

Dominant Parameters Affecting Device Durability for Blue TADF Molecules

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Abstract

Organic light-emitting diodes (OLEDs) have achieved remarkable commercial success in displays for mobile phones and televisions, while blue OLEDs still have a drawback in triplet utilization. Hyperfluorescence OLEDs utilizing thermally activated delayed fluorescence (TADF) represent a promising technology for achieving high efficiency and color-purity. However, their overall performance, including device durability, remains significantly below industrial requirements. In particular, one still has to face the lack of understanding of the relationship between the photophysical properties of TADF materials and their stability. To date, many studies have suggested that shorter exciton lifetimes, which suppress annihilation

processes, could help enhance device lifetimes. In this work, however, we investigate the correlation between device lifetime and the photophysical properties of four TADF emitters and find a noticeable decrease in stability with increasing excited-state energy levels, indicating that higher excited-state energies (S_1+T_1 energies > 5.4 eV) have a substantial impact on device degradation. While improved color purity can be achieved by using a TADF assistant dopant with a shorter emission wavelength, the energy levels must be confined within a specific range to balance efficiency and device lifetime effectively. This study provides practical guidelines for improving device stability and performance.

1. Introduction

Organic light-emitting diodes (OLEDs) are one of the principal technologies of modern and future displays.^[1] Consequently, the three primary light colors—red, green, and blue (RGB)—have been major research targets,^[2] although recent advancements in sensing and communication technologies have also increased interest in invisible light.^[3] These emission colors are essentially determined by the energy levels of organic emitter materials, which can be readily tuned by modifying their molecular structures. Thus, a wide range of highly emissive organic materials with various structures is available, covering the full-color spectrum. However, blue OLEDs that meet industrial requirements have yet to be realized.

The challenge for OLEDs for marketable applications is the simultaneous enhancement of efficiency and stability. External quantum efficiency (EQE) is obviously of prime importance. Therefore, triplet harvesting mechanisms such as triplet-triplet up-conversion (TTU),^[4] phosphorescence,^[5] and thermally activated delayed fluorescence (TADF)^[6] have been extensively investigated. While the theoretical EQE values for phosphorescence- and TADF-based OLEDs achieving nearly 100% internal quantum efficiency (IQE) are higher than that for TTU with an IQE of up to 62.5%, blue OLEDs still rely on the TTU mechanism because of issues with device stability.

Phosphorescence and TADF emitters in green and red enable stable operation with a time to reach 95% of the initial luminance (LT_{95}) exceeding 10,000 hours at 1000 cd m^{-2} . In contrast, blue emitters achieve only several hundred hours, presenting a significant drawback compared to TTU emitters.^[7] This situation intends that high stability is essential performance metric. Since TADF-based OLEDs emerged relatively recently, there may still be room for improving their stability, since the upper limit for device lifetime remains unclear unlike EQE with a defined theoretical limit. The lower device lifetime of blue OLEDs appears to be linked to long-lived triplet excitons with higher energies in phosphorescence and TADF emitters,

which may lead to dissociation events through high-energy states of >5.4 eV formed by triplet-triplet annihilation (TTA) and triplet-polaron annihilation (TPA).^[8–10] Thus, many efforts have been directed towards triplet deactivation—specifically, reducing triplet decay lifetimes and triplet populations. Consequently, the rate constants of reverse intersystem crossing (k_{RISC}) in TADF materials sometimes exceed 10^6 s^{-1} .^[11,12] This feature also contributes to improving efficiency rolloff characteristics by suppressing singlet-triplet annihilation (STA),^[13] thereby enhancing practical efficiencies at high luminance. A more efficient approach for mitigating triplet excitons is TADF-assisted fluorescence, also known as hyperfluorescence. In this mechanism, excitons in TADF molecules rapidly transfer to terminal emitters, avoiding the intersystem crossing (ISC) process in the TADF molecules.^[14] The electroluminescence (EL) spectrum in hyperfluorescence systems depends on the terminal emitter, enabling superior color purity and substantive efficiency enhancement by using emitters with narrow-band emissions. Multiple-resonance (MR) materials, which support TADF properties and exhibit a small full width at half maximum (FWHM), are promising candidates for terminal emitters in hyperfluorescence devices.^[15,16]

The emission spectra of blue terminal emitters would have a peak at around 455–470 nm with FWHM as narrow as possible (corresponding to approximately 2.7 eV for the lowest singlet excited state, S_1). This requirement is due to the specific target in the Commission Internationale de l'Éclairage (CIE) coordinates of $x = 0.131$, $y = 0.046$, as defined by the BT.2020 color space standard.^[17] Therefore, the TADF assistant dopant needs to have relatively high energy levels for both the S_1 and the lowest triplet excited state (T_1). Otherwise, residual emission from TADF materials is observed due to incomplete Förster resonance energy transfer (FRET).^[18] For instance, an advanced blue TADF material named HDT-1 (**Figure 1**) was developed as a blue TADF molecule for sensitizing ν -DABNA with an emission maximum at 469 nm by reducing the charge transfer (CT) character of 3Cz2DPhCzBN with cyan emission.^[19,20] As a result, HDT-1 demonstrated high efficiency and relatively stable operation in hyperfluorescence OLEDs, while moderate FRET efficiency caused inferior CIE coordinates compared to the emission from ν -DABNA alone. In contrast, a compound with higher S_1 and T_1 energy levels, 4PhCz2BN, showed improved CIE coordinates in hyperfluorescence OLEDs using ν -DABNA.^[21] Nevertheless, devices based on 4PhCz2BN exhibited shorter operational lifetimes compared to those based on HDT-1. In general, molecules having different functional groups and geometries exhibit significant differences in stability, regardless of FRET efficiency, suggesting that chemical structures predominantly influence stability.^[22] However, both 4PhCz2BN and HDT-1 share similar components—carbazole-based donors and benzonitrile

