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# Aggregation induced emission of diketopyrrolopyrrole (DPP) derivatives for highly fluorescent red films†

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A large number of diketopyrrolopyrrole (DPP) compounds showing aggregation induced emission (AIE) have been reported in the past few years. However, although DPP compounds exhibited AIE and excellent luminescence properties, their luminescence properties in solid or film states were not much focused on. Here we synthesized and characterized a series of DPP compounds with triphenylamine (TPA) moieties to investigate the AIE properties in the solid film state depending on the functional groups (TPA, BTPA, and MTPA) attached to the TPA moieties. **T2** and **D2** thin films showed excellent fluorescence quantum yields of 31% and 26%, respectively, compared to an **M2** thin film (9%). The restriction of an intramolecular rotation process could inhibit the aggregation induced quenching process and play a key role in achieving highly fluorescent molecules in the solid state.

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# 1. Introduction

Recently, fluorescent  $\pi$ -conjugated organic materials have become the subject of increasing research interest because of their potential applications in organic light-emitting diodes (OLEDs),<sup>1-4</sup> agricultural photoconversion films,<sup>5</sup> light harvesting,<sup>6</sup> optical storage,<sup>7</sup> and chemosensing.<sup>8-10</sup> Because such applications require fluorescent  $\pi$ -conjugated organic materials to be in the solid state (or film state), excellent solid state fluorescence quantum yields are required. However,  $\pi$ -conjugated fluorescent organic molecules commonly exhibit technical limitations owing to aggregation caused quenching (ACQ) resulting from  $\pi$ - $\pi$  stacking interactions and dipoledipole interactions in the solid state.<sup>11,12</sup> Therefore,  $\pi$ -conjugated fluorescent organic molecules have poor solid state fluorescence quantum yields.

In 2001 and 2002, Tang and co-workers and Park and coworkers first described the phenomenon of aggregation induced emission (AIE), in which enhanced emission is observed in the aggregated state.<sup>13,14</sup> AIE has mainly been reported for  $\pi$ -conjugated fluorescent organic materials with functional groups capable of free rotation such as triphenylamine (TPA) or tetraphenylethene (TPE)<sup>15–18</sup> However, the AIE mechanism is difficult to elucidate because this effect is counter to classical concepts of photophysics. The most common mechanisms for the AIE phenomenon include restriction of intramolecular rotation (RIR),<sup>19,20</sup> restriction of intramolecular charge transfer (ICT),<sup>21</sup> twisted intramolecular charge transfer (TICT),<sup>22</sup> and J-aggregate formation.<sup>23</sup> Although a theory that describes the AIE phenomenon universally has not yet been elucidated, considerable research is currently underway to identify systems that exhibit AIE and develop industrial applications.<sup>24,25</sup>

Diketopyrrolopyrrole (DPP) is a well-known  $\pi$ -conjugated fluorescent organic dye that shows excellent fluorescence properties. As DPP is an electron-deficient organic molecule, it can be used as an electron acceptor (EA) for an electron donor (ED) such as electron-rich TPA moieties. Therefore, it is possible to form ED-EA  $\pi$ -conjugated structures with excellent fluorescence and AIE properties by introducing free rotation moieties such as TPA and TPE into DPP.26,27 Previously, some highly emissive  $\pi$ -conjugated AIE-DPPs in the solid state were reported.<sup>16,17</sup> In this study, in order to investigate the luminescence properties of DPP depending on the TPA moieties and to further expand previous research studies for highly emissive AIE-DPPs in the solid state, a series of DPP compounds containing three different TPA moieties (TPA, BTPA, and MTPA) with different donating abilities were designed and synthesized (Scheme 1). The photophysical properties of these compounds were changed in both non-aggregated states



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(in pure tetrahydrofuran (THF)) and aggregated states (in THF/ water mixtures) depending on the TPA moiety introduced into DPP. In addition, thin films of the DPP compounds in poly (methyl methacrylate) (PMMA) were fabricated to observe the AIE phenomenon in the solid film state. The relationship between the photophysical properties and the shapes of the aggregates formed on the surface of the thin films was analyzed using field emission scanning electron microscopy (FE-SEM).

