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A novel tetraphenylethene–carbazole type compound containing the dimesitylboron moiety: aggregation-induced emission enhancement and electroluminescence properties†

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A highly efficient blue light-emitting material based on tetraphenylethene as an aggregation-induced emission enhancement (AIEE) group, carbazole as a hole-transporting group and dimesitylboron as an electronic-transporting group was synthesized and utilized in OLED devices.

Since Tang's innovative work on organic light-emitting diodes (OLEDs) in 1987,[1] OLED devices have attracted considerable interest owing to their potential applications in full-colour flat-panel displays and solid state lighting.[2–5] In order to obtain high-performance OLEDs, many efforts have been made to develop various novel organic materials with desirable properties. To date, the photo-electronic properties of OLEDs devices have been improved greatly. Great success has been made in developing green and red organic light-emitting materials. However, it is still a challenge to design and synthesize blue light-emitting materials of high efficiency, high colour purity, and long operational time due to their wide energy gap. In other words, the process of the injection of holes from the anode and electrons from the cathode in blue light-emitting OLEDs devices is difficult to balance.[6–9] Moreover, the luminescence of many organic luminophores is often weakened or quenched at high concentrations. This phenomenon is widely known as the aggregation-caused quenching effect and was proved to be a thorny obstacle to the fabrication of efficient OLEDs devices.[10,11] Both the above-mentioned factors give rise to the rarity of blue light-emitting materials.

In 2001, Tang and co-workers reported a phenomenon, termed aggregation-induced emission (AIE). They observed that 1-methyl-1,2,3,4,5-pentaphenylsilole is practically non-luminescent in solutions but becomes highly emissive when aggregated.[12] In the subsequent studies, they determined that restriction of intramolecular rotation (RIR) in aggregation state is the major impetus for AIE effect.[13] Based on RIR mechanism, Tang and other groups have discovered a number of AIE-active molecules including siloles, cyanostilbenes, and tetraphenylethene (TPE) derivatives. Among these molecules, tetraphenylethene derivatives enjoy the advantages of facile synthesis and outstanding AIE effect, and are thus considered as good electroluminescence (EL) materials for fabrication of OLEDs devices.[14]

Recently, Tang and co-workers reported an AIE-active molecular combining TPE and dimesitylboron moiety, which is a promising bifunctional EL material with excellent electron-transporting and light-emitting properties.[15] In their subsequent study, they synthesized three AIE-active molecules incorporating TPE and carbazole moiety which are prospective bifunctional EL materials with excellent hole-transporting and light-emitting properties.[16] Their results demonstrated that compounds containing TPE and dimesitylboron as well as TPE and carbazole moieties are attractive materials for organic EL devices attributing to their efficient luminescence and transport performance. Inspired by their results, we are interested in synthesis of a new class of compounds possessing AIE, hole-transporting and electronic-transporting groups. This type of compounds is anticipated to show good thermal stability and multifunctional property. To our knowledge, there are only few reports on this type of compounds.

Herein we first report a novel compound based on tetraphenylethene (as aggregation-induced emission enhancement (AIEE) group), carbazole (as hole-transporting group) and

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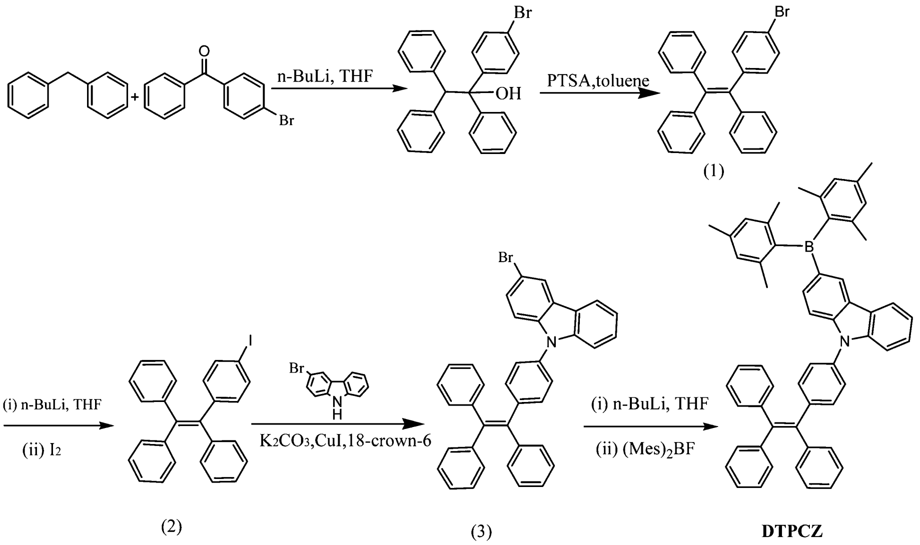
dimesitylboron (as electronic-transporting group). This compound, 3-dimesityboron-9-(4-(1,2,2-triphenylvinyl)phenyl)-9*H*-carbazole (**DTPCZ**), was synthesized by introducing dimesitylboron and TPE moieties to the 3-position and 9-position of carbazole, respectively. The resulting compound **DTPCZ** shows unique AIEE as well as excellent EL, hole-transporting and electron-transporting properties. The OLEDs device using **DTPCZ** as the light emitting layer shows pure blue emission with a luminance efficiency of 4.28 cd A^{-1}.

