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Triphenylethylene carbazole derivatives as a new class of AIE materials with strong blue light emission and high glass transition temperature

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A new class of aggregation-induced emission (AIE) compounds with strong blue-light-emitting properties and a high thermal stability, derived from triphenylethylene carbazole, has been synthesized. Their glass transition temperatures range from 126–151 °C and the maximum fluorescence emission wavelengths are 451–466 nm.

Introduction

A large number of blue-light-emitting materials have been investigated for applications in luminescent devices, such as OLEDs,¹ because emission at blue wavelengths is considered to be the most important. However, the production of blue-light-emitting materials with appropriate levels of brightness and stability is not easy. This difficulty has mainly been attributed to aggregation quenching, or low glass transition temperatures (T_g).

Most luminescent materials have very high luminescence efficiency in dilute solutions, but exhibit relatively weak emission when formed into thin films, owing to the aggregation of molecules in the solid state to form species, such as excimers, which emit far less light.² Aggregation quenching seems to be an intractable problem in the development of devices because organic materials are normally used as thin solid films, in which aggregation inherently accompanies film formation.³ It is thus highly desirable to develop electroluminescent materials that can emit intense light in the solid state and, thereby, overcome the aggregation quenching problem. Indeed, a few rare compounds have been found recently that show significant enhancement of their light-emission upon aggregation or in the solid state. This intriguing phenomenon is named aggregation-induced emission (AIE) and thus these compounds have been named AIE materials.⁴ Since then, AIE materials have been found to be promising emitters for the fabrication of highly efficient electroluminescent devices and stimuli-responsive materials for use in multifunctional switches.⁵ However, discoveries of AIE materials are quite limited and most of them are silole-based compounds.^{4a-f}

The T_g of blue-light-emitting materials is another important factor governing the stability and lifetime of devices. If a device is heated above the T_g of the organic material components, irreversible failure can occur. For example, 4,4'-bis(2,2-diphenylvinyl)-1,1'-biphenyl (DPVBi) is a commercially available

compound, but has a low T_g of 64 °C, undergoes recrystallization after long periods of operation, and has a short device lifetime compared to those of green and red materials.⁶

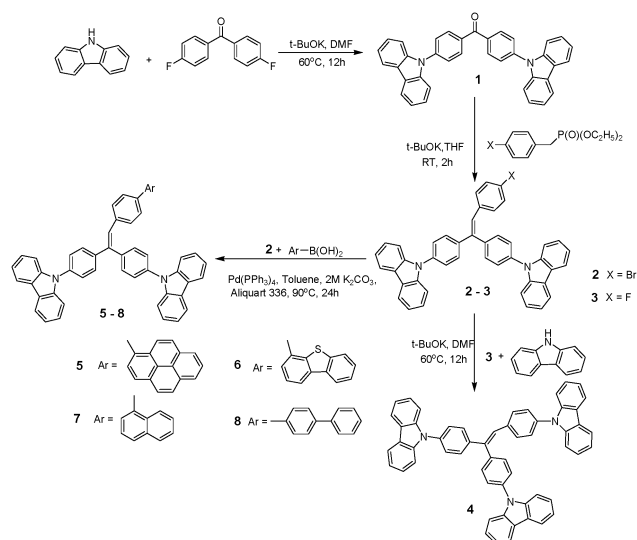
Recently, a number of carbazole derivatives⁷ have been used as organic materials, due to their well known charge-transport properties, luminescence, and high thermal stability. These advantageous properties provoked our interest in introducing the carbazole moiety into AIE materials.

Here, we report a new class of triphenylethylene carbazole derivatives with strong blue light emission, high T_g and AIE effect. It is expected that these molecules, with high thermal stability and the triple functions of blue-light-emitting, AIE-active and charge-transporting properties, are potential materials for blue-light emitters in luminescent devices and fluorescence sensors.

Results and discussion

Synthesis

Our strategy for the synthesis of this new series of carbazole derivatives is outlined in Scheme 1. It is well known that



Scheme 1 Synthetic routes to the desired compounds.

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carbazole is a ‘generalist’ and many groups including halide, alkyl, and aryl halide groups can be attached easily and selectively to positions 3 and/or 6, and when the latter is used, the aryl halide, can be converted readily into other functional groups. Thus, many derivatives of compound **1** can be constructed on the basis of requirements such as high T_g , good solubility, high level of efficiency, *etc.* In addition, intermediate **2** is also a ‘generalist’; it can be formed directly by many kinds of cross-coupling reactions and it is not difficult to convert aryl bromide into other functionalized groups, such as aryl boric acid, aryl tin compounds, aryl aldehydes, *etc.*, which are important intermediates in the construction of conjugate organic molecules as electroluminescent materials through the Suzuki, Heck, and Wittig cross-coupling reactions. In other words, triphenyl-ethylene carbazole can be used to obtain a variety of derivatives according to our needs.

