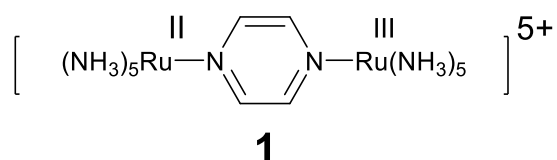


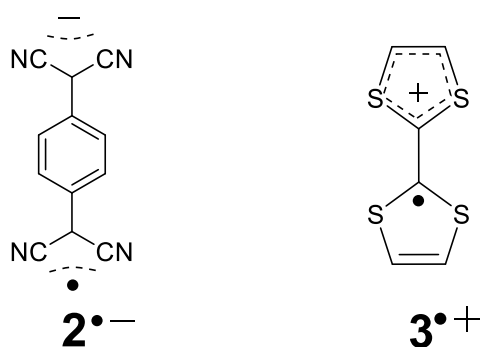
General introduction

1. Scientific history of organic mixed-valence compound research

Mixed valence (MV) is a general term that refers to the inclusion of several different oxidation states within a system. Therefore, MV compounds have multiple redox sites and bridging sites connecting them within a single compound. The bridging sites can be non-covalent or covalent, and the redox sites can be inorganic or organic compound, and a mixture of both. The concept of mixed valence was first introduced for the inorganic complex Creutz-Table complex (**1**)^[1] Near-infrared (NIR) absorption spectra of this complex revealed an electron transfer (ET) between two ruthenium metals, Ru(II) and Ru(III), and this compound has been studied as a typical example of an inorganic MV compound from the 1970s to the present.^[2]



In mixed valence chemistry, it is extremely important to classify MV states by their intramolecular electronic states. For simplicity, the intramolecular electronic state of the MV molecule with two redox sites and one charge is often discussed. It is roughly classified into three possible electronic states: a localized state in which the charge is concentrated on one of the redox sites, a delocalized state with an equally distributed charge at both sites, and an intermediate state. This classification was later systematically summarized by Robin and Day in terms of electronic coupling (H_{AB}). The three classes were named “Class I,” in which the electronic coupling among two redox sites is negligibly small and the charge is localized, “Class III” in which the electronic coupling is quite large and the charge is delocalized, and their intermediate state “Class II”. The classification is still widely used today.^[3] At about the same time as the inorganic MV compounds were found, organic MV compounds were also discovered for tetracyanoquinodimethane (TCNQ) (**2**)^[4] and tetrathiafulvalene (TTF)(**3**)^[5] already synthesized for potential application to organic high charge-transfer (CT) complexes. In 1973, Cowan *et al.* reported that their radical anions (TCNQ^{•-}) and radical cations (TTF^{•+}) are in MV state.^[6]



In 1976, Kosower and Teuerstein *et al.* carried out absorption measurements on a complex consisting of an alkane-bridged bis(pyridinium) dication and a pyridinyl radical. They succeeded to detect the MV by measuring a broad NIR absorption due to CT between redox sites. ^[7] They named this absorption band “intervalence absorption,” and it will be referred to as the “intervalence charge transfer band” (IVCT band) in this doctoral thesis. In organic MV systems, the IVCT band usually appears in the NIR region and does not overlap with other absorption bands. Therefore, it is suitable for identification of the MV state by analyzing the absorption bands. In inorganic MV systems, on the other hand, the IVCT bands are weak and are often masked by ligand-metal CT or metal-ligand CT bands. ^[8] Also, in EPR measurements, electron transfer rate in the molecule of organic MV systems can be kept within the measurement time scale while that in most inorganic MV systems cannot. ^[9] Therefore, soon after the beginning of the study of organic mixed valence, EPR spectroscopy was applied to the evaluation of spin delocalization and localization; an example is the study of diketone by Mazur *et al.* published in 1976. ^[10] In the 1990s, Nelsen *et al.* and Launay *et al.* established respectively a methodology to calculate H_{AB} values from absorption measurements by analyzing the IVCT bands of organic MV compounds based on Marcus-Hush theory. ^[11] This makes it possible to evaluate the Marcus-Hush theory by directly comparing the electron transfer rates calculated from the EPR spectroscopy measurements and the IVCT band analysis. ^[12]

The early work described above, as well as the establishment of measurement and analytical methods, have led many researchers, Lambert etc., to incessant studies on organic MV compounds consisting of various bridging and redox sites. The field of organic MV chemistry is closely linked to “molecular electronics,” the concepts of understanding and controlling the electronic properties within a single molecule as the smallest unit, and applying these to electronic devices, either single molecular systems or assemblies of multiple molecules. ^[13] Each plentiful and interesting information reported so far has contributed to the realization of new electronic devices, and in recent years, organic MV compounds have appeared in a wide range fields of science. ^[8,14]

2. How to determine mixed valence states

2-1 Theoretical interpretation of MV states

To easily understand the MV system, in this section the author assumes a simple symmetrical degenerate organic compound (R-B-R type) with two identical redox sites (R) connected by one bridging site (B), and consider a state in which one charge or spin is added to the R-B-R molecule. Then, Class I can be expressed as $R^{\cdot+}-B-R$, Class II as ${}^{\cdot+}R-B-R \rightleftharpoons R-B-R^{\cdot+}$, and Class III as $[R-B-R]^{\cdot+}$, respectively. Marcus explained the CT process as the system moving from left to right on a potential energy surface consisting of two degenerate parabolic energy surfaces through a transition state. (Figure 1) ^[15]

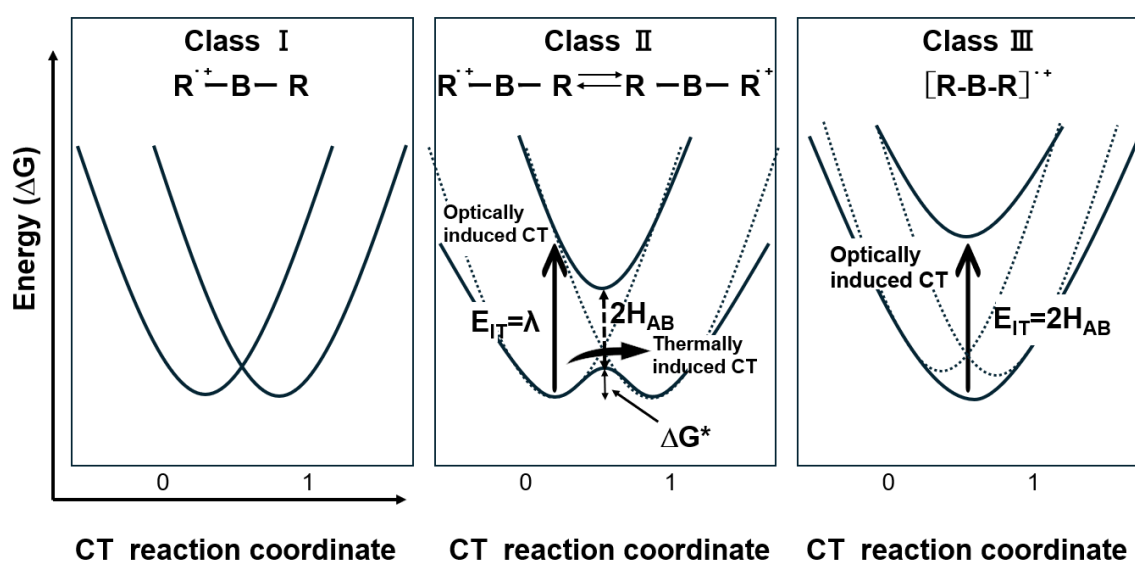


Figure 1. Schematic representation of diabatic and adiabatic surface for a degenerate two-state MV system.

Each of the two energy planes represent the localization of spin to one redox active unit. In Class I state, where there is no electronic interaction between the redox active sites, a diabatic surface as the harmonic potential of the two surfaces is formed and CT barrier exists at the intermediate intersection. In Class II and Class III states with electron interaction, the two non-adiabatic surfaces form two adiabatic surfaces by electronic coupling. These two surfaces are divided by twice the size of the electronic coupling (H_{AB}). In the case of Class II, an activation barrier of ΔG^* exists at the midpoint of the lower adiabatic surface. The thermally induced CT process is carried out by overcoming this activation barrier from left to right. The vertical energy difference between the minimum value of the lower adiabatic plane and the upper adiabatic plane is called the reorganization energy (λ). It represents the total energy required for structural changes in bond lengths and angles within the MV system (internal factor: λ_{in}) and solvent rearrangement (external factor: λ_{out}) through the optically induced CT

process. When λ is constant and the electron coupling rises to $\lambda \leq 2H_{AB}$, the ΔG^* activation barrier disappears and electron/spins delocalize between redox active sites. In this Class III state, optically induced CT process occurs from the lowest point of the lower adiabatic surface to the upper adiabatic surface. Although the energy difference is consistent with $2H_{AB}$, no apparent CT occurs in this transition and the two redox sites have averaged valence states.

2-2 Methods for discriminating MV states based on experimental and theoretical results

The shape of the IVCT band in UV-vis-NIR spectra can be used to determine the MV state roughly; the IVCT band can be identified by stepwise spectral measurements using electrochemical or chemical oxidation. For example, in the R-B-R monoradical cation species, the IVCT band is observed when IVCT is occurring, while by the further oxidation to the dication species, the IVCT band disappears due to the elimination of CT process where both redox sites are completely oxidized. Class II band is generally represented as a broad Gaussian function. Since the energy of the band coincides with the reorganization energy (λ), rigid molecules have lower energies due to the small internal conformational changes during the CT process. The IVCT band of Class II is also characterized by the solvent property: change of the solvent causes a change in λ_{out} due to external factors. On the other hand, Class III has a narrow absorption band with a vibrational structure. This is because the excited state surface has a minimum near the equilibrium shape of the ground state, and the wave packet on the excited state surface created by the Frank-Condon transition can return to the ground state within about 1 picosecond. As for MV systems with strong electronic coupling and “almost delocalized” Class II/Class III boundary, the lack of electronic transitions below $2H_{AB}$ provides a narrow asymmetric band shape where the low-energy side of the band below $2H_{AB}$ is cut off.^[16] No vibrational structure due to strong interactions with symmetric vibrations has been reported by Lambert and Nöll in their study of tetramethoxyphenyl-para-phenylenediamine.^[17] Therefore, it is premature to determine the MV state only by the shape of the IVCT band.

In EPR measurements, the MV state can be determined based on the change in the spectral shape by temperature. Unlike in the Class III state, in the Class II state, the thermally induced CT process is dominated by the activation barrier ΔG^* . Therefore, as the temperature decreases, the CT process weakens and the localization tendency increases. In this view point, the temperature dependence of EPR spectra can be a good indicator of Class II. However, even in a Class II state, if the intramolecular ET process is faster than the EPR measurement time scale, the EPR spectrum shows no temperature dependence, so the MV state cannot be determined only by EPR measurement results.

In addition to the above two spectroscopic methods, quantum chemical calculations assist in the final determination of the MV state. DFT/TD-DFT calculations using the B3LYP function^[18] are mainly used, while for Class II, the BLYP35 function^[19] with a 35% exact exchange term proposed by Kaupp includes solvent effects and provide more accurate information.

2-3 Calculation method of various parameters

The MV state is theoretically determined by two parameters, H_{AB} and λ . As shown in Figure.1, in the case of Class III state, the optical excitation energy from the lowest point to the upper surface in Frank-Condon state coincides with the energy difference $2H_{AB}$, so the electronic coupling is directly determined from the absorption maximum wavenumber $\tilde{\nu}_{\max}$ ($\equiv E_{IT}$) (in cm^{-1}) of the IVCT band. On the other hand, in the case of Class II state, it is calculated based on several theoretical treatments.

Hush reported that the electronic coupling H_{AB} can be calculated by the following equation (Eq.1) when the IVCT band has a completely Gaussian function shape. [20]

$$H_{AB} = \frac{(0.026(\epsilon_{\max} E_{IT} \Delta\tilde{\nu}_{1/2})^{1/2}}{R} \quad (\text{Eq.1})$$

where E_{IT} is the absorption maximum wavelength energy, $\epsilon_{\max}$ the maximum molar absorption coefficient ($\text{M}^{-1} \text{cm}^{-1}$), $\Delta\tilde{\nu}_{1/2}$ the width at half maximum (cm^{-1}), R the CT distance ($\text{\AA}$) which is commonly defined as be the distance between redox centers. However, as described in Section 2-2, it should pay attention that the IVCT band sometimes does not have a Gaussian function shape, and in this case, electronic coupling calculated in the equation in Eq.1 is lower than the actual value. In addition, Nelsen *et al.* reported the possibility that the effective distance (R) between redox centers is affected by delocalization of charges to the bridge. [21]

A more useful equation is that of the Mulliken-Hush Two-State Analysis. [22] (Eq. 2)

$$H_{AB} = \frac{E_{IT}\mu_{ab}}{\Delta\mu_{12}} \quad (\text{Eq.2})$$

where μ_{ab} is the transition moment determined by the integration of the IVCT bands. $\Delta\mu_{12}$ the difference in diabatic dipole moments between the ground and excited states, calculated by Eq.3.

$$\Delta\mu_{12} = \sqrt{(\Delta\mu_{ab})^2 + (4\mu_{ab})^2} \quad (\text{Eq.3})$$

where $\Delta\mu_{ab}$ is the difference in adiabatic dipole moments between the ground and excited states, obtained from quantum chemical calculations.

Mulliken-Hush Two-Mode Analysis [23] employs a two-dimensional model considering the average asymmetric vibrational mode and the average symmetric mode, which can directly calculate the electronic coupling only from the IVCT band without the assistance of quantum chemical calculations. However, this analysis is only applicable to tightly coupled systems (boundary class II/III) with relatively asymmetric IV-CT bands.

In some cases, the H_{AB} is also estimated by Generalized Mulliken-Hush Three-State Analysis [24]. The other analyses mentioned above consider only the super-exchange CT process, however, CT by hopping may occur depending on the energy level relationship between the bridging site and the redox site. If the bridging site also carries spin (or charge), a “bridge band” assigned to the ET between the redox site and the bridging site, as well as the IVCT band may be observed. [25] In addition to the two states, for the three states, it is necessary to obtain more accurate parameters considering transitions

from the ground state to the bridging site. [26]

The reorganization energy (λ) is obtained from experimental results only for the Class II state. In Class II state, optical induced transition energy is consistent with λ , so it can be simply obtained from the IVCT band at $\tilde{\nu}_{max}=\lambda$. The remaining parameters, activation barriers ΔG^* , are closely related to thermal induced CT and can be obtained from Eq.4 only in Class II case by variable-temperature EPR measurements.

$$k_{th} = A \exp\left(-\frac{\Delta G^*}{k_B T}\right) \quad (\text{Eq. 4})$$

where k_{th} is the ET rate obtained by EPR measurement. Using this equation, ΔG^* can be obtained from an Arrhenius plot with T^{-1} on the horizontal axis and $\ln(k_{th})$ on the vertical axis. When H_{AB} and λ are already known, ΔG^* can be calculated by Eq. 5 [22b].

$$\Delta G^* = \frac{\lambda}{4} - H_{AB} + \frac{H_{AB}^2}{\lambda} \quad (\text{Eq.5})$$

3. Basic group of organic MV compounds

3-1 Para-substituted phenylenediamine (PD)

According to Huig's classification, the oxidation behavior of PD is Wurster-type. The structure of PD changes from benzenoid to semiquinoid during one-electron oxidation, followed by to quinoid during two-electron oxidation. (Figure 2)[27] The high stability of the semiquinoid structure makes PD derivatives the first organic radical cation species to be isolated. [28]

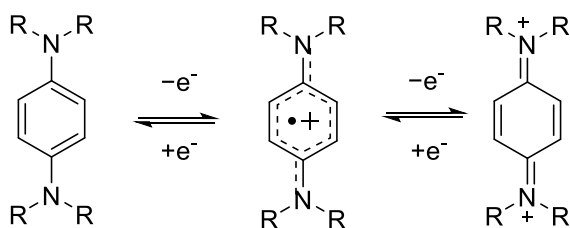
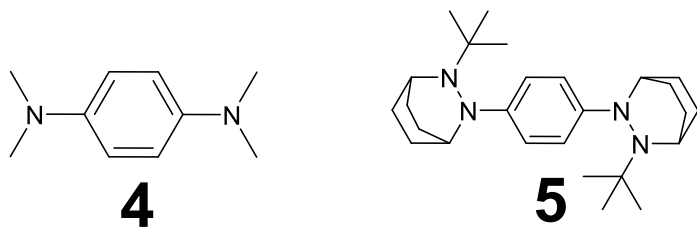


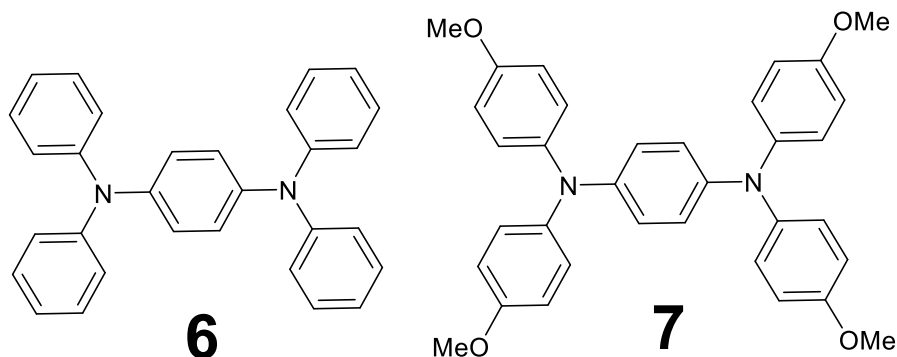
Figure 2. Wurster-type oxidation of PD derivatives.

The PD derivative substituted by methyl groups is tetramethyl-para-phenylenediamine (TMPD) (**4**). The monoradical cation species **4**^{•+} has an IVCT band with a vibrational structure and a symmetrical molecular structure. With the help of theoretical studies, TMPD was determined to be Class III for the following reason. [29] Compared to the localized state, the delocalized state requires reorganization energy for the structure change of one extra neutral amino group from a pyramidal sp^3 orbital to a planar form closer to the sp^2 orbital, while in the case of TMPD, the delocalization energy exceeds the loss of reorganization energy. On the other hand, in the case of bis(hydrazine) PD (**5**) having hydrazine with a large reorganization energy at the redox site, the charge is localized on a single redox center.

[29a]. This indicates that a large reorganization energy tilts the electronic state toward localization.



Tetraphenyl-para-phenylenediamine (TPPD) (**6**) or tetraanisyl-para-phenylenediamine (TAPD) (**7**) is PD derivatives with aryl rings arranged propeller-like around the nitrogen center. The molecular structure of **6**⁺ obtained from X-ray crystal structural analysis and its IR spectra in solvent and solid state are consistent with the results from DFT calculations, proving that (TPPD) (**6**) is a symmetrically delocalized Class III state in both solid and solution states. [30] TPAD is a compound in which the end of TPPD is substituted with a methoxy group. **7**⁺ was found to be a boundary state between Class II and Class III, since the electronic coupling and reorganization energy determined by absorption spectral measurements and Hush theory showed a relationship of approximately $2H_{AB}=\lambda$. [17]



3-2 Para-substituted bis(triarylamine)

Triarylamine (TAA) is a tertiary amine with three aromatic groups, and the nitrogen center is easily oxidized. Among aryl groups, in the case of triphenylamine (TPA), the monoradical cation species obtained by electrochemical oxidation is unstable, and dimerization occurs to generate tetraphenylbenzidine. Although it may become stable in a strongly delocalized class III system, to solve this problem, it is basically necessary to replace all the hydrogens at the para-position to the nitrogen of TPA. [31] Furthermore, TAA has higher electron-donating properties rather than many other inorganic and organic materials due to the resonance delocalization of lone electron pairs throughout the molecular structure, so the nitrogen center of TAA has properties for stable positive charge-generating and transporting. Adding to these photoconductive and hole-transporting properties, the

recent invention of Pd-catalyzed C-N coupling reactions has made it possible to synthesize TAA compounds with the molecular structures and electronic properties envisioned by researchers and developers. This allows to control the MV state of TAA compound and provide sufficient material properties such as thermal stability and amorphous/amorphous film-forming properties. Based on all the characteristics of this compound, TAAs attract attention as a building block for organic optoelectronic materials, with great promise for applications in organic light-emitting diodes (OLEDs) [32], solar cells [33], and organic field-effect transistors (OFETs) [34].

Organic MV chemistry is closely related to the field of electro-optical devices, since MV states are always present in electro-optical devices. Organic MV chemistry mainly focuses on tuning and controlling electronic states in molecules as well as evaluating the conjugation between redox sites by electrical coupling H_{AB} , which will also contribute to the development of electro-optic devices. Based on this background, TAA is one of the most popular redox sites in organic MV chemistry, and there are a lot of papers on para-substituted bis(triaryl amines) (BTA) with para-substituted TAAs connected by conjugated bridges. (Figure 3)



Figure 3. The most popular structure for organic MV compounds.

The nitrogen atom at the center of TAA connected with triaryl rings in a propeller shape, has high planarity in the neutral state among tertiary amines. Therefore, the small structural change of TAA from the neutral state to the radical cation state of the nearly sp^2 orbital planar state provides a low reorganization energy. Thus, the IVCT band appears at longer wavelength side in the NIR region and does not cover other spectra. This advantage makes the analysis of the MV state easier, further facilitating the analysis of the MV state, resulting in the abundance of reports on this compound. [35]

4. Effect of bridging site tuning on organic mixed valence

In this section, the effect of the bridging site on the MV state is evaluated by the electronic coupling H_{AB} , which is an indicator of the electronic communication between redox sites. For example, replacing the bridging site from an acetylene spacer unit to an ethylene unit in the BTA system (Figure 3) changes the MV state from Class II to Class III [36], however, such a change of the entire bridge site

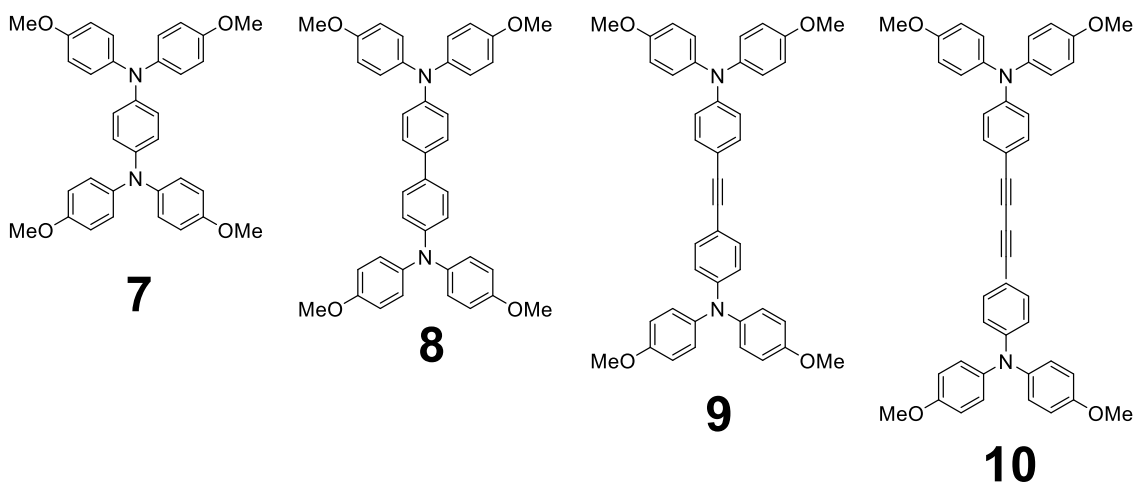
is not included in the “bridging site tuning” in this section. As a fundamental model of BTA system, only the effects on the MV state due to changes in bridging distance, partial substitution, bridging topology and bridging planarity are discussed below.

