Theoretical and Experimental Studies of Organic Semiconductors

Shosei Kubo

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Abbreviations

4CzIPN 2,4,5,6-tetra(9H-carbazol-9-yl)isophthalonitrile ADF Amsterdam density functional Alq₃ tris(8-hydroxyquinolinato)aluminium(III) AMOEBA atomic multipole optimized energetics for biomolecular applications APCI atmospheric pressure chemical ionization B3LYP Becke three-parameter Lee-Yang-Parr BAlq ([1,1'-biphenyl]-4-yloxy)bis[(2-methylquinolin-8-yl)oxy]aluminium bis-TEMPO-bisketal (2,2,4,4,14,14,16,16-octamethyl-7,11,18,21-tetraoxa-3,15-diazatrispiro-[5.2.2.5¹².2⁹.2⁶]henicosane-3,15-diyl)bis(oxidanyl) BmPyPhB 3,3'',5,5''-tetra(pyridin-3-yl)-1,1':3',1''-terphenyl BP86 Becke-Perdew generalized gradient approximation exchange-correlation BSB-Cz 4,4'-bis[(*E*)-4-(9*H*-carbazol-9-yl)styryl]-1,1'-biphenyl bTbK bis-TEMPO-bisketal CBP 4,4'-bis(9*H*-carbazol-9-yl)-1,1'-biphenyl CDBP 9,9'-(2,2'-dimethyl-[1,1'-biphenyl]-4,4'-diyl)bis(9H-carbazole) CE current efficiency CIE International Commission on Illumination (Commission Internationale de l'Éclairage) CP cross-polarization CPME cyclopentyl methyl ether CSA chemical shift anisotropy D-A donor-acceptor DFT density functional theory DMSO dimethyl sulfoxide DNP dynamic nuclear polarization DNP-ssNMR dynamic nuclear polarization enhanced solid-state nuclear magnetic resonance DOS density of states DPEPO bis[2-(diphenylphosphino)phenyl] ether oxide DZ double- ζ valence quality Slater-type orbital DZP singly polarized double- ζ valence quality Slater-type orbital

EHT extended Hückel theory

EL electroluminescence

EML emitting layer

EPR electron paramagnetic resonance

EQE external quantum efficiency

ETL electron-transport layer

FIr6 bis(4',6'-difluorophenylpyridinato)iridium(III) tetrakis(1-pyrazolyl)borate

Flrpic bis[2-(4,6-diffuorophenyl)pyridinato- C^2 ,N](picolinato)iridium(III)

FMO fragment molecular orbital

GDM Gaussian disorder model

GGA generalized gradient approximation

GIAO gauge-including atomic orbital

HOMO highest occupied molecular orbital

HTL hole-transport layer

ICT intramolecular charge transfer

INDO intermediate neglect of differential overlap

IQE internal quantum efficiency

ISC intersystem crossing

ITO indium tin oxide

kMC kinetic Monte Carlo

KS Kohn-Sham

LAMMPS large-scale atomic/molecular massively parallel simulator

Liq lithium quinolin-8-olate

LUMO lowest unoccupied molecular orbital

MD molecular dynamics

MK Merz-Singh-Kollman

MM molecular mechanics

MO molecular orbital

m-MTDATA N^1 -(3-methylphenyl)- N^4 , N^4 -bis{4-[(3-methylphenyl)(phenyl)amino]phenyl}-

 N^1 -phenylbenzene-1,4-diamine

NMR nuclear magnetic resonance

 α -NPD N^4 , $N^{4'}$ -di(naphthalen-1-yl)- N^4 , $N^{4'}$ -diphenyl-[1,1'-biphenyl]-4,4'-diamine

NPT isobaric-isothermal

NVT isochoric-isothermal

OLED organic light-emitting diode

OPV organic photovoltaic cell

P3M particle-particle-mesh PBC periodic boundary condition PBE0 Perdew-Burke-Ernzerhof generalized gradient approximation exchange-correlation along with Hartree-Fock exchange PCM polarizable continuum model PDOS partial density of states PE power efficiency PF Poole-Frenkel PL photoluminescence PLQY photoluminescence quantum yield POPy₂ phenyldi(pyren-1-yl)phosphine oxide PPF dibenzo[*b*,*d*]furan-2,8-diylbis(diphenylphosphine oxide) PTFE polytetrafluoroethylene PV bisbenzimidazo[2,1-a:2',1'-a']anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-10,21-dione PW91 Perdew-Wang generalized gradient approximation exchange-correlation QM quantum mechanics **RISC** reverse intersystem crossing S/N signal-to-noise ssNMR solid-state nuclear magnetic resonance STO Slater-type orbital SZ single- ζ valence quality minimal Slater-type orbital TAB triarylboron TADF thermally activated delayed fluorescence TAPC 4,4'-(cyclohexane-1,1-diyl)bis[*N*,*N*-bis(4-methylphenyl)aniline] TEMPO (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl THF tetrahydrofuran TOF time-of-flight TPD $N^4, N^{4'}$ -bis(3-methylphenyl)- $N^4, N^{4'}$ -diphenyl-[1,1'-biphenyl]-4,4'-diamine TZ2P doubly polarized triple- ζ valence quality Slater-type orbital TZP singly polarized triple- ζ valence quality Slater-type orbital UPS ultraviolet photoelectron spectroscopy UV-vis ultraviolet-visible VASE variable angle spectroscopic ellipsometry vdW van der Waals XC exchange-correlation

XPhos 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl

General Introduction

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1 Backgrounds

1.1 Foundation of organic electronics

Contrary to metal and inorganic compounds, organic molecules had been considered to be an insulator for a long time until the mid-twentieth century. An attention to a possible importance of *electrical properties of organic molecules* has been directed in biochemical catalysis by Szent-Györgyi in 1941 [1], who has later given evidence for photoconductivity in gelatin [2]. In 1948, Eley have shown the electrical conductivity of metal-free and copper phthalocyanines (Fig. 1) [3]. Akamatu and Inokuchi have indicated electrical conductivity of a series of π condugated polycyclic hydrocarbons, violanthrone, isoviolanthrone, and pyranthrone (Fig. 1), in 1952 [4, 5]. Thereafter, Kepler [6] and LeBlanc [7] have discovered photoconductivity of crystalline anthracene (Fig. 1). Such experimental evidences for electrical conductivity of organic molecules have established a concept of *organic semiconductor*. Interest in semiconducting and photoconducting properties of organic molecules have emerged markedly in 1950s.

Apropos of the field of electronics, inorganic materials had been unopposed until the development of organic materials with high electrical conductivity. In 1977, π -conjugated polymers



Figure 1 Examples of organic compounds remarkable in the foundation of organic electronics.

were found to make their electrical conductivity higher by redox treatment [8–10], leading to the Novel Prize in Chemistry in 2000 awarded to Heeger, MacDiarmid, and Shirakawa. This discovery has attracted much attention of many researchers to investigate the semiconducting properties of π -conjugated oligomers and polymers [11]. For the development in organic electronics, it is essential to gain fundamental understanding of the nature of charge transport and electronic excitation phenomena in π -conjugated materials.

1.2 Breakthrough in organic electronics: Development of organic lightemitting diodes

A major breakthrough in the field of organic electronics originates from development of organic light-emitting diodes (OLEDs). The first electroluminescence (EL) phenomenon of acridine derivatives have been found by Bernanose et al. in 1953 using alternating potential applied to cellophane films containing dyes [12, 13]. Pope, Kallmann, and Magnante have observed EL in single-crystalline anthracene and tetracene-doped anthracene under direct current condition [14]. Helfrich and Schneider have observed fluorescence resulting from recombination of holes and electrons in anthracene single crystals using charge injecting electrodes [15]. Although the EL of organic materials has been considered to have potential for practical application in devices, the development of devices utilizing the EL phenomena had not been successful so far. One of the reasons was that high voltage was generally required to inject charges into organic materials and to achieve a significant light output. Therefore, a power-conversion efficiency of the devices had been quite low. In this regard, the work on the application of EL to devices has been done by Tang and VanSlyke in 1987. They have demonstrated that an improved EL efficiency and reduced driving voltage can be achieved by using a double layer of organic thin films, in which each layer was capable of only unipolar charge transport (Fig. 2a) [16]. Shortly thereafter, Adachi et al. have proposed devices with a threelayer structure consisting of hole-transport, emitting, and electron-transport layers (Fig. 2b) [17, 18]. These multilayered devices have enabled ones to choose organic materials such that the morphological, charge transport, recombination, and luminescent properties are compatible with the fabrication and operation of devices.

The early studies on the development of OLEDs have emerged significant interest to both academia and industry. The identification and separation of the role of each layer in OLEDs [16–18] have made an open choice of charge transport and emitting materials from thousands and thousands of organic compounds, and consequently have shown importance of a survey and development of transport and emitting materials. In today's OLEDs, the device generally consists of organic amorphous thin films and is fabricated by vacuum vapor-deposition technique or solution process. To realize highly efficient OLEDs, it is essential to design organic amorphous materials with excellent charge transport and/or luminescent properties. One has to assess the properties of materials and their potential for a practical use in electronic devices. However, it is as if one needs to discover an organic compound with desired properties from an extensive range of chemicals. In the context of a concept of chemical space in cheminformatics, $>10^{23}$ molecules are possible to be considered even if a molecule contains up to a few tens of atoms [19, 20], where it is far too large for practical consideration. Unfortunately, efforts to develop organic materials have yet proceeded largely by trial and error rather than through systematic design. Therefore, it is important to establish a theoretical approach to understand charge transport and luminescent properties of organic materials and to design materials systematically. This thesis aims at the establishment of fundamental science inherent in OLEDs, including charge transport, luminescence phenomena, and morphology of organic amorphous solids.



a) Two-layer OLED

Figure 2 Structures of OLEDs developed (a) by Tang and VanSlyke (two-layer structure) [16] and (b) by Adachi et al. (three-layer structure) [17]. TAPC: 4,4'-(cyclohexane-1,1-diyl)bis[*N*,*N*-bis(4-methylphenyl)aniline]. Alq₃: tris(8-hydroxyquinolinato)aluminium(III). TPD: $N^4, N^{4'}$ -bis(3-methylphenyl)- $N^4, N^{4'}$ -diphenyl-[1,1'-biphenyl]-4,4'-diamine. PV: bisbenzimidazo[2,1-*a*:2',1'-*a*']an-thra[2,1,9-*def*:6,5,10-*d'e'f'*]diisoquinoline-10,21-dione.

Glass substrate

1.3 Multiscale modeling: Conceptual aspect

As stated above, materials used for OLEDs are generally in amorphous state. Hence, to gain insight into their charge transport properties, it is essential to investigate electronic states by taking into account not only the molecule itself but also the nature of amorphous aggregate. Even now in the field of OLEDs, theoretical treatments have often been based on consideration of gas-phase molecules, with effects arising from intermolecular interaction unconsidered. This situation is, however, far apart from real devices. Recently, a concept of *multiscale modeling* have grown in the field of organic electronics and much effort has been made to investigate physics of electronic devices *in silico* as realistically as possible [21–23].

Multiscale modeling is a pursued approach to make sense of a wide range of phenomena. In developing computational methods to investigate complex chemical systems, for example charge transport in organic amorphous systems, it is desired to introduce practical methods to replace the much more time-consuming quantum chemical calculations wherever possible. In 1929, Dirac has introduced this leitmotif as the following statements [24]:

The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.

The concept led the remarkable works in the development of multiscale models for complex chemical systems using both classical and quantum mechanical theory by Karplus, Levitt, and Warshel, to whom the Nobel Prize in Chemistry was awarded in 2013 [25–27]. The core of multiscale modeling is models and related algorithms to couple processes at different spatial and/or temporal scales, and to transform information at one scale and transfer it to another scale, which is known as scale bridging [28]. This approach is multidisciplinary and has been developed in many different communities such as physics, chemistry, biology, ecology, or even socioeconomics. The multiscale modeling enables ones to gain understanding of a microscopic origin of large-scale properties, leading to a deeper knowledge of physical phenomena, and moreover, to design of systems with specific properties. Therefore, the elucidation of device physics through *multiscale modeling and simulation* should be a powerful approach to the establishment of fundamental science inherent in electronic devices.

1.4 Multiscale device simulation and high-throughput material design: Scope of this thesis

One of the aims of this thesis is to *establish methodology of multiscale simulation for electronic devices*. This approach is expected to shed light on device physics from both microscopic molecular-level and practical device-level points of view. This thesis specifically focuses on (i) charge transport in organic amorphous materials (PART I), (ii) morphology of organic materials in amorphous state (PART II), and (iii) luminescent properties of emitting materials and their performance in OLEDs (PART III).

Charge transport in organic amorphous semiconductors is one of the key features for use in OLEDs. In the mechanism of OLEDs, this phenomenon plays an important role in charge transport itself in organic layers, charge recombination in emitting layers, charge blocking at organic layer interfaces, and charge injection from electrodes to organic layers, which are closely related to the performance of devices. For the case of organic amorphous semiconductors, the charge transport mechanism is generally considered to obey hopping-type transport, which assumes that an elementary step of charge transport is a charge transfer among adjacent molecules [29]. This assumption is straightforward because the mean free path that a carrier travels in the solid between subsequent phonon scattering events is less than the order of intermolecular distance at room temperature due to the weak intermolecular coupling of electronic states [30].

One of the remarkable works on hopping-type charge transport in organic amorphous semiconductors has been done by Bässler [31]. They have modeled the nature of organic amorphous systems by introducing two concepts of disorder: energetic (diagonal) disorder and positional (off-diagonal) disorder [32]. The former is related to the energy of an excess charge (hole or electron) on a molecule, henceforth called the hopping site energy, which is determined by its molecular orbital (MO) energy and intermolecular interaction with surrounding molecules. Since intermolecular separations and mutual orientation are varied in amorphous state, the intermolecular interaction and thus the site energy depend on the local structure of the solid. The resulting fluctuation in the site energies are usually referred to as energetic (diagonal) disorder. The latter disorder in the model is subjected to the strength of intermolecular electronic coupling, which also depends on the intermolecular separation and orientation. It is obvious that the local fluctuation in the structure lead to fluctuation in the intermolecular electronic coupling. This type of fluctuation is referred to as positional (off-diagonal) disorder. These disorders were quantified by two simple disorder parameters: the width of Gaussianshaped density of states for energetic disorder and the intermolecular overlap parameter for positional disorder. The model is now called the Gaussian disorder model (GDM) associated

1 Backgrounds

with the Gaussian-distributed disorder. The GDM has succeeded in describing experimentally observed charge transport properties, specifically charge mobility, of organic amorphous semiconductors including effects of temperature [33] and external electric field [34].

Despite the success of the GDM, it should be addressed that in the GDM the model of amorphous systems is essentially based on a lattice model, which treats the molecule as a lattice point. This indicates that the molecule is considered to be a point mass and the mutual intermolecular orientation and molecular orbitals are neglected. Although the effect of mutual orientation is partly introduced by the positional disorder parameter in terms of the GDM, it does not intrinsically originate from the nature of amorphous systems. Consequently, it is somewhat unclear how to link the microscopic molecular-level nature of organic amorphous semiconductors and the macroscopic charge transport properties. To remedy this uncertainty, many attempts have recently been made by means of the aforementioned concept of multiscale modeling [21, 22, 35–41]. However, most of these attempts failed to quantitatively reproduce experimental charge mobilities and the molecular-scale mechanism of charge transport is not yet fully unraveled. Furthermore, experimentally obtained charge mobilities have often been interpreted by fitting of experimental results to the GDM by using its disorder parameters, indicating that these parameters have been regarded as adjustable fitting parameters. This thesis seeks to develop a multiscale and predictive computational model that reflects actual charge transport properties of organic amorphous semiconductors.

Another important issue in this thesis is of morphology of organic amorphous materials. This is also related to the performance of organic electronic devices because it is known to have an impact on material properties related to electronic state [42], charge transport [43–47], light absorption [48] and emission [49], and refraction of light [50]. In the past few decades, organic amorphous solids used in OLEDs have been considered to have isotropic morphology and hence to possess isotropic electrical and/or optical properties [50]. However, some organic materials have recently been found to exhibit preferable molecular orientation in the thin films [50, 51]. Such molecular orientation in the films influences electrical characteristics of devices [52]. In addition, specifically in OLEDs, refractive index of organic layers and molecular orientation of emissive molecules strongly affects a light out-coupling efficiency of the devices, which dominates a theoretical limit of external quantum efficiency (EQE) [53–60]. Therefore, understanding of molecular orientation in organic amorphous materials is essential to reveal underlying science of organic electronic devices and to improve device performances. This thesis tackles this issue to clarify the molecular-level morphology of organic amorphous films from experimental points of view.

Experimental investigation into molecular orientation in organic amorphous solids is im-

portant for the understanding of morphology. In amorphous systems, one of difficulties in detailed analysis is that amorphous systems impede the application of X-ray or neutron diffraction techniques because the systems possess no long-range order contrary to crystalline systems. Several experimental techniques, for example angular-dependent photoluminescence (PL) measurements [61] and variable angle spectroscopic ellipsometry (VASE) [62], can provide information of molecular orientation in organic amorphous films. However, these methods essentially provide only system-averaged information, such as orientation order parameters [63]. Heretofore no appropriate methods for revealing molecular orientation without lack of molecular-level information have been established. This thesis demonstrates potential of solid-state nuclear magnetic resonance (ssNMR) spectroscopy for analysis of molecular orientation in organic amorphous films with atomistic resolution. This technique is expected to be powerful for unraveling molecular-level origins of the performance of organic electronic devices.

For realization of high performance organic electronic devices, it is essential to design and develop organic materials with desired properties. For OLEDs, the design of emitting materials is of main interest and a great deal of effort has been made to develop emitting materials [58, 64–75]. As stated earlier, the development of organic materials has yet proceeded largely by trial and error. To design materials within limited time and human resource, it is necessary to make procedures of material design more cost-effective, or so-called high-throughput. A concept of *high-throughput virtual screening* have emerged in the fields of biological and materials science due to the exponential growth of available computer resource and constant improvement of computational techniques [76–79]. This approach has potential to dive into extensive chemical space for material discovery by combining computer-driven technologies such as cheminformatics and machine learning. On the basis of this concept, this thesis aims at *the development of highly efficient emitting materials by material screening*. To make the procedure for material discovery straightforward wherever possible, this thesis focuses on the material design and screening based only on simple quantum chemical calculations.

2 Outline of this thesis

This thesis consists of three parts and six chapters. PART I investigates charge transport phenomena in organic materials used in OLEDs by means of multiscale charge transport simulation to elucidate the mechanism of charge transport in organic amorphous systems. PART II develops and demonstrates the methodology to gain molecular-level insight into morphology of organic amorphous semiconductors through and experimental approach. PART III designs and develops highly efficient emitting materials used for OLEDs based on high-throughput quantum chemical calculations.

CHAPTER 1 of PART I shows the molecular-scale mechanism of charge transport in organic amorphous systems used for OLEDs. This is accomplished by using a computational simulation with explicit consideration of a molecular structure and intermolecular packing in disordered condensed aggregates. A phenomenon where the charge mobility increases with the applied electric field strength, so-called Poole–Frenkel behavior, is well reproduced in the simulation. Detailed analysis is performed to reveal the molecular-level origin of charge transport, which provides significant progress in understanding charge transport in amorphous organic materials.

CHAPTER 2 of PART I further investigates the molecular-scale mechanism of charge transport and improves the charge transport model presented in CHAPTER 1. In CHAPTER 1, charge transport in organic amorphous systems is considered to occur only via highest occupied MOs (HOMOs) or lowest unoccupied MOs (LUMOs), whereas all other lower- and higher-lying MOs are ignored. CHAPTER 2 shows that charge carriers are effectively transported via lower-/higher-lying MOs as well as HOMOs/LUMOs in organic amorphous systems. Detailed analysis reveals that lower- and higher-lying MOs are *active* in charge transport in addition to the HOMO and LUMO when the site energies between two relevant molecules are similar. From this viewpoint, such MOs are called active *multiple frontier orbitals*, analogous to the concept of frontier orbitals used to explain chemical reactions. The charge transport simulation considering multiple frontier orbitals quantitatively reproduces the experimental mobilities for both hole and electron transport, even though the simulation do not use any adjustable parameters. The findings in CHAPTER 2 also suggest that higher charge mobility may be achieved if as many as possible MOs lie close in energy to the HOMO or LUMO (i.e., are degenerate). Developing materials with multiple frontier orbitals will be a promising strategy to realize highly efficient carrier mobility.

CHAPTER 3 of PART I assesses effects of calculation methods used in the multiscale charge transport simulation demonstrated in CHAPTERS 1 and 2. In the case of charge transport materials used in OLEDs, the multiscale simulation needs to treat a large atomistic system *in silico* because the materials are in amorphous state contrary to ordered crystalline systems, which can be treated within periodic boundary condition. In such a situation, a reduction of computational cost is desired for application of multiscale simulation level used for evaluation of properties relevant to charge transport. The calculations based on semiempirical methods used in CHAPTER 3 to 3 provide reasonable hole mobility of organic amorphous systems. CHAPTER 3

also finds that the use of density functional theory in the multiscale simulation do not always yield better agreement with experimental mobility. Considering the computational cost, the multiscale simulation presented in CHAPTERS 1 to 3 yields reasonable prediction of charge mobility within moderate computational resource and time.

CHAPTER 4 of PART II exemplifies the first application of dynamic nuclear polarization (DNP) enhanced ssNMR (DNP-ssNMR) spectroscopy to an organic semiconductor to reveal molecular orientation in its amorphous state. The molecular orientation in organic semiconductors in amorphous state is considered to strongly affect their performance in electronic devices. The average molecular orientation, or so-called order parameter, can be characterized by techniques such as angular-dependent PL measurements and VASE. However, there are no appropriate methods for determining distribution of molecular orientation. ssNMR has potential to provide detailed information on the structure and dynamics of materials including the distribution of molecular orientation. However, the critical drawback of ssNMR is its low sensitivity and the amount of organic material in a typical sample device is too limited to carry out quantitative analysis. This impedes wider application of ssNMR spectroscopy to organic electronic device systems. To solve this problem, DNP-ssNMR spectroscopy is applied to thin films of an organic semiconductor. The DNP-ssNMR measurements is successfully performed for a single film of a vaccum-deposited organic semiconductor with a sample mass of a few tens of micrograms. The spectra obtained under the DNP condition show an excellent signal-to-noise ratio, enabling quantitative analysis of the molecular orientation distribution. Using this technique, this chapter demonstrates a difference in molecular orientation depending on a preparation processes of thin film, vacuum-deposition and drop-casting methods. The differences revealed by the DNP-ssNMR measurements are related to non-dispersive and dispersive electron transport behavior of the thin films.

CHAPTER 5 of PART III designs and develops new triarylboron (TAB)-based emitters that show both high PL quantum yields (PLQYs) and efficient up-conversion from triplet to singlet states. TAB compounds have a vacant *p*-orbital on the central boron atom, so they possess attractive electron-accepting properties related to their $p-\pi^*$ conjugation. This makes TAB compounds suitable for a number of application such as non-linear optics, anion sensing, hydrogen activation and storage, and optoelectronic materials. The use of TAB as an acceptor of donoracceptor (D–A) systems is expected to provide strong intramolecular charge transfer properties, leading to efficient fluorescence via up-conversion from triplet to singlet states, which is known as thermally activated delayed fluorescence (TADF) or E-type delayed fluorescence [64, 65, 80, 81]. On the basis of this concept, this chapter develops new TAB-based D–A-type TADF emitters composed of an electron-accepting trimesityl boron analogue and electrondonating amine-based units. OLEDs containing the TAB-based emitters show a maximum EQE of 21.6% for a sky-blue OLED and 22.8% for a green OLED. The EQE of 21.6% is the highest value for TADF-based blue OLEDs, while that of 22.8% is the highest among OLEDs with a TAB-based emitter at the time of publication. Both of these EQE far exceed the theoretical limit for conventional fluorescent OLEDs of 5–7.5%. The temperature dependence of transient PL decay curves reveals that the high PLQY and EQE can be attributed to TADF emission originating from the small energy gap between their singlet and triplet states. The results presented in CHAPTER 5 demonstrate high potential of TAB-based TADF emitters as environmentally friendly organic light-emitting compounds that do not contain scarce elements such as rare metals.

CHAPTER 6 of PART III designs and develops blue TADF emitters realizing an EQE of OLED over 25%. Recent interest has focused on TADF emitters that make it possible to fabricate highly efficient *blue* OLEDs. Although considerable efforts have been made in improving the efficiency of blue TADF emitters, there have been few studies demonstrating highly efficient blue TADF emitters with EQE over 20%. Difficulty of developing efficient blue TADF emitters lies in finding a molecular structure that simultaneously incorporates (i) a small energy difference between the lowest excited singlet state (S_1) and the lowest triplet state, (ii) a large oscillator strength between S_1 and the ground state, and (iii) S_1 energy sufficiently high for blue emission. The emitters presented in CHAPTER 6 satisfies the above three requirements. They show blue emission with a PLQY of nearly 100% and high triplet-to-singlet up-conversion yield. In addition, their transition dipole moments are horizontally oriented, resulting in further increase of their electroluminescence efficiency. The work presented in CHAPTER 6 achieves a blue OLED exhibiting a high EQE of 25.9%.

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Part I

Elucidation of Charge Transport in Organic Amorphous Semiconductors Based on Multiscale Simulation

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Chapter 1

Detailed Analysis of Charge Transport in Amorphous Organic Thin Layer by Multiscale Simulation without Any Adjustable Parameters

H OPPING-TYPE charge transport in an amorphous thin layer composed of organic molecules is simulated by combined use of molecular dynamics, quantum chemical, and Monte Carlo calculations. By explicitly considering a molecular structure and disordered intermolecular packing, we reasonably reproduce the experimental hole and electron mobilities and their applied electric field dependence (Poole–Frenkel behavior) without using any adjustable parameters. We find that the distribution of density-of-states originating from the amorphous nature has a significant impact on both the mobilities and Poole–Frenkel behavior. Detailed analysis is also provided to reveal the molecular-level origin of charge transport, including the origin of Poole–Frenkel behavior.

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1.1 Introduction

Charge mobility μ in organic aggregates is a key factor in understanding performance of organic semiconductor devices such as organic light-emitting diodes (OLEDs) [1–3]. Typical organic layers of OLEDs are composed of amorphous thin films. Charge transport in amorphous organic solids is considered to occur through intermolecular charge hopping. Some models have been proposed to describe charge transport in amorphous organic solids. Among these models, the Gaussian disorder model (GDM) [4] successfully describes the macroscopic charge transport properties. However, the model does not consider actual molecules and it has difficulty in revealing molecular-scale behavior of carriers; the disorders, which originate from amorphous structures, are used as adjustable parameters to reproduce experimental mobility data. Although microscopic analyses have also been carried out [5–23] and some useful suggestions have been derived, we only have a limited understanding of the nature of charge transport in amorphous organic layers. In these studies, Marcus theory [24] have frequently been employed to calculate a rate constant of intermolecular charge transfer between molecule *i* and molecule *j*, k_{ij} , which is described as

$$k_{ij} = \frac{2\pi}{\hbar} \frac{|H_{ij}|^2}{(4\pi\lambda k_{\rm B}T)^{1/2}} \exp\left[-\frac{(\lambda + \Delta G_{ij})^2}{4\lambda k_{\rm B}T}\right],\tag{1.1}$$

with $\hbar = h/(2\pi)$, the Planck constant *h*, the Boltzmann constant k_B , and the absolute temperature *T*. Here, H_{ij} is the electronic coupling between molecule *i* and *j*. ΔG_{ij} is the difference of

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Figure 1.1 Molecular structure and frontier orbitals of the isolated CBP obtained by the DFT calculation. MOs are depicted with an isosurface of 0.02 au.

Gibbs free energy between the initial and final states associated with the charge transfer from molecule *i* to *j*. λ is the reorganization energy.

Our goals are to build a computational model reproducing experimental mobilities quantitatively, and to gain understanding of the nature of charge transport in amorphous organic layers by analyzing the model. We have recently carried out simulations in an amorphous organic solid [23]. The calculated mobility was overestimated by two orders of magnitude, which also failed to reproduce the experimental observation that the mobility increased as the applied electric field increased. Here, charge transport process in an amorphous solid of 4,4'-bis(9*H*carbazol-9-yl)-1,1'-biphenyl (CBP; Fig. 1.1), which is a typical host material for OLEDs, was investigated. In the calculations, we considered the energetic disorder (Fig. 1.2, see below for details) and intermolecular packing effect on reorganization energy, both of which were not included in a preceding paper [23].

An amorphous structure containing 4000 CBP molecules was generated using a molecular dynamics (MD) simulation. On the basis of the amorphous structure, electronic coupling and reorganization energy were calculated by quantum chemical calculations. Reflecting the amorphous nature, the calculated electronic coupling were distributed as shown later. The *structural disorder* is often called the *off-diagonal disorder*. In the GDM, mass points are considered instead of real molecules, so the origin of the distribution of electronic coupling is only the distribution of distances between hopping sites. Here, real molecules are considered; not only the distribution of intermolecular distances, but also a relative intermolecular orientation and spatial distribution of frontier orbitals contribute to the distribution of electronic coupling.

