Organic TADF materials design

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Comparative study of thermally activated delayed fluorescent properties of donor–acceptor and donor–acceptor–donor architectures based on phenoxazine and dibenzo[a,j]phenazine

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Abstract

A new thermally activated delayed fluorescence (TADF) compound based on a donor–acceptor (D–A) architecture (D = phenoxazine; A = dibenzo[a,j]phenazine) has been developed, and its photophysical properties were characterized. The D–A compound is applicable as an emitting material for efficient organic light-emitting diodes (OLEDs), and its external quantum efficiency (EQE) exceeds the theoretical maximum of those with prompt fluorescent emitters. Most importantly, comparative study of the D–A molecule and its D–A–D counterpart from the viewpoints of the experiments and theoretical calculations revealed the effect of the number of the electron donor on the thermally activated delayed fluorescent behavior.

Introduction

Thermally activated delayed fluorescence (TADF), which was firstly reported in 1961 by Parker and Hatchard [1], is a fundamental photophysical phenomenon that refers to delayed fluorescence radiated from the singlet excited state (S1) as a consequence of a brief detour to a triplet excited state (Tn) [i.e., intersystem crossing (ISC) and reverse intersystem crossing (rISC)].
Since the revisit of TADF in organic light-emitting diodes (OLEDs) by Adachi in 2012 [2], TADF-active compounds have emerged as emitters in high-performance organic light-emitting diodes (OLEDs) [3-8], biological probes [9], photocatalysis [10], and some others [11]. Specifically, TADF-active purely organic compounds allow for achieving a very high external quantum efficiency (EQE) of OLEDs without using precious metals such as Ir and Pt in the emitter. Thus, the development of TADF-active organic compounds, the establishment of materials design through systematic structure–property relationship (SPR), and the understanding of the TADF mechanism are highly important tasks in this research field.

The singlet–triplet energy splitting between the S1 and T1 states (ΔE_ST) and spin–orbit coupling (SOC) play key roles in manifesting the TADF character of an organic compound. To boost the rISC process, ideally, the ΔE_ST is zero or even negative [12,13], while the SOC is as large as possible. One of the promising molecular design strategies to meet the above-mentioned criteria involves a highly twisted (D)n–(A)m (D: electron donor; A: electron acceptor) system, in which efficient intramolecular charge transfer (ICT) occurs in the singlet excited state (1CT). An efficient rISC can be mediated by mixing the 1CT state with a locally excited triplet state on the donor (3LE_D) or the acceptor (3LE_A) through spin–vibronic coupling [14] or non-Condon effects [15,16].

In 2016, we developed a twisted D–A–D compound POZ-DBPHZ (Figure 1) that exhibits efficient orange-to-red TADF [17], and the OLEDs fabricated with POZ-DBPHZ achieved a high EQE up to 16%. However, the role of the number of donors and molecular symmetry in the TADF character of POZ-DBPHZ remained unexplored, due to the lack of a synthetic method to the asymmetric D–A structure. Herein, we report the synthesis of a new asymmetric D–A compound 1 (Figure 1) as a TADF emitter and its detailed physical properties. Moreover, the developed emitter’s performance was evaluated in an OLED device. To clarify the influence of the donor number and structural symmetry on the physicochemical properties of the DBPHZ-cored D–A system, the properties of D–A compound 1 were compared with those of POZ-DBPHZ. Theoretical calculations further support the impact of the donor numbers in the DBPHZ-cored D–A system.

Results and Discussion

Synthesis of materials

To synthesize the designed D–A molecule 1, an asymmetric dibenzophenazine electrophile was required. Recently, we have established a synthetic method for such a compound, i.e., 3-trifluoromethanesulfonyldibenzo[a,j]phenazine (DBPHZ-OTf in Scheme 1) to prepare linear-type A–D–A–D compounds [18]. Starting from the mono-functionalized compound DBPHZ-OTf, the target compound 1 was successfully synthesized through a Pd-catalyzed Buchwald–Hartwig amination with phenoxazine (POZ) in a good yield as red-brown solid (Scheme 1). The D–A–D counterpart POZ-DBPHZ was synthesized according to the previously reported process [17]. It is noted that the solubility of the D–A compound 1 in organic solvents is lower than that of the D–A–D compound, indicating a more aggregated state of the D–A molecules in the solid state,
due to less steric hindrance on the acceptor plane arising from breaking the symmetry. The synthesized compound 1 was fully characterized by $^1$H and $^{13}$C NMR and IR spectroscopy, MS spectrometry as well as elemental analysis (for the detailed data, see Supporting Information File 1).

**Steady-state PL spectra**

To reveal the photophysical properties of diluted solutions of compound 1, UV–vis absorption and steady-state photoluminescence (PL) spectra were acquired (Figure 2, and the summary of the properties presented in Table 1). The solutions were prepared with a variety of organic solvents at concentrations of ca. $10^{-5}$ M. It is noted that the solubility of 1 in cyclohexane is quite low, and thereby the concentration of the cyclohexane solution and the molar absorption coefficient $\epsilon$ were not determined. As is clearly seen from Figure 2, the absorption spectra were not affected by the dielectric constant of the solvents. In contrast, the emission peaks of the PL spectra drastically red-shifted from cyclohexane ($\lambda_{PL} = 502$ nm) to toluene ($\lambda_{PL} = 608$ nm), and no PL was observed in a more polar solvent such as THF and CHCl$_3$ (Figure 2). In addition, the shape of the PL spectrum changed from a vibrationally resolved shape typical of the emission from a locally excited state (1LE) to a Gaussian-type broad one typical to the emission from a charge–transfer excited state (CT). The CT emission was totally quenched in a solvent that is more polar than toluene (Figure 2). These photophysical observations are consistent with those of the D–A–D-type compound POZ-DBPHZ [17], indicating that one D–A pair is sufficient for generating the CT excited state. In comparison with the photophysical properties of the D–A–D compound, the absorption of 1 ($\lambda_{abs} = 461$ nm) is almost the same as that of POZ-DBPHZ ($\lambda_{abs} = 463$ nm) [17], while the PL emission peak appeared in a slightly blue-shifted region ($\lambda_{PL} = 502$ nm) from D–A–D-type compound ($\lambda_{PL} = 521$ nm for POZ-DBPHZ) in cyclohexane. These data indicate that the effective length of $\pi$-conjugation is not affected by the number of donors, probably due to the right D–A dihedral angle for both compounds in the ground state. In contrary, the slight blue-shift of the PL spectra of the D–A compound 1 compared to POZ-DBPHZ reflects the contribution of an additional donor to relaxation of the molecular geometry in the excited state. The photoluminescence quantum yield ($\Phi_{PL}$) of the D–A compound 1 is lower (0.13 in cyclohexane) than that of the D–A–D compound POZ-DBPHZ (0.33) [17], indicating a dominant non-radiative decay of the excited state for the D–A type compound, which was supported by the theoretical calculations (vide infra).

**Table 1:** Summary of steady-state photophysical data of diluted solutions of 1.a

<table>
<thead>
<tr>
<th>solvent</th>
<th>$\lambda_{abs}$ (nm)</th>
<th>$\lambda_{PL}$ (nm)</th>
<th>$\Phi_{PL}$b</th>
</tr>
</thead>
<tbody>
<tr>
<td>cyclohexane</td>
<td>294, 389, 412</td>
<td>502</td>
<td>0.13</td>
</tr>
<tr>
<td>toluene</td>
<td>296, 393, 415</td>
<td>608</td>
<td>0.16</td>
</tr>
<tr>
<td>THF</td>
<td>295, 392, 415</td>
<td>–</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>CHCl$_3$</td>
<td>295, 394, 416</td>
<td>–</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>

*aSolution concentration: $10^{-5}$ M; b*determined with an integrated sphere; c*saturated solution was used, due to the low solubility in cyclohexane.

![Figure 2](image.png)
In the solid state, the D–A compound 1 showed an emission at around $\lambda_{em} = 560$ nm with a very low $\Phi_{PL} (< 0.1)$ (Figure S1 in Supporting Information File 1). The PL spectrum is similar to that in a CBP host matrix (vide infra). The compound 1 showed an aggregation-induced emission (AIE) behavior in a THF/water system, showing a more red-shifted emission peak at around $\lambda_{em} = 600$ nm when compared with the as-prepared solid state (Figure S2 in Supporting Information File 1). This indicates that in the as-prepared state and aggregation state the molecular stacking modes should be quite different from each other.

**Time-resolved spectroscopic analysis**

To investigate the delayed fluorescence behavior of the D–A compound 1, more detailed photophysical studies were performed using a time-resolved spectroscopic technique (Figure 3). Time-resolved photoluminescence (PL) from a blended film (1 wt % of 1 in Zeonex®) at 300 K showed two-components emission consisting of a prompt fluorescence (PF) that decays within the order of nanoseconds and a delayed fluorescence (DF) that decays in the range of micro to milliseconds (Figure 3a). These PF and DF spectra are exactly overlapped with each other (Figure 3b), which indicated that both emis-

![Figure 3](image-url)

*Figure 3: Time-resolved PL decay profiles (intensity vs delay time) and spectra of 1 in a), b) Zeonex® and c, d) CBP matrix. The energies correspond to the maximum emission peaks.*
ions are radiated from the singlet excited state ($S_1$). Both emission spectra are not well resolved and in a Gaussian-type shape (Figure 2b), suggesting that these emissions have a mixed character of localized ($^1{\text{LE}}$) and charge-transfer state ($^1{\text{CT}}$, Figure 3b). The emission from the $T_1$ state (phosphorescence, PH) at a low temperature (10 K) with the energy of $E_{T1} = 2.26 \text{ eV}$ showed a similar spectral shape to the phosphorescence spectra of the acceptor core (DBPHZ) [17]. This would indicate that the $T_1$ state of the D–A compound is localized on the acceptor unit ($^3{\text{LA}}$). The $\Delta E_{\text{ST}}$ of $I$ was found to be 0.11 eV, which is twice larger than that of POZ-DBPHZ in the same matrix (0.06 eV) [17]. These differences are ascribed to the change in electron density on the acceptor and the electron-donating power of POZ. Therefore, gradual increase of electron-donating strength brings $T_1$ energy closer to the acceptor $T_1$ energy and leads to a smaller $E_{\text{ST}}$ gap. But, the activation energy $E_a$ for the DF process, which was calculated from the Arrhenius plot obtained from the increase of the DF intensity against temperature, was lower for $I$ ($E_a = 27 \text{ meV}$) when compared to POZ-DBPHZ ($E_a = 47 \text{ meV}$, Table 2) in Zeonex®. The directly determined activation energy of the D–A-type compound is half that of the D–A–D compound, which is in contradiction to the $\Delta E_{\text{ST}}$ value (Table 2). If we support the observation with the DF/PF results that present a stronger TADF property for the mono-substituted derivative $I$, the conclusion of misleading $\Delta E_{\text{ST}}$ comparison can be reached. To avoid confusion, a more effective way is to compare only the activation energy of the DF process.

