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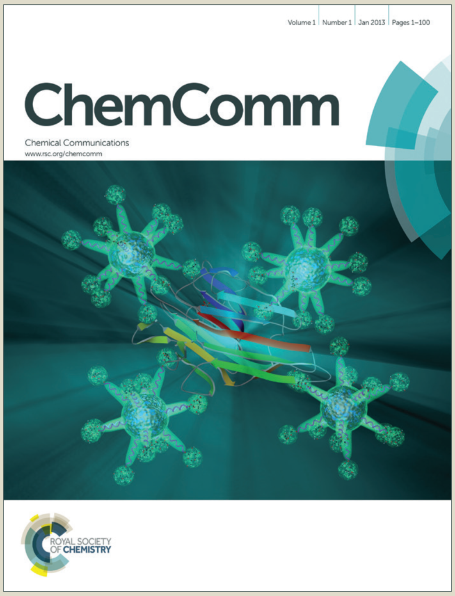

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ARTICLE TYPE

# Excimer Formation in Organic Emitter Films Associated with a Molecular Orientation Promoted by Steric Hindrance

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**White emission with two sharp strong peaks—a molecular emission peak at 455 nm and an excimer emission peak at 591 nm—was obtained by introducing a terphenyl group into a highly twisted core chromophore, which promoted a molecular orientation in the film state suitable for excimer formation.**

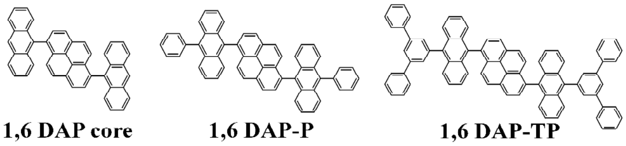
π-Conjugated compounds are useful in a variety of applications, including organic light-emitting diodes (OLEDs)[1], organic thin film transistors (OTFTs)[2], and organic photovoltaic cells (OPVCs)[3]. The key factors that determine their performance in such applications are the molecular structure and the interactions between molecules.[4] Thus, the study of the intermolecular interactions of π-conjugated compounds is very important and has received significant attention.

In the OLED field, excimers commonly result from certain types of intermolecular interactions. Several groups have reported the generation of single molecule white emission using excimers.[5] Excimer emissions typically span a broad wavelength range and are weak signals with intensities similar to those of a shoulder peak. Therefore, in general, clear white emission is difficult to obtain from excimers due to the low intensity of the excimer emission, although excimer emission comes from blue color and the emission is orange color region.

Variable angle spectroscopic ellipsometry (VASE) analysis is useful for determining molecular orientations, given the intermolecular interactions, in a vacuum-deposited film. VASE analysis is integrally related to the molecular structure of the molecules.[6] Previously, we used VASE analysis to characterize the relative orientation of a terphenyl group on a single-core anthracene molecule in a vacuum-deposited film. We found that the orientation of the terphenyl group affects the increased emission efficiency.[7]

In this work, we sought to use molecular orientation effects, derived from a terphenyl group, to ameliorate the weak intensity and broad emission spectrum of an excimer. Molecular orientation effects were first implemented in a highly twisted core group to produce single molecule white emission.

We recently developed a novel dual core system for producing highly efficient organic emitters.[1h,7b] Triple-core chromophores were prepared by extending a dual-core chromophore. The chemical structures of the triple core organic emitters are shown in Scheme 1. Phenyl and bulky terphenyl side groups were attached to the triple-core chromophore. A triple-core chromophore—consisting of a 1,6 DAP core and two triple-core side compounds, 1,6 DAP-P and 1,6 DAP-TP—was synthesized and compared using time-resolved fluorescence spectroscopy, theoretical calculations, VASE measurements, X-ray diffraction (XRD) analysis, and scanning electron microscope (SEM) image.


