# New aggregation-induced emission enhancement materials combined triarylamine and dicarbazolyl triphenylethylene moieties<sup>†</sup>

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A new class of compounds containing triarylamine and dicarbazolyl triphenylethylene moieties with high thermal stability and aggregation-induced emission enhancement properties was synthesized. The glass transition temperature and 5% weight loss temperature of 3B-TPA are up to 214.3 °C and 516.8 °C, respectively. The compounds exhibited significant photoinduced intramolecular charge-transfer properties. The aggregation considerably affected the  $\pi$ - $\pi$ \* transition and resulted in 6–7 nm red shift of the  $\pi$ - $\pi$ \* absorption wavelength at the peak in UV-vis spectra. The compounds could emit intense blue-green light in aggregated states.

## Introduction

Organic luminescent materials with strong solid-state emission have gained great interest for their important use in the applied fields of electroluminescence devices.<sup>1</sup> The aggregation caused by the strong intermolecular  $\pi$ - $\pi$  interaction in the solid state generally debases or quenches the emission.<sup>2</sup> Aggregation quenching is considered as an intractable problem in the development of devices because organic materials are normally used as thin solid films, and that aggregation inherently accompanies film formation. Thus, it is highly desirable to develop luminescent materials that emit intense light in the solid state and can overcome the aggregation-quenching problem. Recently, an unusual phenomenon, where some luminescent molecules have enhanced emission in the solid state, referred to as aggregationinduced emission (AIE)<sup>3</sup> or aggregation-induced emission enhancement (AIEE),<sup>4</sup> has been observed. This phenomenon offers a new path in solving problems on aggregation-caused quenching.

Highly electron-rich triarylamines, which are known to have high hole mobility, have been widely used as hole-transporting materials in multilayer organic electro-luminescence devices.<sup>5</sup> However, triphenylamine (TPA) derivatives have the tendency to crystallize upon exposure to heat resulting in aggregationinduced fluorescence quenching of fluorophores, and often possess low glass transition temperatures ( $T_g$ ) (*i.e.*, poor morphological stability), resulting in low reliability when used in optoelectronic devices. Aggregation quenching and low  $T_g$  are the major reasons for the rare use of TPA derivatives for layer emission in electroluminescent device applications. Consequently, many structural modifications have been made in attempts to develop new TPA derivatives that possess high morphological stability and optoelectronic properties.<sup>6</sup> On the other hand, we have already reported in the recent works a new class of triphenylethylene carbazole derivatives that displayed strong blue light emissions, high  $T_g$  temperatures and AIE effects.<sup>7</sup> We are thus extending these studies by combining dicarbazolyl triphenylethylene and triarylamine units into a single compound *via* synthetic methodology, and to design materials with potential technological applications.

In this article, we present the synthesis of three new compounds in which triphenylamine was mono-, di- and trisubstituted by dicarbazolyl triphenylethylene units. Their thermal and optoelectronic properties are also discussed. The compounds exhibited significant photoinduced intramolecular charge-transfer properties. It was found that the aggregation has a pronounced effect on the  $\pi$ - $\pi$ \* transition. In particular, the three compounds have exhibited aggregation-induced emission enhancement and high levels of thermal stability, which might be promising as luminescent materials.

## **Results and discussion**

## Synthesis

The synthetic routes to the desired compounds are illustrated in Scheme 1. The intermediates 1,7 2,7 4,8 59 and 610 were prepared according to the methods in the literatures. The key intermediate, 3, was prepared from 2 by lithiation with *n*-butyllithium and boronation with trimethyl borate (55% yield). However, we could not obtain compound 3 by Grignard reaction because compound 2 did not react with magnesium (Mg) and failed to produce a Grignard reagent. The target compounds, 1B-TPA, 2B-TPA and 3B-TPA, were synthesized by Suzuki coupling reactions of 3 with the corresponding halogenated triphenylamines 4, 5 and 6 in the presence of a palladium(0) catalyst (36– 53% yield). The products exhibited good solubility in common organic solvents and were purified by silica gel column chromatography using dichloromethane-*n*-hexane as eluent. Their chemical structures were confirmed with proton nuclear magnetic resonance (<sup>1</sup>H-NMR), high resolution mass

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The DSC curves of the samples in the first and second heating runs are shown in Figs 1 and 2, respectively. In the first heating run, only compound **1B-TPA** exhibited a very small melting



Fig. 1 DSC scans of the synthesized compounds at first heating.



