

Cite this: *Chem. Commun.*, 2011, **47**, 11216–11218

www.rsc.org/chemcomm

## Towards high efficiency solid emitters with aggregation-induced emission and electron-transport characteristics†

Wang Zhang Yuan,<sup>ab</sup> Shuming Chen,<sup>c</sup> Jacky W. Y. Lam,<sup>a</sup> Chunmei Deng,<sup>a</sup> Ping Lu,<sup>d</sup> Herman H-Y. Sung,<sup>a</sup> Ian D. Williams,<sup>a</sup> Hoi Sing Kwok,<sup>c</sup> Yongming Zhang<sup>b</sup> and Ben Zhong Tang<sup>\*ae</sup>

Received 9th July 2011, Accepted 1st September 2011

DOI: 10.1039/c1cc14122h

**Combination of an aggregation-induced emission (AIE) moiety and a dimesitylboron group yields a new three-coordinate boron compound exhibiting a synergistic effect: the resultant TPED-MesB shows AIE feature with solid-state emission efficiency up to unity and good electron-transport property, and thus remarkable electroluminescence (EL) performances.**

Design and synthesis of high efficiency solid-state organic materials is of fundamental importance and technical implications for various optoelectronic and photonic applications, such as organic light-emitting diodes (OLEDs),<sup>1</sup> organic lasers,<sup>2</sup> organic light-emitting transistors (OLETs),<sup>3</sup> and sensors.<sup>4</sup> Particularly, for OLEDs, development of multifunctional compounds which are capable of functioning as efficient emitters as well as charge-transport materials is of crucial importance to simplify the device configuration, improve the device duration, enhance the efficiency, and reduce the cost.<sup>5</sup> Therefore, intense endeavors have been made to generate electron- and/or hole-transport emitters in the past decades.<sup>6</sup> Whereas many molecules are highly emissive in dilute solutions, they become weakly fluorescent or non-emissive when aggregated in poor solvents or fabricated as thin films in the solid state. This notorious effect of aggregation-caused quenching (ACQ) has made the development of highly emissive multifunctional organic luminogens a daunting task.

In 2001, our group discovered a novel phenomenon of aggregation-induced emission (AIE): some propeller-like molecules such as siloles and tetraphenylethene (TPE) are non-emissive in solutions but are induced to emit intensely by aggregate

formation.<sup>7</sup> The mechanism of such AIE phenomenon has been identified as the restriction of intramolecular rotation (RIR).<sup>7b</sup> We wondered whether we can create new multifunctional materials through rational simple coupling of different functional moieties, namely AIE chromophores and charge-transport segments. Encouragingly, we recently reported the synthesis of triphenylamine-containing solid emitters with good hole-transport property and solid-state emission efficiency up to unity.<sup>8</sup> Such a win-win strategy eliminated the ACQ effect of triphenylamine without sacrificing its hole-transport property, moreover, giving greatly enhanced emission efficiencies.<sup>8</sup>

The success of obtaining hole-transport and highly luminescent organic solids promoted us to create electron-transport/emitting bifunctional materials. It is known that electron mobility in organic materials is generally orders of magnitude lower than the hole mobility. Therefore, the development of efficient electron-transport materials plays an important role in the improvement of the overall OLED device performance.<sup>9</sup>

So far, several types of electron-transport materials, such as C=N double bond-containing heterocycles, metal-quinolinol complexes, fluoro-substituted compounds, cyano-substituted poly(*p*-phenylenevinylene)s, and three-coordinated organoborons have been developed.<sup>9–11</sup> Among these, the organoboron compounds are particularly attractive and promising due to their unique properties stemming from the p<sub>π</sub>–π\* conjugation between the vacant p orbital on the boron atom with the π\* orbital of the π-conjugated framework.<sup>5,10b,12</sup> Many works have shown the applications of three-coordinate organoboron compounds in nonlinear optical organic material, light-emitting diodes, fluorescent sensing, and so on.<sup>4,13–19</sup> Here, we reported our work on the preparation of electron-transport highly fluorescent solid emitters based on a new approach through combination of AIE-active units (TPE) and the dimesitylboron group. The resulting compound TPEDMesB shows unique AIE characteristics with a solid state efficiency of 100% as well as good electron-transport ability. The OLED employing TPEDMesB as an emitter without an additional electron-transport layer showed bright bluish-green emission with a luminous efficiency of 7.13 cd A<sup>-1</sup>.