# 2. Results and discussion

### 2.1 Design and synthesis

We designed and synthesized a series of DPP compounds incorporating TPA moieties with different donating abilities following the general Suzuki coupling reactions described in the literature (Scheme 1). However, palladium catalysts were used 3–10 times more than that reported in the literature to achieve desirable yields.<sup>15,16</sup>

Compounds **T2**, **D2**, and **M2** were readily synthesized from **D6C** in high yields *via* Suzuki coupling reactions with TPA-BO, BTPA-BO, and MTPA-BO. Characterization of the target compounds by nuclear magnetic resonance (NMR) spectroscopy, mass spectrometry, and elemental analysis confirmed their theoretical molecular structures. It is assumed that **T2**, **D2**,

and M2, which contained TPA moieties, show AIE, but D6C, as a control without TPA moieties, shows ACQ.

### 2.2 Photophysical properties in the solution

The UV-vis absorption and photoluminescence (PL) emission spectra of the DPP compounds in a pure THF solution at a concentration of  $1 \times 10^{-5}$  M are shown in Fig. 1, and the associated photophysical parameters are summarized in Table 1. As shown in Fig. 1a and Table 1, the maximum wavelength of absorption ( $\lambda_{abs. max}$ ) of D6C is 476 nm, whereas T2, **D2**, and **M2** exhibited bathochromic shifts with  $\lambda_{max}$  values of 503, 504, and 513 nm, respectively. As depicted in Fig. 1 and Fig. 2, for T2, D2, and M2, the low energy band at around 500 nm originates from an ICT process, whereas the high energy band at around 400–440 nm is attributed to the n- $\pi^*$ transition of the TPA moieties. Increasing the donating power of the TPA moieties introduced into DPP (MTPA > BTPA > TPA) resulted in a larger bathochromic shift of the maximum wavelength of absorption. Fig. 1b shows the fluorescence emission spectra of the DPP compounds. As shown in Fig. 1b and Table 1, the maximum wavelength of fluorescence ( $\lambda_{em, max}$ ) of D6C is 557 nm, whereas T2, D2, and M2 exhibit bathochromic shifts, with  $\lambda_{em. max}$  values of 590, 602, and 625 nm, respectively. As the donating power of the TPA moieties increased (MTPA > BTPA > TPA), the bathochromic shift of the maximum wavelength of fluorescence became larger. The fluo-



Fig. 1 (a) Absorption and (b) PL spectra of D6C, T2, D2, and M2 in THF at a concentration of  $1 \times 10^{-5}$  mol L<sup>-1</sup>.

Table 1 Photophysical data for D6C, T2, D2, and M2 in THF

Compound	$3_{\max}^{a} (L \text{ mol}^{-1} \text{ cm}^{-1})$	Absorption $\lambda_{abs. max}^{a}$ (nm)	Emission $\lambda_{\rm em.\ max}{}^{a,b}$ (nm)	$\Phi_{\mathrm{f}}{}^{a,b,c}$ (%)	Stokes shift <sup>d</sup> (nm)
D6C	21 700	476	557	67	81
Г2	30 000	503	590	71	87
D2	42 200	504	602	68	98
M2	50 500	513	625	2	112

 $^a$  1 × 10<sup>-5</sup> M concentration of the compounds in pure THF solution.  $^b$  The absorption  $\lambda_{\rm max}$  was used as the excitation wavelength.  $^c$  Fluorescence quantum yields were obtained using an integrating sphere.  $^d$   $\lambda_{\rm em.\ max}$  –  $\lambda_{\rm abs.\ max}$ .

rescence quantum yields ( $\Phi_f$ ) of D6C, T2, D2, and M2 in pure THF solutions (Table 1) were determined to be 67%, 71%, 68%, and 2%, respectively, using an integrating sphere. Although most of the AIE luminophores showed poor fluorescence quantum yields in dilute solutions,<sup>13–15,26–28</sup> T2 and D2 exhibited noticeable fluorescence quantum yields in pure

Table 2 Solubilities of D6C, T2, D2, and M2 at room temperature

	D6C	T2	D2	M2
THF	++++	++	+	+++
$CHCl_3$	++++	++	+	+++

++++: >5.0 × 10<sup>4</sup> mg L<sup>-1</sup>; +++: 5.0 × 10<sup>4</sup>–1.0 × 10<sup>5</sup> mg L<sup>-1</sup>; ++: 5.0 × 10<sup>3</sup>–5.0 × 10<sup>4</sup> mg L<sup>-1</sup>; +: 5.0 × 10<sup>2</sup>–5.0 × 10<sup>3</sup> mg L<sup>-1</sup>.