4-1 Relationship between bridging distance and electronic coupling

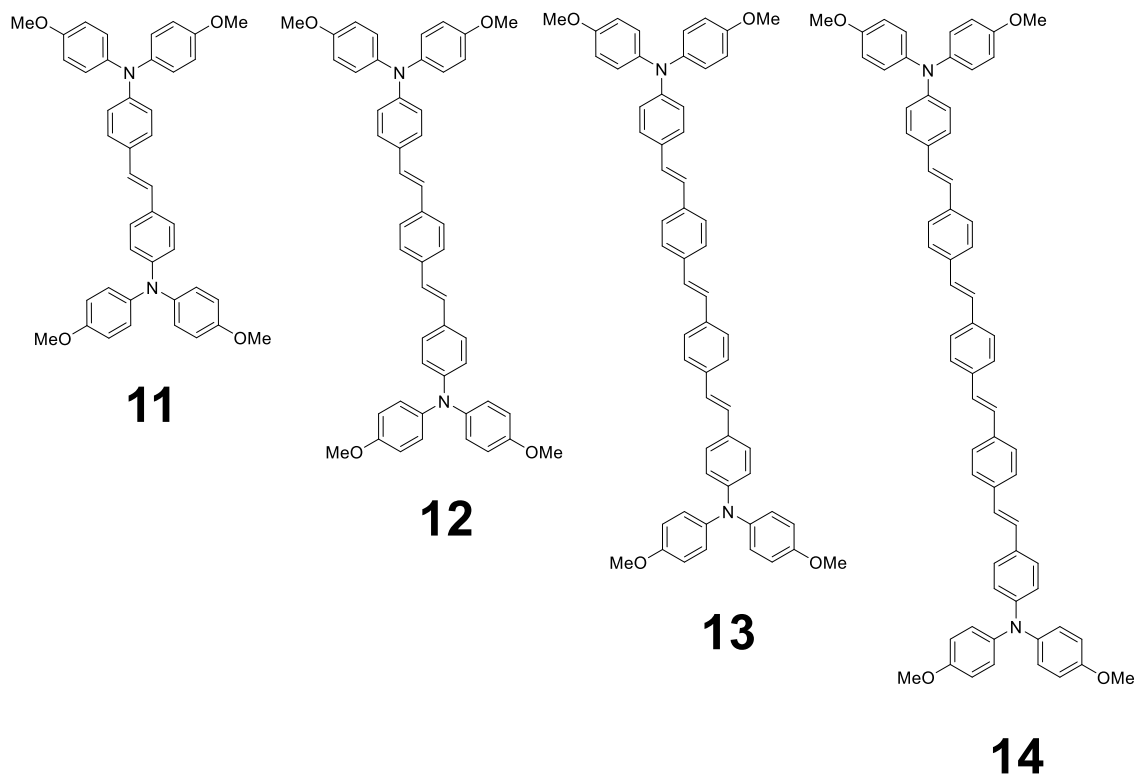
It can be expected that the longer the distance between the redox sites at both ends, the higher the resistance to electronic communication and the smaller the electronic coupling H_{AB} will be. The bridging distance dependence of the H_{AB} can be precisely expressed by the following equation (Eq. 6) when the super-exchange CT occurs in an organic MV system. [37]

$$H_{AB} = H_{AB}^0 \exp\left(-\frac{\beta}{2}Na\right) \quad (\text{Eq. 6})$$

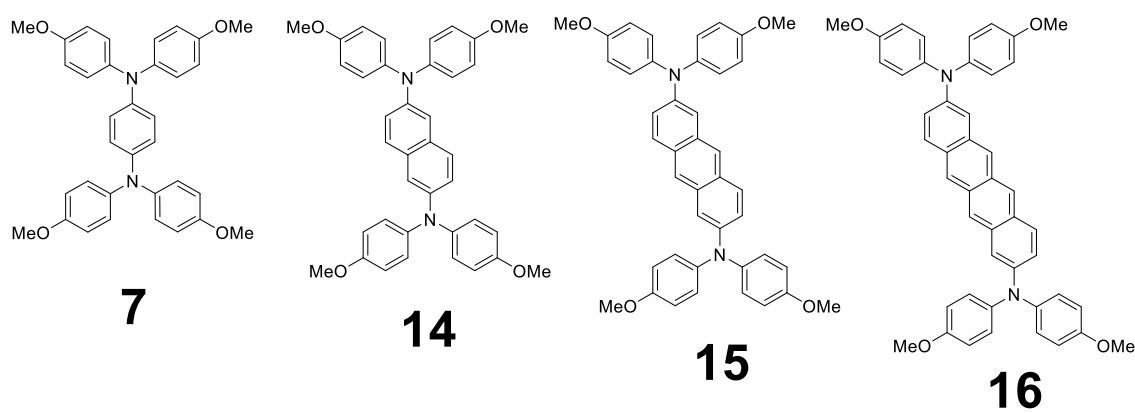
This formula assumes identical repeating bridge units, where β is the decay function, N the number of bridge units and “ a ” the length per bridge unit, while it may also be simply applied to the distance between redox sites as Na . The first study to investigate the relationship between bridging distance and electronic coupling was conducted on four bis(triarylamine) (**7-10**) monoradical cation species, although it did not use a complete homology series. [17a] However, in this study, the electronic coupling decreased exponentially with increasing bridging distance, and the value of decay function β was 0.16 Å⁻¹.



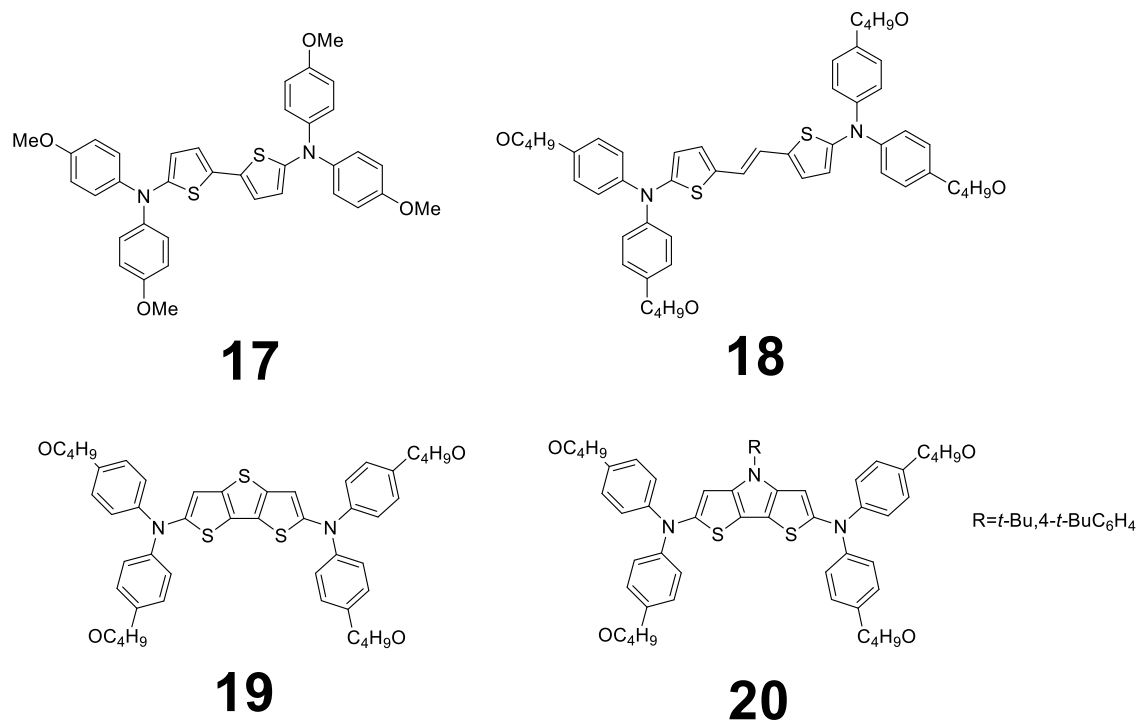
The first study using a complete homology series was the oligo(p-phenylenevinylene)-bridged (OPV-bridged) bis(dianisylamine) system (**11-14**). [38] Barlow *et al.* confirmed the distance dependence of electronic coupling by theoretical calculations and estimated as $\beta = 0.14$ Å⁻¹ for AM1 calculations and $\beta = 0.24$ Å⁻¹ for DFT calculations. Both values were significantly larger than the decay coefficient (0.01 Å⁻¹) previously reported for donor-acceptor systems via OPV wires. [39]



Recently, there were several studies on a homologous series using bis(diarylamine) monoradical cation species bridged with oligoacene. Four types of compounds (**7**, **14-16**) with bridging from benzene to tetracene were successfully synthesized, and IVCT band analysis assigned all the compounds as Class II. The decay constant was calculated as a gentle $\beta = 0.14 \text{ \AA}^{-1}$, suggesting that oligoacene are excellent as molecular wires. ^[40]



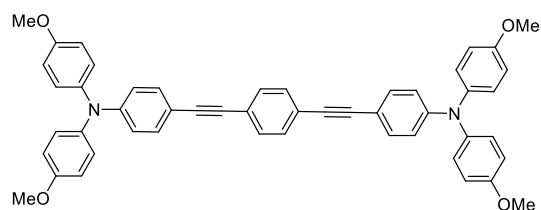
Although all the bridging sites of the organic MV compounds described above are hydrocarbons, there are of course bridging sites containing hetero molecules. For example, thiophene is expected to be used in polymer electronics due to its electron-rich properties. Computational studies have pointed out that as the degree of polymerization of the thiophene bridge increases, the super-exchange CT between the triarylamine units tends from Class III state to Class II state, followed by a hopping CT. ^[41] The same trend was also confirmed in the study of the actually synthesized thiophene-bridged compounds (**17-20**), where the dithienopyrrole-bridged molecule **20**⁺ showed an electronic coupling with $H_{AB} = 5790 \text{ cm}^{-1}$, which was the highest value among the radical cation species in the **BTA system**. On the other hand, EPR results for **20**⁺ showed that the spin density of the bridged site is larger than those of other MV molecules without thiophene, which may assign **20**⁺ to a oxidized bridge compound. ^[42] It is difficult to discuss whether MV radical cation species is an appropriate model of CT, because the extra electronic connections due to the bridges should be eliminated.



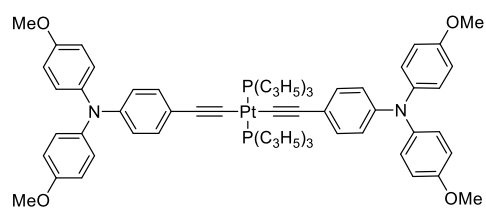
4-2 Relationship between partially substituted bridging site and electronic coupling

Several papers have reported the relationship between structural substitutions in the bridging site and the MV state. The comparison of BTA systems with the center partially substituted with enyhtyl is a good example that clarifying the effect of only partial structural substitution of the bridging site on the MV state, since they can eliminate the effect on the MV state by keeping the bridging distance almost constant. In the comparison of the central part of the bridging unit between benzene (**21**) and platinum-phenylacetylide (**22**), the latter gained 29% more electronic coupling, demonstrating the superiority as

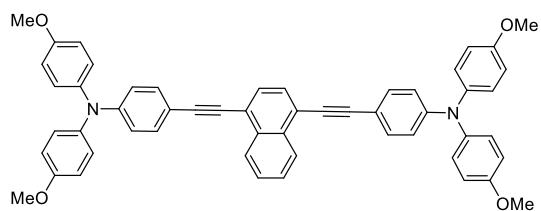
a molecular wire. ^[43] In the study by Lambert *et al.* comparing the electronic coupling among four different centers of the bridge unit, benzene (**21**), naphthalene (**23**), p-dimethoxybenzene (**26**), and anthracene (**27**), “bridge band” assigned to the hopping CT between the bridging and redox site, in addition to as well as IVCT band were observed in the spectral measurements. ^[44] Thus, electronic coupling was calculated by Generalized Mulliken-Hush Three-State Analysis, and **26**⁺ and **27**⁺ showed large H_{AB} . Although super-exchange CT is dominant within organic MV compounds, the contribution of hopping CT to the overall CT depends on the energy difference between the redox site and the bridging site. If the energy of the bridging site is low and the energy difference between the bridging and the redox site is large, the contribution of hopping CT becomes large. The destabilization of the bridge HOMO due to the electron-donating property of the methoxy group and the abundant π -electrons of anthracene results in a smaller HOMO-LUMO gap and a lower energy of the bridge. Thus, the contribution of the hopping CT increased the overall electron coupling. Similarly, p-dimethylbenzene (**28**) substituted with an electron-donating methyl group also increased the electronic coupling. ^[44b,45] Nöll *et al.* also investigated the bridging units thiophene (**24**), furan (**25**), and ethylenedioxythiophene (**29**), and determined that the **24**⁺ and **25**⁺ are Class II states while the more electron-rich **29**⁺ is Class III due to its charge delocalizing on the bridge. **29**⁺ may be assigned to a bridging oxidation compound since the charge likely localizes on the bridging site. However, this assignment is denied by the fact that ethylenedioxythiophene has a higher oxidation potential than TAA. ^[46]



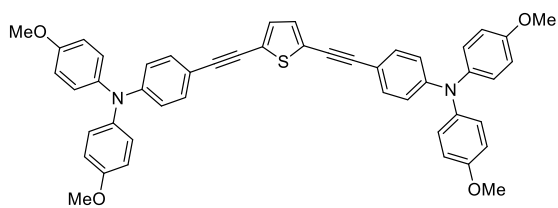
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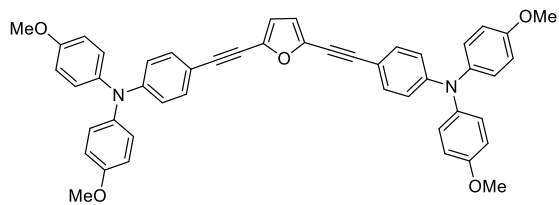
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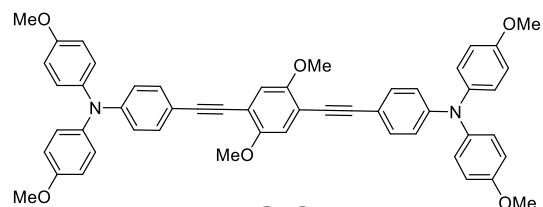
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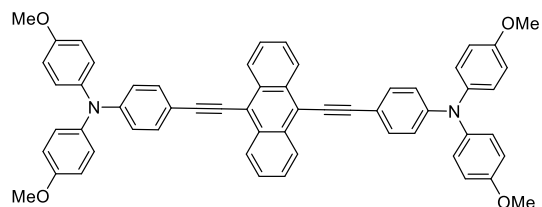
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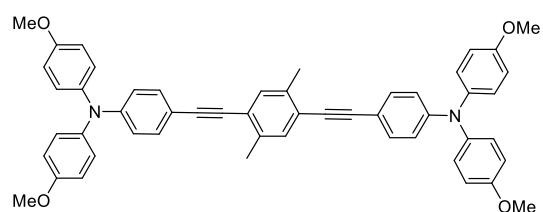
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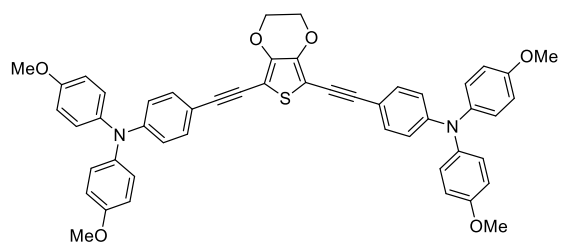
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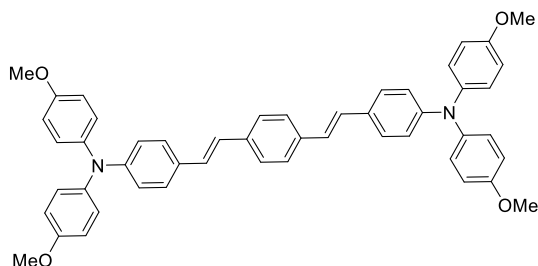
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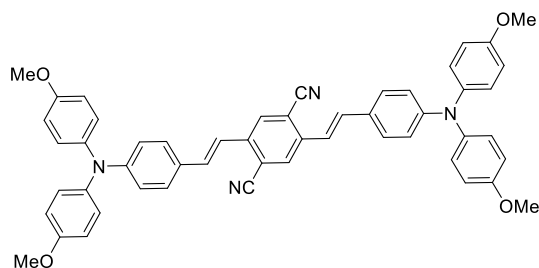
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On the other hand, in OPV-bridged bis(triarylamine) (**30**) substituted with a cyano group, an electron-attraction group, the signal in the variable-temperature EPR measurement changed from five lines to

three lines at 191 K, indicating slower ET, and the electron coupling was estimated to decrease by 33%. [38,47]



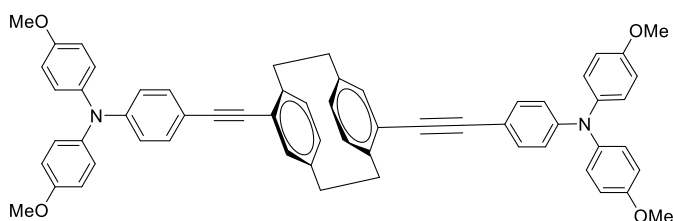
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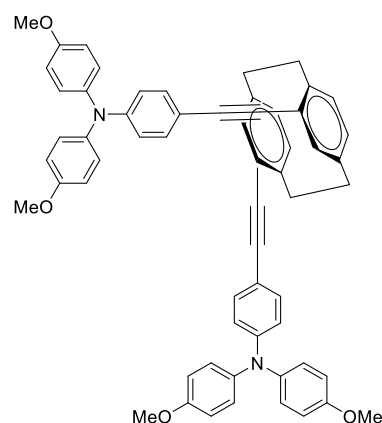
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4-3 Bridging topology and electronic coupling

IVCT is also influenced by the topology of bridging sites. Para-substitution generally has better electronic communication than meta-substitution because the quantum interference of the wavefunction along the conjugation path is constructive for the former while destructive for the latter. [48] Also, ortho-substitution is often disadvantageous for electrical communication because it is a π -conjugated pathway that cannot maintain a planar structure due to steric hindrance. [49] However, compounds not applicable to the case have been discovered, exploring the possibilities for the molecular design of MV systems. For example, the pseudo para-isomer (**31**) and pseudo ortho isomer (**32**) of the cyclophane-bridged BTA monoradical cation did not provide significant difference in electronic coupling, 570 cm^{-1} and 430 cm^{-1} respectively. [45] This may be due to the long enityl bond, which mitigates the steric hindrance caused by the ortho connection.



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Grampp and Lambert *et al.* reported that a compound substituted the 4,6 positions of meta-phenylene-connected double-tolan-bridged bis(dianisylamine) with methoxy groups (**33**) acquired the same degree of electronic coupling as para-phenylene-connected double-tolan-bridged bis(dianisylamine) (**26**) substituted with two methoxy groups ($320\text{ cm}^{-1}, 550\text{ cm}^{-1}$).^[48] In the molecular orbital calculation of **33**⁺ (Figure 4), the metaphenylene group has two non-bonding molecular orbitals, β -HOMO and β -LUMO, and the introduction of an electron-donating methoxy group at positions 4 and 6 destabilizes only the LUMO, widening the HOMO-LUMO energy gap. Since the electron transition from the HOMO to the LUMO corresponds to $2H_{AB}$ in the case of symmetric molecules (Figure 1), **33**⁺ provides a larger electron coupling than the conventional theory.

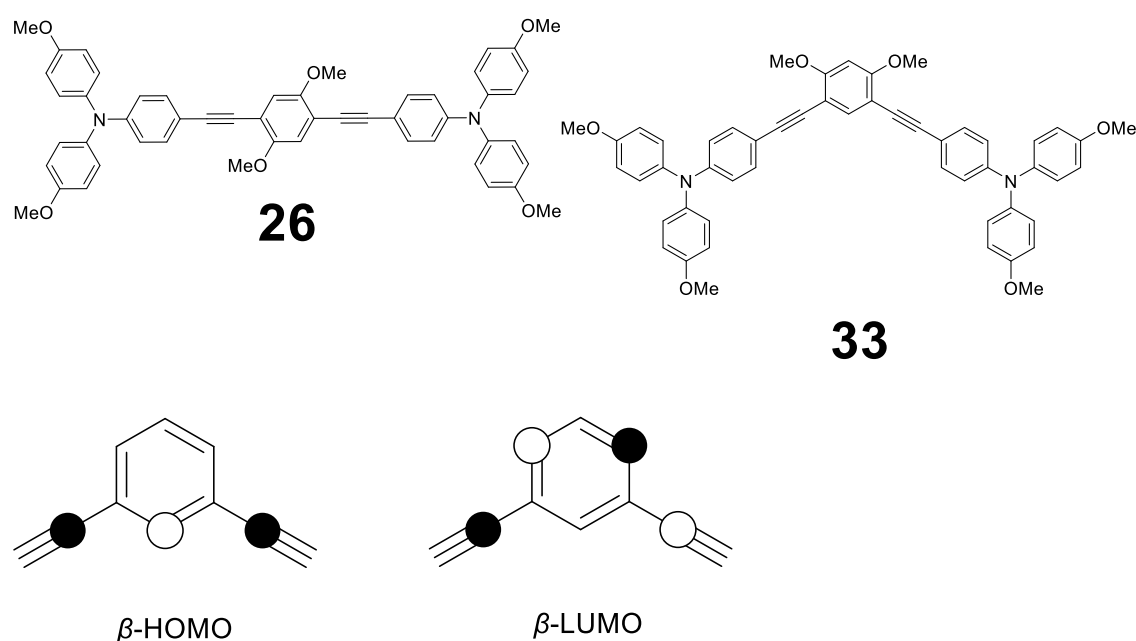
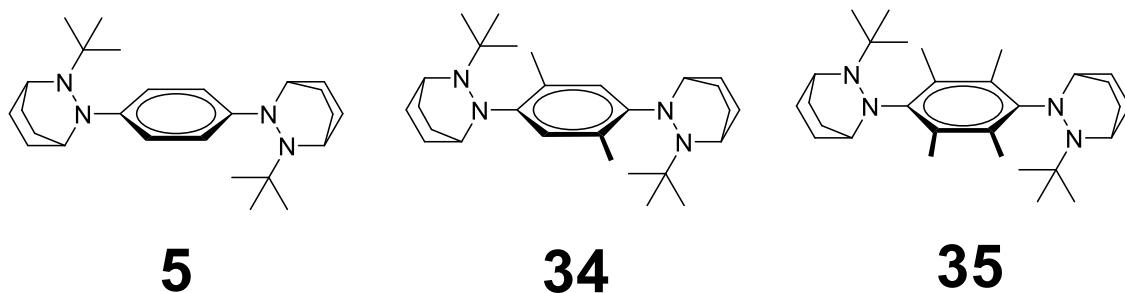


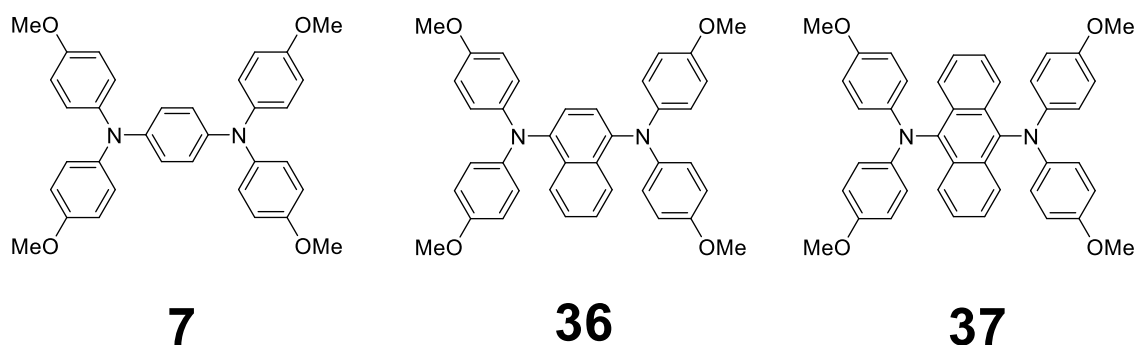
Figure 4. Schematic diagram of molecular orbitals of methyl group in monoradical cation of meta-phenylene-connected double-tolan-bridged bis(dianisylamine).

4-4 Bridging planarity and electronic coupling

The electronic coupling can also be tuned by the change in the planarity of the bridging site; Nelsen *et al.* noted that the *p*-phenylene-bridged bis(hydrazine) monoradical cation (**5**⁺, **34**⁺, **35**⁺) increases its twist angle from the plane as the increase of the substituents on the phenylene spacer. They suggested that the electronic coupling decreases from 2510 cm^{-1} to 1150 cm^{-1} as the torsion angle increases from 48° of **5**⁺ to 66° of **35**⁺ by the calculation.^[12a,21]



Lambert compared analogues (**7,36,37**) of **21,23** and **27** without the enityl linker, and reported that the electronic coupling of anthracene is smaller than that of benzene. ^[50] The torsion angle from the plane of benzene is 27° whereas that of anthracene is 62°, indicating that the loss of electronic coupling due to steric distortion is larger than the gain obtained by reducing the energy gap between the redox site and the bridging site.



5. Effect of redox site adjustment on organic mixed valence

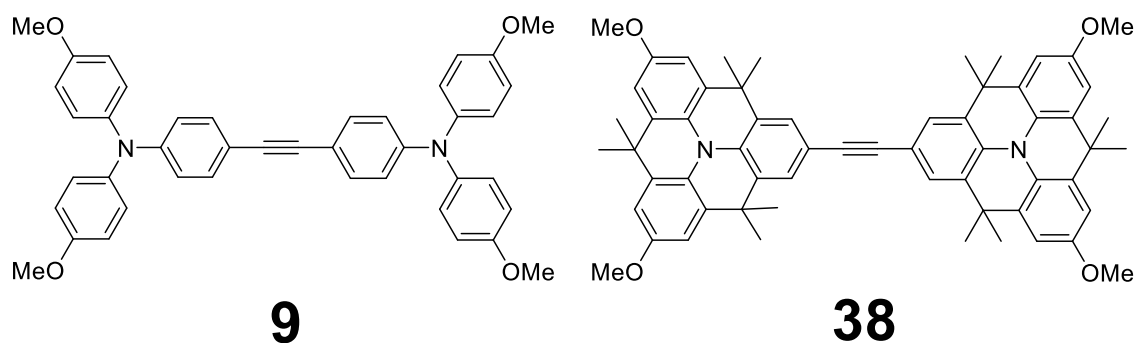
Although hydrazine, dinitro, and TAA have been often employed as redox sites for organic MV compounds, in this section, the redox site groups will not be compared themselves but the effects of partial structural changes on the MV state will be only discussed using by the BTA system as a basic model.

The structural change of the redox site TAA occurs when radical cation species are generated by oxidation. For the structural change, reorganization energy (λ_{in}) due to internal factors is required. Since the MV state is determined by the relationship between λ and H_{AB} , it cannot be controlled solely by increasing or decreasing λ_{in} , however, as shown in Figure 1, in the case of Class II, the larger the λ , the larger the activation barrier ΔG^* . As shown in Eq. 4, λ affects the ET velocity (k_{th}) which is qualitatively evaluated using ΔG^* calculated by variable-temperature EPR measurements.

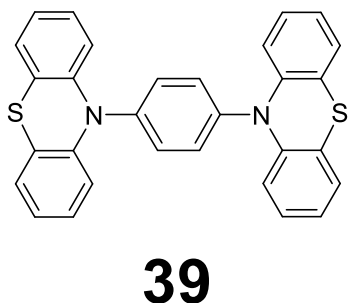
5-1 Effect of changing the rigidity of the redox site on the activation barrier

MV compounds consisting of N-heterotriangulenes (N-HTAs), carbon-bridged TAAs, at redox sites

(**38**) had $\Delta G^* = 4.5 \text{ kJ mol}^{-1}$ [51] This was about half the value of **9** consisting of a simple TAA at the redox site. [52] TAA system with highly structural rigidity has a low λ_{in} due to show little structural change by one-electron oxidation. This result indicates that reorganization energy λ_{in} is effective for reducing the activation barrier energy.



