High-T $_{\rm g}$ carbazole derivatives as a new class of aggregation-induced emission enhancement materials[†]

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A new class of carbazole derivatives was facilely synthesized by Wittig–Horner and Suzuki reactions, and their thermal and photophysical properties were investigated. They exhibited aggregation-induced emission enhancement (AIEE) characteristics and high thermal stability. The glass transition temperatures (T_g) of these compounds ranged from 178 to 231 °C, while their decomposition temperatures (T_d) ranged from 496 to 535 °C. The solubility of the derivatives did not monotonically change with an increasing number of phenylene bridges, but exhibited a clear odd-even effect.

Introduction

Most luminescent compounds exhibit strong luminescence in the dilute solutions. However, in their solid states or in high concentration solutions, their emissions are often reduced or relatively weak.¹ Aggregation quenching is a challenging problem encountered in developing optoelectronic devices because the organic materials normally need to aggregate and form solid thin films in devices.² Chemical, physical and engineering approaches have been used to suppress the aggregation quenching of luminescent molecules, but their effects are limited.³ In contrast to the prevailing thought of preventing the aggregation of luminescent molecules, studies have also suggested the development of new luminescent materials that can emit more efficiently in an aggregated form than in a dissolved form. These new materials with aggregation-induced emission enhancement (AIEE or AIE) properties are luminophores which have significantly enhanced light emission in aggregated form or solid state. They were identified in the pioneering works of Tang et al.4 and Park et al.5 as alternative materials that could overcome aggregation quenching. However, materials with AIEE properties are limited, and most are silole derivatives, 1,1,2,2tetraphenylethene (TPE) derivatives and 1-cyano-trans-1,2-bis-(4-methylbiphenyl)ethylene (CN-MBE) derivatives.⁶ To date, the real cause or mechanism is still unclear, although many mechanisms have been proposed to explain the novel AIEE phenomena, including restriction of intramolecular rotation, formation of J-aggregates, intramolecular planarization, inhibition of photoisomerization and photocyclization, and blockage of nonradiative relaxation pathways of the excited species.7

The thermal stability of organic materials is critical for photoelectronic device stability and lifetime because the heat generated during the electroluminescent process could affect material morphology and device performance. Eventually, this could lead to the degradation of the devices. Hence, a relatively high $T_{\rm g}$ is essential for emissive materials used in optoelectronic applications.

Many organic fluorescent compounds could not be used as emissive materials for fabricated devices because of aggregation quenching in the solid state or undesired low T_g . Recently, the synthesis and application of carbazole derivatives as emissive materials have been of great interest for chemists and material scientists due to their charge-transport properties, luminescence, and thermal stability.⁸ Therefore, we endeavored to attach a carbazole moiety onto AIEE materials.

In this paper, we report a new class of carbazole derivatives with strong light emission properties, high T_g , and AIEE effect. It is expected that the derivatives can be potential light-emitting materials for use in luminescent devices.

Results and discussion

Synthesis

Our strategy to synthesize the carbazole derivatives is outlined in Scheme 1. The key intermediate compounds, bis[4-(9H-carbazol-9-yl)phenyl] methanone 1 and bis[4-(3,6-di-*tert*-butyl-9H-carbazol-9-yl)phenyl]methanone 2, were synthesized according to



Scheme 1 Synthetic routes to the derivatives.

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procedures in the literature previously published by us from bis(4-fluorophenyl) methanone and carbazole or 3,6-ditert-butyl-9H-carbazole, respectively, via N-arylation in a single high-yield step (yield >94%).9 The intermediate compound 3 9,9'-{4,4'-[2-(4-bromophenyl)ethane-1,1-diyl]bis(1,4-phenylene)}bis(9Hcarbazole) was synthesized by the Wittig-Horner reaction of diethyl 4-bromobenzylphosphonate and compound 1 (yield >90%).9 The target compounds, pbc2, p2bc2, pbt2 and p2bt2, were obtained by the Wittig-Horner reaction of 1 or 2 with the respective diphosphonates [tetraethyl 1,4-phenylenebis(methylene)diphosphonate and tetraethyl biphenyl-4,4'-diyl bis(methylene)diphosphonate] (yield 75-87%). The diphosphonates were synthesized by the Arbuzov reaction of triethyl phosphite with the corresponding dibenzyl halides. Other target compounds, p3bc2 and p4bc2, were synthesized by Suzuki coupling reactions of 3 with the corresponding diarylboronic acids (1,4-phenylenediboronic acid and biphenyl-4,4'-divldiboronic acid) in the presence of a palladium(0) catalyst (yield 50-70%).