Fig. 2 DSC scans at second heating (samples after cooled from their melts with a 10  $^{\circ}$ C min<sup>-1</sup> cooling rate).





Scheme 1 Synthetic routes to the compounds.

spectrometer (HRMS), Fourier transform infrared spectroscopy (FT-IR) and elementary analysis (EA).

#### Thermal properties

The thermal stability of organic materials is critical for their applications as luminescent emitters because thermal stability governs the stability and lifetime of devices. If a device is heated above the  $T_g$  of its organic material components, irreversible failure can occur. Hence, a relatively high  $T_g$  is essential for emissive materials used for optoelectronic applications.

Thermal properties were investigated by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). The  $T_g$  values of **1B-TPA**, **2B-TPA** and **3B-TPA** were 137.9, 196.7 and 214.3 °C, respectively, which were much higher than those of the two reported typical AIE-active compounds, 1-methyl-1,2,3,4,5-pentaphenylsilole (MPPS, 54 °C) and 1,1,2,3,4,5-hexaphenylsilole (HPS, 65 °C).<sup>11</sup> The high  $T_g$  is attributed to the effect of the bulky carbazolyl groups. To the best of our knowledge, the  $T_g$  of **3B-TPA** is currently the highest reported for organic luminescent materials with AIE properties. The highest  $T_g$  found for AIE compounds was at 204 °C, which was reported by Tang.<sup>12</sup> As expected,  $T_g$  values increased with a rise in the number of dicarbazolyl triphenylethylene substituents. Trisubstituted **3B-TPA** possessed the highest  $T_g$  of up to 214.3 °C.

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transition peak at 236.5 °C. In the second heating run, only a glass transition could be observed for each compound. This indicates that the compounds exhibited a very low tendency towards crystallization, as no melting peak could be detected, which is ascribed to the starburst structures. Amorphous materials possessing a high  $T_g$  could have a better chance to retain film morphology during device operation.

The  $T_d$  of **1B-TPA**, **2B-TPA** and **3B-TPA** (corresponding to 5% weight loss under N<sub>2</sub> atmosphere) were 438.5, 487.2 and 516.8 °C, respectively (Fig. 3). The  $T_d$  values also showed the same trend as the  $T_g$  values, increasing with the rise in the number of dicarbazolyl triphenylethylene substituents. The trisubstituted **3B-TPA** possessed the highest  $T_d$  of up to 516.8 °C.

The results indicate that the compounds have a very high thermal stability, including high  $T_g$  and  $T_d$ . The thermal stability of organic compounds plays a critical role in both the stability and lifetime of photoelectric devices. Thus, the high level of thermal stability suggests that the synthesized compounds might prove useful for photoelectric materials in fabrication devices.

#### Optical properties and energy levels

To further study the relationship between their molecular structures and optical properties, we investigated the optical properties of these compounds by UV-vis absorption spectroscopy (UV) and photoluminescence spectroscopy (PL). Different organic solvents of cyclohexane (CH), toluene (TOL), dichloromethane (MC), tetrahydrofuran (THF), *N*,*N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were used; herein, these are arranged from the lowest to highest polarity. Note that the spectra of **2B-TPA** are shown in the text as examples; the others are mentioned in the ESI.<sup>†</sup>

Fig. 4 outlines the UV absorption spectra of 2B-TPA in different solvents (5  $\mu$ M) (see also the ESI for the absorption spectra of 1B-TPA and 3B-TPA<sup>†</sup>). There were two main absorption bands in all the compounds: one located at 341-344 nm ( $\lambda$ 1) corresponding to the absorption of the carbazolyl segment, and the other located at 368–389 nm ( $\lambda$ 2) attributed to  $\pi$ - $\pi$ \* transitions. The UV data are summarized in Table 1. It is interesting to note that the compounds show almost the same  $\lambda 1$ values. However, the  $\lambda 2$  and molar absorption coefficient,  $\varepsilon$ , values increased with the number of dicarbazolyl triphenylethylene substituents. For example, in toluene, even if the  $\lambda 1$  of **1B-TPA**, **2B-TPA** and **3B-TPA** were the same at 342 nm, their  $\lambda 2$ values were 370, 384 and 388 nm and their  $\varepsilon$  values were 4.4  $\times$  $10^4$ ,  $7.2 \times 10^4$  and  $11.2 \times 10^4$  M<sup>-1</sup> cm<sup>-1</sup>, respectively. As can be seen from Table 1, solvent polarity had little effect on the absorption wavelengths of these compounds. Since 3B-TPA has a relatively low solubility in CH and its concentration cannot reach 5  $\mu$ M at room temperature, the  $\varepsilon$  in Table 1 and PL intensity in Table 2 were omitted.