The key precursor, compound **1**, bis(4-(9*H*-carbazol-9-yl)phenyl)methanone, was obtained in a single high-yield step from carbazole and bis(4-fluorophenyl)methanone (94% yield); therefore, the synthetic method is much simpler than the two-step procedure starting from bis(4-aminophenyl)methanone that is described in the literature.⁸ The key intermediate compounds **2**, 9,9'-(4,4'-(2-(4-bromophenyl)ethene-1,1-diyl) bis(4,1-phenylene))bis(9*H*-carbazole) and **3** 9,9'-(4,4'-(2-(4-fluoro-phenyl)ethene-1,1-diyl)bis(4,1-phenylene))bis(9*H*-carbazole), were synthesized from compound **1** and the corresponding diethyl 4-halogenobenzylphosphonates through the Wittig–Horner reaction with more than 90% yields. Using a method similar to that described for the synthesis of compound **1**, reaction of compound **3** with carbazole gave the desired product **4**, 9,9',9''-(4,4',4''-(ethene-1,1,2-triyl)tris(4,1-phenylene))tris(9*H*-carbazole). Cross-coupling of the intermediate compound **2** with corresponding aromatic boric acids under Pd-catalyzed Suzuki conditions afforded products **5**, 9,9'-(4,4'-(2-(4-(pyren-1-yl)phenyl)ethene-1,1-diyl)bis(4,1-phenylene))bis(9*H*-carbazole); **6**, 9,9'-(4,4'-(2-(4-(dibenzothiophene-4-yl)phenyl)ethene-1,1-diyl)bis(4,1-phenylene))bis(9*H*-carbazole); **7**, 9,9'-(4,4'-(2-(4-(naphthalen-1-yl)phenyl)ethene-1,1-diyl)bis(4,1-phenylene))bis(9*H*-carbazole); and **8**, 9,9'-(4,4'-(2-(terphenyl-4-yl)ethene-1,1-diyl)bis(4,1-phenylene))bis(9*H*-carbazole), in acceptable yields from 49–65%. All compounds (**1**–**8**) were strictly characterized with proton nuclear magnetic resonance (¹H-NMR), high-resolution mass spectroscopy (HRMS), and elementary analysis (EA).

Thermal properties

The thermal and photophysical properties of these target compounds are summarized in Table 1.

The thermal properties of these compounds were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Similar to the DSC curves of compound **4** (see Fig. 1), all the compounds exhibited a melting peak in the first heating runs. However, no melting peaks or crystallization peaks, except a glass-transition peak, were noticed in the second heating or cooling runs. This indicates very little crystal formation when cooling (even at a cooling rate of only 1 °C min^{−1}) from the melting state, which is expected to yield better electroluminescent materials.

Table 1 Thermal and photophysical properties of target compounds

	$T_g/^\circ\text{C}$	$T_m/^\circ\text{C}$	$T_d/^\circ\text{C}$	$\lambda_{\text{max}}^{\text{abs}}/\text{nm}$	$\lambda_{\text{max}}^{\text{em}}/\text{nm}$
4	143.8	305.7	488.2	343 ^a	463 ^b 452 ^c
5	151.1	255.2	453.3	360	464 466
6	140.2	245.7	486.1	343	464 462
7	126.6	239.3	473.4	342	458 450
8	135.1	290.6	478.5	343	453 451

^a In dichloromethane. ^b In dichloromethane. ^c Solid powder.

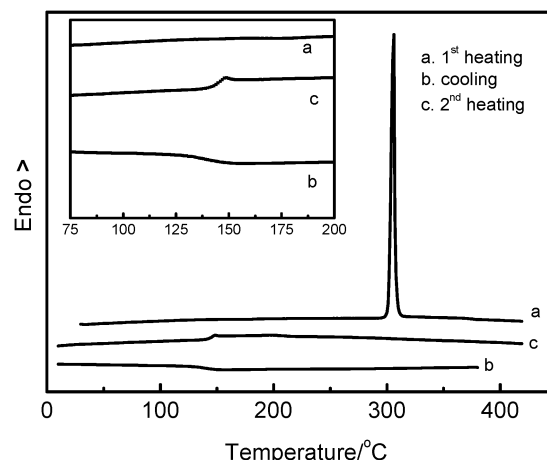


Fig. 1 DSC curves for compound **4** at scan rates of 10 °C min^{−1} (the inset is a magnification of the figure near T_g).