(BN) acceptors—likely possessing comparable chemical stability in terms of bond dissociation energy. This raises the issue that the correlation between chemical structures, photophysical properties, including excited state dynamics, and device stability is still not clearly understood.

To address this gap, we developed a new TADF molecule, 2Cz2PhCz2BN (Figure 1), to enable a reasonable comparison of properties among a series of molecules with carbazole donors and benzonitrile acceptors. Comparisons between different research groups are practically difficult because of variations in methods for estimating photophysical parameters, the diverse selection of peripheral materials in OLEDs, and the absence of standardized criteria for evaluating device stability.^[23] In this study, we properly compared the device stabilities of four TADF molecules and their photophysical properties under consistent fabrication and operating conditions, and explored the degree of association for these parameters. The findings provide deeper insight into molecular design and degradation mechanisms for approaching the target stability.

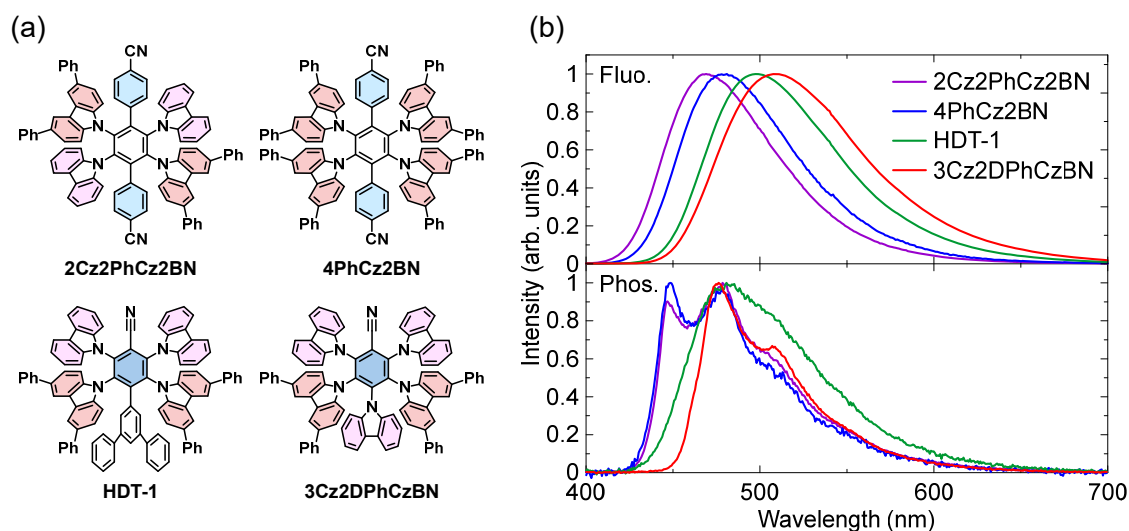


Figure 1. a) Chemical structures for the compounds investigated here. b) Fluorescence spectra and phosphorescence spectra for those molecules in chloroform.

2. Results and discussion

2.1. Synthesis and Characterization

The target compound, 2Cz2PhCz2BN, was synthesized as the scheme described in Methods S1 in the Supporting Information. Two different donor units of carbazole (Cz) and 3,6-diphenylcarbazole (PhCz) were introduced by nucleophilic aromatic substitution (S_NAr) reactions at the fluorine positions starting from 1,4-dibromo-2,3,5,6-tetrafluorobenzene. This

approach requires the following sequence of reactions: first, an S_NAr reaction using two equivalents of PhCz; a subsequent Suzuki coupling reaction to introduce benzonitrile (BN) groups; and finally, an S_NAr reaction for Cz substitutions. When a compound that pre-introduced BN groups (4F2BN) was used as the starting material, PhCz was substituted at four positions, resulting in formation of 4PhCz2BN because of the low solubility of 4F2BN compared to partially reacted intermediates. Similarly, the solubility of 3,6-dibromo-1,2,4,5-tetrakis(carbazole-9-yl)benzene (4Cz2Br) was also low, significantly limiting the yield of the Suzuki coupling reaction in the final step. Additionally, attempts to use 1,4-dibromo-2,5-difluoro-3,6-diiodobenzene as the starting material were unsuccessful, as both Suzuki coupling and Buchwald coupling reactions under standard conditions were inefficient. It is also noteworthy that the first S_NAr reaction with 1,4-dibromo-2,3,5,6-tetrafluorobenzene did not produce isomers with *ortho*- and *meta*-dicarbazole configurations.