**1,6 DAP core** **1,6 DAP-P** **1,6 DAP-TP**

**Scheme 1.** Chemical structures of the synthesized compounds

UV-visible (UV-Vis.) absorption spectra of the synthesized materials in THF solution and the film state are shown in Fig. S4a and b, respectively, while the corresponding photoluminescence (PL) spectra are shown in Fig. S5 (THF solution) and Fig. 1a (film state). UV-Vis. absorption of the three synthesized materials exhibited maximum absorption at 370–405 nm, both in solution and the film states, displaying an absorption wavelength and spectral envelope typical of anthracene. For all three materials, the PL spectra exhibited maximum emission in the blue region at 433–439 nm in a $10^{-5}$ M THF solution. In the vacuum-deposited film (Fig. 1a), the 1,6 DAP core and 1,6 DAP-P produced blue emission at 462 and 455 nm, respectively, similar to that observed in the solution state. By contrast, 1,6 DAP-TP displayed white emission in the film state (Fig. 1a, inset) with distinct peaks at 455 and 591 nm. Blue (455 nm) and orange (591 nm) emission peaks were observed from 1,6 DAP-TP using time-resolved fluorescence spectroscopy in the film state. As shown in Fig. 1b, the 455 nm emission peak exhibited biexponential decay, with a short decay lifetime of 0.2 ns (99.5%) and a longer-lived excited state lifetime of 1.9 ns (0.5%). The 591 nm emission peak displayed longer-lived multiexponential decay with lifetimes of 0.75 ns (66.4%), 2.1 ns (31.8%), and 6.8 ns (1.8%). The longer-lived species that emitted at 591 nm from the 1,6 DAP-TP film was characteristic of molecular interactions.[8] In other words, unlike the solution state which showed a single peak corresponding to PL emission from the molecule, the film system exhibited both an emission peak corresponding to the molecule and an excimer peak produced by molecular interactions. To clarify whether the emission at 591 nm is an excimer peak, excitation spectra were measured along with the UV-Vis.

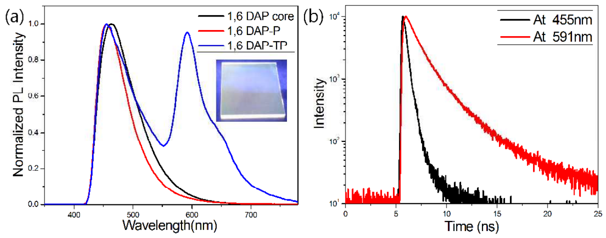


**Fig. 1** (a) Normalized PL spectra of the compounds (vacuum-deposited film on glass, inset: 1,6 DAP-TP film); (b) Time-resolved emission decays obtained from the vacuum-deposited 1,6 DAP-TP films.

absorption spectrum (Fig. S6). The UV-Vis. absorption spectrum matched well with the excitation spectra. The excitation spectra monitored at 455 nm and 591 nm (Fig. S6b and 6c) are very similar, indicating that they arise from the same excitation pathway. These findings are consistent with the 591 nm peak being an excimer emission. In Fig. 1a, the excimer band has a shoulder peak at longer wavelength. This feature can be explained by the vibronic structure.[4g] To check for chemical changes during vacuum deposition, UV-Vis. absorption and PL spectra recorded before and after deposition were compared (Fig. S7). The spectral data from before and after deposition were similar, indicating that no chemical changes occurred during deposition. The 591 nm emission peak resulting from molecular interactions was confirmed to have a sharp full width at half maximum (FWHM) value of 68 nm and relatively high emission intensity. This spectroscopic profile differs from the profiles of general excimer emission which is weak or broad.[5,9]

Given that simple flat moieties, such as anthracene and pyrene, more readily form excimers[10], the 1,6 DAP core would be expected to more easily form excimers compared to 1,6 DAP-TP, which has bulky side groups. Contrary to this expectation, however, excimer formation was observed for 1,6 DAP-TP but not for the 1,6 DAP core (Fig. 1a).

The unusual two-peak white emission spectrum of 1,6 DAP-TP was observed for the film state but not the solution state, indicating that intermolecular interactions generate excimers only in the film. To better understand the characteristics of the film state, XRD patterns were collected and VASE analyses were conducted on the three materials in deposited film states, as summarized in Fig. 2a and S8.