The target compound TPEDMesB was obtained in good yield (82.5%) by the lithiation of 1-(4-bromophenyl)-1,2,2-triphenylethene

<sup>a</sup> Department of Chemistry, The Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong, China.

E-mail: tangbenz@ust.hk

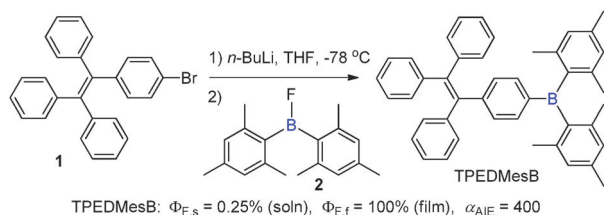
<sup>b</sup> School of Chemistry and Chemical engineering, Shanghai Jiao Tong University, Shanghai 200240, China

<sup>c</sup> Center for Display Research, HKUST, Kowloon, Hong Kong, China

<sup>d</sup> State Key Laboratory of Supramolecular Structure and Materials, Jilin University, Changchun 130023, China

<sup>e</sup> Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

† Electronic supplementary information (ESI) available: Experimental details, NMR, mass and UV-vis spectra, DSC, TGA curves, other EL data and cyclic voltammogram. CCDC 833200. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc14122h

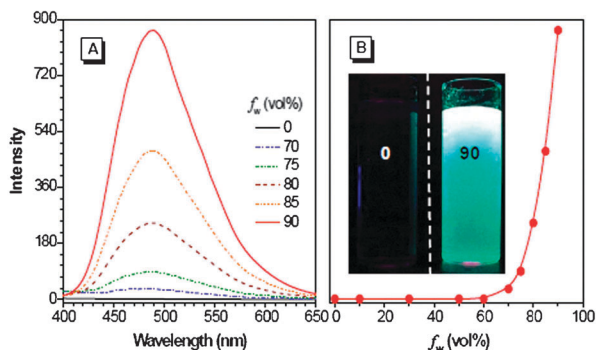


**Scheme 1** The synthetic route to TPEDMesB.

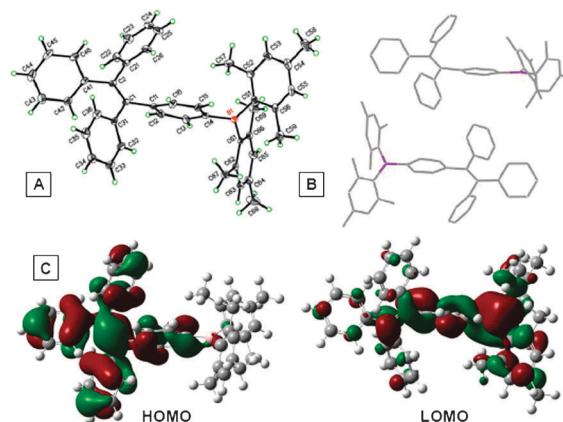
(1) at  $-78\text{ }^\circ\text{C}$  followed by reaction with dimesitylboron fluoride (2) (Scheme 1). Detailed synthetic procedure is provided in ESI†. TPEDMesB was characterized spectroscopically, with satisfactory data obtained (Fig. S1–S3, Table S1, ESI†).

TPEDMesB shows an absorption peak around 338 nm (Fig. S4, ESI†). When illuminated under UV light, no emission is seen from its solutions but intense fluorescence from solid films was observed, indicating that aggregation has turned on its light emission. Further photoluminescence (PL) measurement of TPEDMesB in THF–water mixtures duly verified its AIE-active nature. As shown in Fig. 1, a flat line is recorded for its pure THF solution, and even when the water fraction ( $f_w$ ) is as high as 70%, only a weak PL signal is recorded because the molecules are still genuinely dissolved in the mixture. However, when  $f_w > 80\%$ , addition of even a small amount of water gives sharp promotion in the PL intensity. From the molecular solution in THF to the aggregate suspension in the 90% aqueous mixture, the PL peak intensity of TPEDMesB at 489 nm is increased by 505 times. Comparison of the quantum yield ( $\Phi_F$ ) values of TPEDMesB in the solution and solid states further validates its AIE activity. While the  $\Phi_{F,s}$  value in THF is merely 0.25%, that of its solid films is boosted to 100%, giving an AIE factor ( $\alpha_{AIE} = \Phi_{F,f}/\Phi_{F,s}$ ) as high as 400, which is 6.6-fold higher than that of TPE.<sup>20</sup>