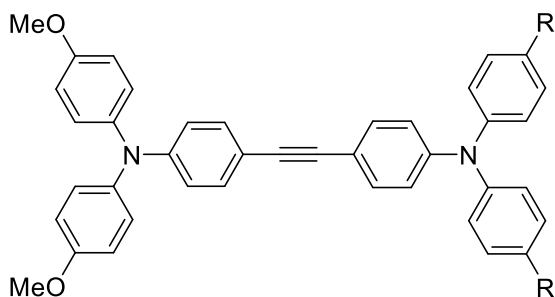
Tethered TAA itself is expected to explore new MV compounds because it can improve the rigidity and stability of the redox site. Kochi *et al.* studied the ET process in a molecule (**39**) having TPPD partially bridged with sulfur. [53] The relatively large reorganization energy of 30 kcal mol^{-1} for **39**⁺ would be attributed to the nonplanarization of phenothiazine.



5-2 Effect of partial substitution on the IVCT band

As the opposite approach discussed in Section 4-2, the energy difference between the redox site and the bridging site was modulated by changing the energy of the redox site; in 2002, Lambert changed the end groups of one TAA to methoxy (**9**), methyl (**40**), chloro (**41**) and cyano (**42**) and compared them. [54] Since the molecular structure of **40-42** is asymmetric, the CT process is represented by a potential energy surface consisted of nondegenerate energy planes. (Figure 5) In this case the optically induced CT energy $\tilde{\nu}_{max}(\equiv E_{IT})$ is the sum of λ and the difference of free energy in the non-adiabatic state ΔG^0 . CV measurements indicated that the redox potential splitting broadens from **9** to **42** due to the increase in electron attraction and the energy position of the IVCT band blue-shifted with the redox

potential splitting. These results suggested a linear relationship between redox potential splitting and ΔG^0 because ΔG^0 tends to be relative to the charge in the nonadiabatic (localized) state of the redox site. The electronic coupling calculated from the two-state analysis was $1020 \pm 50 \text{ cm}^{-1}$ for all four compounds, which is reasonable by considering that all compounds have the same effective CT distance and their substituents show weak effects on the adiabatic dipole moment difference.



- 9** R=OMe
40 R=CH₃
41 R=Cl
42 R=CN

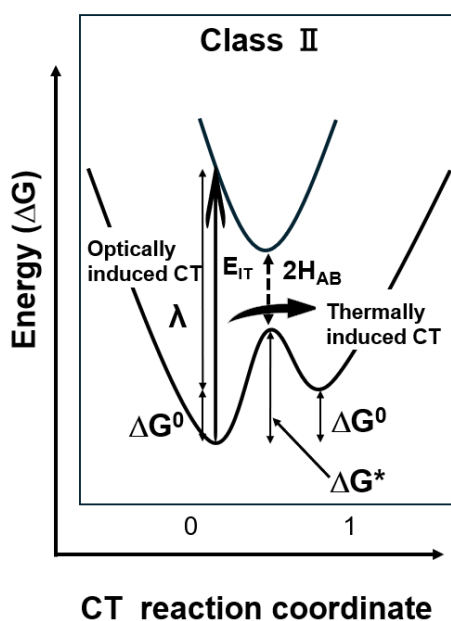
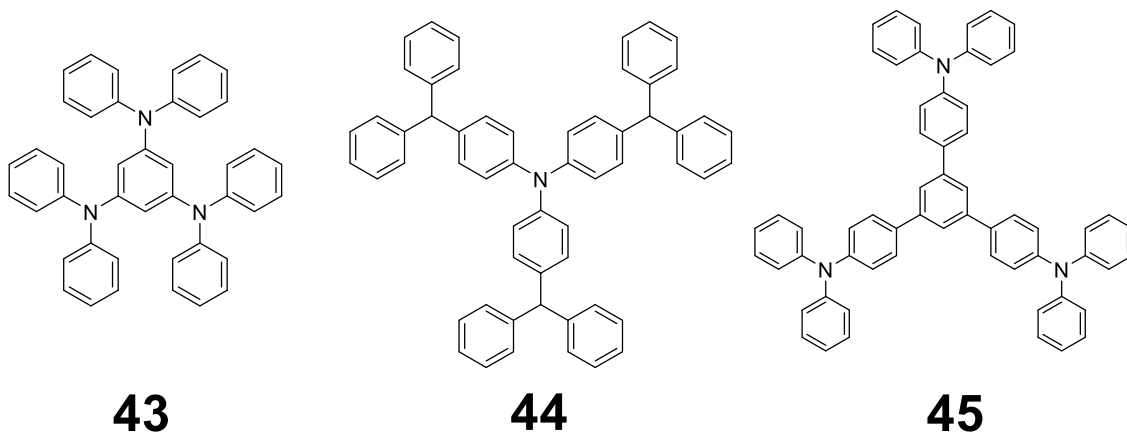


Figure 5. Schematic representation of potential energy surface for a nondegenerate two-state classII system.

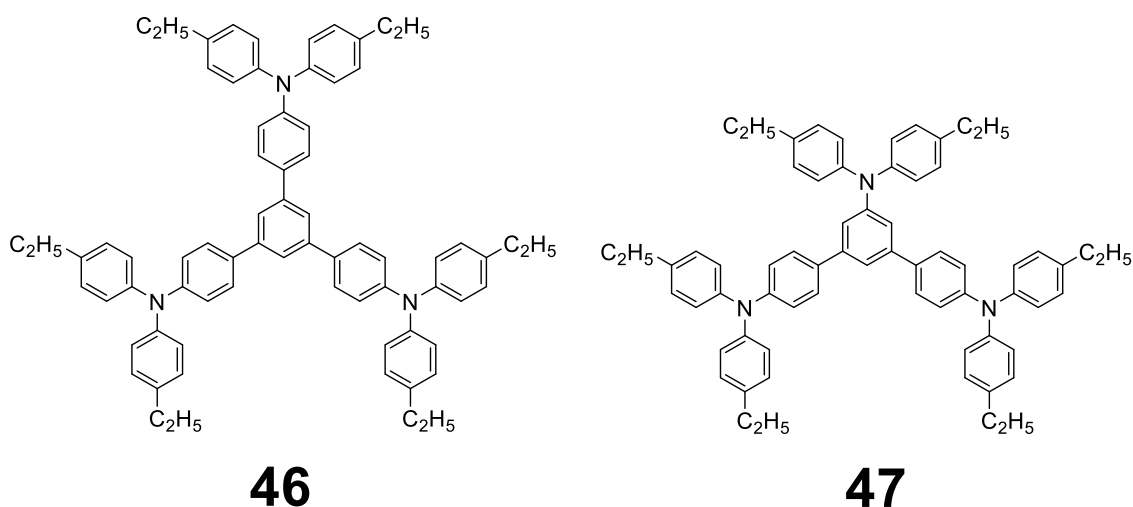
6. Multidimensional organic mixed-valence compounds

Molecules containing three or more redox sites become multidimensional MV states. In this section, assuming a molecule with a terminal redox site and bridged by a central π -conjugated molecule, the molecule with three redox sites would have a triangle conformation. Shirota *et al.* have designed series of 1,3,5-tris(diphenylamino)benzene (TDAB) with a benzene core (**43**), 4,4',4''-tris(diphenylamino)triphenyl amine (TDATA) with a TAA core (**44**), and 1,3,5-tris(4

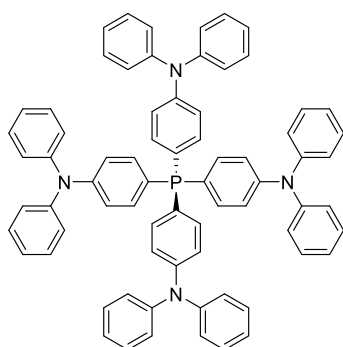
diphenylaminophenyl)benzene (TDAPB) with a triphenylbenzene core (**45**).^[55-57] Among the triangular MV compounds with this extended π -conjugation, **43** achieved the lowest oxidation potential, indicating that the para bond rather than meta bond is more conjugated.



As for **46** in the TDAPB series, both the mono- and dication were determined to be Class II states, and the IVCT band analysis calculated an electronic coupling as small as $H_{AB} = 204 \text{ cm}^{-1}, 224 \text{ cm}^{-1}$. Since the two IVCT bands were almost the same, it was impossible to distinguish and identify the one- and two-electron transfer processes.^[58] In molecule **47**, in which the phenyl ring was partially removed from **46**, the threefold symmetry was broken and the ET processes through the two and three phenyl rings were successfully identified in the mono- and dicationic species. Although the IVCT bands corresponding to the two ET processes were not completely separated, the electron coupling was determined to be 387 cm^{-1} and 230 cm^{-1} from two-dimensional Hush analysis, respectively in the monoradical cation.^[59]

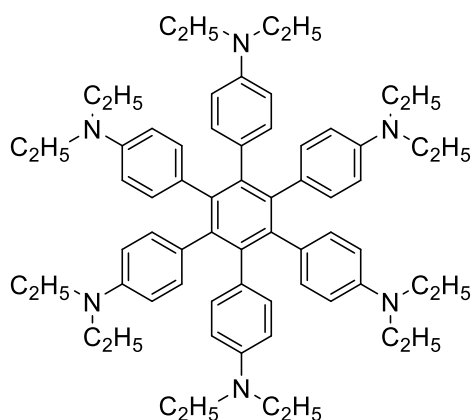


Molecules with four redox sites have a spiro or tetrahedral structure. As for phosphonium cation (**48**) having a pseudo-tetrahedral structure, IVCT bands were observed for its dicationic, tricationic and tetracationic species, and the electronic coupling of them was calculated to be equivalent to that of phenylene-bridged BTA with the same distance between redox sites.^[60] Phosphine bridging seems to be a good alternative to π -conjugated bonds as a molecular wire, but it should be noted that CT is mediated by solvent molecules in the four P-C bonds.



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MV system including six equivalent triarylamine redox sites (**49**) was reported by Kochi *et al.*^[61] CV measurements showed four redox waves assigned to three one-electron and one three-electron oxidations, respectively. Based on the measurements, they succeeded the selective formation of monoradical cation and found that the MV state of **49**⁺ is the boundary state of Class II/Class III. The six-state Mulliken-Hush analysis considering only equivalent interactions between adjacent redox sites calculated an electronic coupling of $1600 \pm 400 \text{ cm}^{-1}$ and a reorganization energy of $5400 \pm 600 \text{ cm}^{-1}$.



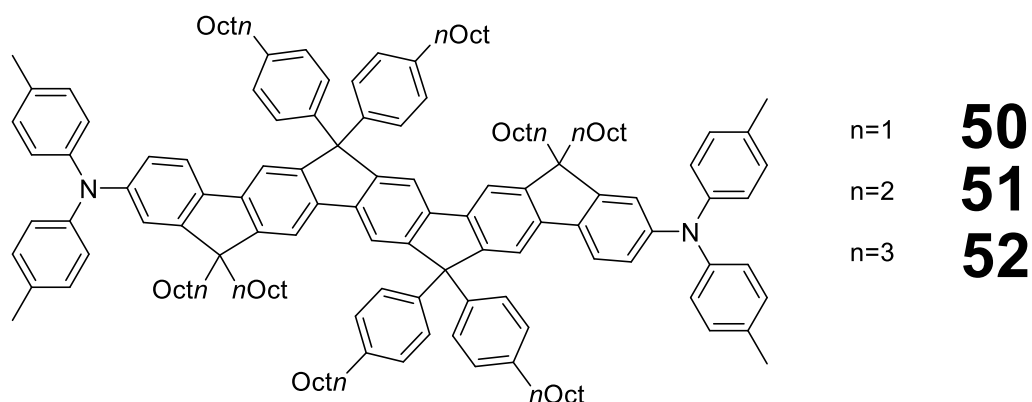
49

7. Conclusion and introduction to this doctoral thesis

TAA is a building unit mostly used for a hole transport material of organic photovoltaics because of its low oxidation potential, stability of radical cation and effective positive charge transport property. Low reorganization energy of TAA also makes IVCT band analysis easy to provide a lot of information about CT in the field of organic MV chemistry. With the invention of coupling reactions using a Pd catalyst, TAA acts as the bridge closely connecting the development of hole transport materials and the advances of organic MV chemistry. For example, a series of studies on the relationship between bridging distance and electronic coupling originated with the discovery of excellent organic molecular wires with one-dimensional long-distance ET. Other many studies on the basic methodology for controlling electronic coupling H_{AB} have been conducted from a variety of aspects such as the changes in bridging topology, planarity and bridge energy by partial substitution.

On the other hand, there are few studies controlling the reorganization energy rather than electronic coupling. This is because the theories and calculation models for λ considering both λ_{in} due to structural changes during molecular oxidation and λ_{out} due to ion-pairing, solvation and the temperature of the medium has not been established compared with those for H_{AB} . If the author select TAA as the redox site and successfully improve the planarity of the neutral state of TAA, it will be possible to suppress λ_{in} and enhance the thermally induced CT process. To improve the planarity of the neutral state of TAA, one of the methods is the bridging of TAA itself. As explained in Section 5-1, there have been some reports on the bridging of TAA, however, the bridged TAAs have been studied as building blocks for constructing two-dimensional π -extended redox-active molecular structures and have rarely been used as organic MV compounds. On the other hand, in Section 4-4, the author introduced studies of organic MV compounds focusing on the planarity of the bridge site. In addition, recently Muellen *et al.* reported a series of BTA radical cations (**50**⁺, **51**⁺, **52**⁺) with ladder-type oligo-pentaphenylene bridging units, in which phenylene as a spacer can be arranged in a plane. They found

that the maximum overlap in the π system resulted in much larger electron coupling than in BTA systems with similar redox site distances. [62]



Thus, the planarity of the compounds affects their electronic coupling. Therefore, planar MV compounds in which the redox sites and bridge sites are connected like a single plate are expected to enhance both optically induced IVCT and thermally induced IVCT due to their small reorganization energy of the redox sites. From the research background, the author decided to study MV compounds with high planarity in which both the redox and bridge site are tethered. Then the author designed and synthesized molecules where ortho positions of the five phenyl rings of TPPD are tethered to each other, and investigated their MV state as discussed in Chapter 1.

Although multi-dimensional MV compounds with three or more redox sites are used as charge-transporting materials in optoelectronic devices, there are quite a few studies on CT of the compounds. [63] Recently, some researchers have reported the study on changes of CT path and electronic state of by changing the bridging topology as well as the bridging distance. [64] The most difficult part of the CT process of multidimensional MV compounds would be the multi-branching properties of CT pathways. The overlap of IVCT bands makes it difficult to distinguish between CT pathways, and further complicates the presence of multiple charges. Therefore, the selective formation of monoradical cation is also important for understanding the CT process. From the research background, the author considered that the design of symmetry-broken multi-dimensional MV compounds would facilitate the identification of CT pathways from IVCT bands. In fact, the author synthesized a molecule with a benzene core where three TAAs are ortho-connected at positions 1, 2, and 3, and identified CT pathways in monoradical cation species, as described in Chapter 2.

On the other hand, multi-branching of CT pathways can be achieved by bridging two redox sites with multiple bridges, however no research on multi-bridged two-site MV systems have reported so far. From the background, the author synthesized a BTA system double bridged with ortho-terphenylophane and investigated the effects of double bridge on intramolecular charge transfer, as discussed in Chapter 3.

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Chapter 1

Oxygen-Bridged Quasi-Planar *para*-Phenylenediamine and Its Oxidized States

1-1 Introduction

Triarylamine (TAA) moiety has been widely recognized as a key redox-active building unit for organic opto- and magneto-electronic materials. Fine tuning of electron delocalization in a unit and/or over nearby ones turns dramatically the overall properties of the compounds from electronic conductive (delocalized) to magnetic (localized) systems.^[1] In parallel, bis(triarylamine) (BTA) radical cations, as open-shell π -bridged triarylamine dimers, have provided an ideal playground for us to gain deeper understandings of basic charge transfer (CT) phenomena in π -conjugated organic molecular systems, and the wealth of information about the molecular structure dependence on the intramolecular CT (ICT) processes has been so far piled up.^[2] The BTA's predominance is closely related to the following points: (i) easy access to various derivatives by using the Pd-catalyzed cross-coupling reactions, enabling fine-tuning of the BTA's electronic states, and (ii) the relatively small reorganization energy of propeller-shaped TAA redox-active units, which effectively shift the optically induced intervalence CT band (IV-CT band) to the near IR (NIR) region, allowing the accurate IV-CT band analysis thanks to the separation from the other absorption bands.^[2]

Derivatives of *p*-phenylenediamine (PDA) radical cations were the most authentically recognized Robin-Day class III^[3] (delocalized) mixed-valence (MV) compounds (Figure 1a). Radical cations of *N,N,N',N'*-tetraalkyl-*p*-phenylenediamine radical cations as a typical two-stage Wurster-type redox system^[4] have been exhaustively examined by Nelsen's group.^[5] Lambert and coworkers have disclosed that *N,N,N',N'*-tetraphenyl-*p*-phenylenediamine (**2**) radical cation and its derivatives are assignable to "almost delocalized"^[6] class III or class III/class II MV systems.^[7]

A series of almost planarized TAAs, where the aryl moieties are fully or partially bridged at the *ortho* positions with respect to the central nitrogen atom, have been explored as versatile building blocks for the construction of two-dimensionally π -extended redox-active molecular architectures.^[8,9] In particular, fully oxygen-bridged *N*-heterotriangulene (trioxatriphenylene: TOT) and its partially bridged derivative (**3**) showed reversible one-electron oxidations (+0.59 and +0.81 V, respectively, vs SCE in DMF) and gave isolable salts of radical cations (Figure 1c).^[10-12] Moreover, the electronic and magnetic properties of TOT^{•+} dimers have been thoroughly investigated as diradical dications.^[13] Turning to the attempts to clarify the electronic states of planarized BTA radical cations, currently there are only a few studies reported regarding this type of compounds. The persistent radical cation of π -extended PDA analogue (**4**) was found to be a planar semiquinoid structure of the PDA moiety, exhibiting the lowest-energy absorption maximum at 702 nm broadening up to 1200 nm in the NIR

region in MeCN (Figure 1c).^[14] More recently, pre-planarized TAA dimer radical cations have been synthesized and characterized as class II MV compounds with low reorganization energies.^[15]

Herein, we focused on globally quasi-planar PDA (**1**), where all the phenyl rings are tethered by four oxygen atoms to embed **3** moieties into the molecular skeleton of **2**, to evaluate the impact by incorporating the structural rigidity into the PDA **2** (Figure 1b). Previously, partially oxygen-bridged quasi-planar bis(triarylamine)s (**5a** and **5b**) had a marked positive effect on the hole-transporting property, thereby leading to a high and anisotropic carrier mobility even in the amorphous film form (Figure 1c).^[16] In this study, we report the structures and fundamental properties of the neutral **1**, the radical cation **1**^{•+}, and dication **1**⁺⁺, and compare to those of the previously investigated non-tethered PDA **2**.^[7]

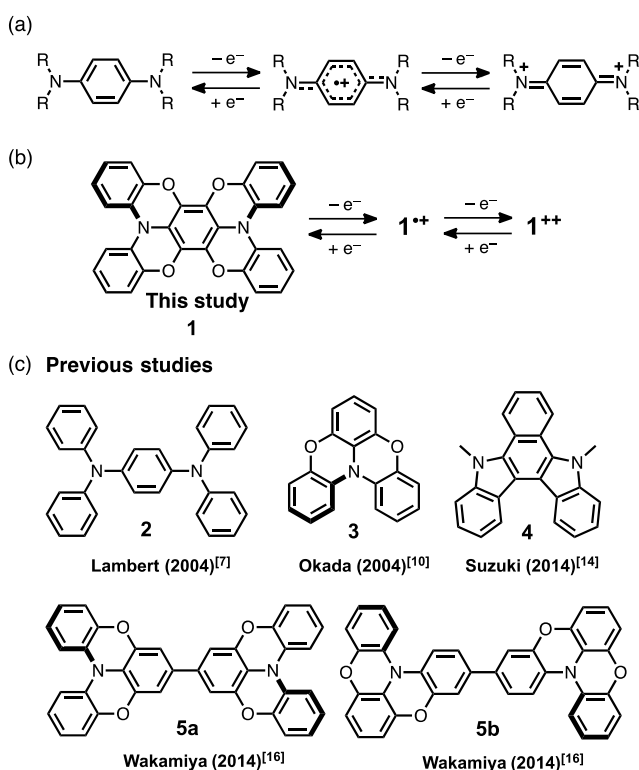
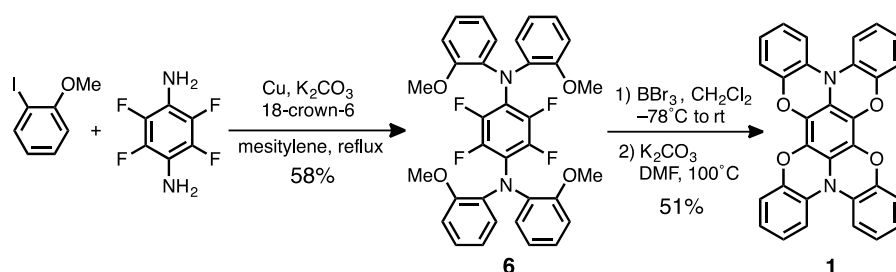


Figure 1. (a) PDA as a typical two-stage Wurster-type redox system, (b) the chemical structures of quasi-planar redox-active **1** as the present target molecule, and (c) the previously studied non-tethered PDA **2** as a reference compound of **1** and the previously reported related compounds **3**–**5**.

1-2 Results and Discussion

The synthesis of the quasi-planar PDA **1** was shown in Scheme 1. Compound **6** was obtained by the Ullmann reaction from 2-iodoanisole and tetrafluoro-*p*-phenylenediamine in 78% yield. The methyl groups of **6** were removed by treatment of tribromoborane, and then, the resulting crude product was subjected to intramolecular cyclization reaction to afford **1** as a greenish green solid in 65% yield from **6**. In dichloromethane solution, the compound **1** showed an absorption band at 370 nm, and

photoexcitation at 350 nm of this solution gave a weak emission at 440 nm with fluorescence quantum yield (Φ_F) of 0.016 (Figure S1). To confirm that the title compound **1** is of the Wurster-type, cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were conducted in dichloromethane at room temperature (Figure S2). Reversible two-stage one-electron oxidation waves were observed at +0.05 (E_1^{ox}) and +0.52 V (E_2^{ox}) vs Fc/Fc⁺, indicating slightly higher electron-donating properties than the non-bridged **2** (+0.10 (E_1^{ox}) and +0.58 V (E_2^{ox}) vs Fc/Fc⁺, remeasured in the same experimental conditions as **1**) (Scheme S3). The redox potential splitting ΔE between the first and second oxidation processes, which is often used as a qualitative index of the electronic coupling strength V between the two redox centers, remains unchanged between **1** (450 mV) and **2** (460 mV), thus suggesting virtually no difference in electronic communication between the corresponding MV radical cations **1**^{•+} and **2**^{•+}.



Scheme 1. Synthesis of **1**.

X-ray diffraction (XRD) analyses of **1** and its radical cation **1**^{•+} were carried out to clarify the structural changes before and after one-electron oxidation. The single crystals of **1** were grown by a slow evaporation of *o*-dichlorobenzene solution. The needle-like orange crystals, suitable for X-ray crystallography, were obtained by a slow evaporation of acetonitrile solution of **1**^{•+}·SbCl₆[−], prepared using equimolar tris(4-bromophenyl)aminium hexachloroantimonate (Magic Blue) as one-electron oxidizing agent. Figures 2a and 2b show the molecular structures of **1** and **1**^{•+}. Both species adopt a quasi-planar geometry, in which the peripheral phenyl rings are warped in the opposite direction so as to have a pseudo-*C*_{2h} symmetrical structure, though they have only a crystallographic inversion center, thus belonging to the point group *C*_i. Moreover, all the nitrogen centers have trigonal planar shape for both **1** and **1**^{•+}, judging from the 360° bond angle sum around the nitrogen atoms. The dihedral angles between the central phenyl ring (A in Figures 2a and 2b) and two peripheral phenyl rings (B and C in Figures 2a and 2b) for **1** (A/B = 25.8°; A/C = 22.8°; B/C = 42.6°) are similar to those for **3** (A/B = 25.5°; A/C = 24.7°; B/C = 43.0°),^[10] whereas the corresponding dihedral angles for **1**^{•+} are reduced to around 80% (A/B = 19.8°; A/C = 18.4°; B/C = 35.2°; note that the B/C angle for **3**^{•+}·FeCl₄[−] was 38.3°).

[12]

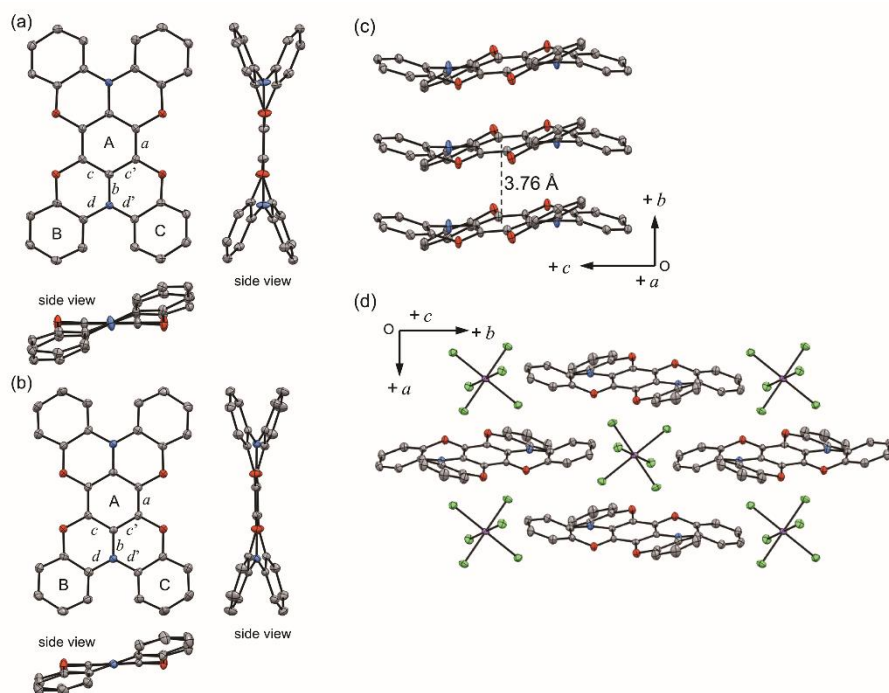


Figure 2. ORTEP views of (a) **1** and (b) **1**⁺ determined from XRD analyses at 153 and 90 K, respectively, and crystal packing of (c) **1** as viewed along the *a* axis and (d) **1**⁺·SbCl₆⁻ as viewed along the *c* axis. (thermal ellipsoids at 50% probability level; hydrogen atoms are omitted for clarity; blue, red, green, and violet ellipsoids designate carbon, nitrogen, oxygen, chlorine, and antimony atoms, respectively).