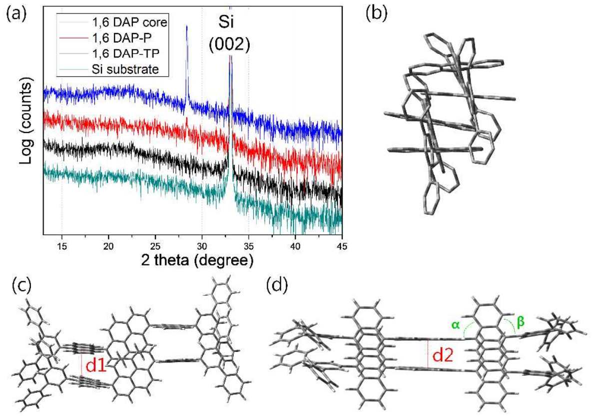


**Fig. 2** (a) Out-of-plane XRD patterns obtained from the 1,6 DAP core, 1,6 DAP-P, and 1,6 DAP-TP (200 nm films deposited on Si substrates); (b) side view of the 1,6 DAP-TP dimer structure; (c) pyrene top view of the 1,6 DAP-TP dimer structure; (d) anthracene top view of the 1,6 DAP-TP dimer structure (calculated at the ωB97XD/6-31G(d) level of theory).

Fig. 2a presents the out-of-plane XRD patterns collected from a 200 nm film deposited on a Si substrate. Unlike the films of the 1,6 DAP core and 1,6 DAP-P, the 1,6 DAP-TP film showed a clear XRD peak at 28.5°, indicating an intermolecular distance of 3.13 Å with a periodic intermolecular spatial arrangement. Also, 1,6 DAP core and 1,6 DAP-P showed amorphous surfaces but 1,6 DAP-TP exhibited sub-micron crystal domain as shown in Fig. S9. Fig. 2b ~ d illustrate a possible dimer stacking model of 1,6 DAP-TP, computed using ωB97XD/6-31G (d)[11] calculations. In the predicted structure, 1,6 DAP-TP has highly twisted core angles of 75.5 ° (α) between the anthracene and pyrene cores, and 83.8° (β) twist core-side angles between the anthracene and bulky side groups of the terphenyl moiety. The values of α and β in the predicted structure were similar to those obtained for a single crystal of 1,6 DAP-TP (78.4° and 81.2° respectively; Fig. S10). The intermolecular anthracene–anthracene distance in the calculated dimer structure of 1,6 DAP-TP was 3.78 Å (d1), and the intermolecular pyrene–pyrene distance was 3.28 Å (d2). These two distance values were similar to the intermolecular distance of 3.13 Å for $2\theta = 28.5°$, based on the 1,6 DAP-TP XRD results. This distance was smaller than the interplanar distance of 4.0 Å required for effective intermolecular interactions, an intense and sharp excimer emission due to periodic intermolecular interactions was observed.[12]

Fig. S8 and 3 show the VASE analysis results and a schematic diagram showing the stacking structures of the 1,6 DAP core, 1,6 DAP-P, and 1,6 DAP-TP. The intermolecular interactions were investigated by analyzing the optical anisotropy in the films of the synthesized materials using VASE. Optical anisotropies were observed in all three films, as shown in Fig. S8. The ordinary (horizontal) and extraordinary (vertical) refractive indices ($n_o$ and $n_e$) and extinction coefficients ($k_o$ and $k_e$) are shown for each film. The VASE results are summarized in Table S1. The difference between $k_o$ and $k_e$ was quite large, especially for 1,6 DAP-TP, suggesting significant dipole orientation along the horizontal direction.[7] 1,6 DAP-TP exhibited an out-of-plane XRD signal but no signals in the in-plane XRD pattern, as shown in Fig. 2a and S11. This result indicates that 1,6 DAP-TP has a horizontal orientation.

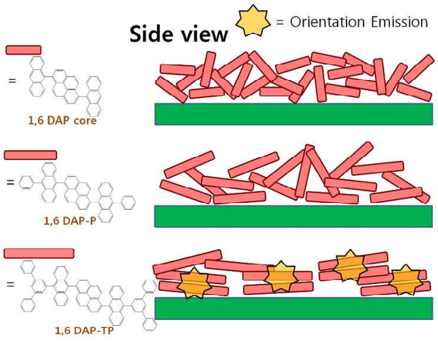


**Fig. 3** Schematic diagram showing the stacking structures of the synthesized compounds.

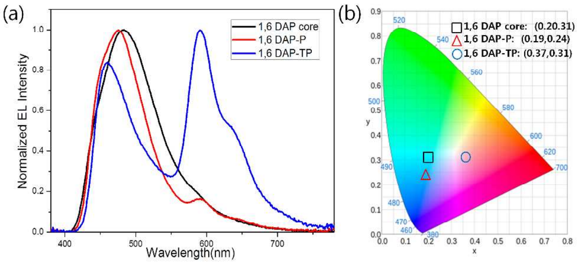


**Fig. 4** (a) Normalized EL spectra, (b) CIE chromaticity diagram of the synthesized compounds using an emitting layer in the OLED device, yielding 10 mA/cm$^2$.