The molecular structure of 2Cz2PhCz2BN was confirmed by X-ray single crystal analysis (Figure S1). The dihedral angles between the carbazole and center phenyl rings are approximately 70° , which falls within the typical range for benzenes substituted with six aromatic rings.^[24] Thus, 2Cz2PhCz2BN features six aromatic rings arranged radially at similar intervals. This conformation differs from that of 4PhCz2BN, which exhibited relatively strong intramolecular interactions between the PhCz rings and the isolated BN rings. The decomposition temperature (T_d) and melting point (T_m) of 2Cz2PhCz2BN were determined to be 556°C and 413°C , respectively (Figure S2), which are relatively similar to those of 4PhCz2BN ($T_d = 580^\circ\text{C}$, $T_m = 420^\circ\text{C}$).

2.2. Electrochemical and Photophysical Measurements

The physical properties of 2Cz2PhCz2BN were initially evaluated in solution to clarify the donor–acceptor (D–A) interactions within the molecule (Figure 1). These properties were primarily compared to those of 4PhCz2BN because of their similar molecular structures. The energy levels of CT type S_1 state proportionally decreased with increasing donor strengths. Since the Cz donor is weaker than the PhCz donor, 2Cz2PhCz2BN exhibited a fluorescence maximum that was blue-shifted by 10 nm compared to that of 4PhCz2BN (Figure S3 and Table S1). Conversely, a red-shift of 16 nm was observed relative to 4Cz2BN, which contains four Cz donors. This trend strongly correlates with the energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of these compounds, specifically due to slight shifts in the HOMO levels while the LUMO levels remained consistent (Figure S4 and Table S2). The theoretical calculations showed good

agreement with the experimental results (Table S3). The similar LUMO energies of 2Cz2PhCz2BN and 4PhCz2BN help in achieving comparable charge balance in OLEDs when using standard p-type host materials, such as 3,3'-di(9*H*-carbazol-9-yl)-1,1'-biphenyl (mCBP). The T_1 levels of 2Cz2PhCz2BN and 4PhCz2BN were found to be nearly identical because of the same local triplet excited state (3LE) of the twisted acceptor part (BN–Ph–BN),^[21] resulting in a slight difference in the S_1 – T_1 gap (ΔE_{ST} = 0.06 for 2Cz2PhCz2BN and 0.01 eV for 4PhCz2BN in chloroform, respectively). However, the photoluminescence (PL) quantum yield (Φ) of 2Cz2PhCz2BN was sufficiently high, measured at 82%, compared to 92% for 4PhCz2BN in chloroform. Optical measurements conducted in other solvents exhibited a similar trend (Figures S5 and Table S4).

2.3. Device Fabrication and Characterization

The OLED characteristics were assessed using the previously optimized device structure of ITO/HAT-CN (10 nm)/Tris-PCz (30 nm)/electron blocking layer (EBL) (5 nm)/emissive layer (EML) (30 nm)/SF3-TRZ (10 nm)/35-wt%-Liq:SF3-TRZ (30 nm)/Liq (2 nm)/Al (100 nm) (Methods S2 and Figures S6–S7), where both the EBL and host material were mCBP (Devices A–B).^[21] Additionally, 9-phenyl-9*H*-3,9'-bicarbazole (CCP) was tested as both the EBL and host material (Devices C–D). In the EML, TADF emitters were doped at a concentration of 20 wt% into the host matrices. Devices B and D represent hyperfluorescence systems incorporating ν -DABNA as the terminal emitter. Devices A1–D1 are based on 2Cz2PhCz2BN, while Devices A2–D2 utilize 4PhCz2BN.

The maximum EQE of Device A1 was lower than 10%, which can be attributed to the comparatively low Φ value of 60 % for 2Cz2PhCz2BN in an mCBP host (**Figure 2** and S8, and Table S5). However, Device B1 demonstrated an improved EQE of 15.5% with nearly the same EL spectra and CIE values as the reference device with a ν -DABNA-only emitter. The CIE values of (0.12, 0.13) for Device B1 were slightly improved compared to those for Device B2 based on 4PhCz2BN owing to the blue-shifted spectrum of the assistant dopant (Figure S9) and better FRET efficiency (vide infra). This level of color purity surpasses that of previously reported OLEDs employing ν -DABNA as the terminal emitter.^[19,22,25,26] Further improvements in EQE, exceeding 20%, were achieved using the CCP host in Device D1, while maintaining the same CIE values of (0.12, 0.13). Although the device durability of the hyperfluorescence system was significantly enhanced compared to that of the ν -DABNA-only device (LT_{50} = >40 h at 1000 cd m⁻² versus LT_{50} = 31 h at 100 cd m⁻², respectively),^[16] 2Cz2PhCz2BN-emitter

based devices exhibited lower stability than corresponding 4PhCz2BN-emitter based devices (Figure 2). Notably, the charge transport properties, efficiencies, and EL spectra for Devices D1 and D2 were very similar, indicating that the TADF emitters predominantly determine the device stability. While we previously speculated that the reduced stability of 4PhCz2BN compared to HDT-1 might be due to conformational disorder in its molecular structure,^[21] the conformationally ordered 2Cz2PhCz2BN was also found to exhibit poor stability. Therefore, it is essential to conduct a detailed analysis to identify the intrinsic factors contributing to this instability.