THF solution. Consequently, it is assumed that **T2** and **D2** had lower energy dissipation *via* rotation of TPA moieties than **M2**.

### 2.3 Solubility and planarity

The solubilities of the synthesized DPP compounds in THF and CHCl<sub>3</sub> (CF) are shown in Table 2. The solubilities were found to be high in both THF and CF, decreasing in the order of **D6C** > **M2** > **T2** > **D2**. In **T2** and **D2**,  $\pi$ - $\pi$  stacking interactions are strengthened owing to the increased planarity achieved by introducing bulky aromatic substituents at the Br positions of the **D6C** structure. Therefore, the solubilities of **T2** and **D2** are



Fig. 2 Electron density distributions of the frontier molecular orbitals of D6C, T2, D2, and M2.

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lower than that of D6C.<sup>29</sup> In contrast, M2 exhibited higher solubility than T2 and D2 because M2 had a branched methoxy substituent at the *para* positions of TPA inhibiting intermolecular  $\pi$ - $\pi$  stacking in M2 compared to T2 and D2.<sup>12,30</sup>

### 2.4 Computational analysis

The electronic structures of DPP compounds, and the HOMO and LUMO of each compound were analyzed by computational calculations (DFT/B3LYP/6-31G, Gaussian 09 program package) to investigate the relationship between the photophysical properties. The HOMOs, LUMOs, and electron density distributions of the frontier molecular orbitals for the optimized structures of the DPP compounds are shown in Fig. 2. The calculated band gaps of D6C, T2, D2, and M2 (2.77, 2.5, 2.48, and 2.45 eV, respectively) increased in the order of M2 < D2 < T2 < D6C. T2, D2, and M2 showed separated electron cloud distributions between the HOMO and the LUMO, whereas it seemed similar between the HOMO and LUMO of D6C. Notably, the LUMOs of T2, D2, and M2 had higher electron densities in the DPP core than the HOMOs because the electron-rich TPA moieties functioned as EDs, whereas the electron-deficient DPP core functioned as an EA. Therefore, it seemed evident that DPP compounds with TPA moieties had more ICT characteristics between the ED and the EA than the one without TPA moieties. These results suggest that expanding the  $\pi$ -conjugation system of DPP with electron donating moieties induced separation between the HOMO and the LUMO. As shown in Fig. 1, the absorption and PL spectra of T2, D2, and M2 exhibited bathochromic shifts relative to those of D6C.

### 2.5 AIE characteristics in THF/H<sub>2</sub>O mixtures

To examine the optical behavior of the synthesized DPP compounds in the aggregated states, different amounts of water, which is a poor solvent for luminophores, were added to the pure THF solutions to induce aggregation. Fig. 3 and 4 show the absorption spectra and PL spectra with the corresponding optical images of the DPP compounds in THF/water mixtures with water fractions ( $f_w$ ) of 0%–90%. The optical images of PL were obtained under illumination of a 365 nm UV lamp. As shown in Fig. S1,† the optical properties of the mixtures were analyzed after sonicating for an hour to disperse the precipitated molecules. Fig. 5 shows the plot of *I* (the PL intensity in the THF/water mixture)/ $I_0$  (the PL intensity in pure THF) *versus* water fractions of the DPP compounds.

The concentration of each compound was maintained at  $1 \times 10^{-4}$  mol L<sup>-1</sup> in aqueous mixtures. As shown in Fig. 3, the absorption tails of T2, D2, and M2 in the THF/water mixture were extended into the long wavelength region (600-700 nm) with increasing water fractions. According to the literature, the extended absorptions indicate the formation of aggregates of the nanoparticles in the presence of water, and the level-off tails in the visible region are attributed to the Mie scattering caused by the nanosized particles.31 As shown in the PL spectra in Fig. 4b-d, substitution of TPA moieties at the Br positions of D6C affected the optical properties. In the pure THF solution, D6C showed strong yellowish green light, T2 and D2 showed strong orange light, and M2 was nearly nonluminescent. The PL intensity of D6C was not changed significantly from  $f_w = 0\%$  to 60%. However, the intensity began to decrease dramatically from  $f_w$  = 70% to 90%. This fluorescence quenching can be explained by the ACQ phenom-



Fig. 3 Absorption spectra of (a) D6C, (b) T2, (c) D2, and (d) M2 in THF/water mixtures with different water fractions (f<sub>w</sub>).