The extent of the horizontal alignment increased in the order of 1,6 DAP core, 1,6 DAP-P, and 1,6 DAP-TP. That is, the orientation effects increased upon introduction of the phenyl and terphenyl side groups into the molecule. This trend was understood in terms of the relatively linear compound, which was maximized by the introduction of extended bulky side groups in the 1,6 DAP-TP series. The horizontal alignment promoted the formation of excimers in 1,6 DAP-TP, as shown in Fig. 3.

The HOMO-1, HOMO, LUMO, and LUMO+1 levels of the three compounds are shown in Fig. S12. The electron density distributions were found to be distributed across the anthracene group, indicating that electron transfer between the ground state and the excited state could only occur within the anthracene moiety. The UV-Vis. and PL spectra could be tuned based on the anthracene group properties. The sharp 591 nm emission in the PL spectrum (Fig. 1a) of 1,6 DAP-TP was understood as arising from the intermolecular interactions of the anthracene planes. The reason for the large difference in wavelength between the peak of the original molecule and the excimer peak in the PL spectrum of the 1,6 DAP-TP film remains unclear. A possible explanation is that it arises from the substantial overlap of the anthracene molecules, with DFT calculations (Fig. 2b) showing 67% overlap between adjacent anthracenes.[10a, 12b]

OLED devices were fabricated to examine the effects of the intermolecular orientations and excimers on the electroluminescence (EL). The OLED device structure was ITO / 2-TNATA(60 nm) / NPB (15 nm) / synthesized materials (35 nm) / Alq$_3$ (20nm)/ LiF (1 nm) / Al (200 nm). Fig. S13 shows the energy diagrams of the materials used. As in the EL spectrum shown in Fig. 4(a), the 1,6 DAP core and the 1,6 DAP-P compounds displayed EL maxima that yielded blue emission at 484 and 476 nm, respectively. 1,6 DAP-TP was verified to produce white emission due to a two-peak emission profile in the blue and orange, at 460 and 591 nm. As with the PL spectrum in the film state, the excimer emission at 591 nm was intense and sharp. As shown in Fig. 4(b), the CIE values of the 1,6 DAP core and the 1,6 DAP-P were in the blue region, (0.20, 0.31) and (0.19, 0.24), respectively. 1,6 DAP-TP yielded a CIE of (0.37, 0.31), very close to pure white (0.33, 0.33). These results suggested the introduction of molecular interaction effects that promoted anisotropic orientations that affected the EL and PL spectra. Interestingly, the CIE value obtained from 1,6 DAP-TP changed from (0.39, 0.32) at 6 V to (0.37, 0.31) at 10 V, a relatively insignificant change relative to the magnitude of the voltage change. Other excimer OLED devices have yielded CIE x and y values that have changed remarkably by around 0.1 with increasing voltage.[5b] The device performances of 1,6 DAP, 1,6 DAP-P, and 1,6 DAP-TP at 10 mA/cm$^2$ corresponded to luminance efficiencies of 4.97, 3.81, and 3.43 cd/A, respectively.

In conclusion, a bulky terphenyl group was introduced into a highly twisted triple core chromophore to promote anisotropic intermolecular alignment (orientation effects). White emission with two sharp intense emissions at 455 and 591 nm from a single molecule was obtained as a result of the orientation effects, which controlled excimer formation as a result of the linear molecular shape. The optimized compound was used as the emitting layer in an OLED device that exhibited CIE values of (0.37, 0.31), very close to pure white, confirming that the EL spectrum did not change significantly with the voltage. The approach developed here using 1,6-DAP-TP may be applied to other OLED lighting applications that require a main emitter that produces two-color white emission.

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## Notes and References

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# Excimer Formation in Organic Emitter Films Associated with a Molecular Orientation Promoted by Steric Hindrance

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White emission with two sharp strong peaks was obtained by introducing a terphenyl group into a highly twisted core chromophore, which promoted a molecular orientation in the film state suitable for excimer formation.