As shown in Figure 2c, quasi-planar **1** displays one-dimensional on-top π -stacked columns along the *b* axis with intermolecular distance of 3.76 Å, and hence, we anticipated the high and anisotropic carrier mobility like **5a** and **5b**.^[16] However, the preliminary time-resolved microwave conductivity (TRMC) measurements^[17] gave disappointing results (Figure S4). In the **1**⁺·SbCl₆⁻ salt, the quasi-planar π -radicals were fully isolated from each other due to the presence of counteranions (Figure 2d).

Turning next to the structural deformations when going from **1** to **1**⁺ (Table 1), a bond alternation (Δd) was confirmed upon one-electron oxidation of **1**, generating the the semiquinoidal structure of **1**⁺: the shortening of bonds *a* and *b* and the elongation of bonds *c* (*c'*) and *d* (*d'*). However, the bond alternation in **1**⁺ was not so noticeable as compared with the corresponding reported structural deformations from **2** to **2**⁺ (Figure S5 and Table S2),^[7a] probably due to the geometrical constraint of **1** brought about by the four oxygen tethers. This trend is also supported by the so-called bond length alternation (BLA) parameter,^[18] a measure of the quinoidal deformation: the BLA parameter of 0.029 Å for **1**⁺ was half of 0.06 Å for **2**⁺. In addition, the dihedral angle (ϕ) between the central phenyl ring (A) and the nitrogen trigonal plane changes from 22.5° for **1** to 16.6° for **1**⁺, while the change from 55.8° for **2** to 15.2° for **2**⁺ was reported,^[7a] hence indicating the planarity as the PDA radical cations remains virtually unchanged between **1**⁺ and **2**⁺.

The molecular structures for **1**, **1⁺**, and **1⁺⁺** were optimized at the (U) ω B97X-D^[19] level of theory with 6-31+G** split valence basis set including diffuse and polarization functions.^[20] The quasi-planar **1** has two different conformers due to the combinations of the axial helicity (*P/M*) of the peripheral two phenyl rings on both sides of the PDA unit: the C_{2h} symmetric (*PM*) and D_2 -symmetric (*PP* or *MM*) conformations (Figure S6). As shown in Figure 2, the XRD analysis indicated that both **1** and **1⁺** adopted the pseudo- C_{2h} symmetric structures in the solid state. Additionally, the computed energy difference between the two conformers for **1**, **1⁺**, and **1⁺⁺** was within 0.5 kcal mol⁻¹: the relative energy of the optimized C_{2h} -symmetric structures for **1**, **1⁺**, and **1⁺⁺** were estimated to be -0.05, +0.42, and +0.35 kcal mol⁻¹, respectively, as compared to the optimized D_2 -symmetric ones. Hence, the DFT results for the C_{2h} -symmetric structures of **1**, **1⁺**, and **1⁺⁺** were utilized throughout this article. Note that the following discussion basically does not change by the calculated results obtained for the optimized D_2 -symmetric structures (Figure S7). The DFT-optimized geometrical parameters for **1** and **1⁺** showed a good accordance with those obtained from the XRD analyses (Table 1). The DFT-computed BLA parameters for **1⁺** and **1⁺⁺** were estimated to be 0.038 and 0.077, respectively, thus again suggesting the quinoidal deformation does not proceed even in the dication **1⁺⁺**, probably due to the geometrical constraint of **1**.

Table 1. Comparisons of the selected bond lengths^a (Å) and the dihedral angles ϕ (°) between the central phenyl ring and the nitrogen trigonal plane for **1** and **1⁺** in **1⁺⁺**·SbCl₆⁻ salt determined by XRD analyses as well as the corresponding DFT computed values

	1	1⁺	Δd	1 (C_{2h}) ^b	1⁺ (C_{2h}) ^b	1⁺⁺ (C_{2h}) ^b
<i>a</i>	1.382(2)	1.373(3)	-0.009(4)	1.389	1.376	1.367
<i>b</i>	1.409(2)	1.375(3)	-0.034(4)	1.405	1.367	1.336
<i>c</i>	1.383(2)	1.410(3)	+0.027(4)	1.389	1.409	1.428
<i>c'</i>	1.390(1)	1.395(3)	+0.005(3)	1.389	1.409	1.428
<i>d</i>	1.407(1)	1.417(3)	+0.010(3)	1.405	1.419	1.424
<i>d'</i>	1.409(2)	1.423(3)	+0.014(4)	1.405	1.419	1.424
ϕ	22.5	16.6		23.8	19.2	15.2

^aDesignation of selected bonds is given in Figure 2. ^b(U) ω B97X-D/6-31+G** optimized geometrical parameters.

As discussed above, it has been found that the quasi-planar **1** undergoes the modest quinoidal deformation through the two-stage redox reactions. To ascertain the electronic structures of the oxidized species of **1**, the in-situ absorption spectral change upon electrochemical oxidation was recorded by using an optically transparent thin-layer electrochemical cell (Figure 3). Upon one-electron oxidation, the disappearance of the band at 370 nm for **1** followed by the appearance of two new bands at 487 and 1456 nm for **1⁺** with an isosbestic point at 394 nm (Figure 3a). The observed

lowest energy NIR band with a partially resolved vibrational progression demonstrates that the radical cation of **1** adopts a symmetrical charge-delocalized class III structure.^[5,21] The class III structure of **1**^{•+} was also supported by time-dependent density functional theory (TD-DFT) calculations for the symmetric C_{2h} -optimized structure of **1**^{•+} at the U ω B97X-D/6-31+G** level of theory (Figure 4). The lowest energy charge resonance band at 1456 nm is assignable to the electronic transition from the HOMO(β) to LUMO(β) [$D_1 \leftarrow D_0$ excitation energy: 1436 nm ($f = 0.29$)], which is in good agreement with the observed absorption maximum. The second absorption band can be attributed to the HOMO–2(β) to LUMO(β) transition [$D_3 \leftarrow D_0$ excitation energy: 421 nm ($f = 0.07$)]. Note that the non-tethered radical cation **2**^{•+} exhibited a broad featureless IV-CT band, seemingly being expected to a typical charge-localized class II compound, and however, **2**^{•+} has been elucidated to belong to class III right at the border to class II.^[7] The further oxidation from **1**^{•+} to **1**⁺⁺ resulted in a rapid decrease of the charge resonance band of **1**^{•+}, and instead, a new band of **1**⁺⁺ appeared at 790 nm with an isosbestic point at 958 nm (Figure 3b). TD-DFT// ω B97X-D/6-31+G** calculations for the closed-shell dicationic state of **1**⁺⁺ also indicated that the lowest energy band at 790 nm corresponds to the HOMO–LUMO transition [$S_1 \leftarrow S_0$ excitation energy: 835 nm ($f = 0.57$)] (Figure S8).

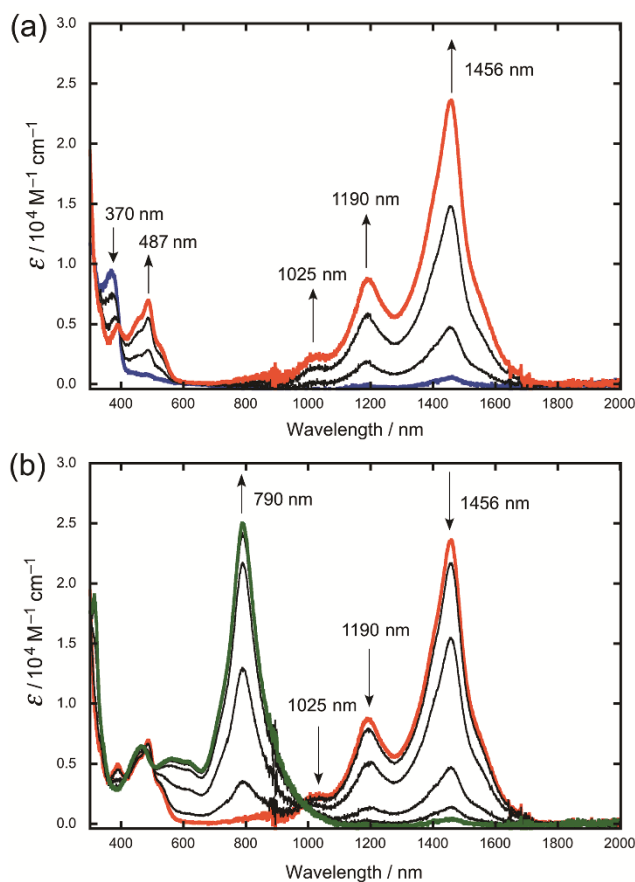


Figure 3. UV/Vis/NIR absorption spectral change upon stepwise electrochemical oxidation: (a) from **1** (blue line) to $1^{+\bullet}$ (red line), and (b) from $1^{+\bullet}$ (red line) to 1^{++} (green line), recorded in dichloromethane (at 0.1 mM) containing 0.1 M $[n\text{-Bu}_4\text{N}]^+[\text{BF}_4]^-$ at 298 K.

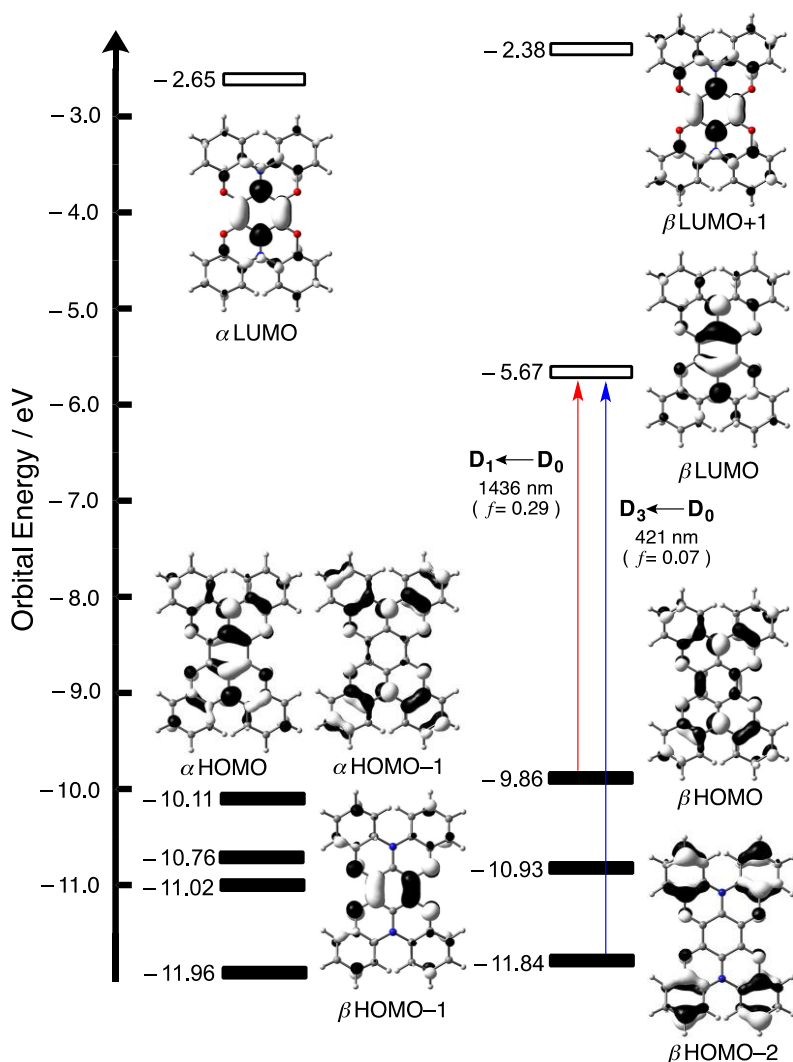


Figure 4. Frontier Kohn-Sham orbital energy level diagram for the C_{2h} -symmetric structure of 1^{++} at the $U\omega B97X\text{-D}/6\text{-}31\text{+G}^{**}$ level of theory. The red and blue arrows represent the major contributions related to the observed lowest and next lowest energy electronic transitions, respectively.

Electron paramagnetic resonance (EPR) spectroscopy was utilized to extract more information about charge delocalization over the class III radical cation $1^{+\bullet}$. The sample of the EPR spectroscopy was prepared by dissolving the $1^{+\bullet} \cdot \text{SbCl}_6^-$ salt in dichloromethane at a concentration of 1 mM. Tris(4-bromophenyl)aminium hexachloroantimonate (Magic Blue) was found to be the right chemical oxidizing agent for preparation of the monocations of **1** selectively, and an excess of the Magic Blue

did not generate any dicationic species $\mathbf{1}^{++}$. In a similar way, silver hexafluoroantimonate ($\text{Ag}^+[\text{SbF}_6]^-$) served as a one-electron oxidizing agent for $\mathbf{1}$ (Figure S9a). In contrast, the compound $\mathbf{1}$ dissolved in concentrated sulfuric acid while forming a dark blue colored solution, which was in good agreement with the absorption spectrum for $\mathbf{1}^{++}$ in Figure 3b (Figure S9b), thereby indicating a selective formation of dicationic species of $\mathbf{1}$.^[22]

As shown in Figure 5a, a five-line spectrum centered at $g = 2.0022$ was observed at 303 K. This spectrum of $\mathbf{1}^{++}$ was well simulated by the following hyperfine coupling constants: $|a_{\text{N}}| = 0.498$ mT (2N); $|a_{\text{H}}| = 0.082$ mT (8N), 0.054 mT (8N), which are in good accordance with the results of DFT-computed Fermi contact analysis (Figure 5b). Thus, the observed EPR spectrum proved that the unpaired electron is fully delocalized over the radical cation $\mathbf{1}^{++}$. More importantly, the variable temperature EPR measurements displayed that the EPR spectral shape remained unchanged in the measured temperature range (193–303 K), strongly suggesting the static charge/spin delocalization of $\mathbf{1}^{++}$ (Figure S10).

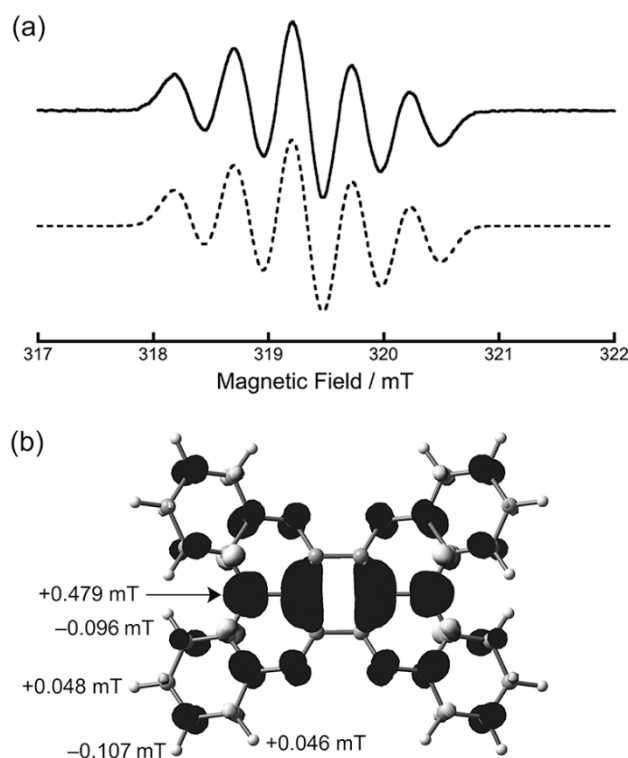


Figure 5. Observed X-band EPR spectrum of $\mathbf{1}^{++}$ in CH_2Cl_2 at 298 K, and its simulated spectrum (broken line), and (b) the spin density distribution (isodensity threshold: 0.002 e bohr⁻³) of $\mathbf{1}^{++}$ and the hyperfine coupling constants at the U ω B97X-D/6-31+G** level of theory.

For the charge-delocalized class III compounds, the optical transition energy at the charge resonance band maximum ($\tilde{\nu}_{\text{max}}$) enables us to evaluate the strength of electronic coupling (V) between the diabatic states in the PDA radical cations ($\tilde{\nu}_{\text{max}} = 2V$), as a measure of the extent of electronic

communication between the redox-active units.^[2] The value of V for the present quasi-planar radical cation $\mathbf{1}^{+\bullet}$ can be estimated to be 3430 cm^{-1} , thus indicating a large electronic coupling enough for the charge delocalization, as compared to those of the biphenyl-bridged and stilbene-bridged BTA radical cations ($V \sim 2800\text{ cm}^{-1}$).^[2] Despite the similar dihedral angle between the central phenyl ring (A) and the nitrogen trigonal plane for both $\mathbf{1}^{+\bullet}$ and $\mathbf{2}^{+\bullet}$, as described before, the non-tethered radical cation $\mathbf{2}^{+\bullet}$ has been known to have a much larger electronic coupling V ($\sim 5790\text{ cm}^{-1}$, judging from the $\tilde{\nu}_{\text{max}}/2$ value in dichloromethane),^[7a] which is close to double that of $\mathbf{1}^{+\bullet}$. This discrepancy arises from the electronic effect of the oxygen-bridges. As noted before, the electronic coupling in the MV systems with two redox-active centers is directly related to the HOMO(β)–LUMO(β) gap and, more importantly, the electronic transition energy between them at the symmetrical molecular structures.^[2,23–25] As seen from the comparison of the orbital energy diagrams in Figures 5 and S11, the HOMO(β) of $\mathbf{1}^{+\bullet}$ is destabilized by the oxygen-bridges, while the LUMO(β) of $\mathbf{1}^{+\bullet}$, to some extent, stabilizes, in comparison with those of $\mathbf{2}^{+\bullet}$, thereby resulting in the lower transition energy (6964 cm^{-1} ; $V_{\text{DFT}} = 3482\text{ cm}^{-1}$) for $\mathbf{1}^{+\bullet}$ than that (13831 cm^{-1} ; $V_{\text{DFT}} = 6916\text{ cm}^{-1}$) for $\mathbf{2}^{+\bullet}$. More interestingly, the reorganization energies for triphenylamine and **3** as redox-active units for **1** and **2**, were calculated at the $\omega\text{B97X-D/6-31+G}^{**}$ level of theory to be 917 cm^{-1} and 1768 cm^{-1} , respectively.^[26] This suggests the oxygen-bridges induce an increase in the reorganization energy of TAA as the redox-active unit, negatively affecting the electronic communication in the present quasi-planar $\mathbf{1}^{+\bullet}$. Nevertheless, it can be safely said that $\mathbf{1}^{+\bullet}$ is still in the class III system.

1-3 Conclusions

In summary, the combination of electrochemistry, in situ optical spectroscopic measurements during electrochemical oxidation, X-ray diffraction analyses, EPR measurements, and theoretical calculations has revealed characteristics of oxygen-bridged quasi-planar PDA (**1**) and its oxidized species ($\mathbf{1}^{+\bullet}$ and $\mathbf{1}^{++}$). These oxidized species have been generated preferentially by choice of oxidizing agents. In particular, the radical cation $\mathbf{1}^{+\bullet}$ has been characterized to be a charge-delocalized class III compound, having a medium-sized electronic coupling due to the electronic effect by the oxygen-bridges as well as the rather large reorganization energy originating from the structural rigidity of the oxygen-bridges, and an exquisite balance of both parameters might ensure the charge-delocalization on $\mathbf{1}^{+\bullet}$.

1-4 Experimental Section

General: All the purchased reagents were of standard quality, and used without further purification. All the purchased solvents were purified, dried, and degassed by standard procedures. Column chromatography was performed with silica gel (Kanto Chemical Co., Inc., silica gel 60N, spherical neutral). ^1H and ^{13}C NMR spectra were measured by a JEOL JNM-AL400 FT-NMR spectrometer. Chemical shifts of NMR spectra were determined

relative to internal tetramethylsilane (TMS) standard (δ), and are given in parts per million (ppm). Crystallographic data for **1** and $\mathbf{1}^{++} \cdot \text{SbCl}_6^-$ were collected at 153 K for **1** and 90 K for $\mathbf{1}^{++} \cdot \text{SbCl}_6^-$ on a Rigaku Saturn724+ (4×4 bin mode) diffractometer using graphite-monochromated Mo K α radiation ($\lambda = 0.71075$ Å for **1** and 0.71073 Å for $\mathbf{1}^{++} \cdot \text{SbCl}_6^-$) generated from a rotating anode. The structures were solved by direct method [SHELXS-2014 (Sheldrick, 2014) for **1** and SHELXT 2018/2 (Sheldrick, 2018) for $\mathbf{1}^{++} \cdot \text{SbCl}_6^-$] and refined by full-matrix least-squares procedures on F^2 [SHELXL-2014 (Sheldrick, 2014) for **1** and SHELXL 2018/3 (Sheldrick, 2018) for $\mathbf{1}^{++} \cdot \text{SbCl}_6^-$]. The non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were located on the calculated positions, and refined isotropically as a riding model. UV/Vis-NIR absorption spectra were obtained with a Perkin-Elmer Lambda 950 spectrometer. High resolution (HR) electrospray ionization (ESI) mass spectra were acquired using a Thermo Fischer EXACTIVE mass spectrometer. Fluorescence spectra were recorded on an absolute PL quantum yield measurements system (HAMAMATSU Quantaaurus-QY). The redox properties were evaluated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in CH_2Cl_2 solution at 298 K with 0.1 M tetra-*n*-butylammonium tetrafluoroborate (TBABF₄) as supporting electrolyte (scan rate 100 mV s⁻¹) using an ALS/chi Electrochemical Analyzer model 612A. A three-electrode assembly was used, which was equipped with a platinum disk (2 mm²) and a platinum wire as the working and counter electrodes, respectively, and Ag/0.01 M AgNO₃ (acetonitrile) was used as the reference electrode. The redox potential were referenced against a ferrocene/ferrocenium ($\text{Fc}^{0/+}$) redox potential measured in the same electrolytic solution. Spectroelectrochemical measurements were carried out with a custom-made optically transparent thin-layer electrochemical (OTTLE) cell (light pass length = 1 mm) equipped with a platinum mesh and a platinum coil as the working and counter electrodes, respectively, and Ag/0.01 M AgNO₃ (acetonitrile) was used as the reference electrode. The potential was applied with an ALS/chi Electrochemical Analyzer model 612A. ESR spectra were recorded on a JEOL JES-X310 X-band ESR spectrometer, in which temperature was controlled by a JEOL ES-13060DVT5 variable temperature unit. A Mn²⁺/MnO solid solution was used a reference.

Compound **2** was purchased from TCI chemicals and used without further purification to remeasure the electrochemical properties in comparison with those of compound **1** in the same experimental conditions. The crystallographic data for **2** and $\mathbf{2}^{++}$ were taken from Ref. [7a] (CCDC 221196 and 221197).

Synthesis of 6: A mixture of 2-iodoanisole (0.94 g, 4.0 mmol), 2,3,5,6-tetrafluoro-1,4-phenylenediamine (0.16 g, 0.89 mmol), K₂CO₃ (0.48 g, 3.5 mmol), copper powder (80 mg, 1.3 mmol), and 18-crown-6 (30 mg, 0.11 mmol) in mesitylene (100 mL) was refluxed under argon atmosphere for 24 h with stirring. The resulting reaction mixture was filtered, and the residue was washed with CH₂Cl₂. The filtration was evaporated in vacuo, and then the residue was triturated and washed well with water and *n*-hexane to afford **6** (0.42 g, 78%) as a dark purple solid; m.p. 205–207°C; ¹H NMR (400 MHz, acetone-*d*₆) δ 7.00–7.10 (m, 8H), 6.84–6.91 (m, 8H), 3.67 (s, 12H); ¹³C{¹H} NMR (100 MHz, acetone-*d*₆) δ 154.6, 137.0, 125.8, 125.6, 122.0, 114.2, 56.4 (seemingly, additional two signals in the aromatic region are accidentally overlapped, or considerably diminished by the C–F coupling.); HRMS(ESI) *m/z*: [M+Na]⁺ Calcd for C₃₄H₂₈F₄N₂O₄Na: 627.1883; found 627.1869.

Synthesis of 1: A mixture of **6** (0.22 g, 0.36 mmol), BBr₃ (0.63 g, 2.5 mmol) in dichloromethane (30 mL) was stirred for 24 h at –78°C under argon atmosphere. After returning to room temperature, the product is poured into pure water and extracted with ethyl acetate, and layer was dried over Na₂SO₄. After evaporation of the solvent, the crude product was dissolved in DMF (30 mL). After addition of K₂CO₃ (0.69 g, 5.0 mmol), the mixture was stirred at 120°C under argon atmosphere for 72 h. The cooled reaction mixture was filtered, and the residue was washed with water and acetone to yield **1** (110 mg, 65%) as a greenish gray solid; m.p. 273°C (decomp.); ¹H NMR (400 MHz, CS₂ (a small amount of CDCl₃ was added) δ 7.29 (dd-like, *J*_{H,H} = ca. 8, 2 Hz, 4H), 6.99–6.87 (m, 12H); HRMS(ESI) *m/z*: [M]⁺ calcd for C₃₀H₁₆N₂O₄ 468.1110; found 468.1110. ¹³C NMR spectrum of **1** was not measurable due to an extremely low solubility in common organic solvents.