All of the target compounds were characterized with proton and carbon nuclear magnetic resonance spectroscopy (¹H-NMR, ¹³C-NMR), high-resolution mass spectroscopy (MS), and elemental analyses (EA).

Solubility and thermal properties

The solubility and thermal properties of the target compounds are summarized in Table 1. Solubility is important to the practical applications of conjugated organic luminescent materials for the purification of the product and fabrication of the electroluminescent device through spin-coating or ink-jet printing processes. However, the solubility of many highly conjugated organic luminescent materials is quite low. Introducing a tertbutyl group into a luminescent molecular structure often serves to improve its solubility. In this study, the tert-butyl groups were introduced into the 3,6-positions of the carbazolyl moieties in the compounds pbt2 and p2bt2. As can be seen in Table 1, comparing with the analogous pbc2 and p2bc2, pbt2 and p2bt2 showed markedly increased solubilities (S) of 30 and 54 g/L, respectively, which are much higher than those of pbc2 (0.19 g/L) and p2bc2 (9.5 g/L). The solubility of pbc2, p2bc2, p3bc2 and p4bc2 did not monotonically change with an increasing number of phenylene bridges but exhibited a clear odd-even effect. This means that the solubility values of pbc2 (0.19 g/L) and p3bc2 (0.36 g/L), which contain an odd number of phenylene bridges, are lower than those of p2bc2 (9.5 g/L) and p4bc2 (6.3 g/L), which contain an even number of phenylene bridges. The odd-even effect of the solubility is most likely associated with the twist angle of oligo-

 Table 1
 Solubility and thermal properties of the compounds

Compd	$S (g/L)^a$	T_g (°C)	$T_m (^{\circ}C)$	T_d (°C)
pbc2	0.19	178	380	509
p2bc2	9.5	178	363	535
p3bc2	0.36	186	386	533
p4bc2	6.3	192	399	525
pbt2	30	230	412	534
p2bt2	54	231	399	496
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^a Dichloromethane as solvent.

phenylene spacers which influences their molecular packing in the solid state. To the best of our knowledge, the odd-even effects of wholly aromatic rigid molecules have rarely been reported, but it is well known that organic molecules consisting of long alkyl chains show odd-even effects in phase transition temperatures and material properties.¹⁰ Among the four compounds, **p2bc2** exhibited the highest solubility.

The thermal properties were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Table 1 shows that the T_g values were high, which was attributed to the effect of the bulky carbazolyl groups. The T_g values (178-231 °C) are much higher than those of the common organic luminescent materials reported in the literature, such as 4,4'-bis(2,2-diphenylvinyl)-1,19-biphenyl (DPVBi, 64 °C) and 2-methyl-9,10-di(2-naphthyl)anthracene (MADN, 120 °C).¹¹ They are also higher than those of the two typical AIEE-active 1-methyl-1,2,3,4,5-pentaphenylsilole compounds reported. (MPPS, 54 °C) and 1,1,2,3,4,5-hexaphenylsilole (HPS, 65 °C).¹² To the best of our knowledge, such T_g values are currently the highest reported for organic luminescent materials with AIEE properties.

Table 1 also shows that the introduction of *tert*-butyl groups could improve not only the solubility but also the T_g . Compared with **pbc2**, the T_g of **pbt2** was raised by 52 °C.

