ChemComm

Largely blue-shifted emission through minor structural modifications: molecular design, synthesis, aggregation-induced emission and deep-blue OLED application†

Jing Huang,‡[a] Ning Sun,‡[b] Pengyu Chen,[a] Runli Tang,[a] Qianqian Li,[a] Dongge Ma*[b] and Zhen Li*[a]

By simply introducing additional groups with different size and conjugation degree to the 2,2′-positions of BTPE, four BTPE derivatives are prepared which give blue or deep-blue EL emissions when used as emitters in non-doped OLEDs, as the result of the tuned dihedral angles of the biphenyl cores (up to ∼89°), providing a new approach to design AIE luminogens with blue and deep-blue emissions.

Tremendous efforts have been devoted to develop AIE (aggregation-induced emission) luminogens for their unique advantages over normal luminogens with the aggregation caused quenching (ACQ) effect and promising applications in OLEDs and sensors, pioneered by Ben Zhong Tang *et al.* since 2001.[1] Among the reported AIE fluorophores, tetraphenylethene (TPE) is an iconic unit with facile synthesis and a splendid AIE effect.[2] So far, the direct linkage of some aromatic rings to TPE could largely improve their performance as emitting layers in OLEDs, however, the emission wavelength red-shifted to a large degree[3,4] (Chart S1, ESI†), leading to the scarcity of good blue and deep-blue AIE luminogens. And actually, this is still a big challenge in the research field of AIE emitters. For example, by just linking two TPE blocks together, the resultant 4,4′-bis(1,2,2-triphenylvinyl)biphenyl (BTPE) exhibits electroluminescence (EL) performance with a current efficiency up to 7.3 cd A^{-1},[5] much higher than that of TPE (0.45 cd A^{-1}). But the EL emission is red-shifted from deep blue to sky blue (445 to 488 nm), due to the good conjugation effect between the two pieces of TPE moieties.

As the development of blue and deep-blue emitters is the bottleneck for the commercial application of OLEDs,[6] it is essential to explore some new approaches to obtain AIE luminogens with blue or deep-blue emissions. Our previous research indicated that, to yield efficient blue or even deep blue TPE-based luminogens, the π-system of TPE would be inevitably prolonged, however, simultaneously, the conjugation between the aromatic blocks should be controlled.[7] Based on this consideration, we have also succeeded in obtaining four BTPE derivatives with blue or deep blue emissions, just by modifying the linkage modes of two TPE blocks.[7c] Furthermore, it is noteworthy that the modification of the dihedral angle is another efficient approach to adjust the conjugation effect of two aromatic blocks in basic organic chemistry, besides the linkage mode mentioned above. In this communication, with the aim to explore new approaches for the design of blue or even deep blue AIE emitters, four new BTPE derivatives, namely methyl-BTPE, isopro-BTPE, Ph-BTPE and Cz-BTPE with different dihedral angles of the biphenyl cores were intelligently designed (Chart 1) and synthesized (Scheme S1, ESI†). Fortunately, the results confirmed our idea.

The thermal properties of the new compounds were investigated by thermal gravimetric analysis (TGA, Fig. S1, ESI†) and differential scanning calorimetry (DSC, Fig. S2, ESI†). As listed in Table S1 (ESI†), the four BTPE derivatives exhibit high thermal decomposition temperatures (T_d, corresponding to 5% weight loss) ranging from 374 to 447 °C. Among them, Ph-BTPE and Cz-BTPE possess higher T_d values than methyl-BTPE and isopro-BTPE due to the incorporation of aromatic groups. Their glass transition temperatures (T_g) are in the range of 88–162 °C. The highest T_g value was observed for

[a] *Department of Chemistry, Hubei Key Lab on Organic and Polymeric Opto-Electronic Materials, Wuhan University, Wuhan 430072, China. E-mail: lizhen@whu.edu.cn, lichemlab@163.com; Fax: +86-27-68755363; Tel: +86-27-68755363*

[b] *Institute of Applied Chemistry, The Chinese Academy of Sciences, Changchun 130022, China. E-mail: mdg1014@ciac.jl.cn*