Density functional theory calculations: DFT calculations were performed with using a long-range corrected hybrid Hartree–Fock/density functional theory (HF/DFT) method including short-range Hartree–Fock exchange plus empirical atom-atom dispersion correction (*ω*B97X-D).^[19, 27] Full geometrical optimizations for the neutral and oxidized states of **1** and **2** were carried out, and furthermore, their local minimum structures were confirmed by performing subsequent frequency analyses. Excitation energies were examined on the basis of time-dependent density functional theory (TD-DFT)^[28] by using the (U) *ω*B97X-D optimized structures. All the computations employed the 6-31+G** basis sets.^[20] All these computational approaches are implemented in Gaussian 16 package of ab initio quantum chemical calculation.^[29]

References and Notes

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Chapter 2

A Three-Redox-Center Organic Mixed-Valence System: Optically and Thermally Assisted Charge Transfer in Radical Cation of Tris(triarylamine) Connected through 1,2,3-Benzenetriyl Bridge

2-1 Introduction

Partially oxidized oligotriarylamine have always played a central role as benchmark organic mixed-valence (MV) molecular systems.^[1–5] This can be ascribed to both the robustness of the radical cations generated on the triarylamine (TA) redox-active centers^[6–8] and their synthetic availability.^[9] The intervalence charge-transfer (IVCT) in the MV compounds is affected not only by the choice of a redox-active center but also by the choice of a π -conjugated bridging unit linking the redox-active centers, and the bridging topology between the redox-active centers has been recognized as a pivotal factor governing the IVCT process.^[1,2] In particular, the substitution pattern of the redox-active centers via the phenylene π -bridge were extensively studied to develop the so-called topology rule for the strength in the electronic coupling (V) between the neutral and charged redox-active units in the organic MV systems: *para*- or *ortho*-phenylene-bridging leads to a larger V , whereas *meta*-phenylene-bridging to a relatively smaller V .^[10–13]

As shown in Figure 1a, historically, Bonvoisin and co-workers commenced the optically assisted IVCT band analysis on oligotriarylamine radical cations with *meta*-topology such as *meta*-phenylene-bridged bis(triarylamine) (**4a**) and/or the 1,3,5-benzenetriyl-bridged tris(triarylamine) (TTA; **5**) radical cations.^[14,15] Thereafter, the charge-transfer process for oxidized species of hexakis(triarylamine)s (HTAs; **6**) was precisely delineated by Lambert and co-workers.^[16,17] Moreover, by utilizing the dialkylanilino moieties in place of TA redox-active centers, the toroidal charge-delocalization in **7** has been fulfilled by Kochi et al.^[18,19] In those fully amino-group-substituted MV systems, *ortho*-topology was taken in consideration in conjunction with an overcrowdedness due to *ortho*-substitution. Additionally, we have demonstrated that the V of *ortho*-phenylene-bridged BTA (**2**) radical cation was comparable in magnitude to that for *para*-phenylene-bridged BTA (**3**) radical cation, while *meta*-phenylene-bridged BTA (**4b**) radical cation exhibits a smaller V , thus leading to the above-mentioned archetypal topology rule.^[12,13]

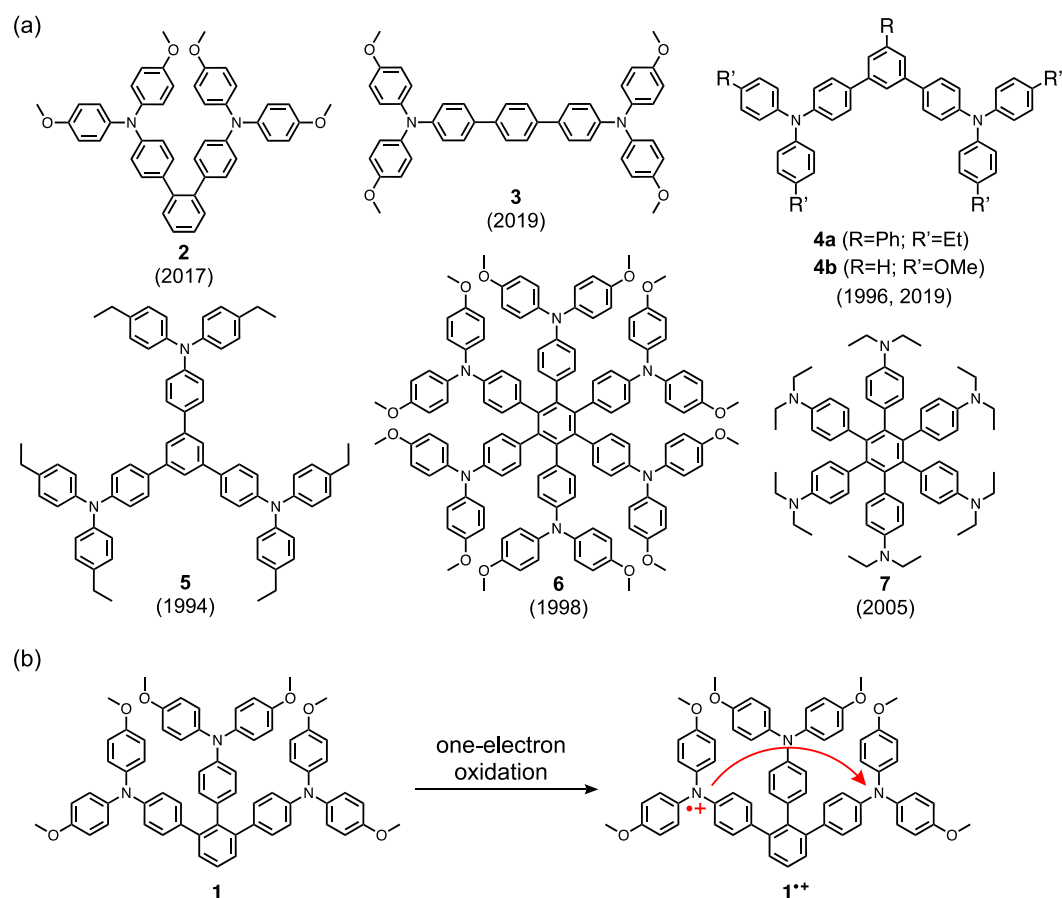
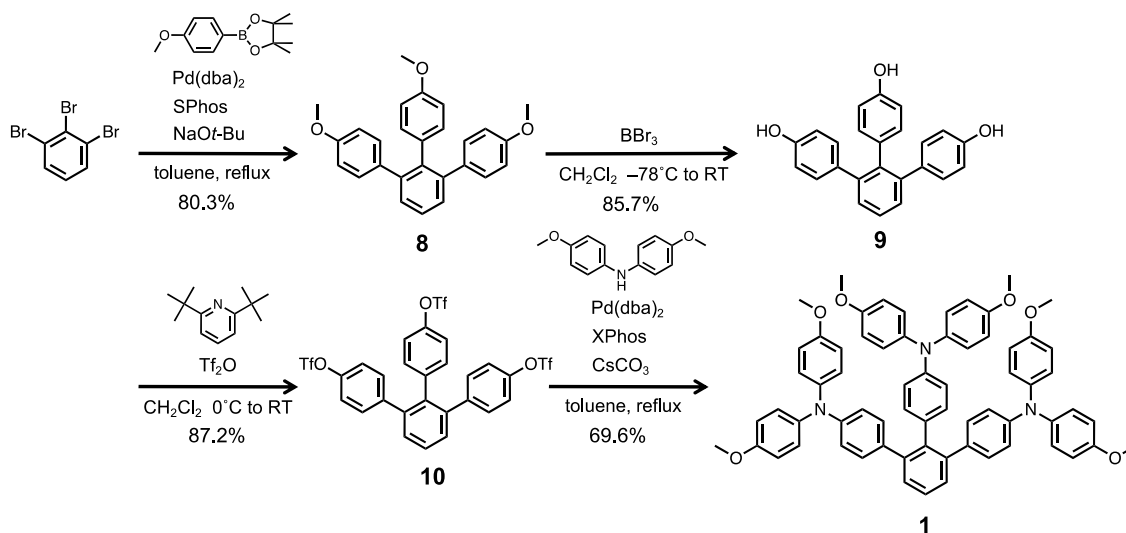


Figure 1. (a) Previously studied phenylene-bridged BTAs **2–4**, and oligotriarylamines having multi-redox-active centers **5–7**, and (b) the three-redox-center TTA **1** connected through 1,2,3-benzenetriyl bridge and its MV radical cation of interest in this study.

Though the various features on the intramolecular charge-transfer (ICT) processes are being clarified by those oligotriarylamine-based organic MV compounds, the investigation on organic MV systems with multi-redox-active centers, also referred to as multi-dimensional organic MV systems,^[2] is still in its infancy with some exceptions.^[14–23] Having found that thermally assisted IVCT process in the *ortho*-phenylene-bridged BTA radical cation **2^{•+}** was observable by the variable-temperature electron spin resonance (VT-ESR) spectroscopy,^[12] we became interested in exploring the ICT in three-redox-center organic MV radical cation **1^{•+}** where three TA redox-active centers were arranged in a side-by-side fashion via 1,2,3-benzenetriyl bridging unit (Figure 1b). In the present study, we elucidated the optically and thermally assisted IVCT processes of **1^{•+}** from the absorption and VT-ESR spectroscopic analyses.

2-2 Results and Discussion

TTA **1** was obtained in four steps according to the routes shown in Scheme 1, starting from the Suzuki-Miyaura coupling reaction of 1,2,3-tribromobenzene and 4-methoxyphenylboronic acid pinacol ester.^[24] Compound **8** with three *p*-anisyl groups was demethylated with boron tribromide (BBr₃),^[25] and then, the hydroxy groups of compound **9** was triflated using triflic anhydride (Tf₂O) and a hindered pyridine.^[26] Finally, the Buchwald-Hartwig amination reaction^[27] of the tris(triflate) **10** and dianisylamine afforded **1** as a white crystalline solid.



Scheme 1. Synthesis of TTA **1**.

Slow diffusion of *n*-pentane into a CH₂Cl₂ solution of **1** gave colorless prismatic crystals suitable for X-ray structure analysis (Supporting information, Table S1 and Figure S1). As shown in Figure 2, the separations between the central nitrogen atom and the two peripheral nitrogen atoms of **1** were estimated to be 6.756 Å and 8.450 Å, respectively, designating the central TA slightly closer to one of the two peripheral TAs. Note that two nitrogen atoms were separated by 7.963 Å for **2** (Figure 2b). The dihedral angles between the 1,2,3-benzenetriyl ring and each of the NC₃ planes of three TAs were confirmed to be quite large (62.4°, 64.7°, and 39.2°), probably due to an increase in the steric congestion of **1**. Note that the corresponding dihedral angles for **2** were 42.7° and 48.2°, respectively (Figure 2b). One of the three TAs of **1** became possible to take a smaller dihedral angle due to the larger nitrogen–nitrogen separation of 8.450 Å, that is, alleviation of congestion. The observed large dihedral angles were also confirmed by the geometrical optimization (*C*₂-symmetry) of **1** at the B3LYP/6-31G* level of theory (Supporting Information, Figure S5).

Inspection of the Kohn-Sham orbitals at the optimized geometry of **1**, furthermore, suggested that the HOMO was mainly localized on the central TA, while the HOMO-1 was localized on the peripheral

TAs, and the HOMO-2 delocalized over three TAs. In addition, the small energy gaps within 0.14 eV between the HOMO, HOMO-1, and HOMO-2, of **1** clearly indicated a quasi-degeneracy of the frontier orbitals (Supporting Information, Figure S6).

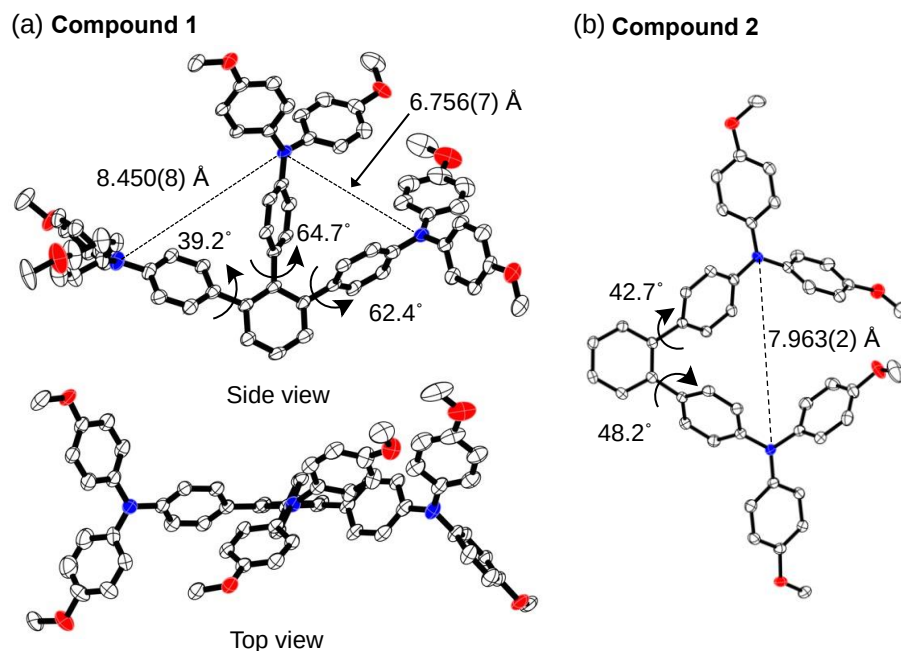
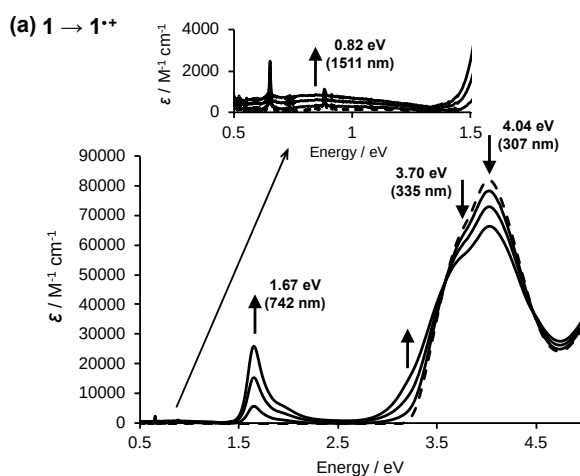


Figure 2. ORTEP views with the selected geometrical parameters of (a) **1** determined from XRD analyses (thermal ellipsoids at 50% probability level; hydrogen atoms are omitted for clarity; blue- and red-colored ellipsoids designate nitrogen and oxygen atoms, respectively) and (b) **2** for comparison. The XRD data of **2** were taken from CCDC 1554271 (Ref. [12]).

To gain an insight into the qualitative strength of the electronic coupling in $\mathbf{1}^{\bullet+}$, the redox behavior of **1** was measured by the electrochemical analysis [cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in 0.1 M $[n\text{Bu}_4\text{N}]^+[\text{BF}_4]^-/\text{CH}_2\text{Cl}_2$ (ca. 1 mM) at room temperature (Supporting information, Figure S2)]. The single reversible oxidation wave was seen in the cyclic voltammogram, and the oxidation reaction was found to be comprised of three consecutive one-electron oxidation processes by the differential pulse voltammogram. The oxidation potentials are determined to be $E_1 = +0.13$ V (1e), $E_2 = +0.20$ V (1e), and $E_3 = +0.26$ V (1e) by the simulation of the observed DPV. The potential difference between E_1 and E_2 ($\Delta E = 0.07$ V) indicated the electronic stabilization of $\mathbf{1}^{\bullet+}$, to some extent, due to the dynamic charge/spin delocalization between three triarylamine redox centers, as compared to $\mathbf{1}^{2+}$. This is because the ΔE value corresponds to $(2RT/F)\ln 2$ ($= 0.036$ V at 298 K) in the case of molecular systems with non-interacting redox centers.^[28-30] Such a redox behavior of **1** was similar to that of **2**.^[12]

The optically assisted IVCT in oligo(triarylamine)-based MV compounds can be characterized by the electronic absorption band observed in the near IR (NIR) region.^[2,5] The UV/Vis/NIR absorption spectral changes were monitored by using an optically transparent thin-layer electrochemical cell^[31] during stepwise electrochemical oxidation of **1** in CH₂Cl₂ (Figure 3). As shown in Figure 3a, during the course of the oxidation going from **1** to **1**^{•+}, the absorption band at 4.04 eV (307 nm) with a shoulder at around 3.70 eV (335 nm) gradually decreased with increasing intensity of the weak IVCT absorption band at 0.82 eV (1511 nm). The triarylaminium-localized π - π^* transitions at 1.67 eV (742 nm)^[6] increased simultaneously associated with two isosbestic points at 3.58 and 4.50 eV. The single-point TD-DFT calculation at the UB3LYP/6-31G* optimized charge-delocalized C₂-symmetric structures for **1**^{•+} underestimated the IVCT transition energy [0.23 eV (5303 nm), $f=0.09$] (Supporting Information, Figure S8). However, the symmetric optimized structure was predicted with the spin density being localized on the central TA redox-active center by the DFT geometrical optimization for **1**^{•+} with use of the BLYP-based hybrid functional with 35% exact exchange (BLYP35/SVP)^[32] including the solvation effect by the conductor-like polarizable continuum (CPCM) model^[33] [CH₂Cl₂ ($\epsilon = 8.93$)] (Supporting Information, Figure S9 and Figure 4).



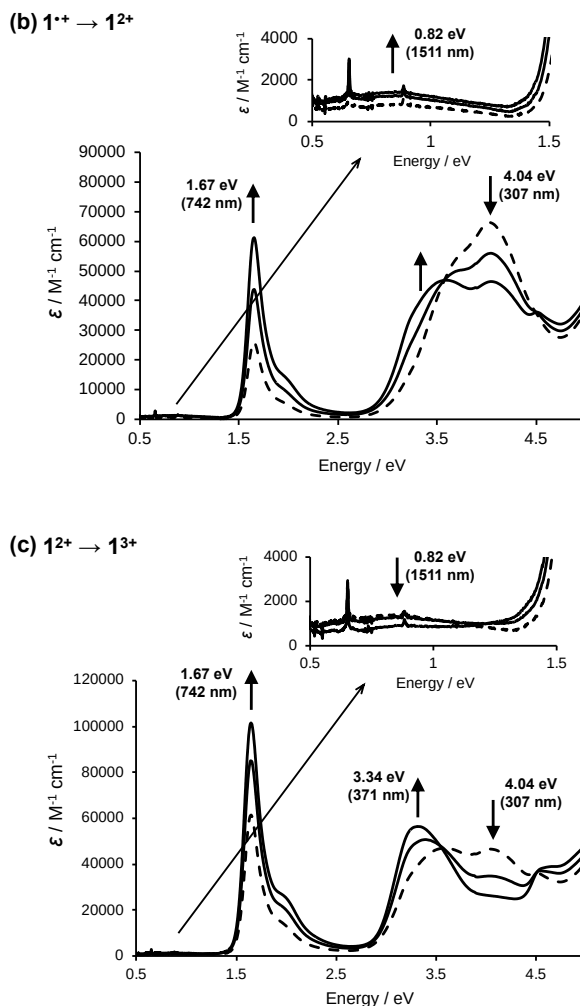


Figure 3. UV/Vis-NIR absorption spectral changes during electrochemical oxidation (a) from **1** (broken line) to $1^{+\bullet}$ (solid line), (b) from $1^{+\bullet}$ (broken line) to 1^{2+} (solid line), and (c) from 1^{2+} (broken line) to 1^{3+} (solid line) in CH_2Cl_2 (at 1×10^{-4} M) at 298 K.

The IVCT transition can be assigned as the lowest-energy transition from βHOMO and/or $\beta\text{HOMO}-1$ (the MO localized on the peripheral TAs) to βLUMO (the MO localized the central TA) by the subsequent single-point TD-DFT calculation at the same level of theory. (Supporting Information,

Figure S9). The IVCT transition energies ($\bar{h}_{\text{IVCT}}^{\text{DFT}}$) were then estimated by DFT as 0.69 eV (1802 nm; $f = 0.017$) and 0.69 eV (1788 nm; $f = 0.018$), which are in reasonable agreement with the observed IVCT band maximum. Hence, the BLYP35 computations supported the present TTA MV radical cation was classified into class II MV system,^[34] where the generated charge was localized on the central TA redox-active center. More interestingly, the charge/spin localized asymmetric local minimum structure for $1^{+\bullet}$ has also been found together with the partially charge/spin localized asymmetric saddle-point

structure at the BLYP35/SVP+CPCM (CH₂Cl₂) level of theory (Supporting Information, Figures S10 and S11). As a whole, the DFT-predicted energy diagram for the intramolecular charge/spin transfer process in TTA radical cation **1**^{•+} are shown in Figure 4. Hence, in contrast to the degenerate MV system such as **2**^{•+},^[12] **1**^{•+} can be expected to be a nondegenerate MV system.^[2,35] During further oxidation to **1**²⁺, the intensity of IVCT band and triarylaminium-localized π - π^* transition band continued to increase to almost 2-fold larger than that of **1**^{•+} (Figure 2b), indicating that **1**²⁺ is still in the MV state. Finally, the IVCT band at 0.82 eV disappeared by oxidation up to **1**³⁺, and the intensity of the triarylaminium-localized π - π^* band at 1.67 eV reached up to nearly 3-fold relative to that of **1**^{•+} (Figure 2c). Note that the stepwise chemical oxidation of **1** also reproduced the same spectral changes as those in Figure 2 (Supporting Information, Figure S3).

For the charge/spin-localized class II MV compound **1**^{•+} in the framework of Mulliken-Hush theory, the value of V can be derived by Eq. (1):^[36–38]

$$V = \frac{\mu_{ab}}{\Delta\mu_{12}} \tilde{\nu}_{\max} = \frac{\mu_{ab}}{\sqrt{(\Delta\mu_{ab})^2 + 4(\mu_{ab})^2}} \tilde{\nu}_{\max} \quad (1),$$

where m_{ab} is the transition moment between the adiabatic states (m_{ab}), which can be determined from the integration of the IVCT band (Supporting Information, Figure S4), $\tilde{\nu}_{\max}$ the energy of the IVCT band maximum (6618 cm⁻¹; Figure 3), Dm_{12} the difference in the diabatic dipole moments between the ground and excited states, which was calculated by using both of m_{ab} and the DFT-computed adiabatic dipole moment difference (Dm_{ab}) of 20.5 Debye [BLYP35/SVP+CPCM(CH₂Cl₂)]. Noteworthy is that the direction of the adiabatic dipole moment change in **1**^{•+} by the optically assisted IVCT is parallel to the direction of connecting line between the central TA and the 1,2,3-benzenetriyl bridging unit, whereas that in **2**^{•+} is parallel to the direction of connecting line between two TAs (Supporting Information, Figure S12). From the IVCT band analysis, the value of V for **1**^{•+} in CH₂Cl₂ has been determined to 874 cm⁻¹, which was comparable to that of **2**^{•+} (794 cm⁻¹).^[12] More interestingly, additional IVCT bands corresponding to the direct charge/spin transfer between two peripheral TA redox-active centers were not confirmed for **1**^{•+}, in contrast with the Bonvoisin's TTA radical cation possessing two kinds of charge/spin transfer pathways.^[15]

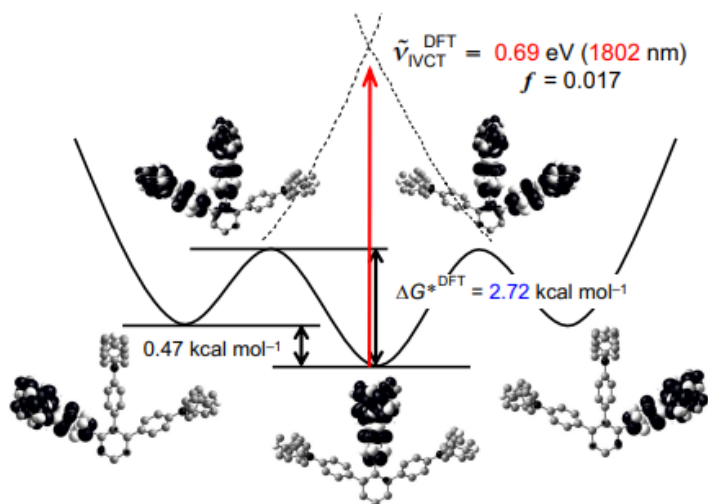


Figure 4. DFT- and TD-DFT-predicted energy diagram for the intramolecular charge/spin transfer process of $1^{\bullet+}$ [BLYP35/SVP+CPCM(CH₂Cl₂)]. The depicted symmetrical and asymmetrical molecular structures with spin density distribution were determined by the geometrical optimization at BLYP35/SVP+CPCM(CH₂Cl₂) level of theory.