The DSC curves of the samples in the first and second heating runs are shown in Fig. 1 and Fig. S1 (see Electronic Supplementary Information, ESI[†]), respectively. All compounds exhibited a melting peak in the first heating run. The melting peak temperatures of pbc2, p2bc2, p3bc2, p4bc2, pbt2 and p2bt2 were 380, 363, 386, 399, 412 and 399 °C, respectively. Compound p2bc2 possessed the lowest melting temperature. Moreover, a clear cold-crystallization peak occurred near 250 °C in the curve of p3bc2. After heating over 400 °C, melts of the samples were cooled down to room temperature at 10 °C/min. Then, the second heating runs were carried out. All compounds had clear glass transition peaks. The compounds p2bc2, pbt2 and p2bt2 had no melting or crystallization peaks, but a glass transition peak occurred in the second heating runs. This indicates that there was very little crystal formation when cooling from the melted state. In other words, the three compounds were difficult to crystallize from their melts. However, pbc2, p3bc2 and p4bc2



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

exhibited crystallization from their melts. In their DSC curves, besides the melting transition peak, all the three compounds possessed a clear cold-crystallization peak.

The DSC curve of **pbc2** showed two melting peaks at 355 and 377 °C in the second heating run. Fig. 2 shows three DSC heating curves with different thermal histories for comparison: (a) the synthesized sample on the first heating run; (b) the sample after 10 °C/min cooling from melt: and (c) the sample after rapidly cooling from melt. Only one melting peak existed for the samples in (a) and (c) which had different peak positions at 355 and 379 °C, respectively. However, (b) resulted in two melting peaks, a low-temperature peak at 354 °C and a hightemperature peak at 377 °C, corresponding to the peaks from (a) and (c), respectively. Clearly, the high-temperature peak depended on the cooling rate, and it could form only after a very slow process. Although the sample was rapidly cooled at a rate of about 150 °C/min, the size of the peak (c) is similar to the low-temperature peak of (b). The low-temperature peak was considered to come from a cold-crystallization process because both curves (b) and (c) had clear cold-crystallization transitions. Double or multiple melting endotherms are often found in semicrystalline polymers crystallized isothermally from the melt at selected crystallization temperatures. These may result from the melting of crystals with different stabilities (dual morphology mechanism) or the melting recrystallization and remelting process (reorganization mechanism).13 Because no meltingrecystallization process was observed in this study, it means that the double melting endotherms could be explained by the dual morphology mechanism.

The T_d of these compounds (corresponding to 5% weight loss under N₂ atmosphere) were in the range of 496–535 °C (Table 1 and Fig. S2†), whereas the T_d of MADN was only at 397 °C.¹¹ The T_d values of the compounds were higher than those of the reported AIEE-active compounds, MPPS (309 °C) and HPS (351 °C).¹² The results indicate that the compounds had very high levels of thermal stability. The thermal stability of organic compounds is critical to the stability and lifetime of photoelectric devices. Thus, the high level of thermal stability suggested that



Fig. 2 DSC curves of **pbc2** recorded under different conditions: (a) the synthesized compound upon first heating; (b) the second heating after 10 °C/min cooling from the melt; and (c) the second heating after rapidly cooling from the melt.

the synthesized compounds could be useful as photoelectric materials.

Although the *tert*-butyl group is an alkyl group usually considered to improve solubility while simultaneously lowering T_g and thermal stability, introducing it into **pbt2** and **p2bt2** improved not only the solubility but also the T_g and thermal stability. The excellent solubility and high thermal stability of the compounds make them potential materials for photoelectric devices fabricated through the solution process.