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Figure 1.2 Schematic illustration of energetic disorder. *A* and *I* are electron affinity and ionization potential in amorphous state, respectively.

In addition to the structural disorder, molecules (hopping sites) are distributed in energy in amorphous solids (Fig. 1.2), because different molecules undergo a different intermolecular interaction. The distribution of energy is called the *energetic disorder* or *diagonal disorder*. We calculated the energetic disorder by considering an electrostatic interaction and polarization effect of neighboring molecules. The energy of a hole/electron on molecule *i*, $\Delta E_i^{+/-}$ (the superscript + and – signs indicate the energy for hole and electron, respectively), can be written as

$$\Delta E_i^+ = E_{i,\text{neigh}}^+ - E_{i,\text{neigh}}^0 + I_{\text{isol}}, \qquad (1.2)$$

$$\Delta E_i^- = E_{i,\text{neigh}}^- - E_{i,\text{neigh}}^0 - A_{\text{isol}}.$$
(1.3)

Here, I_{isol} and A_{isol} are the ionization potential and electron affinity of an isolated CBP molecule, respectively. $E_{i,neigh}^+$, $E_{i,neigh}^-$, and $E_{i,neigh}^0$ are the sum of the electrostatic interaction and polarization effect of neighboring molecules, for positively charged (+), negatively charged (-), and the neutral state (0) of molecule *i*, respectively. Therefore, ΔG_{ij} in eq. (1.1) can be expressed as

$$\Delta G_{ij} = \Delta E_j - \Delta E_i - q \mathbf{F} \cdot \mathbf{r}_{ij}, \qquad (1.4)$$

where ΔE_k (k = i, j) is ΔE_k^+ or ΔE_k^- for hole or electron transport, q is the charge of a carrier, F is the externally applied electric field (|F| = F) and r_{ij} is the vector connecting the center of molecule i to that of molecule j (displacement of the carrier).

The reorganization energy was calculated taking into account steric influence of neighboring molecules with the quantum mechanics (QM)/molecular mechanics (MM) method. Using the calculated electronic coupling, ΔG_{ij} , and reorganization energy, the rate constants of charge transfer were calculated from eq. (1.1). The charge transport process was simulated using a kinetic Monte Carlo (kMC) method based on the MD-constructed amorphous structure and the calculated rate constants, which provided charge mobilities. To confirm validity of the calculations, we also performed time-of-flight (TOF) experiments. The experimental data were consistent with those reported previously [20, 25, 26]. More details of the computational and experimental methods are summarized in the following sections.

1.2 Computational and experimental methods

1.2.1 Overview

The simulations of charge transport process for amorphous structure containing 100, 1000, 4000, and 8000 molecules of CBP were performed. Here, the methodology for the 4000 CBP system is described. We performed the simulations also for the other systems in the same manner as performed for the 4000 CBP system. Unless otherwise noted, the result for the 4000 CBP system was used in the discussion. The MD simulation was performed on the large-scale atomic/molecular massively parallel simulator (LAMMPS) code [27]. All quantum chemical calculations were carried out using the Gaussian 09 program package [28]. The kMC simulations were performed using our in-house program.

1.2.2 Molecular dynamics simulation

The amorphous structure containing 4000 CBP molecules was generated with a MD simulation. The Dreiding force field [29] was used to describe interatomic potential. The bond length parameters in the force field were modified to reproduce an optimized molecular structure obtained by a density functional theory (DFT) calculation. The DFT calculation was performed with the Becke three-parameter Lee–Yang–Parr (B3LYP) functional [30] and 6-31G* basis set. The DFT-optimized bond angles were reproduced by the MD simulation without modification of the force field. The sufficiently large cubic cell was generated and periodic boundary condition was applied to the cell. A Lennard–Jones (12, 6) potential was used as a model for the van der Waals (vdW) interaction with tail correction [31], which is a correction for thermodynamic quantities that takes into account the homogeneous long range vdW interaction. The particle–particle–particle–mesh (P3M) method [32] was used to calculate the

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coulombic interaction between atoms. To determine the atomic partial charges, we performed a DFT calculation on the DFT-optimized molecule and then used the Merz–Singh–Kollman scheme [33], which is a method for calculating atomic charges to fit the electrostatic potential on molecular surfaces.

As an initial structure of the MD simulation, the DFT-optimized molecules were placed with random orientation at random positions in the generated cell. To mimic vacuum vapordeposition process, the MD simulation was performed in an isochoric-isothermal (NVT) ensemble under 573 K for 10 ps followed by a simulation in an isobaric-isothermal (NPT) ensemble under 298 K and 1.0×10^{-4} Pa for 1.0 ns using a Nosé–Hoover thermostat and barostat [34, 35]. During the simulation in the NPT ensemble, the simulation cell shrank and finally reached a constant volume. We obtained the cubic cell of the condensed structure with a side length of 14.55 nm and the density of the generated structure was calculated to be 1.04 g cm⁻³. Finally, to eliminate the deviation from the stable structure originating from molecular vibration, energy minimization was performed.

1.2.3 Reorganization energy

The reorganization energy was calculated by DFT calculations based on Nelsen's four-point method [36]. Reorganization energy is described by the sum of energy change arising from geometric change in the molecules during charge transfer. The contribution of energy change can be split into two terms: $\lambda = \lambda_1 + \lambda_2$. λ_1 and λ_2 can be expressed as

$$\lambda_1 = E_c(\boldsymbol{Q}_n) - E_c(\boldsymbol{Q}_c), \qquad (1.5)$$

$$\lambda_2 = E_{\rm n}(\boldsymbol{Q}_{\rm c}) - E_{\rm n}(\boldsymbol{Q}_{\rm n}), \qquad (1.6)$$

where E_n and E_c denote the molecular energies of the neutral and charged states, and Q_n and Q_c represent the optimized geometries of the neutral and charged states, respectively [15]. In most cases, reorganization energy is calculated for an isolated molecule. However, interactions with neighboring molecules in aggregate state are considered to affect reorganization energy. Here, we introduced a QM/MM approach [37] to quantify such environmental influences. The reorganization energy including the influences is denoted by λ_{aggr} . For 45 randomly sampled molecules (out of 4000 molecules in the aggregate structure), we calculated λ_{aggr} by the QM/MM method. DFT (B3LYP/6-31G*) and the Dreiding force field were used for the QM and MM regions, respectively. The neighboring molecules within 3.0 nm were included and their geometries were frozen during the calculation. Partial charges of the atoms in the MM region were incorporated into the QM Hamiltonian. The partial charges were set to be same values as those used in the MD simulation. The calculated average value of λ_{aggr} was

 (0.105 ± 0.009) eV for hole and (0.373 ± 0.027) eV for electron (95% confidence interval), respectively. We also calculated the reorganization energy for the isolated CBP molecule, λ_{isol} . λ_{isol} (0.129 eV and 0.516 eV for hole and electron, respectively) is larger than λ_{aggr} , owing to the absence of steric effect from neighboring molecules.

1.2.4 Electronic coupling

The electronic coupling was calculated using the extended Hückel method as described in previous works [15, 18, 23]. The calculation was performed for all pairs with a center-to-center distance within a cutoff distance of 2.5 nm (167 993 pairs). The cutoff distance is validated by H_{ij} versus the intermolecular distance plots (Fig. 1.3), which show that the molecular pairs with a center-to-center distance longer than 2.5 nm have a negligibly small H_{ij} (<10⁻⁴ meV). Figure 1.4 shows the distributions of the calculated electronic coupling for hole and electron. Some examples of the intermolecular packings are shown in Fig. 1.5. From the examples and the intermolecular distance dependence of electronic coupling, we found that the electronic coupling are *not solely* determined by the intermolecular distances.

1.2.5 Energetic disorder

We calculated the energetic disorder by considering the electrostatic interaction and polarization effect of neighboring molecules. $E_{i,\text{neigh}}^{0/+/-}$, the sum of the two terms, is then expressed as

$$E_{i,\text{neigh}}^{0/+/-} = E_{i,\text{c-c}}^{0/+/-} + E_{i,\text{c-d}}^{0/+/-}.$$
(1.7)

Here, the superscripts 0, +, and – represent neutral, positively charged, and negatively charged states of molecule *i*, respectively. $E_{i,c-c}^{0/+/-}$, defined by

$$E_{i,c-c}^{0/+/-} = \sum_{j \neq i} \sum_{k} \sum_{k'} \frac{q_{i,k}q_{j,k'}}{4\pi\varepsilon_0} \frac{1}{|\mathbf{r}_{ij,kk'}|},$$
(1.8)

is the electrostatic interaction energy between the atomic partial charges of molecule *i* and neighboring molecules, where $q_{i,k}$ and $q_{j,k'}$ are an atomic partial charge of atom *k* in molecule *i* and that of atom *k'* in molecule *j*, respectively, and $r_{ij,kk'}$ is a vector connecting atom *k* in molecule *i* to atom *k'* in molecule *j*. Atomic partial charges of charged and neutral molecules were obtained by the same method as used for the MD simulation. $E_{i,c-c}^{0/+/-}$ was calculated taking into account neighboring molecules with a center-to-center distance within 3.0 nm. $E_{i,c-d}^{0/+/-}$ is the polarization effect of neighboring molecules, which effectively moderates the interaction between atomic partial charges. This effect can be regarded as the interaction between atomic



Figure 1.3 Correlation between electronic coupling H_{ij} and intermolecular (center-to-center) distance for (a) hole and (b) electron transport.



Figure 1.4 Distribution of electronic coupling H_{ij} for (a) hole and (b) electron transport.




Figure 1.5 Examples of intermolecular packings. H_{ij}^+ and H_{ij}^- are the electronic couplings for hole and electron transport, respectively. (a) Molecular pairs which have the largest coupling. (b) Molecular pairs which have a small coupling in spite of a short distance. (c) Molecular pairs which have a large coupling in spite of a long distance. Note that the distributions of frontier orbitals are significantly depend on the conformation of the molecule in the aggregate structure.



Figure 1.6 Probability densities (p. d.) of site energy for (a) hole and (b) electron transport. The distribution was centered on the average energy level. Solid lines show the Gaussian probability density function, which is zero-centered and whose standard deviation is set to be the sample standard deviation of the calculated site energies.

partial charges in molecule *i* and induced dipole moments on atoms in neighboring molecules. Hence, $E_{i,c-d}^{0/+/-}$ can be approximately written as

$$E_{i,c-d}^{0/+/-} = \sum_{j \neq i} \sum_{k} \sum_{k'} -\frac{q_{i,k}}{4\pi\varepsilon_0} \frac{\mu_{j,k'} \cdot \mathbf{r}_{ij,kk'}}{|\mathbf{r}_{ij,kk'}|^3},$$
(1.9)

where $\mu_{j,k'}$ is the induced dipole moment on atom k' in neighboring molecule j. $\mu_{j,k'}$ can be described as $\mu_{j,k'} = \alpha_{j,k'} E_{j,k'}$, where $\alpha_{j,k'}$ is the atomic polarizability and $E_{j,k'}$ is the electric field at the position of atom k' in molecule j caused by the atomic partial charges in molecule i and its neighbors within 3.0 nm other than molecule j. We used atomic polarizability implemented in the atomic multipole optimized energetics for biomolecular applications (AMOEBA) polarizable force field [38]. By eqs. (1.7) to (1.9), we can determine the energies of the positively charged state ($E_{i,neigh}^+$), negatively charged state ($E_{i,neigh}^-$), and neutral state ($E_{i,neigh}^0$) for molecule i, leading to eqs. (1.2) and (1.3) and the resulting Gibbs free energy change expressed by eq. (1.4). The distribution of energy levels obtained in this work obeyed a Gaussian distribution (Fig. 1.6) and its sample standard deviation was 0.107 eV and 0.102 eV for hole and electron, respectively.

-500

0

x (Å)



-500

0

x (Å)

Figure 1.7 Examples of the simulated charge transport trajectories. The external electric field is applied along the x-axis. (a,b) For hole and electron transport under $F^{1/2} = 300 \text{ V}^{1/2} \text{ cm}^{-1/2}$, respectively. (c,d) For hole and electron transport under $F^{1/2} = 1300 \text{ V}^{1/2} \text{ cm}^{-1/2}$, respectively.



Figure 1.8 Calculated charge mobility μ for hole and electron transport with various size of system. The mobility was calculated for three orthogonal axes in (a) 100, (b) 1000, (c) 4000, and (d) 8000 CBP systems.

1.2.6 Kinetic Monte Carlo simulation

Using rate constants of the charge transfer from molecule *i* to *j*, k_{ij} , calculated by the Marcus equation [eq. (1.1)], a kMC calculation was performed to simulate the experimental TOF measurements. The simulation was performed under 298 K until the charge moved a distance *L* along *F*, with periodic boundary condition applied for each axes. We set *L* to be 100 nm. 10⁴ trials were performed to obtain TOF transient curves and the travelling time of the carriers, *t*. Examples of the simulated trajectories are shown in Fig. 1.7. The charge mobility μ was calculated from $\mu = L/(tF)$ for the three orthogonal directions, *x*-, *y*-, and *z*-axes. The calculated mobilities for the three directions are shown in Fig. 1.8. An anisotropy of the mobility was observed for the MD-constructed amorphous structures which consist of 100 or 1000 CBP molecules. For the structures containing 4000 or 8000 CBP molecules, the anisotropy almost disappeared, and the average values of mobility calculated for the three directions were consistent for 4000 and 8000 systems. The average mobilities are provided in the following discussion.

1.2.7 Time-of-flight experiment

The charge mobility was experimentally measured for a CBP thin film using TOF equipment (TOF-401-3, Sumitomo Heavy Industries Advanced Machinery, Japan). A TOF sample with the structure of indium tin oxide (50 nm)/CBP ($3.9 \mu m$)/Al (20 nm) was fabricated by vacuum-deposition. A nitrogen gas laser (KEC-150, Usho Optical Systems, Japan) with a wavelength of 337 nm was used to generate the photocarriers.

1.3 Results and discussion

Figure 1.9 compares the experimentally obtained and calculated mobilities for hole and electron transport. The experimental mobilities (black filled and black open symbols in Fig. 1.9) showed a positive linear $F^{1/2}$ -dependence, often called Poole–Frenkel (PF)-type behavior, commonly observed in organic amorphous materials [1, 4, 39]. Open circles in Fig. 1.9 consider the intermolecular packing effect in the calculation of reorganization energy but the energetic disorder is not considered. The calculated mobilities significantly deviated from the experimental values, being one or two orders of magnitude larger. In addition, the calculated negative $F^{1/2}$ -dependence is not compatible with the experiments. Open squares in Fig. 1.9 show the calculated mobilities incorporating the energetic disorder but the intermolecular packing effect on reorganization energy is not considered. By considering the energetic disorder, the experimentally obtained positive $F^{1/2}$ -dependence was reproduced.



Figure 1.9 Calculated and experimental charge mobilities μ for (a) hole and (b) electron transport. Black filled diamonds: measured by TOF experiments. Black open diamonds, downward triangles, and upward triangles: experimental data from refs. [20], [25], and [26], respectively. Open circles: calculated with λ_{aggr} and without energetic disorder (e. d.). Filled squares: calculated with λ_{aggr} and with energetic disorder (e. d.). Filled squares: calculated with λ_{aggr} and with energetic disorder.

The mobility is more than one order of magnitude smaller compared with the experiments for electron transport. By incorporating both the energetic disorder and the intermolecular packing effect on reorganization energy, we obtained the filled squares in Fig. 1.9. The calculated mobilities showed better agreement with the experimentally obtained values. The slightly worse agreement for electron transport is proposed to reflect difficulty in calculating unoccupied orbitals.

Here, we investigate the origin of the PF behavior, the positive $F^{1/2}$ -dependence of charge mobility. Figure 1.9 indicated that the PF behavior was reproduced when the energetic disorder was incorporated in the simulations, but not reproduced when the energetic disorder was not incorporated. Therefore, the energetic disorder plays a crucial role in the PF behavior. To investigate the mechanism of influence of the energetic disorder on the $F^{1/2}$ -dependence of mobility, we calculated the number of hops during the transport (*n*), the number of hopping sites used at least once during the transport (*v*), and the mean time required for each individual charge hopping, $\tau = t/n$ (*t* is the time required for the transport between electrodes), with and without the energetic disorder (see Table 1.1. The intermolecular packing effect on reorganization energy was considered in all cases.). When the energetic disorder was

Condition	$F^{1/2}$ (V ^{1/2} cm ^{-1/2})	п	v	τ (ps)
Hole (with energetic disorder)	300	220 324	1265	2.6
Hole (with energetic disorder)	1300	1022	266	4.3
Electron (with energetic disorder)	300	128 683	1176	58.8
Electron (with energetic disorder)	1300	1136	185	74.9
Hole (w/o energetic disorder)	300	4729	1257	0.4
Hole (w/o energetic disorder)	1300	405	235	0.9
Electron (w/o energetic disorder)	300	12 584	1325	5.2
Electron (w/o energetic disorder)	1300	507	179	19.4

Table 1.1 The number of hops (*n*), the number of used hopping sites (*v*), and the mean time required for each individual charge hopping ($\tau = t/n$).

Note: Intermolecular packing effect on reorganization energy is considered in all cases.

included in the simulations, *n* decreased by two orders of magnitude with $F^{1/2}$ increasing from $300 V^{1/2} \text{ cm}^{-1/2}$ to $1300 V^{1/2} \text{ cm}^{-1/2}$, while τ had the same order of magnitude regardless of *F*. Since $\mu = L/(tF) = L/(n\tau F)$, the PF behavior is mainly attributed to the decrease in *n* with *F*. Again, *L* is the distance between the electrodes. When $F^{1/2} = 300 V^{1/2} \text{ cm}^{-1/2}$ and under the existence of the energetic disorder, *n* is larger than *v* by two orders of magnitude, indicating that the same sites are repeatedly used. Hence, the charge carriers frequently move back and forth during the transport. This *round-trip* of carriers is enhanced by the energetic disorder; without the energetic disorder, *n* has the same order as or is one order of magnitude larger than that of *v*. Different from the case of $F^{1/2} = 300 V^{1/2} \text{ cm}^{-1/2}$, the difference of *n* and *v* is much smaller when $F^{1/2} = 1300 V^{1/2} \text{ cm}^{-1/2}$, regardless of whether the energetic disorder is incorporated or not. To summarize, the energetic disorder causes frequent back and forth hopping of carriers and entails large *n* under weak *F*, but not under strong *F*. This results in the PF behavior.

When we compare the simulations with and without the energetic disorder under the same $F^{1/2}$, not only *n* but also τ become larger by incorporation of the energetic disorder. Both factors affect the reduced mobility for the case with energetic disorder. When we compare hole and electron transport with the same $F^{1/2}$ and energetic disordered state, *n* and *v* are not significantly different but τ is one to two orders of magnitude larger for electron transport. The larger τ induces a smaller mobility for electrons in spite of the maximum electronic coupling for electron transport (70 meV) being larger than that of hole transport (41 meV). This implies that charge mobility is not solely determined by the largest electronic coupling.

These characteristics can be explained at the molecular level. Figure 1.10 shows the num-



Figure 1.10 n_i^{in} versus their site energies under various conditions. (a,b) For hole and electron under $F^{1/2} = 300 \text{ V}^{1/2} \text{ cm}^{-1/2}$, respectively. (c,d) For hole and electron under $F^{1/2} = 1300 \text{ V}^{1/2} \text{ cm}^{-1/2}$, respectively. $\langle \Delta E^+ \rangle$ and $\langle \Delta E^- \rangle$ are average values of site energies, ΔE_i^+ and ΔE_i^- , respectively.



Figure 1.11 Charge mobilities μ calculated without low-energy sites for (a) hole and (b) electron transport. Open circles, open upward triangles, and open downward triangles: 1%, 3%, and 5% of low-energy sites removed, respectively. Filled squares: calculated with all hopping sites.

ber of hops into site *i* (denoted by n_i^{in}) versus their site energies ($\Delta E_i^{+/-}$). When $F^{1/2} = 300 \text{ V}^{1/2} \text{ cm}^{-1/2}$, n_i^{in} is nearly exponential with the site energies (Fig. 1.10a,b), indicating that the charges mainly use *low-energy* sites (black filled area in Fig. 1.2) during the transport, that is, charge carriers tend to jump into low-energy hopping sites. Here, we note that the *low-energy* site for hole (electron) has a positively (negatively) high energy for the hopping site, as shown in Fig. 1.2. When the charge carriers escape from the low-energy hopping sites, they tend to back into the low-energy sites owing to the difference of site energies. Hence, the charge carriers frequently move forward and backward between the low-energy sites and neighboring sites under $F^{1/2} = 300 \text{ V}^{1/2} \text{ cm}^{-1/2}$.

The small number of low-energy sites significantly decreases charge mobility under weak *F* as demonstrated in the following manner. Figure 1.11 shows the mobility versus $F^{1/2}$ with low-energy 1%, 3%, and 5% of all sites removed. From Fig. 1.11, the mobility is found to be significantly influenced by the small number (1–5%) of low-energy sites when $F^{1/2} = 300 V^{1/2} \text{ cm}^{-1/2}$; it is often considered that low-energy sites trap carriers. Our results suggest that the carriers hop back and forth between the low-energy sites and neighboring sites. The carriers are not frozen in the low-energy sites, but the *round-trip* of carriers consequently consumes much time; therefore, this may also be comprehended as a kind of *trap*.

On the contrary, when $F^{1/2} = 1300 \text{ V}^{1/2} \text{ cm}^{-1/2}$, the correlation between n_i^{in} and the site energy is weak (Fig. 1.10c,d). Figure 1.11 clearly shows that the mobility does not change irrespective of the existence of low-energy sites at $F^{1/2} = 1300 \text{ V}^{1/2} \text{ cm}^{-1/2}$, indicating that these sites do not work as *traps*. The charge carriers tend to move along with *F* regardless of



Figure 1.12 Charge mobilities μ calculated under various conditions for (a) hole and (b) electron transport. Filled squares: all the pairs are used. Open circles (overlapped with filled squares): pairs with $H_{ij} < 0.1$ meV are removed. Open diamonds: pairs with $H_{ij} < 1.0$ meV are removed. Upward open triangles: pairs with $H_{ij} < 2.0$ meV are removed. Downward open triangles: pairs with $H_{ij} < 3.0$ meV are removed.

the energetic disorder.

Next, we discuss influence of the electronic coupling distribution on the mobility. The electronic coupling was distributed over the range of 0–41 meV and 0–70 meV for hole and electron, respectively (Fig. 1.4). The kMC simulations were also performed without molecular pairs with $H_{ij} < 0.1$, 1.0, 2.0, and 3.0 meV, and the calculated mobilities are shown in Fig. 1.12. The molecular pairs with $H_{ij} < 0.1$ meV do not affect charge transport (open circles in Fig. 1.12 are overlapped with filled squares). However, the contributions of the pairs with $H_{ij} < 1.0$, 2.0, and 3.0 meV are significant, especially at strong *F*. When the pairs with $H_{ij} < 3.0$ meV are removed (downward open triangles in Fig. 1.12), the mobility decreases by three or four orders of magnitude. This result clearly shows that the pairs with $H_{ij} < 3.0$ meV is frequently used as charge hopping sites although the electronic coupling is much smaller than the maximum coupling (41 meV and 70 meV for hole and electron hopping, respectively). Hence, the decrease in charge mobility by removing pairs with $H_{ij} < 1.0-3.0$ meV is attributed to the change in charge transport paths. This result indicates that in amorphous aggregates, weakly coupled pairs significantly contribute to charge mobility by forming effective charge transport paths

1.4 Conclusions

especially at strong F.

From the above discussion, in amorphous thin layers, the charge mobility is not simply determined by the maximum electronic coupling and therefore the maximum hopping rate constant, although charge mobility are often discussed by hopping rate constant. This feature is different from that of crystalline solids. Thus, consideration of different hierarchical structures is crucial for the understanding of charge mobility in amorphous organic aggregates.

1.4 Conclusions

In conclusion, the charge mobility of the organic amorphous solid was quantitatively reproduced without any adjustable parameters, by taking into account both the disorder of the energy level of hopping sites and the disordered structure. The PF behavior was also reproduced, and its origin was attributed to the influence of the energetic disorder on the charge transport trajectory; under weak F, the charge carriers go back and forth owing to the difference of the site energies, however, under strong F, the charge carriers tend to move simply along F. In amorphous organic solids, molecular pairs with relatively small electronic coupling are found to largely contribute to charge mobility, indicating that they form effective paths for charge transport.

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Chapter 2

Parameter-Free Multiscale Simulation Realizing Quantitative Prediction of Hole and Electron Mobilities in Organic Amorphous System with Multiple Frontier Orbitals

> N amorphous organic semiconducting systems, hole and electron transfer has been considered to occur based on the overlap of highest occupied molecular orbitals (HOMOs) and that of lowest unoccupied molecular orbitals (LU-MOs) between two adjacent molecules, respectively. Other molecular orbitals (MOs), HOMO-1, HOMO-2, ..., and LUMO+1, LUMO+2, ..., have been neglected in charge transport calculations. However, these MOs could potentially contribute to charge transport. In this study, our multiscale simulations show that carriers are effectively transported not only via HOMOs or LUMOs but also via other MOs when the MOs are close in energy. Because these multiple MOs are active in charge transports, here we call them *multiple frontier orbitals*. Molecules with multiple frontier orbitals are found to possess high carrier mobility. The findings in this study provide guidelines to aid design of materials with excellent charge transport properties.

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2.1 Introduction

Charge transport in organic semiconductors are important to understand performance of organic semiconductor devices such as organic light-emitting diodes (OLEDs) [1], organic fieldeffect transistors [2], and organic photovoltaic cells [3]. Much effort has been devoted to investigating the charge transport properties of organic semiconductors, typically in terms of charge mobility μ [4]. In organic *amorphous* systems, one successful description of charge transport is called the Gaussian disorder model [5]. However, because this model, which is based on hopping-type charge transport, does not take actual molecules into account, it is not straightforward to unveil the relationship between the molecular structure and charge transport properties of a material, even though this relationship is important for material design and device optimization. An explicit consideration of molecules in aggregates should be used in charge transport models to access molecular-level insight into charge transport processes [6–16].

In our previous studies, a hopping-type charge transport process in amorphous aggregates of materials used in OLEDs was investigated by a multiscale simulation including quantum chemical, molecular dynamics (MD), and kinetic Monte Carlo (kMC) calculations [12, 15]. To simulate charge transport in organic amorphous systems, an amorphous aggregate is generated by an MD simulation. In the hopping-type charge transport model, the elementary step of charge transport is charge hopping between two adjacent molecules of relevance. For various molecules or molecular pairs in the MD-constructed amorphous aggregate, the hopping site energy difference, electronic coupling, and reorganization energy associated with charge transfer are calculated, which are crucial factors determining the rate of charge hopping [4]. Starting from the molecular structure of an organic material, multiscale simulation enables us to hierarchically link the microscopic (structural and/or electronic) details to the macroscopic charge transport properties.

Disorder in an amorphous system yields *distribution* of hopping site energy and *distribution* of electronic coupling between adjacent hopping sites [4, 11]. By explicitly considering these distributions, our multiscale simulations reasonably reproduced an experimentally observed positive dependence of charge mobility versus electric field (*F*), $\partial \ln \mu / \partial F^{1/2} > 0$, which is called Poole–Frenkel-type field dependence. The experimental hole mobility was well reproduced by the multiscale simulation *without use of adjustable parameters* [15]. However, for electron transport, the agreement between simulated and experimental mobilities was not satisfactory. Because accurate physical insight into charge transport phenomena in actual organic devices has not been fully unraveled, the molecular- to device-level (i.e., multiscale) approach to investigate charge transport still needs to be further refined.

It is currently unclear if charge transport occurs only through the highest occupied molecular orbital (HOMO) or lowest unoccupied molecular orbital (LUMO) of a molecule. We envisaged that not only the HOMO or LUMO but also other molecular orbitals (MOs) may potentially contribute to charge transport. However, all previous studies simulating charge transport in organic amorphous systems do not consider MOs other than the HOMO and LUMO, except for crystalline [17, 18] or liquid crystalline [19, 20] systems. In this study, we consider the involvement of multiple MOs in charge transport in organic *amorphous* systems. Figure 2.1 shows a flowchart of our new multiscale charge transport simulation. This multiscale simulation results in excellent agreement of calculated and experimental mobilities for both hole and electron transport, as shown later. The simulations clearly show that not only the HOMO and LUMO but also other MOs are active in charge transport. From this viewpoint, we call such MOs *multiple frontier orbitals*, which are analogous to frontier orbitals in the context of chemical reactions. This study also shows that these other MOs, such as lowerlying occupied MOs (HOMO-1, HOMO-2, ...) or higher-lying unoccupied MOs (LUMO+1, LUMO+2, ...), increase charge mobility when the energy levels lie close to the HOMO or LUMO, respectively (i.e., are degenerate or quasi-degenerate). Thus, molecules with (quasi-)degenerate MOs that can behave as active multiple frontier orbitals are promising to realize highly efficient charge carrier transport.