Fig. 4 Optical images and PL spectra of (a) D6C, (b) T2, (c) D2, and (d) M2 in THF/water mixtures with different water fractions (f<sub>w</sub>).



Fig. 5 Plot of / (the PL intensity in the THF/water mixture)/ $I_0$  (the PL intensity in pure THF) versus the water fractions ( $f_w$ ) of (a) D6C, (b) T2, (c) D2, and (d) M2.

enon, which is typical of organic fluorescent molecules. In contrast, **T2**, **D2**, and **M2** showed different fluorescence behavior in the aggregated state. As shown in Fig. 4b, with gradual addition of water to the THF solution, the emission of **T2** rapidly weakened when  $f_w \leq 40\%$ . However, as shown in

Fig. 3b and S2b,† with the formation of aggregates at  $f_w \ge 50\%$ , the emission of T2 also increased. As shown in Fig. 5b, the maximum intensity of PL was 1.1-fold higher at  $f_w = 80\%$  than that in the pure THF solution. In addition, small dual peaks at 590–610 nm and 620–640 nm are observed at  $f_w =$ 

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50% and 60%. This phenomenon could be related to the irregular formation of aggregated nanoparticles. As shown in Fig. S1b,<sup>†</sup> because T2 aggregated abruptly, it was irregularly aggregated inside the nanoparticles. Therefore, T2 precipitated from the aqueous mixtures at  $f_w$  = 50% and 60%, and certain different emissions could be observed from the dispersion of precipitated irregular aggregates. The changes in the PL spectra of the DPP compounds in THF/water mixtures were also related to the solvent effect. TICT is caused by the twisting of a single bond between the ED and EA as the solvent polarity increases, achieved here by adding water to THF solution.<sup>27</sup> The DPP core functioned as an EA, and the TPA moieties functioned as EDs. Consequently, the former peak (590-610 nm) of T2 is assigned to a local excited state (LE), and the latter one (620 nm-640 nm) could be related to the TICT state, which is shown in the longer wavelength region in an equilibrium state at  $f_w = 50\%$  and 60%. The PL intensity of mixtures with high water fractions at  $f_w$  = 70% and 80% was enhanced compared to the intensity of pure THF solution due to the increased RIR process. At  $f_w$  = 90%, the net outcome PL intensity was slightly decreased, and the spectrum of the mixture shifted to a longer wavelength region. This may be related to the TICT state originating from the high solvent polarity due to the high water fraction. Thus, the measured luminescence properties of T2 aqueous mixtures showed no regularity at high water fractions. As shown in Fig. 4c, the emission of D2 also weakened rapidly until  $f_w \leq 30\%$ . However, as shown in Fig. 3c and S2c,<sup>†</sup> with the formation of aggregates at  $f_{\rm w} \ge 40\%$ , the emission of D2 also increased. As shown in Fig. 5c, the maximum intensity of PL was about 1.6-fold higher at  $f_w = 60\%$  than that in the pure THF solution. In addition, dual peaks at 590-610 nm and 620–640 nm are observed at  $f_w$  = 50% and 60%. This phenomenon could also be related to the irregular formation of aggregated nanoparticles. As shown in S1c,† irregular aggregates of **D2** precipitated from the aqueous mixtures from  $f_w = 30\%$  to 60% and showed opaque dispersion from  $f_w$  = 70% to 90%. In addition, the dual peaks at 550-590 nm and 600-630 nm were observed for the aqueous mixture from  $f_w = 40\%$  to 90% are shown in Fig. 3c. In contrast to T2, an intense former peak (550-590 nm) of D2 could be related to the aggregation state, and the latter one (600 nm-625 nm) is assigned to an LE state from  $f_w$  = 40% to 90%. The environment inside the irregularly formed aggregated nanoparticles is less polar than the medium outside, which explains why the aggregate emission state is blue-shifted from that of the LE state.<sup>32</sup> The enhancement of the net outcome PL intensities at  $f_{\rm w} \ge 40\%$  was