Optical properties and energy levels

The optical properties of the compounds were investigated by UV-vis absorption spectroscopy (UV) and photoluminescence spectroscopy (PL) in dichloromethane (DCM) solution and in the solid state. Fig. 3 show the UV and PL spectra of p2bc2 as an example. The spectra of the other compounds are provided in ESI (Fig. S3 and Fig. S4[†]). The maximum absorption wavelengths (λ_{max}^{abs}) and emission wavelengths (λ_{max}^{em}) of **pbc2**, **p2bc2**, **p3bc2**, **p4bc2**, **pbt2** and **p2bt2** appeared at $\lambda_{max}^{abs} = 374$ nm, 368 nm, 364 nm, 362 nm, 379 nm and 371 nm, and $\lambda_{max}^{em} = 487$ nm, 466 nm, 459 nm, 458 nm, 488 nm and 470 nm in DCM (Table 2). Both λ_{max}^{abs} and λ_{max}^{em} in DCM were monotonically blue-shifted with the increasing number of phenylene bridges, which implies that increasing the number of phenylene bridges causes a significant decrease in the conjugated extent of the molecules. However, the λ_{max}^{em} in solid state did not show a similar pattern, and compound p3bc2 exhibited the shortest emission wavelength. Comparing the λ_{max}^{em} of **pbc2**, **p2bc2**, **p3bc2** and **p4bc2** in solution and in solid state, pbc2 exhibited a 5 nm blue-shift, while the others exhibited a 13 nm, 2 nm and 1 nm red-shift, respectively. The compound pbt2 had a 7 nm blue-shift, and p2bt2 did not change.

The quantum yield values (Φ_{FL}) of the compounds in DCM and cyclohexane (CHX) (10 μ M) were determined by the standard method using 9,10-diphenylanthracene (DPA) as the standard. Table 2 shows that the compounds have high Φ_{FL} in the poor solvent CHX. The Φ_{FL} values ranged from 37% to 68%. Compound **pbt2** exhibited the highest fluorescence efficiency ($\Phi_{FL} = 68\%$). In comparison, the compounds showed lower fluorescence efficiency in good solvents, namely, DCM and tetrahydrofuran (THF), and the Φ_{FL} values ranged from 4.7 to 8.6% and from 3.2 to 14%, respectively. The 'solutions' in poor



Fig. 3 UV and PL spectra of **p2bc2** in DCM and in solid state (concentration of the solutions: $10 \ \mu$ M).

Compd	λ_{max}^{abs} (nm) DCM	λ_{max}^{em} (nm)		$\phi_{FL}(\%)^a$		
		DCM	Solid	CHX	DCM	THF
pbc2	374	487	482	46	7.2	5.3
P2bc2	368	466	479	58	8.6	7.9
P3bc2	364	459	461	54	8.0	4.9
P4bc2	362	458	470	37	4.7	3.2
Pbt2	379	488	481	68	8.5	13.0
P2bt2	371	470	470	56	8.5	14.0

 a Fluorescence quantum yields measured using 9,10-diphenylanthracene as standard.

solvent (CHX) with higher Φ_{FL} were visually clear and macroscopically homogenous with no precipitate. It was considered that the solute molecules formed nanodimensional aggregates through intermolecular associations causing restricted vibrorotational motions with reduced non-radiative relaxations and increased fluorescence quantum efficiency.

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), which are related to the redox potentials, are 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, cyclic voltammetry (CV) analyses were carried out. The CV curve of **p2bc2** is shown in Fig. 4. The CV curves for all compounds are provided in ESI (Fig. S5†). The HOMO energy levels were obtained using the onset oxidation potentials. The energy band gaps (ΔE_g) of the compounds were estimated from the onset wavelengths 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 ΔE_g values are listed in Table 3. The ΔE_g values of the compounds were found to be in the range of 2.85–3.05 eV. Compounds **pbt2** and **p4bc2** exhibited the narrowest energy band gap and the widest energy band gap, respectively. Data in Table 3 show that the ΔE_g values depended on the number of phenylene bridges: the larger the number of phenylene bridges linked, the larger the ΔE_g value was. The HOMO values ranged from 5.21 to 5.58 eV. Compounds **p2bc2**

Table 3 Energy levels of the compounds

Compd	HOMO (eV)	LUMO (eV)	$\Delta E_{g} (eV)$
pbc2	5.58	2.68	2.90
p2bc2	5.21	2.23	2.98
p3bc2	5.29	2.26	3.03
p4bc2	5.25	2.20	3.05
pbt2	5.21	2.36	2.85
p2bt2	5.50	2.56	2.94

and **pbt2** had the lowest HOMO levels, and **pbc2** had the highest HOMO level. The HOMO levels of **pbc2** and **p3bc2** with an odd number of phenylene bridges were higher than those of **p2bc2** and **p4bc2** with an even number of phenylene bridges. The LUMO values ranged from 2.20 to 2.68 eV. Compound **p4bc2** possessed the lowest LUMO level, while **pbc2** possessed the highest LUMO level.