From material

Chemical structure

4,000 molecules

Toward

device

Macroscopic

properties

Molecule j

Electrostatic interaction

Site energy

 E_i^{H-p} / E_i^{L+p}



Figure 2.1 Molecular structure of 4,4'-bis(9H-carbazol-9-yl)-1,1'-biphenyl (CBP) and flowchart of the multiscale charge transport simulation.

Charge-transfer rate constant

k^{pq}

Charge transport property

kMC simulation

2.2 Computational methods

2.2.1 Overview of charge transport model

Here, we denote HOMO–p and LUMO+p as the pth MO (p = 0, 1, ...). Note that HOMO–0 and LUMO+0 (i.e. p = 0) indicate the HOMO and LUMO, respectively. Molecules in an amorphous aggregate have different conformations, resulting in different hopping site energies. We investigated the effect of conformation on site energy, which has not been considered in our previous works [12, 15]. In addition, we included intermolecular effects, an electrostatic interaction and polarization effect of neighboring molecules in an amorphous aggregate, in the calculation of site energy as in ref. [15]. The site energy was calculated including these effects based on the energy of the corresponding MO for an isolated molecule. Such intraand intermolecular effects cause distribution of site energy, which is called *energetic disorder* or *diagonal disorder*. We defined the site energies for the HOMO–p and LUMO+p of the *i*th molecule in the amorphous aggregate as

$$E_i^{\mathrm{H}-p} = \Delta \varepsilon_i - \varepsilon_i^{\mathrm{H}-p}, \qquad (2.1)$$

$$E_i^{L+p} = \Delta \varepsilon_i + \varepsilon_i^{L+p}, \qquad (2.2)$$

where the superscript H–*p* and L+*p* indicate the HOMO–*p* and LUMO+*p*, respectively. $\Delta \varepsilon_i$ is the sum of the electrostatic interaction and polarization effect of a carrier on the *i*th molecule. ε_i^{H-p} and ε_i^{L+p} are the eigenenergies of the HOMO–*p* and LUMO+*p*, respectively, of the *i*th molecule in an isolated state retaining its molecular structure in the amorphous aggregate; these eigenenergies include the conformational effect of each molecule. Different site energies for respective molecules result in a rugged energy landscape (Fig. 2.2). A charge in a certain MO can hop to an adjacent MO. The calculations in this study were conducted for multiple adjacent molecular sites with numerous different MOs for each molecule.

2.2.2 Quantum chemical calculation and molecular dynamics simulation

In this study, we investigated charge transport in an amorphous solid of 4,4'-bis(9*H*-carbazol-9-yl)-1,1'-biphenyl (CBP; its molecular structure is shown in Fig. 2.1). The amorphous model of CBP was constructed by a MD simulation. The quantum chemical calculations and MD simulations were performed using the Gaussian 09 program package [21] and the largescale atomic/molecular massively parallel simulator (LAMMPS) program package [22], respectively. We first performed a structure optimization for an isolated CBP based on a density functional theory (DFT) calculation using the Becke three-parameter Lee–Yang–Parr (B3LYP)



Figure 2.2 Schematic illustration of the energy landscape of site energies including lower- and higherlying MOs as well as the HOMO and LUMO. E_i^{H-p} and $E_i^{L+p'}$ denote the site energies of the HOMO–pand LUMO+p' of the *i*th molecule, and E_j^{H-q} and $E_j^{L+q'}$ are those of the HOMO–q and LUMO+q' of the *j*th molecule. Dashed lines connecting two MOs represent possible hopping paths for a carrier on the HOMO–p or LUMO+p' of the *i*th molecule (represented as red and blue open circles, respectively) to various MOs of adjacent molecules *j*, *k*, etc. The thickness of the black dashed lines reflects the hopping rate constant.



Figure 2.3 Change in the density of the amorphous aggregate consisting of 4000 CBP molecules, CBP-4000-A, during the MD simulation. A similar result was obtained for CBP-4000-B.

functional [23, 24] and 6-31G* basis set. We note that the B3LYP functional was used only for the structure optimization and the calculation of reorganization energy (see below for details). The DFT-optimized CBP molecule was used as an initial molecular structure to construct amorphous aggregates. To confirm the reproducibility of charge transport simulations, we generated two amorphous models consisting of 4000 CBP molecules with different initial intermolecular structures by MD simulations. These structures are referred to as CBP-4000-A and CBP-4000-B. In the MD simulations, the Dreiding force field [25] was used, and the bond lengths and angles of the DFT-optimized molecule were applied as the equilibrium bond length and angle parameters of the force field. The coulombic interaction between atoms was calculated based on the particle-particle-particle-mesh (P3M) method [26] using atomic partial charges for the DFT-optimized molecule determined by the Merz-Singh-Kollman scheme [27]. The MD simulations were performed as follows: (i) an isochoric-isothermal (NVT) run at 573 K for 0.1 ns; (ii) an isobaric-isothermal (NPT) run at 298 K and 1.0×10^{-4} Pa for 1.0 ns using a Nosé-Hoover thermostat and barostat [28, 29]. Figure 2.3 confirms that the density of the amorphous aggregates has reached equilibrium within the above MD simulation time. In more precise, site energy and electronic coupling fluctuate due to the molecular vibrations [30-33]. The calculation of site energy and electronic coupling over a long time interval provides reasonable statistical time averages, but is time-consuming. Here, we performed energy minimization at the end of MD simulation. The resulting structures are with a side length and density of 14.6 nm and 1.04 g cm⁻³, respectively, for CBP-4000-A and 14.5 nm and 1.05 g cm⁻³, respectively, for CBP-4000-B. Unless otherwise noted, we used CBP-4000-A for the discussion

in this study.

2.2.3 Molecular orbital energy and electronic coupling

The energy of the HOMO–*p* and LUMO+*p* of the *i*th molecule, ε_i^{H-p} and ε_i^{L+p} , respectively, and the electronic coupling between the HOMO–*p* or LUMO+*p* of the *i*th molecule and the HOMO–*q* or LUMO+*q* of the *j*th molecule, H_{ij}^{pq} , were calculated based on the extended Hückel method [12, 15, 34, 35]. H_{ij}^{pq} is expressed as

$$H_{ij}^{pq} = \frac{\beta_{ij}^{pq} - (\alpha_i^p + \alpha_j^q) S_{ij}^{pq}/2}{1 - (S_{ii}^{pq})^2},$$
(2.3)

where $\alpha_i^p = \langle \psi_i^p | \hat{H}_{ij} | \psi_i^p \rangle$, $\beta_{ij}^{pq} = \langle \psi_i^p | \hat{H}_{ij} | \psi_j^q \rangle$, and $S_{ij}^{pq} = \langle \psi_i^p | \psi_j^q \rangle$. Here, \hat{H}_{ij} is the Hamiltonian of *i*-*j* dimer system. ψ_i^p and ψ_j^q are the HOMO-*p* or LUMO+*p* of the *i*th molecule and the HOMO-*q* or LUMO+*q* of the *j*th molecule, respectively. To calculate electronic coupling, the molecular pairs with a center-to-center distance of less than 2.5 nm (167 993 and 168 103 pairs for CBP-4000-A and CBP-4000-B, respectively) were included.

2.2.4 Electrostatic and polarization interactions

The calculation of the sum of the electrostatic interaction and polarization effect of a carrier on the *i*th molecule, $\Delta \varepsilon_i$, is summarized in ref. [15]. The neighboring molecules within a cutoff distance of 3.0 nm were considered in the calculation of $\Delta \varepsilon_i$. The atomic multipole optimized energetics for biomolecular applications (AMOEBA) polarizable force field [36] was used to provide atomic polarizability to calculate the dipole moments induced on neighboring molecules.

2.2.5 Reorganization energy

Reorganization energy is commonly calculated for isolated molecules, however, it has been reported that intermolecular packing in an aggregated state influences reorganization energy [15, 37, 38]. To incorporate the intermolecular steric influence of neighboring molecules into the reorganization energy, we used a quantum mechanics (QM)/molecular mechanics (MM) approach [39, 40]. The reorganization energy associated with the charge transfer from the *i*th to the *j*th molecule, λ_{ij} , was calculated based on Nelsen's four-point method [41]. DFT (B3LYP/6-31G^{*}) and the Dreiding force field were used for the QM and MM regions, respectively. The neighboring molecules within a cutoff distance of 3.0 nm were included in the MM region, and their geometries were frozen during the calculation. The atomic partial

charges of the neighboring molecules were embedded in the QM Hamiltonian. To lower the computational cost, we used an average value of λ_{ij} , $\langle \lambda_{ij} \rangle$, over randomly sampled molecules [0.105 eV/0.373 eV (45 molecules in CBP-4000-A) and 0.112 eV/0.385 eV (50 molecules in CBP-4000-B) for hole/electron transport, respectively] in the calculation of charge-transfer rate constants.

2.2.6 Charge-transfer rate constant

Using the calculated values of electronic coupling, site energy, and reorganization energy, the rate constant of charge hopping from the *p*th MO of the *i*th molecule to the *q*th MO of the *j*th molecule, k_{ii}^{pq} , was calculated based on Marcus theory [42]:

$$k_{ij}^{pq} = \frac{2\pi}{\hbar} \frac{|H_{ij}^{pq}|^2}{(4\pi \langle \lambda_{ij} \rangle k_{\rm B} T)^{1/2}} \exp\left[-\frac{(\langle \lambda_{ij} \rangle + \Delta E_{ij}^{pq} - q_{\rm c} \boldsymbol{F} \cdot \boldsymbol{r}_{ij})^2}{4 \langle \lambda_{ij} \rangle k_{\rm B} T}\right],\tag{2.4}$$

where $\hbar = h/(2\pi)$, *h* is the Planck constant, $k_{\rm B}$ is the Boltzmann constant, $q_{\rm c}$ is the charge of a carrier, F(|F| = F) is the external applied electric field, *T* is the absolute temperature, and r_{ij} is the vector connecting the *i*th and *j*th molecules. Here, ΔE_{ij}^{pq} is the difference between the site energies of the *p*th MO of the *i*th molecule and the *q*th MO of the *j*th molecule, which is defined as $\Delta E_{ij}^{pq} = E_j^{\rm H-q} - E_i^{\rm H-p}$ or $\Delta E_{ij}^{pq} = E_j^{\rm L+q} - E_i^{\rm L+p}$ for hole or electron transfer, respectively.

2.2.7 Kinetic Monte Carlo simulation

The simulations of charge transport process in a thin film consisting of the MD-constructed amorphous model of CBP were carried out by a kMC method implemented in our in-house program. All simulations were performed at 300 K under periodic boundary condition until the carriers migrated a distance (*L*) of 100 nm along *F*. *F* was set in the same direction as the *x*-, *y*-, or *z*-axis. The calculated mobilities for the three orthogonal directions were essentially the same, reflecting the isotropic nature of the amorphous system. The calculated mobilities provided in this study are the average values for these directions. We simulated 10⁴ trajectories of the carrier per direction for each of the *x*-, *y*-, and *z*-directions (3×10^4 trajectories in total) to determine the transit time *t*. The mobility μ was calculated from $\mu = L/(tF)$. Figure 2.4 shows a comparison of the calculated mobilities for CBP-4000-A and CBP-4000-B.



Figure 2.4 Charge mobility μ calculated for the two MD-constructed amorphous models of CBP, CBP-4000-A and CBP-4000-B, for (a) hole and (b) electron transport in the eight-MO model. Experimental data (black symbols) from refs. [15] (filled circles), [10] (open diamonds), [43] (open downward triangles), and [44] (open upward triangles) are also shown. Although slight variation of the calculated hole mobilities was found depending on the final structure of the amorphous model, the calculated mobilities were almost within the variation obtained experimentally.

2.3 Results and discussion

Figure 2.5 shows the density of states (DOS) for the MD-constructed amorphous CBP system. The total DOS calculated for ε_i^{H-p} or ε_i^{L+p} , which reflects the effect of various conformations of molecules in the amorphous aggregate, is distributed, even though the total DOS does not contain the effect of the intermolecular interactions (Fig. 2.5a). This clearly indicates that the energetic disorder partly originates from ε_i^{H-p} or ε_i^{L+p} , that is, different molecular conformations. When both $\Delta \varepsilon_i$ (intermolecular effect) and ε_i^{H-p} or ε_i^{L+p} (intramolecular effect) were considered in the site energy calculations [eqs. (2.1) and (2.2)], the total DOS turned to that in Fig. 2.5b, which was much broader than that considering only ε_i^{H-p} or ε_i^{L+p} (Fig. 2.5a). Here, we call the DOS for respective MOS partial DOS. It is noteworthy that the partial DOS for the HOMO–1 and LUMO+1 mostly overlapped with those for the HOMO and HOMO–1 was 55.1 meV and that between the LUMO and LUMO+1 was 3.4 meV. These results suggest that both the HOMO–1 and LUMO+1 will contribute to charge transport, which is actually the case, as shown later. The energy levels of HOMO–p and LUMO+p with $p \ge 2$ are energetically separated from those with $p \le 1$ (larger than 0.3 eV on average), suggesting these MOS make a smaller or negligible contribution to charge transport.

Next, we consider *structural disorder* (known also as *off-diagonal disorder*), that is, the distribution of electronic coupling. Here, the electronic coupling between the HOMO–*p* or LUMO+*p* of the *i*th molecule and the HOMO–*q* or LUMO+*q* of the *j*th molecule is denoted as H_{ij}^{pq} (i, j = 1, ..., 4000; p, q = 0, 1, ...). Figure 2.6 compares the probability densities of $|H_{ij}^{pq}|$, $p(|H_{ij}^{pq}|)$, in the cases in which one-, two-, four-, and eight-MOs were considered. When multiple MOs were included, the distribution of $|H_{ij}^{pq}|$ was wider than that for the one-MO. The maximum values of $|H_{ij}^{pq}|$ in the eight-MO model, 133 and 125 meV for holes and electrons, respectively, are larger than those in the one-MO model of 41 and 70 meV, respectively. This suggests that charges will hop effectively using MOs with $p \ge 1$ in terms of the electronic coupling. However, the following charge transport simulations clearly reveal that the MOs with $p \ge 2$ do not contribute to charge transport because of their unfavourable energy levels (Fig. 2.5b).

Figure 2.7 shows the calculated hole and electron mobilities as a function of $F^{1/2}$ considering one-, two-, four-, and eight-MOs as hopping sites. The calculated mobilities considering two-MOs (HOMO–1 or LUMO+1 in addition to the HOMO or LUMO) are higher than those considering only one-MO (HOMO or LUMO). Much lower- and higher-lying MOs (HOMO–2, HOMO–3, ..., and LUMO+2, LUMO+3, ...) did not influence mobilities. This result indicates



Figure 2.5 Density of states (DOS) for the amorphous CBP system calculated for (a) the site energy with intramolecular effect (without considering intermolecular interactions), ε_i^{H-p} or ε_i^{L+p} , which corresponds to MO energy, and (b) the site energy with both intra- and intermolecular interactions, $E_i^{H-p} = \Delta \varepsilon_i - \varepsilon_i^{H-p}$ or $E_i^{L+p} = \Delta \varepsilon_i + \varepsilon_i^{L+p}$. A Gaussian broadening of 25 meV was applied. Partial DOS for HOMO to HOMO-7 and LUMO to LUMO+7 are also shown. Total DOS is plotted as a superposition of the partial DOS for the eight-MOs. $\langle \varepsilon_i^{H} \rangle$, $\langle \varepsilon_i^{L} \rangle$, $\langle E_i^{H} \rangle$, and $\langle E_i^{L} \rangle$ denote the peak energies of the partial DOS for HOMO or LUMO of the corresponding cases. The energies are represented as relative values to the respective peak energies, $\langle \varepsilon_i^{H} \rangle$, $\langle \varepsilon_i^{L} \rangle$, $\langle E_i^{H} \rangle$, and $\langle E_i^{L} \rangle$.



Figure 2.6 Probability densities of electronic coupling $|H_{ij}^{pq}|$, $p(|H_{ij}^{pq}|)$, for the cases in which one-, two-, four-, and eight-MOs were included.



Figure 2.7 Calculated and experimental charge mobilities μ for (a) hole and (b) electron transport as a function of $F^{1/2}$. The calculated results for two-, four-, and eight-MO models overlapped. The colored open diamonds represent the mobilities assuming that all eight-MOs are quasi-degenerate; they possess an energy difference originating only from the intermolecular interaction (i.e., $E_i^{\text{H}-p} = \Delta \varepsilon_i$ and $E_i^{\text{L}+p} = \Delta \varepsilon_i$; its standard deviation is ~0.1 eV). The experimental data are also shown as black symbols with the same notation as in Fig. 2.4.

that the MOs contribute to charge transport only when they lie close in energy, even if the relevant electronic coupling is considerable. Experimental data obtained by a time-of-flight method [10, 15, 43, 44] are also shown in Fig. 2.7. The two-MO model resulted in excellent agreement with the experimental data for both hole and electron transport. Of course, the four- and eight-MO models also reproduced the experimental data, but these models are less computationally efficient than the two-MO model.

To obtain further details, we calculated the number of carrier hops from the *q*th MO of the *j*th molecule to the *p*th MO of the *i*th molecule, n_{ii}^{qp} (note that n_{ii}^{pq} represents the hopping in the opposite direction). Using n_{ji}^{qp} , the number of incoming carriers from all adjacent MOs to the *p*th MO of the *i*th molecule can be expressed as $n_i^p = \sum_{j,q} n_{ji}^{qp}$. Figure 2.8 shows the sum of n_i^p over all 4000 molecules in the aggregate, $n^p = \sum_i n_i^p$, which reflects the frequency of using the *p*th MOs in the amorphous system during charge transport over a distance of 100 nm along F (all values are the average of 30 000 trials of the kMC simulation). It is clear that the HOMO-1 and LUMO+1 were frequently used as well as the HOMO and LUMO during hole and electron transport, respectively. In electron transport, the contributions of the LUMO+1 and LUMO are nearly equal $(n^1 \approx n^0)$. In contrast, the HOMO-1 was used slightly less frequently than the HOMO for hole transport ($n^1 < n^0$), reflecting the smaller energy difference between the LUMO and LUMO+1 (3.4 meV on average) compared to that between the HOMO and HOMO-1 (55.1 meV on average). This readily explains the larger increase of electron mobility than that of hole mobility when we include the contributions of the HOMO-1 and LUMO+1 in addition to the HOMO and LUMO (Fig. 2.7). Figure 2.8 also reveals that the contributions of MOs with $p \ge 2$ were much smaller than those of the HOMO, HOMO-1, LUMO, and LUMO+1 (see Fig. 2.9 for MOs with $p \ge 4$). This is consistent with the negligible contributions of these MOs to the charge mobilities in Fig. 2.7. According to Marcus equation [eq. (2.4)], the rate constant for charge hopping from lower-lying MO (HOMO–*p* with large *p*) to HOMO is larger than that for hopping between two HOMOs due to the large difference in site energy. Therefore, holes occupying HOMO-p with large p were immediately transferred to HOMO or HOMO-1 during a few tens of hopping steps in our simulations, which were negligibly short compared with the whole charge hopping process (shorter than 1/100 of the whole process, see Fig. 2.10a), in spite that no assumption was made for a probability of charge injection among the multiple MOs and that the internal conversion of carriers was not considered. In addition to HOMO and HOMO-1, HOMO-2 and HOMO-3 were used sometimes (Fig. 2.10a), because the high energy edges of HOMO-2 and HOMO-3 are within the energy distribution of HOMO and HOMO-1 (see Fig. 2.5b). This indicates that the phenomenon originates from the distribution of site energy, that is, energetic disorder. The same picture



Figure 2.8 Number of incoming carriers from all adjacent MOs to *p*th MOs in the amorphous system, n^p , as a function of $F^{1/2}$ for (a) hole and (b) electron transport in the four-MO model. n^p is averaged over 30 000 trials of the kMC simulation.



Figure 2.9 Number of incoming carriers from all adjacent MOs to *p*th MOs in the amorphous system, n^p , as a function of $F^{1/2}$ for (a) hole and (b) electron transport in the eight-MO model. n^p is averaged over 30 000 trials of the kMC simulation.



Figure 2.10 Change in charge occupation of *p*th MOs for (a) hole and (b) electron transport in the eight-MO model. 100 trials of the kMC simulation at $F^{1/2} = 800 \text{ V}^{1/2} \text{ cm}^{-1/2}$ are superposed. The first 200 hopping steps are expanded in the inset.

holds true for electron hopping (Fig. 2.10b and Fig. 2.5b).

The above discussion and Fig. 2.7 reveal that MOs with close energy levels to those of HOMO and LUMO are involved in charge transport in organic amorphous systems. These MOs are active in charge transport, so we call such multiple MOs *multiple frontier orbitals*. The above results and discussion also indicate that high charge mobility can be achieved when as many as possible MOs lie close in energy to the HOMO or LUMO (i.e., are degenerate or quasi-degenerate). We obtained very high hole and electron mobilities (blue and red open diamonds in Fig. 2.7a,b, respectively) when the eight-MOs in our amorphous system were close in energy. The hole and electron mobilities of the eight-MO model with degenerate MOs were more than one order of magnitude higher than those of the one-MO model without degenerate MOs (blue and red open circles in Fig. 2.7a,b, respectively). We found that all the MOs were used almost equally when the eight-MOs were close in energy, as shown in Fig. 2.11 (n^p versus $F^{1/2}$).

Here, we present detailed molecular-level analysis of the contributions of nine MO pairs that are combinations of three MOs, LUMO, LUMO+1, and LUMO+2 for electron transport (Fig. 2.12; the calculated results for hole transport are summarized in Fig. 2.13). Figure 2.12 shows the number of electron hops between the LUMO+p of the *i*th molecule and the LUMO+q of the *j*th molecule, n_{ij}^{pq} and n_{ji}^{qp} , for the pair consisting of the 1207th and 2650th molecules in our amorphous system, corresponding to the four-MO model in Fig. 2.7 (and Fig. 2.8), as an example. This is one of the most frequently used molecular pairs in electron transport. There are various intermolecular packings in the amorphous aggregate, and the intermolecular orientations and distances between two molecules strongly affect their electronic coupling. In Fig. 2.12, although the intermolecular orientation and distance remain the same, the intermolecular overlap between two MOs strongly depends on the spatial distribution of the respective MOs. The various overlaps influence the electronic coupling. The electronic coupling between the two LUMO+1's of the two molecules $(|H_{1207,2650}^{11}| = 30.4 \text{ meV}; \text{ the MO})$ pair in a red box in Fig. 2.12) is the largest among the nine MO pairs because of the sufficient overlap between the two MOs (both MOs are localized at the contacting part). In contrast, the electronic couplings are smaller when one (MO pairs in green boxes in Fig. 2.12) or both (MO pairs in blue boxes) of the relevant MOs are localized far from the contacting part of the two molecules. Figure 2.12 also shows the site energy difference, $\Delta E_{1207,2650}^{pq}$ where $p, q \leq 2$. We clearly found that the LUMO+2 was not used for electron transport because the site energy differences between the LUMO and LUMO+2 or the LUMO+1 and LUMO+2 were larger than 0.3 eV, and the values of $n_{1207,2650}^{pq}$ were negligibly small; that is, it is energetically unfavourable for the charge to hop to the LUMO+2 for these MO pairs. The site energy differences between



Figure 2.11 Number of incoming carriers from all adjacent MOs to *p*th MOs in the amorphous system, n^p , as a function of $F^{1/2}$ for (a) hole and (b) electron transport where all eight MOs, HOMO to HOMO–7 or LUMO to LUMO+7, are quasi-degenerate. n^p is averaged over 30 000 trials of the kMC simulation.



Electron transport (CBP#1207 & CBP#2650)

Figure 2.12 Examples of MO pairs for electron transport with $p \le 2$ (LUMO to LUMO+2), depicted with an isosurface of 0.02 au. The red, green, and blue boxes indicate the MO pairs in which the two MOs exhibit sufficient overlap (red), one of the relevant MOs is localized on a contacting part of the relevant molecule (green), and both of the relevant MOs are localized far from the contacting part (blue), respectively. The electronic coupling $|H_{ij}^{pq}|$, site energy difference ΔE_{ij}^{pq} , and number of hops between the *p*th MO of the *i*th molecule and the *q*th MO of the *j*th molecule, n_{ij}^{pq} and n_{ji}^{qp} , for each pair are also provided. n_{ij}^{pq} and n_{ji}^{qp} are averaged over 30 000 trials of the kMC simulation at $F^{1/2} = 800 \text{ V}^{1/2} \text{ cm}^{-1/2}$.



Figure 2.13 Examples of MO pairs for hole transport with $p \le 2$ (HOMO to HOMO–2), depicted with an isosurface of 0.02 au. The electronic coupling $|H_{ij}^{pq}|$, site energy difference ΔE_{ij}^{pq} , and number of hops between the *p*th MO of the *i*th molecule and the *q*th MO of the *j*th molecule, n_{ij}^{pq} and n_{ji}^{qp} , for each pair are also provided. n_{ij}^{pq} and n_{ji}^{qp} are averaged over 30 000 trials of the kMC simulation at $F^{1/2} = 800 \text{ V}^{1/2} \text{ cm}^{-1/2}$.
(a) Hole transport								
n ^{pq}	НОМО	HOMO-1	HOMO-2	HOMO-3				
НОМО	5118.2	1454.6	0.2	0.3				
HOMO-1	1454.8	288.2	0.3	0.2				
HOMO-2	0.3	0.4	0.6	0.7				
HOMO-3	0.4	0.4	0.7	0.7				
(b) Electron transport								
(b) Electron	transport							
(b) Electron n^{pq}	transport LUMO	LUMO+1	LUMO+2	LUMO+3				
$\frac{(b) \text{ Electron}}{n^{pq}}$ LUMO	LUMO 1030.6	LUMO+1 1600.0	LUMO+2 0.3	LUMO+3 0.0006				
$\frac{(b) \text{ Electron}}{n^{pq}}$ $\frac{1}{10000000000000000000000000000000000$	LUMO 1030.6 1600.0	LUMO+1 1600.0 1423.4	LUMO+2 0.3 0.3	LUMO+3 0.0006 0.001				
(b) Electron n^{pq} LUMO LUMO+1 LUMO+2	LUMO 1030.6 1600.0 0.4	LUMO+1 1600.0 1423.4 0.4	LUMO+2 0.3 0.3 0.03	LUMO+3 0.0006 0.001 0.008				
(b) Electron n^{pq} LUMO LUMO+1 LUMO+2 LUMO+3	LUMO 1030.6 1600.0 0.4 0.1	LUMO+1 1600.0 1423.4 0.4 0.1	LUMO+2 0.3 0.3 0.03 0.03 0.05	LUMO+3 0.0006 0.001 0.008 0.02				

Table 2.1 Number of carrier hops from *p*th to *q*th MOs summed over all possible molecular pairs, $n^{pq} = \sum_{i,j} n^{pq}_{ij}$, for (a) hole and (b) electron transport.

Note: All values are averaged over 30 000 trials of the kMC simulation at $F^{1/2} = 800 \text{ V}^{1/2} \text{ cm}^{-1/2}$.

the two LUMOs, $\Delta E_{1207,2650}^{00}$, between the LUMO and LUMO+1, $\Delta E_{1207,2650}^{01}$ and $\Delta E_{1207,2650}^{10}$, and between the two LUMO+1's, $\Delta E_{1207,2650}^{11}$, were comparable ($\approx 100 \text{ meV}$). Thus, the number of hops for these MO pairs is solely determined by the electronic coupling between the two relevant MOs; the largest electronic coupling, which is found for the two LUMO+1's, results in the largest number of hops ($n_{1207,2650}^{11} = 103.3$ and $n_{2650,1207}^{11} = 103.0$).

The same discussion holds for the whole amorphous system. Table 2.1 shows the number of hops from *p*th to *q*th MOs, $n^{pq} = \sum_{i,j} n_{ij}^{pq}$, for the whole system. It is found that the charge hopping involving not only the HOMO and LUMO but also the HOMO-1 and LUMO+1 strongly contributes to charge transport in the whole system. Table 2.1 also clearly indicates that the MO pairs with $p \ge 2$ or $q \ge 2$ were rarely used in both hole and electron transport. The charge transport simulation including the charge hopping involving the HOMO-1 and LUMO+1 in addition to the HOMO and LUMO successfully described the charge transport properties for the amorphous aggregate of CBP.