† Electronic supplementary information (ESI) available: Experimental section and chart of TPE and TPE-based luminogens; synthetic scheme, TGA and DSC curves, UV spectra, AIE curves, CV plots, calculated dihedral angels, EL curves, NMR spectra and thermal, electrochemical and photophysical data for methyl-BTPE, isopro-BTPE, Ph-BTPE and Cz-BTPE. See DOI: 10.1039/c3cc49313j

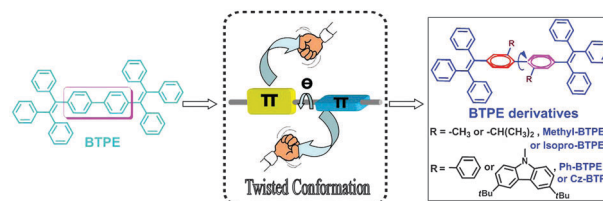‡ Contributed equally to this manuscript.

Chart 1 Chemical structures of BTPE and its derivatives developed in this work.

Cz-BTPE as a result of its largest molecular weight and more rigid bulky carbazole units, while methyl-BTPE shows the lowest one, probably due to its more twisted conformation caused by the non-conjugated methyl groups.

The maximum absorption wavelengths ($\lambda_{abs,max}$) of methyl-BTPE, isopro-BTPE, Ph-BTPE and Cz-BTPE are 315, 315, 328 and 328 nm (Fig. S3, ESI†), respectively, which are much blue-shifted, as large as 25 nm, compared to that of BTPE (340 nm), disclosing their shorter π-conjugation lengths. To confirm their AIE feature, THF and water were chosen as the solvent pair for their good miscibility. Fig. S4 (ESI†) shows the PL spectra of the new luminogens in THF–water mixtures with different water fractions (f_w). It is clearly seen that, in pure THF solutions, the PL curves are all practically flat lines parallel to the abscissa, demonstrating the weak emission property in the solution state. However, when the water fraction is over 80%, the emission intensities increase swiftly, indicating the formation of nano-aggregates. From a pure THF solution to the THF–H_2O mixture with 95% water content, the emission intensities increase over 240-fold. The quantitative enhancement of emission was evaluated by the PL quantum yields (Φ_F), using 9,10-diphenylanthracene as the standard. From a pure solution in THF to the aggregate state in 99% aqueous mixture, the Φ_F values increased from nearly 0 to 21.9%, 42.7%, 49.9% and 25.4% for methyl-BTPE, isopro-BTPE, Ph-BTPE, and Cz-BTPE, respectively (Fig. 1). It is noteworthy that Ph-BTPE possesses the highest quantum yield under identical conditions, probably because it bears more freely rotated phenyl rotors, the key factor for the distinct AIE effect. Furthermore, we have also investigated the PL properties of the luminogens in the solid state. As shown in Fig. 1B, the solid films of methyl-BTPE, isopro-BTPE and Ph-BTPE exhibit blue emission ranging from 455–469 nm, much blue-shifted than those of their aggregates in THF–H_2O mixtures. This is probably due to the change from crystal states to amorphous ones.[2] Compared to BTPE with a PL peak at 499 nm in the solid films, the conjugation lengths of the four luminogens are effectively shortened as a result of the adjusted molecular torsion degree.

Density Functional Theory (DFT) calculations (B3LYP/6-31g*) were carried out to investigate the structure–property relationship of the new compounds. As shown in Fig. 2 and Fig. S6 (ESI†), the
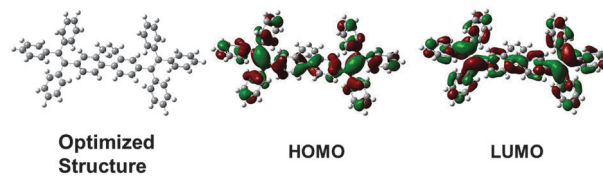

Fig. 2 Calculated molecular orbital amplitude plots of HOMO and LUMO levels and optimized molecular structures of methyl-BTPE.