AIEE properties

To determine whether these compounds are AIEE active, the fluorescent behaviors of their diluted mixtures were studied in a mixture of water/THF with different water fractions. As the compounds were insoluble in water, increasing the water fraction in the mixed solvent could thus change their existing forms from a solution or well-dispersed state in the pure THF to the aggregated particles in the mixtures with high water content.

The PL spectra of 5 μ M of **p2bc2** in the water/THF mixtures with different contents of water are shown in Fig. 5 (the PL spectra for all compounds are provided in ESI, Fig. S6†). The **p2bc2** in THF exhibited weak PL intensity (~60 a. u.). However, the fluorescent intensity was significantly enhanced when the water fraction exceeded 30%. The enhancement of fluorescent intensity from 60 to 305 a. u. was observed as the water fraction of the water/THF mixture increased from 30% to 60%. Similar phenomena were observed for the other compounds. Since the molecules of the compounds aggregated in the mixtures with higher water content, enhanced fluorescent intensity was attributed to aggregation. Therefore, the compounds were characterized as AIEE-active. The emission images of the compounds in pure THF and in a 90 : 10 (v/v) water/THF mixture under





Fig. 5 PL spectra of **p2bc2** in water/THF mixtures. The inset depicts the changes in PL peak intensity.



Fig. 6 The emission images of the compounds in pure THF (a) and a 90:10 (v/v) water/THF mixture (b) under 365 nm UV illumination at room temperature.

365 nm UV illumination at room temperature are shown in Fig. 6. The compounds in high water fractions of water/THF mixtures exhibited stronger emission than the compounds in pure THF solution.

The changes of PL maximum emission wavelength of the compounds in a 60 : 40 (v/v) water/THF mixture in relation to the emission in THF solution are shown in Fig. 7. Compounds **pbc2** and **p2bc2** were blue-shifted by 7 and 1 nm, respectively, while the other compounds **p3bc2**, **p4bc2**, **pbt2** and **p2bt2**, were red-shifted by 6, 4, 4 and 4 nm, respectively. The different PL behaviors seem to be related to their molecular and packing structures.

The absorption spectra of **p2bc2** in the water/THF mixtures are shown in Fig. 8 (the UV spectra for all compounds are provided in ESI, Fig. S7†). The spectral profile was virtually unchanged when up to $\sim 30\%$ water fraction was added to the THF solution. When the water fraction was further increased,



Fig. 7 Changes of PL emission wavelength of the compounds in a 60:40 (v/v) water/THF mixture in relation to the emission in THF solution.



Fig. 8 UV absorption spectra of p2bc2 in water/THF mixtures with different volume fractions of water.



Fig. 9 Photoluminescent Φ_{FL} of the compounds in water/THF mixtures with different volume fractions of water.

the entire spectrum started to rise. The increase in the absorbance in the entire spectral region was due to light scattering of the nano-aggregates, which effectively decreased light transmission through the mixture. The abrupt broad change in the shape of the absorbance for the mixture with >50% water fraction agreed well with the sudden jump in the PL intensity and Φ_{FL} (Fig. 5 and 9). These results confirm that the **p2bc2** molecules started to markedly aggregate when the mixture contained >30% of water. Fig. S8† shows that the UV spectra were all red-shifted in the 60 : 40 (v/v) water/THF mixture relative to the sample dissolved in THF solution. The maximum absorption wavelengths of **pbc2**, **p2bc2**, **p3bc2**, **p4bc2**, **pbt2** and **p2bt2** were red-shifted by 18, 32, 20, 27, 12 and 14 nm, respectively. Compounds **p2bc2** and **p4bc2**, with an even number of phenylene bridges, exhibited a significant red-shift compared with **pbc2** and **p3bc2**.