2.4 Conclusions

In conclusion, we proposed a multiscale simulation scheme that considers lower- and higherlying MOs in addition to HOMO and LUMO to investigate charge transport in amorphous systems of organic materials. To our knowledge, this is the first study that explicitly includes multiple MOs in the calculation of charge transport in an *amorphous* system. As for crystalline or liquid crystalline systems, a few reports considering lower- or higher-lying MOs were found [17–20]. In these studies, the electronic state of hopping sites was obtained using mathematical techniques, such as a symmetric orthogonalization [17] or symmetry-adapted linear combination [19, 20]. However, these approaches have high computational cost or cannot be applied to systems without structural symmetry. In contrast, our simple simulation scheme can be widely applied with reasonable cost irrespective of the structural symmetry of the system. Our simulations quantitatively reproduced experimentally determined mobilities for both hole and electron transport. The detailed analysis revealed that not only the HOMO and LUMO but also the HOMO-*p* and LUMO+p' contributed markedly to the charge transport in the amorphous solid when their energy levels were comparable to those of the HOMO or LUMO. Thus, multiple frontier orbitals can be actively involved in charge transport. These findings indicate that (quasi-)degenerate MOs play a crucial role in charge transport. Designing materials with multiple frontier orbitals will be a promising approach to realize excellent charge transport properties.

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Chapter 2

Chapter 3

Effects of Calculation Levels on Multiscale Charge Transport Simulation in Organic Amorphous Systems

> HARGE transport is a key parameter that determines performance of organic electronic devices, and has been investigated experimentally and computationally. Recently, multiscale charge transport simulations have been carried out because molecular- to device-level understanding are necessary to elucidate charge transport in organic semiconductors. In the case of organic light-emitting diodes, charge transport materials are in amorphous state, which needs to be treated as a large atomistic system in silico in contrast to ordered crystalline systems with periodic boundary condition. In such a situation, it is challenging to design charge transport materials using the multiscale simulation in a high-throughput manner. The reduction of computational cost is desired for the realization of high-throughput multiscale simulation. In this study, on the basis of our developed charge transport simulation, we investigate the effects of calculation levels including semiempirical method and density functional theory (DFT) on charge transport properties to assess the accuracy and cost of computation. The calculation level is found to significantly affect charge transport properties such as hopping site energy or electronic coupling. The semiempirical-based simulation provides reasonable prediction of charge mobility of organic materials, whereas the DFT-based simulation does not yield best agreement with experiments. Considering the computational cost, the use of semiempirical method is found to be reasonable and cost-effective to predict charge mobility. Our charge transport simulation is promising approach to design excellent organic amorphous semiconductors.

Chapter 3 Effects of Calculation Levels on Multiscale Charge Transport Simulation in Organic Amorphous Systems

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Introduction 3.1

Developing organic materials with desired optoelectronic properties is essential for realization of highly efficient organic electronics devices, such as organic light-emitting diodes (OLEDs) [1], organic photovoltaic cells [2], and organic field-effect transistors [3]. A quantum chemical-based computational approach has been utilized to design materials because high performance computing technology has been available for material chemists. Recently, we have successfully developed highly efficient emitters for OLEDs exhibiting thermally activated delayed fluorescence by means of high-throughput screening based on quantum chemical calculations [4-10]. The screening of emitting materials can be conducted by single-molecule calculations because the photophysical properties predominantly depend on its molecular structure. Another property of organic materials, charge transport property, is also related to the device efficiency. In contrast to photophysical properties, charge transport largely depends not only on molecular structure itself but also intermolecular packing. The high-throughput screening is challenging because *ab initio* simulation of charge transport ranging from molecular- to device-level demands very high computational cost. To design excellent charge transport materials in a high-throughput way, prediction of charge transport properties such as charge mobility should be more cost-efficient. On the other hand, it is also important to develop more reliable computational approach for charge transport simulation. Therefore, a compromise between the cost and accuracy of the methods needs to be judged when one uses in silico approaches in design of organic semiconductors. In this study, we investigated effects of computational methods used in our recently developed charge transport simulation [11–13] on charge transport properties.

Charge transport materials used for OLEDs are usually in amorphous state. Therefore, it is essential to explicitly consider conformational and intermolecular disorders. To investigate charge transport properties in organic amorphous systems, combined use of molecular mechanical [or molecular dynamics (MD)] and quantum chemical calculations have been utilized in several groups [11-22]. It is often called a multiscale simulation since the target system of these calculations ranges from microscopic molecular- to macroscopic device-level. In a general multiscale simulation, an organic amorphous system is modeled by MD [11-13, 15-17, 19–21] or Monte Carlo simulations [14, 22], and an electronic state relevant to charge transport is evaluated based on quantum chemical calculations. A simulation of charge transport in organic amorphous systems is generally based on hopping-type charge transport mechanism [23]. In this mechanism, the energy of respective orbitals on a molecule (site energy) as well as the electronic coupling and the reorganization energy between two molecules associated with charge hopping are crucial factors determining the hopping rate. Macroscopic charge transport is simulated based on the charge hopping rate constant. Several approaches, including a master equation for drift-diffusion of carriers [15, 17, 22], application of the Einstein relation of charge diffusion [16, 20, 24], and a kinetic Monte Carlo (kMC)-based simulation [11–14, 17, 19, 21], have been developed to obtain macroscopic properties, such as charge mobility and current density-voltage characteristics. A benefit of the multiscale simulation is that it provides the relationship between the microscopic (structural and/or electronic) nature and the macroscopic charge transport properties.

A critical drawback of the multiscale simulation is that an *in silico* amorphous system should be sufficiently large due to its un-periodic structure. To overcome this situation, some parametrizations have been proposed by several groups [18]: for example, a disordered-lattice model imitating amorphous systems such as the Gaussian disorder model (GDM) [25] and some models extended from the GDM [26–28], or alternatively, a coarse-grained off-lattice model describing the morphology and properties related to charge transport [29, 30]. These strategies are expected to reduce computational cost significantly, however, Kordt et al. have pointed out that the parametrization relies on approximations that are made in model construction and may not always hold true for the system of interest [18]. The model for predicting charge transport properties should reflect the real system.

In our recent studies [11–13, 19], we have used all-atom amorphous systems composed of 4000 molecules and $\sim 10^5$ molecular pairs without parametrization. In return for the use of such large atomistic systems, we have utilized a semiempirical method, extended Hückel the-



Figure 3.1 Structures of molecules used in this study.

ory (EHT) [31], for the calculation of site energy and electronic coupling to reduce computational cost. For charge transport material used in OLEDs, 4,4'-bis(9*H*-carbazol-9-yl)-1,1'biphenyl (CBP; Fig. 3.1), the mobility calculated by our multiscale charge transport simulation successfully agreed with the experimental mobility quantitatively without any use of adjustable parameters [13]. However, for another material, $N^4, N^{4'}$ -di(naphthalen-1-yl)- $N^4, N^{4'}$ diphenyl-[1,1'-biphenyl]-4,4'-diamine (α -NPD; Fig. 3.1), the agreement between the calculated and experimental mobilities was insufficient as shown later. In this work, we compare three calculation methods, EHT, intermediate neglect of differential overlap (INDO), density functional theory (DFT), to assess the validity. Among them, the DFT-based calculation requires high computational cost for an immense number of molecules and molecular pairs in the system. From the comparison, the EHT calculations were found to be reasonable and cost-effective to predict charge mobility of organic amorphous semiconductors.

3.2 Computational methods

3.2.1 Overview

To assess the effects of calculation method on the charge transport properties, we conducted the multiscale charge transport simulation for amorphous systems of α -NPD and CBP. Since these materials are known to be capable of hole transport, we focused the simulations for hole transport. Our multiscale simulation treats the amorphous system constructed by an all-atom MD simulation. On the basis of the MD-constructed amorphous system, the site energy, electronic coupling, and reorganization energy, and then intermolecular charge transfer rate constant were calculated for the actual molecules and molecular pairs by taking into account their amorphous-natured disorders. We performed kMC calculations to simulate charge transport process and to obtain the charge mobility. Our model considers contributions of not only highest occupied molecular orbital (HOMO) but also low-lying HOMO–p (p = 1, 2, ...; p = 0 indicates HOMO), which have often been neglected for a typical charge transport simulation scheme. Our previous study clearly revealed that low-lying molecular orbitals (MOs) largely contribute charge transport when they energetically lie close to HOMO [13].

The calculations of site energy and electronic coupling were carried out using EHT and INDO approximation [32] as semiempirical methods. DFT was also used. The details of computation are provided in following sections.

3.2.2 Construction of amorphous models

Amorphous aggregates used in this study were constructed using all-atom MD simulations as described in refs. [11-13]. All the MD simulations were performed using the large-scale atomic/molecular massively parallel simulator (LAMMPS) code [33]. A supercell system composed of 4000 molecules with random molecular orientations in a cubic cell was used as an initial structure. A density of the initial structures is less than $0.1 \,\mathrm{g}\,\mathrm{cm}^{-3}$. Periodic boundary condition was applied to the supercell. An initial molecular conformation in the system was obtained by a DFT optimization using the Becke three-parameter Lee-Yang-Parr (B3LYP) functional [34, 35] and 6-31G* basis set, performed by the Gaussian program package [36]. In the MD simulations, the Dreiding force field [37] was used as an interatomic potential, and the parameters for bond lengths and angles in the force field were replaced with those obtained by the DFT calculation. The coulombic interaction between atoms was calculated by the particle-particle-mesh (P3M) method [38] using atomic partial charges for the DFToptimized molecules determined by the Merz-Singh-Kollman (MK) scheme [39]. The MD simulations were performed as follows: (i) an isochoric-isothermal (NVT) run at 573 K for 0.1 ns; (ii) an isobaric-isothermal (NPT) run at 298 K and 1.0×10^{-4} Pa using a Nosé–Hoover thermostat and barostat [40, 41] until the density of the system converged. To alleviate undesired distortion of molecular structure in the aggregated system, energy minimization was performed at the end of MD run.

3.2.3 Calculation of site energy

To incorporate the contribution of MOs lying lower than HOMO in energy to charge transport, we introduce the site energy for the HOMO–p of molecule *i* as [13]

$$E_i^{\mathrm{H}-p} = \Delta \varepsilon_i - \varepsilon_i^{\mathrm{H}-p}.$$
(3.1)

where ε_i^{H-p} is the eigenenergy of the HOMO-*p* of molecule *i*. Respective molecules in the amorphous aggregate have different ε_i^{H-p} because of their different conformations. $\Delta \varepsilon_i$ is the sum of electrostatic and polarization energy for the carrier on molecule *i*, which originates

from intermolecular interaction between the carrier and neighboring molecules in the amorphous aggregate. ε_i^{H-p} was calculated at EHT, INDO, and DFT levels using the Gaussian program package. The B3LYP functional and 6-31G* basis set was used in the DFT calculation of the eigenenergy. To obtain $\Delta \varepsilon_i$, electrostatic interaction and the dipole moment induced on neighboring molecules were calculated [11] using the atomic partial charges of molecules by the MK scheme and the atomic multipole optimized energetics for biomolecular applications (AMOEBA) polarizable force field [42]. The neighboring molecules with an intermolecular distance within 3.0 nm were considered in the calculation of $\Delta \varepsilon_i$.

3.2.4 Calculation of electronic coupling

The electronic coupling between two MOs relevant to charge transfer in a *i*-*j* molecular dimer system was calculated according to the site-energy corrected splitting scheme introduced by Valeev et al. [43]. To quantify the coupling between not only HOMOs but also other lowerlying MOs, we define the HOMO-*p* of molecule *i* and the HOMO-*q* of molecule *j* as ψ_i^p and ψ_j^q , respectively [13]. These MOs were calculated within an isolated monomer system retaining its molecular structure in the amorphous system. The electronic coupling between ψ_i^p and ψ_j^q in the dimer system, H_{ij}^{pq} , can be expressed as following equation [43] by means of the Löwdin's symmetric transformation [44]:

$$H_{ij}^{pq} = \frac{\beta_{ij}^{pq} - (\alpha_i^p + \alpha_j^q) S_{ij}^{pq} / 2}{1 - (S_{ii}^{pq})^2},$$
(3.2)

with $\alpha_i^p = \langle \psi_i^p | \hat{H}_{ij} | \psi_i^p \rangle$, $\beta_{ij}^{pq} = \langle \psi_i^p | \hat{H}_{ij} | \psi_j^q \rangle$, and $S_{ij}^{pq} = \langle \psi_i^p | \psi_j^q \rangle$. Here, \hat{H}_{ij} is the Hamiltonian of the relevant dimer system. We calculated H_{ij}^{pq} at EHT and INDO levels using the Gaussian program package. The calculation was conducted for the molecular dimers with an intermolecular distance within 2.5 nm (125 873 and 167 993 dimers for α -NPD and CBP, respectively).

For comparison, we also calculated H_{ij}^{pq} at DFT level, using the fragment molecular orbital (FMO) approach [45] implemented in the Amsterdam density functional (ADF) program [46–48]. In the DFT calculation, \hat{H}_{ij} in eq. (3.2) is replaced with the Kohn–Sham (KS) Hamiltonian of the dimer system. The ADF program has the feature that directly provides α_i^p and β_{ij}^{pq} as diagonal and off-diagonal matrix elements of the KS Hamiltonian, respectively, and S_{ij}^{pq} as overlap matrix elements [49]. The calculations were performed using the Becke–Perdew generalized gradient approximation (GGA) exchange–correlation (XC) functional (BP86 in ADF) [34, 50] and the Perdew–Wang GGA XC functional (PW91 in ADF) [51]. We tested the validity of several Slater-type orbital (STO) basis sets for both functionals using a single- ζ valence

quality minimal STO basis set (SZ basis set in ADF), a double- ζ valence quality STO (DZ) basis set, a singly polarized double- ζ valence quality STO (DZP) basis set, a singly polarized triple- ζ valence quality STO (TZP) basis set, and a doubly polarized triple- ζ valence quality STO (TZP) basis set [52]. Except for the SZ basis set, all the basis sets we tested provided almost the same results as shown in Figs. 3.2 and 3.3 as discussed later. For safety, we used the TZP basis set in the following charge transport simulations. The calculation of electronic coupling in amorphous systems should be carried out for a tremendous number of molecular dimers (~10⁵ dimers, see above). The DFT calculations are impossible at present. Thus we conducted the computation at DFT not for all the molecular dimers but for randomly selected 128 dimers in the amorphous system (the calculation is henceforth referred to as the 128-dimers calculation). Note that the same 128 dimers were used among the respective calculations.

We estimated the values of electronic coupling at DFT level for *all the dimers* within the cutoff distance of 2.5 nm, based on those for 128 dimers. We first compared the values calculated by the semiempirical methods (EHT and INDO) for the same 128 dimers and for all the dimers. We confirmed that the 128-dimer calculation provided reasonable distribution compared to the all-dimers calculation (Fig. 3.4). Figure 3.5a,c,e,g show correlations and two-dimensional probability density functions p(x, y) of electronic coupling between EHT/INDO and DFT levels (x: log $|H_{ij}^{pq}|$ at EHT/INDO level, y: that at DFT level). The DFT-based electronic coupling for *all the dimers* were determined by stochastically sampling values from the one-dimensional probability density function, p(x = x', y), where x' is the EHT/INDO-calculated value for the respective dimers. We confirmed that the correlations for the sampled electronic coupling were consistent with the referenced correlations (Fig. 3.5a,c,e,g versus Fig. 3.5b,d,f,h).

3.2.5 Charge transport simulation

The charge transport simulations in a thin film consisting of the MD-constructed amorphous aggregate were performed using a kMC algorithm implemented in our in-house program [13]. A rate constant of hole transfer from HOMO–*p* of molecule *i* to HOMO–*q* of molecule *j*, k_{ij}^{pq} , was calculated based on Marcus theory [53], in which k_{ij}^{pq} is expressed as

$$k_{ij}^{pq} = \frac{2\pi}{\hbar} \frac{|H_{ij}^{pq}|^2}{(4\pi \langle \lambda_{ij} \rangle k_{\rm B} T)^{1/2}} \exp\left[-\frac{(\langle \lambda_{ij} \rangle + \Delta E_{ij}^{pq} - q_{\rm c} \boldsymbol{F} \cdot \boldsymbol{r}_{ij})^2}{4 \langle \lambda_{ij} \rangle k_{\rm B} T}\right],\tag{3.3}$$



Figure 3.2 Probability density functions of electronic coupling, $p(\log |H_{ij}^{pq}|)$, calculated using DFT with different functionals and basis sets in the amorphous systems of (a) α -NPD and (b) CBP. The contributions of HOMO and HOMO–1 were included. All the distributions were obtained from the calculations for the same 128 dimers used in the DFT-based calculation. No significant difference between the distributions was obtained for two functionals, BP86 and PW91. The DZ, DZP, TZP, and TZ2P basis sets provided almost same distributions irrespective of the functional. The SZ estimated smaller electronic coupling for both two functionals compared to the other basis sets.

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Figure 3.3 Correlation of electronic coupling calculated using different methods, EHT, INDO, BP86/SZ, BP86/DZ, BP86/DZP, BP86/TZP, BP86/TZ2P, PW91/SZ, PW91/DZ, PW91/DZP, PW91/TZP, and PW91/TZ2P. The correlation was obtained from the calculations with different methods for the same 128 dimers used in the DFT-based calculation. The contributions of HOMO to HOMO–7 were included. The contours represent two-dimensional probability density of each correlation plot. (a) For the amorphous system of α -NPD.







Figure 3.4 Probability density functions of electronic coupling, $p(\log |H_{ij}^{pq}|)$, calculated using EHT and INDO for the amorphous systems of (a) α -NPD and (b) CBP. The distributions were obtained from the calculations for the same 128 dimers used in the DFT-based calculation. The results calculated for the all-dimers are also shown for comparison. The contributions of HOMO and HOMO–1 were included. This figure indicates that the 128-dimers calculation provided statistically reasonable distributions of electronic coupling. Note that contribution of the dimers with electronic coupling smaller than 10^{-4} eV (gray region) was negligible for charge transport.



Figure 3.5 Correlations of electronic coupling between the semiempirical method (EHT or INDO) and DFT (BP86/TZP), which were used for the estimation of electronic coupling at DFT level. (a,c,e,g): The reference correlations obtained by the calculation for the same 128 dimers used in the DFT-based calculation. (b,d,f,h): The correlations obtained by the estimated electronic coupling. The contours represent two-dimensional probability density of each correlation plot. (a–d) For the amorphous system of α -NPD.





where $\hbar = h/(2\pi)$, h is the Planck constant, $k_{\rm B}$ is the Boltzmann constant, q_c is the charge of a carrier, T is the absolute temperature, F is the external applied electric field (|F| = F), r_{ij} is the vector connecting molecule *i* and *j*, and ΔE_{ij}^{pq} is the site energy difference defined as $\Delta E_{ij}^{pq} = E_i^{H-q} - E_i^{H-p}$. The calculated reorganization energies associated with hole transfer, $\langle \lambda_{ii} \rangle$, for α -NPD and CBP were taken from those reported previously (0.289 eV [12] and 0.105 eV [13], respectively). The calculations included intermolecular influence of adjacent molecules in the aggregated state [54, 55] by quantum mechanics (QM)/molecular mechanics (MM) method [56, 57]. All kMC simulations were performed with periodic boundary condition applied in x-, y-, and z-axes. A transport process of carriers was simulated until the carriers migrated a distance (L) of 100 nm along F, which was applied in the same direction as the x-, y-, or z-axis. The transit time of the carriers, t, was determined from 10^4 kMC trials per direction of $F(3 \times 10^4 \text{ trials in total})$ and the mobility μ was calculated from $\mu = L/(tF)$. Reflecting isotropic nature of the MD-constructed amorphous system, the resulting mobilities possessed no anisotropic feature among the three orthogonal directions. To investigate the effect of calculation levels on the calculated mobility, we used several combinations of the site energy and electronic coupling with different calculation levels, EHT, INDO, and DFT.

3.3 Results and discussion

3.3.1 Site energy

Figure 3.6 shows the density of states (DOS) of occupied state for the amorphous systems of α -NPD and CBP calculated at EHT, INDO, and DFT levels. The DOS and partial DOS (pDOS) were obtained by summation of site energies for all the 4000 molecules in the MD-constructed amorphous aggregate. Gaussian broadening of 25 meV was applied in the summation. The standard deviations (widths) of pDOS are provided in Table 3.1, which ranged from 0.106–0.177 eV. The energy levels of HOMO–*p* relative to HOMO are also summarized in the table. The different calculation methods provided different results. This originates from the conformational contribution to site energy [the term of ε_i^{H-p} in eq. (3.1), see Fig. 3.7 for the distribution of ε_i^{H-p}]. In the case of α -NPD (Fig. 3.6a), the INDO- and DFT-calculated DOS were similar for HOMO and HOMO–1 (0–1 eV), whereas the EHT-calculated HOMO and HOMO–1 were distributed in narrower region (0–0.6 eV). The difference was more significant for HOMO–2 and HOMO–3. In contrast, in the case of CBP (Fig. 3.6b), the EHT-calculated DOS agreed well with the DFT-calculated one from HOMO to HOMO–3, while INDO provided significantly different results; the energy split between HOMO–1 and HOMO–2 was



Figure 3.6 DOS of occupied state for the amorphous systems of (a) α -NPD and (b) CBP calculated using EHT, INDO, and DFT (B3LYP/6-31G*). All the DOS were obtained by summation of site energies for all 4000 molecules in the MD-constructed amorphous aggregate, with Gaussian broadening of 25 meV applied. pDOS of HOMO to HOMO-3 are also shown. E_{on}^{H} denotes the onset energy for the pDOS of HOMO and the energy is represented relative to E_{on}^{H} . The MOS lying lower by >0.3 eV in energy than the HOMO (gray region) do not contribute to charge transport [13].

Table 3.1 Standard deviations of pDOS for HOMO–p, σ^{H-p} , and energy shift relative to pDOS of HOMO on average, $\langle E_i^{H-p} \rangle - \langle E_i^H \rangle$, calculated using EHT, INDO, and DFT (B3LYP/6-31G*) in the amorphous systems of α -NPD and CBP.

Material	Method	МО	p	$\sigma^{\mathrm{H}-p}$ (eV)	$ \begin{array}{c} \langle E_i^{\mathrm{H}-p} \rangle - \langle E_i^{\mathrm{H}} \rangle \\ (\mathrm{eV}) \end{array} $
a-NPD	EHT	НОМО	0	0.133	0.000
		HOMO-1	1	0.131	0.090
		HOMO-2	2	0.132	0.467
		HOMO-3	3	0.131	0.500
	INDO	HOMO	0	0.177	0.000
		HOMO-1	1	0.168	0.309
		HOMO-2	2	0.150	0.956
		HOMO-3	3	0.159	1.127
	DFT	HOMO	0	0.155	0.000
		HOMO-1	1	0.152	0.244
		HOMO-2	2	0.137	0.680
		HOMO-3	3	0.136	0.791
CBP	EHT	HOMO	0	0.112	0.000
		HOMO-1	1	0.108	0.064
		HOMO-2	2	0.107	0.365
		HOMO-3	3	0.107	0.370
	INDO	HOMO	0	0.130	0.000
		HOMO-1	1	0.111	0.146
		HOMO-2	2	0.108	1.146
		HOMO-3	3	0.107	1.161
	DFT	HOMO	0	0.111	0.000
		HOMO-1	1	0.107	0.056
		HOMO-2	2	0.107	0.338
		HOMO-3	3	0.106	0.372



Figure 3.7 Distribution of eigenenergy (conformational contribution to the DOS) of occupied state for the amorphous systems of (a) α -NPD and (b) CBP calculated using EHT, INDO, and DFT (B3LYP/6-31G*). The same Gaussian broadening as in Fig. 3.6 was applied. Partial distributions of HOMO to HOMO–3 are also shown. E_{on}^{H} denotes the onset eigenenergy of HOMO and the energy is represented relative to E_{on}^{H} . In the case of CBP (b), the conformational contribution does not dominate the final DOS regardless of the calculation method (see Fig. 3.6), whereas for α -NPD (a), INDO and DFT provide the broader distributions resulting in the broader DOS (Fig. 3.6 and Table 3.1).

larger (1.0 eV) than those for EHT and DFT (~0.30 eV). These results suggest that the calculated DOS significantly depends on the calculation levels and neither of EHT and INDO universally provide energy levels that are similar to those obtained by DFT.

Figure 3.8 compares the calculated DOS and experimental results of ultraviolet photoelectron spectroscopy (UPS) by Greiner et al. [58]. The calculated DOS was scaled to compare the shape of calculated DOS with the UPS spectra. For all the cases, the experimental spectra (black broken curves) near the valence band edge (<1 eV) were well reproduced by the sum of contribution of HOMO to HOMO–3 (colored solid curves) using different scaling factors (the factors are shown in the respective figures). The UPS spectra in a deep energy region (>1 eV for α -NPD, >1.5 eV for CBP) could not be reproduced by the calculated DOS. However, such low-lying states can be neglected for the charge transport simulation because the MOs lying lower by >0.3 eV in energy than the HOMO do not contribute to charge transport [13] (therefore, the MOs lying lower than HOMO–2 can be neglected, see Table 3.1). Influence of computational inaccuracy in the DOS at the deep energy region is negligible when we consider charge transport.

In the aspect of computational cost, the calculation of site energy for 4000 molecules in the amorphous system at INDO level required eight times longer computation time compared to EHT (using 20 CPU threads for both EHT and INDO calculations). Moreover, the computation at DFT using 128 threads takes over 1000 times longer time compared to the 20-thread calculation at EHT level.

3.3.2 Electronic coupling

Figure 3.9 compares the distributions of electronic coupling calculated by EHT, INDO, and DFT methods. For the cases of EHT and INDO (the calculations were conducted for all the dimers, 125 873 and 167 993 dimers for α -NPD and CBP, respectively), the electronic coupling of α -NPD and CBP distributed mainly around 10^{-3} eV and the maximum values were up to the order of $10^{-2}-10^{-1}$ eV. A considerable number of dimers with much smaller electronic coupling was found. However, as previously reported [11], contribution of dimers with electronic coupling smaller than 10^{-4} eV (gray region in Fig. 3.9) was negligible for charge transport, which was also confirmed in this work. The INDO calculation yielded larger electronic coupling than the EHT-calculated one, which is consistent with the investigation reported by Huang and Kertesz [59].

The results of the DFT-based calculation using BP86/TZP and PW91/TZP for the 128 dimers are also shown in Fig. 3.9. The dimers were selected randomly but each calculation was carried out for the same 128 dimers. We confirmed that the 128-dimers calculation



Figure 3.8 Comparison between the calculated DOS (solid lines) and experimental results obtained by UPS [58] (dashed lines) for the amorphous systems of (a) α -NPD and (b) CBP. The energy is represented relative to the onset energy of UPS spectra. The energy was scaled and Gaussian broadening was applied for the calculated DOS as shown in the respective panels.



Figure 3.9 Probability density functions of electronic coupling, $p(\log |H_{ij}^{pq}|)$, calculated using EHT, INDO, and DFT (BP86/TZP and PW91/TZP) for the amorphous systems of (a) α -NPD and (b) CBP. The contributions of HOMO and HOMO–1 were included. The distributions for DFT were obtained from the calculations for the same 128 dimers in the amorphous systems. The curves for BP86/TZP and PW91/TZP are almost overlapped. The right panels show enlarged view for the region of large electronic coupling. Arrows indicate the shifts of the distributions in logarithmic scale relative to the EHT (the corresponding ratios are given in the parentheses).

provided statistically reasonable distributions of electronic coupling (see Fig. 3.4). No functional dependence of the distributions was obtained for BP86/TZP and PW91/TZP (overlapped green and red curves in Fig. 3.9). In addition, for the 128 dimers, the results were found to be consistent when we used the other basis sets, DZ, DZP and TZ2P (the SZ basis set yielded smaller electronic coupling, see Fig. 3.2). Compared to both EHT and INDO, the DFT-calculated electronic coupling distributed in larger electronic coupling region. As shown by arrows in the right panel of Fig. 3.9, the shifts in largest edge of the DFT-calculated distribution were found to be 0.24 (α -NPD) and 0.15 (CBP) in logarithmic scale with respect to the EHT-calculated one, which corresponds to 1.7 (α -NPD) and 1.4 (CBP) times larger electronic coupling.

For further investigation, a correlation of electronic coupling calculated at EHT, INDO, and DFT levels is shown in Fig. 3.10. The same 128 dimers selected above were used to calculate electronic coupling not only at DFT level but also at EHT and INDO levels. It is clear from Figs. 3.3 and 3.10 that the DFT-calculated electronic couplings (e.g. BP86/TZP and PW91/TZP) strongly correlated, indicating that the electronic coupling is functional and basis set independent (except for the SZ basis set as shown in Fig. 3.3). In contrast, the correlations among EHT, INDO and DFT are weak. This suggests that the electronic coupling of a given dimer is varied among the calculation level we used, leading to change in microscopic charge hopping behavior. Fig. 3.10 shows that, at the region around 10^{-3} eV, the INDO-calculated electronic coupling was slightly larger on average than that calculated by EHT, and DFT yielded slightly larger electronic coupling than INDO. The difference in the magnitude of electronic coupling among the calculation levels was more significant at the region below 10^{-4} eV (Fig. 3.3). A similar correlation has been reported by Rühle et al. [17]. However, as stated above, the discrepancy in the distributions at small coupling region (< 10^{-4} eV) arising from different calculation levels should have no significant effect on charge transport.