However, solvent polarity exerted a great effect on the PL emission, as shown in Fig. 5 and Table 2. The PL intensities (I) and quantum yield ( $\Phi$ ) of the solutions of the three compounds decreased with increasing solvent polarity. The  $\Phi$  of **1B-TPA**, **2B-TPA** and **3B-TPA** were 0.57, 0.67 and 0.73 in CH (lowest polarity, the  $\Phi$  were very high), and 0.19, 0.20 and 0.20 in DMSO (highest polarity), respectively. In CH, the  $\Phi$  were approximately 3.0-, 3.4-, and 3.7-fold higher as compared with those in the



Fig. 4 UV-vis absorption spectra of **2B-TPA** in different solvents (5  $\mu$ M).

Table 1 UV data of the compounds in different solvents (5  $\mu$ M)

Solv.	1B-TPA			2B-TPA			3B-TPA		
	λ1	λ2	ε/10 <sup>4</sup>	λ1	λ2	ε/10 <sup>4</sup>	λ1	λ2	ε/10 <sup>4</sup>
СН	341	368	5.0	341	379	7.8	341	387	_
TOL	342	370	4.4	342	384	7.2	342	388	11.2
MC	343	368	4.6	343	379	7.6	342	386	11.4
THF	343	368	4.9	342	380	7.7	341	387	11.8
DMF	344	369	4.9	342	381	7.5	342	387	11.3
DMSO	344	370	4.5	343	381	7.5	342	390	11.3

 Table 2
 PL data of compounds in different solvents<sup>a</sup>

		CH	TOL	MC	THF	DMF	DMSO
1B-TPA	Φ	0.57	0.38	0.25	0.22	0.17	0.19
	λ	467	473	494	491	516	519
	Ι	265	147	105	93	64	63
2B-TPA	$\Phi$	0.67	0.47	0.34	0.32	0.22	0.20
	λ	461	468	496	493	522	527
	Ι	419	304	226	216	124	113
3B-TPA	$\Phi$	0.73	0.49	0.37	0.37	0.22	0.20
	λ	456	465	498	495	524	529
	Ι		385	279	276	145	131

<sup>*a*</sup>  $\Phi$ : quantum yield; I: PL intensity (a.u.);  $\lambda$ : maximum emission wavelength.



Fig. 5 PL emission spectra of 2B-TPA in different solvents (5 µM).



Fig. 6 Fluorescent images of **2B-TPA** dissolved in different solvents taken under irradiation at  $365 \text{ nm} (5 \mu \text{M})$ .

DMSO. As illustrated in Fig. 5, the maximum emission wavelength ( $\lambda$ ) of each compound progressively shifted to a longer wavelength when the polarity of the solvent increased from CH to DMSO. The  $\lambda_{em}$  of **1B-TPA**, **2B-TPA** and **3B-TPA** were 467, 461 and 456 nm in CH, and 519, 527 and 529 nm in DMSO, respectively. Compared with the  $\lambda$  in CH solutions, the  $\lambda$  values in DMSO solutions red-shifted by 52, 66 and 73 nm for **1B-TPA**, **2B-TPA** dissolved in different solvents taken under irradiation at 365 nm are shown in Fig. 6. As can be seen, the fluorescence colors completely differ from each other. Thus, the emission properties of this group of molecules highly depend on the solvent polarity.

The large bathochromic shift combined with the decreased  $\Phi$  might be related to the stabilization of the excited state. This behavior is frequently observed in highly polarized molecules exhibiting enlarged dipoles and charge-transfer characters in their excited states referred to as intramolecular charge-transfers (ICT).<sup>13</sup> Since solvent polarity had little effect on the absorption wavelengths of the compounds, their solvatochromisms might be caused by photo-induced ICT in the excited state, suggesting that the ICT excited state had a larger dipolar moment compared with the ground state, due to substantial charge redistribution.