The time-resolved spectroscopic analysis of the emitter (10 wt % $I$) in an OLED matrix, 4,4’-bis(N-carbazolyl)-1,1’-biphenyl (CBP), revealed that the emission at 300 K yields a weaker DF when compared to the Zeonex® matrix (Figure 3c). In addition, the emission in CBP was more complicated, due to the emission spectra that move around with delay time (Figure S3, Supporting Information File 1). At 5.1 ns, the emission peak from PF was observed in a red-shifted region (by approximately 41 nm) than that observed in Zeonex® ($\lambda_{em} = 524 \text{ nm}$) (Figure S3a in Supporting Information File 1). Thereafter, there was a monotonic red shift in the emission peak and the gradual increment during the delay time from 0 ns to 150 ns, and the largest red-shifted spectrum was found at 613 nm (at 150 ns) (Figure S3a, Supporting Information File 1). From 168 ns to 5 $\mu s$ delay time, the emission peak plateaued at around $\lambda_{em} = 607 \text{ nm}$ (Figure S3b, Supporting Information File 1), then from 5 $\mu s$ to 32 $\mu s$, a significant hypsochromic shift of the emission peak was observed down to 560 nm, and the emission peak stayed at this value (Figure S3c, Supporting Information File 1). This behavior brings the proposition that the PF in the nanosecond range based on a CT character with a little contribution from the $^1{\text{LE}}$ state have inhomogeneous energies. Firstly, the $^1{\text{LE}}$ state decays, and then decays of the lower-energy excited states follow. The triplet energy level of $I$ is 2.08 eV, which is lower than that in Zeonex® (2.26 eV). A closer inspection of the transient curves and inset spectra at microsecond delays let us notice that the spectra shift slightly to lower energies (Figure S3 in Supporting Information File 1). This behavior is not unusual in CT-based emitters and can be explained by local interactions between the dipole moment of the host and the excited state dipole moment of the TADF molecule [19].

The activation energy for the TADF process of the D–A compound $I$ is as low as 15 meV. Nevertheless, the TADF efficiency of the D–A compound in CBP is much lower when compared to that in Zeonex® and its D–A–D counterpart (Table 2). First, the DF/PF ratio is much smaller in CBP than in Zeonex®, suggesting a smaller triplet contribution to the overall emission. If we compare compound $I$ with the previously studied D–A–D compound, the $\Phi_{PL}$ is slightly lower, but the highest impact is related with DF/PF, where POZ-DBPHZ has the twice higher value which in total should give a much lower performance in the device for $I$.

**Thermal stability**

To fabricate the OLED devices by thermal evaporation techniques, a high thermal stability is required. To evaluate the effect of the donor number on the thermal stability of the

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**Table 2: Summary of the general photophysical properties of compound 1.**

<table>
<thead>
<tr>
<th>Compd.</th>
<th>host</th>
<th>$\lambda_{em}$ [nm]</th>
<th>$\Phi_{PL}$</th>
<th>$\tau_{PF}$ [ns]</th>
<th>$\tau_{DF}$ [ps]</th>
<th>$DF/PF$</th>
<th>$E_a$ [eV]</th>
<th>$S_1$ [eV]</th>
<th>$T_1$ [eV]</th>
<th>$\Delta E_{\text{ST}}$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Zeonex®</td>
<td>524</td>
<td>32.5</td>
<td>15.37 ± 1.35</td>
<td>6.9 ± 0.43</td>
<td>5.01</td>
<td>0.028</td>
<td>2.37</td>
<td>2.26</td>
<td>0.11</td>
</tr>
<tr>
<td>POZ-DBPHZ</td>
<td>Zeonex®</td>
<td>530</td>
<td>29.5</td>
<td>10.23 ± 0.16</td>
<td>26.4 ± 1.50</td>
<td>4.72</td>
<td>0.047</td>
<td>2.48</td>
<td>2.40</td>
<td>0.08</td>
</tr>
<tr>
<td>1</td>
<td>CBP</td>
<td>565</td>
<td>68.5</td>
<td>16.11 ± 0.38</td>
<td>2.96 ± 0.18</td>
<td>0.98</td>
<td>0.015</td>
<td>2.19</td>
<td>2.08</td>
<td>0.11</td>
</tr>
<tr>
<td>POZ-DBPHZ</td>
<td>CBP</td>
<td>595</td>
<td>79.0</td>
<td>2.7 ± 0.21</td>
<td>0.47 ± 0.04</td>
<td>1.94</td>
<td>0.019</td>
<td>2.28</td>
<td>2.26</td>
<td>0.02</td>
</tr>
</tbody>
</table>

*aThe maximum wavelength of photoluminescence spectra; bPhotoluminescence quantum yield in degassed; cPrompt fluorescence lifetime; dDelayed fluorescence lifetime; eThe ratio of delayed fluorescence (DF) to prompt fluorescence (PF); fActivation energy of the triplet to singlet transfer (error ± 0.01 eV); gsinglet and triplet energy (error ± 0.03 eV); hEnergy splitting (error ± 0.05 eV). All parameters estimated at 300 K.*
DBPHZ-cored D–A type emitter, the degradation temperature \( T_d \) (5 wt % loss) was investigated by thermogravimetric analysis (TGA), which showed a high \( T_d \) (5 wt % loss under N\(_2\) atmosphere) of compound 1 (342 °C) (Figure S4a in Supporting Information File 1), which is high enough for a thermal deposition process. However, when compared with the D–A–D counterpart, the \( T_d \) of 1 is much lower (by 111 °C) than that of POZ-DBPHZ (453 °C) [17]. These data would support that the increase in the sterically hindered donors in emitting molecule suppress intermolecular contact to enhance the thermal stability.

**OLED fabrication and characterization**

The OLED device was fabricated and characterized in the CBP host (Figure 4). The HOMO–LUMO values obtained from the electrochemical measurement (Figure S5 in Supporting Information File 1) were used to evaluate whether the emitter works in a previously analyzed device structure [17]. The OLED device structure applied the following configuration: –ITO/NPB[{N,N’-di(1-naphthyl)-N,N’-diphenyl-(1,1’-biphenyl)-4,4’-diamine} (40 nm)/10% of 1 in CBP (20 nm)/TPBi [2,2’,2’’-(1,3,5-benzinetriyl)-tris(1-phenyl-1H-benzimidazole)] (20 nm)/BCP (bathocuprine)] (20 nm)/LiF (1 nm)/Al (100 nm)– (Figure 4).

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**Figure 4:** The characteristics of the OLED devices: a) electroluminescence spectra; b) current density-bias characteristics; c) EQE–current density characteristics; d) luminance–current density characteristics.
The external quantum efficiency (EQE) was measured at around 11.4%, where the device fabricated with the previously studied D–A–D compound POZ-DBPHZ showed 16%. As for luminescence, a high luminescence of 27,060 cd/m² was obtained, which is slightly lower than that we previously reported (>35,000 cd/m²) [17]. A positive aspect about the device fabricated with compound 1 is the lower efficiency roll-off when compared with the previously studied D–A–D emitter. As the result, the efficiency is higher for the D–A compound 1 above 10,000 cd/m², and at the luminance, the EQE was kept around 10%, whereas in the case of doubly donor-substituted compound POZ-DBPHZ, the EQE dropped below 10% [17].

Theoretical calculations
We performed electronic structure calculations on both the D–A (1) and D–A–D (POZ-DBPHZ) compounds to understand better their respective TADF mechanisms and the efficacy of introducing two electronic donors on the acceptor unit. The calculations employed density functional theory (DFT) with the long-range corrected ωPBE functional and the 6-31G(d,p) basis set. Tuning of the range separation parameter was performed for both molecules [20] with the results collected in Table S1 (Supporting Information File 1). The Tamm–Dancoff (TDA) approximation was used in all excited state calculations and solvent effects were included by means of the polarizable continuum model (PCM) associated with a perturbative state specific solvation method using toluene as solvent. The photophysics of both molecules was analyzed using a unified approach for photophysical rate calculations that employs the nuclear ensemble method as implemented in the NEMO software [21,22] interfaced with the QChem 5.0 program suite [23]. A total of 500 geometries were sampled for each molecule and for each relevant electronic state. From these calculations, emission spectra were computed along with fluorescence, phosphorescence, and ISC rates, providing us insight into the mechanism behind the photophysical behavior of the molecules under analysis in this work.

Taking fluorescence properties as starting point, the simulations point out considerable similarity between the spectra of the D–A and D–A–D compounds. As shown in Figure S6 (Supporting Information File 1), the calculated fluorescence peaks lie at 510 nm and 505 nm for the D–A and D–A–D compounds, respectively. These results agree very well with those obtained from the measurement in Zeonex® (Table 2), which has a similar dielectric constant as toluene (≈2.3), the solvent used in the calculations. A comparison with results from steady-state PL spectra (Table 1), however, show that the predicted peak matches measurements made with cyclohexane, but appear to be blue shifted with respect to measurements in toluene. Considering that cyclohexane has a only a slightly lower dielectric constant (≈2.0) than toluene, it is reasonable that calculations would produce similar predictions, which makes the red-shifted experimental emission in toluene more surprising. In addition to similarities in fluorescence energy, the D–A (1) and D–A–D (POZ-DBPHZ) compounds share very close calculated fluorescence rates (2.2 × 10⁻⁷ s⁻¹ and 1.8 × 10⁻⁷ s⁻¹, respectively) which translate into prompt fluorescence lifetimes of 45 ns and 54 ns, respectively. These values are in the same order of magnitude as the experimental lifetimes shown in Table 2, further indicating the appropriateness of the theoretical approach.

From the first singlet excited state, we have estimated ISC rates for both molecules. Table S5 in Supporting Information File 1 shows the calculated ISC rates from S₁ to the first five triplet states. For both molecules, the estimated rate values are comparable or larger than those for fluorescence, which makes the ISC process competitive. Comparing all available processes from the S₁ state, we are able to estimate probabilities for each transition (detailed in Supporting Information File 1, Table S8 and Table S9). In the case of the D–A compound 1, the singlet population is expected to split mostly into T₁ (33%) and T₂ states (42%), with about 2% probability expected for prompt fluorescence. On the other hand, for the D–A–D compound POZ-DBPHZ, transitions to T₁ display 48% probability whereas fluorescence has around 4%. The remaining probabilities are mostly distributed between transfers to T₂ and T₃ with about 20% each.