3.3.3 Charge transport simulation

Figure 3.11 compares charge mobilities obtained from the charge transport simulations using the different combinations of calculation levels, EHT+EHT, INDO+INDO, EHT+DFT, and INDO+DFT, where X+Y denotes that the site energy and electronic coupling were calculated at the computational level X and Y, respectively. The BP86/TZP-based electronic coupling was used as the DFT and the DFT-based electronic coupling for all the dimers was determined using the correlation of EHT versus DFT (Fig. 3.5a,e) and INDO versus DFT (Fig. 3.5c,g) for EHT+DFT and INDO+DFT, respectively, as described in the method section. Experimental results of TOF measurements [11, 12, 60–64] are also shown for comparison. We first compare



Figure 3.10 Correlation of electronic coupling calculated using different methods, EHT, INDO, and DFT (BP86/TZP and PW91/TZP). The correlation was obtained by the calculations with different methods for the same 128 dimers used in the DFT-based calculation. The contributions of HOMO to HOMO–7 were included. The contours represent two-dimensional probability density of each correlation plot. (a) For the amorphous system of α -NPD.



Figure 3.10 (contd.) (b) For the amorphous system of CBP.



Figure 3.11 Hole mobilities μ of (a) α -NPD and (b) CBP as a function of a square root of applied electric field, $F^{1/2}$, calculated using different combinations of calculation levels. The notation X+Y in the legend denotes that the site energy and electronic coupling were calculated at the computational level X and Y, respectively. The contributions of HOMO and HOMO–1 were included in the charge transport simulations. Experimental data (black symbols) for α -NPD [12, 60, 61] and CBP [11, 62–64] are shown for comparison (α -NPD: filled circles, ref. [12]; open squares, ref. [60]; open triangles, ref. [61]. CBP: filled circles, ref. [11]; open squares, ref. [62]; open triangles, ref. [63]; open rhombuses, ref. [64]).

the results of EHT+EHT- and INDO+INDO-based simulations (light blue circles and squares in Fig. 3.11). In the case of α -NPD (Fig. 3.11a), the result of EHT+EHT-based simulation exhibited better agreement with the experimental result. Although the electronic coupling is larger for INDO compared to EHT, the EHT+EHT-based simulation provided higher mobility than the INDO+INDO. There are two origins for the higher mobilities of the EHT+EHT-based simulation. One is the contribution of the HOMO–1, which increases hole mobility several times [13]. Compared to the EHT-calculated energy difference of HOMO and HOMO–1 (0.090 eV), the INDO-calculated difference was 0.309 eV (Table 3.1) and the contribution of HOMO–1 was negligible. The second origin is the narrower DOS in the EHT than the INDO (Fig. 3.6a). This leads smaller site energy difference, resulting in faster charge hopping [see eq. (3.3)]. In contrast, in the case of CBP (Fig. 3.11b), both EHT+EHT- and INDO+INDObased simulations quantitatively reproduced the experimental mobility. The differences of electronic coupling, width of DOS, and energy gap between HOMO and HOMO–1 canceled out in the charge transport simulations, resulting in almost the same mobilities.

In the case of EHT+DFT and INDO+DFT (orange triangles and diamonds in Fig. 3.11), the simulations yielded higher mobilities compared to the EHT+EHT and INDO+INDO, respectively. Here, the site energies were calculated by EHT or INDO method. Therefore, the difference is found to originate from the larger electronic coupling at DFT level compared to the semiempirical methods (Figs. 3.9 and 3.10). For α -NPD (Fig. 3.11a), the increase of mobility resulted in the improved agreement between the EHT+DFT-based result and experimental mobility. In contrast, the calculated mobility by the EHT+DFT-based simulation for CBP was significantly deviated from the experiments; the other methods, EHT+EHT, INDO+INDO, and INDO+DFT, provided far better agreement with the experiments (Fig. 3.11b). Note that for α -NPD, the DFT+DFT-based simulation would provide a result similar to that based on INDO+DFT because the INDO- and DFT-calculated DOS were similar (Fig. 3.6a). The results of DFT+DFT- and EHT+DFT-based simulation for CBP would also be similar because of the same reason (Fig. 3.6b).

Our previous study have indicated that the calculated mobility depends on the MDconstructed amorphous structure. The one order of magnitude different mobility was observed in different MD-constructed aggregates, although the MD procedure is completely the same [13]. Considering the fact, we can say that the calculated mobility is reasonable when the mobility is within one order of magnitude different from experiments.

It should be noted that this stochastic approach must be used with careful consideration to whether the modeled system reflects the actual system of interest. In summary, the EHT+EHT-based simulation quantitatively predicted the experimental mobilities for CBP. For α -NPD, it was the second best choice that yielded the reasonable value of mobility. Therefore, among several methods in this study, the EHT+EHT-based multiscale charge transport simulation is reasonable and cost-effective choice for prediction of charge mobility in organic amorphous semiconductors.

3.4 Conclusions

In summary, we demonstrated the effects of calculation level on the properties inherent in charge transport phenomena of organic amorphous semiconductors. Our multiscale charge transport simulation based on the semiempirical method, EHT, provided reasonable mobilities of the amorphous systems. We also demonstrated the realization of simulation in amorphous systems using DFT-calculated properties by means of the stochastic estimation of electronic coupling, which is based on the computation only for a portion of the whole amorphous system. However, the combined use of semiempirical and DFT methods in the simulation did not always yield the best agreement with experimental mobilities, in spite of far larger computational time used compared to the all-semiempirical approaches. Considering such a situation, the use of EHT-based simulations is the reasonable choice among the calculation levels we used, which yields reasonable prediction of charge mobility within much lower computational resource and time. Our multiscale charge transport simulation is a promising *in silico* approach to predict charge mobility and design excellent organic amorphous semiconductors.

CHAPTER 3 is the author's version of an unpublished work that will be submitted for publication.

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Part II

Investigation into Morphology of Organic Amorphous Semiconductors

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Chapter 4

Analysis of Molecular Orientation in Organic Semiconducting Thin Films Using Static Dynamic Nuclear Polarization Enhanced Solid-State NMR Spectroscopy

More than the example of the distribution of an analysis of amorphous phenyldi (pyren-1-yl)-phosphine oxide (POPy₂). The ³¹P DNP-ssNMR spectra exhibit a sufficient signal-to-noise ratio to quantify the distribution of molecular orientation analysis of amorphous phenyldi (pyren-1-yl)-phosphine oxide (POPy₂). The ³¹P DNP-ssNMR spectra exhibit a sufficient signal-to-noise ratio to quantify the distribution of molecular orientation analysis of a sufficient signal-to-noise ratio to quantify the distribution of molecular orientation in amorphous films; the P=O axis of a vacuum-deposited and drop-cast POPy₂ shows anisotropic and isotropic distribution, respectively. The different molecular orientation reflects the molecular origin of the different charge transport behavior.

Chapter 4 Analysis of Molecular Orientation in Organic Semiconducting Thin Films Using Static Dynamic Nuclear Polarization Enhanced Solid-State NMR Spectroscopy

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Introduction 4.1

Organic thin-film semiconductor devices, such as organic light-emitting diodes (OLEDs), organic photovoltaic cells (OPVs), and organic thin-film transistors, are expected to be the next generation devices owing to their light-weight, cost effectiveness, and flexible properties. Thus, organic semiconductors have been extensively studied over the last few decades [1-3]. The properties inherent in these devices, such as charge carrier mobility, light emission, and light out-coupling, depend on intra- and inter-molecular structures, including the orientation of organic molecules in the devices.

Organic molecules in OLEDs and OPVs are often in amorphous state, which limits the application of diffraction techniques based on X-rays and neutrons for detailed analysis of the molecular orientation in organic amorphous films. The molecular orientation can be determined by angular-dependent photoluminescence measurements [4, 5], and variable angle spectroscopic ellipsometry [6, 7]; however, these methods provide only average values, such as orientation order parameters. There are currently no appropriate methods for revealing distribution of molecular orientation in an amorphous aggregate.

Solid-state nuclear magnetic resonance (ssNMR) spectroscopy is a powerful technique for analyzing the structure and dynamics of materials with both crystalline and amorphous morphologies [8–12]. Thus, it may be possible to perform detailed analysis of the structure of semiconducting materials in organic devices. However, most ssNMR studies are based on bulk samples [13–18] and reports on thin film samples are rare [19]. One reason for this lack of previous studies is that the limited amount of organic material in the devices results in a low signal-to-noise (S/N) ratio.

To enhance the sensitivity of NMR, dynamic nuclear polarization (DNP) enhanced ssNMR

(DNP-ssNMR) spectroscopy has recently attracted considerable attention [20–26]. In DNPssNMR experiments, radicals dispersed in a sample are polarized by microwave irradiation leading to high electron polarization. The resulting electron polarization is transferred to the ¹H population in the sample. In most cases, the enhanced ¹H polarization is further transferred to other nuclei, typically by cross-polarization (CP). Although most recent DNPssNMR measurements have been performed under magic angle spinning conditions [20–26], Bechinger's group reported a static DNP-ssNMR measurement, which provided insight into the structure of membrane polyproteins in lipid bilayers [27, 28].

Here, we performed static DNP-ssNMR measurements for an organic semiconductor, phenyldi(pyren-1-yl)phosphine oxide (POPy₂; Fig. 4.1a). POPy₂ has electron transport properties [29], and is thus frequently used in OLEDs. As shown later, we detected different electron transport behavior depending on different preparation methods, vacuum-deposition and drop-casting methods (Fig. 4.1b).

4.2 Experimental methods

4.2.1 Preparation of samples for DNP-ssNMR measurement

General procedures

We selected a bisnitroxide radical, (2,2,4,4,14,14,16,16-octamethyl-7,11,18,21-tetraoxa-3,15diazatrispiro[5.2.2.5¹².2⁹.2⁶]henicosane-3,15-diyl)bis(oxidanyl) [bis-TEMPO-bisketal; also referred to as bTbK, TEMPO: (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl] [30] (Fig. 4.1a), as the polarizing agent, because our thermogravimetric measurements (Fig. 4.2) revealed that bTbK can be sublimed before decomposition. A concentration of radicals is the main factor affecting the signal enhancement, because strong electron–electron exchange coupling among radicals are reported to decrease the DNP efficiency [31]. Thus, we used a radical doping concentration of 0.25 wt%. Electron paramagnetic resonance (EPR) spectra of sublimed bTbK doped in POPy₂ showed essentially the same spectra as the drop-cast spectra, as shown in Fig. 4.3. The EPR signals were well-resolved, indicating that the radicals in the sample films did not possess any notable electron–electron exchange coupling.

POPy₂ was purchased from Lumtec (sublimed grade) and used without further purification. bTbK was synthesized according to ref. [31] and purified by temperature gradient sublimation. Ultrathin glass (SiO₂) substrates [$(3.5 \times 17 \times 0.03) \text{ mm}^3$] were pre-treated with the same procedure as that used for standard device fabrication as follows: pre-cleaning with acetone



Figure 4.1 (a) Molecular structure of $POPy_2$ and bTbK. (b) Schematic illustration of sample preparation. The films on glass (SiO₂) or PTFE are inserted into a 5-mm φ quartz tube.



Figure 4.2 Thermogravimetric profiles of bTbK. Solid lines were measured under vacuum (50 Pa) condition. Dashed lines were measured under argon gas flow. The sublimation temperature, between 138 and 192 °C, was much lower than the decomposition temperature (T_d) of 271 °C, confirming that bTbK is suitable for vacuum-deposition process.



Figure 4.3 EPR spectra of bTbK (0.25 wt%) doped in POPy₂. For (a) vacuum-deposited and (b) drop-cast films on SiO₂.



Figure 4.3 (contd.) For (c) vacuum-deposited and (d) drop-cast films on PTFE.

and propan-2-ol followed by ultraviolet/ozone irradiation for 30 min. Polytetrafluoroethylene (PTFE) substrates $[(3.5 \times 18 \times 0.25) \text{ mm}^3]$ were pre-cleaned with acetone and propan-2-ol. The thickness of organic films was measured by a stylus surface profiler [Dektak 6M, Bruker (Veeco Instruments)].

Vacuum-deposited amorphous films

Vacuum-deposited amorphous thin films were prepared on SiO_2 or PTFE substrates by codeposition of POPy₂ and bTbK with deposition rates of 2 and 0.005 nm s⁻¹, respectively. These conditions resulted in a bTbK concentration of 0.25 wt%. The thickness of the resulting organic films was 1.5 µm (~52 µg for each substrate). The thickness was thinner than a typical sample thickness required for time-of-flight (TOF) experiments (normally, thicker than several micrometers), which is a most frequently used method to measure transient photocurrent.

Drop-cast amorphous films

POPy₂ (15 mg) and bTbK (0.038 mg, 0.25 wt%) were dissolved in deoxygenated chloroform (1 mL) and stirred at 30 °C for 2 h. The resulting solution was drop-cast on SiO₂ or PTFE substrates. The solution was dried *in vacuo* for 3 h at 30 °C. The thickness of the resulting organic films was 2.8 μ m.

4.2.2 DNP-ssNMR measurement

We performed ³¹P CP DNP-ssNMR experiments under static condition to obtain chemical shift anisotropy (CSA) spectra, which give information on ³¹P=O orientation. The POPy₂ films on the substrates were set perpendicular to the external magnetic field, B_0 (Fig. 4.1b). The DNP-ssNMR measurements were performed with a wide-bore 9.4 T magnet and a solidstate NMR spectrometer (Avance III, Bruker BioSpin) equipped with a gyrotron producing 263 GHz microwaves, a microwave transmission line, a cooling unit based on liquid nitrogen, and a ¹H-³¹P double resonance single coil static DNP-ssNMR probe with the 5-mm rf solenoidal coil axis orientation transverse to the external magnetic field B_0 . The measurement temperature was (90 ± 5) K. An adiabatic CP pulse sequence was used with a CP contact time of 2.0 ms, a 90° pulse width of 2.0 µs, and an acquisition time of 5.1 ms. All the samples showed two components with different ¹H spin-relaxation times (T_{1H}) as shown in Table 4.1. The recycle delay times were set to be 1.3 times of the longest T_{1} values. Two dummy scans were applied before the acquisition. Before the Fourier transformation, we applied an exponential line-broadening of 200 Hz. The chemical shifts of the ³¹P spectra were externally referenced to aqueous 85% phosphoric acid (0 ppm) at room temperature. The DNP signal enhancement factor ($\varepsilon_{on/off}$) was calculated from the ratio of the integral signal intensity of the DNP-on and -off spectra. All the experimental parameters and conditions were identical for the on and off

Substrate	Preparation method	# of sheets	$T_{^{1}\mathrm{H}}(\mathbf{s})$	$^{31}{ m P}~arepsilon_{ m on/off}$
SiO ₂	Vacuum-deposition	12	0.44 / 17.8	3.0
		1	0.38 / 21.6	6.0
	Drop-casting	15	2.2 / 23.0	2.0
PTFE	Vacuum-deposition	10	0.59 / 20.0	10
	Drop-casting	15	0.74 / 16.7	9.3

Table 4.1 ¹H spin–lattice relaxation times (T_{1H}) and DNP signal enhancement factors ($\varepsilon_{on/off}$) for the amorphous POPy₂.

spectra except for the number of scans. In most cases the number of scans was identical, but when the number of scans was different, a compensation factor was applied.

4.2.3 Charge mobility measurement by time-of-flight experiment

We fabricated vacuum-deposited or drop-cast devices for TOF measurements. The device structure was indium tin oxide (ITO; 50 nm)/POPy₂ (3.8 µm for vacuum-deposited and 3.6 µm for drop-cast device)/Al (20 nm). For the vacuum-deposited device, the POPy₂ layer was fabricated by sublimation onto the surface of ITO *in vacuo* (10^{-4} Pa) with a deposition rate of 2 nm s⁻¹, and then an aluminum (Al) electrode was formed by vapor-deposition [0.2 nm s⁻¹; (1.4-2.5) × 10^{-3} Pa]. For the drop-cast device, the POPy₂ layer was prepared from 1 mL of the chloroform solution of POPy₂ (7.5 mg mL^{-1}). Then, an Al electrode was formed by vapor-deposition [0.2 nm s⁻¹; (1.4-2.5) × 10^{-3} Pa]. TOF measurements were performed at 300 K using TOF equipment (TOF-401-3, Sumitomo Heavy Industries Advanced Machinery, Japan) to obtain electron mobility.

4.3 Results and discussion

Figure 4.4 shows the ³¹P CSA spectra of POPy₂ with and without DNP enhancement. According to reports from Bechinger's group [27, 28], we calculated the DNP enhancement factor ($\varepsilon_{on/off}$) to be the ratio of the integral signal intensity of the CSA spectra with and without DNP enhancements. The values of $\varepsilon_{on/off}$ for the vacuum-deposited and drop-cast films on SiO₂ (12 sheets for the vacuum-deposited films; 15 sheets for the drop-cast films) were 3.0 and 2.0, respectively (Fig. 4.4a,b). Figure 4.4c shows the ³¹P CSA spectrum of a single sheet of a POPy₂ thin film with a measurement time of ~16 h. Compared with the stacked samples in Fig. 4.4a,b, the $\varepsilon_{on/off}$ value increased to 6.0. Through the DNP enhancement, we successfully obtained the CSA spectrum with a sufficient S/N ratio from the sample of even a single sheet.



Figure 4.4 ³¹P CSA spectra of POPy₂ with (black) and without (gray) DNP enhancement for (a) the vacuum-deposited films on SiO₂ (12 sheets), (b) the drop-cast films on SiO₂ (15 sheets), and (c) the vacuum-deposited film on SiO₂ (1 sheet).



Figure 4.5 ³¹P CSA spectra of POPy₂ with (black) and without (gray) DNP enhancement for (a) the vacuum-deposited films on PTFE (10 sheets) and (b) the drop-cast films on PTFE (15 sheets).



Figure 4.6 Schematic illustration of the orientation of chemical shift tensor for $POPy_2$. The relationship between the P=O orientation and the chemical shift is also shown in a calculated CSA spectrum assuming completely random orientation.

Note that the POPy₂ films on PTFE substrates (10 sheets for the vacuum-deposited films; 15 sheets for the drop-cast films) exhibited $\varepsilon_{on/off}$ values of 10 and 9.3, respectively (Fig. 4.5). These values are much higher than those on SiO₂. This difference in the values of $\varepsilon_{on/off}$ for the samples on SiO₂ and PTFE is likely caused by the different degree of sample heating under microwave irradiation to SiO₂ and PTFE substrates [27].

The CSA patterns of the vacuum-deposited and drop-cast POPy₂ were spread over a wide chemical shift range from 100 to -100 ppm depending on the P=O direction of POPy₂. The experimentally obtained CSA spectra were axially symmetric (Figs. 4.4 and 4.5). From the structural symmetry of POPy₂, the principal axes of chemical shift tensor can be assigned as shown in Fig. 4.6. This assignment is confirmed by gauge-including atomic orbital (GIAO) calculations. The signal at -100 ppm, labeled σ_{\parallel} , corresponds to the parallel alignment of P=O axis relative to B_0 (the angle between the unique principal axis of the uniaxial chemical shift tensor, σ_{\parallel} , and the P=O axis was calculated to be 3.2°). The signal at 100 ppm, labeled σ_{\perp} , corresponds to the perpendicular alignment of the P=O axis relative to B_0 . For the vacuumdeposited POPy₂ (Fig. 4.7a), increased signal intensity around -100 ppm was observed compared with the drop-cast sample (Fig. 4.7b), indicating the greater contribution of the P=O axis parallel to the B_0 . In the case of POPy₂ on PTFE substrates, the CSA patterns with completely random molecular orientation were obtained for the drop-cast and vacuum-deposited samples (Fig. 4.5). This result suggests the possibility that the POPy₂ molecules did not orient on the PTFE substrates. However, the PTFE substrates are not completely flat and thus detailed analysis of the molecular orientations was not performed.



Figure 4.7 Experimental ³¹P CSA spectra of POPy₂ (a) vacuum-deposited and (b) drop-cast on SiO_2 (1 sheet) with DNP enhancement (black line). The best-fit simulated spectra are shown by the red lines.



Figure 4.8 Experimental ³¹P CSA spectra of POPy₂ (a) vacuum-deposited (b) and drop-cast on SiO₂ (1 sheet) with DNP enhancement (black lines) and the best-fit simulated spectra assuming an Gaussian-type orientation distribution function $p(\theta) \propto \exp[-\sin^2 \theta/(2\sigma^2)]$ (red lines).



Figure 4.9 Orientation distributions $p(\theta)$ for POPy₂ (a) vacuum-deposited on SiO₂ and (b) drop-cast on SiO₂, defined by a Gaussian-type function (red lines) and by an expansion of Legendre polynomials [eqs. (4.1) to (4.3), dashed lines]. Owing to the symmetry, the values of $p(\theta)$ with $\theta > 90^{\circ}$ are folded in that between 0° and 90°.

Table 4.2 Principal values of chemical shift tensor (σ_{\parallel} and σ_{\perp}), order parameters ($\langle P_2 \rangle, \langle P_4 \rangle, \langle P_6 \rangle$), and Gaussian line-broadening factor (BF) for the vacuum-deposited and drop-cast POPy₂ films determined from the best-fit simulated CSA spectra in Fig. 4.7.

Sample	σ_{\parallel} (ppm)	σ_{\perp} (ppm)	$\langle P_2 \rangle$	$\langle P_4 \rangle$	$\langle P_6 \rangle$	BF (ppm)
Vacuum-deposited	114.3	-93.4	0.15	0.031	-0.0010	8.4
Drop-cast	110.1	-88.4	-0.019	0.0059	-0.0014	7.2

To quantify the distribution of molecular orientation, the experimental CSA spectra were fitted by the Legendre moment expansion approach [8, 32, 33]. The simulated spectra assuming a Gaussian-type orientation distribution function showed slightly poor reproducibility (Figs. 4.8 and 4.9). Because the CSA spectra of POPy₂ have the axially symmetric pattern, the orientation distribution function $p(\theta)$ was defined by an expansion of Legendre polynomials $P_n(\cos \theta)$ as follows.

$$p(\theta) = \sum_{n} \frac{2n+1}{2} \langle P_n \rangle P_n(\cos \theta), \quad n = 0, 2, 4, 6, \dots$$
(4.1)

$$\int_0^{\pi} p(\theta) \sin \theta \, \mathrm{d}\theta = 2\langle P_0 \rangle = 1 \tag{4.2}$$

$$\langle P_n \rangle = \frac{\int_0^{\pi} p(\theta) P_n(\cos \theta) \sin \theta \, \mathrm{d}\theta}{\int_0^{\pi} p(\theta) \sin \theta \, \mathrm{d}\theta}$$
(4.3)

Here, θ is the angle between the P=O axis and B_0 , and B_0 is normal to the SiO₂ substrate (Fig. 4.6). The function $p(\theta)$ gives the probability of finding a molecule at a particular orientation of θ . The experimental data were fitted by least squares minimization. The fitting parameters were the principal values of σ_{\parallel} and σ_{\perp} , *n*th order parameters $\langle P_n \rangle$ (n = 2, 4, 6), and a Gaussian line-broadening factor. Higher order parameters ($n \ge 8$) were ignored because the contribution of the 6th order parameter was negligibly small, as shown in Table 4.2.

The CSA spectra of the vacuum-deposited and drop-cast samples were well reproduced by the best-fit simulated spectra, shown by the red curves in Fig. 4.7. The best-fit parameters are shown in Table 4.2. The thick red curves in Fig. 4.10 represent $p(\theta)$ for the vacuum-deposited and drop-cast samples. The respective contributions of $P_n(\cos \theta)$ are also shown in Fig. 4.10. For the vacuum-deposited film, the probability of finding a P=O orientation at $\theta = 0$ was highest and decreased with increasing θ . This originates from the large contribution of the order parameter $\langle P_2 \rangle$ of 0.15 in addition to $\langle P_0 \rangle$. We detected some contribution from $\langle P_4 \rangle$, but that of $\langle P_6 \rangle$ is negligible. For the drop-cast film, the contributions of $\langle P_n \rangle$, where *n* is higher than two are quite small (Fig. 4.10b) and the CSA spectrum is mostly determined by



Figure 4.10 Orientation distributions $p(\theta)$ (thick red lines) and contributions of respective terms (thin lines) of Legendre polynomials $P_n(\cos \theta)$ for POPy₂ (a) vacuum-deposited and (b) drop-cast on SiO₂. Owing to the symmetry, the values of $p(\theta)$ with $\theta > 90^{\circ}$ are folded in that between 0° and 90°.

 $\langle P_0 \rangle$, indicating that the P=O axis of POPy₂ is isotropically oriented in the drop-cast film.

The difference in molecular orientation can be expected to affect photocurrent transient behavior of POPy₂. Indeed, the transient photocurrent of the vacuum-deposited and drop-cast films of POPy₂, measured by the TOF technique, exhibited different behavior, as shown in Fig. 4.11. The vacuum-deposited POPy₂ showed a *non-dispersive* photocurrent with a clear bending point, while the drop-cast POPy₂ exhibited a featureless *dispersive* photocurrent. This difference in the electron transport behavior was considered to originate from the different molecular orientation revealed by the DNP-ssNMR experiments shown above.

4.4 Conclusions

In summary, we performed DNP-ssNMR measurements of vacuum-deposited and drop-cast POPy₂ thin films. Under the DNP-enhanced condition, we obtained the ³¹P CSA spectra with a S/N ratio sufficient for orientation analysis. The analysis of CSA spectra based on the Legendre moment expansion approach revealed the quantitative orientation distribution of the vacuum-deposited and drop-cast amorphous POPy₂ thin films. The vacuum-deposited POPy₂ favors a perpendicular orientation of the P=O axis to the SiO₂ substrate, while the drop-cast POPy₂ exhibits an isotropic random orientation. This difference in molecular orientation affects the photocurrent transient behavior.

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Figure 4.11 Transient photocurrent curves. (a) For the vacuum-deposited POPy₂.



Figure 4.11 (contd.) (b) For the drop-cast $POPy_2$.

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Chapter 4

Part III

Material Design and Development of Highly Efficient Organic Light-Emitting Diodes Based on Quantum Chemical Calculations

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Chapter 5

Triarylboron-Based Fluorescent Organic Light-Emitting Diodes with External Quantum Efficiencies Exceeding 20%

> **T**RIARYLBORON compounds have attracted much attention, and found wide use as functional materials because of their electron-accepting properties arising from the vacant *p*-orbitals on the boron atoms. In this study, we design and synthesize new donor-acceptor-type triarylboron emitters that show thermally activated delayed fluorescence. These emitters display sky-blue to green emission and high photoluminescence quantum yields of 92–100% in host matrices. Organic light-emitting diodes using these emitting molecules as dopants exhibit high external quantum efficiencies of 14.0–22.8%, which originate from efficient up-conversion from triplet to singlet states and subsequent efficient radiative decay from singlet to ground states.

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5.1 Introduction

Triarylboron (TAB) compounds have a vacant *p*-orbital on the central boron atom so they possess attractive electron-accepting properties. Donor–acceptor (D–A) systems with a TAB acceptor and amine-based donor groups have received considerable interest because of their strong intramolecular charge transfer (ICT) properties [1–13]. The ICT character of TAB-based D–A compounds strongly influences their photophysical and photochemical properties [2–5], and makes them useful for non-linear optics [1], anion sensing [6, 7], hydrogen activation and storage [8], and optoelectronics [9–13].

However, a limited number of TAB D–A compounds have been used as emitters in organic light-emitting diodes (OLEDs) because the external quantum efficiency (EQE, η_{EQE}) of such devices has been relatively low [9–12]. One origin of the low η_{EQE} is spin statistics [14]; conventional fluorescent materials can convert only 25% of electrogenerated singlet excitons into light, and the remaining 75% of generated triplet excitons are deactivated as heat. Considering that the light out-coupling efficiency of OLEDs is typically 20–30% [15, 16], the theoretical maximum η_{EQE} of OLEDs with conventional fluorescent emitters is limited to 5–7.5%. Thus, efficient conversion of triplet excitons into light is needed to realize OLEDs with high η_{EQE} .

To extract light from triplet excitons, phosphorescent organometallic materials have been used as emitters in OLEDs [17–19]. Phosphorescent organometallic emitters can theoretically convert 100% of excitons into light because of strong spin-orbit coupling, so have been frequently used in OLEDs [19]. Several TAB-based organometallic phosphorescent emitters have been reported [20–22].