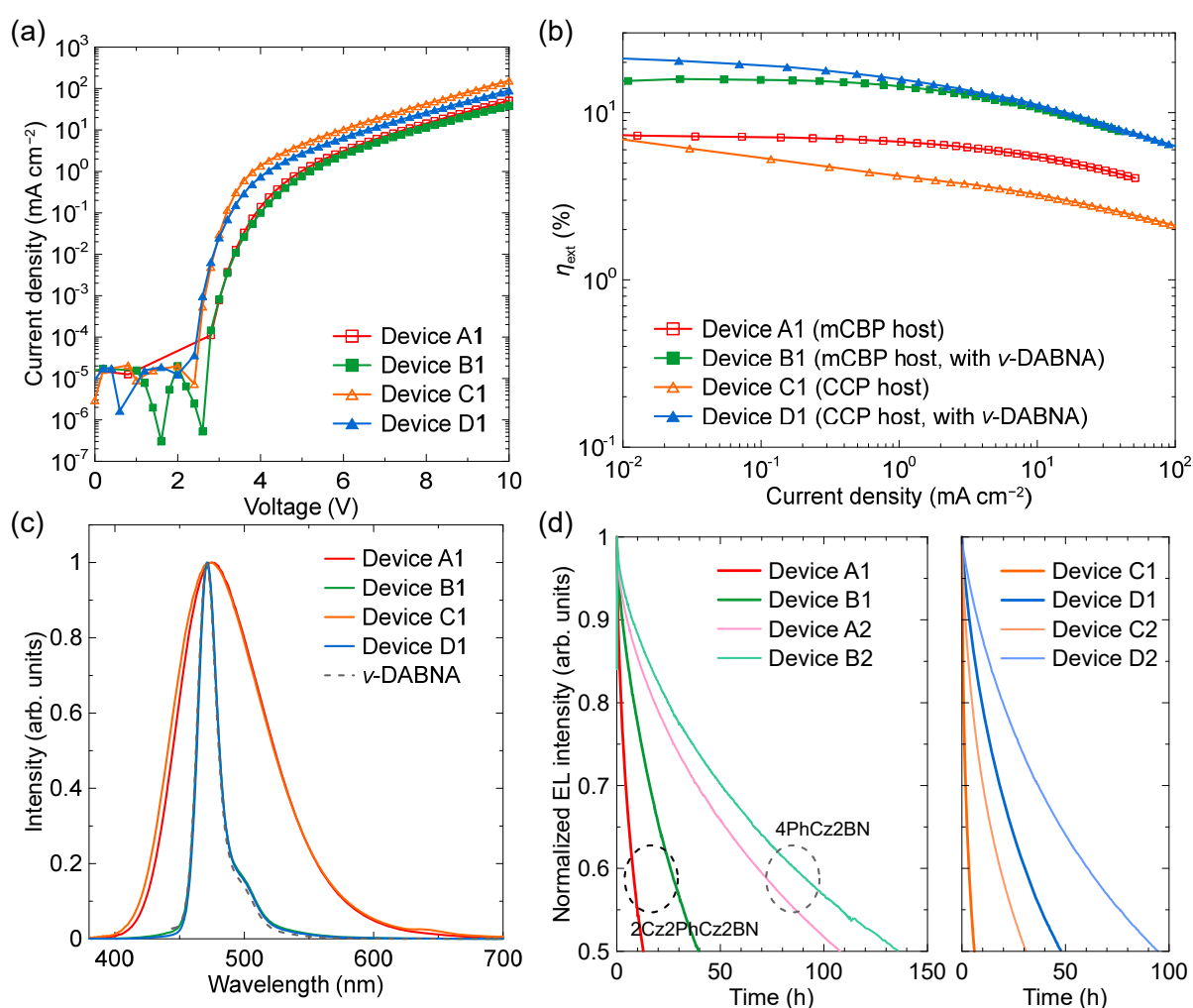


Figure 2. Device performances for 2Cz2PhCz2BN-based devices (Devices A1–D1). a) Current density–voltage characteristics. b) EQE–current density characteristics. c) EL spectra at 1000 cd m⁻². d) Luminance change versus operational time at an initial luminance of 1000 cd m⁻² for Devices A–B with mCBP host and Devices C–D with CCP host.