As can be seen, relatively high T_g values are observed. The T_g values of all compounds are above 126 °C, while that of compound **5** is the highest (151 °C), due to the bulky pyrenyl group. This T_g value is 2.3-fold higher than that of DPVBi (64 °C) and much higher than that (120 °C) of 2-methyl-9,10-di-(2'-naphthyl)anthracene (MADN), two typical blue-light emitters.⁹ It is also much higher than that of 1-methyl-1,2,3,4,5-pentaphenylsilole (MPPS, 54 °C) and 1,1,2,3,4,5-hexaphenylsilole (HPS, 65 °C), two typical AIE-active compounds.¹⁰

The decomposition temperature (T_d) is defined as the temperature at which 5% weight loss occurs during heating. As shown by the TGA curves presented in Fig. 2, the compounds were highly stable, as they started to decompose at 453–488 °C.

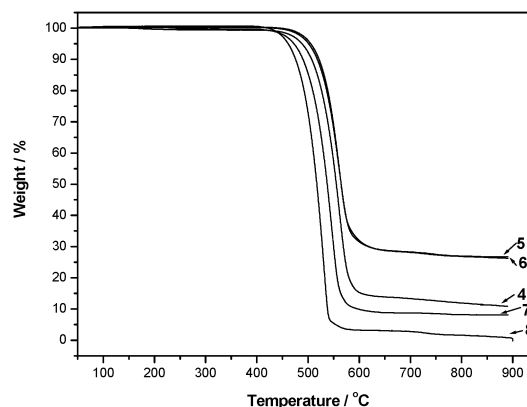


Fig. 2 TGA curves of compounds **4**–**8**.

The T_d values of the compounds were also much higher than that of the above AIE-active compounds, MPPS (309 °C) and HPS (351 °C).¹⁰

Thermal behavior of organic compounds has a critical influence on both the stability and the lifetime of luminescent devices. The results presented here show the potential of these new materials as blue-light-emitting materials in organic luminescent devices.

AIE properties

All of the compounds, except compound **5**, exhibit a blue shift in their emission in the solid state, compared to in dichloromethane solution. However, solidification of many blue luminescence materials produces a red-shift their emission spectra, which is clearly undesirable.

Almost no photoluminescence (PL) signal could be detected from a dilute solution of the compounds in tetrahydrofuran (THF). Fig. 3 shows the corresponding emission spectra of compound **4** in aqueous THF with different water/THF ratios. The emission from the THF solution of **4** was so weak that almost no PL signal was recorded. However, a dramatic enhancement of luminescence was observed for the 60 : 40 (v/v)

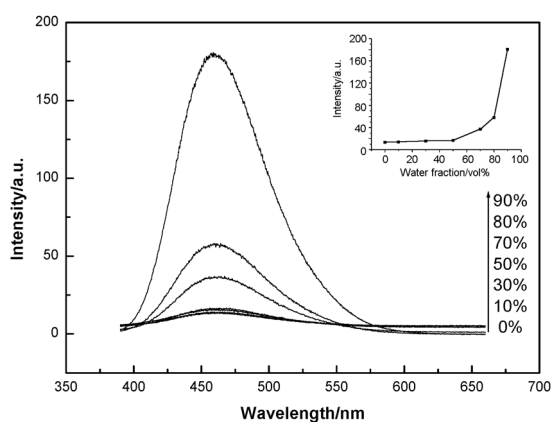


Fig. 3 PL spectra of **4** in water–THF mixtures. The inset depicts the changes of PL peak intensity.

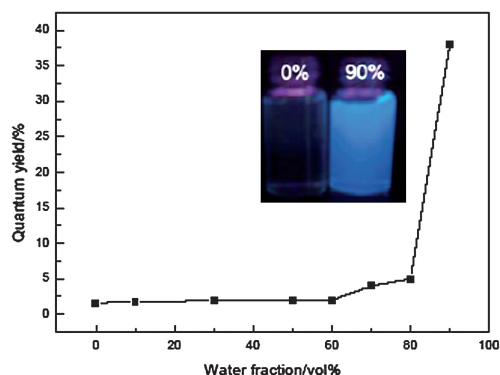


Fig. 4 Variation of PL quantum yield of **4** depending on water fractions in the THF–water mixture. Inset is the emission images of **4** in pure THF (left, 10^{-5} mol L⁻¹) and in the THF–water mixture (right, 90% water). The images were taken at room temperature under UV light ($\lambda_{\text{ex}} = 365$ nm).

water–THF mixture. While the PL intensity in THF is only 15, it is boosted to 180 in 90 : 10 (v/v) water–THF. Similar effects were observed for the other compounds.