The target compound **DTPCZ** was obtained by a multi-step reaction. First, the key intermediate (3-bromo-9-(4-(1,2,2-triphenylvinyl)phenyl) carbazole) was synthesized *via* the modified Ullmann reaction of 1-(4-iodophenyl)-1,2,2-triphenylethene and 3-bromocarbazole in the presence of 18-crown-6, K_2CO_3 and CuI catalyst system in DMF at 140 °C with 19.4% yield, and then, **DTPCZ** was obtained by reacting the key intermediate with *n*-BuLi, followed with adding dimesitylboron fluoride under N_2 at −78 °C with 36% yield. The detailed synthetic route and chemical structure of **DTPCZ** confirmed by ^{1}H and ^{13}C nuclear magnetic resonance spectroscopy, mass spectrometry, and elemental analysis are presented in ESI.† Scheme 1 illustrates the synthetic route of **DTPCZ**.

The photophysical properties of **DTPCZ** (5.0 μM) in various solvent systems were initially studied. Fig. S1 (ESI)† depicts the absorption spectra of **DTPCZ** in *n*-hexane, dichloromethane, tetrahydrofuran (THF), acetonitrile, and dimethylsulfoxide. Two absorption peaks at *ca.* 312 and 350 nm are observed in these solvents, corresponding to $\pi \rightarrow \pi^*$ transitions of skeleton and intramolecular charge transfer (ICT), respectively. The absorption data are displayed in Table S1 (ESI).† The fluorescence spectra of **DTPCZ** were depicted in Fig. S2 (ESI).† With the increasing polarity of the solvents, a bathochromic shift of 70 nm ranging from 383 nm (in hexane) to 453 nm (in CH_3CN) was observed. Such a distinct solvatochromism indicated that intramolecular charge transfer from the tetraphenylethene–carbazole moiety to dimesitylboron moiety takes place during the excitation process. There is not much difference in the spectral characteristics of **DTPCZ** in these solvents.

It has been reported that the AIE of some TPE derivatives in organic solvents could be induced in the presence of polar co-solvent.[15] As such, the effect of water on AIE of **DTPCZ** in different THF–water solvent mixtures was investigated. Herein, THF and water act as the solvent and non-solvent, respectively. Fig. 1a depicts the photoluminescence (PL) spectra of **DTPCZ** in various THF–water solvent mixtures at an excitation wavelength of 350 nm. **DTPCZ** displays very weak PL emission in pure THF with a fluorescence quantum yield (Φ) of 0.38% (the PL peak is at 425 nm). There is no significant change in spectral characteristics of **DTPCZ** when the water volume fraction (f_w) of the THF–water solvent mixtures is 0.0–60% v/v. However, the PL peak shifts to 475 nm (Table S1, ESI†) and the PL intensity increases drastically when (f_w) is > 60% v/v. The higher the f_w = 65–95% v/v, the stronger the emission intensity. When f_w is 80% v/v, a small increase in f_w can promote a large increase in PL intensity. When f_w is 95% v/v, the PL intensity reaches the maximum. Fig. 1b depicts the plot of $[(I/I_o) - 1]$ against f_w, where I_o and I are the PL intensities without and with water in the THF–water mixtures. It is obvious that water could induce the PL of **DTPCZ** in THF–water solvent mixture, attributing to the AIE of **DTPCZ** in high water content of solvent mixture.