2.4. Relation between Photophysical Parameters and Device Stability

To gain a deeper understanding of the relationship between molecular properties and device durability, four TADF compounds depicted in Figure 1 were intensively examined. The emission spectra in the doped film for these materials are displayed in **Figure 3**. The excited state energies and TADF properties for these compounds exhibit slight variations ($S_1 = 2.75\text{--}2.93\text{ eV}$, $\Delta E_{ST} = 0.04\text{--}0.13\text{ eV}$ in Figure S10 and $\tau_d = 1.6\text{--}5.7\text{ }\mu\text{s}$), facilitating an exploration of the impact of excitonic processes on stability. It is practically impossible to achieve exactly the same carrier balance and recombination events since TADF molecules also share charge carrier transport. However, the same device configuration and similar molecular structures of TADF materials with the same building blocks helps minimize intrinsic variables causing degradation during device operation. The LT_{95} values at 1000 cd m^{-2} for the TADF-based devices with 20 wt%-TADF emitters in the EML were found to be 0.3 h for 2Cz2PhCz2BN, 1.3 h for 4PhCz2BN,^[21] 29 h for HDT-1,^[19] and 200 h for 3Cz2DPhCzBN.^[20,27] These lifetimes were plotted against several parameters in **Table 1** on a semi-log graph in **Figure 4** to identify the most dominant factor contributing to degradation, although each parameter should have some influence. The data plot suggests a correlation between the excited state energies of S_1 and T_1 for TADF molecules and device durability. We do not focus on the details of the statistical analysis here because of the limited sample size. The HOMO-LUMO energy levels play a role in charge injection and transport, with deeper LUMO levels in TADF molecules in the mCBP host potentially reducing interfacial recombination, which often affects device degradation.^[28] For these molecules, the acceptor structures were classified into two types, indicating similar electron-transporting properties for HDT-1 and 3Cz2DPhCzBN, as well as for 2Cz2PhCz2BN and 4PhCz2BN. However, markedly different stability within these groups implies the presence of other more critical factors. Some reports have pointed to a potential relationship between shorter exciton lifetimes and stability, with k_r^2 related to singlet-singlet annihilation (SSA) possibly impacting stability.^[27,29] Nevertheless, this correlation was found to be weaker than those for the energy level differences. While theoretically, an increased k_{RISC} should lead to enhanced lifetime,^[30] emitters with very fast k_{RISC} are not robust materials because they mostly have heavy atoms forming weaker bonds. Thus, a rational comparison between the molecules with similar chemical stabilities is necessary. The previous research using a compound based on Cz donor and BN acceptor revealed that minor modulation of k_{RISC} in the same compound did not alter excited state stability.^[31] Similarly, here, faster k_{RISC} and reduced triplet accumulation did not result in extended device lifetimes. Meanwhile, a recently proposed

parameter, $k_{\text{r}}k_{\text{eq}} = 4k_{\text{r}}k_{\text{RISC}}/(3k_{\text{r}} + 4k_{\text{ISC}})$, which has expressed a correlation with efficiency roll-off characteristics and should relate to bimolecular annihilation processes such as STA and TTA, was also plotted.^[32] The analysis suggests that exciton losses by annihilations are likely independent of device lifetime. On the other hand, the observed correlation between stability and combined excited state energy levels for $S_1 + T_1$ (Figure 4e) supports the influences of all SSA, TTA, and STA. These results indicate that the probability of chemical bond dissociation increases with rising energy levels of higher states generated through annihilation processes, and this effect appears to be more significant than the increase in the number of annihilation events when the exciton lifetime becomes longer. Importantly, a small energy difference of 0.2 eV significantly changes the device lifetime, resulting in 100-fold increase, as indicated by the exponential regression model.

Note that the eye-sensitivity drastically decreases in the deep blue region, resulting in only 10% luminous efficacy for pure blue compared to pure green. Consequently, the experimental condition at an initial luminance of 1000 cd m^{-2} for lifetime measurements meant the driving conditions with different radiances for these four emitter materials. In particular, 2Cz2PhCz2BN was evaluated under 1.5 times stronger irradiance than 3Cz2DPhCzBN, potentially shortening the device lifetime. However, the overall trend of the plots is expected to remain unchanged even after adjusting for these differences through an accelerated degradation simulation, viz. $\text{LT}_{95}' = \text{LT}_{95} \times \sim 1.5^n$, where n is the acceleration factor typically ranging 1.3–1.8.

In the hyperfluorescence system, excitons can be rapidly transferred to the terminal emitter by FRET, suggesting that the excited state energy levels of the terminal emitters seem to be of greater importance. Indeed, the terminal emitter with the lower triplet energy exhibited a longer device lifetime, although higher triplet energy facilitating TADF led to slightly higher efficiencies.^[33] However, hyperfluorescence devices using the identical terminal emitter (ν -DABNA), assisted by these TADF emitters and exhibiting only a small fraction of emission from TADF emitters, demonstrated the same trend of the lifetimes as the TADF-based devices (Figure S11). This result underscores the crucial role of the assistant dopant in realizing stable pure blue OLEDs. Note that the 3Cz2DPhCzBN-assisted hyperfluorescence device exhibited a substantial fraction of emission originating from 3Cz2DPhCzBN, resulting in a FRET efficiency of only 33%, which makes it difficult to fairly evaluate the properties of the hyperfluorescence system (Figure S12). A comparison of device lifetimes between the hyperfluorescence and corresponding TADF devices is of particular interest (11 h versus 29 h for HDT-1, 2.2 h versus 1.3 h for 4PhCz2BN, and 0.8 h versus 0.3 h for 2Cz2PhCz2BN). Here,