Thermally activated delayed fluorescence (TADF) has recently been used as a different approach to acquire light from triplet excitons [23–28]. TADF emitters, which often have D–A frameworks, can convert the lowest triplet state (T₁) to the lowest excited singlet state (S₁) through reverse intersystem crossing (RISC) by thermal activation [23–28]. Although early TADF-based OLEDs showed relatively low η_{EQE} [24, 25], recent TADF emitters possess the outstanding performance [23, 26–28]. The number of highly efficient TADF emitters is increasing rapidly at present, but is still limited compared with a multitude of phosphorescence emitters. In particular, there are few reports of TAB-based TADF [29, 30] because it is still challenging to use versatile TAB-based D–A frameworks as TADF emitters, even though the strong π -electron accepting ability related to the $p-\pi^*$ conjugation of TAB materials should be beneficial to realize TADF.

Here, we report TAB-based TADF emitters, named PXZ-Mes₃B (1), 2DAC-Mes₃B (2), and DAC-Mes₃B (3), composed of an electron-accepting trimesitylboron analogue (Mes₃B) and three amine-based electron-donating units (Fig. 5.1a). OLEDs using 1, 2, and 3 as emitting dopants exhibit high η_{EQE} of up to 22.8%, far exceeding the theoretical limit for normal fluorescent emitters of 5–7.5%. Specifically, the η_{EQE} of 21.6% for a sky-blue OLED containing 2 is the highest value for TADF-based blue OLEDs, while that of 22.8% is the highest value for OLEDs with a TAB emitter.

5.2 Experimental methods

5.2.1 Synthesis and characterization

General procedures

Compounds 1, 2, and 3 were synthesized in two steps according to Scheme 5.1. Bromosubstituted precursors 4, 5, and 6 were synthesized by copper-catalyzed Ullmann coupling of 2-bromo-5-iodo-1,3-dimethylbenzene (7) with corresponding amine-based donor units. Lithiation of 4, 5, and 6 in diethyl ether (Et_2O) or cyclopentyl methyl ether (CPME) and subsequent treatment with dimesitylboron fluoride (8) gave 1, 2, and 3 in overall yields of 39–61%. Et_2O or CPME is needed for lithiation and subsequent reactions; using tetrahydrofuran (THF) gave mainly debrominated compounds, resulting in quite low yields. 1, 2, and 3 were stable in air and water and were purified by column chromatography on silica gel and temperature-



Figure 5.1 (a) Molecular structure of TAB emitters. Torsion angles between donor and acceptor units, α , are also shown. (b) Calculated HOMO and LUMO distributions of **1**, **2**, and **3**, depicted with an isosurface of 0.03 au.



Scheme 5.1 Preparation of the TAB emitters 1, 2, and 3. Reagents/conditions: (i) CuI, L-proline, DMSO, K_2CO_3 , 110 °C; (ii) *n*-BuLi, dimesitylboron fluoride, Et₂O or CPME, 0 °C to r.t.

gradient sublimation.

¹H, ¹³C, and ¹¹B NMR spectra were recorded with a JEOL ECA-600 spectrometer (600 MHz for ¹H, 151 MHz for ¹³C, and 193 MHz for ¹¹B) and a Bruker Avance III 800 US Plus spectrometer (800 MHz for ¹H and 201 MHz for ¹³C). Chemical shifts are reported in δ ppm, determined against the signal from residual protons in the deuterated solvents for ¹H NMR and solvent peaks for ¹³C NMR as internal standards, whereas those in ¹¹B NMR were relative to boron trifluoride diethyl etherate (BF₃ · OEt₂; 0.00 ppm). Thin-layer chromatography was performed on plates coated with 0.25 mm of silica gel 60F-254 (Merck). Column chromatography was performed using silica gel PSQ 60B (Fuji Silysia). All reactions were carried out under an argon atmosphere.

10-(4-Bromo-3,5-dimethylphenyl)-10H-phenoxazine (PXZ precursor, 4)



Scheme 5.2 Synthesis of 4.

10*H*-Phenoxazine (**9**; 2.00 g, 10.9 mmol), 7 (4.06 g, 13.1 mmol), copper(I) iodide (CuI; 412 mg, 2.17 mmol), L-proline (499 mg, 4.33 mmol), and potassium carbonate (K_2CO_3 ; 6.02 g, 43.6 mmol) were mixed in dry dimethyl sulfoxide (DMSO; 6.0 mL), and stirred at 120 °C for 48 h. The reaction mixture was poured into water and extracted with dichloromethane (CH₂Cl₂; 75 mL × 3). The organic phase was dried over anhydrous sodium sulfate (Na₂SO₄), filtered, and concentrated under reduced pressure. The obtained crude product was purified by silica-gel column chromatography (eluent: 1:4 CH₂Cl₂/hexane, $R_f = 0.43$) to give 1.92 g (2.93 mmol) of **4** as a pale yellow solid in 44% yield.

¹H NMR (600 MHz, CDCl₃): δ (ppm) = 7.06 (s, 2 H), 6.70–6.50 (m, 6 H), 5.93 (d, *J* = 8.1 Hz, 2 H), 2.46 (s, 2 H).

¹³**C NMR (151 MHz, CDCl₃):** δ (ppm) = 144.0, 141.6, 137.5, 134.3, 130.2, 127.6, 123.3, 121.5, 115.6, 113.4, 24.14.

APCI-MS (m/z): $[M + H]^+$ calcd. for C₂₀H₁₇BrNO, 366.0494; found, 366.0489.



Figure 5.2 NMR spectra of **4** in CDCl₃. (a) 1 H and (b) 13 C NMR spectrum.



10-[4-(Dimesitylboraneyl)-3,5-dimethylphenyl]-10*H*-phenoxazine (PXZ-Mes₃B, **1**)

Scheme 5.3 Synthesis of 1.

To a stirred solution of 4 (1.01 mg, 2.77 mmol) in dry Et_2O (5 mL) at 0 °C was added dropwise *n*-butyllithium (*n*-BuLi) in hexane (1.6 M, 1.86 mL, 2.97 mmol). The mixture was stirred for 1 h at 0 °C. To this mixture was added **8** (891 mg, 3.32 mmol) in Et_2O at 0 °C. After stirring for 16 h, the resulting precipitate was filtered and recrystallized from CH_2Cl_2 /hexane to give 1.30 g (2.44 mmol) of **1** as yellow crystals in 88% yield.

¹H NMR (600 MHz, CDCl₃): δ (ppm) = 6.87 (s, 2 H), 6.79 (s, 2 H), 6.77 (s, 2 H), 7.22–7.19 (m, 10 H), 6.66 (d, *J* = 7.2 Hz, 2 H), 6.64–6.57 (m, 8 H), 5.97 (d, *J* = 7.6 Hz, 2 H), 2.29 (s, 6 H), 2.06 (s, 6 H), 2.05 (s, 6 H), 2.03 (s, 6 H).

¹³C NMR (201 MHz, CDCl₃): δ (ppm) = 148.0, 144.0, 143.6, 140.9, 140.4, 139.7, 139.1, 134.3, 129.2, 128.9, 128.8, 123.2, 121.1, 115.3, 113.2, 22.95, 22.92, 22.86, 21.26.

¹¹B NMR (193 MHz, CDCl₃): δ (ppm) = 75.28.

APCI-MS (m/z): $[M + H]^+$ calcd. for C₃₈H₃₉BNO, 536.3125; found, 536.3115.

Elemental analysis: calcd. (%) for C₃₈H₃₈BNO: C, 85.23; H, 7.15; N, 2.62; found: C, 85.35; H, 7.10; N, 2.74.



Figure 5.3 NMR spectra of **1** in CDCl₃. (a) 1 H and (b) 13 C NMR spectrum.



Figure 5.3 (contd.) (c) ¹¹B NMR spectrum.
9-(4-Bromo-3,5-dimethylphenyl)-*N*³,*N*³,*N*⁶,*N*⁶-tetraphenyl-9*H*-carbazole-3,6-diamine (2DAC precursor, **5**)



Scheme 5.4 Synthesis of 5.

 N^3 , N^3 , N^6 , N^6 -Tetraphenyl-9*H*-carbazole-3,6-diamine (**10**; 1.20 g, 2.40 mmol), 7 (893 mg, 2.88 mmol), CuI (91.4 mg, 0.48 mmol), L-proline (110 mg, 0.96 mmol), and K₂CO₃ (1.68 g, 4.80 mmol) were mixed in dry DMSO (6.0 mL), and stirred at 120 °C for 48 h. The reaction mixture was poured into water and extracted with CH₂Cl₂ (75 mL × 3). The organic phase was dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The obtained crude product was purified by silica-gel column chromatography (eluent: 1:4 CH₂Cl₂/hexane, $R_f = 0.31$) to give 1.49 g (2.18 mmol) of **5** as a pale yellow solid in 91% yield.

¹H NMR (600 MHz, CDCl₃): δ (ppm) = 7.76 (s, 2 H), 7.30 (m, 4 H), 7.23–7.18 (m, 10 H), 7.06 (d, J = 7.8 Hz, 8 H), 6.93 (t, J = 7.2 Hz, 4 H), 2.52 (s, 6 H).

¹³C NMR (151 MHz, CDCl₃): δ (ppm) = 148.6, 140.7, 140.4, 138.5, 136.2, 129.2, 126.5, 126.4, 126.1, 124.2, 122.9, 121.8, 118.8, 111.0, 24.20.

APCI-MS (m/z): $[M + H]^+$ calcd. for C₄₄H₃₄BrN₃, 684.2014; found, 684.1994.



Figure 5.4 NMR spectra of 5 in $CDCl_3$. (a) ¹H and (b) ¹³C NMR spectrum.

9-[4-(Dimesitylboraneyl)-3,5-dimethylphenyl]- N^3 , N^3 , N^6 , N^6 -tetraphenyl-9*H*-carbazole-3,6diamine (2DAC-Mes₃B, **2**)



Scheme 5.5 Synthesis of 2.

To a stirred solution of 5 (1.20 g, 1.76 mmol) in dry CPME (10 mL) at 0 °C was added dropwise *n*-BuLi in hexane (1.6 M, 1.21 mL, 1.94 mmol). The mixture was stirred for 30 min at 0 °C. To this mixture was added **8** (613 mg, 2.29 mmol) in CPME at 0 °C. After stirring for 16 h at room temperature, the reaction mixture was poured into saturated aqueous ammonium chloride (NH₄Cl) solution and extracted with CH₂Cl₂. The organic phase was dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The obtained crude product was purified by silica-gel column chromatography (eluent: 1:4:15 CH₂Cl₂/toluene/hexane, $R_f = 0.31$) to give 1.01 g (1.18 mmol) of **2** as a yellow solid in 67% yield.

¹H NMR (800 MHz, CDCl₃): δ (ppm) = 7.76 (d, J = 1.6 Hz, 2 H), 7.36 (d, J = 8.8 Hz, 2 H), 7.24–7.16 (m, 10 H), 7.13 (s, 2 H), 7.08 (d, J = 7.2 Hz, 8 H), 6.93 (t, J = 7.2 Hz, 4 H), 6.79 (d, J = 12 Hz, 4 H), 2.30 (s, 6 H), 2.11 (s, 6 H), 2.09 (s, 6 H), 2.04 (s, 6 H).

¹³C NMR (201 MHz, CDCl₃): δ (ppm) = 148.7, 147.0, 143.9, 142.6, 141.0, 140.7, 140.6, 139.8, 138.5, 138.1, 129.2, 129.0, 128.9, 126.0, 125.6, 124.2, 122.9, 121.8, 118.8, 111.3, 23.12, 23.08, 23.02, 21.41.

¹¹B NMR (193 MHz, CDCl₃): δ (ppm) = 74.76.

APCI-MS (m/z): $[M + H]^+$ calcd. for C₆₂H₅₈BN₃, 854.4646; found, 854.4681.

Elemental analysis: calcd. (%) for C₆₂H₅₆BN₃: C, 87.20; H, 6.61; N, 4.92; found: C, 87.49; H, 6.43, N, 5.02.



Figure 5.5 NMR spectra of **2** in CDCl₃. (a) ¹H and (b) ¹³C NMR spectrum.



Figure 5.5 (contd.) (c) ¹¹B NMR spectrum.

9-Benzyl-*N*,*N*-diphenyl-9*H*-carbazol-3-amine (**12**)



Scheme 5.6 Synthesis of 12.

9-Benzyl-3-iodo-9*H*-carbazole (**11**; 5.11 g, 13.3 mmol), tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct $(Pd_2(dba)_3 \cdot CHCl_3; 70.4 \text{ mg}, 67.8 \mu \text{mol})$, tri-*tert*-butylphosphonium tetrafluoroborate $(P(t-Bu)_3 \cdot HBF_4; 78.6 \text{ mg}, 271 \mu \text{mol})$, sodium *tert*-butoxide (*t*-BuONa; 1.91 g, 19.9 mmol), and diphenylamine (2.47 g, 14.6 mmol) were dissolved in dry toluene (120 mL). The mixture was stirred at 100 °C for 18 h. After cooling, the reaction mixture was poured into water and extracted with toluene (80 mL × 3). The organic phase was dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was purified by silica-gel column chromatography (eluent: 1:4 CH₂Cl₂/hexane, $R_f = 0.29$) to give 4.29 g (10.1 mmol) of **12** as a colorless solid in 76% yield.

¹H NMR (600 MHz, DMSO- d_6): δ (ppm) = 8.10 (d, J = 8.4 Hz, 1 H), 7.97 (d, J = 1.8 Hz, 1 H), 7.67–7.61 (m, 2 H), 7.42 (d, J = 7.8 Hz, 1 H), 7.32–7.19 (m, 10 H), 7.15 (t, J = 7.5 Hz, 1 H), 6.80 (d, J = 8.4 Hz, 4 H), 6.93 (t, J = 7.5 Hz, 2 H).

¹³C NMR (151 MHz, DMSO-*d*₆): δ (ppm) = 148.1, 140.6, 139.9, 139.8, 137.5, 135.5, 129.3, 126.6, 126.5, 126.0, 125.7, 123.9, 122.4, 122.1, 121.7, 120.9, 120.1, 118.9, 111.2, 109.9, 23.43. APCI-MS (*m*/*z*): $[M + H]^+$ calcd. for C₃₁H₂₅N₂, 425.2018; found, 425.2013.



Figure 5.6 NMR spectra of **12** in DMSO- d_6 . (a) ¹H and (b) ¹³C NMR spectrum.

N,*N*-Diphenyl-9*H*-carbazol-3-amine (**13**)



Scheme 5.7 Synthesis of 13.

12 (4.24 g, 10.0 mmol) in dry anisole (30 mL) was added to a suspension of aluminium chloride (AlCl₃; 7.98 g, 60.0 mmol) in dry anisole (10 mL) at 0 °C. The reaction mixture was stirred at 65 °C for 24 h and then poured into water and extracted with toluene (100 mL × 2). The organic phase was dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was purified by silica-gel column chromatography (eluent: 1:1 CH₂Cl₂/hexane, $R_f = 0.34$) to give 1.90 g (5.69 mmol) of **13** as a pale green solid in 57% yield.

¹H NMR (600 MHz, DMSO- d_6): δ (ppm) = 11.4 (s, 1 H), 8.06 (d, J = 7.8 Hz, 1 H), 7.95 (d, J = 1.8 Hz, 1 H), 7.56–7.50 (m, 2 H), 7.40 (t, J = 8.0 Hz, 1 H), 7.27 (t, J = 9 Hz, 4 H), 7.21 (dd, J = 8.7, 2.0 Hz, 1 H), 7.13 (t, J = 7.4 Hz, 1 H), 7.02 (d, J = 9.0 Hz, 4 H), 6.96 (t, J = 7.5 Hz, 2 H).

¹³C NMR (151 MHz, DMSO- d_6): δ (ppm) = 148.2, 140.4, 138.3, 137.3, 129.2, 125.8, 125.7, 123.5, 122.2, 121.8, 121.4, 120.5, 119.0, 118.5, 112.2, 111.1.

APCI-MS (m/z): $[M + H]^+$ calcd. for C₂₄H₁₉N₂, 335.1548; found, 335.1550.



Figure 5.7 NMR spectra of **13** in DMSO- d_6 . (a) ¹H and (b) ¹³C NMR spectrum.



9-(4-Bromo-3,5-dimethylphenyl)-N,N-diphenyl-9H-carbazol-3-amine (DAC precursor, 6)

Scheme 5.8 Synthesis of 6.

13 (1.20 g, 3.59 mmol), 7 (1.34 mg, 4.31 mmol), CuI (137 mg, 0.72 mmol), L-proline (166 mg, 1.44 mmol), and K_2CO_3 (995 mg, 7.20 mmol) were mixed in dry DMSO (7.2 mL), and stirred at 120 °C for 48 h. The reaction mixture was poured into water and extracted with CH_2Cl_2 (75 mL × 3). The organic phase was dried over anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure. The obtained crude product was purified by silica-gel column chromatography (eluent: 1:4 CH_2Cl_2 /hexane, $R_f = 0.36$) to give 1.27 g (2.46 mmol) of **6** as a colorless solid in 69% yield.

¹H NMR (600 MHz, DMSO- d_6): δ (ppm) = 8.16 (d, J = 7.2 Hz, 2 H), 8.03 (d, J = 2.4 Hz, 2 H), 7.49 (s, 2 H), 7.46–7.34 (m, 3 H), 7.29–7.16 (m, 6 H), 7.00 (d, J = 8.4 Hz, 4 H), 6.95 (t, J = 6.9 Hz, 2 H), 2.48 (s, 6 H).

¹³C NMR (151 MHz, DMSO-*d*₆): δ (ppm) = 148.1, 140.6, 139.9, 139.8, 137.5, 135.5, 129.3, 126.6, 126.5, 126.1, 125.7, 123.9, 122.4, 122.1, 121.7, 120.9, 120.1, 118.9, 111.2, 109.9, 23.42. APCI-MS (*m*/*z*): $[M + H]^+$ calcd. for C₃₂H₂₆BrN₂, 517.1279; found, 517.1284.



Figure 5.8 NMR spectra of **6** in DMSO- d_6 . (a) ¹H and (b) ¹³C NMR spectrum.

9-[4-(Dimesitylboraneyl)-3,5-dimethylphenyl]-*N*,*N*-diphenyl-9*H*-carbazol-3-amine (DAC-Mes₃B, **3**)



Scheme 5.9 Synthesis of 3.

To a stirred solution of **6** (1.03 g, 2.00 mmol) in dry CPME (2.0 mL) at 0 °C was added dropwise *n*-BuLi in hexane (1.6 M, 1.38 mL, 2.20 mmol). The mixture was stirred for 30 min at 0 °C. To this mixture was added **8** (644 mg, 2.40 mmol) in CPME (3 mL) at 0 °C. After stirring for 16 h at room temperature, the reaction mixture was poured into saturated aqueous NH₄Cl solution and extracted with CH₂Cl₂. The organic phase was dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The obtained crude product was purified by silica-gel column chromatography (eluent: 1:4:15 CH₂Cl₂/toluene/hexane, $R_f = 0.27$) to give 1.12 g (1.66 mmol) of **3** as a pale yellow solid in 83% yield.

¹H NMR (800 MHz, CDCl₃): δ (ppm) = 7.98 (d, J = 8.0 Hz, 1 H), 7.92 (d, J = 1.6 Hz, 1 H), 7.45–7.36 (m, 3 H), 7.25–7.20 (m, 6 H), 7.15–7.10 (m, 6 H), 6.95 (t, J = 7.2 Hz, 2 H), 6.80 (d, J = 17 Hz, 4 H), 2.30 (s, 6 H), 2.11 (s, 6 H), 2.10 (s, 6 H), 2.05 (s, 6 H).

¹³C NMR (201 MHz, CDCl₃): δ (ppm) = 148.8, 147.0, 143.9, 142.6, 141.4, 141.0, 140.7, 140.5, 139.8, 138.2, 138.1, 129.0, 126.1, 125.7, 124.5, 123.2, 122.9, 121.7, 120.6, 119.9, 118.7, 111.1, 110.3.

¹¹**B NMR (193 MHz, CDCl₃):** δ (ppm) = 76.38.

APCI-MS (m/z): $[M + H]^+$ calcd. for C₅₀H₄₈BN₂, 687.3911; found, 687.3898.

Elemental analysis: calcd. (%) for C₅₀H₄₇BN₂: C, 87.45; H, 6.90; N, 4.08; found: C, 87.62; H, 6.83; N, 4.15.



Figure 5.9 NMR spectra of **3** in $CDCl_3$. (a) ¹H and (b) ¹³C NMR spectrum.



Figure 5.9 (contd.) (c) 11 B NMR spectrum.

5.2.2 Measurement of photophysical properties

Ultraviolet–visible (UV–vis) absorption and photoluminescence (PL) spectra of 1, 2, and 3 in various solvents were measured with UV–vis (UV-3150, Shimadzu, Japan) and PL (FluoroMax-4, Horiba Scientific, Japan) spectrometers, respectively. PL spectra of film samples were measured with the same PL spectrometer. For PL experiments, the excitation wavelengths were the absorption peak wavelengths (λ_{abs}) for the solution samples. For film samples, the excitation wavelengths were 340 nm for 1 doped in 4,4'-bis(9*H*-carbazol-9-yl)-1,1'-biphenyl (CBP), and 280 nm for 2 and 3 doped in bis[2-(diphenylphosphino)phenyl]-ether oxide (DPEPO), which correspond to λ_{abs} of the host materials. PL lifetimes were measured using a fluorescence lifetime measurement system (Quantaurus-Tau C11367-02, Hamamatsu Photonics, Japan). PL quantum yields (PLQY, Φ_{PL}) were measured using an absolute PLQY measurement system (Quantaurus-QY C11347-01, Hamamatsu Photonics, Japan). Ionization potentials (I_p) of neat films were measured with an atmospheric photoelectron spectrophotometer (AC-3, Riken Keiki, Japan). The electron affinities (E_a) of the emitters were estimated from their I_p and optical band gap. All the film samples were fabricated by vacuum-deposition at ~10⁻⁵ Pa on clean quartz glass substrates.

5.2.3 Device fabrication and measurement of OLED performance

We fabricated OLEDs with structures shown in Fig. 5.10. The energy levels of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of 1, 2, and 3 were determined from the I_p and absorption spectra of the neat films (Figs. 5.11 and 5.12). The OLEDs have the following structures: device I is ITO (50 nm)/TAPC (80 nm)/1 (16 wt%) in CBP (40 nm)/BAlq (30 nm)/Liq (1 nm)/Al (80 nm); device II and III are ITO (50 nm)/TAPC (70 nm)/2 or 3 (16 wt%) in DPEPO (30 nm)/BmPyPhB (30 nm)/Liq (1 nm)/Al (80 nm), where ITO, TAPC, BAlq, Liq, and BmPyPhB are indium tin oxide, 4,4'-(cyclohexane-1,1-diyl)bis[N,N-bis(4-methylphenyl)aniline], ([1,1'-biphenyl]-4-yloxy)bis[(2-methylquinolin-8-yl)oxy]aluminium, lithium quinolin-8-olate, and 3,3",5,5"-tetra-(pyridin-3-yl)-1,1':3',1''-terphenyl, respectively. OLEDs with an active area of 4 mm² were fabricated by vacuum-deposition at $\sim 10^{-5}$ Pa on clean ITO-coated glass substrates with a deposition apparatus (SE-4260, ALS Technology, Japan). Encapsulations of devices with a glass cap using epoxy glue were carried out in a nitrogen-filled glove box. Calcium oxide as a desiccant was incorporated into the glass cap. OLED characteristics were measured with a source meter (2400, Keithley, Japan) and an absolute EQE measurement system equipped with an integrating sphere (C9920-12, Hamamatsu Photonics, Japan).







Figure 5.11 Dependence of photoelectron emission yield on photon energy for neat films of (a) **1**, (b) **2**, and (c) **3**.



Figure 5.12 UV-vis absorption spectra of neat films of (a) 1, (b) 2, and (c) 3.

Compound	Calc.			Expt. ^a					
	α^b (°)	f^{c}	$\Delta E_{\rm ST}^{\ \ d}$ (meV)	λ_{abs}^{e} (nm)	$\lambda_{\mathrm{PL}}^{f}$ (nm)	Φ _{PL} ^g (%)	${\Phi_{\mathrm{PL}}}^h$ (%)		
1	87.3	0.0002	8	399	509	44	20		
2	51.5	0.0995	21	387	495	84	51		
3	53.0	0.0838	19	375	477	91	54		

Table 5.1Calculated properties and experimental photophysical properties (solution) of 1, 2, and 3.

^{*a*} Measured in O₂-free toluene (1×10^{-5} M) at r.t.

^b Torsion angle between the donor unit and adjacent phenyl ring.

^{*c*} Oscillator strength.

^{*d*} Calculated energy gap between S_1 and T_1 .

^{*e*} UV–vis absorption peak wavelength.

^{*f*} PL emission peak wavelength.

^g PLQY.

^{*h*} PLQY of as-prepared solution.

5.3 Results and discussion

5.3.1 Material design

To realize efficient TADF emission, a very small energy gap between S_1 and T_1 (ΔE_{ST}) is required to promote RISC [23, 26–28]. ΔE_{ST} generally decreases when the exchange interaction between HOMO and LUMO of a molecule weakens [31]. We selected the widely used Mes₃B unit as an electron-accepting segment [1–13], which has methyl groups at the ortho position of C–B bonds that protect the B atom from oxygen (O₂) and water. As an electron-donating unit, we used phenoxazine (PXZ), bis(diphenylamino)carbazole (2DAC), and diphenylaminocarbazole (DAC) units (Fig. 5.1a) aiming to minimize ΔE_{ST} .

We performed geometry optimization of 1, 2, and 3 by density functional theory (DFT) calculations using the PBE0 functional [32] and 6-31G* basis set implemented in the Gaussian 09 program package [33]. The optimized structures of 1, 2, and 3 show that 1 has a larger torsion angle (α) between the donor unit and adjacent phenyl ring than 2 and 3 because of steric repulsion arising from the H atoms at the 1,9-positions of PXZ and those on the phenyl ring (Table 5.1). The HOMO and LUMO of 1, 2, and 3 are mainly distributed on the electron-donating units and electron-accepting Mes₃B unit, respectively, indicating efficient separation of HOMO and LUMO (Fig. 5.1b). The overlap of the HOMO and LUMO of 1 is smaller than those of 2 and 3. The difference of HOMO–LUMO overlap, which is closely related to α , affects ΔE_{ST} and oscillator strength (f) of 1, 2, and 3 [34]. Time-dependent DFT calculations showed

that 1 has relatively small ΔE_{ST} and *f*, whereas 2 and 3 possess larger ΔE_{ST} and *f* (Table 5.1).

5.3.2 Photophysical properties

Figure 5.13a shows the steady-state UV–vis absorption and PL spectra of 1, 2, and 3 in toluene; photophysical data of 1, 2, and 3 are given in Table 5.1. The compounds show λ_{abs} around 380 nm, and the broad structureless PL spectra with emission peaks (λ_{PL}) in the green to skyblue region (Table 5.1). The absorption and PL spectra of 1, 2, and 3 in various solvents show their ICT character (Figs. 5.14 and 5.15); the absorption spectra were almost independent of solvent polarity (Fig. 5.14), whereas the PL spectra showed a marked red shift as solvent polarity increased (Fig. 5.15). These results indicate that the absorption and emission of 1, 2, and 3 result from ICT transitions, which originate from their spatially separated HOMO and LUMO. Figure 5.13b shows the PL spectra of 1, 2, and 3 in host matrices. The green emitter 1 (T₁ level = 2.40 eV) was doped in CBP (2.58 eV). Sky-blue emitters 2 (2.51 eV) and 3 (2.54 eV) were doped in DPEPO (3.00 eV) to prevent back transfer of excited energy from guest to host [35]. The PL spectra of these films only show the fluorescence of the dopants, suggesting efficient energy transfer from the host to the guest molecules (Fig. 5.13b).

The Φ_{PL} of **1**, **2**, and **3** in O₂-free toluene (1: $\Phi_{PL} = 44\%$; **2**: 84%; **3**: 91%) were larger than those of as-prepared solutions containing O₂ (1: $\Phi_{PL} = 20\%$; **2**: 51%; **3**: 54%). This is because some T₁ excitons transferred from S₁ to T₁ via intersystem crossing (ISC) are quenched by dissolved O₂, so T₁ \rightarrow S₁ RISC is inhibited [23, 24, 27]. We also measured Φ_{PL} of **1**, **2**, and **3** doped in host matrices (CBP for **1**, DPEPO for **2** and **3**). The highest Φ_{PL} of **1**, **2**, and **3** (16 wt%) in host matrices were 92%, 100%, and 87%, respectively, at room temperature.

Up-conversion from T_1 to S_1 was confirmed by the transient PL measurements of 1, 2, and 3 in host matrices (Fig. 5.16). For 1, delayed PL decay components were observed in both CBP matrix and O₂-free toluene (Fig. 5.16a and Fig. 5.17a). In contrast, 2 and 3 exhibited small amounts of delayed PL components both in DPEPO matrix and O₂-free toluene (Fig. 5.16b,c and Fig. 5.17b,c).