The photo-induced ICT of the compounds was supported by the molecular orbital (MO) calculation studies. On the basis of the density functional method at the HF/3-21G level after optimizing the structure,<sup>14</sup> the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) of **1B-TPA** were obtained, as shown in Fig. 7. The calculation results showed that **1B-TPA** exhibited the complete separation of the HOMO and the LUMO. The majority of the electron distribution of the HOMO was located on the triarylamine moiety; however, the electron distribution of the LUMO was located on the triphenylethylene moiety. The complete localization of HOMO and LUMO means the HOMO  $\rightarrow$  LUMO transition becomes a typical photo-induced intramolecular charge transfer transition, which is desirable for the efficient energy transfer.<sup>15</sup>

However, since the solvent polarity has little effect on the emission of the siloles system, typical AIE compounds included HPS, MPPS *etc*, the ICT mechanism has been ruled out in the AIE and AIEE process of the siloles system.<sup>16</sup> The above PL results in different solvents evidently demonstrate the likelihood



Fig. 7 The calculated spatial distributions of the LUMO and the HOMO of **1B-TPA**.

of the involvement of the ICT mechanism in the AIEE process of our synthesized compounds.

It is also interesting to note that the number of dicarbazolyl triphenylethylene substituents exerted little effect on their emission wavelengths in their solid states. As shown in Fig. 8, the maximum emission wavelengths ( $\lambda$ ) of the three compounds were about 482.7 nm. However, in CH and TOL, the order of the  $\lambda$  values followed the order of **1B-TPA > 2B-TPA > 3B-TPA**. In sharp contrast, in MC, THF, DMF and DMSO, the  $\lambda$  values followed the order of **3B-TPA > 1B-TPA**.

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), which are related



Fig. 8 The PL spectra of the compounds recorded from their TLC plates.



Fig. 9 A CV curve of 2B-TPA in MC.

 Table 3
 The energy levels of the compounds

Compound	HOMO/eV	LUMO/eV	$\Delta E_{\rm g}/{\rm eV}$
1B-TPA 2B-TPA 2D TDA	5.19 5.15	2.37 2.38 2.27	2.82 2.77 2.75

to the redox potentials, have been identified as two important parameters for electroluminescent materials because of their relationship with the hole-/electron-injecting capability of organic light-emitting devices. To measure the HOMO levels of the synthesized compounds, CV analyses were carried out. The CV curve of 2B-TPA, as an example, is shown in Fig. 9 (the other CV curves are shown in the ESI<sup>†</sup>). The HOMO energy levels were obtained using the onset oxidation potential. The energy band gaps ( $\Delta E_{s}$ ) of the compounds were estimated from the onset wavelength of their UV absorptions. The LUMO energy levels were obtained from the HOMO energy and the energy band gap ( $\Delta E_g = HOMO - LUMO$ ). The HOMO, LUMO and  $\Delta E_{\rm g}$  values are listed in Table 3. The  $\Delta E_{\rm g}$  values of the compounds were found to be in the range of 2.75-2.82 eV, which is below the value (3 eV) that common organic light materials possess. As can be seen, the  $\Delta E_{\rm g}$  values decreased with an increase in the number of dicarbazolyl triphenylethylene substituents. Therefore, compounds 3B-TPA and 1B-TPA exhibited the narrowest energy band gap and the widest energy band gap, respectively. HOMO values ranged from 5.12-5.19 eV. The HOMO values also depended on the number of the dicarbazolyl triphenylethylene substituents: the larger the number, the smaller the HOMO value. However, LUMO values ranged from 2.37-2.38 eV and were very close to each other.

#### **AIEE** properties

To determine whether **1B-TPA**, **2B-TPA** and **3B-TPA** are AIEE active, the fluorescent behaviors of their diluted mixtures were studied in a mixture of water–DMF under different water fractions. Since the compounds were insoluble in water, increasing the water fraction in the mixed solvent could change their



Fig. 10 PL spectra of 2B-TPA in water–DMF mixtures (5 µM).

existing forms from a solution or well-dispersed state in the pure DMF to the aggregated particles in the mixtures with high water content.