As has been established for the BTA-based organic MV systems,^[39–41] an insight into the thermally assisted IVCT process of $1^{\bullet+}$ was directly monitored by VT-ESR spectroscopy at X-band frequencies. As shown in Figure 5, the sample generated by chemical oxidation of **1** by 0.5 equivalent of AgSbF₆ gave a hyperfine-structured ESR spectrum of $1^{\bullet+}$ in CH₂Cl₂ at 298 K. The spectrum was reasonably reproduced by hyperfine interactions of the radical spin with ¹⁴N nuclei ($|a_{Na}| = 0.45$ mT) and two sets of equivalent ¹H nuclei ($|a_{Ha}| = 0.12$ mT (2H), $|a_{Hc}| = 0.08$ mT (4H)) in the central triarylamine redox-center and two equivalent ¹⁴N nuclei ($|a_{Nb}| = 0.24$ mT (2N)) and two sets of equivalent ¹H nuclei ($|a_{Hb}| = 0.06$ mT (4H), $|a_{Hd}| = 0.04$ mT (8H)) in two peripheral TA redox-active centers (Figure 5b), indicating the generated charge/spin was dynamically delocalized over the three TAs at room temperature. As shown in Figure 6a, temperature-dependence of the ESR spectra of $1^{\bullet+}$ in CH₂Cl₂ clearly showed a thermally assisted IVCT process between three TA redox-active centers, thereby indicating the radical cation $1^{\bullet+}$ can be classified into charge-localized class II MV systems. This is in accordance with the aforementioned results on the optical IVCT band analysis. The IVCT rate constants (k_{th}) at various temperatures were determined by spectral simulations with the Heinzer's dynamic ESR-EXN program based on the stochastic Liouville scheme, which simulates the ESR line shape when there exists the intramolecular dynamic spin transfer among the multi-redox-active centers (Figure 6b).^[42] As shown in Figure 7, in the present dynamic ESR simulations, the spin configurations of 50% at the central TA and 25% at the peripheral two TAs has been assumed on the basis of the DFT-predicted energy profile (Figure 4), and the fictitious hyperfine coupling constants, a_N , a_{H1} (2H), and

$a_{\text{H}_2}(4\text{H})$, for each of three TA redox-active centers were estimated to be 0.9, 0.24, and 0.16 mT, respectively. The activation barrier (ΔG^*) for the thermally assisted IVCT in $\mathbf{1}^{*+}$ in CH_2Cl_2 was evaluated to be 986 cm^{-1} ($2.82\text{ kcal mol}^{-1}$) from the Arrhenius plots of $\ln(k_{\text{th}})$ versus $1/T$ in the temperature range (Figure S13). It should be noted that the experimentally determined activation barrier (DG^*) for $\mathbf{1}^{*+}$ showed good agreement with the TD-DFT-computed value [950 cm^{-1} ($2.72\text{ kcal mol}^{-1}$)] at the BLYP35/SVP+CPCM(CH_2Cl_2) level of theory (Figure 4). Again, the direct charge/spin transfer pathway between two peripheral TA redox-active centers could not be extracted from the VT-ESR analysis for $\mathbf{1}^{*+}$, as can be seen from the energy diagram in Figure 4. This is probably because the electronic coupling value via *meta*-phenylene bridge ($200 \sim 300\text{ cm}^{-1}$)^[13,15] is smaller than that via *ortho*-phenylene bridge ($\sim 800\text{ cm}^{-1}$)^[12] thus leading to a high activation barrier through *meta*-phenylene bridge. Hence, it is strongly suggested that the thermally assisted IVCT pathway between two peripheral TA redox-active centers is virtually forbidden due to such high activation barrier.

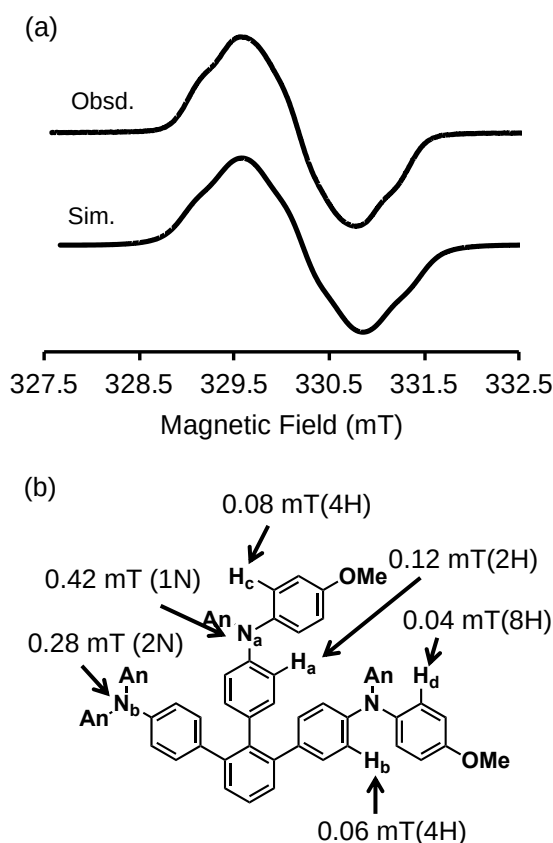


Figure 5. (a) Observed and simulated X-band ESR spectrum at 298 K, and (b) the designation of nitrogen and hydrogen nuclei used in the simulation together with the hyperfine coupling constants.

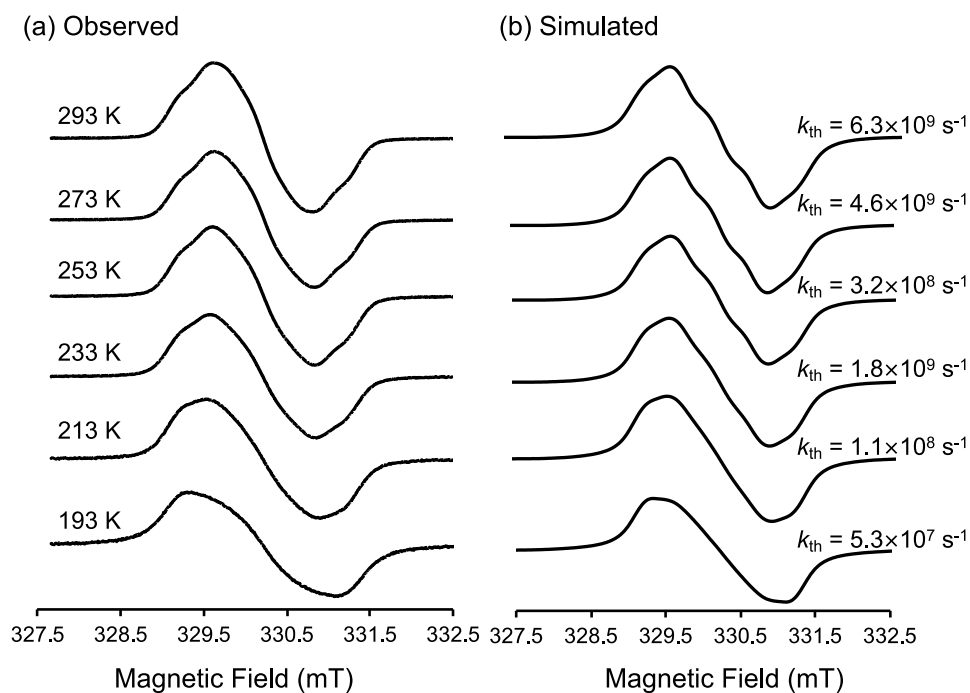


Figure 6. (a) Observed X-band VT-ESR spectra and (b) simulated spectra with determined IVCT rates (k_{th}) of $\mathbf{1}^{\bullet+}$ in CH_2Cl_2 at 1×10^{-4} M.

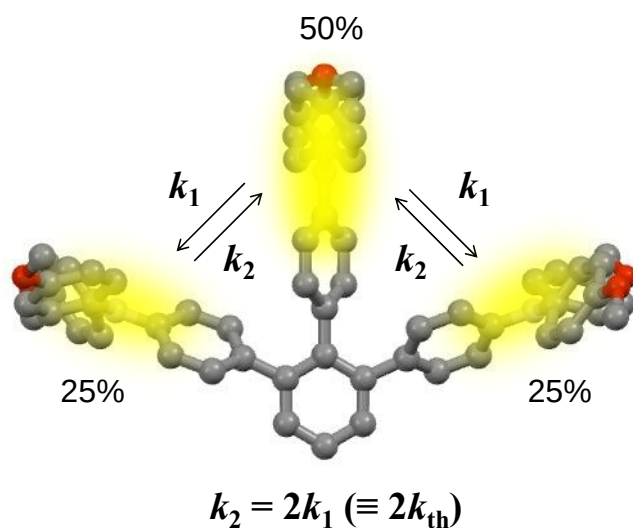


Figure 7. Spin configurations for the dynamic ESR analysis of $\mathbf{1}^{\bullet+}$.

2-3 Conclusions

The foregoing results unequivocally demonstrated that the present radical cationic species of tris(triarylamine), bearing three triarylamine redox-centers in a side-by-side fashion via 1,2,3-

benzentriyl bridge, exhibited optically and thermally assisted IVCT phenomenon, and these features were fully characterized by the Mulliken-Hush analysis of the observed IVCT band, the exchange rate analysis based on VT-ESR measurements, and the DFT-based analysis. As opposed to the previously studied tris(triarylamine) radical cation with trigonal topology, the present tris(triarylamine) radical cation was found to be a nondegenerate MV system, and the overall charge/spin transfer pathway was revealed by the dynamic ESR simulation on the basis of the DFT prediction with use of the BLYP35 functional. More noteworthy is that the IVCT pathway through *ortho*-phenylene overwhelms the IVCT pathway through *meta*-phenylene, probably due to a large difference in electronic couplings for *ortho*- and *meta*-conjugation. The present study may provide a clue for designing multi-dimensional MV systems to control many aspects of electronic communication.

2-4 Experimental Section

General: All the purchased reagents were of standard quality, and used without further purification. All the solvents were purified, dried, and degassed by standard procedures. Column chromatography was performed with silica gel (Kanto Chemical Co., Inc., silica gel 60N, spherical neutral). ^1H and ^{13}C NMR spectra were measured by a JEOL JNM-AL400 FT-NMR spectrometers. Chemical shifts of NMR spectra were determined relative to internal tetramethylsilane (TMS) standard (δ), and are given in parts per million (ppm). UV/Vis-NIR absorption spectra were obtained with a Perkin-Elmer Lambda 950 spectrometer. High resolution (HR) electrospray ionization (ESI) mass spectra were acquired using a Thermo Fischer EXACTIVE mass spectrometer. Crystallographic data for **1** were collected at 144 K on a Rigaku Saturn70 CCD diffractometer using graphite monochromated Mo K α radiation ($\lambda = 0.71075 \text{ \AA}$) generated from a rotating anode. The data collection and processing was performed with CrystalClear software.^[43] The structures was solved by direct method [SHELXT-2014/5]^[44] and refined by full-matrix least-squares procedures on F^2 [SHELXL-2018/1]^[45]. The non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were located on the calculated positions, and refined isotropically as a riding model. All the calculations except for the refinement procedures were performed by using CrystalStructure crystallographic software package.^[46] The redox properties were evaluated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in CH_2Cl_2 solution at 298 K with 0.1 M tetra-*n*-butylammonium tetrafluoroborate (TBABF $_4$) as supporting electrolyte (scan rate 100 mV s $^{-1}$) using an ALS/chi Electrochemical Analyzer model 612A. A three-electrode assembly was used, which was equipped with a platinum disk (2 mm 2) and a platinum wire as the working and counter electrodes, respectively, and Ag/0.01 M AgNO $_3$ (acetonitrile) was used as the reference electrode. The redox potentials were referenced against a ferrocene/ferrocenium (Fc $^{0/+}$) redox potential measured in the

same electrolytic solution. The computational simulation for the observed differential pulse voltammogram was conducted according to the method of Bond and co-workers.^[47] Spectroelectrochemical measurements were carried out with a custom-made optically transparent thin-layer electrochemical (OTTLE) cell (light pass length = 1 mm) equipped with a platinum mesh and a platinum coil as the working and counter electrodes, respectively, and Ag/0.01 M AgNO₃ (acetonitrile) was used as the reference electrode. The potential was applied with an ALS/chi Electrochemical Analyzer model 612A. ESR spectra were recorded on a JEOL JES-X310 X-band ESR spectrometer, in which temperature was controlled by a JEOL ES-13060DVT5 variable temperature unit.

Synthesis of 2: A mixture of 1,2,3-tribromobenzene (4.00 g, 12.7 mmol), 4-methoxyphenylboronic acid pinacol ester (10.7 g, 44.5 mmol), NaOt-Bu (6.48 g, 67.4 mmol), SPhos (0.80 g, 1.9 mmol), and Pd(dba)₂ (1.00 g, 1.74 mmol) in toluene (100 mL) was refluxed with stirring under argon atmosphere for 24 h. The reaction mixture was washed with brine and the organic layer was dried over Na₂SO₄. After evaporation of the solvent, the crude product was chromatographed on silica gel (dichloromethane : *n*-hexane = 1:4 as eluent) to afford **2** (4.06 g, 80.3%) as a white solid; ¹H NMR (400 MHz, CDCl₃) δ = 3.69 (s, 3H), 3.75 (s, 6H), 6.54 (d, *J* = 8.8 Hz, 2H), 6.69 (dd, *J* = 6.7 Hz, 2 Hz, 4H), 6.69 (dd, *J* = 6.7 Hz, 2 Hz, 4H), 6.72 (d, *J* = 8.8 Hz, 2H), 7.34-7.38 (m, 2H+1H); ¹³C NMR (100 MHz, CDCl₃) δ = 55.0, 55.1, 112.8, 113.0, 126.9, 129.3, 130.8, 132.1, 132.6, 134.5, 138.6, 141.6, 157.4, 157.8.

Synthesis of 3: To a dichloromethane (20 mL) solution of **2** (1.19 g, 3.00 mmol), BBr₃ (13.5 mL, 1.0 M in dichloromethane) was added at -78 °C, and the mixture was stirred at room temperature for 1 day. The reaction mixture was cooled to 0 °C, then quenched with H₂O. The mixture was extracted with dichloromethane and ethyl acetate. The combined organic layer was dried over Na₂SO₄, filtrated, and concentrated under vacuum. The residue was purified by column chromatography on silica gel (toluene : ethyl acetate = 1 : 1 as eluent) to afford white powder **3** (0.91 g, 85.7%); ¹H NMR (400 MHz, THF-*d*₈) δ = 6.27 (d, *J* = 8.8 Hz, 2H), 6.41 (d, *J* = 8.4 Hz, 4H), 6.48 (d, *J* = 8.4 Hz, 2H), 6.72 (d, *J* = 8.8 Hz, 4H), 7.08-7.19 (m, 2H+1H), 7.86 (s, 1H), 7.99 (s, 2H); ¹³C NMR (100 MHz, THF-*d*₈) δ = 114.1, 114.2, 126.3, 128.8, 130.6, 130.9, 132.5, 133.4, 138.9, 142.1, 155.6, 155.9.

Synthesis of 4: To a dichloromethane (30 mL) solution of **3** (0.91 g, 2.6 mmol) and 2,6-di-*tert*-butylpyridine (1.5 mL, 6.8 mmol), Tf₂O (4.3 mL, 26 mmol) was added at 0 °C, and the mixture was stirred at room temperature for 1 day. The reaction mixture was cooled to 0 °C, then quenched with 1M HCl (15 mL). The combined organic layer was dried over Na₂SO₄, filtrated, and concentrated under vacuum. The residue was purified by column chromatography on silica gel (*n*-hexane : ethyl

acetate = 4 : 1 as eluent) to afford white powder **4** (1.68 g, 87.2%); ^1H NMR (400 MHz, CDCl_3) δ = 6.84 (dd, 6.6 Hz, 2.2 Hz, 4H), 6.95 (dd, 6.7 Hz, 2 Hz, 4H), 7.50-7.47 (m, 2H+2H), 7.53-7.57 (m, 2H+1H); ^{13}C NMR (100 MHz, CDCl_3) δ = 117.0, 120.2, 120.5, 120.7, 128.4, 130.0, 131.4, 132.9, 137.1, 139.0, 140.1, 141.2, 148.0, 148.2.

Synthesis of 1: A mixture of **4** (750 mg, 1.00 mmol), 4,4'-dimethoxydiphenylamine (1.37 g, 5.98 mmol), $\text{Pd}(\text{dba})_2$ (100 mg, 0.17 mmol), XPhos (100 mg, 0.21 mmol), and CsCO_3 (3.00 g, 9.20 mmol) in toluene (30 mL) was refluxed under argon atmosphere for 1 day with stirring. The reaction mixture was washed with brine and the organic layer was dried over Na_2SO_4 . After evaporation of the solvent, the crude product was chromatographed on silica gel (dichloromethane : *n*-hexane = 1:1 as eluent), then purified by HPLC to afford **1** (688 mg, 69.6%) as a white crystal; ^1H NMR (400 MHz, acetone- d_6) δ = 3.75 (s, 6H), 3.77 (s, 12 H), 6.68 (s, 2H), 6.73 (d, J = 9.0 Hz, 4H), 6.81 (d, J = 9.0 Hz, 4H), 6.85-6.96 (m, 8H+4H+2H), 7.01 (d, J = 9.0 Hz, 8H), 7.35-7.42 (m, 2H+1H); ^{13}C NMR (100 MHz, acetone- d_6) δ = 55.7, 115.5, 115.6, 120.5, 121.9, 126.4, 127.2, 128.0, 129.5, 131.4, 133.3, 134.4, 135.3, 140.0, 141.8, 142.2, 142.7, 147.5, 148.0, 156.6, 157.0; HRMS (ESI): m/z calcd for $\text{C}_{66}\text{H}_{57}\text{N}_3\text{O}_6$ $[\text{M}]^+$: 987.4247; found: 987.4237; Elemental analysis (%) calcd for $\text{C}_{66}\text{H}_{57}\text{N}_3\text{O}_6$: C, 80.22; H, 5.81; N, 4.25. Found: C, 80.23; H, 5.96; N, 4.11.

Density functional theory calculations: Quantum chemical calculations were performed with using a hybrid Hartree–Fock/density functional theory (HF/DFT) method (B3LYP).^[48] Full geometrical optimizations for **1** and **1 $^{++}$** were carried out, and furthermore, their local minimum structures were confirmed by performing subsequent frequency analyses. Excitation energies were examined on the basis of time-dependent density functional theory (TD-DFT)^[49] by using the B3LYP/6-31G* optimized structures. All the computations employed the 6-31G* basis sets.^[50] In addition, the symmetric and asymmetric optimized structures for **1 $^{++}$** were determined by using the BLYP35 functional with the SVP basis sets,^[32,51-53] and their excitation energies were also computed on the basis of TD-DFT at the same level of theory. In addition, the solvent effect has been included by the CPCM version of polarizable continuum solvent model for CH_2Cl_2 (ϵ = 8.93).^[33] All these computational approaches are implemented in Gaussian 16 package of ab initio quantum chemical calculation.^[54]

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Chapter 3

Diaza[1.1](4,4'')*ortho*-terphenylophane: A Doubly-Bridged Organic Mixed-Valence Model System

3-1 Introduction

Electron transfer properties of π -conjugated molecular systems are being continuously investigated in conjunction with growing interest in various research areas such as organic photovoltaics,^[1,2] organic photocatalysts including water splitting,^[3,4] organic-based electrodes for batteries,^[5,6] and so forth. Charge transport through single-molecule junctions has been, in particular, actively examined and discussed for realization of molecular-scale devices.^[7-10] An emerging trend at the forefront is seemingly entering a phase to control the quantum interference (QI) pathways of charges over more complicated molecules with an interplay of molecular orbital interactions and the transient structural deformations.^[11-14] In a tutorial review by Lambert,^[15] the QI effect through multi-branched molecular structure has been introduced as an example of the more complex structure, where it has been demonstrated that the quantum of conductance even in the case of two-branches does not necessarily correspond to the sum of each branch.

In association with the intensive studies on single-molecule electron transport, various insights on intramolecular charge transfer phenomena have also been accumulated by utilizing π -bridged bis(triarylamine) (BTA) radical cations as an ideal purely organic mixed-valence (MV) model system showing intervalence charge-transfer (IVCT).^[16-21] In the MV compounds, the two important parameters: the reorganization energy λ and the electronic coupling V govern a whole picture of IVCT. It has been clarified that those parameters were effectively tuned by various factors such as selections of both bridging unit and redox-active center, bridge length, bridge topology, molecular configuration, in the so-called singly π -bridged 2-site MV system, where the two redox-active centers were linked by a single- π -bridge. In contrast, there has been no reports on multiply π -bridged 2-site organic MV compounds.

Herein, we focused on the doubly π -bridged 2-site MV model compound including triarylamine moieties as redox-active centers. As shown in Figure 1, our previous study on phenylene-bridged BTA radical cations has demonstrated that the electronic coupling of 794 cm^{-1} for *ortho*-phenylene-bridged BTA radical cation (*ortho*-BTA $^{\bullet+}$) was comparable in magnitude to that of 860 cm^{-1} for *para*-phenylene-bridged one (*para*-BTA $^{\bullet+}$).^[22,23] Thus, we anticipated that the selection of *ortho*-terphenylene bridge enabled us to prepare diaza[1.1](4,4'')*ortho*-terphenylophane (**1**) as a doubly π -bridged BTA option with a reasonable electronic coupling between two redox-centers (Figure 1).

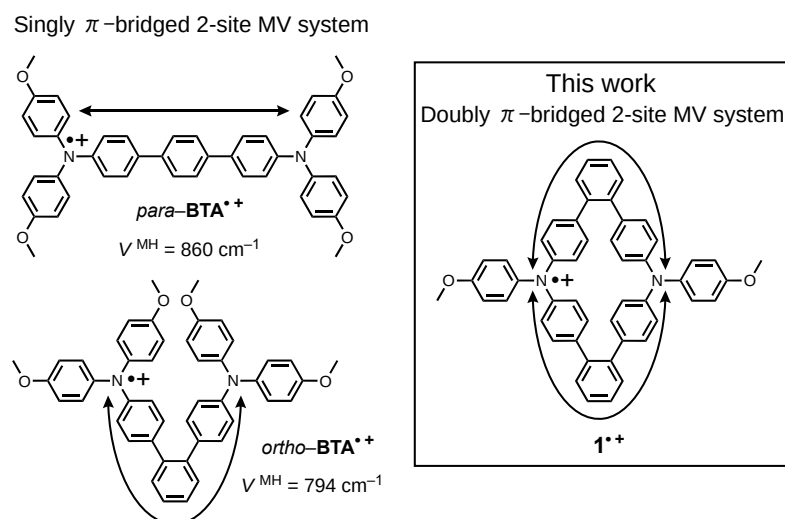


Figure 1. Previously reported BTA MV compounds, *para*-BTA $^{\bullet+}$ and *ortho*-BTA $^{\bullet+}$, as a singly π -bridged 2-site MV system (left) and **1** $^{\bullet+}$ as a doubly π -bridged 2-site MV system (right). The superscript on V designates that the electronic coupling was evaluated on the basis of the Mulliken-Hush theory.

In the present study, we report the first analysis of doubly π -bridged organic MV model system **1** $^{\bullet+}$ in comparison with singly π -bridged *ortho*-BTA $^{\bullet+}$. Prior to the detailed evaluation of **1** $^{\bullet+}$ as a MV compound, the value of $2V$ for *ortho*-BTA $^{\bullet+}$ and **1** $^{\bullet+}$ was roughly estimated by the single-point calculations of a neutral state at radical cation geometries (neutral in cation geometry (NCG) method^[24,25]). As shown in Figure 2, the HOMO and HOMO-1 energy level diagrams for *ortho*-

BTA^{•+} and **1^{•+}** on the basis of NCG method (B3LYP/6-31G*) show the electronic coupling constant of **1^{•+}** was almost double that of *ortho*-**BTA^{•+}**, thus suggesting the strengthening of the electronic coupling V between two redox-centers due to the double- π -bridge. In addition, it should be noted that the orientation of p-orbitals on the two nitrogen-redox-centers to the *ortho*-phenylene plane underwent a considerable change by the double- π -bridging, thus leading to a difference in reorganization energy λ between *ortho*-**BTA^{•+}** and **1^{•+}** (Figure 2).

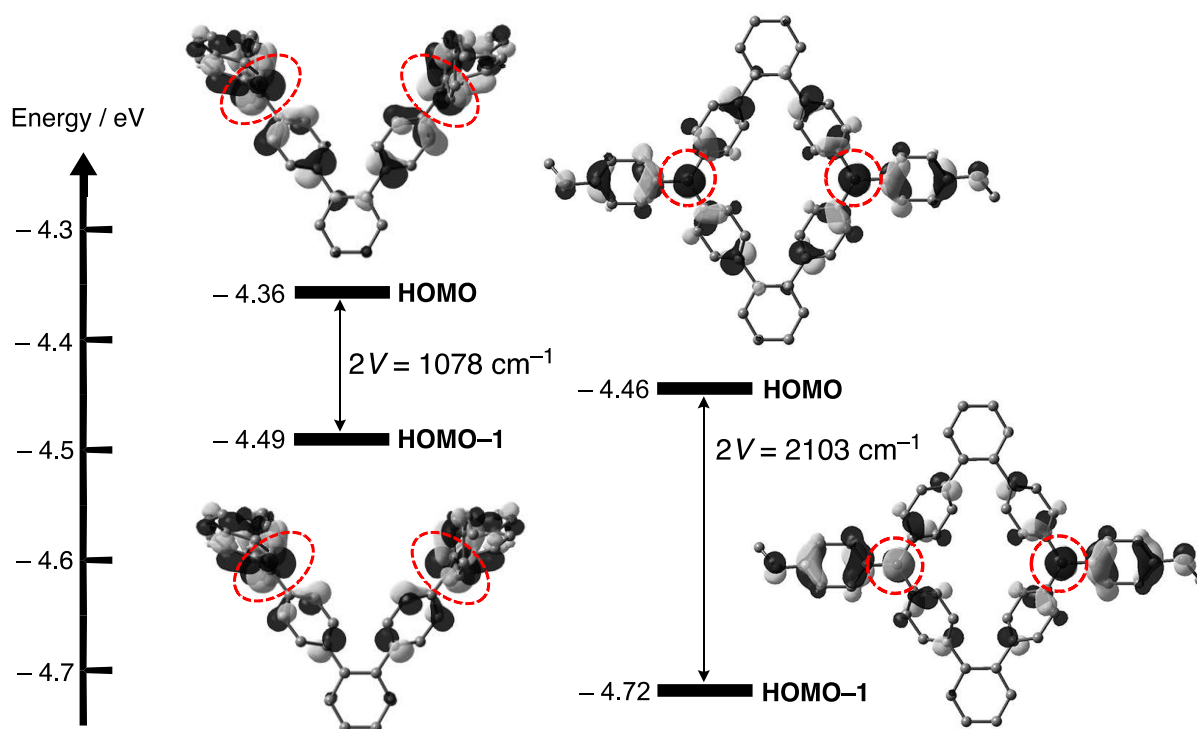
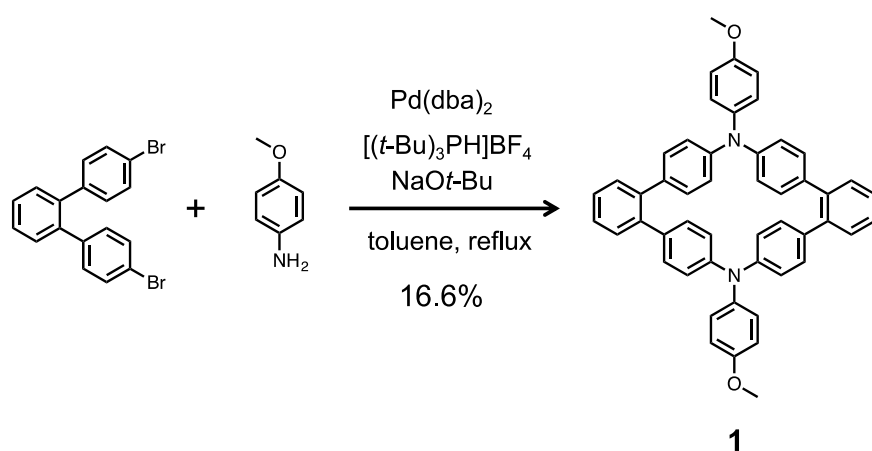


Figure 2. HOMO and HOMO-1 energy diagram for *ortho*-**BTA** and **1** at the optimized geometries for radical cations of *ortho*-**BTA** and **1** on the basis of NCG method (B3LYP/6-31G*). The p-orbitals on the nitrogen redox-centers are encircled by the dashed red line.