The quantitative enhancement of emission was estimated by the PL quantum yields (Φ_{FL}) of compound **4** in mixtures of water and THF in various proportions, using 9,10-diphenylanthracene (DPA) as the standard. As seen from Fig. 4, the Φ_{FL} of the THF solution was very low ($\Phi_{\text{FL}} = 0.016$), and was almost unchanged when water was added up to 60% (v/v), but started to increase swiftly upon addition of water to 80% (v/v).

When the volume fraction of water in the water–THF mixture was increased to 90%, Φ_{FL} rose to 0.38, which is about 24-fold higher than that of THF. The above results indicate that the compound molecules started to aggregate markedly when the volume fraction of water reached 80%. Since water is a non-solvent of these compounds, the molecules must have aggregated in the water–THF mixtures with higher water content. Apparently, the emissions are induced by aggregation of the compounds; in other words, they are AIE-active.

Fig. 5 shows the effect of temperature on the PL relative peak intensity of the compounds in dilute solutions. It can be seen that the relative peak intensity of the DPA is almost unchanged during the temperature increase from 75K. In contrast, all of the new compounds have dramatic decreases near the melting point of THF. But, the extent of the decrease is not the same for each compound. The peak intensity of **6**, which contains a benzo-thiophene group, at 75K is about 120-fold higher than that at room temperature; the value is about 40-fold for compounds **4** and **7**, and less than 10-fold for compounds **5** and **8**. The results indicate that the AIE effect of frozen compound molecules in the solid are similar to those due to aggregation in the liquid, due to the restriction of rotation of groups.

The effect of temperature on the peak wavelength is different between AIE compounds such as compound **4** and non-AIE compounds such as DPA. As seen from Fig. 6, the two peak wavelengths of compound **4** are red-shifted with increasing temperature, but they are blue-shifted for DPA.

Fig. 7 shows online pictures of the solvent evaporation procedure of a drop of **4** solution in dichloromethane placed on a weighing paper. Early in its development, the spot was wet and could scarcely be visualized under irradiation at 365 nm (Fig. 7a). But as the solvent evaporated, the image became brighter and

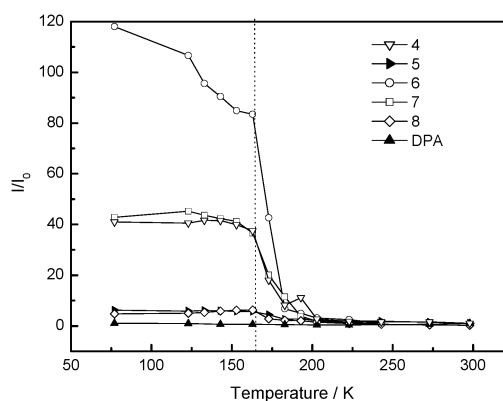


Fig. 5 Effect of temperature on the PL relative peak intensity of the compounds, and DPA, in THF.