The PL spectra of 5 µM 2B-TPA in water–DMF mixtures with different water contents are shown in Fig. 10. The 2B-TPA in DMF exhibited a weak PL intensity (~125 a.u.). However, the fluorescence intensity was significantly enhanced when the water fraction exceeded 15%. The enhancement of the fluorescence intensity from 125 to 245 a.u. was observed as the water fraction of the water-DMF mixture increased from 15% to 20%. Similar phenomena were observed for the other two compounds (see the ESI<sup>†</sup>). Therefore, the compounds were characterized as AIEEactive. However, the starting points for the PL enhancement of 1B-TPA, 2B-TPA and 3B-TPA differed from each other and were at 20, 15 and 10% water fraction, respectively. The reason for the difference is that the three compounds possessed different solubilities in the mixed solvents. Clearly, the huge 3B-TPA had the lowest solubility, and thus, was the one most easily aggregated and precipitated from the mixed solvents.

The emission images of **2B-TPA** taken under 365 nm UV illumination at room temperature in pure DMF and mixed solvents with different water fractions, as well as the TLC thin film, are shown in Fig. 11. As can be seen, there is a wide difference in the emissive brightness and color among the samples. When the water content was up to 20%, the solution exhibited very strong blue-green emission (Fig. 11b-e).



Fig. 11 Emission images of **2B-TPA** taken under 365 nm UV illumination at room temperature in (a) DMF solution, (b) 15%, (c) 20%, (d) 25%, and (e) 90% (water fraction, v%) (5  $\mu$ M); (f) the TLC plate.

Moreover, the solid thin film also emitted very strong blue-green fluorescence (Fig. 11f).

Figs 12 and 13 illustrate the PL intensity and maximum emission wavelength of the compounds. As can be seen in Fig. 12, the intensities of **2B-TPA** and **3B-TPA** exhibited a slight decrease in PL enhancement upon the addition of water before the starting point, but an increase in the PL intensities of the three compounds was observed with the further addition of water after the starting points. After reaching a maximum, the PL intensities of the three compounds decreased with the increase in water content. This phenomenon was often observed in some compounds with AIE or AIEE properties, but the reasons remain unclear. Thus far, there are two possible explanations for this phenomenon. First, after the aggregation, only the molecules on the surface of the nanoparticles emitted light and contributed the fluorescence intensity upon excitation, leading to to a decrease in fluorescence intensity. However, the restriction of intramolecular rotations of the aromatic rings around the carbon-carbon single bonds in the aggregation state could enhance light emission. The net outcome of these antagonistic processes depends on which process plays a predominant role in affecting the fluorescence behavior of the aggregated molecules.<sup>17</sup> Second, when water is added, the solute molecules can aggregate



Fig. 12 PL intensities of the compounds in water–DMF mixtures (5  $\mu$ M).



Fig. 13 PL maximum emission wavelengths of the compounds in water– DMF mixtures (5  $\mu$ M).

into two kinds of nanoparticle suspensions: crystal particles and amorphous particles. The former leads to an enhancement in the intensity of photoluminescence emission, while the latter leads to a reduction in intensity.<sup>7</sup> Thus, the measured overall PL intensity data depends on the combined actions of the two kinds of nanoparticles. However, it is hard to control the formation of nanoparticles in high water content. Thus, the measured photoluminescence intensity often shows no regularity in high water content.

As shown in Fig. 13, the PL maximum emission wavelength of the compounds exhibited significant blue shifts after the starting points of PL enhancement. The blue shifts of **1B-TPA**, **2B-TPA** and **3B-TPA** in the 90 : 10 (v/v) water–DMF mixture in relation to the emission in DMF solution were 34, 39 and 39 nm, respectively. Their maximum emission wavelengths in the 90 : 10 (v/v) water–DMF mixture (483, 484 and 485nm, respectively) were very close to each other and closer to the emission wavelengths of their film samples, mentioned above (482.7 nm).

The absorption spectra of **2B-TPA** in the water–DMF mixtures (5  $\mu$ M) are shown in Fig. 14. The spectral profile was markedly changed when >15% water was added to the DMF solution. The entire spectrum started to increase in absorption, indicating the formation of nanoscopic aggregates of **2B-TPA**.



Fig. 14 UV-vis absorption spectra of **2B-TPA** in water–DMF mixtures with different volume fractions of water ( $5 \mu M$ ).