The Φ of **DTPCZ** in f_w = 95% is 56%, which is enhanced by 148 times in comparison to that in THF and the corresponding PL peak intensity of **DTPCZ** at 475 nm increases by 256 times. These data strongly indicate the prominent aggregation-induced emission enhancement (AIEE) characteristics of **DTPCZ**, which can be attributed to the RIR process in the aggregate formation which populates the radioactive decay of the excitons and makes the luminogen fluoresce strong.[17] **DTPCZ** in THF–water mixtures (f_w = 65–95% v/v) are macroscopically homogenous with no sign of precipitates, thereby suggesting the aggregates are nano-dimensional. The morphology of these nano-aggregrates was investigated by SEM



Scheme 1 Synthetic route of DTPCZ.

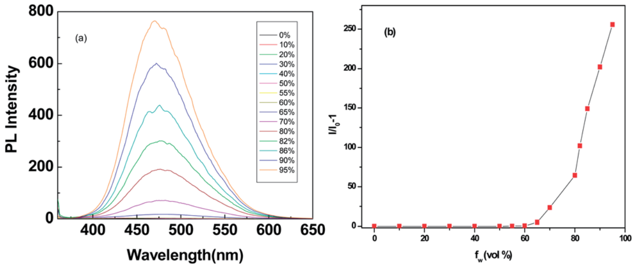


Fig. 1 (a) PL spectra of **DTPCZ** in various water contents of THF–water mixtures at excitation 350 nm. (b) Plot of $(I/I_o) - 1$ against water volume fraction (f_w), where I_o and I are the PL intensities without and with water in the THF–water mixtures. The intensity was monitored at excitation/emission wavelengths of 350/475 nm.

and TEM. Fig. S3 (ESI)† shows the SEM image of the nano-aggregrates of **DTPCZ** obtained from THF–water (1 : 9) mixture. **DTPCZ** is highly aggregrated to form some nanoparticles with diameters of less than 100 nm. The inset of Fig. S3† displays the TEM image of the nano-aggregrates of **DTPCZ**. Spherical nanoparticles of diameter *ca.* 50–100 nm is clearly observed. These results confirm that **DTPCZ** could form nano-aggregrates in high water contents of solvent mixtures and these nano-aggregrates possess strong PL emission. **DTPCZ** does not form nano-aggregrates such as in organic solvents and so no or very weak PL is found. Thin film of **DTPCZ** was fabricated on a glass substrate and its PL property was taken. Fig. S4 (ESI)† displays the PL spectrum of thin film of **DTPCZ** at an excitation wavelength of 350 nm. A strong blue emission band at 464 nm (Table S1, ESI†) is observed which is similar to that of the nano-aggregates of **DTPCZ**. Our results demonstrate that once the **DTPCZ** molecules are aggregated, the PL properties of **DTPCZ** will be produced and the PL emission band will depend on the particle size and/or polydispersity of the nano-aggregates.

To obtain better insight on geometrical structure and electronic properties of **DTPCZ** was studied with DFT/B3LYP/6-31G (d,p) method by using the polarized continuum model (PCM). Coordinates of **DDBICZ** from DFT calculation are deposited in Table S2 (ESI).† The optimal structure and the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) distributions of **DTPCZ** are shown in Fig. S5 (ESI).† The optimal geometry shows that the TPE moiety is twisted from the plane of the carbazole and the dimesitylboron moiety forms propeller-like conformation at the 3-position of carbazole. We infer that the intramolecular rotation (IMR) process of the TPE unit and dimesitylboron moiety of **DTPCZ** can effectively consume the excited state energy, resulting in non-radiative decay process of the luminogens in the solution state, and when **DTPCZ** is aggregated as nano-suspensions or solid films, the intramolecular rotations are impeded and the propeller-like configuration hinder the emission quenching caused by intermolecular π–π stacking interaction, thus endowing the aggregates with intense emission.

The electron density of the HOMO is localized on the backbone of carbazole and TPE while the electron density of the LUMO is localized mainly on the dimesitylboron moiety and slightly on the backbone of carbazole and TPE. Thus, the electronic transition from the ground state to the first excited state mainly involves the ICT from the backbone of carbazole and TPE as the electron-donor to the dimesitylboron moiety as the electron-acceptor.

The thermal properties of **DTPCZ** were investigated by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC), as displayed in Fig. S6 and S7 (ESI),† respectively. The decomposition temperature (T_d based on 5% weight loss) at 241 °C, the glass transition temperature (T_g) at 123 °C and the melting temperature (T_m) at 202 °C were determined from the TGA and DSC curves, respectively. These data are summarized in Table S1 (ESI).† Our results indicate that **DTPCZ** have excellent thermal properties which should be adequate for optoelectronic device applications.