the S_1 state of ν -DABNA is considered to be primarily generated via FRET from the TADF assistant dopant, as direct charge recombination and Dexter energy transfer are unlikely to play a significant role. This interpretation is supported by the slight changes observed in the J - V characteristics upon ν -DABNA doping (e.g., Figure 2a, Devices A1 and B1), and by the fact that Dexter energy transfer is generally suppressed under optimized conditions with a low doping concentration of the terminal emitter. The FRET efficiency of 2Cz2PhCz2BN is approximately 90%, which is significantly higher than that of HDT-1 (67%) (Figure S12). These values are well supported by the FRET radius between the TADF assistant dopant and ν -DABNA, calculated as 3.07 nm, 2.95 nm, 2.56 nm, and 2.27 nm for 2Cz2PhCz2BN, 4PhCz2BN, HDT-1, and 3Cz2DPhCzBN, respectively (Figure S13). Thus, the hyperfluorescence device using 2Cz2PhCz2BN more effectively suppresses triplet excitons in the TADF material. In addition, 2Cz2PhCz2BN exhibits an emission peak nearly identical to that of ν -DABNA (Figure 2b), which results in a reduced total S_1 energy after FRET and contributes to an extended device lifetime. Although HDT-1 has a similar S_1 energy to ν -DABNA as estimated from the onset of the emission spectrum, the majority of its emission appears at longer wavelengths, leading to a relatively narrow distribution centered at higher energies after FRET. As a result, the hyperfluorescence device using HDT-1 exhibited a shorter lifetime. While the residual emission from HDT-1 in the hyperfluorescence device may contribute to the improved lifetime compared to a hypothetical case of 100% FRET from HDT-1 to ν -DABNA, the operational stability of ν -DABNA emission is still considered to be primarily governed by the properties of the TADF material.

To meet the industrial requirement of LT_{95} of 5,000 hours at 1000 cd m^{-2} , the excited state energies should be maintained as low as possible, with an extrapolated target of $<5.3 \text{ eV}$ according to Figure 4. Meanwhile, the energy level of monochromatic pure blue light at 467 nm is 2.66 eV, which must be exceeded. This necessitates TADF assistant dopants with precisely controlled S_1 and T_1 energy levels and efficient FRET capabilities. Meanwhile, molecular degradation fundamentally depends on chemical stability, suggesting the possibility of boosting lifetime in different molecular systems. For example, 4,6-diphenyl-1,3,5-triazine (TRZ) as an acceptor may lead to the development of robust TADF materials.^[12] Although Cz donor and BN acceptor exhibit greater stability compared to other building blocks such as 9,10-dihydro-9,9-dimethylacridine (DMAC) donor and triarylphosphine oxide ($\text{Ar}_3\text{P}=\text{O}$) acceptor,^[34] the weak bonds within the molecules should be thoroughly excluded or strengthened, for example, bridged ring systems decreasing flexibility and entropy gain upon bond dissociation are useful and thus found in commercial applications.^[9]

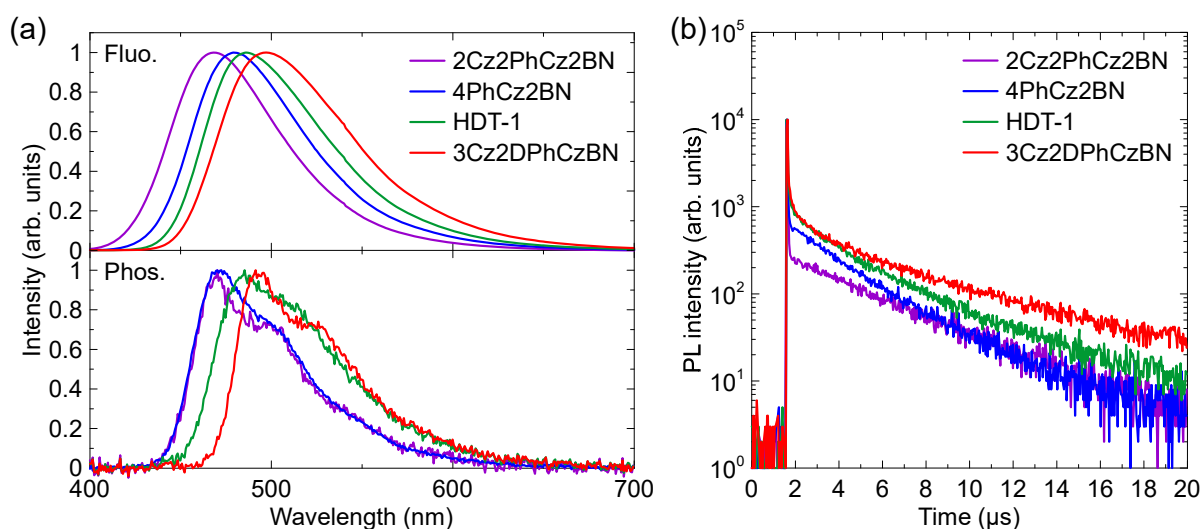


Figure 3. a) Fluorescence and phosphorescence, and b) PL transient decay spectra for 2Cz2PhCz2BN, 4PhCz2BN, HDT-1, and 3Cz2DPhCzBN doped in mCBP films with the concentration of 20 wt%.