electron clouds in both HOMO and LUMO levels of methyl-BTPE, isopro-BTPE and Ph-BTPE are mainly located on TPE units, demonstrating the weak intramolecular charge transfer. However, the electron distribution of the HOMO and LUMO orbitals is centralized at carbazole and TPE separately for Cz-BTPE, indicating that the electron-donating property of the carbazole group provided the better hole-transporting ability of the luminogen. Moreover, the dihedral angles between the adjacent phenyl blades of the two TPE units are 88.6°, 84.5°, 57.4° and 50.0° for methyl-BTPE, isopro-BTPE, Ph-BTPE and Cz-BTPE (Fig. S7, ESI†), respectively, much higher than that of BTPE (35.5°). Thus, all the four luminogens adopt more twisted conformations in comparison with BTPE, corresponding to their blue-shifted maximum absorptions. In other words, the π-conjugation lengths of the four derivatives are effectively shortened through the introduction of methyl, isopropyl, phenyl and carbazolyl groups to the 2,2′-positions of the biphenyl cores.

The good thermal stabilities and efficient light emissions in the solid state of the four BTPE derivatives prompted us to investigate their electroluminescence properties. Non-doped OLED devices with a configuration of ITO/MoO_3 (10 nm)/NPB (60 nm)/EML (15 nm)/TPBi (35 nm)/LiF (1 nm)/Al (100 nm) were fabricated. In these OLED devices, MoO_3, NPB, and TPBi worked as the hole-injection, hole-transporting, and hole-blocking layers, respectively, and methyl-BTPE, isopro-BTPE, Ph-BTPE and Cz-BTPE served as emitters. Fig. S8 (ESI†) and Fig. 3 show the current density–voltage–brightness (J–V–L) characteristics, current efficiency versus current density curves and EL spectra of the OLEDs. As listed in Table 1, the device based on Cz-BTPE exhibits a lower turn-on voltage (4.9 V) than those of other emitters (5.3 V), due to the introduction of hole-dominated
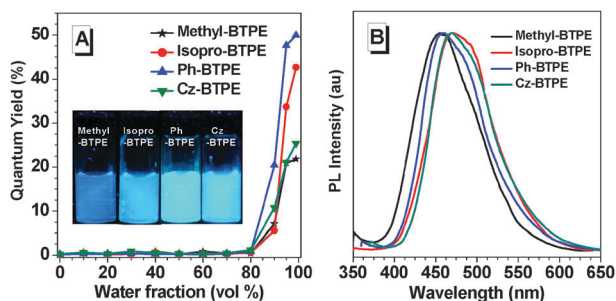

Fig. 1 (A) Plots of fluorescence quantum yields determined in THF–H_2O solutions using 9,10-diphenylanthracene (Φ = 90% in cyclohexane) as standard versus water fractions. Inset: photos of the four luminogens in the THF–water mixture (f_w = 95%) taken under illumination of a 365 nm UV lamp. (B) PL spectra of solid thin films of the four luminogens. The thin films were spin-coated onto ITO glass in a dilute THF solution with a concentration of 1 mg mL^{-1}.
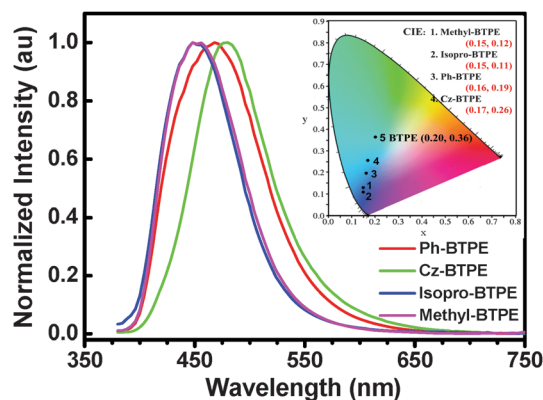

Fig. 3 EL spectra of multilayer EL devices of methyl-BTPE, isopro-BTPE, Ph-BTPE and Cz-BTPE. Inset: CIE coordinates of the devices. Device configurations: ITO/MoO_3 (10 nm)/NPB (60 nm)/EML (15 nm)/TPBi (35 nm)/LiF (1 nm)/Al.