**Fig. 15** The relationship between the absorption peaks ( $\lambda 1$  and  $\lambda 2$ ) of the compounds and water fraction in water–DMF mixtures (5  $\mu$ M).

The light scattering, or Mie effect, of the nanoaggregates suspensions in the solvent mixtures effectively decreased light transmission in the mixture and caused the apparent high absorbance and level-off tail in the visible region of the UV absorption spectrum.<sup>18</sup>

Fig. 15 shows the relationship between the peak positions of the two absorption bands,  $\lambda 1$  and  $\lambda 2$ , of the compounds and the water fraction. It can be seen that the  $\lambda 1$  values had almost no change during water addition. However,  $\lambda 2$  exhibited a redshifted abrupt change corresponding to the abrupt change in PL spectra. This indicates that the aggregation has a pronounced effect on  $\pi$ - $\pi$ \* transitions. The  $\lambda 2$  of **1B-TPA**, **2B-TPA** and **3B-TPA** in the 90 : 10 (v/v) water-DMF mixture in relation to those in DMF solution red-shifted by 7, 6 and 7 nm, respectively.

#### Conclusions

A new class of compounds containing dicarbazolyl triphenylethylene and triarylamine units was synthesized. The compounds possessed high thermal stability and AIEE properties. The glass transition temperature and 5% weight loss temperature of the trisubstituted compound (**3B-TPA**) are up to 214.3 °C and 516.8 °C, respectively. The  $T_g$  value is the highest ever reported to date for materials with AIE or AIEE properties. The compounds exhibited photo-induced intramolecular charge-transfer properties. The PL spectra blue-shifted after aggregation. The aggregation considerably affected the  $\pi$ - $\pi$ \* transition and resulted in 6–7 nm red shift of the  $\pi$ - $\pi$ \* absorption wavelength at the peak in UV-vis spectra. The number of the dicarbazolyl triphenylethylene substituents exerted little effect on the emission wavelengths of the compounds in the solid state.

#### Experimental

All starting reagents and chemicals were purchased from Alfa-Aesar and used as received. Analytical grade N,N-dimethylformamide (DMF) was purified by distillation under an inert nitrogen atmosphere. Tetrahydrofuran (THF) was distilled from sodium benzophenone. Ultra-pure water was used in the experiments. All other analytical-grade solvents were purchased from Guangzhou Dongzheng Company and used without further purification. Intermediates bis(4-(9*H*-carbazol-9-yl)phenyl)methanone (1) and 9,9'-(4,4'-(2-(4-bromophenyl)ethene-1,1-diyl)bis(4,1-phenylene))bis(9*H*-carbazole) (2) were synthesized according to procedures in previously published by us.<sup>7</sup> The halogenated triphenylamines 4-bromo-N,N-diphenylbenzenamine (4),<sup>8</sup> 4-bromo-N-(4-bromo phenyl)-N-phenylbenzenamine (5)<sup>9</sup> and tris(4-iodophenyl)amine (6)<sup>10</sup> were prepared according to the literature procedures.

Proton nuclear magnetic resonance (<sup>1</sup>H-NMR) spectra were measured on a Mercury-Plus 300 spectrometer (CDCl<sub>3</sub> or DMSO-d<sub>6</sub> as solvent and tetramethylsilane (TMS) as the internal standard). Mass spectra (MS) were measured on a Thermo MAT95XP-HRMS spectrometer. Elemental analyses (EA) were performed with an Elementar Vario EL elemental analyzer. Fluorescence spectra were measured on a Shimadzu RF-5301pc spectrometer with a slit width of 1.5 nm for both excitation and emission. Differential scanning calorimetry (DSC) curves were obtained with a NETZSCH thermal analyzer (DSC 204) at