caused via the RIR process of the TPA moiety through the formation of aggregates. Interestingly, both T2 and D2 showed poor fluorescence in aqueous mixtures with low water fractions. It is assumed that because the high polarity of water caused an intramolecular charge separation of DPP compounds, the energy of the first singlet excited state was lowered and thereby alleviated the transition of the molecule into other states such as the triplet state with corresponding fluorescence quenching.<sup>33</sup> As shown in Fig. 3d, 4d, and S1d,<sup>†</sup> the emissions of M2 aqueous mixtures rapidly enhanced with the formation of aggregates at  $f_w \ge 40\%$ . The maximum PL intensity was about 600-fold higher at  $f_w = 60\%$  than that in the pure THF solution. Also, intensive dual peaks at 570-600 nm and 610–650 nm are observed from  $f_w = 40\%$  to 60%. The newly arisen former peak (570-600 nm) of M2 could be related to the aggregation state originating from the irregularly formed aggregated nanoparticles, and the latter one (610 nm-650 nm) is assigned as the TICT state from  $f_w = 40\%$  to 60%. However, the aggregation state disappeared from 70% to 90%. The net outcome PL intensity of M2 aqueous mixtures from  $f_w = 70\%$ to 90% decreased compared to that at  $f_w$  = 50% and 60% but still showed AIE properties. The above results indicated that the luminescence properties of DPP compounds could be changed depending on the degree of aggregation with the corresponding water fractions in THF/water mixtures. In addition, the RIR process by TPA moieties plays an important role in the emission behavior of the aggregated molecules.<sup>34</sup>

#### 2.6 Fabrication of DPP compound/PMMA thin films

DPP compound/PMMA thin films were fabricated to observe the AIE properties of the DPP compounds while minimizing the solvent effects. The surface properties of the fabricated thin films were investigated through FE-SEM. As shown in Fig. 6, the thicknesses of the thin films formed on quartz plates were measured by FE-SEM. The fabricated films had a thickness of about 11 µm to minimize the effects caused by the differences in thicknesses. Fig. 7 shows the FE-SEM images of the surfaces of the thin films. As shown in Fig. 7a, the surface of the D6C/PMMA thin film was uniform with agglomerated particles of about 20-30 nm size. However, as shown in Fig. 7b-d, the surfaces of the T2/PMMA, D2/PMMA, and M2/PMMA thin films were not uniform, and the agglomerated particles were bulkier than those in the D6C/PMMA thin film. The differences observed in the surface images of these DPP compound/PMMA thin films were related to the solubility and planarity of the DPP compounds, as described earlier.



Fig. 6 FE-SEM images of the cross-sections of DPP compound/PMMA thin films: (a) D6C, (b) T2, (c) D2, and (d) M2.



Fig. 7 FE-SEM images of the surface of DPP compound/PMMA thin films: (a) D6C, (b) T2, (c) D2, and (d) M2.



Fig. 8 (a) Absorption and (b) PL spectra of D6C, T2, D2, and M2 in PMMA films.

Consequently, **D6C** showed relatively uniform aggregation in the thin film owing to its relatively low planarity. In contrast, **T2**, **D2**, and **M2** were non-uniformly aggregated in the polymer matrix due to their higher planarity than **D6C**.

# 2.7 Photophysical properties of DPP compound/PMMA thin films

The normalized absorption and emission spectra, photophysical data, and optical images of the thin films are depicted in Fig. 8, Table 3, and Fig. 9, respectively. The spectra were normalized to ensure the reliability of the data because of the lack of uniformity in the thin films. The absorption and emission spectra of the thin films tended to exhibit bathochromic shifts compared with those in the solution. The absorbance spectra of **D6C**, **T2**, **D2**, and **M2** bathochromically shifted by 4, 5, 5,

### Table 3 Photophysical data for D6C, T2, D2, and M2 in PMMA films

Compound	Absorption $\lambda_{abs. max}^{a}$ (nm)	Emission $\lambda_{\rm em.\ max}^{a,b}$ (nm)	$\Phi_{\mathrm{f}}{}^{a,b,c}$ (%)	Stokes shift <sup>d</sup> (nm)
D6C	480	574	11	94
T2	508	614	31	106
D2	509	611	26	102
M2	517	640	9	123

<sup>*a*</sup> 5 mol% of the compounds in a PMMA thin film coated on a quartz plate. <sup>*b*</sup> The absorption  $\lambda_{\text{max}}$  was used as the excitation wavelength. <sup>*c*</sup> Fluorescence quantum yields were obtained using an integrating sphere. <sup>*d*</sup>  $\lambda_{\text{em. max}} - \lambda_{\text{abs. max}}$ .

and 4 nm, respectively, relative to those in the pure THF solution. The PL spectra of D6C, T2, D2, and M2 also bathochromically shifted by 17, 24, 9, and 15 nm, respectively, relative to



Fig. 9 Optical images of D6C/PMMA, T2/PMMA, D2/PMMA, and M2/ PMMA films.

those in the pure THF solutions. The fluorescence quantum yields of the D6C, T2, D2, and M2 thin films were 11%, 31%, 26%, and 9%, respectively.