Table 1. Electrochemical properties in solution and photophysical characteristics in 20 wt%-doped film of mCBP for 2Cz2PhCz2BN, 4PhCz2BN, HDT-1, and 3Cz2DPhCzBN

Compound	HOMO [eV] ^{a)}	LUMO [eV] ^{a)}	λ_{PL} [nm]	S_1 [eV]	T_1 [eV]	ΔE_{ST} [eV]	Φ_{PL} [-] ^{b)}	Φ_p/Φ_d [-] ^{b)}	τ_p [ns]	τ_d [μs]	k_p [10 ⁸ s ⁻¹]	k_r [10 ⁷ s ⁻¹]	k_{ISC} [10 ⁸ s ⁻¹]	k_{RISC} [10 ⁵ s ⁻¹]	$k_r k_{eq}$ [10 ⁵ s ⁻¹]
2Cz2PhCz2BN	-5.59	-2.58	468	2.93	2.80	0.13	0.60	0.21/0.39	6.7	4.1	1.5	3.1	1.2	5.9	1.3
4PhCz2BN	-5.55	-2.60	479	2.84	2.80	0.04	0.87	0.25/0.62	4.9	1.6	2.1	5.3	1.6	20	5.5
HDT-1	-5.73	-2.85	486	2.79	2.73	0.06	0.86	0.18/0.68	7.2	2.9	1.4	2.5	1.1	16	3.0
3Cz2DPhCzBN	-5.65	-2.80	497	2.75	2.64	0.11	0.94	0.15/0.79	5.8	5.7	1.7	2.7	1.5	11	1.7

^{a)}Estimated from redox potential in cyclic voltammetry. ^{b)}Measured under Ar in films.