The single-crystal structure of TPEDMesB was attained to illustrate the AIE effect. As depicted in Fig. 2A, the TPEDMesB molecule is highly twisted so when it is dissolved in solvents, multiple phenyls undergo active intramolecular rotations which dissipate the exciton energy effectively, making it non-emissive in solution. However, when it is aggregated as nano-suspensions or solid films, on one hand, the intramolecular



**Fig. 1** (A) PL spectra of TPEDMesB in THF and THF–water mixtures. (B) Plot of PL peak intensity at 489 nm vs. water fraction ( $f_w$ ) of the aqueous mixture. Luminogen concentration: 20  $\mu\text{M}$ ; excitation wavelength: 360 nm. Inset: solution of TPEDMesB in THF ( $f_w = 0\%$ ) and its suspension in a THF–water mixture with  $f_w = 90\%$ ; photographs taken under UV illumination.



**Fig. 2** (A) ORTEP drawing, (B) molecular packing in crystals, and (C) B3LYP/6-31G(d) calculated molecular orbital amplitude plots of HOMO and LUMO levels of TPEDMesB.

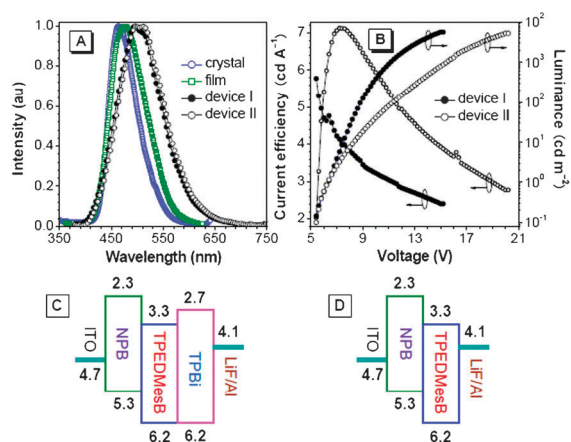
rotations are impeded, and on the other hand, the propeller-like configuration prevents the formation of detrimental excimers or exciplexes *via*  $\pi$ – $\pi$  stackings (Fig. 2B), thus endowing the aggregates with intense emission.

The B3LYP/6-31G(d) calculated HOMO and LUMO levels of TPEDMesB are shown in Fig. 2C. The electron cloud in HOMO level is mainly located on the TPE unit, whereas that of the LUMO level is predominantly located on the boron atom and the surrounding aromatic rings, revealing the electron transfer in the molecules.

The thermal properties of TPEDMesB was examined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements. The results reveal the decomposition temperature for a 5% weight loss ( $T_d$ ) and melting temperature ( $T_m$ ) of TPEDMesB are 359 and 206  $^\circ\text{C}$  (Fig. S6, ESI†), respectively, indicating it is thermally stable. No glass-transition temperature, however, was detected.

Due to its high thermal stability and efficient film emission, we then used TPEDMesB to fabricate EL devices. We first constructed an organic light-emitting diode (device I) with the configuration of ITO/NPB (60 nm)/TPEDMesB (20 nm)/TPBi (40 nm)/LiF (1 nm)/Al (100 nm),<sup>21</sup> where TPEDMesB serves as emitter and NPB and TPBi work as hole-transport and electron-transport layers, respectively. The EL spectrum of the device peaks at 496 nm (Fig. 3), which is slightly red-shifted from the PL peaks of the thin film (478 nm) and nanoaggregates (489 nm) of TPEDMesB, but far from the crystal emission (463 nm), indicating that the EL emission should be from the amorphous TPEDMesB layer. The device performance is good (Table 1 and Fig. S7, ESI†), with maximum luminance ( $L_{\text{max}}$ ), maximum current efficiency ( $CE_{\text{max}}$ ), power efficiency ( $PE_{\text{max}}$ ), and external quantum efficiency ( $EQE$ ) being 5581  $\text{cd m}^{-2}$ , 5.78  $\text{cd A}^{-1}$ , 3.2  $\text{lm W}^{-1}$  and 2.3%, respectively.