Table 1 EL performances of methyl-BTPE, isopro-BTPE, Ph-BTPE and Cz-BTPE[a]

	λ_{EL} (nm)	V_{on} (V)	L_{max} (cd m^{-2})	$\eta_{P,max}$ (lm W^{-1})	$\eta_{C,max}$ (cd A^{-1})	$\eta_{ext,max}$ (%)	CIE (x, y)
Methyl-BTPE	451	5.3	1976	0.98	1.53	1.3	0.15, 0.12
Isopro-BTPE	451	5.3	1127	1.43	1.86	1.7	0.15, 0.11
Ph-BTPE	467	5.3	6497	2.13	3.10	1.9	0.16, 0.19
Cz-BTPE	479	4.9	9911	2.55	3.74	1.9	0.17, 0.26

[a] Abbreviations: V_{on} = turn-on voltage at 1 cd m^{-2}, L_{max} = maximum luminance, $\eta_{P,max}$, $\eta_{C,max}$ and $\eta_{ext,max}$ = maximum power, current and external efficiencies, respectively. CIE = Commission International de l'Eclairage coordinates at 100 mA cm^{-2}.

carbazole units, which is consistent with its electron clouds distribution and the diminished energy gap between the emitter and the hole-transporting layer (NPB).

Generally, devices based on the aromatic-substituted BTPE derivatives show better EL performance than the alkyl-substituted ones. In detail, devices based on methyl-BTPE and isopro-BTPE exhibit maximum luminances (L_{max}) of 1976 and 1127 cd m^{-2}, maximum current efficiencies ($\eta_{C,max}$) of 1.53 and 1.86 cd A^{-1}, and maximum power efficiencies ($\eta_{P,max}$) of 0.98 and 1.43 lm W^{-1}, respectively. And both of the devices show deep-blue emissions (451 nm) with Commission International de l'Eclairage (CIE) coordinates of (0.15, 0.12) and (0.15, 0.11), due to the introduction of the non-conjugated alkyl groups and *ortho*-interaction of 2-methyl or 2-isopropyl substituents. Interestingly, although the molecular structures of these two emitters are slightly different, with methyl or isopropyl groups attached to the biphenyl cores, isopro-BTPE showed better EL performance than methyl-BTPE.

Much better EL performance were obtained for Ph-BTPE and Cz-BTPE with L_{max}, $\eta_{C,max}$, and $\eta_{P,max}$ of 6497 and 9911 cd m^{-2}, 3.10 and 3.74 cd A^{-1}, and 2.13 and 2.55 lm W^{-1}, respectively, showing a more efficient exciton combination in the emissive layers as expected. Blue emissions were observed from both of the devices based on Ph-BTPE and Cz-BTPE, with CIE coordinates of (0.16, 0.19) and (0.17, 0.26). As discussed above, Ph-BTPE bears two more freely rotatable phenyl rings, leading to its higher quantum yield in the aggregated state. Therefore, when fabricated as an emissive layer in the device, it exhibits higher luminance and efficiencies than methyl-BTPE and isopro-BTPE, since the radiative channel was activated in the solid state. On the other hand, the aromatic phenyl ring with larger size is obviously more conjugated than methyl and isopropyl groups, thus the conjugation length of Ph-BTPE should be longer than those of methyl-BTPE and isopro-BTPE, as partially confirmed by their UV-vis and EL spectra. As we know, carbazole is a vesatile material used in opto-electronic applications due to its good hole-transporting ability, and generally, the direct linkage of carbazole to other chromophores through 3,6-positions will actually cause a distinct

bathochromic shift. Thus, to control the conjugation between the carbazolyl and TPE moieties, Cz-BTPE is constructed from BTPE and carbazole units through carbon–nitrogen bonds with a less conjugation effect. However, the dihedral angle of the biphenyl core in Cz-BTPE is smaller than those of the other derivatives caused by the much stronger π–π interactions between the planar carbazolyl moieties and the BTPE skeleton. Hence, the device based on Cz-BTPE shows longer EL emission with greatly enhanced efficiencies, but still in the region of blue emission.