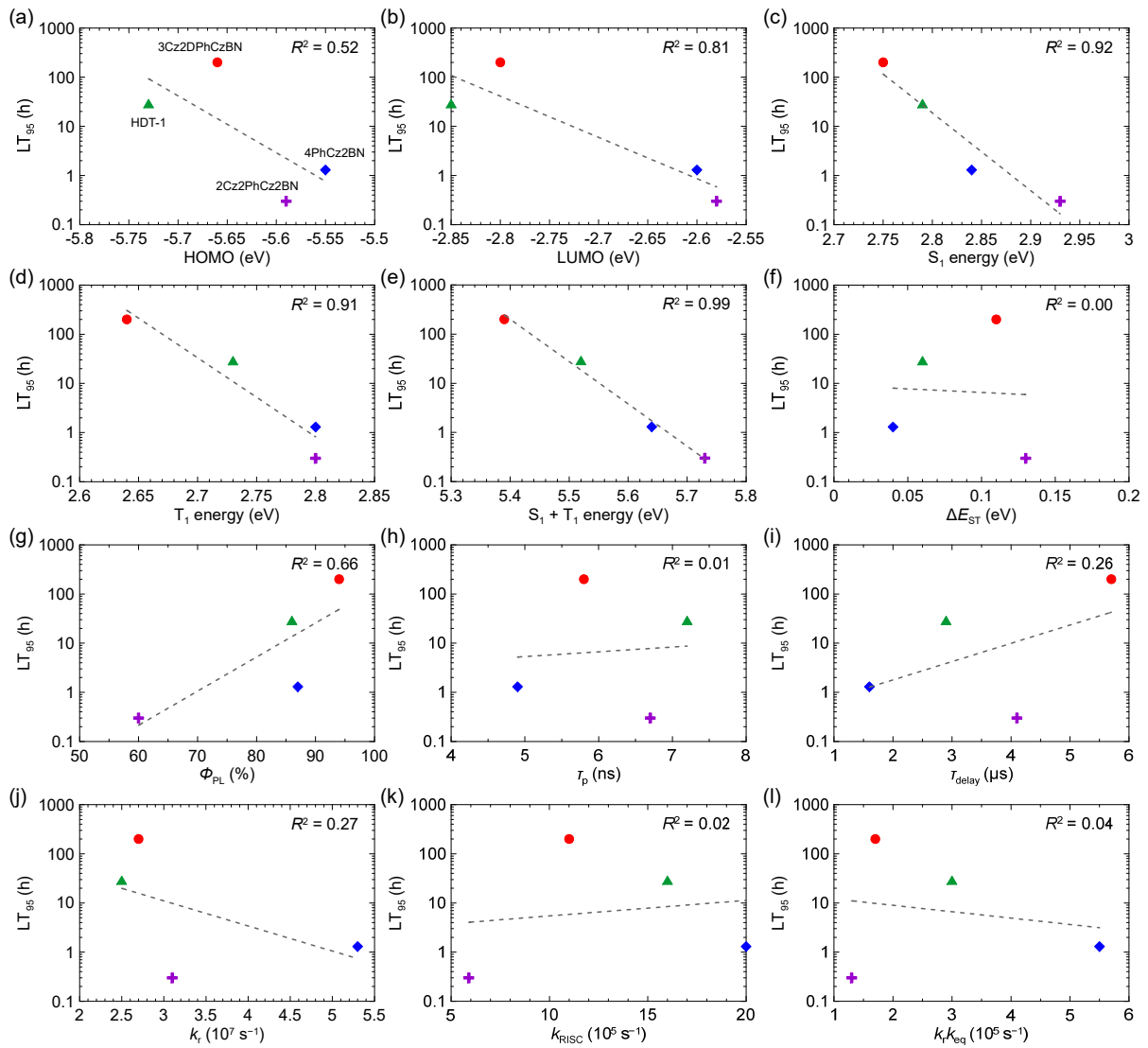


Figure 4. Graph of the relation between device durability and various parameters; a) HOMO level, b) LUMO level, c) S_1 energy level, d) T_1 energy level, e) $S_1 + T_1$; f) $\Delta E_{ST} = S_1 - T_1$ g) Quantum yield; h) prompt lifetime; i) delayed lifetime; j) radiative rate constant from S_1 , k) reverse intersystem crossing rate constant; l) $k_r k_{RISC} \approx k_r k_{RISC} / k_{ISC}$ which might correlate to roll-off characteristics. Red circle: 3Cz2DPhCzBN. Green triangle: HDT-1. Blue rhombus: 4PhCz2BN. Purple cross: 2Cz2PhCz2BN. R^2 : coefficient of determination.

3. Conclusion

In this study, we developed a new D–A type TADF molecule, 2Cz2PhCz2BN, for use in deep-blue OLEDs. The hyperfluorescence device employing ν -DABNA, sensitized by 2Cz2PhCz2BN, exhibited an EL spectrum nearly identical to the corresponding device without the assistant dopant, achieving excellent CIE coordinates of (0.12, 0.13). This performance is notably superior to previously reported hyperfluorescence devices, owing to the sufficiently high energy levels of 2Cz2PhCz2BN. Although the optimized device demonstrated an adequately high EQE of 21.4%, comparable to that of the device using the TADF molecule 4PhCz2BN, its durability was significantly worsened. This result indicates that the TADF assistant dopant drastically limits the stability to a lower level. Thus, the four TADF materials were compared to elucidate the most critical parameter inducing the degradation, suggesting a log-linear relationship with excited state energy levels, while less correlation with rate constants. This result aligns with the previous report discussing chemical bond dissociation via higher excited states > 5.4 eV.^[10]

Although improvements in device operational lifetimes and efficiency can be expected through device engineering approaches such as the use of tandem structures and microcavity effects, performance enhancement from the perspective of molecular science is particularly necessary at present. A possible guideline for the molecular design of TADF materials for highly efficient and stable deep blue OLEDs would be as follows. It must avoid excessive blue-shift of emission, increasing the energy levels. For efficient RISC and small ΔE_{ST} , the T_1 energy level needs to be very close to the S_1 energy level. Thus, optimal S_1 energy would be ca. 2.7 eV, while the emission band should be as narrow as possible to maximize a spectrum overlap for efficient FRET from the TADF material to the terminal emitter. Indeed, it is possible to derive narrow CT emission of < 50 nm by structurally engineered D–A molecules.^[35] Meanwhile, MR materials can be a candidate for assistant dopants as MR-TADF-sensitized MR-emitter devices.^[26,36] However, the performance requirements for assistant dopants, including fast RISC and applicability to relatively high doping concentrations of > 20 wt%, are still challenges for MR materials. The suppression of concentration quenching and carrier traps of MR materials also allows the terminal emitter to increase doping concentrations for high FRET efficiency. Another strategy for realizing complete FRET is the rigid TADF molecular structure with homogeneous CT emission.^[22] In any case, chemical robustness has been essential for stable operation, suggesting that the quest for highly luminescent molecules consisting of stronger chemical bonds is considered a reasonable target. Since all organic compounds, including host and charge transport materials, have a chance to contribute to improving device

durability,^[37] it is conceivable that new material designs achieve practical device lifetime in TADF-based blue OLEDs.

4. Experimental Section/Methods

General: Commercially available materials for the synthesis were used as received from the suppliers. Details of instruments and physical measurements are given in Table S6.

Synthesis and Characterizations: The synthetic procedures and characterization data for each material are described in Methods S1 and NMR spectra are given in Data S1.

Quantum calculations: The computations were mainly performed using the computer facilities at the Research Institute for Information Technology, Kyushu University. Molecular orbital calculations were performed using the program Gaussian 16. The geometries were optimized at the ω b97xd/6-31G(d,p). The TD-DFT calculations were conducted at the B3LYP/6-31+G(d,p) level for the calculations of the excited state.

Preparation of organic films for photophysical measurements: Organic thin-films for optical measurements were fabricated on clean quartz and silicon substrates by thermal evaporation at a pressure lower than 1×10^{-4} Pa. The substrates were cleaned with acetone and isopropanol and then treated with UV/ozone to remove adsorbed organic species before deposition.

OLED fabrication and performance characterization: The fabrication and measurement procedures are described in Methods S2.

X-ray single crystal analysis: Single crystals suitable for X-ray structural analysis were obtained by vacuum sublimation. X-ray crystallographic information files (CIFs) are available. [CCDC 2429915 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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