The electrochemical property of **DTPCZ** was investigated by cyclic voltammetry. Fig. S8 (ESI)† depicts the cyclic voltammogram (CV) of **DTPCZ** which exhibits two reversible oxidation and reduction peaks. The oxidation peak at 0.76 V is attributing to the oxidation of carbazole moiety and the other oxidation peak at 1.35 V is from the oxidation of TPE moiety. The two reversible reduction peaks at −0.897 and −0.475 V are corresponding to the reduction of triarylboron and TPE moieties, respectively. The CV curves remain unchanged under multiple successive potential scans, indicating the excellent redox stability of **DTPCZ**. The HOMO and LUMO energy level and energy band gap (E_g) are determined from the CV curves and summarized in Table S1 (ESI).† The energy band gap is in consistent with the ICT band (*vide supra*) of **DTPCZ**.

In order to evaluate the potential application of **DTPCZ** as luminescent material in EL device, a multi-layer device (Device A) with the configuration of indium tin oxide (ITO)/*N*,*N*′-di-1-naphthyl-*N*,*N*′-diphenylbenzidine (NPB) (60 nm)/**DTPCZ** (20 nm)/2,2′,2″-(1,3,5-benzinetriyl)tris(1-phenyl-1-*H*-benzimidazole) (TPBi) (10 nm)/tris(8-hydroxyquinolinolato) aluminium (Alq_3) (30 nm)/LiF (1 nm)/Al (200 nm) was fabricated by vacuum deposition, in which NPB and Alq_3 functioned as the hole-transporting layer and the electron-transporting layer, respectively. TPBi and **DTPCZ** worked as the hole-blocking layer and the emitting layer, respectively. Fig. 2a depicts the EL spectra of Device A at driving voltages of 6.0–16.0 V, which remain unchanged when the driving voltage increases from 6.0 to 16.0 V. The EL spectrum has a peak maximum of 464 nm and CIE coordinates (0.18, 0.21) which is identical to the PL spectrum of the solid thin film of **DTPCZ**. Fig. 2b and c display the current density–voltage–luminance curve and luminance efficiency–current density curve of Device A, respectively. Device A exhibits good performance with a turn-on voltage of 6.0 V, a maximum luminance of 4624 cd m^{-2} at 16.2 V and a maximum luminescent efficiency of 4.28 cd A^{-1} at 10.5 V. Table S3 (ESI)† summarizes the EL properties of **DTPCZ**. The data indicate that **DTPCZ** is a promising blue light emitting material for fabrication of OLEDs. Although the maximum luminance and luminance efficiency of the EL device of **DTPCZ** might not be as high as in some of the blue EL devices reported before,[15,16] the novel compound is promising for application in OLEDs as emitting

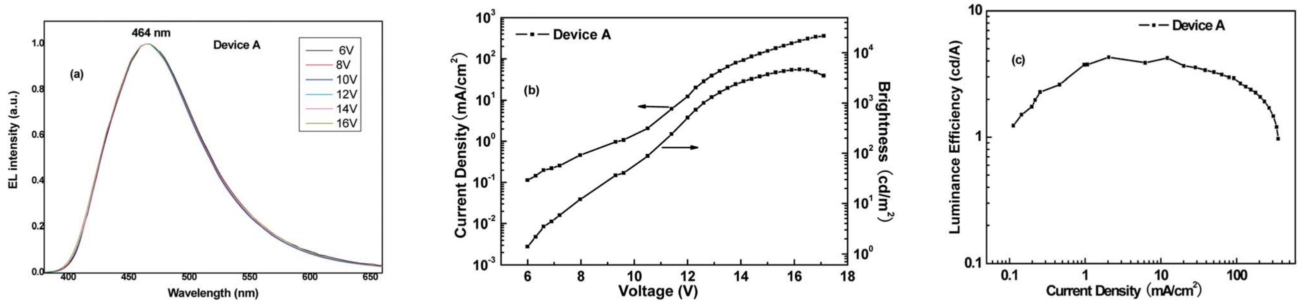


Fig. 2 (a) Electroluminescent spectra, (b) current density–voltage–luminance curves and (c) current density–luminance efficiency curve of Device A.

material due to its excellent thermal, electrochemical and charge-transporting properties.

In summary, a novel compound (**DTPCZ**) with AIEE behaviour through combination of TPE, carbazole and dimesitylboron moieties has successfully synthesised. **DTPCZ** is demonstrated to be a promising EL material for the non-doped EL device, displaying the same pure blue emission (464 nm) with CIE coordinates (0.18, 0.21) at various driving voltages. The fabricated Device A has a turn-on voltage of 6.0 V, a maximum luminance of 4624 cd m^{-2} and a maximum luminance efficiency of 4.28 cd A^{-1}. Finally, our work provides a new strategy of developing highly efficient EL materials.