3-2 Results and Discussion

The title compound **1** was prepared in 16.6% yield from the Buchwald-Hartwig amination reaction^[26] between 4,4''-dibromo-*o*-terphenyl and *p*-anisidine as shown in Scheme 1. In air-saturated dichloromethane solution, the compound **1** showed an absorption maximum at 330 nm, and

photoexcitation at 320 nm of this solution resulted in a clear emission at 460 nm with fluorescence quantum yield (Φ_F) of 29% (Figure 3). In degassed dichloromethane solution, the quantum yield increased up to 36%. Additionally, the compound **1** was fluorescent even in the solid state ($\Phi_F = 13.5\%$). Upon one-electron chemical oxidation with AgSbF_6 salt in dichloromethane, a continuous decrease in emission intensity at 460 nm was observed, and no additional emission bands appeared for neither $\mathbf{1}^{\bullet+}$ or $\mathbf{1}^{2+}$ (Figure S1).



Scheme 1. Preparation of doubly π -bridged BTA **1**.

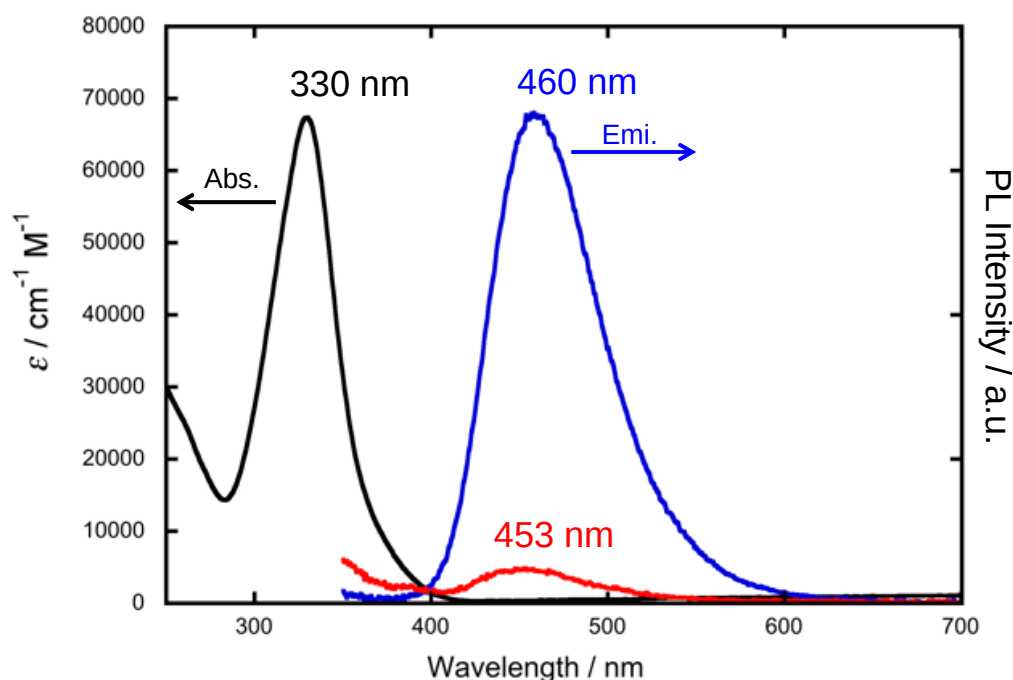


Figure 3. Absorption (black line) and photoluminescence (PL; blue line) spectra of **1** in dichloromethane (10 μ M) and in the solid state (red line) at r.t. The emission spectra were obtained at the excitation wavelength of 320 nm for dichloromethane solution and 300 nm for the solid state. An increase of the PL intensity observed in shorter wavelength region than 400 nm (red line) is a Rayleigh scattering tail of the exciting light at 300 nm.

The electronic transitions to the singlet excited states of **1** were calculated at the B3LYP/6-31G* level of theory using the time-dependent DFT (TD-DFT) approach for the optimized ground-state molecular geometry of **1**. As shown in Figure 4, the unoccupied frontier orbitals were localized on the *o*-terphenylene bridges, while the occupied frontier orbitals were of triarylamine redox-center localized ones, and therefore, the HOMO-LUMO (H – L) transition ($S_1 \leftarrow S_0$) of **1** was virtually forbidden (410 nm, $f=0.0001$) similar to that of triarylamines. The absorption band at 330 nm can be assigned to the $S_2 \leftarrow S_0$ (H-1 $\rightarrow$ L; 365 nm, $f=0.32$), $S_3 \leftarrow S_0$ (H $\rightarrow$ L+1; 353 nm, $f=0.56$), and $S_4 \leftarrow S_0$ (H $\rightarrow$ L+2; 342 nm, $f=0.23$) electronic excitations.

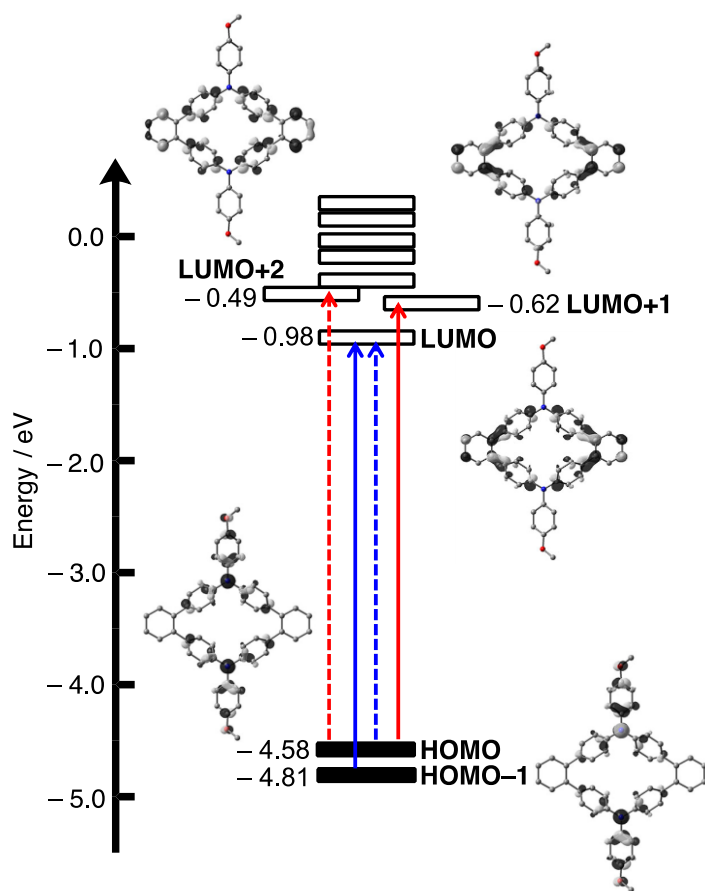


Figure 4. Frontier Kohn-Sham orbitals and their energy levels for **1** at the B3LYP/6-31G* level of theory. The arrows denote the major contributions related to the $S_1 \leftarrow S_0$ (dashed blue), $S_2 \leftarrow S_0$ (solid blue), $S_3 \leftarrow S_0$ (solid red), and $S_4 \leftarrow S_0$ (dashed red) electronic transitions on the basis of single-point TD-DFT calculations (B3LYP/6-31G*).

To check the electron-donating ability of **1** and its oxidative stability, the redox properties of **1** were investigated at room temperature in dichloromethane by means of cyclic voltammetry (CV) and differential pulse voltammetry (DPV) while comparing with the previously reported data^[22] for *ortho*-**BTA** (Figure 5). The two reversible redox waves were detected in the CV and the DPV, respectively, hence indicating stepwise oxidation of **1** through **1^{•+}** to **1²⁺**. The first oxidation potential of **1** ($E_1 = +0.25$ V (1e) vs $\text{Fc}^{0/+}$) exhibited an anodic shift of +0.05 V, as compared with *ortho*-**BTA** ($E_1 = +0.20$ V (1e) vs $\text{Fc}^{0/+}$), reflecting the impact of double- π -bridging in **1**. The second oxidation potential of **1** ($E_2 = +0.38$ V (1e) vs $\text{Fc}^{0/+}$) was found to be more anodically shifted than that of *ortho*-

BTA ($E_2 = +0.29$ V (1e) vs $\text{Fc}^{0/+}$), indicating the larger redox potential splitting $\Delta E \equiv E_2 - E_1 = 130$ mV for **1** than that for *ortho*-**BTA** ($\Delta E = 90$ mV). The strength of ΔE can be frequently utilized as a qualitative indicator for electronic communication between two redox-centers in 2-site MV systems,^[27] thus promising a large electronic coupling in **1**^{•+}.

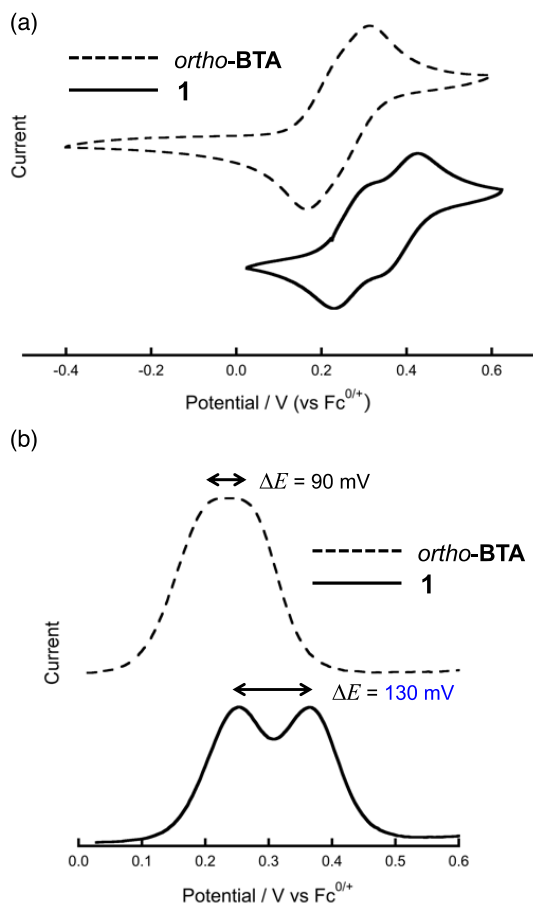


Figure 5. (a) Cyclic voltammograms and (b) differential pulse voltammograms of **1** (solid curve) and *ortho*-**BTA** (dashed curve) measured in 0.1 M $[n\text{Bu}_4\text{N}]^+[\text{BF}_4]^-$ /dichloromethane (ca. 1 mM) at a scan rate of 0.1 V s^{-1} . The potential values were corrected for ferrocene/ferrocenium redox couple ($\text{Fc}^{0/+}$) as an internal standard.

Herein, prior to the detailed analysis and discussion on the MV state of **1**^{•+}, we briefly overview the experimental procedures and the analyses to extract the two kinds of key parameters, the reorganization energy λ and the electronic coupling V , while referring to the schematic representation

of adiabatic free energy surfaces (FESs) for degenerate MV states (Figure 6).^[16,17,20] The separated diabatic FESs corresponding to those of two identical redox-active centers are mixed to result in two adiabatic FESs shown in Figure 6, as a result of electronic coupling V between the redox-active centers through interaction with the π -bridge orbitals. The abscissa axis designates the charge transfer coordinate X indicating two minima of the lower adiabatic FESs at $X = 0$ and 1. The lower energy double-well FES means the existence of charge/spin localized ground state for one-electron oxidized MV state, which is referred to as charge-localized class II MV state in the Robin-Day classification.^[28] At $X = 0$ and 1 (and at this point, the MV molecule adopts the asymmetric geometrical structure), the energy gap between upper and lower FESs equals with λ , and hence, the quantum chemical single-point transition energy calculation at this point gives the theoretical estimation of λ . Moreover, at $X = 0.5$ (and at this point, the MV molecule adopts the symmetric geometrical structure), the energy gap between upper and lower FESs equals with $2V$, and hence, the same single-point transition energy calculation at this point provides the theoretical estimation of $2V$. Experimentally, the value of λ is directly obtained from the optical absorption band maximum (the so-called IVCT band maximum) corresponding to the electron transition at $X = 0$ and 1, and the optical transition causes the optically assisted IVCT. Additionally, the integration of the observed IVCT band is proportional to the transition dipole moment μ_{ab} , and the value of V can be finally evaluated from the energy of the IVCT band maximum and the change of static dipole moment before and after the charge transfer event, in addition to the transition dipole moment. To determine the change of static dipole moment, the charge transfer distance is needed for the studied MV system. However, in the organic MV systems such as BTA radical cations, the exact charge transfer distance is difficult to define, simply because the generated charge/spin on one redox-active center is partially delocalized on the periphery. Therefore, the change of static dipole moment is usually estimated from the quantum chemical calculations of adiabatic dipole moment difference.

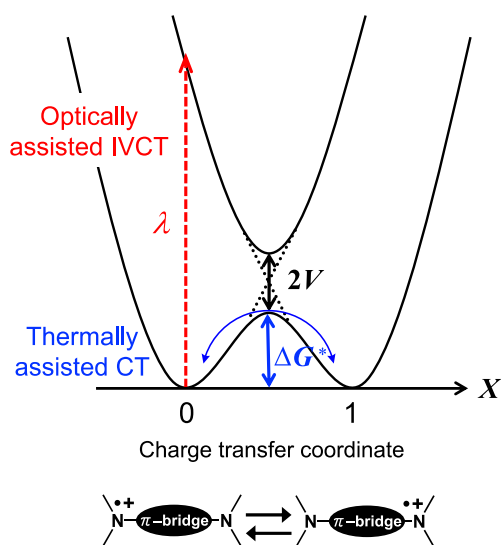


Figure 6. Schematic representation of adiabatic free energy surfaces (FES) for a 2-site MV compound (such as BTA radical cations) with degenerate MV states classified into a charge-localized class II MV system ($0 < 2V < \lambda$). The values of $2V$ and ΔG^* are determined at the crossing point of the diabatic FESs ($X = 0.5$), where the MV compound adopts a symmetrical structure.

From the viewpoint of thermally assisted IVCT for 2-site MV systems, the activation barrier ΔG^* at $X=0.5$ along the lower FES in Figure 6 determines the ease of charge delocalization between two redox-active centers: the lower the activation barrier becomes, the more delocalized the charge/spin is. Theoretically, the value of ΔG^* can be obtained by the energy difference between the charge-localized asymmetric structure (at $X = 0$ and 1) and the charge-delocalized symmetric structure (at $X = 0.5$), when both structures are optimized quantum-chemically as well. Experimentally, the value of ΔG^* can be evaluated by the ESR spectroscopy. As is often the case with the BTA radical cations,^[29–31] if the solution ESR line-shape exhibits a temperature dependency in measurable temperature range, the rate constant k_{th} of the IVCT at each temperature can be derived from the spectral simulations, and hence the Arrhenius plot gives the activation barrier ΔG^* . However, we cannot discern whether the

charge/spin is delocalized statically or dynamically, in case of the value of k_{th} exceeding the ESR time-scale in the measured temperature range. Obviously, the MV system with $\Delta G^* = 0$, that is $\lambda \leq 2V$, is of charge-delocalized class III MV system in the Robin-Day classification.^[28]

Above-mentioned analytical procedures are also applicable to the present doubly π -bridged BTA radical cation **1**^{•+}. The key parameters, the reorganization energy λ and the electronic coupling V , obtained in this way affect a whole picture of the IVCT process. The larger the reorganization energy λ is, the more the double-well of the lower-energy FES in Figure 6 deepens, leading to the charge localization. The larger the electronic coupling V is, the shallower the double-well becomes, leading to the dynamic charge delocalization. As an extreme case such as $\lambda \leq 2V$, the double-well FES degenerates into a single well FES, where the charge is statically delocalized over the MV system, resulting in the charge-delocalized class III MV state. It should be noted that the observed IVCT absorption band shape also tells us the degree of charge delocalization in the MV system:^[32] the small electronic coupling of $0 < 2V < \lambda$ gives a symmetric Gaussian-shaped IVCT band, while the large electronic coupling of $2V > \lambda$ an asymmetric IVCT band with cut-off in the lower-energy side. Hence, we can safely judge the charge-localized class II or charge-delocalized class III MV systems whether the observed IVCT band shape is symmetric or asymmetric.

To confirm the electronic states of the oxidized species of **1**, the changes in the optical absorption spectra during the electrochemical oxidation in dichloromethane were recorded by using an optically transparent thin-layer electrochemical cell^[33] (Figure S2); firstly, a weak band due to the formation of **1**^{•+} grew at 0.59 eV (2097 nm) in the near IR (NIR) region, accompanied by an intense absorption band due to the triarylaminium-localized π - π^* transition^[18,20,34] at 1.61 eV (769 nm), and secondly, the weak band gradually disappeared, whereas the intense π - π^* band continued to increase until further oxidation to **1**²⁺. This indicates that the observed lowest-energy weak band can be characterized as the IVCT band for **1**^{•+}. The optical absorption spectrum of **1**^{•+}, which was generated with 1 equiv. AgSbF₆

as an oxidizing agent in dichloromethane, is shown in Figure 7, together with the IVCT band for *ortho*-**BTA**^{•+}. The DFT geometrical optimizations by using the BLYP-based hybrid functional^[35,36] with 35% exact exchange term and the SVP basis set^[37] (BLYP35/SVP)^[38] obviate the overestimation of charge-delocalized geometries originating from the self-interaction error,^[39] and in particular, the selection of exchange-correlation functionals is of great importance for the organic MV systems.^[40,41] Additionally, the solvation effect was included by the conductor-like polarizable continuum (CPCM) model (dichloromethane ($\epsilon = 8.93$) in the present case).^[42] The BLYP35-optimization for **1**^{•+} provided the charge-localized asymmetric structure as energetically most stable structure, as shown in Figure 9b. The single-point TD-DFT calculation (BLYP35/SVP) at the asymmetrical geometry of **1**^{•+} indicated that the lowest-energy electronic transition corresponds to the IVCT transition from HOMO(β) to LUMO(β) [$D_1 \leftarrow D_0$], and the transition energy was computed to be 0.69 eV (1792 nm; $f = 0.11$), in reasonable agreement with the observed IVCT band maximum of 2097 nm (Figure S3 and Figure 7). Moreover, the intense absorption band at 1.61 eV (769 nm) is assignable to the $D_2 \leftarrow D_0$ (H-1 and H-2 $\rightarrow$ L; 707 nm, $f = 0.18$) and $S_3 \leftarrow S_0$ (H-3 $\rightarrow$ L; 702 nm, $f = 0.30$) electronic excitations (Figure S4). Hence, judging from the computational result as well as the observed symmetric IVCT band shape, it can be safely said that **1**^{•+} was classified into the charge-localized class II MV system similar to *ortho*-**BTA**^{•+}. Additionally, the observed optical excitation energy of the IVCT band ($\tilde{\nu}_{\max}$) corresponds to the reorganization energy (λ) for the charge-localized Robin-Day class II MV systems,^[28] The doubly π -bridged **1**^{•+} had the reorganization energy of 4769 cm⁻¹ (= 2097 nm in wavelength), which was in contrast to the value of 6135 cm⁻¹ (= 1630 nm in wavelength) in the singly-bridged analog of *ortho*-**BTA**^{•+} (Figure 7).

On the basis of Mulliken-Hush theory, the electronic coupling (V) was evaluated by Eq. (1):^[43–45]

$$V = \frac{\mu_{ab}}{\Delta\mu_{12}} \tilde{\nu}_{\max} = \frac{\mu_{ab}}{\sqrt{(\Delta\mu_{ab})^2 + 4(\mu_{ab})^2}} \tilde{\nu}_{\max} \quad (1),$$

where μ_{ab} is the transition dipole moment between the adiabatic states, which can be determined from the integration of the IVCT band, $\tilde{\nu}_{\max}$ the energy of the IVCT band maximum, $\Delta\mu_{12}$ the difference in the diabatic dipole moments between the ground and excited states, which is calculated by using both of μ_{ab} and the DFT-computed adiabatic dipole moment difference ($\Delta\mu_{ab}$) of 36.4 Debye [BLYP35/SVP+CPCM(CH₂Cl₂)]. From the lowest-energy band fitting to several Gaussian functions, the observed IVCT band fit well with a single Gaussian function, indicating the charge localized class II MV system of **1**^{•+}. Based on the IVCT band analysis, the electronic coupling V for **1**^{•+} in dichloromethane was evaluated to be 656 cm⁻¹. It should be noted that the experimentally determined value for **1**^{•+} was quite small as compared with the rough estimation by the NCG method (1052 cm⁻¹; Figure 1), and furthermore it was a smaller value than that for *ortho*-**BTA**^{•+} (794 cm⁻¹; Figure 7).

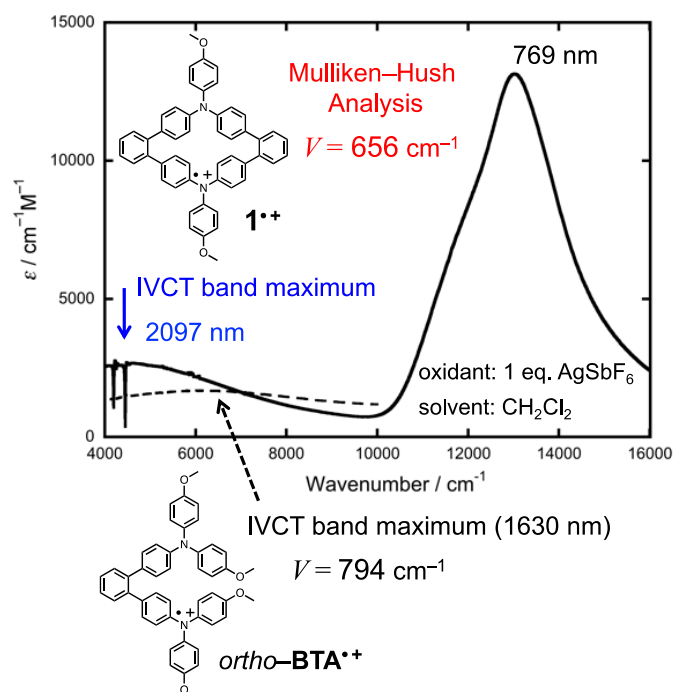


Figure 7. UV/Vis/NIR optical absorption spectrum of **1**^{•+} generated with 1 equiv. AgSbF₆ as an oxidizing agent in dichloromethane (at 0.1 mM) at r.t. The IVCT band of *ortho*-**BTA**^{•+} generated

under the same conditions was also shown in dashed line.

Alternatively, the thermally assisted IVCT picture of $\mathbf{1}^{\bullet\bullet}$ is provided by the variable-temperature ESR (VT-ESR) spectroscopy. As shown in Figure 8, a five-line spectrum was observed at 293 K, thereby indicating the dynamic delocalization of spin/charge between two triarylamine redox-active centers at room temperature. However, the ESR spectral shape of $\mathbf{1}^{\bullet\bullet}$ in dichloromethane remained unchanged in the measured temperature range (193 – 293 K). The observed spectrum of $\mathbf{1}^{\bullet\bullet}$ at 293 K was well characterized by the splitting of the main five-line by the two equivalent nitrogen nuclei from the two redox-active centers [$|a_N| = 0.45$ mT (2N)] and relatively smaller splitting by the two sets of hydrogen nuclei surrounding the two nitrogen redox-active centers [$|a_{H1}| = 0.08$ mT (8H); $|a_{H2}| = 0.06$ mT (4H)]. The observed temperature-independent spectral behavior strongly suggested that the rate of the thermally assisted IVCT in $\mathbf{1}^{\bullet\bullet}$ (k_{th}) was rapid enough compared to the ESR time-scale ($> 10^9$ s $^{-1}$), indicating a shallow activation barrier (ΔG^*) in the adiabatic double-well FES for the thermally assisted IVCT of doubly π -bridged $\mathbf{1}^{\bullet\bullet}$ (Figure 6). In contrast, the VT-ESR measurements for singly π -bridged *ortho*-**BTA** $^{\bullet\bullet}$ exhibited a clear temperature-dependent spectral change with the ΔG^* value of 3.09 kcal mol $^{-1}$.^[22] Hence, it was demonstrated that the double- π -bridging in a 2-site MV system effectively enabled the dynamic charge-delocalization in comparison with the usual singly π -bridged one. The activation barrier (ΔG^*) can be represented by the electronic coupling V and the reorganization energy λ by Eq. (2):^[43]

$$\Delta G^* = \frac{(I - 2V)^2}{4\lambda} \quad (2)$$

From the experimentally determined values for both V (656 cm $^{-1}$) and λ (4769 cm $^{-1}$; Figure 7), the ΔG^* value was calculated to be 1.79 kcal mol $^{-1}$, thus certainly providing a small value for the observation of dynamic charge-delocalization in $\mathbf{1}^{\bullet\bullet}$ within the ESR time-scale.