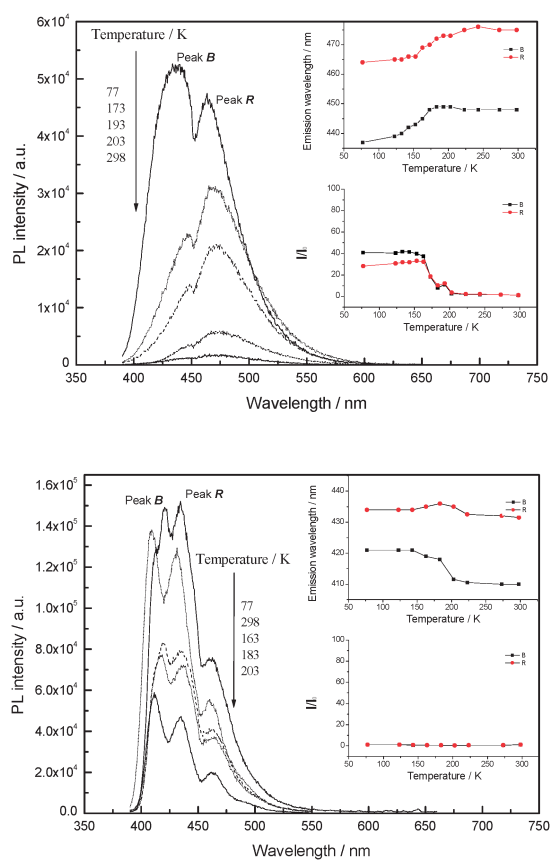


Fig. 6 Effect of temperature on the peak wavelength and intensity of compound **4** (top) and DPA (bottom) (insets: right upper is the peak wavelength vs. temperature and right lower is the relative PL intensity vs. temperature).

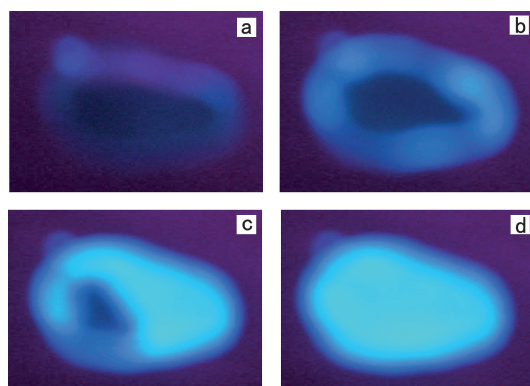


Fig. 7 Photographs taken online of a drop of **4** solution in CH_2Cl_2 on a weighing paper under irradiation at 365 nm (time: a = 1 s; b = 3 s; c = 5 s and d = 7 s).

brighter (Fig. 7b,c), finally reaching full-size brightness after the solvent had evaporated to dryness (Fig. 7d). This indicates that these novel molecules are AIE-active.

Off/on switching properties

Application of the synthesized compounds to on/off fluorescence switches was investigated with a spot of **4** on a thin-layer

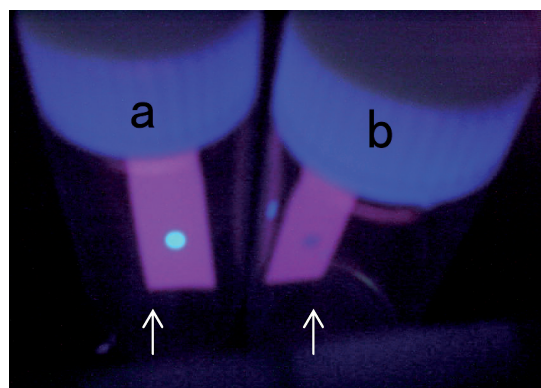


Fig. 8 On/off fluorescence switching of compound **4** on TLC plates without vapor (a) and in CH_2Cl_2 vapor (b) under UV light (365 nm) illumination at room temperature.

chromatography (TLC) plate (Fig. 8). Under UV light illumination (wavelength 365 nm) at room temperature, the spot showed bright blue fluorescence, which was switched off reversibly in an atmosphere of dichloromethane vapor. A probable explanation is that solvation of the vapor of a good solvent releases the interaction of solid molecules to a greater extent and causes free rotation of single bonds of the AIE molecules, leading to non-emission. Because AIE materials possess the on/off fluorescence switching property in some organic vapors, it is suggested that this could be one of their most important potential applications, in the photoswitch field as a chemical vapor sensor.

Simulated conformation

The structure and optimized geometry of compound **4** are shown in Fig. 9. It can be seen that the three phenyl rings rotate to some degree relative to each other (dihedral angle θ : $\text{C}(17)\text{--}\text{C}(20)\text{--}\text{C}(21)\text{--}\text{C}(27) = -54.2^\circ$, $\text{C}(22)\text{--}\text{C}(21)\text{--}\text{C}(20)\text{--}\text{C}(23) = -52.7^\circ$, $\text{C}(20)\text{--}\text{C}(22)\text{--}\text{C}(41)\text{--}\text{C}(46) = -39.0^\circ$), which demonstrates a twisted configuration of the compound in the isolated state (single molecule) due to the bulky carbazole group substituents on the benzene rings of triphenylethylene. Although the mechanism underlying the AIE phenomenon is still unclear, the twisted configuration is a common structural characteristic of