 ΔE_{ST} values were evaluated from Arrhenius plots for rate constant of RISC [27]. We obtained similar ΔE_{ST} for **1**, **2**, and **3** in host matrices (Table 5.2), which are close to that of one of the most efficient TADF emitters, 2,4,5,6-tetra(9*H*-carbazol-9-yl)isophthalonitrile (4CzIPN; $\Delta E_{\text{ST}} = 83 \text{ meV}$) [27]. The experimental errors of ΔE_{ST} for **2** and **3** were large because of the small fraction of their delayed components, especially at low temperature.



Figure 5.13 (a) Normalized UV–vis absorption (dashed lines) and PL (solid lines) spectra of 1 (green), **2** (sky-blue), and **3** (blue) in toluene $(1.0 \times 10^{-5} \text{ M})$. (b) Normalized PL spectra of **1** (green) doped in CBP (16 wt%), and **2** (sky-blue) and **3** (blue) doped in DPEPO (16 wt%).



Figure 5.14 UV-vis spectra of (a) **1**, (b) **2**, and (c) **3** in various solvents.



Figure 5.15 PL emission spectra of (a) 1, (b) 2, and (c) 3 in various solvents.



Figure 5.16 Temperature dependence of transient PL characteristics for (a) 1 doped in CBP (16 wt%), (b) 2 doped in DPEPO (16 wt%), and (c) 3 doped in DPEPO (16 wt%).



Figure 5.17 Transient PL characteristics of (a) **1**, (b) **2**, and (c) **3** in toluene $(1.0 \times 10^{-5} \text{ M})$ at room temperature.

Table 5.2 Performance of TAB-based OLEDs and photophysical properties of 16 wt% guest:host filmsof 1, 2, and 3.

Film	$\eta_{\mathrm{EQE}}{}^{a}$ (%)	CIE $(x, y)^b$	$\lambda_{\rm EL}^{\ c}$ (nm)	$\lambda_{\mathrm{PL}}{}^d$ (nm)	${\Phi_{\mathrm{PL}}}^e$ (%)	$\Delta E_{\rm ST}^{f}$ (meV)
1:CBP	22.8	(0.22, 0.55)	502	504	92	71 ± 6
2:DPEPO	21.6	(0.18, 0.43)	492	487	100	58 ± 21
3:DPEPO	14.0	(0.17, 0.30)	488	477	87	62 ± 23

^{*a*} Maximum external quantum efficiency.

^b CIE coordinates of EL emission.

^{*c*} EL emission peak wavelength.

^{*d*} PL emission peak wavelength.

^e PLQY.

^{*f*} Energy gap between S_1 and T_1 .

5.3.3 Performance of OLEDs

We fabricated OLEDs using 16 wt% of **1**, **2**, and **3** in host matrices as emitting layer. The electroluminescence (EL) emission peaks (λ_{EL}) of device I–III were observed in the green to sky-blue region (Fig. 5.18a and Table 5.2). No other emission from host materials or any other layers was observed for device I–III, suggesting that all excitons generated in the devices are effectively confined in the emitting layers. The International Commission on Illumination (Commission Internationale de l'Éclairage, CIE) coordinates of device II and III (Table 5.2) are close to those of OLEDs using the typical sky-blue phosphorescent emitter bis[2-(4,6-di-fluorophenyl)pyridinato-C², N](picolinato)iridium(III) (FIrpic) [36].

Figure 5.18b reveals that the maximum η_{EQE} of device I, II, and III were 22.8%, 21.6%, and 14.0%, respectively, far higher than the theoretical limit for conventional fluorescent emitters (5–7.5%), indicating that efficient upconversion of excitons from T₁ to S₁ is realized in these devices. In particular, device I showed low efficiency roll-off (Fig. 5.18b); its η_{EQE} remains extremely large even at practical luminance levels, with values of 19.1% at 500 cd m⁻² (for display application) and 14.2% at 3000 cd m⁻² (for lighting application).

5.4 Conclusions

We synthesized new TAB-based emitters, **1**, **2**, and **3**, that achieved both high Φ_{PL} and low ΔE_{ST} . A sky-blue OLED using **2** as an emitter exhibited the maximum η_{EQE} of 21.6%; the highest value for TADF-based blue OLEDs. A green OLED with **1** as an emitter showed the maximum η_{EQE} of 22.8%, which is the highest for OLEDs with a TAB emitter to date. These high η_{EQE} are attributed to TADF emission originating from efficient up-conversion from T₁ to S₁. Further modification of D–A-type TAB-based TADF frameworks will provide OLEDs with enhanced performance and full-color tuning.

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Figure 5.18 (a) EL spectra of device I–III at luminance of 100 cd m⁻². (b) η_{EQE} -current density (*J*) characteristics of device I–III.

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Chapter 5

Chapter 6

Blue Organic Light-Emitting Diodes Realizing External Quantum Efficiency over 25% Using Thermally Activated Delayed Fluorescence Emitters

> MPROVING performance of blue organic light-emitting diodes (OLEDs) is needed for full-color flat-panel displays and solid-state lighting sources. The use of thermally activated delayed fluorescence (TADF) is a promising approach to efficient blue electroluminescence. However, difficulty of developing efficient blue TADF emitters lies in finding a molecular structure that simultaneously incorporates (i) a small energy difference between the lowest excited singlet state (S₁) and the lowest triplet state (T₁), ΔE_{ST} , (ii) a large oscillator strength, *f*, between S₁ and the ground state (S₀), and (iii) S₁ energy sufficiently high for blue emission. In this study, we develop TADF emitters named CCX-I and CCX-II satisfying the above requirements. They show blue photoluminescence and high triplet-to-singlet up-conversion yield. In addition, their transition dipole moments are horizontally oriented, resulting in further increase of their electroluminescence efficiency. Using CCX-II as an emitting dopant, we achieve a blue OLED showing a high external quantum efficiency (EQE) of 25.9%, which is one of the highest EQEs in blue OLEDs reported previously.

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6.1 Introduction

Organic light-emitting diodes (OLEDs) are now used commercially in full-color displays for smartphones and televisions and have great potential to provide energy-savings for application over large-areas in solid-state lighting sources and for flexible flat-panel displays [1–3]. Great improvement of electroluminescence (EL) efficiency of OLEDs has been achieved by harnessing phosphorescence [4, 5], triplet-triplet annihilation [6], and thermally activated delayed fluorescence (TADF) [7, 8]. An internal quantum efficiency (IQE) of 100% has been realized for green TADF OLEDs [9]. However, it remains challenging to develop highly efficient blue OLEDs. Recently, TADF materials have attracted considerable attention because of their potential for converting all electrogenerated singlet and triplet excitons into light [8]. Since 2012, the luminescence efficiency of blue-to-green TADF emitters has been significantly improved [9–37]. The external quantum efficiency (EQE, η_{EQE}) of sky-blue [16] and green [9, 38, 39] TADF-based OLEDs has been increased to 30%. Nevertheless, there have been few studies demonstrating highly efficient blue TADF emitters with η_{EOE} over 20% [12–15].

 η_{EQE} of an OLED can be written as $\eta_{EQE} = \eta_{IQE} \times \eta_{out}$, where η_{IQE} and η_{out} are the IQE and light out-coupling factor of the device, respectively. For a TADF-based OLED, η_{IOE} can

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be expressed as

$$\eta_{\text{IQE}} = \left[\frac{1}{4}\Phi_{\text{p}} + \left\{\frac{3}{4} + \frac{1}{4}(1 - \Phi_{\text{p}})\right\}\frac{\Phi_{\text{d}}}{1 - \Phi_{\text{p}}}\right]\gamma,\tag{6.1}$$

where γ is the carrier balance ratio of holes and electrons, and Φ_p and Φ_d are the contributions from prompt fluorescence and delayed fluorescence to the photoluminescence (PL) quantum yield (PLQY, Φ_{PL}), respectively, i.e., $\Phi_{PL} = \Phi_p + \Phi_d$ [40]. Φ_{PL} of a TADF emitter can be increased by reducing an energy difference between the lowest excited singlet state (S₁) and the lowest triplet state (T₁), ΔE_{ST} , and simultaneously increasing an oscillator strength (*f*) between the S₁ and ground state (S₀) [26, 41]. A small ΔE_{ST} and large *f* are satisfied when the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of a TADF emitter are moderately separated in space. This HOMO–LUMO separation can be realized in TADF emitters containing covalently linked electron-donating and accepting units [9, 26, 41]. As well as a small ΔE_{ST} and large *f*, blue TADF emitters have the additional requirement of a high S₁ energy. These three requirements limit the choice of electron-donating and accepting units, making it difficult to achieve blue TADF-based OLEDs with a high IQE.

In this study, we developed highly efficient blue TADF emitters, 3-(9H-[3,9'-bicarbazol]-9-yl)-9H-xanthen-9-one (CCX-I) and 3-(9'H-[9,3':6',9''-tercarbazol]-9'-yl)-9H-xanthen-9-one (CCX-II), simultaneously satisfying (i) a small ΔE_{ST} , (ii) a large *f*, and (iii) a high S₁ energy (Fig. 6.1). Both CCX-I and CCX-II show efficient blue PL and high triplet-to-singlet conversion efficiency. Furthermore, CCX-I and CCX-II tend to orient parallel to the glass substrate. These features enhance the η_{EQE} of CCX-I- and CCX-II-based OLEDs. A CCX-II-based OLED shows a maximum η_{EQE} of 25.9% with the International Commission on Illumination (Commission Internationale de l'Éclairage, CIE) coordinates of (0.15, 0.22). This performance is comparable to that of the blue phosphorescent OLED based on bis(4',6'-di-fluorophenylpyridinato)iridium(III) tetrakis(1-pyrazolyl)borate (FIr6) as an emitting dopant [the η_{EQE} of 25% and CIE coordinates of (0.14, 0.23)] [42]. With an out-coupling sheet, the maximum η_{EQE} of our devices increased to 33.3%.

6.2 Experimental methods

6.2.1 Quantum chemical calculation

Geometries of the ground state of CCX-I and CCX-II were optimized by density functional theory (DFT) calculations. The excitation energies of S_1 and T_1 were obtained by time-



Figure 6.1 Molecular structure of CCX-I and CCX-II. Electron-donating and electron-accepting units are indicated by red and blue, respectively. α is the torsion angle between the electron-donating and electron-accepting units. Calculated HOMO and LUMO distributions were depicted with an isosurface of 0.02 au.
dependent DFT calculations. All the calculations were performed using the PBE0 functional [43] and 6-31G* basis set implemented in the Gaussian 09 program package [44].

6.2.2 Synthesis and characterization

General procedures

Reactions were performed under an argon atmosphere. Column chromatography was performed with silica gel PSQ 60B (Fuji Silysia). ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded with a Bruker Avance III 800 US Plus spectrometer (800 MHz for ¹H and 201 MHz for ¹³C). Chemical shifts are reported in δ ppm, determined against the signal from residual protons in the deuterated solvents for ¹H NMR and solvent peaks for ¹³C NMR as internal standards. Atmospheric pressure chemical ionization (APCI) mass spectra were measured with a Bruker micrOTOF-Q II mass spectrometer (Bruker, Germany). Spectral grade solvents and starting materials were purchased from commercial sources and used without further purification. The respective donor units of CCX-I and CCX-II, 9*H*-3,9'-bicarbazole (BCZ) and 9'*H*-9,3':6',9'' -tercarbazole (TCZ), respectively, were synthesized according to ref. [45]. The acceptor unit of the emitters, 3-bromo-9*H*-xanthen-9-one (BXTN), was prepared according to ref. [46]. A host material used for OLEDs, dibenzo[*b*,*d*]furan-2,8-diylbis(diphenylphosphine oxide) (PPF), was also synthesized as in ref. [47]. CCX-I, CCX-II, and PPF were used after purification by temperature-gradient sublimation.

3-(9H-[3,9'-Bicarbazol]-9-yl)-9H-xanthen-9-one (CCX-I)

A mixture of BCZ (359 mg, 1.08 mmol), BXTN (297 mg, 1.08 mmol), tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct $(Pd_2(dba)_3 \cdot CHCl_3; 23.3 mg, 0.0225 mmol)$, 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (XPhos; 40.6 mg, 0.0852 mmol) and sodium *tert*-butoxide (*t*-BuONa; 158 mg, 1.64 mmol) in toluene (9 mL) was stirred under reflux for 12 h. After cooling to room temperature, the reaction mixture was extracted with chloroform (CHCl₃). The organic layer was washed with water and then dried over anhydrous magnesium sulfate (MgSO₄). After filtration and evaporation, the crude product was purified by flash chromatography (silica gel, eluent: CHCl₃) and recrystallized from toluene to provide 429 mg of CCX-I as a yellow-green solid in 76.4% yield.

¹**H NMR** (800 MHz, CDCl₃): δ (ppm) = 8.64 (d, J = 8.2 Hz, 1 H), 8.43 (dd, J = 7.9, 1.7 Hz, 1 H), 8.32 (d, J = 2.1 Hz, 1 H), 8.20 (d, J = 8.2 Hz, 2 H), 8.14 (d, J = 8.2 Hz, 1 H), 7.87 (d, J = 1.4 Hz, 1 H), 7.80 (m, 2 H), 7.76 (dd, J = 8.2, 2.1 Hz, 1 H), 7.67 (d, J = 8.2 Hz, 1 H), 7.62 (dd, J = 8.2, 2.1 Hz, 1 H), 7.57 (d, J = 8.2 Hz, 1 H), 7.54 (dt, J = 8.2, 6.9, 1.4 Hz, 1 H), 7.47 (dt, J = 8.2, 6.9, 1.4 Hz, 1 H), 7.43 (m, 4 H), 7.39 (t, J = 6.9 Hz, 1 H), 7.31 (ddd, J = 7.7, 6.0, 2.1 Hz, 2 H).

¹³C NMR (201 MHz, CDCl₃): δ (ppm) = 176.39, 157.22, 156.32, 143.43, 141.75, 140.74, 139.11, 135.15, 130.91, 128.91, 127.13, 126.89, 125.92, 125.89, 125.20, 124.44, 123.61, 123.20, 122.17, 122.02, 121.40, 120.83, 120.67, 120.33, 119.74, 119.67, 118.01, 115.28, 111.04, 110.23, 109.73.

APCI-MS (m/z): $[M + H]^+$ calcd. for $C_{37}H_{23}N_2O_2$, 527.1760; found, 527.1991.

Elemental analysis: calcd. (%) for C₃₇H₂₂N₂O₂: C, 84.39; H, 4.21; N, 5.32; found: C, 84.65; H, 4.24; N, 5.29.



Figure 6.2 NMR spectra of CCX-I in CDCl₃. (a) ¹H NMR spectrum and (b) enlarged view of the region 7.0-9.0 ppm.



Figure 6.2 (contd.) (c) 13 C NMR spectrum.

3-(9'*H*-[9,3':6',9''-Tercarbazol]-9'-yl)-9*H*-xanthen-9-one (CCX-II)

A mixture of TCZ (1.00 g, 2.02 mmol), BXTN (553 mg, 2.01 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (41.6 mg, 0.0402 mmol), XPhos (76.6 mg, 0.161 mmol) and *t*-BuONa (290 mg, 3.02 mmol) in toluene (20 mL) was stirred under reflux for 23 h. After cooling to room temperature, the reaction mixture was extracted with CHCl₃. The organic layer was washed with water and then dried over anhydrous MgSO₄. After filtration and evaporation, the crude product was purified by flash chromatography (silica gel, eluent: CHCl₃) and recrystallized from toluene to provide 1.39 g of CCX-II as a yellow-green solid in 99.7% yield.

¹H NMR (800 MHz, CDCl₃): δ (ppm) = 8.70 (d, J = 8.9 Hz, 1 H), 8.44 (dd, J = 8.2, 2.1 Hz, 1 H), 8.31 (d, J = 2.1 Hz, 2 H), 8.17 (d, J = 8.2 Hz, 4 H), 7.95 (d, J = 2.1 Hz, 1 H), 7.86 (d, J = 8.9 Hz, 4 H), 7.84 (dd, J = 8.2, 2.1 Hz, 2 H), 7.69 (dd, J = 8.6, 1.7 Hz, 1 H), 7.59 (d, J = 7.6 Hz, 1 H), 7.49 (t, J = 8.2 Hz, 1 H), 7.41 (m, 8 H), 7.30 (m, 4 H).

¹³C NMR (201 MHz, CDCl₃): δ (ppm) = 176.45, 157.37, 156.42, 143.14, 141.73, 139.88, 135.37, 131.44, 129.27, 127.03, 126.74, 126.07, 124.82, 124.64, 123.34, 122.27, 122.11, 121.08, 120.47, 120.01, 119.95, 118.14, 115.57, 114.54, 109.71.

APCI-MS (*m*/*z*): [M]⁻ calcd. for C₃₆H₂₄N₃, 691.2260; found, 691.2464.

Elemental analysis: calcd. (%) for C₄₉H₂₉N₃O₂: C, 85.07; H, 4.23; N, 6.07; found: C, 85.03; H, 4.24; N, 6.05.



Figure 6.3 NMR spectra of CCX-II in $CDCl_3$. (a) ¹H NMR spectrum and (b) enlarged view of the region 7.0–9.0 ppm.



Figure 6.3 (contd.) (c) 13 C NMR spectrum.

6.2.3 Device fabrication and measurement of OLED performance

We fabricated OLEDs with structures shown in Fig. 6.4. The OLEDs have the following structures: device A is ITO (50 nm)/TAPC (70 nm)/6 wt% CCX-I:DPEPO (30 nm)/BmPyPhB (40 nm)/Liq (1 nm)/Al (80 nm); device B is ITO (50 nm)/TAPC (70 nm)/CDBP (10 nm)/X wt% CCX-I:PPF or CCX-II:PPF (20 nm)/PPF (10 nm)/BmPyPhB (30 nm)/Liq (1 nm)/Al (80 nm) with X = 6, 10, or 15, where ITO, TAPC, DPEPO, BmPyPhB, Liq, and CDBP are indium tin oxide, 4,4'-(cyclohexane-1,1-diyl)bis[*N*,*N*-bis(4-methylphenyl)aniline], bis[2-(diphenylphosphino)phenyl] ether oxide, 3,3'',5,5''-tetra(pyridin-3-yl)-1,1':3',1''-terphenyl, lithium quinolin-8-olate, and 9,9'-(2,2'-dimethyl-[1,1'-biphenyl]-4,4'-diyl)bis(9*H*-carbazole), respectively. OLEDs with an active area of 4 mm² were fabricated by vacuum-deposition at ~10⁻⁵ Pa on clean ITO-coated glass substrates with a deposition apparatus (SE-4260, ALS Technology, Japan). After fabrication, devices were encapsulated with a desiccant and a glass cap using epoxy glue in a nitrogen-filled glove box. OLED characteristics were measured with a source meter (2400, Keithley, Japan) and an absolute EQE measurement system equipped with an integrating sphere (C9920-12, Hamamatsu Photonics, Japan).

6.2.4 Angular-dependent photoluminescence measurement and optical simulation of OLEDs

Angular-dependent photoluminescence measurements were carried out to analyze orientation of transition dipole moment of the emitters in vacuum-deposited films. 6 wt% CCX-I:PPF and CCX-II:PPF films were prepared by vacuum-deposition on fused silica substrates. Angular-dependent p-polarized PL intensity was measured by a system equipped with a 375nm continuous-wave diode laser (DPS-5004, Neoarc, Japan), a rotation stage, a polarized filter, and a calibrated multichannel spectrometer (PMA-12, Hamamatsu Photonics, Japan) combined with a collimator and optical fiber. PL intensities at 453 nm were monitored while rotating the stage at a fixed excitation angle of 45°. A fused silica half-cylinder prism was attached to the sample substrate using index-matching fluid. The analysis of the experimental data was performed using the opto-electrical device simulator Setfos (Fluxim, Switzerland), providing a ratio of the transition dipole moment aligned horizontally with respect to the substrate, Θ_h . Θ_h is related to orientation order parameter *S*, which is commonly used to quantify molecular orientation, as [9]

$$S = \frac{4(1 - \Theta_{\rm h})^2 - \Theta_{\rm h}^2}{4(1 - \Theta_{\rm h})^2 + 2\Theta_{\rm h}^2}.$$
(6.2)

Optical simulations of OLEDs were performed with Setfos. The optical model used





Figure 6.4 OLED structures and energy level diagrams.

in the simulations was a glass substrate $(0.7 \text{ mm})/\text{ITO} (50 \text{ nm})/\text{TAPC} (x \text{ nm})/\text{CDBP} (10 \text{ nm})/\text{emitting layer (EML, 20 nm})/PPF (10 nm)/BmPyPhB (y nm)/Al (80 nm), where x and y are the thicknesses of the hole-transport layer (TAPC) and the electron-transport layer (BmPyPhB), respectively. In the simulations, the emissive dipoles were assumed to be localized in the interface between the CDBP layer and EML. The <math>\Theta_{\rm h}$ obtained by the angular-dependent PL measurements was used to express the orientation of emissive dipoles.

6.2.5 Measurement of photophysical properties

Ultraviolet–visible (UV–vis) absorption and photoluminescence (PL) spectra were measured with UV–vis (UV-3150, Shimadzu, Japan) and PL (FluoroMax-4, Horiba Scientific, Japan) spectrometers, respectively. $\Phi_{\rm PL}$ was measured using an absolute PLQY measurement system (Quantaurus-QY C11347-01, Hamamatsu Photonics, Japan). Transient PL measurements were performed using a fluorescence lifetime measurement system (Quantaurus-Tau C11367-02, Hamamatsu Photonics, Japan). All the film samples were fabricated by vacuum-deposition on clean fused silica substrates.

From the transient PL decay curves, we determined lifetimes of prompt (τ_p) and delayed (τ_d) fluorescence and prompt and delayed components of the PLQY, Φ_p and Φ_d , respectively. From these values and Φ_{PL} ($\Phi_{PL} = \Phi_p + \Phi_d$), we calculated rate constants for prompt fluorescence (k_p), delayed fluorescence (k_d), intersystem crossing (ISC, k_{ISC}), and reverse ISC (RISC, k_{RISC}) as previously reported [48].

6.3 Results and discussion

6.3.1 Material design

We chose a carbazole derivative with a deep HOMO level as a donor moiety and xanthone with a shallow LUMO level as an acceptor moiety. The HOMOs and LUMOs of the geometry-optimized CCX-I and CCX-II were predominantly distributed over the electron-donating and electron-accepting units, respectively, and were well separated spatially, as shown in Fig. 6.1. Torsion angles (α) between the electron-donating and electron-accepting units of CCX-I and CCX-II were calculated to be 50.0° and 51.2°, respectively (Fig. 6.1). These angles allow for moderate HOMO–LUMO overlap. As shown in Table 6.1, the calculated $\Delta E_{\rm ST}$ of CCX-I and CCX-II are smaller than that of 2,4,5,6-tetra(9*H*-carbazol-9-yl)isophthalonitrile (4CzIPN) [8], one of the most efficient TADF materials developed to date. In addition, the calculated values of *f* and S₀ \rightarrow S₁ excitation energies of CCX-I and CCX-II are larger than that of 4CzIPN,

Emitter	HOMO (eV)	LUMO (eV)	HOMO-LUMO gap (eV)	f^a	$S_1^{\ b}$ (eV)	T_1^c (eV)	$\Delta E_{\rm ST}^{\ d}$ (eV)
CCX-I	-5.49	-1.93	3.55	0.1076	2.76	2.71	0.050
CCX-II	-5.50	-2.03	3.47	0.1292	2.73	2.68	0.050
4CzIPN	-5.97	-2.45	3.52	0.0375	2.45	2.26	0.185

Table 6.1Calculated electronic properties.

^{*a*} Oscillator strength of the $S_0 \rightarrow S_1$ transition.

^{*b*} $S_0 \rightarrow S_1$ excitation energy.

^{*c*} $S_0 \rightarrow T_1$ excitation energy.

^{*d*} Energy difference between S_1 and T_1 .

indicating that CCX-I and CCX-II may be efficient blue TADF materials.

6.3.2 Performance of OLEDs

For blue OLEDs, A choice of appropriate host materials is crucial for effective energy transfer from host to emitting materials. First, we examined DPEPO [49], a widely used host material for blue TADF-based OLEDs. We fabricated an OLED using CCX-I as an emitting dopant, termed CCX-I-6A (device A in Fig. 6.4). The CCX-I-6A showed poor device performance; the maximum $\eta_{\rm EQE}$ was 8.2% and drastically decreased at luminance (L) greater than 100 cd m $^{-2}$ (cross marks in Fig. 6.5). Figure 6.6a shows the EL spectra measured at current densities (*J*) of 1, 25, 60, and 100 mA cm⁻². The EL intensity in the range of 500–800 nm increased with increasing J. The bottom of Fig. 6.7 shows difference of EL spectra obtained by subtracting the EL spectrum measured at $J = 1 \text{ mA cm}^{-2}$ from those measured at $J = 25, 60, \text{ and } 100 \text{ mA cm}^{-2}$. Two emission bands, with maxima at 520 and 580 nm, appeared in the difference spectra. The latter emission band can be assigned to emission from the TAPC layer [50]. The former emission band may be assigned to emission from an exciplex formed between TAPC and CCX-I; the peak wavelength of 520 nm (2.4 eV) corresponds to the energy difference between the HOMO of TAPC and the LUMO of CCX-I. To verify this exciplex emission, we measured PL spectra of 50 wt% CCX-I:TAPC, neat CCX-I, and neat TAPC films fabricated by vacuumdeposition (Fig. 6.7). The PL spectrum of the 50 wt% CCX-I:TAPC film was clearly different from those of the CCX-I and TAPC neat films, suggesting that the emission from the 50 wt% CCX-I:TAPC film originates from the exciplex formed between CCX-I and TAPC. The PL spectrum of the 50 wt% CCX-I:TAPC film also agreed well with the emission band at 520 nm in the difference spectra. Meanwhile, the EL spectrum of TAPC agreed well with the emission band at 580 nm in the difference spectra. These observations suggest that emission from the TAPC layer and the exciplex are responsible for the EL emission in the range of 500-800 nm,



Figure 6.5 η_{EQE} -*L* characteristics of the devices and photos of CCX-II-6B and CCX-II-6B-OC.



Figure 6.6 (a) EL spectra of CCX-I-6A at $J = 1, 25, 60, \text{ and } 100 \text{ mA cm}^{-2}$, with corresponding luminance of 88, 961, 1027, and 706 cd m⁻², respectively. (b) EL spectra of CCX-I-6B at $J = 1, 25, 60, \text{ and } 100 \text{ mA cm}^{-2}$, with corresponding luminance of 133, 2278, 3783, and 5012 cd m⁻², respectively.



Figure 6.7 EL difference spectra of CCX-I-6A (solid lines) and PL spectra of CCX-I, TAPC, and 50 wt% CCX-I:TAPC film together with EL spectrum of TAPC [50] (dashed lines). The difference spectra was obtained by subtracting the EL spectrum measured at $J = 1 \text{ mA cm}^{-2}$ from those measured at J = 25, 60, and 100 mA cm⁻².

leading to the poor performance of CCX-I-6A.

To prevent the formation of the exciplex, CDBP was inserted as an interlayer between the TAPC and emitting layers (CCX-I-6B, device B with X = 6 in Fig. 6.4). CDBP has a high T₁ energy (3.0 eV [51]) and functions as an exciton-blocking layer. In addition, we replaced DPEPO with PPF. PPF shows a higher T₁ energy than DPEPO, and hence, T₁ excitons are expected to be confined more effectively in the emitters when PPF is used as a host. To avoid triplet energy transfer from the emitting layer to the BmPyPhB layer, a thin PPF layer was inserted as an exciton-blocking layer between the emitting and BmPyPhB layers. Figure 6.6b shows the EL spectra of CCX-I-6B measured at J = 1, 25, 60, and 100 mA cm⁻². Unlike CCX-I-6A, no notable change in the spectra was observed in the range of 500–800 nm. The EL spectrum shows a single emission band with a peak at 468 nm assigned to emission from the 6 wt% CCX-I:PPF layer. Importantly, the η_{EQE} -L characteristics were considerably improved; the maximum η_{EQE} of 17.6% (triangles in Fig. 6.5). Figure 6.8a shows the J-V-L characteristic of CCX-I-6B.

By replacing CCX-I with CCX-II in CCX-I-6B, we fabricated CCX-II-based OLEDs (CCX-II-XB, device B with X = 6, 10, 15 in Fig. 6.4). Square, rhombus, and filled circle marks in Fig. 6.5 show the η_{EQE} -L characteristics for the CCX-II-based OLEDs. At X = 6, we obtained the maximum η_{EQE} of 25.9%, which is the highest value reported for blue TADF-OLEDs to date. The *J*-*V*-*L* characteristics of CCX-II-6B are shown in Fig. 6.8a. The EL peak wavelength of CCX-II-6B was 471 nm, corresponding to CIE coordinates of (0.15, 0.22) (the left photograph in Fig. 6.5). The η_{EQE} and color purity are comparable to those obtained with the blue phosphorescent emitter, FIr6, which exhibits the CIE coordinates of (0.14, 0.23) [42]. When using a light out-coupling sheet with microlens array (CCX-II-6B-OC), we obtained an η_{EQE} of 33.3%. The η_{EQE} remained at 21.9% even at luminance of 1000 cd m⁻² (open circles and the right photograph in Fig. 6.5). Increasing the doping concentration improved the efficiency roll-off in the η_{EQE} -L characteristics. For X = 15, a maximum power efficiency of 52.5 lm W⁻¹ and a current efficiency of 47.5 cd A⁻¹ were obtained (Fig. 6.8b). These values are high compared with those of other blue TADF-based OLEDs reported to date [12–15, 17–22]. The device characteristics of the CCX-II-and CCX-II-based OLEDs are listed in Table 6.2.