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References

1 C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.*, 1987, **51**, 913.

2 J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, *et al.*, *Nature*, 1990, **347**, 539.

3 L. S. Hung and C. Chen, *Mater. Sci. Eng., R*, 2002, **39**, 143.

4 U. Mitschke and P. Bäuerle, *J. Mater. Chem.*, 2000, **10**, 1471.

5 Y. Shirota, *J. Mater. Chem.*, 2000, **10**, 1.

6 L. M. Leung, W. Y. Lo, S. K. So, K. M. Lee and W. K. Choi, *J. Am. Chem. Soc.*, 2000, **122**, 5640.

7 M. T. Lee, C. H. Liao, C. H. Tasi and C. H. Chen, *Adv. Mater.*, 2005, **17**, 205.

8 C. C. Wu, Y. T. Lin, K. T. Wong, R. T. Chen and Y. Y. Chen, *Adv. Mater.*, 2004, **16**, 61.

9 Y. Zhang, L. L. Zhang, R. S. Wang and X. M. Pan, *J. Mol. Graphics Modell.*, 2012, **34**, 46.

10 (*a*) S. W. Thomas III, G. D. Joly and T. M. Swager, *Chem. Rev.*, 2007, **107**, 1339; (*b*) A. C. Grimsdale, K. L. Chan, R. E. Martin, P. G. Jokisz and A. B. Holmes, *Chem. Rev.*, 2009, **109**, 897.

11 J. Huang, N. Sun, Y. Q. Dong, R. L. Tang, P. Lu, P. Cai, Q. Q. Li, D. G. Ma, J. G. Qin and Z. Li, *Adv. Funct. Mater.*, 2013, **23**, 2329.

12 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.

13 J. Chen, B. Xu, X. Y. Ouyang, B. Z. Tang and Y. Cao, *J. Phys. Chem. A*, 2004, **108**, 7522.

14 (*a*) 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; (*b*) S. K. Kim, Y. Park, I. N. Kang and J. W. Park, *J. Mater. Chem.*, 2007, **17**, 4670; (*c*) 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; (*d*) Z. Zhao, J. W. Y. Lam, C. Y. K. Chan, S. Chen, J. Liu, P. Lu, M. Rodriguez, J. L. Maldonado, G. Ramos-Ortiz, H. H. Y. Sung, I. D. Williams, H. Su, K. S. Wong, Y. Ma, H. S. Kwok, H. Qiu and B. Z. Tang, *Adv. Mater.*, 2011, **23**, 5430; (*e*) C. Y. K. Chan, Z. Zhao, J. W. Y. Lam, J. Liu, S. Chen, P. Lu, F. Mahtab, X. Chen, H. H. Y. Sung, H. S. Kwok, Y. Ma, I. D. Williams, K. S. Wong and B. Z. Tang, *Adv. Funct. Mater.*, 2012, **22**, 378; (*f*) 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; (*g*) B. Xu, Z. Chi, H. Li, Xi. Zhang, X. Li, S. Liu, Y. Zhang and J. Xu, *J. Phys. Chem. C*, 2011, **115**, 17574; (*h*) Z. Zhao, J. W. Y. Lamb and B. Z. Tang, *J. Mater. Chem.*, 2012, **22**, 23726.

15 W. Z. Yuan, S. M. Chen, J. W. Y. Lam, C. M. Deng, P. Lu, H. H.-Y. Sung, I. D. Williams, H. S. Kwok, Y. M. Zhang and B. Z. Tang, *Chem. Commun.*, 2011, **47**, 11216.

16 Z. J. Zhao, C. Y. K. Chan, S. M. Chen, C. M. Deng, J. W. Y. Lam, C. K. W. Jim, Y. N. Hong, P. Lu, Z. F. Chang, X. P. Chen, P. Lu, H. S. Kwok, H. Y. Qiu and B. Z. Tang, *J. Mater. Chem.*, 2012, **22**, 4527.

17 J. Zhou, Z. F. Chang, Y. B. Jiang, B. R. He, M. Du, P. Lu, Y. N. Hong, H. S. Kwok, A. J. Qin, H. Y. Qiu, Z. J. Zhao and B. Z. Tang, *Chem. Commun.*, 2013, **49**, 2491.