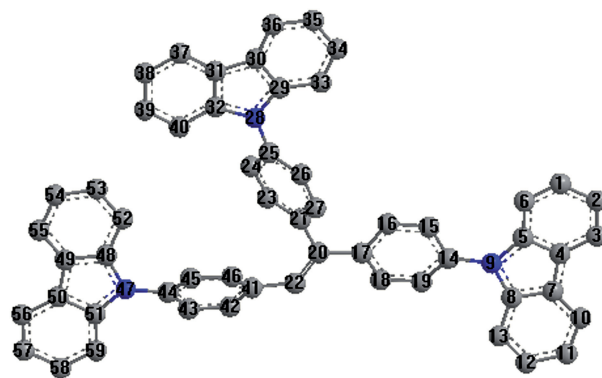


Fig. 9 The lowest-energy conformer optimized using the MM2 force field for compound **4**. Hydrogen atoms are omitted for clarity.

reported AIE molecules of either siloles,^{4a} or 1-cyano-*trans*-1,2-bis-(4'-methylbiphenyl)ethylene (CN-MBE).^{4h}

Conclusions

In this work, we have developed a new class of AIE-active compounds, triphenylethylene carbazole derivatives. They exhibit a strongly enhanced emission in the aggregated state, and on/off fluorescent switching which is sensitive to organic vapor. The derivatives are all blue-light emitters and their $\lambda_{\text{max}}^{\text{em}}$ are in the range 450–466 nm. These new derivatives have rather high levels of thermal stability: their T_{gs} are in the range 126–151 °C, and their T_{d} values are all above 450 °C. It is suggested that they are potential materials for blue light emitters in OLEDs and fluorescence sensors.

Experimental

All reagents and chemicals purchased from Alfa Aesar were used as received. Analytical grade 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 solvents were purchased as analytical grade from Guangzhou Dongzheng Company, and used without further purification. ¹H-NMR spectra were measured on a Mercury-Plus 300 spectrometer with chemical shifts reported as ppm (in CDCl₃, TMS as internal standard). Mass spectra were measured with Thermo spectrometers (MAT95XP-HRMS and DSQ-MS). Elemental analysis was done with an Elementar Vario EL Elemental Analyzer. Fluorescence spectra were determined with a Shimadzu RF-5301PC spectrometer and the slit width was 3 nm for both excitation and emission. Differential scanning calorimetry (DSC) curves were obtained with a TA thermal analyzer (Q10) at a heating rate of 10 °C min⁻¹ under a N₂ atmosphere. Thermogravimetric analyses (TGA) were performed with a TA thermal analyzer (A50) under a N₂ atmosphere with a heating rate of 20 °C min⁻¹.

Synthesis of bis(4-(9*H*-carbazol-9-yl)phenyl)methanone 1

Carbazole (16.7 g, 100 mmol) was dissolved in anhydrous DMF (150 mL) in a flask fitted with a magnetic stirrer and condenser. Potassium *tert*-butoxide (11.8 g, 105 mmol) was added and the mixture was heated at 70 °C for 10 min and bis(4-fluorophenyl)methanone (10.9 g, 50 mmol) was added with stirring for 12 h. The mixture was cooled to room temperature, poured into ice-water, filtered, and the crude residue was recrystallized from acetone. A white powder was obtained (24.1 g, 94% yield).

¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.36 (t, 4 H), 7.48 (t, 4 H), 7.58 (d, 4 H), 7.82 (d, 4 H), 8.19 (d, 8 H); MS (FAB) m/z : 512 ([M]⁺, calcd for C₃₇H₂₄N₂O, 512.6); Anal. calcd for C₃₇H₂₄N₂O: C 86.69, H 4.72, N 5.46; O 3.12, found: C 86.72, H 4.68, N 5.44.

Synthesis of 9,9'-(4,4'-(2-(4-bromophenyl)ethene-1,1-diyl)bis(4,1-phenylene))bis(9*H*-carbazole) 2

A solution of compound 1 (10.3 g, 20 mmol) and diethyl-4-bromobenzylphosphonate (6.2 g, 20 mmol) in anhydrous tetrahydrofuran (100 mL) was stirred under a N₂ atmosphere at 0 °C. Potassium *tert*-butoxide (2.2 g, 20 mmol) was added quickly and

the mixture was stirred continuously for 2 h at room temperature. The reaction mixture was precipitated into ethanol, the crude product was collected, and washed with ethanol three times. The crude product was recrystallized from dichloromethane–*n*-hexane (1 : 20, v/v) to obtain 11.6 g white powder in 87% yield. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.05 (d, 2H), 7.11 (s, 1H), 7.27–7.57 (m, 16H), 7.58–7.71 (m, 6H), 8.10–8.24 (m, 4H); MS (FAB) m/z : 666 ([M]⁺, calcd for C₄₄H₂₉N₂Br, 665.62); Anal. calcd for C₄₄H₂₉N₂Br: C 79.40, H 4.39, Br 12.00, N 4.21; found: C 79.42, H 4.42, N 4.16.