From the angular-dependent PL measurements of 6 wt% CCX-I- and CCX-II-doped PPF films, we found that the transition dipole moments of CCX-I and CCX-II were horizontally oriented with respect to the glass substrate, resulting in enhanced light out-coupling of devices. The ratios of the horizontal dipole (Θ_h) for 6 wt% CCX-I- and CCX-II-doped PPF films were



Figure 6.8 (a) J-V-L characteristics of CCX-I-6B and CCX-II-6B. (b) Current efficiency (CE) and power efficiency (PE) of CCX-II-15B as a function of *L*.

Devices	EQE _{max} ^a (%)	EQE _{100/500/1000} ^b (%)	$\frac{PE_{max}^{c}}{(lm W^{-1})}$	$\operatorname{CE}_{\max}^{d}$ (cd A ⁻¹)	$\lambda_{\rm EL}^{\ e}$ (nm)	CIE $(x, y)^f$
I-6B	17.6	13.7 / 10.9 / 9.0	24.7	28.3	468	(0.16, 0.21)
II-6B	25.9	20.2 / 16.3 / 14.4	35.9	41.1	471	(0.15, 0.22)
II-10B	24.5	21.8 / 19.0 / 17.0	44.9	44.8	476	(0.16, 0.26)
II-15B	24.0	22.1 / 19.7 / 18.4	52.5	47.5	480	(0.16, 0.29)
II-6B-OC	33.3	28.9 / 24.2 / 21.9	54.4	55.4	469	(0.16, 0.22)

Table 6.2OLED performance of devices based on CCX-I and CCX-II.

^{*a*} Maximum η_{EQE} .

 b $\eta_{\rm EOE}$ at luminance of 100, 500, and 1000 cd m⁻².

^{*c*} Maximum power efficiency.

^{*d*} Maximum current efficiency.

^{*e*} EL peak wavelength at luminance of 1000 cd m^{-2} .

 f CIE coordinates at luminance of 1000 cd m⁻².

determined to be 0.75 and 0.83, which correspond to the orientation order parameters (*S*) of -0.17 and -0.36, respectively (Fig. 6.9). Optical simulations based on these *S* values showed that CCX-I-6B and CCX-II-6B can potentially exhibit η_{out} of 25.0% and 29.5%, respectively (Fig. 6.10). Using the relation, $\eta_{IQE} = \eta_{EQE}/\eta_{out}$, we calculated the η_{IQE} values of CCX-I-6B and CCX-II-6B to be 70.4% and 87.8%, respectively. These η_{IQE} values are higher than those of conventional fluorescent OLEDs. Thus, the high performance of CCX-I-6B and CCX-II-6B results from the efficient TADF and horizontal orientation of CCX-I and CCX-II molecules.

6.3.3 Photophysical properties

Figure 6.11 shows UV–vis absorption and PL spectra of CCX-I and CCX-II in toluene solution $(1.0 \times 10^{-5} \text{ M})$. The absorption intensity was larger for CCX-II than that for CCX-I, reflecting the greater *f* value of CCX-II than that of CCX-I (Table 6.1). From the absorption edges (423 nm for both CCX-I and CCX-II), the HOMO–LUMO gaps of CCX-I and CCX-II were confirmed to be sufficiently wide for blue emission. The PL peak wavelengths (λ_{PL}) for CCX-I and CCX-II were 453 and 450 nm, respectively. In the dilute toluene solution, CCX-I and CCX-II showed pure blue emission. We also fabricated 6 wt% CCX-I:PPF and CCX-II:PPF films by vacuum-deposition. PLQYs of the 6 wt% CCX-I:PPF and CCX-II:PPF doped films were both nearly 100% [(97.2 ± 4.0)% and (104.0 ± 4.0)%, respectively] when the emitter was directly excited. When PPF was excited, the PLQYs decreased to (88.6 ± 4.0)% and (96.8 ± 4.0)%, respectively. The decrease in PLQY suggests that energy loss occurs during the energy transfer from PPF to the emitter. Figure 6.12a shows PL spectra of the 6 wt% CCX-II:PPF films was 468 nm



Figure 6.9 Angular-dependent p-polarized PL intensities of 6 wt% CCX-I:PPF and CCX-II:PPF films.



Figure 6.10 Calculated η_{out} as a function of the thicknesses of the hole-transport layer (HTL) and electron-transport layer (ETL) for (a) CCX-I-6B and (b) CCX-II-6B.



Figure 6.11 PL (solid lines) and UV-vis (dashed lines) spectra of CCX-I and CCX-II in toluene $(1.0 \times 10^{-5} \text{ M})$.



Figure 6.12 (a) PL spectra of 6 wt% CCX-I:PPF and CCX-II:PPF films. (b) Temperature dependence of transient PL characteristics for a 6 wt% CCX-II:PPF film.

and 465 nm, respectively, and no emission from PPF was observed. The PL spectra of CCX-I and CCX-II in the PPF host were red shifted by 15 nm compared to those in toluene solution.

Figure 6.12b shows temperature dependence of transient PL decay curves for the 6 wt% CCX-II:PPF film. In addition to prompt fluorescence, long tailed fluorescence was observed. The delayed fluorescence increased with increasing temperature, indicating that it is involved in a thermal activation process. Rate constants of the prompt fluorescence, TADF, ISC, and RISC together with contributions from prompt and delayed components to PLQY are summarized in Table 6.3. Using the method previously reported [40], we calculated the IQE at 298 K to be 70.6% and 88.7% for CCX-I and CCX-II, respectively. The IQE calculated from this analysis was in good agreement with that obtained from optical simulations (70.4% and 87.8% for CCX-I and CCX-II, respectively). This agreement indicates that excitons are well confined in the emitting layers and losses occurred only in the emitting layer. Figure 6.13 shows the temperature dependence of the PLQY, RISC efficiency, and IQE of CCX-II doped films. The PLQY of CCX-II is independent of temperature and remained at nearly 100%. The IQE also remained over 80%, suggesting that ΔE_{ST} was sufficiently small to induce RISC at room temperature. From Arrhenius plots of the rate constant of RISC, the ΔE_{ST} values of CCX-I and CCX-II were estimated to be 70 and 31 meV, respectively (Fig. 6.14), which are smaller than that of 4CzIPN (83 meV).

6.4 Conclusions

In conclusion, we developed efficient TADF emitters, CCX-I and CCX-II, with small ΔE_{ST} and large *f*. When the emitters were doped into host matrices, CCX-I and CCX-II showed high PLQYs and blue emission. OLEDs containing CCX-II as an emitting dopant achieved the maximum EQE of 25.9%, which is the highest reported to date among blue TADF-based OLEDs. The OLEDs also showed good color purity with the CIE coordinates of (0.15, 0.22). Further device optimization, using host materials that produce a higher IQE than that of PPF, would allow additional improvement in the performance of CCX-I- and CCX-II-based OLEDs.

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Table 6.3 Temperature dependence of lifetimes, PLQYs and rate constants for (a) the 6 wt% CCX-II:PPF and (b) 6 wt% CCX-II:PPF systems.

(a) 6	wt% C	CX-I:PP	F						
<i>T^a</i> (K)	$\tau_{\rm p}^{\ b}$ (ns)	τ_d^c (µs)	${\Phi_{ ext{PL}}}^d_{(\%)}$	$\Phi_{\mathrm{p}}^{\ e}$ (%)	Φ_{d}^{f} (%)	$\frac{k_{\rm p}{}^{g}}{(10^{7}{ m s}^{-1})}$	$\frac{k_{\rm d}{}^{h}}{(10^{3}{ m s}^{-1})}$	$\frac{k_{\rm ISC}}{(10^7 { m s}^{-1})}$	$\frac{k_{\rm RISC}^{j}}{(10^3 {\rm s}^{-1})}$
200	8.32	24.9	89.1	76.7	12.5	9.22	4.99	1.28	5.81
220	8.29	18.0	101.8	89.1	12.7	10.7	7.14	1.34	8.15
240	8.10	15.2	83.5	72.4	11.1	8.95	7.34	1.19	8.47
260	7.98	14.5	98.9	82.3	16.9	10.3	11.6	1.74	14.0
280	7.82	14.5	93.4	73.6	19.8	9.41	13.7	1.99	17.4
298	7.77	12.2	88.6	67.7	20.9	8.71	17.2	2.06	22.5
(b) 6 wt% CCX-II:PPF									
(0) 0	wt% C	CX-II:PI	PF						
$\frac{(b) \ 6}{T^a}$ (K)	$\frac{\text{wt\% Co}}{\tau_{p}^{b}}$ (ns)	$\frac{\tau_d^c}{(\mu s)}$	$\frac{\Phi_{\rm PL}^{d}}{(\%)}$	$\Phi_{\rm p}^{\ e}$ (%)	Φ _d ^f (%)	$k_{\rm p}^{g}$ (10 ⁷ s ⁻¹)	$\frac{k_{\rm d}{}^{h}}{(10^{3}{ m s}^{-1})}$	$\frac{k_{\rm ISC}{}^i}{(10^7{\rm s}^{-1})}$	$\frac{k_{\rm RISC}^{j}}{(10^3 \rm s^{-1})}$
$(0) \ 0$ T^a (K) 200	$\frac{\text{wt\% C}}{\tau_{p}^{b}}$ (ns) 7.30	$\frac{\tau_{d}^{c}}{(\mu s)}$	$\frac{\Phi_{\rm PL}^{\ \ d}}{(\%)}$ 95.3	Φ _p ^e (%) 86.9	Φ _d ^f (%) 8.3	$\frac{k_{\rm p}^{g}}{(10^{7}{ m s}^{-1})}$ 13.7	$\frac{k_{\rm d}^{\ h}}{(10^3{ m s}^{-1})}$ 66.9	$\frac{k_{\rm ISC}^{\ i}}{(10^7 {\rm s}^{-1})}$ 1.79	$\frac{k_{\text{RISC}}^{j}}{(10^{3} \text{s}^{-1})}$ 77.3
	$\frac{\text{wt% Co}}{\tau_{\text{p}}^{b}}$ (ns) 7.30 7.35	$\frac{\tau_d^c}{(\mu s)}$ $\frac{\tau_d^c}{15.2}$	$\frac{\Phi_{\rm PL}^{\ \ d}}{(\%)}$ 95.3 96.6	$\Phi_{\rm p}^{\ e}$ (%) 86.9 85.5	Φ_{d}^{f} (%) 8.3 11.2	$\frac{k_{\rm p}{}^g}{(10^7{\rm s}^{-1})}$ 13.7 13.6		$\frac{k_{\rm ISC}{}^{i}}{(10^{7}{\rm s}^{-1})}$ 1.79 1.97	$\frac{k_{\rm RISC}^{j}}{(10^{3}{\rm s}^{-1})}$ 77.3 76.6
$ \begin{array}{r} (6) & 6 \\ \overline{T^a} \\ (K) \\ \overline{200} \\ 220 \\ 240 \\ \end{array} $	$ \frac{\tau_{\rm p}^{\ b}}{(\rm ns)} = \frac{\tau_{\rm p}^{\ b}}{7.30} \\ 7.35 \\ 7.18 $	$\frac{\tau_{d}^{c}}{(\mu s)}$ $\frac{\tau_{d}^{c}}{15.2}$ $\frac{15.6}{14.0}$	$ \frac{\Phi_{\rm PL}^{\ \ d}}{(\%)} $ 95.3 96.6 95.9	$\Phi_{\rm p}^{\ e}$ (%) 86.9 85.5 83.8	Φ_{d}^{f} (%) 8.3 11.2 12.1		$ \begin{array}{r} k_{\rm d}^{\ h} \\ (10^3 {\rm s}^{-1}) \\ 66.9 \\ 65.2 \\ 73.5 \\ \end{array} $	$\frac{k_{\rm ISC}^{\ i}}{(10^7 {\rm s}^{-1})}$ 1.79 1.97 2.26	$\frac{k_{\rm RISC}{}^{j}}{(10^{3} {\rm s}^{-1})}$ 77.3 76.6 88.2
	$ \frac{\tau_{\rm p}^{\ b}}{(\rm ns)} \\ 7.30 \\ 7.35 \\ 7.18 \\ 7.15 $	$ \begin{array}{r} CX-II:PI \\ \overline{\tau_d}^c \\ (\mu s) \\ \overline{15.2} \\ 15.6 \\ 14.0 \\ 13.2 \\ \end{array} $	$ \frac{\Phi_{\rm PL}^{\ d}}{(\%)} $ 95.3 96.6 95.9 95.9		$ \begin{array}{c} \Phi_{d}^{\ f} \\ (\%) \\ 8.3 \\ 11.2 \\ 12.1 \\ 14.7 \\ \end{array} $		$ \begin{array}{r} k_{\rm d}{}^{h} \\ (10^{3} {\rm s}^{-1}) \\ 66.9 \\ 65.2 \\ 73.5 \\ 79.5 \\ \end{array} $	$\frac{k_{\rm ISC}{}^{i}}{(10^{7} {\rm s}^{-1})}$ 1.79 1.97 2.26 2.64	$\begin{array}{c} k_{\rm RISC}{}^{j}\\ (10^{3}{\rm s}^{-1})\\ 77.3\\ 76.6\\ 88.2\\ 98.6\end{array}$
$ \begin{array}{c} (6) & 6 \\ \hline T^a \\ (K) \\ \hline 200 \\ 220 \\ 240 \\ 260 \\ 280 \\ \end{array} $	$ wt% Co \tau_p^{\ b} (ns) 7.30 7.35 7.18 7.15 6.82 $	$ \begin{array}{r} CX-II:PJ \\ \overline{\tau_d}^c \\ (\mu s) \\ 15.2 \\ 15.6 \\ 14.0 \\ 13.2 \\ 10.5 \\ \end{array} $	$\frac{\Phi_{\rm PL}^{\ d}}{(\%)}$ 95.3 96.6 95.9 95.9 95.9 95.2	$\Phi_{\rm p}^{\ e}$ (%) 86.9 85.5 83.8 81.1 79.2	$\begin{array}{c} \Phi_{d}{}^{f} \\ (\%) \\ \hline 8.3 \\ 11.2 \\ 12.1 \\ 14.7 \\ 16.1 \end{array}$		$ \begin{array}{r} k_{d}^{h} \\ (10^{3} s^{-1}) \\ 66.9 \\ 65.2 \\ 73.5 \\ 79.5 \\ 95.3 \\ \end{array} $	$\frac{k_{\rm ISC}{}^{i}}{(10^{7} {\rm s}^{-1})}$ 1.79 1.97 2.26 2.64 3.05	$\begin{array}{c} k_{\rm RISC}{}^{j} \\ (10^{3} {\rm s}^{-1}) \\ 77.3 \\ 76.6 \\ 88.2 \\ 98.6 \\ 120 \end{array}$

^{*a*} Temperature.

^b Lifetime of prompt fluorescence.

^{*c*} Lifetime of delayed fluorescence.

^d PLQY of overall fluorescence ($\Phi_{\rm PL} = \Phi_{\rm p} + \Phi_{\rm d}$).

^{*e*} PLQY of prompt fluorescence.

^{*f*} PLQY of delayed fluorescence.

^g Rate constant of prompt fluorescence.

^{*h*} Rate constant of delayed fluorescence.

^{*i*} Rate constant of ISC.

^{*j*} Rate constant of RISC.



Figure 6.13 Temperature dependence of PLQY, RISC efficiency, and IQE for the 6 wt% CCX-II:PPF system.



Figure 6.14 Arrhenius plots of the rate constant of RISC for (a) the 6 wt% CCX-I:PPF and (b) 6 wt% CCX-II:PPF systems. The ΔE_{ST} values were obtained by least-squares fitting (red solid lines).

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Concluding Remarks

This thesis investigated charge transport in organic amorphous semiconductors, morphology of organic materials in amorphous state, and luminescent properties of emitting materials and their performance in organic light-emitting diodes (OLEDs), from both computational and experimental points of view. The results and findings in this thesis are summarized as follows.

PART I (CHAPTERS 1 to 3) developed methodology of *multiscale charge transport simulation* and investigated charge transport in organic amorphous semiconductors used for OLEDs. The multiscale simulation is based on the combined use of quantum chemical, molecular dynamics (MD), and kinetic Monte Carlo calculations, which can bridge the scales from molecules to practical devices. The motivation of the simulation is to elucidate the relationship between charge transport mechanism and properties of a single molecule itself. In the simulation, the explicit consideration of molecules in amorphous systems enables ones to investigate not only the electronic states of molecule but also the nature of amorphous state and its effects on charge transport properties.

In CHAPTER 1 of PART I, the calculated charge mobilities were reasonably reproduced the experimentally observed hole mobility, including the dependence of external electric field on the mobility, so-called Poole–Frenkel (PF) behavior. The simulation provided the detailed picture of charge hopping mechanism in the disordered system that results in the PF behavior. The detailed analysis also revealed how the electronic coupling of molecules relevant to charge hopping influences charge transport. Interestingly, charge transport in the amorphous system was dominated by the molecular pairs not with significantly large electronic coupling but with moderate coupling, which can form effective charge transport paths in the system. This finding is possibly a contrast to the cases of organic crystalline systems. Furthermore, it should be addressed that the simulation does not rely on any adjustable parameters that are used to fit experimental data. This approach is useful to ones in assessing charge transport properties of a given organic material for predicting purposes.

CHAPTER 2 of PART I raised the question whether charge transport in organic amorphous systems originates from charge hopping only through highest occupied or lowest unoccupied molecular orbitals (HOMOs or LUMOs). The multiscale charge transport simulation

in CHAPTER 2 indicated that charge carriers are effectively transported via lower- or higherlying molecular orbitals as well as HOMOs or LUMOs in the system. The detailed insight revealed that this transport mechanism is essential when the site energies of molecules relevant for charge hopping are close in energy, viz., (quasi-)degenerate. On the basis of these findings, this chapter proposed that the molecular orbitals contributed to charge transport should be addressed as *multiple frontier orbitals*, which are analogous to the concept of frontier orbitals describing chemical reactions. As a consequence of taking multiple frontier orbitals into account, the agreement of calculated mobilities with the experimental results was improved compared to the simulation demonstrated in CHAPTER 1. The author believes that the findings presented in CHAPTER 2 should pave the way for a promising strategy to realize highly efficient charge transport materials.

CHAPTER 3 of PART I evaluated the effects of calculation level on the multiscale charge transport simulation. The multiscale simulation of organic amorphous systems needs to treat a large atomistic system *in silico* because the systems possess disordered nature in their structure, whereas ordered crystalline systems can be treated using a unit cell and periodic boundary condition. In this regard, the reduction of computational cost is desired for the multiscale simulation. The results presented in CHAPTER 3 showed that the use of high-cost computational method does not always provide better agreement with experimentally obtained charge mobilities. The higher level of theory demanded much more computational resource and time, which is not practical for use in large scale simulation. Considering such a situation, the semiempirical methods employed in CHAPTERS 1 to 3 can be considered to yield reasonable prediction of charge mobility within moderate computational resource and time. The author hopes that the multiscale charge transport simulation demonstrated in PART I should be a promising *in silico* approach to design excellent organic charge transport materials, and ultimately, to explore extensive chemical space for material discovery.

PART II (CHAPTER 4) demonstrated the methodologies that shed light on molecular-level insight into morphology of organic amorphous materials. In the past few decades, organic amorphous solids have been considered to possess isotropic morphology. However, it is now known that the isotropic nature does not always inhere in organic amorphous systems due to the existence of preferable molecular orientation in the solids. It is therefore essential to understand the morphology because it has remarkable impacts on the performance of opto-electronic devices. Although many experimental investigations have proceeded to elucidate morphology of organic amorphous materials, the methodology that provides molecular-level information on the morphology is not yet well established.

CHAPTER 4 of PART II exemplified the first application of dynamic nuclear polarization

(DNP) enhanced solid-state nuclear magnetic resonance (ssNMR) (DNP-ssNMR) spectroscopy to an electron transporting phosphine oxide to investigate molecular orientation in its amorphous state. Although molecular orientation in organic amorphous solids can be analyzed by several measurement techniques, the methods essentially provide only system-averaged information on molecular orientation. CHAPTER 4 demonstrated that the application of DNP-ssNMR spectroscopy enables ones to reveal molecular orientation in amorphous solids without lack of molecular-level information, for example, distribution of molecular orientation. This chapter also succeeded in obtaining the DNP-enhanced signals sufficient for the quantitative analysis of molecular orientation. The results presented in CHAPTER 4 showed that the phosphine oxide exhibits different molecular orientation depending on the preparation methods of thin films. This difference in molecular orientation was found to affect the photocurrent transient behavior, indicating the different charge transport properties.

The work presented in PART II provided molecular-level insight into morphology of organic amorphous solids and its effect on their properties from the experimental point of view. The author believes that this approach lead to a powerful tool to clarify the relationship between morphology of organic amorphous systems and their properties, and moreover, to design morphology for realization of high performance organic electronic devices.

PART III (CHAPTERS 5 and 6) designed and developed efficient emitting materials for use in OLEDs. The materials demonstrated in CHAPTERS 5 and 6 both exhibited thermally activated delayed fluorescence (TADF). This is accomplished by designing donor–acceptor frameworks so that they possess not only a small energy gap between the lowest excited singlet and lowest triplet states but also a large oscillator strength, leading to efficient reverse intersystem crossing from the triplet to singlet states and fast radiative decay from the singlet state. The resulting emitters exhibited green (CHAPTER 5), sky-blue (CHAPTER 5), and blue (CHAPTER 6) emission with the high photoluminescence quantum yields in host matrices. The analysis of photophysical properties of the emitters confirmed that the triplet excitons are effectively upconverted to singlet ones in the host matrices. As a consequence, the excitons generated in the OLEDs were effectively converted into light via the singlet excitons, resulting in the high external quantum efficiencies. The works presented in PART III provided the clear guideline to aid design of TADF emitters and exemplified its applicability. The author expects that a combination of this guideline and cheminformatics should be a more powerful and high-throughput tool for realization of excellent TADF-based OLEDs.

To conclude, this thesis aimed at the establishment of fundamental science inherent in organic electronics through the investigations on charge transport, morphological, and luminescent properties of organic materials. The core concept of this thesis, multiscale simulation, is expected to progress to the next stage to investigate wider range of phenomena, for example in OLEDs, charge transport in multilayered film stacks, charge recombination, exciton dynamics and transport, and light propagation. The author believes that it will lead to a concept of *in silico design and fabrication of organic electronic devices*, which enables ones to tailor organic materials, device structures, and even fabrication processes completely in a computer. This concept should be a promising approach to discover excellent organic materials and electronic devices. Owing to the growth of computational technologies, material scientists are now allowed to tackle complex problems in organic electronics to shed light on underlying science, however, they have not yet gained complete understanding of organic electronics. A continuous challenge is therefore essential to gain further insight into device physics and related material properties. The author hopes that the findings presented in this thesis will aid ones to grasp *in-depth knowledge of organic electronics*.

List of Publications

Part I

Chapter 1

"Detailed analysis of charge transport in amorphous organic thin layer by multiscale simulation without any adjustable parameters"

H. Uratani, **S. Kubo**, K. Shizu, F. Suzuki, T. Fukushima, and H. Kaji *Sci. Rep.* **2016**, *6*, 39128.

CHAPTER 1 is the author's version of a submitted work that was subsequently accepted for publication in *Scientific Reports*, copyright © Springer Nature, after peer review. The contents of supplemental material in the publication are included in this chapter. To access the final edited and published work see the following website: https://doi.org/10.1038/srep39128

Chapter 2

"Parameter-free multiscale simulation realising quantitative prediction of hole and electron mobilities in organic amorphous system with multiple frontier orbitals"

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S. Kubo and H. Kaji
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Sci. Rep. 2018, 8, 13462.

CHAPTER 2 is the author's version of a submitted work that was subsequently accepted for publication in *Scientific Reports*, copyright © Springer Nature, after peer review. The contents of supplemental material in the publication are included in this chapter. To access the final edited and published work see the following website: https://doi.org/10.1038/s41598-018-31722-w

Chapter 3

"Effects of Calculation Levels on Multiscale Charge Transport Simulation in Organic Amorphous Systems"

S. Kubo, K. Moriwaki, and H. Kaji

CHAPTER 3 is the author's version of an unpublished work that will be submitted for publication.

Part II

Chapter 4

"Analysis of molecular orientation in organic semiconducting thin films using static dynamic nuclear polarization enhanced solid-state NMR spectroscopy" K. Suzuki, **S. Kubo**, F. Aussenac, F. Engelke, T. Fukushima, and H. Kaji *Angew. Chem. Int. Ed.* **2017**, *56*, 14842–14846. *Angew. Chem.* **2017**, *129*, 15038–15042.

CHAPTER 4 is the author's version of a submitted work that was subsequently accepted for publication in *Angewandte Chemie International Edition* and *Angewandte Chemie*, copyright © Wiley-VCH, after peer review. The contents of supplemental material in the publication are included in this chapter. To access the final edited and published work see the following website: https://doi.org/10.1002/anie.201707208
Part III

Chapter 5

"Triarylboron-based fluorescent organic light-emitting diodes with external quantum efficiencies exceeding 20%"

K. Suzuki, **S. Kubo**, K. Shizu, T. Fukushima, A. Wakamiya, Y. Murata, C. Adachi, and H. Kaji *Angew. Chem. Int. Ed.* **2015**, *54*, 15231–15235.

Angew. Chem. 2015, 127, 15446–15450.

CHAPTER 5 is the author's version of a submitted work that was subsequently accepted for publication in *Angewandte Chemie International Edition* and *Angewandte Chemie*, copyright © Wiley-VCH, after peer review. The contents of supplemental material in the publication are included in this chapter. To access the final edited and published work see the following website: https://doi.org/10.1002/anie.201508270

Chapter 6

"Blue organic light-emitting diodes realizing external quantum efficiency over 25% using thermally activated delayed fluorescence emitters"

T. Miwa, **S. Kubo**, K. Shizu, T. Komino, C. Adachi, and H. Kaji *Sci. Rep.* **2017**, *7*, 284.

CHAPTER 6 is the author's version of a submitted work that was subsequently accepted for publication in *Scientific Reports*, copyright © Springer Nature, after peer review. The contents of supplemental material in the publication are included in this chapter. To access the final edited and published work see the following website: https://doi.org/10.1038/s41598-017-00368-5

Other publications

"Purely organic electroluminescent material realizing 100% conversion from electricity to light"

H. Kaji, H. Suzuki, T. Fukushima, K. Shizu, K. Suzuki, **S. Kubo**, T. Komino, H. Oiwa, F. Suzuki, A. Wakamiya, Y. Murata, and C. Adachi *Nat. Commun.* **2015**, *6*, 8476.

"Highly efficient electroluminescence from a solution-processable thermally activated delayed fluorescence emitter"

Y. Wada, K. Shizu, **S. Kubo**, K. Suzuki, H. Tanaka, C. Adachi, and H. Kaji *Appl. Phys. Lett.* **2015**, *107*, 183303.

"Highly efficient solution-processed host-free organic light-emitting diodes showing an external quantum efficiency of nearly 18% with a thermally activated delayed fluorescence emitter" Y. Wada, K. Shizu, **S. Kubo**, T. Fukushima, T. Miwa, H. Tanaka, C. Adachi, and H. Kaji *Appl. Phys. Express* **2016**, *9*, 032102.

"Adamantyl substitution strategy for realizing solution-processable thermally stable deep-blue thermally activated delayed fluorescence materials"

Y. Wada, S. Kubo, and H. Kaji

Adv. Mater. 2018, 30, 1705641.

"Effects of structural and energetic disorders on charge transports in crystal and amorphous organic layers"

F. Suzuki, S. Kubo, T. Fukushima, and H. Kaji

Sci. Rep. 2018, 8, 5203.

"Thermally activated delayed fluorescent materials combining intra- and intermolecular charge transfers"

D. Zhang, K. Suzuki, X. Song, Y. Wada, **S. Kubo**, L. Duan, and H. Kaji *ACS Appl. Mater. Interfaces* **2019**, *11*, 7192–7198.

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Assoc. Prof. Atsushi Goto	Mr. Sotaro Higaki
(currently Division of Chemistry and Biological	Mr. Rin Wakayama
Chemistry, School of Physical and Mathemati-	Mr. Yasuaki Wakisaka
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Shosei Kubo Shosei Kubo