In summary, four new BTPE derivatives with tunable dihedral angels of the biphenyl cores have been successfully constructed. The ingenious introduction of methyl, isopropyl, phenyl and carbazyl groups with different size and conjugation degree has resulted in their blue or deep blue EL emissions, compared to BTPE with sky-blue emission (488 nm) and CIE coordinates of (0.20, 0.36). This is in accordance with our design idea and has shed some light on the further molecular design.

Notes and references

1 (a) J. Luo, Z. Xie, J. W. Y. Lam, L. Cheng, H. Chen, C. Qiu, H. S. Kwok, X. Zhan, Y. Liu, D. Zhu and B. Z. Tang, *Chem. Commun.*, 2001, 1740; (b) Y. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Commun.*, 2009, 4332; (c) Y. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Soc. Rev.*, 2011, **40**, 5361.
2 Y. Dong, J. W. Y. Lam, A. Qin, J. Liu, Z. Li, B. Z. Tang, J. Sun and H. S. Kwok, *Appl. Phys. Lett.*, 2007, **91**, 011111.
3 Z. Zhao, J. W. Y. Lam and B. Z. Tang, *J. Mater. Chem.*, 2012, **22**, 23726.
4 (a) W. Z. Yuan, P. Lu, S. Chen, J. W. Y. Lam, Z. Wang, Y. Liu, H. S. Kwok, Y. Ma and B. Z. Tang, *Adv. Mater.*, 2010, **22**, 2159; (b) Z. Zhao, S. Chen, J. W. Y. Lam, P. Lu, Y. Zhong, K. S. Wong, H. S. Kwok and B. Z. Tang, *Chem. Commun.*, 2010, **46**, 2221; (c) Y. Liu, S. Chen, J. W. Y. Lam, P. Lu, R. T. K. Kwok, F. Mahtab, H. S. Kwok and B. Z. Tang, *Chem. Mater.*, 2011, **23**, 2536; (d) Z. Chang, Y. Jiang, B. He, J. Chen, Z. Yang, P. Lu, H. S. Kwok, Z. Zhao, H. Qiu and B. Z. Tang, *Chem. Commun.*, 2013, **49**, 594; (e) Y. Liu, Y. Lv, H. Xi, X. Zhang, S. Chen, J. W. Y. Lam, R. T. K. Kwok, F. Mahtab, H. S. Kwok, X. Tao and B. Z. Tang, *Chem. Commun.*, 2013, **49**, 7216.
5 Z. Zhao, S. Chen, X. Shen, F. Mahtab, Y. Yu, P. Lu, J. W. Y. Lam, H. S. Kwok and B. Z. Tang, *Chem. Commun.*, 2010, **46**, 686.
6 (a) C. W. Tang and S. A. Vanslyke, *Appl. Phys. Lett.*, 1987, **51**, 913; (b) T. P. I. Saragi, T. Spehr, A. Siebert, T. Fuhrmann-Lieker and J. Salbeck, *Chem. Rev.*, 2007, **107**, 1011; (c) P. E. Burrows, G. Gu, V. Bulovic, Z. Shen, S. R. Forrest and M. E. Thompson, *IEEE Trans. Electron Devices*, 1997, **44**, 1188; (d) J. N. Moorthy, P. Venkatakrishnan, P. Natarajan, Z. Lin and T. J. Chow, *J. Org. Chem.*, 2010, **75**, 2599.
7 (a) J. Huang, X. Yang, J. Wang, C. Zhong, L. Wang, J. Qin and Z. Li, *J. Mater. Chem.*, 2012, **22**, 2478; (b) J. Huang, N. Sun, J. Yang, R. Tang, Q. Li, D. Ma, J. Qin and Z. Li, *J. Mater. Chem.*, 2012, **22**, 12001; (c) J. Huang, N. Sun, Y. Dong, R. Tang, P. Lu, P. Cai, Q. Li, D. Ma, J. Qin and Z. Li, *Adv. Funct. Mater.*, 2013, **23**, 2329.