Synthesis of 9,9'-(4,4'-(2-(4-fluorophenyl)ethene-1,1-diyl)bis(4,1-phenylene))bis(9*H*-carbazole) 3

The compound was prepared using the procedure described for 2 but using diethyl-4-fluorobenzylphosphonate instead of diethyl-4-bromobenzylphosphonate in 85% yield.

¹H NMR (300 MHz, CDCl₃) δ (ppm): 6.97 (t, 2 H), 7.15–7.19 (m, 2 H), 7.31–7.37 (m, 4 H), 7.43–7.56 (m, 10 H), 7.56–7.70 (m, 7 H), 8.19 (dd, 4 H); MS (EI), m/z : 604 ([M]⁺, calcd for C₄₄H₂₉FN₂, 604.71); Anal. calcd for C₄₄H₂₉FN₂: C 87.39, H 4.83, F 3.14, N 4.63; found: C 87.41, H 4.85, N 4.60.

Synthesis of 9,9'-(4,4'-(ethene-1,1,2-triyl)tris(4,1-phenylene))tris(9*H*-carbazole) 4

Carbazole (0.85 g, 5 mmol) was dissolved in anhydrous DMF (20 mL) in a flask fitted with a magnetic stirrer and condenser. Potassium *tert*-butoxide (0.61 g, 5.3 mmol) was added to the above solution, heated at 70 °C for 10 min and 3 (3.35 g, 5 mmol) was added with stirring for 12 h. The mixture was cooled to room temperature, and poured into ice-water. The mixture was filtered and the crude product was purified by column chromatography on silica, eluting with dichloromethane–*n*-hexane (1 : 1, v/v) to yield 4 as an off-white powder (2.85 g, 76% yield). ¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.29 (s, 1 H), 7.34 (t, 6 H), 7.41–7.57 (m, 16 H), 7.64–7.77 (m, 8 H), 8.18 (m, 6 H); ¹³C NMR (125 MHz, CDCl₃) δ (ppm): 141.76, 141.65, 140.75, 140.69, 140.61, 138.95, 137.45, 137.37, 136.50, 136.13, 132.02, 131.03, 129.02, 128.50, 127.49, 126.89, 126.48, 126.07, 126.00, 123.52, 123.49, 120.48, 120.34, 120.13, 120.10, 109.85, 109.78, 109.67; FT-IR (KBr) ν (cm⁻¹): 3049 (Ar and =C–H stretching), 1598, 1514, 1452, 1334, 1228, 835, 750, 723; MS (FAB), m/z : 752 ([M + H]⁺, calcd for C₅₆H₃₇N₃, 751); Anal. calcd for C₅₆H₃₇N₃: C 89.45, H 4.96, N 5.59; Found: C 89.23, H 4.75, N 5.83%.

General procedure for synthesis of compounds 5–8

To a solution of 2 (1.33 g, 2 mmol) and the corresponding boric acid (2 mmol) in toluene (20 mL), 2 M aqueous K₂CO₃ solution (3 mL) was added and the mixture was stirred for 30 min under an argon atmosphere. Then, the Pd(PPh₃)₄ catalyst (0.05 g) was added all at once to the mixture. The reaction mixture was stirred at 90 °C for 24 h. After cooling, the product was extracted with dichloromethane–water. The organic layers were collected and dried under Na₂SO₄. The concentrated product was purified by silica gel column chromatography (dichloromethane–*n*-hexane from 1 : 5 to 1 : 1, v/v) to obtain pure products 5–8.

Compound 5

^1H NMR (300 MHz, CDCl_3) δ (ppm): 7.29–7.51 (m, 11 H), 7.57 (dd, 6 H), 7.65–7.78 (m, 8 H), 8.03 (t, 3 H), 8.12 (s, 2 H), 8.17–8.26 (m, 8 H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm): 141.87, 141.25, 140.76, 140.14, 139.27, 137.28, 137.23, 137.11, 136.05, 132.06, 131.48, 130.95, 130.66, 130.45, 129.71, 129.14, 128.98, 128.41, 127.60, 127.48, 127.39, 126.85, 126.03, 126.00, 125.17, 125.08, 124.90, 124.86, 124.69, 123.50, 120.37, 120.08, 109.87, 109.74; FT-IR (KBr) ν (cm^{-1}): 3039 (Ar and =C–H stretching), 1597, 1513, 1450, 1315, 1226, 839, 746, 719; MS (FAB), m/z : 786 ($[\text{M}]^+$, calcd for $\text{C}_{60}\text{H}_{38}\text{N}_2$, 786); Anal. calcd for $\text{C}_{60}\text{H}_{38}\text{N}_2$: C 91.57, H 4.87, N 3.56; Found: C 91.42, H 5.01, N 3.48%.