heating and cooling rates of 10 °C min<sup>-1</sup> under N<sub>2</sub> atmosphere. Thermogravimetric analyses (TGA) were performed with a thermal analyzer (TA Instruments Inc. A50) under N<sub>2</sub> atmosphere with a heating rate of 20 °C min<sup>-1</sup>. The fluorescence quantum yields ( $\Phi$ ) of all the compounds in different solvents or DMF-water mixtures were evaluated using 9,10-diphenylanthracene, as in ref. 19 The solid-state PL spectra of the compounds on TLC plates (aluminium TLC plate, Merck, Silica 60 F254) were measured according to the literature procedure.<sup>20</sup> Cyclic voltammetry (CV) measurement was carried out on a Shanghai Chenhua electrochemical workstation CHI660C in a three-electrode cell with a Pt disk counter electrode, a Ag/AgCl reference electrode, and a glassy carbon working electrode. All CV measurements were performed under an inert argon atmosphere with supporting electrolyte of 0.1M n-Bu<sub>4</sub>NClO<sub>4</sub> in dichloromethane at scan rate of 100 mV s<sup>-1</sup> using ferrocene (Fc) as the standard. The lowest unoccupied molecular orbital/highest occupied molecular orbital (LUMO/HOMO) energy gaps  $\Delta E_g$ for the compounds were estimated from the absorption edge of the UV-vis absorption spectra.

The DMF–water mixtures with different water fractions were prepared by slowly adding distilled water into the DMF solution of samples under ultrasound at room temperature. For example, a 70% water fraction mixture was prepared in a volumetric flask by adding 7 mL distilled water into 3 mL DMF solution of the sample. The concentrations of all of the samples were adjusted to 5  $\mu$ M after adding distilled water.

## Synthesis of 4-(2,2-bis(4-(9*H*-carbazol-9-yl)phenyl)vinyl) phenylboronic acid (3)

Compound 2 (6.0 g,  $9.0 \times 10^{-3}$  mol) was dissolved in anhydrous THF (100 mL) and n-butyllithium (2.2 M/hexane, 6 mL, 0.0132 mol) was added, dropwise, under an argon atomosphere at -78 °C. After stirring for 5 h, B(OCH<sub>3</sub>)<sub>3</sub> (2.2 mL) was added quickly at -78 °C and the mixture was stirred overnight allowing the temperature to rise gradually to room temperature. Then, the reaction mixture was acidified with hydrochloric acid (2 M) for 2 h. The mixture was extracted with dichloromethane (3  $\times$ 50 mL) and the organic layer was dried with anhydrous sodium sulfate. After removing the solvent under reduced pressure, the crude product was purified by silica gel column chromatography using acetone/CH<sub>2</sub>Cl<sub>2</sub> (1:20, v/v) as eluent to yield 3 (2.1 g, yield 55%). <sup>1</sup>H-NMR (300 MHz, DMSO-d<sub>6</sub>) δ: 7.137 (s, 1 H, >C=CH-), 7.25-7.58 (m, 16 H), 7.62-7.78 (m, 8 H), 7.976 (s, 2 H, -B(OH)<sub>2</sub>), 8.20-8.30 (m, 4 H, carbazole-H); MS (EI), m/ z: 586 ([M-(B(OH)<sub>2</sub>)]<sup>+</sup>, calcd for C<sub>44</sub>H<sub>29</sub>, 585); anal. calc. for C44H31BN2O2: C 83.81, H 4.96, N 4.44; found: C 83.64, H 4.89, N 4.48.

# Synthesis of 4'-(2,2-bis(4-(9*H*-carbazol-9-yl)phenyl)vinyl)-*N*,*N*-diphenylbi phenyl-4-amine (1B-TPA)

Compounds 4 (0.315 g, 0.5 mmol) and 3 (0.162 g, 0.5 mmol) were dissolved in toluene (15 mL), then  $K_2CO_3$  (2 M, 1.5 mL) and Aliquat 336 (5 drops) were added. After stirring for 45 min under an argon atmosphere, the Pd(PPh<sub>3</sub>)<sub>4</sub> (catalytic amount) was added and the reaction mixture was stirred at 85 °C for 24 h. Then, the mixture was cooled to room temperature and extracted

with dichloromethane–water. The organic layer was collected and dried with Na<sub>2</sub>SO<sub>4</sub>. The crude product was purified by silica gel column chromatography using *n*-hexane–CH<sub>2</sub>Cl<sub>2</sub> = 2 : 3 (v/v) as eluent, to obtain pure product (0.22 g, yield 53%). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.07 (dd, 4 H, Ph–H), 7.20 (m, 5 H, Ph–H, >C=CH–), 7.31 (dd, 8 H, carbazole-H, Ph–H), 7.40–7.72 (m, 22 H, carbazole–H, Ph–H), 8.14–8.19 (d, 4 H, carbazole–H); FT-IR (KBr)  $\nu/\text{cm}^{-1}$ : 3030 (Ar and =C–H stretching), 2922, 2851, 1593, 1513, 1448, 1227, 817, 750, 625; MS (EI), *m/z*: 829 ([M]<sup>+</sup>, calcd for C<sub>63</sub>H<sub>43</sub>N<sub>3</sub>, 829); anal. calc. for C<sub>62</sub>H<sub>43</sub>N<sub>3</sub>: C 89.72, H 5.22, N 5.06; found: C 89.69, H 5.15, N 5.12.