The fluorescence quantum yield of M2 in the film state (9%) exhibited a 4.3-fold enhancement compared with that in the pure THF solution (2%) through the AIE process. However, although T2 and D2 exhibited AIE properties in THF/water mixtures, they showed decreased quantum yield in the thin films compared to the values in the pure THF solutions. In general, when fluorescent organic molecules form planar aggregates,  $\pi$ - $\pi$  stacking and intermolecular interactions increase, which may cause ACQ.<sup>35</sup> As shown in Fig. 7b and c, the surface images of T2 and D2 showed more bulky and planar forms than D6C because of increased planarity. Consequently, more  $\pi$ - $\pi$  stackings and intermolecular interactions may arise in the thin films of T2 and D2 than D6C. However, the fluorescence quantum yields of T2 (31%) and D2 (26%) in the film state were 2.3-2.8-fold that in a thin film of D6C (control, 11%) and 2.97-3.63-fold that in a thin film of M2. It is because obviously the AIE process originates from the RIR process of the TPA moieties and inhibits the ACQ process in a trade-off relationship. Therefore, it is clear that T2 and D2 had AIE characteristics in the film state and their fluorescence quantum yields in the solid state (thin film) were much higher than that of M2.

# 3. Conclusions

A series of diketopyrrolopyrrole compounds incorporating three different triphenylamine moieties were synthesized, and their photophysical properties were analyzed in pure THF solutions, THF/water mixtures, and thin films. All the diketopyrrolopyrrole compounds with triphenylamine moieties showed different red emissions with aggregation induced emission characteristics. The difference in the luminescence properties of the prepared diketopyrrolopyrrole compounds was attributed to the different functional groups attached to the triphenylamine moieties, and the fluorescence quantum yields of solid thin films of diketopyrrolopyrrole were changed as 9%, 26%, and 31%. Consequently, this work provided some insight into tuning the triphenylamine moieties for obtaining highly emissive diketopyrrolopyrrole compounds in the solid film state. Therefore, diketopyrrolopyrrole with optimal triphenylamine moieties could also become excellent solid state emissive materials by aggregation induced emission.

### 4.1 General

TPA-BO, BTPA-Pre, and MTPA-Pre were purchased from Tokyo Chemical Industry. PMMA with a number-average molecular weight  $(M_{\rm p})$  of 350 000 was purchased from Aldrich and was used as received. All other chemicals were purchased from commercial suppliers and used as received without further purification. The intermediates 3,6-bis(4-bromophenyl)-2,5dihydropyrrolo[3,4-c]pyrrole-1,4-dione (DPPH), 4-[bis(biphenyl-4-yl)amino]phenylboronic acid (BTPA-BO), and 4-(bis(4-methoxyphenyl)amino)phenylboronic acid (MTPA-BO) were synthesized efficiently according to literature procedures.<sup>15,36,37</sup> Transparent glass substrates were provided by NTP, Inc. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance III 500 spectrometer at 500 MHz in CHCl<sub>3</sub>-d or dichloromethane-d with tetramethylsilane (TMS) as an internal standard. Elemental analysis was performed with a Thermo Scientific Flash EA 1112 elemental analyzer. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were recorded on an Applied Biosystems Voyager-DE STR Biospectrometry Workstation using cyano-4-hydroxycinnamic acid (CHCA) as a matrix. UV-vis absorption spectra were recorded using a PerkinElmer Lambda 25 spectrophotometer. PL spectra and absolute fluorescence quantum yields were obtained using PerkinElmer LS 55 and Jasco International FP-8500ST spectrofluorometers, respectively. FE-SEM images were acquired using a Zeiss MERLIN Compact field emission scanning electron microscope; Pt was coated on the samples using a JEOL MSC-101 sputter coater for 40 s at a current strength of 40 mA to avoid charging of the surface. Density functional theory (DFT) calculations were performed with the Gaussian 09 program package using the 6-31G(d,p) Pople basis set for all elements and the conventional B3LYP exchange correlation function.