Transfers to higher lying triplet states may end up relaxing to the lowest triplet state by means of internal conversion. In this sense, it is important to look into the energy gaps between triplet states of both molecules. Considering the average gaps taken from all the conformations sampled in the nuclear ensemble from the T₁ state geometry, we obtain T₁ to T₂ gaps of approximately 0.4 eV for both compounds. This significant value suggests the possibility of the T₂ population not necessarily decaying to T₁ instantly. In contrast, the average energy difference between two adjacent triplet levels above T₂ is approximately 0.1 eV for both molecules, which indicates that internal conversion should be very efficient.

Following the above observations, we estimated rISC rates from the first two triplet states of both molecules and the results are collected in Table S6 and Table S7 (Supporting Information File 1). It is worth noting, that the D–A–D compound POZ-DBPHZ presents rISC rates that are larger than those of its D–A counterpart 1 by roughly one order of magnitude, which suggests that the addition of an extra donor unit is able to improve the TADF efficiency. For both triplet states, rISC transfers to S₁ are overwhelmingly larger than those to higher...
singlet states. Similarly, these transfer rates to $S_1$ are orders of magnitude larger than estimated phosphorescence rates (Table S3 in Supporting Information File 1). The analysis of the probabilities associated with each transfer mechanism from $T_1$ and $T_2$ (shown in Table S8 and Table S9 of Supporting Information File 1) indicates that the expected depopulation mechanism for the first two triplet states is dominated by an rISC back to the first excited singlet state, which is responsible for the TADF behavior observed in both molecules.

The rate estimates finally allow us to paint a picture of the TADF mechanism of the two compounds. This is schematically shown in Figure 5, along with the calculated rates for each of the represented processes. In addition, we present natural transition orbitals (NTOs) for the three excited states most relevant for the TADF mechanism. These NTOs demonstrate the similar CT character of the $S_1$ state of both compounds, which helps explain their coinciding fluorescence spectra. Finally, the NTOs for the triplet states indicate a possible source for the difference in their TADF efficiencies. Whereas the first two triplet states of the D–A compound 1 correspond mostly to excitations localized in the acceptor fragment, the $T_1$ and $T_2$ states on the D–A–D molecule POZ-DBPHZ display a mixed CT/LE character. It is known that having two states with different electronic characters allows for larger spin–orbit couplings, so we would expect these couplings to be larger in the case of the D–A molecule when comparing with the D–A–D compound. This is indeed the case, as the average spin–orbit coupling for the $T_1$ to $S_1$ transition in the D–A compound 1 is 0.462 meV, whereas for the D–A–D compound POZ-DBPHZ it is 0.177 meV. However, the average energy gap taken from all geometries in the nuclear ensemble for this transition is 0.37 eV for the D–A–D compound and 0.71 eV for the D–A molecule. As such, the higher similarity in electronic character between the singlet and triplet states of the D–A–D molecule was enough to decrease the average energy gap without compromising significantly the spin–orbit coupling, resulting in an overall better TADF performance.

Conclusion
In conclusion, we have developed a new D–A-type TADF compound and investigated its physicochemical properties for comparison with the corresponding D–A–D analogue. The number of donor units has no effect on the absorption, due to the highly twisted D–A(–D) structures, while an additional donor unit led to a slight red shift in photoluminescence by the stabilization of the charge-transfer singlet excited states ($^1$CT). Most importantly, the additional donor unit not only lowers the $^1$CT energy but also is bringing the $T_1$ energy to the approximation of the $^3$LE$_A$ energy, leading to a narrower singlet–triplet energy gap and a more efficient TADF process, when compared with the mono-donor-substituted compound. On one hand, the comparison of the activation energy for the TADF process for the two compounds gave an inversed order of energy. In addition, the one-less number of donor units in the molecular scaffold led to lower solubility in organic solvents and thermal stability, presumably due to the less steric hindrance around the $\pi$-extended conjugated acceptor unit with the unsymmetric molecule structure. The OLEDs fabricated with the D–A emitter achieved a good EQE up to 11%, which exceeds the theoretical
maximum (ca. 5%) of prompt fluorescent emitter-based OLEDs. The additional donor gave a better EQE of the OLED device than that fabricated with the D–A compound, due to a less efficient TADF process. Taken together the experimental and theoretical calculations, the role of the additional donor unit in the TADF mechanism is boosting the rISC process by balancing the singlet–triplet energy gap and spin–orbit coupling. The results showcased herein would allow for designing efficient TADF emitters more flexibly in the future.

Supporting Information

Supporting Information File 1
General information, synthetic procedures, spectral data, photophysical data, and theoretical calculation data. [https://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-18-48-S1.pdf]

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References
22. NEMO, Version 0.2.0; de Sousa, L. E.; https://github.com/LeonardoESousa/NEMO.
Goldey, M.; Horn, P. R.; Jacobson, L. D.; Kaliman, I.; Khaliullin, R. Z.;
Ku, T.; Landau, A.; Liu, J.; Proynov, E. I.; Rhee, Y. M.; Richard, R. M.;
Rohrdanz, M. A.; Steele, R. P.; Sundstrom, E. J.; Woodcock, H. L., III;
Zimmerman, P. M.; Zuev, D.; Albrecht, B.; Alguire, E.; Austin, B.;
Beran, G. J. O.; Bernard, Y. A.; Berquist, E.; Brandhorst, K.;
Chen, S. H.; Closser, K. D.; Crittenden, D. L.; Diedenhofen, M.;
Fusil-Molnar, L.; Ghysels, A.; Golubeva-Zadorozhnaya, A.; Gomes, J.;
Hanson-Heine, M. W. D.; Harbach, P. H. P.; Hauser, A. W.;
Lawler, K. V.; Levchenko, S. V.; Lin, C. Y.; Liu, F.; Livshits, E.;
Lochan, R. C.; Luenser, A.; Manohar, P.; Manzer, S. F.; Mao, S.-P.;
Mardirossian, N.; Mareovich, A. V.; Maurer, S. A.; Mayhall, N. J.;
Neuscamman, E.; Oana, C. M.; Olives-Amaya, R.; O'Neil, D. P.;
Parkhill, J. A.; Perrine, T. M.; Pererati, R.; Prociuk, A.; Rehn, D. R.;
Rosta, E.; Russ, N. J.; Sharada, S. M.; Sharma, S.; Small, D. W.;
Sodt, A.; Stein, T.; Stöck, D.; Su, Y.-C.; Thom, A. J. W.;
Watson, M. A.; Wenzel, J.; White, A.; Williams, C. F.; Yang, J.;
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Abstract
The interest in organic materials exhibiting thermally activated delayed fluorescence (TADF) significantly increased in recent years owing to their potential application as emitters in highly efficient organic light emitting diodes (OLEDs). Simple modification of the molecular structure of TADF compounds through the selection of different electron-donating or accepting fragments opens great possibilities to tune the emission properties and rates. Here we present the synthesis of a series of novel pyrimidine–carbazole emitters and their photophysical characterization in view of effects of substituents in the pyrimidine ring on their TADF properties. We demonstrate that electron-withdrawing substituents directly connected to the pyrimidine unit have greater impact on the lowering of the energy gap between singlet and triplet states ($\Delta E_{ST}$) for efficient TADF as compared to those attached through a phenylene bridge. A modification of the pyrimidine unit with CN, SCH$_3$, and SO$_2$CH$_3$ functional groups at position 2 is shown to enhance the emission yield up to 0.5 with pronounced TADF activity.

Introduction
The first reports on highly efficient thermally activated delayed fluorescence (TADF) mechanism and its successful realization in organic light emitting diodes (OLEDs) by Adachi and co-workers [1,2] have drawn the attention to the design and synthesis of various emissive donor–acceptor organic compounds. Efficient triplet harvesting in TADF compounds leads to internal quantum efficiencies up to 100% and electroluminescence yields exceeding 20% [3,4]. TADF OLEDs usually contain pure organic molecules, which avoid expensive noble metals and allow broad possibilities of molecular design. One of
the main requirement for efficient TADF is a negligible energy difference between the lowest singlet and triplet states (ΔE<sub>ST</sub>) which is often obtained in (hetero)aromatic compounds possessing twisted electron-donor (D) and acceptor (A) fragments with strong intramolecular charge transfer (ICT) [5-7]. Moreover, the number and nature of various side units on the emitter framework can also affect the properties of TADF compounds [3]. Among the electron-donating units, 9,10-dihydroacridine, carbazole or phenoxazine derivatives often are used as D units, while the π-electron-deficient nitrogen heterocycles such as triazine, diazines or aromatics containing cyano and sulfone groups are popular acceptor units for the construction of highly efficient TADF emitters [8-11]. Pyrimidine (1,3-diazine) owing to its aromaticity, significant π-deficiency, strong electron affinity, high luminous efficiency, good electrical and optical properties, and easy chemical modification is a desired structural unit in organic structures targeted for numerous applications including organic photovoltaic solar cells (OPV) [12-14], organic field-effect transistors (OFETs) [15-17], chemical and biosensors [18-23], and OLEDs [3,7-9,24]. In case of TADF emitters, a pyrimidine ring is often connected with a donor unit through a phenylene group as a conjugate π-spacer (s) [25-28]. As the majority of research describes TADF compounds with D–A–D layout, reports on TADF properties of pyrimidine emitters where the pyrimidine moiety is directly bonded with a donor moiety are scarce [29-31], though several examples of such pyrimidine-based conjugates found utility as high triplet energy hosts [32,33]. Envisaging the potential of the pyrimidine–carbazole pair for achieving efficient deep-blue emission, we were interested to study the influence of substituents in position 2 of the pyrimidine ring on the TADF properties of pyrimidine–carbazole emitters. For this purpose, we performed the synthesis of novel 4,6-bis(3,6-di-tert-butyl-9H-carbazol-9-yl)pyrimidines modified with various substituents in position 2 of the pyrimidine ring (Figure 1).

For comparison, analysis of the TADF properties of a similar pyrimidine–carbazole emitter tCbz-mPYR is also included in this paper [29]. To enhance the electron-accepting character of the pyrimidine moiety some electron-withdrawing groups, namely cyano, bromo or sulfonyl groups were introduced directly or through a phenylene bridge into position 2 of the pyrimidine ring.

Results and Discussion

Synthesis

Due to the versatile reactivity of a methythio group in the pyrimidine nucleus [34,35] we used 4,6-bis(3,6-di-tert-butyl-9H-carbazol-9-yl)-5-methyl-2-methylthiopyrimidine (tCbz-mPYR) as a starting material for the synthesis of 2-substituted pyrimidine emitters (Scheme 1). Compound tCbz-mPYR was synthesized by using the palladium-catalyzed Buchwald–Hartwig amination reaction of 4,6-dichloro-5-methyl-2-methylpyrimidine with 3,6-di-tert-butylcarbazole according to the procedure reported by us previously [29].