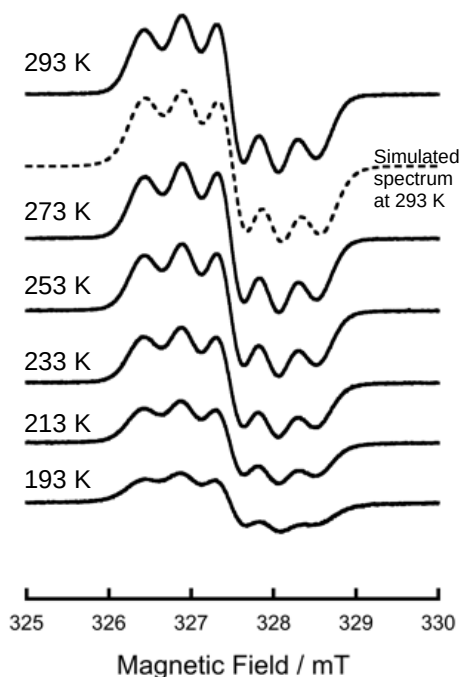


Figure 8. Observed X-band variable-temperature ESR spectra of $\mathbf{1}^{\bullet+}$ generated with 1 equiv. AgSbF_6 as an oxidizing agent in dichloromethane (at 0.1 mM). The simulated spectrum for the observed one at 293 K was depicted in dashed line.

The DFT- and TD-DFT-computed energy profiles are summarized in Figure 9 for the singly π -bridged *ortho*- $\text{BTA}^{\bullet+}$ and the doubly π -bridged $\mathbf{1}^{\bullet+}$ at the BLYP35/SVP level of theory. For both compounds, the charge-localized asymmetric structures were optimized as the energetically most stable structures. Note that no other asymmetric structures were found for $\mathbf{1}^{\bullet+}$ in which the charge was mainly localized on one *o*-terphenylene-bridge. The DFT-computed V for *ortho*- $\text{BTA}^{\bullet+}$ and $\mathbf{1}^{\bullet+}$ was estimated to be 651 and 959 cm^{-1} , respectively, as the lowest excitation energies computed at the optimized symmetric structures ($2V$ in Figure 9). In contrast to the values obtained by the simplistic NCG method, it was found that the value of V for $\mathbf{1}^{\bullet+}$ was reduced to approximately 1.5 times that for *ortho*- $\text{BTA}^{\bullet+}$ on the basis of the BLYP35/SVP level of theory. However, the experimentally determined value of V (656 cm^{-1}) for $\mathbf{1}^{\bullet+}$ is still low as compared with the theoretical prediction (959

cm⁻¹), and the origin is currently unclear. For the experimental determination of V according to Eq. (1), the adiabatic dipole moment difference ($\Delta\mu_{ab}$) is solely dependent on the DFT calculations. Hence, there may be room for improvement of the value of V by considering further on the validity of computational values of $\Delta\mu_{ab}$.

The DFT-computed activation barriers (ΔG^*) for *ortho*-BTA^{••} and **1**^{••} were determined to be 2.66 and 1.40 kcal mol⁻¹, respectively, by the energy difference between the symmetric and asymmetric structures, thereby indicating that the thermally assisted IVCT rate could be accelerated by double- π -bridge between two redox-active centers in accordance with the VT-ESR results. Note that the DFT-computed ΔG^* value of 1.40 kcal mol⁻¹ showed good consistency with the ΔG^* value obtained from Eq. (2) (1.79 kcal mol⁻¹). Such a low activation barrier for **1**^{••} was considered to be derived from the small reorganization energy: both *ortho*-BTA^{••} and **1**^{••} showed a similar trend of experimental and theoretical λ with significant reduction by the double- π -bridge. Indeed, the slight geometrical change was seen in the symmetric and asymmetric structures of **1**^{••} optimized at BLYP35/SVP level of theory, as show in Figure 10. Only the peripheral anisyl group underwent a quinoidal distortion as well as a decrease in the dihedral angle against the sp² plane of the nitrogen redox-active center (Figure 10b).

Herein, the spin state of the dication of **1** is worth a mention in passing. On the basis of UB3LYP/6-31G* level of theory, it was predicted that the closed-shell singlet state lay 6.2 kcal mol⁻¹ above the triplet state, and furthermore, the singlet–triplet energy difference ΔE_{S-T} was estimated to be -1.0 kcal mol⁻¹ according to the DFT-based broken symmetry approach,^[46–48] indicating the open-shell singlet ground state of **1**^{2•}. As a result, the small ΔE_{S-T} value means very weak spin-spin interaction. As shown in Figure S5, the observed ESR spectrum in a frozen dichloromethane matrix exhibited a single resonance with no definite fine structure at 123 K. Moreover, the forbidden resonance was not observed in the half-field region (the inset in Figure S5), strongly suggesting virtually no intramolecular magnetic interaction between two spins-1/2 in **1**^{2•}.

In the present study, unexpectedly, the electronic coupling for doubly π -bridged **1**^{•+} (656 cm⁻¹) has become smaller than that for singly π -bridged *ortho*-**BTA**^{•+} (794 cm⁻¹). However, as is apparent from the ESR study, the activation barrier ΔG^* of **1**^{•+} has been lowered enough to realize the dynamic charge/spin delocalization, in comparison with *ortho*-**BTA**^{•+}. In the recent studies,^[49,50] it has been clarified that the charge delocalization in a MV system is governed by an exquisite balance of two key parameters, the reorganization energy λ and the electronic coupling V . Although the activation barrier ΔG^* increases with decreasing electronic coupling V , a whole picture of the IVCT process possibly leads to a dynamic or static charge delocalization by a greater decrease of reorganization energy λ , as compared to the small electronic coupling. For the present doubly π -bridged **1**^{•+}, it is inferred that the rigidity of triarylamine redox-active units due to the macrocyclization by two *o*-terphenylene bridges brought about a small reorganization energy.

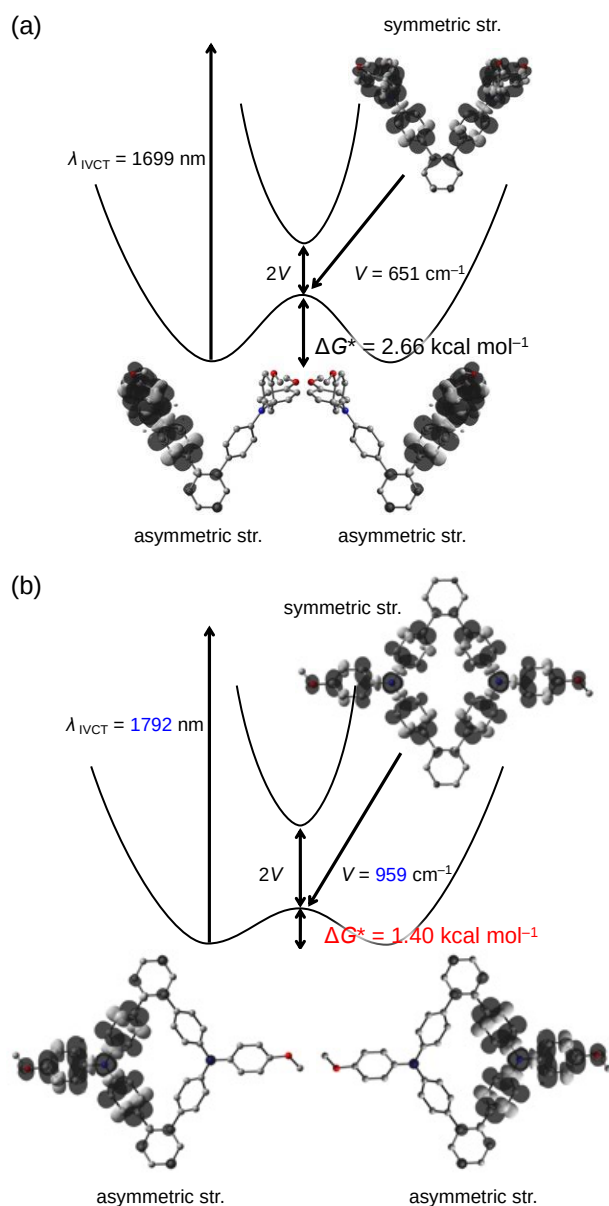
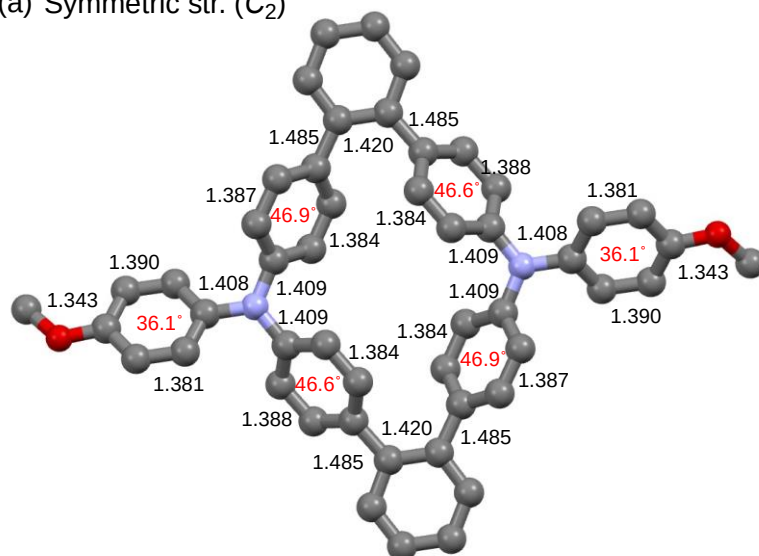


Figure 9. DFT-predicted energy diagrams for the optically and thermally assisted IVCT of (a) *ortho*-BTA^{•+} and (b) **1**^{•+} [BLYP35/SVP+CPCM(CH₂Cl₂)]. The depicted symmetrical and asymmetrical molecular structures with spin density distribution were determined by the geometrical optimization at BLYP35/SVP+CPCM(CH₂Cl₂) level of theory.

(a) Symmetric str. (C_2)



(b) Asymmetric str. (C_1)

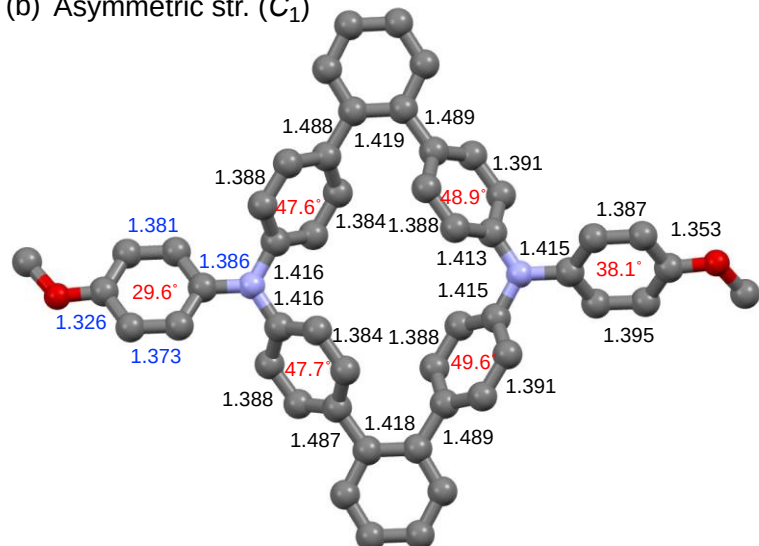


Figure 10. DFT-optimized geometrical parameters for (a) symmetric structure (C_2 -symmetry) and (b) asymmetric structure (C_1 -symmetry) of **1^{••}** at the BLYP35/SVP+CPCM(CH_2Cl_2) level of theory; the bond length (in Å) is written in black, the dihedral angle of peripheral phenyl groups to the sp^2 plane of the nitrogen redox-center (shown in yellow triangles) in red. The left-side triarylamine moiety in the asymmetric structure is the spin/charge-localized center, and the relatively short bond lengths are written in blue.

3-3 Conclusions

In conclusion, this work explored the intramolecular charge/spin transfer in a newly designed 2-site organic MV compound where two redox-active centers were connected by double- π -bridge. Contrary to the simplistic theoretical prediction that the electronic coupling of doubly π -bridged MV system

becomes larger than that of singly π -bridged one, it has been found that the doubly π -bridged MV compound possessed a smaller electronic coupling than the singly π -bridged one as a reference compound, on the basis of the optically assisted IVCT band analysis. However, in the thermally assisted IVCT process, the doubly π -bridged MV compound exhibited virtually dynamic charge-delocalization, whereas the singly π -bridged MV gave temperature-dependent ESR spectral change originating from the significant activation barrier. This work exemplifies the possibility that multi-branched organic MV systems give rise to unexpected charge delocalization among the redox-active centers. Such compounds also expand the molecular design possibilities toward the realization of molecular-scale devices. Further studies on this line are in progress.

3-4 Experimental Section

General: 4,4''-dibromo-*o*-terphenyl and *p*-anisidine were purchased from TCI chemicals and used without further purification. All the other purchased reagents were of standard quality, and used without further purification. All the purchased solvents were purified, dried, and degassed by standard procedures. Column chromatography was performed with silica gel (Kanto Chemical Co., Inc., silica gel 60N, spherical neutral). ^1H and ^{13}C NMR spectra were measured by a JEOL JNM-AL300 and JNM-AL400 FT-NMR spectrometers. Chemical shifts of NMR spectra were determined relative to internal tetramethylsilane (TMS) standard (δ), and are given in parts per million (ppm). UV/Vis-NIR absorption spectra were obtained with a Perkin-Elmer Lambda 950 spectrometer. High resolution (HR) electrospray ionization (ESI) mass spectra were acquired using a Thermo Fischer EXACTIVE mass spectrometer. Fluorescence spectra were recorded on an absolute PL quantum yield measurements system (HAMAMATSU Quantaurus-QY). The redox properties were evaluated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in CH_2Cl_2 solution at 298 K with 0.1 M tetra-*n*-butylammonium tetrafluoroborate (TBABF₄) as supporting electrolyte (scan rate 100 mV s⁻¹) using an ALS/chi Electrochemical Analyzer model 612A. A three-electrode assembly was used, which was equipped with a platinum disk (2 mm²) and a platinum wire as the working

and counter electrodes, respectively, and Ag/0.01 M AgNO₃ (acetonitrile) was used as the reference electrode. The redox potentials were referenced against a ferrocene/ferrocenium (Fc^{0/+}) redox potential measured in the same electrolytic solution. Spectroelectrochemical measurements were carried out with a custom-made optically transparent thin-layer electrochemical (OTTLE) cell (light pass length = 1 mm) equipped with a platinum mesh and a platinum coil as the working and counter electrodes, respectively, and Ag/0.01 M AgNO₃ (acetonitrile) was used as the reference electrode. The potential was applied with an ALS/chi Electrochemical Analyzer model 612A. ESR spectra were recorded on a JEOL JES-X310 X-band ESR spectrometer, in which temperature was controlled by a JEOL ES-13060DVT5 variable temperature unit.

Synthesis of 1: A mixture of 4,4''-dibromo-*o*-terphenyl (2.00 mmol, 776 mg), *p*-anisidine (2.00 mmol, 246 mg), Pd(dba)₂ (0.17 mmol, 100 mg), [(*t*-Bu)₃PH]BF₄ (0.34 mmol, 100 mg), sodium *tert*-butoxide (6.00 mmol, 576 mg) in anhydrous toluene (200 mL) was refluxed with stirring under argon atmosphere for 48 h. The reaction mixture was cooled down to room temperature and washed with brine. The organic layer was dried over Na₂SO₄, and the solvent was evaporated *in vacuo*. The crude product was purified by column chromatography on silica gel (dichloromethane : toluene = 1:1), and recrystallized from methanol to afford **1** as a white powder (116 mg (0.166 mmol), 16.6%). ¹H NMR (400 MHz, CD₂Cl₂): δ = 7.48 (m, 4H), 7.39 (m, 4H), 7.04 (d, *J* = 8.0 Hz, 8H), 6.97 (d, *J* = 8.4 Hz, 4H), 6.92 (d, *J* = 8.0 Hz, 8H), 6.80 (d, *J* = 8.4 Hz, 4H), 3.72 ppm (s, 6H); ¹³C NMR (75 MHz, CDCl₃): δ = 154.7, 147.8, 141.2, 139.6, 135.3, 131.2, 130.0, 127.5, 124.9, 123.5, 114.4, 55.5 ppm; HRMS (ESI): *m/z* calcd for C₅₀H₃₈N₂O₂: 698.2933 [M]⁺; found: 698.2928.

Density functional theory calculations: Quantum chemical calculations were performed with using a hybrid Hartree–Fock/density functional theory (HF/DFT) method (B3LYP).^[51] Full geometrical optimizations for *ortho*-TBA^{•+}, **1**, **1**^{•+}, and **12**^{•+} were carried out, and furthermore, their local minimum structures were confirmed by performing subsequent frequency analyses. Excitation energies were examined on the basis of time-dependent density functional theory (TD-DFT)^[52] by using the B3LYP/6-31G* optimized structures. All the computations employed the 6-31G* basis sets.^[53] In addition, the symmetric and asymmetric optimized structures for *ortho*-TBA^{•+} and **1**^{•+} were determined by using the BLYP35 functional with the SVP basis sets,^[37,40,41] and their excitation energies were also computed on the basis of TD-DFT at the same level of theory. In addition, the solvent effect has been included by the CPCM version of polarizable continuum solvent model for CH₂Cl₂ ($\epsilon = 8.93$).^[37] All these computational approaches are implemented in Gaussian 16 package of ab initio quantum chemical calculation.^[54]

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General Conclusion

Understanding and controlling the electronic properties of molecules is important for realizing the concept of "molecular electronics" applied to electronic devices such as single-molecule systems or assemblies of multiple molecules. From this point of view, study on the intramolecular charge transfer (CT) phenomenon in mixed valence (MV) compounds leads to understand the CT phenomenon in single molecules and contributes to the development of electronic devices such as hole transport materials. The main objective of organic MV chemistry is to establish a methodology for controlling two parameters the electronic coupling (H_{AB}) and reorganization energy (λ). There are many studies to control the electronic coupling by changing the distance, the topology and planarity of the bridging site as well as the energy of the bridging site by chemical modification. However, these studies are limited to one-dimensional intramolecular CT between two acid reduction sites. In multidimensional MV compounds with three or more redox sites, multiple IVCT bands appear at the same positions, making it difficult to identify the intramolecular CT pathway. There are not many studies on CT of multidimensional MV compounds despite their use as charge transport materials. In addition, there are few studies controlling the reorganization energy rather than electronic coupling. This is because the theories and calculation models for λ considering both λ_{in} due to structural changes during molecular oxidation and λ_{out} due to ion-pairing, solvation and the temperature of the medium has not been established compared with those for H_{AB} .

In this research background, the author focused on molecules with multiple triarylamine (TAA) at the redox sites and bridged by π -conjugated molecules, and analyzed the charge transfer processes mainly appearing during oxidation in the molecules by spectroscopic and theoretical methods. This thesis consists of three chapters and the following is the outline of each chapter.

In Chapter 1, the author synthesized tetraphenyl-p-phenylenediamine **1** (TPPD) with high structural rigidity, in which the ortho positions of the phenyl rings are partially tethered by four oxygen atoms. The author investigated the effect of oxygen bridges on the mixed-valence (MV) state of monoradical cation species by comparing it with non-tethered TPPD **2**. UV-vis-NIR absorption measurements of the tethered molecule **1**⁺ showed an IVCT band with a vibrational structure, indicating that it is in a charge delocalized state (Class III), and this result was supported by time-dependent density functional theory (TD-DFT) calculations. Variable-temperature EPR measurements also showed no change in the shape of the spectrum during temperature-variable measurements at 193–303 K, determining that **1**⁺ is in a charge delocalized state (Class III state). Although it was expected that the planarity of this compound would increase due to the increase in structural rigidity by tethering, X-ray crystal structure analysis showed that the peripheral phenyl rings in **1**⁺ were distorted in the opposite direction so as to

have a pseudo- C_{2h} symmetrical structure. No significant difference in planarity between 1^+ and 2^+ was observed since no significant change in the dihedral angles of the central and peripheral phenyl rings occurred before and after the tethering. Although the structural effect of the tethering on electronic communication was not considered, the electronic coupling of molecule 1^+ calculated from the IVCT band was reduced to about half that of molecule 2^+ . The quantum chemical calculation suggested that the HOMO (β) of 1^+ is destabilized by the oxygen-bridges, while the LUMO (β) of 1^+ , to some extent, stabilizes, in comparison with those of 2^+ . That is, the HOMO-LUMO gap energy of the radical cation species, corresponding to the electronic coupling, was reduced by the electronic effect of the oxygen-bridges. Quantum chemical calculations also revealed that the partial tethering expected to be effective in suppressing the reorganization energy, actually increases the reorganization energy.

In Chapter 2, the author synthesized a triad molecule **3** in which the 1, 2, and 3 positions of benzene were replaced with TAA, and analyzed the multidimensional MV state. CV and DPV measurements for three oxidation potentials of this molecule confirmed the stability of the monoradical cation species 3^+ by the relatively large potential difference between the first and second oxidation potentials. Based on this result, the author prepared molecule 3^+ by chemical oxidation and performed variable-temperature EPR measurements. The EPR spectrum showed temperature dependence, determining it to be in class II MV state. The result of quantum chemical calculations using BLYP35/SVP was in good agreement with that of the spectroscopic measurements. The calculation also showed a minimum structure and a saddle point structure in addition to the most stable structure of 3^+ , indicating that 3^+ is in a non-degenerate MV state. Dynamic EPR simulations based on DFT calculations agreed with the experimental values when 25% of the spins were placed in the TAA at both ends and 50% in the central TAA, which also supported the non-degenerate MV state. As for CT pathways of molecule 3^+ , CT from the central TAA site to the TAA sites at both ends as well as that between the TAA sites at both ends were expected, however only one type of IVCT band was observed in the UV-vis-NIR absorption measurements. In addition, quantum chemical calculations showed that the direction of the change in adiabatic dipole moment due to optically induced IVCT was parallel to the direction of the line connecting the central TAA and the bridge unit. These results, including that from dynamic EPR simulation, indicated that only the former CT (CT from the central TAA site to the TAA sites) occurs. From these results, the author concluded that charge transfer through the *m*-phenylene bridge is prohibited due to weaker electronic coupling and higher activation barrier than that through the *o*-phenylene bridge. In this chapter, the author pointed out that topology control is an important factor in multidimensional MV systems with multiple electron transfer pathways.

In Chapter 3, the author synthesized bis(triarylamine) (BTA) **4** doubly bridged by orthophenylene, and compared the electronic state of the monoradical cation species with that of the single-bridged BTA **5** to investigate the doubly bridged effect on the intramolecular charge/spin transfer process. Both molecules were determined to be Class II based on the shape of the IVCT bands and the results of

quantum chemical calculations. Contrary to the simple theoretical prediction that the electronic coupling of the double-bridged MV system would be larger than that of the single-bridged MV system, the electronic coupling calculated by the IVCT band analysis was smaller for molecule **4**⁺. In addition, the reorganization energy calculated from the IVCT bands was found to be lower for molecule **4**⁺. This tendency was observed in variable-temperature EPR measurements i.e. only single-bridged molecule **5**⁺ showed temperature-dependent spectral changes while molecule **4**⁺ showed thermally induced CT over the measurement time scale, suggesting that the activation barrier of molecule **4**⁺ was lowered due to the decrease in reorganization energy, leading to more dynamic charge delocalization. This study points out that dynamic charge delocalization proceeds when the reduction in electronic coupling is exceeded by the large reduction in reorganization energy, and suggests that multi-branched organic MV systems may lead to unexpected charge delocalization. This is the first study in the organic MV field to attempt to control the electronic coupling by increasing the number of electron transfer paths by bridging.

As described above, in this thesis, in order to clarify an important research topic in organic mixed-valence chemistry "How and which site does charge/spin behave in molecules having an oxidation number gap among multiple redox active sites?", the author investigated the localized/delocalized state of electrons in MV compounds with TAA at the redox site by various spectroscopic analyses and quantum chemical calculations. In particular, in Chapter 2, the author analyzed the complex electronic state of the multidimensional MV compound and succeeded in identifying the CT pathway. Furthermore, in Chapters 1 and 3, the author synthesized and compared molecules with different redox sites and bridging sites to evaluate their effect on charge/spin transfer using electronic bonds and activation barriers as indicators. Through all these studies, the author found that the structural rigidity of the entire molecule by bridging and the expansion of the electron transfer pathway by double bridging could provide new methods of CT control and proposed one of the methodologies for controlling and adjusting photo- and thermally induced CT. Thus, this thesis provided a useful guide for a broader and deeper understanding of the fundamental electronic properties of organic mixed-valence compounds and controlling them.

List of Publications

- (1) Oxygen-Bridged Quasi-Planar para-Phenylenediamine and Its Oxidized States
Koshi Yoshida, Kai Hikida, Takayuki Tanaka, Shu Seki, and Akihiro Ito, *Eur. J. Org. Chem.* **2024**, 27, e202400030.
- (2) A Three-Redox-Center Organic Mixed-Valence System: Optically and Thermally Assisted Charge Transfer in Radical Cation of Tris(triarylamine) Connected through 1,2,3-Benzenetriyl Bridge
Masashi Uebe, Koshi Yoshida, Shu Seki, Akihiro Ito, submitted for publication
- (3) Diaza[1.1](4,4'')ortho-terphenylophane: A Doubly-Bridged Organic Mixed-Valence Model System
Koshi Yoshida, Fumiya Takasaki, Masashi Uebe, Shu Seki, Akihiro Ito, in revision

The following paper is not included in this thesis:

Facile synthesis of an ambient stable pyreno[4,5-*b*]pyrrole monoanion and pyreno[4,5-*b*:9,10-*b'*]dipyrrole dianion: from serendipity to design
Sharvan Kumar, Koshi Yoshida, Yusuke Hattori, Tomohiro Higashino, Hiroshi Imahori, Shu Seki, *Chem. Sci.* **2022**, 13, 1594.