### 4.2 Syntheses of compounds

3,6-Bis(4-bromophenyl)-2,5-dihexyl-2,5-dihydropyrrolo-3,4cpyrrole-1,4-dione (D6C). A solution of DPPH (6 g, 13.52 mmol) in N-methyl-2-pyrrolidone (NMP) (70 mL) was stirred at room temperature under a nitrogen atmosphere. After stirring for 2 h, potassium tert-butoxide (t-BuOK) (4.83 g, 43.04 mmol) was added dropwise. After stirring for 2 h, 1-iodohexane (17.320 g, 81.67 mmol) was added dropwise. The resulting solution was stirred for another 2 h at 45 °C and then cooled to room temperature. The reaction mixture was directly evaporated at 180 °C using a vacuum rotary evaporator with an oil bath. The crude product was purified by column chromatography using CH<sub>2</sub>Cl<sub>2</sub> as the eluent to obtain bright orange crystals of **D6C** (4.63 g, 56% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$ (ppm): 7.62-7.67 (m, 8H), 3.69-3.72 (t, J = 7.75 Hz, 4H), 1.52–1.55 (t, J = 7 Hz, 4H), 1.17–1.24 (m, 12H), 0.81–0.84 (t, J = 7 Hz, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 162.59, 147.63, 132.39, 130.28, 127.11, 126.00, 110.07, 42.02, 31.37, 29.54, 26.53, 22.63, 14.12. MALDI-TOF MS: m/z 615.00 (100%, M + H<sup>+</sup>). Elemental analysis: calcd for  $C_{30}H_{34}Br_2N_2O_2$ : C,

58.65; H, 5.58; Br, 26.01; N, 4.56; O, 5.21. Found: C, 58.62; H, 5.57; N, 4.54; O, 5.24.

3,6-Bis(4'-(diphenylamino)-1,1'-biphenyl-4-yl)-2,5-dihexyl-2,5dihydropyrrolo-3,4-c-pyrrole-1,4-dione (T2). A mixture of Pd(PPh<sub>3</sub>)<sub>4</sub> (100 mg, 0.091 mmol), D6C (0.28 g, 0.46 mmol), and TPA-BO (0.40 g, 1.38 mmol) in dry THF (40 mL) was stirred for 30 min at room temperature under a nitrogen atmosphere. After increasing the temperature of the mixture to 60 °C, an aqueous solution of K<sub>2</sub>CO<sub>3</sub> (3.65 M, 5 mL) was added dropwise and the resulting mixture was maintained at this temperature for 12 h. The reaction mixture was then poured into water and extracted with CH2Cl2. The combined organic layers were dried over anhydrous MgSO<sub>4</sub> and then evaporated to dryness. The crude product was purified by column chromatography using  $CH_2Cl_2$ : hexane (3:1, v/v) as the eluent to obtain red crystals of T2 (0.35 g, 80% yield). <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>), δ (ppm): 7.88–7.89 (m, 4H), 7.73–7.75 (m, 4H), 7.55-7.57 (m, 4H), 7.26-7.30 (m, 8H), 7.11-7.14 (m, 12H), 7.04–7.07 (m, 4H), 3.78 (t, J = 7.5 Hz, 4H), 1.56–1.62 (m, 4H), 1.19–1.26 (m, 12H), 0.83 (d, J = 7 Hz, 6H). <sup>13</sup>C NMR (125 MHz,  $CD_2Cl_2$ ),  $\delta$  (ppm): 163.13, 148.62, 148.23, 148.03, 143.56, 133.77, 129.91, 129.84, 128.30, 127.22, 127.14, 125.35, 123.90, 123.79, 110.40, 42.39, 31.82, 29.93, 26.91, 23.05, 14.31. MALDI-TOF MS: m/z 943.7 (100%, M<sup>+</sup>). Elemental analysis: calcd for C<sub>66</sub>H<sub>62</sub>N<sub>4</sub>O<sub>2</sub>: C, 84.04; H, 6.63; N, 5.94; O, 3.39. Found: C, 84.04; H, 6.62; N, 5.97; O, 3.38.