Compound 6

^1H NMR (300 MHz, CDCl_3) δ (ppm): 7.30–7.36 (m, 7 H), 7.45–7.52 (m, 6 H), 7.55–7.61 (m, 6 H), 7.63–7.76 (m, 10 H), 7.83 (t, 1 H), 8.16–8.23 (m, 6 H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm): 141.77, 141.50, 140.76, 139.49, 139.37, 139.16, 138.40, 137.32, 137.24, 136.82, 136.43, 136.34, 135.75, 132.08, 130.10, 129.01, 128.02, 127.46, 126.86, 126.77, 126.05, 126.00, 125.14, 124.42, 123.50, 122.61, 121.73, 120.56, 120.37, 120.08, 109.86, 109.81; FT-IR (KBr) ν (cm^{-1}): 3047 (Ar and =C–H stretching), 1599, 1512, 1446, 1336, 1226, 835, 746, 721; MS (FAB), m/z : 768 ($[\text{M}]^+$, calcd for $\text{C}_{56}\text{H}_{36}\text{N}_2\text{S}$, 768); Anal. calcd for $\text{C}_{56}\text{H}_{36}\text{N}_2\text{S}$: C 87.47, H 4.72, N 3.64, S 4.17; Found: C 87.57, H 4.81, N 3.56, S 4.35%.

Compound 7

^1H NMR (300 MHz, CDCl_3) δ (ppm): 7.30–7.37 (m, 7 H), 7.42–7.58 (m, 14 H), 7.64–7.77 (m, 8 H), 7.89 (d, 1 H), 7.93 (d, 1 H), 7.98 (d, 1 H), 8.17–8.21 (dd, 4 H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm): 141.86, 141.10, 140.74, 139.70, 139.67, 139.23, 137.24, 137.18, 136.03, 133.84, 132.01, 131.44, 129.92, 129.59, 129.14, 128.94, 128.34, 127.76, 127.44, 126.89, 126.82, 126.11, 126.02, 125.98, 125.80, 125.38, 123.48, 120.36, 120.06, 109.85, 109.71; FT-IR (KBr) ν (cm^{-1}): 3043 (Ar and =C–H stretching), 1597, 1514, 1450, 1336, 1226, 835, 746, 721; MS (FAB), m/z : 712 ($[\text{M}]^+$, calcd for $\text{C}_{54}\text{H}_{36}\text{N}_2$, 712); Anal. calcd for $\text{C}_{54}\text{H}_{36}\text{N}_2$: C 90.98, H 5.09, N 3.93; Found: C 91.13, H 4.80, N 4.14%.

Compound 8

^1H NMR (300 MHz, CDCl_3) δ (ppm): 7.28 (s, 1 H), 7.31–7.41 (m, 6 H), 7.45–7.52 (m, 6 H), 7.54–7.61 (m, 7 H), 7.63–7.74 (m, 14 H), 8.20 (d, 4 H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm): 141.91, 141.05, 140.76, 140.72, 140.60, 140.28, 139.34, 139.31, 139.22, 137.25, 137.20, 136.18, 132.02, 130.20, 129.06, 128.96, 128.82, 127.54, 127.39, 127.24, 127.01, 126.84, 126.68, 126.02, 125.99, 123.54, 123.49, 120.41, 120.35, 120.11, 120.06, 109.86, 109.79; FT-IR (KBr) ν (cm^{-1}): 3030, 3449 (Ar and =C–H stretching), 1595, 1512, 1450, 1336, 1228, 835, 744, 719; MS (FAB), m/z : 738 ($[\text{M}]^+$, calcd for $\text{C}_{56}\text{H}_{38}\text{N}_2$, 738); Anal. calcd for $\text{C}_{56}\text{H}_{38}\text{N}_2$: C 91.03, H 5.18, N 3.79; Found: C 91.12, H 5.34, N 3.58%.

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