#### Synthesis of 4'-(2,2-bis(4-(9*H*-carbazol-9-yl)phenyl)vinyl)-*N*-(4'-(2,2-bis(4-(9*H*- carbazol-9-yl) phenyl)vinyl)biphenyl-4-yl)-*N*-phenylbiphenyl-4-amine (2B-TPA)

5 (0.15 g, 0.375 mmol) and 3 (0.47 g, 0.75 mmol) were dissolved in toluene (20 mL), and then K<sub>2</sub>CO<sub>3</sub> (2 M, 2.5 mL) and 5 drops of Aliquat 336 were added. The mixture was stirred for 45 min under an argon atmosphere at room temperature. Then the Pd(PPh<sub>3</sub>)<sub>4</sub> catalyst (catalytic amount) was added and the reaction mixture was stirred at 85 °C for 24 h. After cooling, the reaction mixture was extracted with dichloromethane-water. The organic layer was collected and dried with Na<sub>2</sub>SO<sub>4</sub>. The crude product was purified by silica gel column chromatography (*n*-hexane– $CH_2Cl_2 = 1$ : 1, v/v) to obtain pure product (0.19 g, yield 36%). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.15–7.25 (m, 7 H), 7.32 (m, 12 H, carbazole-H, Ph-H), 7.40-7.72 (m, 44 H, carbazole-H, Ph-H), 8.14-8.19 (d, 8 H, carbazole-H); FT-IR (KBr) *v*/cm<sup>-1</sup>: 3035 (Ar and =C-H stretching), 1594, 1513, 1448, 1227, 817, 747, 623; MS (FAB), m/z: 1414([M]+, calcd for C106H71N5, 1414); anal. calc. for C<sub>106</sub>H<sub>71</sub>N<sub>5</sub>: C 89.99, H 5.06, N 4.95; found: C 90.01, H 5.12, N 4.91.

# Synthesis of tris(4'-(2,2-bis(4-(9*H*-carbazol-9-yl) phenyl)vinyl) biphenyl-4- yl)amine (3B-TPA)

6 (0.21 g, 0.33 mmol) and 3 (0.63 g, 1.0 mmol) were dissolved in toluene (25 mL), and then K<sub>2</sub>CO<sub>3</sub> (2 M, 3.0 mL) and 5 drops of Aliquat 336 were added. The mixture was stirred for 45 min under an argon atmosphere at room temperature. Then the Pd(PPh<sub>3</sub>)<sub>4</sub> catalyst (catalytic amount) was added and the reaction mixture was stirred at 85 °C for 48 h. After cooling, the reaction mixture was extracted with dichloromethane-water. The organic layer was collected and dried over Na<sub>2</sub>SO<sub>4</sub>. The crude product was purified by silica gel column chromatography (*n*-hexane–CH<sub>2</sub>Cl<sub>2</sub> = 2: 3, v/v) to obtain pure product (0.32 g, yield 48%). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.20–7.25 (m, 9 H), 7.32 (m, 12 H, carbazole-H, Ph-H), 7.40-7.72 (m, 66 H, carbazole-H, Ph-H), 8.14-8.19 (d, 12 H, carbazole-H); FT-IR (KBr)  $\nu/cm^{-1}$ : 3030 (Ar and =C-H stretching), 1594, 1508, 1448, 1313, 1227, 812, 747, 720, 623; MS (FAB), m/z: 1999([M]+, calcd for C<sub>150</sub>H<sub>99</sub>N<sub>7</sub>, 1999); anal. calc. for C<sub>150</sub>H<sub>99</sub>N<sub>7</sub>: C 89.99, H 4.99, N 4.90; found: C 89.95, H 4.94, N 4.96.

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