In order to remove the methythio group in tCbz-mPYR and to obtain the 2-unsubstituted pyrimidine derivative 1, a hydrogenolysis reaction employing Raney Ni was carried out. Efficient methods for the introduction of aryl moieties into methythio-substituted nitrogen heterocycles such as tCbz-mPYR are a Ni(0)-catalyzed cross-coupling reaction with Grignard reagents [34,36] or the Liebeskind–Srogl reaction employing arylboronic acids [37-39]. Taking into account a large assortment of arylboronic acids and the simplicity of the method, we chose the Liebeskind–Srogl cross-coupling reaction for the synthesis of the target 2-arylpymidines derivatives. Thus, heating tCbz-mPYR with phenyl-, 4-cyanophenyl-, 3-cyanophenyl-, or 3-bromophenylboronic acid at 130 °C in dioxane in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub>, copper(I) 3-methylsalicylate (CuMeSal), and Cs<sub>2</sub>CO<sub>3</sub> as a catalyst system furnished the corresponding 2-substituted pyrimidines 2a–d. For the introduction of cyano and 4-(tert-butyl)phenylthio groups into position 2 of the pyrimidine, the conversion of the methythio group to the better leaving methylsulfonyl group was necessary to perform. A suitable oxidant for this purpose appeared to be oxone [40]. Thus, the oxidation of tCbz-mPYR with oxone proceeded in DMF at 80 °C to provide the 2-methylsulfonyl derivative 3 in 92% yield. Then, treatment of compound 3 with NaCN or 4-(tert-butyl)thiophenol led to the formation of the 2-cyano- and 2-(4-tert-butylphenylthio) derivatives 4 and 5 in 65% and 77% yield, respectively. Finally, compound 5 in the reaction with oxone furnished 2-(4-tert-butylphenylsulfonyl) derivative 6 in reasonable 68% yield. <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and HRMS were employed to confirm the structures of the synthesized compounds (see Figures S1–S27 in Supporting Information File 1).
Scheme 1: Synthesis of 4,6-bis(3,6-di-tert-butyl-9H-carbazol-9-yl)-5-methyl-2-substituted pyrimidines 1–6. Reagents and conditions: i – Raney Ni, MeOH, 90 °C, 2 h; ii – arylboronic acid (1.3 equiv), Pd(PPh$_3$)$_4$ (5 mol %), Cs$_2$CO$_3$ (2 equiv; 1 equiv in case of meta-substituted boronic acids), copper(I) 3-methylsalicylate (2.2 equiv), dioxane, 130 °C, 4 h, argon; iii – oxone (2.5 equiv), DMF, 80 °C, 3 h; iv – NaCN (2.2 equiv), THF, reflux, 3.5 h; v – 4-t-BuC$_6$H$_4$SH (1.1 equiv), Et$_3$N (1.1 equiv), THF, 50 °C, overnight, argon.

R = H (a, 48%), 4-CN (b, 35%); 3-CN (c, 19%), 3-Br (d, 55%)

1 (16%) → i → tCbz-mPYR → ii → 2a–d → iii → CN

4 (65%) → iv → 3 (92%)

3 (92%) → v → 5 (77%)

5 (77%) → ii → 6 (68%)
DFT analysis
To assess the structural and electronic properties of the chromophores tCbz-mPYR and 1–6, quantum chemical calculations were performed. DFT analysis revealed that all studied compounds were of similar molecular geometry with partially twisted carbazole units (in the order of 45–47°). The steric hindrance between the carbazole fragments and the pyrimidine core was enhanced by introducing a methyl group in position 5 of the latter [29], enabling sufficient HOMO–LUMO decoupling. Single-bonded phenyl substituents (compounds 2a–d) are almost coplanar with the pyrimidine core (dihedral angle 0.5–1.5°), while a phenyl group connected with the pyrimidine ring via a sulfur atom (compounds 5 and 6) is twisted out of the pyrimidine plane and is not conjugated with the pyrimidine ring. Despite the similar molecular structures, the studied chromophores showed somewhat different electronic properties, mainly due to the variation of the acceptor structure. The DFT computed spatial distribution of frontier molecular orbitals (FMOs) of compounds tCbz-mPYR and 1–6 is presented in Figure 2. A comparison of the electronic structures revealed that the electron density distribution in the HOMO is rather similar for all molecules and tended to localize on the electron-donat-

<table>
<thead>
<tr>
<th>compound</th>
<th>HOMO</th>
<th>LUMO</th>
<th>compound</th>
<th>HOMO</th>
<th>LUMO</th>
</tr>
</thead>
<tbody>
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<td><img src="image1" alt="HOMO" /> <img src="image2" alt="LUMO" /></td>
<td><img src="image3" alt="HOMO" /> <img src="image4" alt="LUMO" /></td>
<td>2d</td>
<td><img src="image5" alt="HOMO" /> <img src="image6" alt="LUMO" /></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td><img src="image7" alt="HOMO" /> <img src="image8" alt="LUMO" /></td>
<td><img src="image9" alt="HOMO" /> <img src="image10" alt="LUMO" /></td>
<td>3</td>
<td><img src="image11" alt="HOMO" /> <img src="image12" alt="LUMO" /></td>
<td></td>
</tr>
<tr>
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<td><img src="image13" alt="HOMO" /> <img src="image14" alt="LUMO" /></td>
<td><img src="image15" alt="HOMO" /> <img src="image16" alt="LUMO" /></td>
<td>4</td>
<td><img src="image17" alt="HOMO" /> <img src="image18" alt="LUMO" /></td>
<td></td>
</tr>
<tr>
<td>2b</td>
<td><img src="image19" alt="HOMO" /> <img src="image20" alt="LUMO" /></td>
<td><img src="image21" alt="HOMO" /> <img src="image22" alt="LUMO" /></td>
<td>5</td>
<td><img src="image23" alt="HOMO" /> <img src="image24" alt="LUMO" /></td>
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</tr>
<tr>
<td>2c</td>
<td><img src="image25" alt="HOMO" /> <img src="image26" alt="LUMO" /></td>
<td><img src="image27" alt="HOMO" /> <img src="image28" alt="LUMO" /></td>
<td>6</td>
<td><img src="image29" alt="HOMO" /> <img src="image30" alt="LUMO" /></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 2:** HOMO and LUMO spatial distributions of carbazole–pyrimidine TADF compounds.
ing carbazole moiety partially extending to the pyrimidine ring. The main differences in the electronic structure can be observed in the LUMO distribution. For the 2-methylthio- and 2-(tert-butylphenyl)thio-substituted compounds (tCbz-mPYR and 5) or the corresponding sulfonyl derivatives (3 and 6), the LUMO is localized over the electron-withdrawing pyrimidine unit with low extension to tCbz, being very similar to the LUMO distribution for pyrimidine derivative 1 without a substituent at the position 2 of the pyrimidine ring. The π-electron density distribution in the LUMO of compounds bearing a phenyl (2a), para/meta-cyanophenyl, and meta-bromophenyl moiety (2b–d) at position 2 of the pyrimidine ring tends to localize over the pyrimidine ring and nearby phenyl groups, resulting in a lower HOMO–LUMO overlap. A similar LUMO localization is observed for compound 4 with a 2-cyano group.

The energies of the HOMO level were in the range from −5.50 eV to −5.70 eV with lower values for those compounds bearing electron-withdrawing groups (Table 1). The LUMO energies varied from −1.38 eV for compound 5 with a phenylthio group to −2.15 eV for compound 2b bearing a p-cyanophenyl group in position 2 of the pyrimidine ring. The S0 → S1 transition energies ranged from 3–3.4 eV with lower values for the CN/Br/phenyl-substituted compounds due to the larger conjugation length of the acceptor unit (also evidenced by larger FWHM values of fluorescence spectra for compounds with stronger CT emission (e.g., compounds 1 and 4). The phosphorescence (PH) spectra of the carbazole–pyrimidine TADF compounds were rather intriguing. 10 K PH spectra of compounds tCbz-mPYR, 1, 3, 5, and 6 clearly resembled that of individual tCbz units, peaking at about 418 nm [29], while for the rest of the compounds the PH spectra were red-shifted, though still maintaining the vibronic structure. However, the closer inspection of the PH spectra, see Figure S29 in Supporting Information File 1, revealed that all PH spectra coincided with that of the tCbz unit. Actually, the lowest-energy 0–0’ vibronic peak was of very low intensity for compounds 2a–d or 4 as well as the intensity ratio of high-energy replicas was also different, though the T1 energy was the same for all carbazole–pyrimidine compounds. The compounds 2a–d and 4 have one common feature, namely, their acceptor unit is modified with various phenyl-like fragments, increasing the flexibility of the molecular structure, probably altering the electron–vibronic coupling. A similar behavior was observed

Table 1: DFT computed S0→S1 transition energies, oscillator strengths of S0→S1 transitions, and ΔEST values of carbazole–pyrimidine TADF compounds.