Due to the electron-deficient nature of boron atom, three-coordinated boron compounds can be used as efficient electron-transport materials.<sup>12</sup> To check whether TPEDMesB shows good electron-transport property, we fabricated device II, in which the TPBi layer was eliminated. The EL performances are shown in Fig. 3 and summarized in Table 1. Compared to device I, device II is turned on by the same voltage ( $V_{\text{on}} = 6.3\text{ V}$ ) with similar EL spectrum profile and comparable intensity



**Fig. 3** (A) PL and EL spectra of TPEDMesB, (B) current efficiency–luminance–voltage plots of its multilayer light-emitting diodes with a general device configuration of ITO/NPB/X/LiF/Al [X = TPEDMesB/TPBi (device I), X = TPEDMesB (device II)], and the energy diagrams of (C) device I and (D) device II.

**Table 1** EL performances of TPEDMesB based devices<sup>a</sup>

Device	$\lambda_{\max}$ / nm	$V_{\text{on}}$ / V	$L_{\max}$ /cd m <sup>-2</sup>	$PE_{\max}$ /lm W <sup>-1</sup>	$CE_{\max}$ /cd A <sup>-1</sup>	EQE (%)
I	496, 512	6.3	5581	3.4	5.78	2.3
II	496, 512	6.3	5170	3.2	7.13	2.7

<sup>a</sup> Device configuration: ITO/NPB (60 nm)/X/LiF (1 nm)/Al (100 nm); for device I: X = TPEDMesB (20 nm)/TPBi (40 nm); for device II: X = TPEDMesB (60 nm); abbreviations:  $\lambda_{\max}$  = EL peak,  $V_{\text{on}}$  = turn on voltage,  $L_{\max}$  = maximum luminance,  $PE_{\max}$  = maximum power efficiency,  $CE_{\max}$  = maximum current efficiency, and  $EQE$  = maximum external quantum efficiency.

( $L_{\max} = 5170 \text{ cd cm}^{-2}$ ); Moreover, it emits even more efficiently ( $CE_{\max} = 7.13 \text{ cd A}^{-1}$ ) due to the lower contact resistance. Evidently, TPEDMesB is serving as emissive component as well as electron-transport material in the EL device, which should be ascribed to an optimal energy match and charge-balance of the device, as can be seen from the energy alignment (Fig. 3C). The bifunctional property of TPEDMesB helps to simplify device structure, shorten fabrication process and lower production cost, and moreover enhance the device performance.

In summary, through combination of a typical AIE luminogen TPE and dimesitylboron moiety, a new bluish-green emitter TPEDMesB with AIE activity and excellent electron-transport property has been obtained. This molecule has been demonstrated to be a promising bifunctional material in the fabrication of a non-doped EL device, giving maximum current efficiency of  $7.13 \text{ cd A}^{-1}$ . Moreover, the work presented herein shows a new strategy on creating novel electron-transport high efficiency solid organics. The expansion of applicability of such strategy to create further multifunctional materials, such as oxadiazole- and 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY)-containing organics, and the study of ambipolar

compounds with AIE activities and high solid-state efficiencies is under way in our lab.

We thank the support from the Research Grants Council of Hong Kong (603509, HKUST2/CRF/10, and 604711).