3,6-Bis(4'-(di(1,1'-biphenyl-4-yl)amino)-1,1'-biphenyl-4-yl)-2,5-dihexyl-2,5-dihydropyrrolo-3,4-c-pyrrole-1,4-dione (D2). Compound D2 was prepared according to a procedure similar to that for T2, using BTPA-BO (0.61 g, 1.38 mmol) instead of TPA-BO to produce red crystals of D2 (0.47 g, 82% yield). <sup>1</sup>H NMR (500 MHz,  $CD_2Cl_2$ ),  $\delta$  (ppm): 7.89–7.91 (d, J = 8.5 Hz, 4H), 7.76-7.78 (d, J = 8.5 Hz, 4H), 7.59-7.63 (m, 12H), 7.54-7.57 (m, 8H), 7.41-7.44 (m, 8H), 7.29-7.33 (m, 4H), 7.22–7.25 (m, 12H), 3.74–3.80 (m, 4H), 0.80–1.60 (m, 22H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 163.10, 148.22, 147.89, 146.80, 143.38, 140.74, 136.23, 134.02, 129.48, 128.99, 128.21, 128.13, 127.19, 127.04, 126.94, 126.75, 124.99, 124.09, 110.03, 42.36, 31.46, 29.90, 29.69, 29.58, 26.65, 22.69. Elemental analysis: calcd for C<sub>90</sub>H<sub>78</sub>N<sub>4</sub>O<sub>2</sub>: C, 86.64; H, 6.30; N, 4.49; O, 2.56. Found: C, 86.08; H, 6.44; N, 4.42; O, 3.12.

3,6-Bis(4'-(bis(4-methoxyphenyl)amino)-1,1'-biphenyl-4-yl)-2,5-dihexyl-2,5-dihydropyrrolo-3,4-cpyrrole-1,4-dione (M2). Compound M2 was prepared according to a procedure similar to that for T2, using MTPA-BO (0.48 g, 1.38 mmol) instead of TPA-BO and  $CH_2Cl_2$ : methanol (400:1, v/v) instead of  $CH_2Cl_2$ : hexane (3:1, v/v) as the eluent to produce deep red crystals of M2 (0.34 g, 70% yield). <sup>1</sup>H NMR (500 MHz,  $CDCl_3$ ),  $\delta$  (ppm): 7.88–7.90 (d, J = 8.5 Hz, 4H), 7.69–7.71 (d, J = 8.5 Hz, 4H), 7.48 (d, J = 2 Hz, 2H), 7.47 (d, J = 2 Hz, 2H), 7.09-7.13 (m, 8H), 6.99-7.00 (t, J = 1.5 Hz, 4H), 6.85-6.88 (m, 8H), 3.79-3.82 (m, 16H), 0.82-1.69 (m, 22H). <sup>13</sup>C NMR (125 MHz,  $CDCl_3$ ),  $\delta$  (ppm): 163.12, 156.35, 149.13, 148.22, 143.61, 140.72, 131.43, 129.42, 127.76, 127.14, 126.71, 126.30, 120.34, 114.99, 109.90, 55.71, 42.35, 31.45, 29.67, 26.65, 22.69, 14.17. Elemental analysis: calcd for  $C_{70}H_{70}N_4O_6$ : C,

79.07; H, 6.64; N, 5.27; O, 9.03. Found: C, 79.05; H, 6.74; N, 5.26; O, 8.98.

### 4.3 Investigation of solubility

The solubility properties of the synthesized compounds in THF and  $CHCl_3$  were examined to observe the planarity of the compounds. The prepared compounds were added to the solvents at various concentrations, and the solutions were sonicated for 5 min using an ultrasonic cleaner ME6500E. The solutions were left to stand for 24 h at room temperature and checked for precipitation to determine the solubility of the synthesized compounds.<sup>29</sup>

### 4.4 Fabrication of thin films

According to literature procedures, PMMA thin films doped with the synthesized compounds were prepared on quartz plates by the doctor blade technique using CHCl<sub>3</sub> solutions with a fixed PMMA concentration of 5 wt% showing optimal coatability. The synthesized compounds were added to PMMA/ CHCl<sub>3</sub> solutions at a concentration of 3 mol% relative to the quantity of PMMA monomer units. More than 3 mol% concentrations were out of the detection limit of UV and PL analyzing equipment. The cast films were dried under vacuum for 24 h at 80 °C.<sup>38</sup>

### Conflicts of interest

The authors declare no competing financial interest.

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