<table>
<thead>
<tr>
<th>Compd.</th>
<th>fS0→S1</th>
<th>E S0→S1 (eV)</th>
<th>E S0→T1 (eV)</th>
<th>ΔE S1T1 (meV)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>tCbz-mPYR</td>
<td>0.3940</td>
<td>3.4265</td>
<td>3.1380</td>
<td>289</td>
<td>−5.53</td>
<td>−1.42</td>
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<tr>
<td>1</td>
<td>0.3999</td>
<td>3.4508</td>
<td>3.1400</td>
<td>311</td>
<td>−5.53</td>
<td>−1.39</td>
</tr>
<tr>
<td>2a</td>
<td>0.0383</td>
<td>3.4094</td>
<td>2.9911</td>
<td>418</td>
<td>−5.51</td>
<td>−1.52</td>
</tr>
<tr>
<td>2b</td>
<td>0.0360</td>
<td>2.9562</td>
<td>2.7535</td>
<td>203</td>
<td>−5.61</td>
<td>−2.15</td>
</tr>
<tr>
<td>2c</td>
<td>0.0473</td>
<td>3.1616</td>
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<td>261</td>
<td>−5.57</td>
<td>−1.89</td>
</tr>
<tr>
<td>2d</td>
<td>0.0465</td>
<td>3.2820</td>
<td>2.9518</td>
<td>330</td>
<td>−5.55</td>
<td>−1.71</td>
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<tr>
<td>3</td>
<td>0.3959</td>
<td>3.2132</td>
<td>2.9251</td>
<td>288</td>
<td>−5.66</td>
<td>−1.79</td>
</tr>
<tr>
<td>4</td>
<td>0.0496</td>
<td>3.0245</td>
<td>2.7858</td>
<td>239</td>
<td>−5.70</td>
<td>−2.09</td>
</tr>
<tr>
<td>5</td>
<td>0.4100</td>
<td>3.4377</td>
<td>3.1390</td>
<td>299</td>
<td>−5.50</td>
<td>−1.38</td>
</tr>
<tr>
<td>6</td>
<td>0.3779</td>
<td>3.2706</td>
<td>2.9864</td>
<td>284</td>
<td>−5.63</td>
<td>−1.71</td>
</tr>
</tbody>
</table>

*S0→S1 transition oscillator strength; *S0→S1 transition energies; *S0→T1 transition energies; *Singlet–triplet energy gap; *HOMO energies; *LUMO energies.
for similar pyrimidine TADF compounds [42]. Moreover, fluorescence line shapes of compounds 2a and 2d were different from the rest of compounds with low-energy shoulder. More detailed analysis (see Figure S30 in Supporting Information File 1) revealed the presence of room-temperature phosphorescence (RTP), perturbing the lineshape of PL spectra. The estimated singlet-triplet energy gaps ($\Delta E_{ST}$) of carbazole–pyrimidine TADF compounds were in the range of 159–530 meV, systematically decreasing for compounds with stronger acceptor unit (see Figure S28d in Supporting Information File 1). $\Delta E_{ST}$ was large for the majority of compounds, however, for compounds 2b, 3, 4, and 6 modified with CN and SO$_2$CH$_3$ groups $\Delta E_{ST}$ was as low as 159 meV, promising for efficient thermally activated triplet upconversion.

Fluorescence decay transients of 1 wt % PMMA films of carbazole–pyrimidine TADF compounds are shown in Figure 4. Typical for TADF compounds temporal profiles having two decay regimes were observed when the initial decay was of prompt fluorescence and the latter one was of TADF. The PF decay rate ($1\text{–}4 \times 10^8 \text{ s}^{-1}$) was typical for directly bound carbazole–pyrimidine TADF compounds [43,44], though a somewhat lower value was estimated for compound 3 modified with a methylsulfonyl group. More insights could be drawn by analyzing the fluorescence quantum yield ($\Phi_F$) as well as radiative ($k_r$) and non-radiative ($k_{nr}$) fluorescence decay rates (see Table 2). The $\Phi_F$ was typical for carbazole–pyrimidine TADF compounds [31,43,44], in the range of 0.01–0.07 and decreased for compounds with stronger acceptor units (see Figure S28b in Supporting Information File 1). The radiative decay rate was in the range of $1.3\text{–}13.0 \times 10^6 \text{ s}^{-1}$. Typically, $k_r$ was larger for compounds with weaker acceptor units and a lower CT fluorescence strength (see Figure S28c in Supporting Information File 1). In case of $k_{nr}$, a similar analysis is hardly possible, as $k_{nr}$ accounts for two different rates, namely internal conversion to $S_0$ and intersystem crossing. However, some faint trends could be seen, as compounds with the strongest donor units tend to have the larger $k_{nr}$ (compounds 2b–d).

In case of delayed fluorescence, more complicated fluorescence temporal profiles were observed, aggravating its analysis. DF decay transients were perturbed by conformational disorder, typical for D–A TADF compounds in solid films [41,45–47]. The presence of conformational disorder made exponential fitting of DF transients hardly possible due to the multieponential temporal profiles of the DF decay. Unfortunately, TADF decay rates were inaccessible. Similar emission decay transients were also estimated for RTP compounds 2a and 2d both at singlet and triplet emission peaks (see Figure S31 in Supporting Information File 1). The largest DF quantum yield, ranging from 0.34–0.49, was estimated for compounds tCzb-mPYR, 3, and 4 with the lowest $\Delta E_{ST}$, modified with CN, SCH$_3$, and SO$_2$CH$_3$ functional groups directly at the pyrimidine unit. The introduction of phenyl substituents (compounds 2a–d) or S-aryl units (compounds 5 and 6) at position 2 of the pyrimidine ring
Table 2: Fluorescence parameters of carbazole–pyrimidine TADF compounds.

<table>
<thead>
<tr>
<th>Compd.</th>
<th>λ_{abs} (nm)^a</th>
<th>ε (M(^{-1})cm(^{-1}))(^b)</th>
<th>λ_{PL} (nm)</th>
<th>Φ_{PF}^d</th>
<th>Φ_{DF}^e</th>
<th>(k_{DF} \times 10^8) s(^{-1})</th>
<th>(k_{k} \times 10^6) s(^{-1})</th>
<th>(k_{nr} \times 10^8) s (\Phi_{DF}/\Phi_{PF}^i)</th>
<th>ΔE_{ST} (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>tCbz-mPYR</td>
<td>339</td>
<td>22000</td>
<td>415</td>
<td>0.05</td>
<td>0.40</td>
<td>2.5</td>
<td>13.0</td>
<td>2.4</td>
<td>8.0</td>
</tr>
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<td>33420</td>
<td>411</td>
<td>0.07</td>
<td>0.11</td>
<td>1.4</td>
<td>9.3</td>
<td>1.3</td>
<td>1.6</td>
</tr>
<tr>
<td>2a</td>
<td>339</td>
<td>29100</td>
<td>411</td>
<td>0.03</td>
<td>0.06</td>
<td>2.1</td>
<td>6.8</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>2b</td>
<td>339</td>
<td>34200</td>
<td>468</td>
<td>0.01</td>
<td>0.24</td>
<td>3.1</td>
<td>3.0</td>
<td>3.1</td>
<td>24.0</td>
</tr>
<tr>
<td>2c</td>
<td>339</td>
<td>28700</td>
<td>410</td>
<td>0.01</td>
<td>0.18</td>
<td>3.0</td>
<td>3.7</td>
<td>3.0</td>
<td>18.0</td>
</tr>
<tr>
<td>2d</td>
<td>339</td>
<td>30700</td>
<td>447</td>
<td>0.01</td>
<td>0.05</td>
<td>4.2</td>
<td>2.4</td>
<td>4.1</td>
<td>5.0</td>
</tr>
<tr>
<td>3</td>
<td>357</td>
<td>23000</td>
<td>440</td>
<td>0.06</td>
<td>0.49</td>
<td>0.7</td>
<td>4.0</td>
<td>0.6</td>
<td>8.2</td>
</tr>
<tr>
<td>4</td>
<td>358</td>
<td>19700</td>
<td>460</td>
<td>0.01</td>
<td>0.34</td>
<td>1.1</td>
<td>1.3</td>
<td>1.0</td>
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</tr>
<tr>
<td>5</td>
<td>341</td>
<td>27400</td>
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<tr>
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<td>355</td>
<td>23000</td>
<td>441</td>
<td>0.04</td>
<td>0.02</td>
<td>1.2</td>
<td>5.1</td>
<td>1.1</td>
<td>0.5</td>
</tr>
</tbody>
</table>

^a Absorption peak in toluene; \(^b\) Molar absorption coefficient in toluene; \(^c\) Fluorescence peak in 1 wt % PMMA; \(^d\) Prompt fluorescence quantum yield 1 wt % PMMA; \(^e\) Delayed fluorescence quantum yield 1 wt % PMMA; \(^f\) Fluorescence decay rates 1 wt % PMMA; \(^g\) Radiative decay rates 1 wt % PMMA; \(^h\) Nonradiative decay rates 1 wt % PMMA; \(^i\) Prompt and delayed fluorescence quantum yield ratio 1 wt % PMMA; \(^j\) Singlet–triplet energy gap 1 wt % PMMA.

Figure 4: Fluorescence decay transients of 1 wt % PMMA films of carbazole–pyrimidine TADF compounds in oxygen-free conditions.

led to lower Φ_{DF}, probably due to the enlarged nonradiative decay rate. Interestingly, ΔE_{ST} was remarkably larger for tCbz-mPYR despite its high Φ_{DF}. In this case, rISC probably was promoted by efficient triplet upconversion through spin-vibronically bound T\(_n\) energy levels [48].

Conclusion

In summary, a series of novel pyrimidine–carbazole TADF emitters bearing different substituents in position 2 of the pyrimidine moiety were successfully prepared by using Liebeskind–Srogl cross-coupling, hydrogenolysis, oxidation reactions of 4,6-bis(3,6-di-tert-butyl-9-carbazolyl)-5-methyl-2-methylthiopyrimidine and following nucleophilic substitution of the methylsulfonyl group with sodium cyanide and 4-(tert-butyl) thiophenol. The thorough photophysical analysis was carried out to assess the impact of different substituents in position 2 of the pyrimidine ring. It was shown that HOMO–LUMO overlap and the resulting ΔE_{ST} can be easily minimized, enabling rather efficient TADF. We have shown that electron-withdrawing substituents connected directly to the pyrimidine unit have a larger impact on TADF efficiency in comparison with those attached through a phenylene bridge. The largest delayed fluorescence quantum yield, ranging from 0.34–0.49, was estimated for compounds with CN, SCH\(_3\), and SO\(_2\)CH\(_3\) functional groups at the position 2 of the pyrimidine unit. We believe that our findings on the TADF properties of
differently substituted carbazole–pyrimidines will be useful for molecular design of high-performance TADF emitters in the future.

**Experimental**

**General information**

Reagents and solvents were purchased directly from commercial suppliers and solvents were purified by known procedures. Melting points were determined in open capillaries with a digital melting point IA9100 series apparatus (ThermoFischer Scientific) and were not corrected. Thin-layer chromatography was performed using TLC aluminum sheets with silica gel (Merck 60 F254). Visualization was accomplished by UV light. Column chromatography was performed using silica gel 60 (0.040–0.063 mm, Merck). NMR spectra were recorded on a Bruker Ascend 400 (400 MHz and 100 MHz for $^1$H and $^{13}$C, respectively). $^1$H NMR and $^{13}$C NMR spectra were referenced to residual solvent peaks. High-resolution mass spectrometry (HRMS) analyses were carried out on a Dual-ESI Q-TOF 6520 (Agilent Technologies) mass spectrometer.