## Notes and references

- (a) S. R. Forrest, *Org. Electron.*, 2003, **4**, 45; (b) M. Shimizu and T. Hiyama, *Chem.-Asian J.*, 2010, **5**, 1516.
- (a) M. D. McGehee and A. J. Heeger, *Adv. Mater.*, 2000, **12**, 1655; (b) I. D. W. Samuel and G. A. Turnbull, *Chem. Rev.*, 2007, **107**, 1272.
- (a) J. Zaumseil and H. Sirringhaus, *Chem. Rev.*, 2007, **107**, 1296; (b) F. Cicoira and C. Santato, *Adv. Funct. Mater.*, 2007, **17**, 3421.
- X. Y. Liu, D. R. Bai and S. Wang, *Angew. Chem.*, 2006, **118**, 5601.
- S.-L. Lin, L.-H. Chan, R.-H. Lee, M.-Y. Yen, W.-J. Kuo, C.-T. Chen and R.-J. Jeng, *Adv. Mater.*, 2008, **20**, 3947.
- (a) Y. Shirota, M. Kinoshita, T. Noda, K. Okumoto and T. Ohara, *J. Am. Chem. Soc.*, 2000, **122**, 11021; (b) R.-Y. Wang, W.-L. Jia, H. Aziz, G. Vamvounis, S. Wang, N.-X. Hu, Z. D. Popović and J. A. Coggan, *Adv. Funct. Mater.*, 2005, **15**, 1483; (c) H. Zhang, C. Huo, J. Zhang, P. Zhang, W. Tian and Y. Wang, *Chem. Commun.*, 2006, 281; (d) M. Kinoshita, H. Kita and Y. Shirota, *Adv. Funct. Mater.*, 2002, **12**, 780.
- (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) Q. Zeng, Z. Li, Y. Dong, C. Di, A. Qin, Y. Hong, L. Ji, Z. Zhu, C. K. W. Jim, G. Yu, Q. Li, Z. Li, Y. Liu, J. Qin and B. Z. Tang, *Chem. Commun.*, 2007, 70; (d) S. Dong, Z. Li and J. Qin, *J. Phys. Chem. B*, 2009, **113**, 434; (e) Z. Li, Y. Q. Dong, J. W. Y. Lam, J. Sun, A. Qin, M. Häubler, Y. P. Dong, H. H. Y. Sung, I. D. Williams, H. S. Kwok and B. Z. Tang, *Adv. Funct. Mater.*, 2009, **19**, 905.
- 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.
- A. P. Kulkarni, C. J. Tonzola, A. Babel and S. A. Jenekhe, *Chem. Mater.*, 2004, **16**, 4556, and references therein.
- (a) D. Izuhara and T. M. Swager, *J. Mater. Chem.*, 2011, **21**, 3579; (b) Z. M. Hudson and S. Wang, *Dalton Trans.*, 2011, **40**, 7805, and references therein.
- Y. Shirota and H. Kageyama, *Chem. Rev.*, 2007, **107**, 953.
- (a) P. Chen, R. A. Lalancette and F. Jäkle, *J. Am. Chem. Soc.*, 2011, **133**, 8802; (b) C. D. Entwistle and T. B. Marder, *Angew. Chem., Int. Ed.*, 2002, **41**, 2927; (c) C. D. Entwistle and T. B. Marder, *Chem. Mater.*, 2004, **16**, 4574.
- H. Doi, M. Kinoshita, K. Okumoto and Y. Shirota, *Chem. Mater.*, 2003, **15**, 1080.
- (a) A. Wakamiya, K. Mori and S. Yamaguchi, *Angew. Chem., Int. Ed.*, 2007, **46**, 4273; (b) S. Yamaguchi, T. Shirasaka and K. Tamao, *Org. Lett.*, 2000, **2**, 4129; (c) C.-H. Zhao, A. Wakamiya, Y. Inukai and S. Yamaguchi, *J. Am. Chem. Soc.*, 2006, **128**, 15934; (d) M. Elbing and G. C. Bazan, *Angew. Chem., Int. Ed.*, 2008, **47**, 834.
- A. Lorbach, M. Bolte, H. Li, H.-W. Lerner, M. C. Holthausen, F. Jäkle and M. Wagner, *Angew. Chem., Int. Ed.*, 2009, **48**, 4584.
- N. Matsumi, K. Naka and Y. Chujo, *J. Am. Chem. Soc.*, 1998, **120**, 5112.
- Y. Zhou, J. W. Kim, R. Nandhakumar, M. J. Kim, E. Cho, Y. S. Kim, Y. H. Jang, C. Lee, S. Han, K. M. Kim, J.-J. Kim and J. Yoon, *Chem. Commun.*, 2010, **46**, 6512.
- Z. Yuan, J. C. Collings, N. J. Taylor, T. B. Marder, C. Jardin and J. F. Halet, *J. Solid State Chem.*, 2000, **154**, 5.
- A. Loudet and K. Burgess, *Chem. Rev.*, 2007, **107**, 4891.
- 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.
- ITO = indium tin oxide; NPB = 1,4-bis[(1-naphthylphenyl)amino]biphenyl (hole-transport layer); TPBi = 1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene (electron-transport layer).