Photophysical properties were analyzed in $10^{-5}$ M toluene solutions as well as 1 wt % PMMA (poly(methyl methacrylate)) films. The solid-state samples were prepared by dissolving the compounds and polymer or host material at appropriate ratios in toluene solution and then wet-casting the solutions on quartz substrates. The absorption spectra were recorded by a Lambda 950 UV–vis–NIR spectrometer (Perkin Elmer). The fluorescence quantum yields ($\Phi_F$) in ambient air were estimated by the integrating sphere method [49] in integrating sphere (Sphere Optics) coupled to a CCD spectrometer PMA-12 (Hamamatsu) via optical fibers excited with a CW xenon lamp. $\Phi_F$ and $\Phi_{PF}$ values were estimated according to [50]. Time-integrated fluorescence, phosphorescence spectra as well as fluorescence decay kinetics were recorded with a time-gated intensified iCCD camera iStar DH340T (Andor) with a spectrograph SR-303i (Shamrock) coupled with nanosecond YAG:Nd$^{3+}$ laser NT 242 with an optical parametric generator (Ekspla, pulse width 7 ns, 1 kHz frequency, 100 nJ pulse energy). Fluorescence decay transients were obtained by exponentially increasing the delay and integration time [51]. Phosphorescence spectra were recorded at 10 K temperature after a 100 μs delay with a 49 ms integration time. Solid-state samples were mounted in a closed cycle He cryostat (Cryo Industries 204 N) for PL measurements in oxygen-free conditions.

Quantum chemical calculations were carried out by using density functional theory at the B3LYP/6-31G(d) level as implemented in a software package Gaussian 09 [52]. The solvation behaviour of the surrounding toluene was estimated by the polarizable continuum model. Although the B3LYP/6-31G(d) theory level due to the neglected long-range exchange interaction can give less accurate results for calculated molecular geometries and transition energies [53], however, it should be sufficient for brief analysis.

**Procedures and product characterization**

4,6-Bis[3,6-di(tert-butyl)-9H-carbazol-9-yl]-5-methylpyrimidine (1). Compound 1 was synthesized in a manner similar to [30]. A mixture of compound tCbz-mPyR (90 mg, 0.13 mmol, 1 equiv), Raney nickel (270 mg, 3 equiv by mass), prepared before reaction according to [54], and methanol (3 mL) were placed in a screw-cap vial equipped with a magnetic stirring bar. The reaction mixture was heated at 90 °C under stirring for 2 h. Then, Raney nickel was filtered off and washed with hot chloroform. The filtrate was concentrated and the obtained residue was purified by column chromatography using chloroform/petroleum ether 2:1 to pure chloroform as an eluent to give 13.5 mg (16%) of compound 1. Mp > 300 °C (from 2-propanol); $^1$H NMR (400 MHz, CDCl$_3$) δ 1.52 (s, 36H, (CH$_3$)$_3$), 2.01 (s, 3H, CH$_3$), 7.48 (d, J = 8 Hz, 4H, CH$_{Cbz}$), 7.62 (d, J = 8 Hz, 4H, CH$_{Cbz}$), 8.18 (s, 4H, CH$_{Cbz}$), 9.23 (s, 1H, CH$_p$) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 15.2, 31.9, 34.9, 110.7, 116.6, 121.8, 124.2, 124.7, 137.8, 144.6, 157.1, 160.2 ppm; HRMS–ESI (m/z): [M + H]$^+$ calcd for C$_{45}$H$_{55}$N$_4$, 649.4265; found, 649.4265.

2-Aryl-4,6-bis[3,6-di(tert-butyl)-9H-carbazol-9-yl]-5-methylpyrimidines 2a–d

**General procedure.** 4,6-Bis(3,6-di-tert-butyl-carbazol-9-yl)-5-methyl-2-methylthiopyrimidine (50 mg, 0.072 mmol), the corresponding boronic acid (0.094 mmol), CuMeSal (34 mg, 0.158 mmol), Pd(PPh$_3$)$_4$ (4.2 mg, 0.0036 mmol), Cs$_2$CO$_3$ (46.8 mg, 0.144 mmol, in case of meta-substituted boronic acid, 1 equiv) and dioxygen (3 mL) were placed in a screw-cap vial equipped with a magnetic stirring bar and flushed with argon for 10 min. The reaction mixture was heated at 130 °C under stirring for 4 h. Then, dioxygen was removed by distillation under reduced pressure, water (40 mL) was added to the residue, and the mixture was extracted with chloroform (3 × 25 mL). The combined extracts were washed with brine, dried with anhydrous Na$_2$SO$_4$, filtered, and chloroform was removed by distillation under reduced pressure. The residue was purified by column chromatography using chloroform/petroleum ether (1:1 for compound 2a; 1:2 for compounds 2b, 2c; 1:4 for compound 2d) as an eluent to give the corresponding product.

4,6-Bis[3,6-di(tert-butyl)-9H-carbazol-9-yl]-5-methyl-2-phenylpyrimidine (2a). Yield 48%; mp > 320 °C (from 2-propanol); $^1$H NMR (400 MHz, CDCl$_3$) δ 1.54 (s, 36H, (CH$_3$)$_3$), 7.52–7.59 (m, 7H, ArH, CH$_{Cbz}$) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) ppm; 1.52 (s, 36H, (CH$_3$)$_3$); 7.48 (d, J = 8 Hz, 4H, CH$_{Cbz}$), 7.62 (d, J = 8 Hz, 4H, CH$_{Cbz}$), 8.18 (s, 4H, CH$_{Cbz}$), 9.23 (s, 1H, CH$_p$) ppm; HRMS–ESI (m/z): [M + H]$^+$ calcd for C$_{45}$H$_{55}$N$_4$, 649.4265; found, 649.4265.
4.6-Bis[3,6-di-(tert-butyl)-9H-carbazol-9-yl]-2-(4-cyano-phenyl)-5-methylpyrimidine (2b). Yield 35%; mp 266–270 °C (from 2-propanol); 1H NMR (400 MHz, CDCl3) δ 8.54 (s, 36H, (CH3)3C), 2.00 (s, 3H, CH3), 7.54 (d, J= 8.61 Hz, 4H, CHCbz), 7.64 (dd, J= 8.61 Hz, J= 1.69 Hz, 4H, CHCbz), 7.82 (d, J= 8.35 Hz, 2H, ArH), 8.21 (d, J= 1.61 Hz, 4H, CHCbz), 8.70 (d, J= 8.35 Hz, 2H, ArH) ppm; 13C NMR (100 MHz, CDCl3) δ 15.2, 32.0, 34.9, 39.4, 111.2, 116.5, 124.0, 124.6, 128.4, 128.7, 131.1, 136.9, 137.9, 144.4, 160.2, 163.0 ppm; HRMS–ESI (m/z): [M + H]+ calcd for C55H56N6S, 725.4578; found, 725.4576.

4.6-Bis[3,6-di-(tert-butyl)-9H-carbazol-9-yl]-2-(3-cyano-phenyl)-5-methylpyrimidine (2c). Yield 19%; mp 233–236 °C from 2-propanol); 1H NMR (400 MHz, CDCl3) δ 1.56 (s, 36H, (CH3)3C), 1.95 (s, 3H, CH3), 7.43 (d, J= 8.0 Hz, 1H, ArH), 8.77 (s, 1H, ArH) ppm; 13C NMR (100 MHz, CDCl3) δ 15.4, 32.0, 34.9, 110.9, 114.3, 116.7, 118.9, 119.7, 124.1, 124.7, 128.8, 132.6, 137.7, 140.9, 144.7, 160.5 ppm; HRMS–ESI (m/z): [M + H]+ calcd for C55H56N6S, 725.4578; found, 725.4576.

4.6-Bis[3,6-di-(tert-butyl)-9H-carbazol-9-yl]-2-(3-bromo-phenyl)-5-methylpyrimidine (2d). Yield 55%; mp > 250 °C; 1H NMR (400 MHz, CDCl3) δ 1.54 (s, 36H, (CH3)3C), 1.95 (s, 3H, CH3), 7.40 (t, J= 7.88 Hz, 1H, ArH), 7.53 (d, J= 8.6 Hz, 4H, CHCbz), 7.63 (dd, J= 8.68 Hz, J= 1.92 Hz, 4H, CHCbz), 7.67 (m, 1H, ArH), 8.20 (d, J= 1.64 Hz, 4H, CHCbz), 8.53 (dt, J= 8.0 Hz, J= 1.24 Hz, 1H, ArH), 8.72 (t, J= 1.72 Hz, 1H, ArH) ppm; 13C NMR (100 MHz, CDCl3) δ 15.2, 32.0, 34.9, 110.9, 116.6, 119.2, 123.0, 124.1, 124.6, 127.0, 130.3, 131.2, 134.0, 137.8, 139.0, 144.5, 160.4, 161.7 ppm; HRMS–ESI (m/z): [M + H]+ calcd for C51H58BrN4S, 803.3683; found, 803.3675.

4.6-Bis[3,6-di-(tert-butyl)-9H-carbazol-9-yl]-5-methyl-2- methylsulfonylpyrimidine (3). A mixture of compound 1CbzMpyr (60 mg, 0.086 mmol), oxone (133.2 mg, 0.217 mmol, 2.5 equiv by active component), and DMF (3 mL) were stirred at 80 °C for 3 h. After completion of the reaction, water (40 mL) was added to reaction mixture and the aqueous solution was extracted with chloroform (3 × 25 mL). The combined extract was washed with brine twice, dried with anhydrous Na2SO4, filtered, and chloroform was removed by distillation under reduced pressure. The residue was purified by column chromatography using chloroform/petroleum ether 2:1 as an eluent to give 58 mg (92%) of compound 3. Mp > 350 °C (from 2-propanol); 1H NMR (400 MHz, CDCl3) δ 1.52 (s, 36H, (CH3)3C), 2.03 (s, 3H, CH3), 3.45 (s, 3H, CH3SO2), 7.54 (d, J= 8.65 Hz, 4H, CH), 7.64 (dd, J= 8.67 Hz, J= 1.89 Hz, 4H, CH), 8.15 (d, J= 1.68 Hz, 4H, CH) ppm; 13C NMR (100 MHz, CDCl3) δ 16.5, 31.9, 34.9, 39.4, 111.2, 116.7, 122.6, 124.4, 125.2, 137.3, 145.6, 160.8, 162.5, 163.8 ppm; HRMS–ESI (m/z): [M + H]+ calcd for C46H32N4O3S, 727.4040; found, 727.4034.

4.6-Bis[3,6-di-(tert-butyl)-9H-carbazol-9-yl]-5-methylpyrimidine-2-carbonitrile (4). A mixture of compound 3 (50 mg, 0.069 mmol), NaN3 (7.4 mg, 0.151 mmol), and THF (2 mL) was refluxed under stirring for 3.5 h. After completion of the reaction, THF was removed by distillation under reduced pressure, water (30 mL) was added to the residue, and the aqueous solution was extracted with chloroform (3 × 25 mL). The combined extract was washed with brine, dried with anhydrous Na2SO4, filtered, and chloroform was removed by distillation under reduced pressure. The residue was purified by column chromatography using chloroform/petroleum ether 1:2 as an eluent to give 30 mg (65%) of compound 4. Mp > 320 °C (from 2-propanol); 1H NMR (400 MHz, CDCl3) δ 1.43 (s, 36H, (CH3)3C), 1.92 (s, 3H, CH3), 7.40 (d, J= 8.63 Hz, 4H, CHCbz), 7.55 (dd, J= 8.66 Hz, J= 1.93 Hz, 4H, CHCbz), 8.07 (d, J= 1.67 Hz, 4H, CHCbz) ppm; 13C NMR (100 MHz, CDCl3) δ 16.4, 31.9, 34.9, 111.0, 115.4, 116.8, 123.8, 124.3, 125.1, 137.2, 142.4, 145.6, 160.7 ppm; HRMS–ESI (m/z): [M + H]+ calcd for C46H32N3S, 674.4217; found, 674.4213.
4,6-Bis[3,6-dit(tert-butyl)-9H-carbazol-9-yl]-2-[4-(tert-butyl)phenylsulfonyl]-5-methylpyrimidine (6). Compound 6 was synthesized from compound 5 according to the procedure described for compound 3.

References

Post-synthesis from Lewis acid–base interaction: an alternative way to generate light and harvest triplet excitons

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Review

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Abstract

The changes in absorption and emission of fluorescent materials with the introduction of Lewis acids have been frequently observed due to either physical or chemical interactions. In this mini-review, we elaborate how Lewis acids adjust the optical properties and the bandgap of luminescent materials by simple coordination reactions. It is common that fluorescent materials containing Lewis basic nitrogen heterocycles are more likely to provide the feasible band gap modulation. The essence of such phenomenon originates from Lewis acid–base coordination and adducts, which highly depends on the electron-accepting property of the Lewis acids. This intermolecular mechanism, considered as post-synthesis of new luminescent compounds offers promising applications in sensing and electroluminescence by manipulating the frontier molecular orbital energy levels of organic conjugated materials, simply based on Lewis acid–base chemistry.

Introduction

Organic light emitting diodes (OLEDs) show great potential to dominate the next generation of flat-panel displays and efficient light sources attributed to the advantages of self-illumination, high efficiency, wide color gamut, and flexibility [1-3]. In OLEDs photons are mainly generated by radiative recombination in the emitting layer [4]. Therefore, the development of efficient luminescent materials and the exploration of new luminescent mechanisms are one of the core tasks in academic research. The most common luminescent materials are fluorescent compounds. Based on the spin statistics, the fluorescent emitters can only use singlet excitons for light generation [5]. In contrast, phosphorescent materials based on metal complexes
could achieve a high internal quantum efficiency (IQE) up to 100% through intersystem crossing (ISC) [6, 7]. In 2012, Adachi et al. first reported purely organic thermally activated delayed fluorescent (TADF) materials, which achieved nearly 100% exciton utilization via reverse intersystem crossing (RISC) [8]. Meanwhile, novel materials based on new luminescence mechanisms such as hybridized local and charge-transfer (HLCT) and doublet emission have been designed and demonstrated [9, 10]. However, the development of these materials often requires complicated molecular design and synthesis [11, 12]. Alternatively, it is also possible to produce light emission by molecular exciplexes composed of multiple molecules [13]. The exciplex contains new excited states through charge transfer between a donor molecule and an acceptor molecule. This provides a simple way to create new luminescence processes through the intermolecular interactions of existing molecules [14].

It has been reported that new emitters can be realized by adding a Lewis acid to a fluorescent conjugated compound [15, 16]. Lewis acids are common complexing agents [17] and are frequently used to dope conjugated polymers to enhance their conductivity while the luminescence is completely quenched [18, 19]. In contrast, in the presence of nitrogen-containing heterocycles in the fluorescent materials, the addition of a Lewis acid tended to induce red-shifted absorption and emission, shedding light on the fact that the Lewis acid interacts easily with the nitrogen-containing fluorescent materials. This interaction mechanism is the coordination between Lewis acids and bases, which can finely adjust the optoelectronic properties of the fluorescent molecules, such as band gaps, peak wavelengths, and even frontier molecular orbitals if bound together [20]. The traditional way to manipulate the optoelectronic properties of the emitters highly depends on the molecular design and structures, including linkers, donor and acceptor units, which requires complex and time-consuming molecular synthesis and optimization [21-23]. In contrast, the introduction of specific Lewis acid–base pairs in existing molecules can be utilized to achieve brand new luminescent properties. In this mini-review, we summarize unique electron donor and acceptor materials which regulate luminescent properties via Lewis acid–base interactions and briefly explain the exploration of their chemical nature and interaction mechanisms.

Review

Lewis acids as electron acceptors

Some Lewis acids have good solubility in common organic solvents, which makes it easy to fabricate films for optoelectronic applications [24]. Because of their strong electrophilicity [25], Lewis acids may dominate charge distributions of the fluorescent materials featured with electron-rich nitrogen-containing heterocycles, resulting in the change of energy levels and spectra. The following will illustrate Lewis acids used in the exploration of luminescent materials and mechanisms due to Lewis acid–base interactions. The chemical structures of some candidate Lewis acids are shown in Figure 1.

In 2002, Monkman reported the addition of camphor sulfonic acid (CSA) to the fluorescent polymer poly{2,5-pyridylene-co-1,4-[2,5-bis(2-ethylhexyloxy)phenylene]} (compound 1 in Figure 2) containing pyridine groups led to the protonation effect [26]. CSA has strong acidity and low volatility, which is feasible to be bound with pyridine groups. As shown in Figure 3a, the protonation by CSA resulted in a significant red-shift in the photoluminescence (PL) spectrum, which was simi-
Figure 2: Chemical structures of Lewis basic fluorescent polymer poly(2,5-pyridylene-co-1,4-[2,5-bis(2-ethylhexyloxy)]phenylene) 1 and D–A–D compound 2,5-bis([N,N-diphenylamino)phenyl]thiazolothiazole 2.

Figure 3: (a) Normalized PL spectra of films with compound 1 doped with different Lewis acids. (b) PL spectra of compound 2 under different acid conditions in dichloromethane. (c) EL spectra of devices with compound 2 doped with CSA at different concentrations. Figure 3a was reprinted with permission from [26], Copyright 2002 American Chemical Society. This content is not subject to CC BY 4.0. Figure 3b and 3c were reproduced from [27] with permission from The Royal Society of Chemistry. This content is not subject to CC BY 4.0.

lar to the cases caused by other Lewis acids such as methanesulfonic acid (MSA) and dichloracetic acid (DCA). Wang et al. used HCl, TFA, and BBr3 as dopants which were respectively added to the donor–acceptor–donor (D–A–D) molecule 2,5-bis([N,N-diphenylamino)phenyl]thiazolothiazole (compound 2 in Figure 2) containing thiazolothiazole units. As shown in Figure 3b, four different colors ranged from green, yellow, red and NIR regions, i.e., a dramatic wavelength shift of 215 nm [27]. Light-emitting devices were fabricated by adding different concentrations of CSA into the fluorescent compound and a wide range of color tunability was observed in the EL spectra (see Figure 3c).

In 2009, Welch et al. employed the Lewis acid B(C6F5)3 (BCF) to bind to nitrogen atoms at the basic site a of π-conjugated polymer, providing a simple strategy to regulate the optical properties of the A–D–A chromophore with charge transfer excited state properties [28]. In 2019, Wang et al. constructed a novel exciplex system by using the Lewis acids B(C6F5)3 and B(C6H5)3 as electron acceptors, respectively [29]. B(C6F5)3 displays high chemical stability and Lewis acidity [30]. Moreover, its good solubility endows the possibility to form Lewis acid–base adducts in films by solution processing. The strong electron attraction of the fluorine substituents on the benzene rings of B(C6F5)3 is responsible for its stronger Lewis acidity compared to B(C6H5)3, and reacted efficiently with the basic fluorescent materials.

In 2011, Hayashi investigated the modification of pyridyl-conjugated polymer films with the Lewis acid BF3 [31]. Through repeated acid–base treatment, the polymer film can achieve reversible color changing. Due to the poor solubility, the doped polymer film was simply prepared by BF3 vapor treatment. The schematic diagram is shown in Figure 4. It is clear that the film achieved a gradient of colors from top to bottom under 365 nm UV light, which confirmed that the emission was sensitive to BF3 concentration. Yang et al. used also TFA to shape the fluorescence emission based on the protonation effect between the dissociated H+ and the fluorescent material [32].
Lin et al. used the Lewis acids B(C₆F₅)₃ and AlCl₃ to regulate the optoelectronic properties of a fluorene-based copolymer with an sp² nitrogen heteroatom via supramolecular coordination [33]. The PL emission in solution showed an obvious red-shifted profile. The polymer LED with different molar equivalents of Lewis acids was investigated. The EL peak wavelength was gradually red-shifted with increasing the concentration of the Lewis acid, changing from 440 nm to 520 nm. In order to further explore the doping mechanism of Lewis acid on organic semiconductors, Yurash et al. found that B(C₆F₅)₃ possessed the best doping effect and thus increased the conductivity, compared with BF₃, BBr₃, and AlCl₃, respectively, mixed in the low bandgap conjugated polymer materials. This is ascribed to the formation of Lewis acid–base adducts [34].

Fluorescent materials as electron donors

Hancock et al. compared the PL and EL spectra of the π-conjugated heterocyclic oligomer 6,6'-bis(2-(1-pyrenyl)-4-octylquinoline) (BPYQ, compound 3 in Figure 5), which could be tuned in the whole visible range through the complex reaction...
with CSA [35]. This is supposed to be the first EL example of the protonated organic semiconductor. Compound 3 is an aromatic end-capped oligoquinoline, with both quinoline and pyridine as N-containing heterocycles rich in electrons, which are the key structural factors leading to acid discoloration. At the same time, Kappaun et al. synthesized a series of conjugated alternating and statistical copolymers (poly[2,7-(9,9-dihexylfluorenyl)-alt-(2,6-pyridinyli)]) (compound 4 in Figure 5) and (poly[2,7-(9,9-dihexylfluorenyl)-stat-(2,6-pyridinyli)]) (compound 5 in Figure 5) with pyrene and pyridine units [36]. The pyridine groups in the conjugated polymer contain basic sites presumably induced by nitrogen atoms, where protonation occurred.

In 2012, Zalar et al. synthesized the conjugated polymer F8Py (compound 6 in Figure 5), in which the incorporation of the pyridine co-monomer provides a lone pair of electrons for binding Lewis acids [37]. The formation of acid–base adducts accurately regulated the band gap of the luminescent polymer. The PL spectra in solution showed the evident red-shift upon mixing the polymer with the Lewis acid (Figure 6a). This property was also successfully demonstrated in OLEDs to modify the electroluminescence (EL) characteristics (Figure 6b).

In 2020, Yang et al. designed and synthesized a blue fluorescent material CzPA-F-PD (compound 7 in Figure 5), which consisted of the twisted A–π–D–π–A structure with N-(4-aminophenyl)carbazole (CzPA) as electron donor unit, pyridine as electron acceptor unit, and 9,9-dioctylfluorene (F) as π-conjugated linker [32]. Compound 7 showed remarkable dual-fluorescence properties when mixed with a very small amount of trifluoroacetic acid (TFA). As shown in Figure 6c, the PL spectra in solution were dominated by the amount of TFA. At the appropriate ratio, the solution-processed device with compound 7 as single emission layer generated broadband white light emission under EL process (see Figure 6d).

In 2016, Yamaguchi et al. designed and synthesized a series of 5-N-arylaminothiazoles with 4-pyridyl groups at the 2-position (compounds 8–12 in Figure 5), which behaved as strong Lewis basic sites [38]. After adding BCF to compound 12, a new emission peak was generated in the orange-red region, accom-
Basic nitrogen atoms tend to interact with the Lewis acids, dis- 
cussing in this review and thus lead to a significant shift of their 
optoelectronic properties. It has been confirmed that organic 
molecules containing pyrimidine, pyrazine, and indole groups 
display similar interactions upon the addition of Lewis acids 
[40-42].

**Lewis acid–base interaction mechanisms**

**Chemical essence of Lewis acid–base interaction**

All the above discussed fluorescent materials share the common 
characteristics of Lewis basicity. Therefore, the changes in band 
gaps and colors of the donor materials is essentially attributed to 
a Lewis acid–base complexation reaction. In order to clarify the 
coordination reaction of nitrogen atoms, Bazan’s group de-
signed a conjugated polymer containing pyridine and thiazole 
groups and small molecule 15 (Figure 8) and compared the 
$^1$H NMR spectra and $^19$F NMR spectra after the addition of 
1 equivalent B(C$_6$F$_3$)$_3$ at various temperatures from 230 to 
300 K (see Figure 9) [43].

As shown in Figure 9a, when the temperature reached 280 K, 
the aromatic resonances became intense, implying the appear-
ance of a new species, which was assigned to the Lewis 
acid–base adduct. Fifteen new resonance peaks were also ob-
served in the $^19$F NMR spectrum (see Figure 9b), which were 
different from the same chemical environment of fluorine atoms 
in the original B(C$_6$F$_3$)$_3$. To further explore the interaction of 
the Lewis acid–base pairs, Huang et al. added B(C$_6$F$_3$)$_3$ to pyri-
dine group-capped diketopyrrolopyrrole (DPP) molecules, i.e., 
DPPPy-Py-3F (16), DPPPy-Py-3F (17), and DPPPy-Py-Ph-F (18, 
Figure 8), and determined the $^{11}$B NMR spectra (Figure 9c) 
[44]. When coordinated with nitrogen atoms, the resonance 
peak shifted slightly from ca. −10 to 0 ppm, which suggested the 
interaction between boron and nitrogen atoms.

Wang’s group studied the interaction of compound 14 re-
spectively with B(C$_6$F$_3$)$_3$ and B(C$_6$H$_3$)$_3$ by X-ray photoelec-
troscopy (XPS) [29]. The B(1s) signal showed peaks at 
190.61 and 191.08 eV, respectively. This is close to the re-
ported characteristic B–N binding energy (190.5 eV) in B–N

**Figure 7:** Photos of a solution of compound 12 and B(C$_6$F$_3$)$_3$ at different ratios in toluene under a 365 nm UV lamp. Figure 7 was reproduced from [38] © 2016 K. Yamaguchi et al., published by Wiley-VCH Verlag GmbH & Co. KGaA, distributed under the terms of the Creative Commons Attribution-NonCommercial 4.0 International License, https://creativecommons.org/licenses/by-nc/4.0/. This content is not subject to CC BY 4.0.
crystals. Despite the weak signals of boron in these two Lewis acids, it was assumed that compound 14 formed a B–N coordination bond when doped with B(C$_6$F$_5$)$_3$ and B(C$_6$H$_5$)$_3$, respectively.

**Luminescent mechanisms**
In view of the phenomenon that Lewis acid–base coordination contributes to a decrease of the band gap and bathochromic shifts of absorption and emission, it is essential to explore the
mechanisms. Welch et al. supposed that the strong electrophilic Lewis acid triggers charge transfer with nitrogen-containing heterocycles containing lone-pair electrons. Consequently, it reduces the electron density of the π-conjugated system and the characteristics of the excited states, accounting for the decrease of band gap [27,37,43]. In 2018, Li et al. used density functional theory (DFT) to investigate the energy levels of polymers 19 (P1) and 20 (P2, Figure 10) containing pyrazine groups before and after the addition of B(C₆F₅)₃ (see Figure 11a) [45]. Considering the electrostatic potential surface (EPS) maps (see Figure 11b) of the pyrazine-containing polymers before and after B(C₆F₅)₃ coordination, it is likely that B(C₆F₅)₃ sacrificed the electron density of the polymer skeleton and turned it from an electron-rich to an electron-deficient species. This was assumed to be the reason for the decrease of the band gap. Meanwhile, the LUMO levels estimated from electrochemistry experiments (see Figure 11c and 11d) were also depressed from −3.60 eV (compound 19) to −3.96 eV (compound 19/B(C₆F₅)₃) and from −3.59 eV (compound 20) to −4.12 eV (compound 20/B(C₆F₅)₃), which were consistent with the theoretical calculation results.

Yang and co-workers compared the energy level distributions of the HOMO and LUMO of CzPA-F-PD (compound 7 in Figure 5) before and after protonation, which were diverse [32]. The cyclic voltammogram (CV) curves of CzPA-F-PD and CzPA-F-PD-H⁺ showed that the energy levels of both the HOMO and LUMO of CzPA-F-PD-H⁺ decreased relative to
those of CzPA-F-PD, and the LUMO level decreased more significantly. According to the theoretical calculation results, the HOMO and LUMO distributions of CzPA-F-PD-H⁺ were more spatially separated, the charge transfer characteristics of the excited states turned to be stronger, and the localized excited states characteristics was reduced. The energy level gap between S₁ and T₁ (ΔE_S⁰) of CzPA-F-PD-H⁺ was 0.16 eV, which is significantly lower than the 0.39 eV of CzPA-F-PD [32].

The formation of exciplexes, e.g., with the donor-like 35DCzPPy (compound 14 in Figure 5) and acceptor-like Lewis acids, effectively reduces the energy gap between S₁ and S₀ and thus leads to a red-shift of emission (Figure 12a), as claimed by Xie and Wang’s group [29]. The absorption of both 35DCzPPy:B(C₅F₆)₅ and 35DCzPPy:B(C₆H₄)₃ were nearly identical to that of their constituting materials, which suggested that there existed no new ground-state in the exciplex films (Figure 12b). The reduction of the LUMO energy level would correlate closely with the protonation effect on the pyridine unit of the donor. More importantly, delayed fluorescence profiles of the exciplexes were detected (see Figure 12c, τ₁ = 57.07 ns and τ₂ = 158.20 ns), which proved the possibility to harvest triplet excitons based on Lewis acid–base adducts. Therefore, the OLED using 35DCzPPy:B(C₆F₆)₅ as the emitting layer exhibited a maximum external quantum efficiency of ∼6.2%, surpassing the upper limit (ca. 5%) of the conventional fluorescent material 35DCzPPy [29,39]. As illustrated in Figure 12a, BCF can narrow down the bandgap of the exciplex because of the stronger electrophilicity of the fluorine atoms. Similarly, Yamaguchi et al. used molecular modifications to introduce stronger electron donors to luminescent molecules and obtained stronger spectral changes [38]. This demonstrates that stronger Lewis acids and Lewis bases will result in stronger charge transfer. Moreover, stronger electron donors or more accessible nitrogen-containing groups would interact easily via Lewis acid coordination. As shown in Figure 13b, the energy levels determined from the optimized structures of compounds 21 and 22 (Figure 13a) by DFT suggest that pyridine is a better binding site than thiophene [43].

The effect of steric hindrance on the Lewis acid–base binding should not be ignored. If there is large steric hindrance of the Lewis basic molecules, it will hinder the coordination with a Lewis acid. For example, Bazan’s group investigated the analogous compounds 21 and 22 shown in Figure 13a, featuring the same nitrogen heterocycles but with different steric hindrances. Subsequently, the ability of their coordination with B(C₆F₄)₃ and BBr₃ was compared, respectively [43]. As displayed in Figure 13c and 13d, the UV–vis–NIR absorption spectra manifested that the larger steric hindrance interrupted the binding of BCF more effectively than that of BBr₃.

**Figure 12:** (a) UV–vis absorbance and (b) PL spectra (excited by 330 nm) for 35DCzPPy (compound 14), B(C₆F₄)₃, B(C₅H₅)₂, 35DCzPPy:B(C₅F₆)₅ (1:1), and 35DCzPPy:B(C₆H₄)₃ (1:1) in films. (c) Fluorescence decay curves for the solid films of 35DCzPPy, 35DCzPPy:B(C₆H₄)₃, and 35DCzPPy:B(C₅F₆)₅ recorded at photoluminescence maxima (385, 435, and 509 nm) at room temperature. Figure 12 was reprinted from [29], Chemical Engineering Journal, vol. 380, by M. Zhang; G. Xie; Q. Xue; H. Wang, “Electroluminescence of intra-molecular exciplexes based on novel Lewis acid borane acceptors and a high triplet level donor”, article no. 122527, Copyright (2020), with permission from Elsevier. This content is not subject to CC BY 4.0.
Conclusion

For fluorescent materials containing nitrogen atoms with Lewis basic nature, it is easily found that the addition of suitable Lewis acids can lead to a dramatic red-shift in the absorption and emission of the mixtures. The electrophilic Lewis acid as electron acceptor frequently reacts with the nitrogen-containing heterocyclic conjugated molecules, ascribed to the charge redistributions of the molecules. This governs their optoelectronic properties and most likely rouses the non-radiative triplet excitons of reverse intersystem crossing.

Lewis acid–base chemistry provides a simple and effective way to finely regulate the optoelectronic properties of fluorescent materials, avoiding the complicated molecular synthesis. Lewis acid–base interactions found some promising applications in band gap engineering, photoluminescence, and electroluminescence. The in-depth study of the mechanisms of this phenomenon could inspire the innovation in cutting-edge researches beyond organic light-emitting diodes [29,32], e.g., organic thin-film transistors [45,46], organic photovoltaics [47], and chemical sensing [48].

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References

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