To have a quantitative estimation parameters of the AIEE property, photoluminescent Φ_{FL} was calculated for the derivatives in mixtures of water and THF in various proportions (v/v) using DPA as the standard. Fig. 9 shows that the Φ_{FL} values of the THF solutions were low and remained almost unchanged up to 30% water, but it started to increase swiftly upon the addition of 50% water. However, the extent of the increase was not the same for each compound. When the volume fraction of water in the water/THF mixture was increased to 50%, the Φ_{FL} of **p4bc2**

rose to 49%, which is about 16-fold higher than that in THF (3%). With the same water fraction, the Φ_{FL} of **pbt2** was only five-fold higher than that in pure THF solution.

However, a further increase of the water fraction resulted in a decrease of photoluminescent intensity and photoluminescent Φ_{FL} . This phenomenon was often observed in some compounds with AIEE properties, and the reasons remain unclear. There are two possible explanations for this phenomenon. First, after the aggregation, only the molecules on the surface of the nanoparticles emit light and contribute to the fluorescent intensity upon excitation, and this leads to a decrease in fluorescent 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 played a predominant role in affecting the fluorescent behavior of the aggregated molecules.¹⁴ Second, when water is added, the solute molecules can aggregate into two kinds of nanoparticle suspensions: crystal particles and amorphous particles. The former would lead to an enhancement of the intensity of photoluminescent emission, while the latter would lead to reduction of intensity.9 Thus, the measured overall PL intensity data depend 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 photoluminescent intensity and photoluminescent Φ_{FL} were not regular (Fig. 5 and 9).

Conclusions

A new class of carbazole derivatives with high thermal stability and AIEE properties was synthesized. The highest T_g of the compounds was 231 °C, which is the highest value ever reported for the materials with AIEE properties to date. The solubility of the compounds exhibited a clear odd-even effect with an increasing number of phenylene bridges. The excellent solubility and high thermal stability of these compounds make them potential materials for the fabrication of photoelectric devices fabricated by the solution process.

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. 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. 3,6-Di-*tert*-butyl-9H-carbazole,¹⁵ tetraethyl 1,4-phenylenebis-(methylene)diphosphonate,¹⁶ tetraethyl biphenyl-4,4'-diylbis-(methylene)diphosphonate,¹⁷ and diethyl 4-bromobenzylphosphonate¹⁸ were prepared according to known procedures. Compounds **1**, **2**, and **3** were synthesized according to procedures in the literature previously published by us.⁹

Proton and carbon nuclear magnetic resonance (¹H-NMR and ¹³C-NMR) spectra were measured on a Mercury-Plus 300 spectrometer [CDCl₃, 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. Photoluminescence spectra (PL) were measured on a Shimadzu RF-5301pc spectrometer with a slit width of 1.5 nm for both excitation and emission. UV-vis absorption spectra (UV) were recorded on a Hitachi UV-vis spectrophotometer (U-3900). Differential scanning calorimetry (DSC) curves were obtained with a NETZSCH thermal analyzer (DSC 204) at a heating rate of 10 °C/min under N₂ atmosphere. Thermogravimetric analyses (TGA) were performed with a thermal analyzer (TA Instruments Inc. A50) under N₂ atmosphere with a heating rate of 20 °C/min. The fluorescence quantum yields (Φ_{FL}) of all the compounds in THF or THF/water mixture were evaluated using 9,10-diphenylanthracene as the reference.¹⁹

Cyclic voltammetry (CV) measurement was carried out on a Shanghai Chenhua electrochemical workstation CHI660C in a three-electrode cell with a Pt disk working electrode, a Ag/AgCl reference electrode, and a glassy carbon counter electrode. All CV measurements were performed under an inert argon atmosphere with supporting electrolyte of 0.1 M tetrabutylammonium perchlorate (n-Bu₄NClO₄) in dichloromethane at a scan rate of 100 mV/s using ferrocene (Fc) as standard. The HOMO energy levels were obtained using the onset oxidation potentials from the CV curves. The lowest unoccupied molecular orbital/highest occupied molecular orbital (LUMO/HOMO) energy gaps ΔE_g for the compounds were estimated from the onset absorption wavelengths of UV absorption spectra.

The THF/water mixtures with different water fractions were prepared by slowly adding distilled water into the THF 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 THF solution of the sample. The concentrations of all samples were adjusted to 5 μ M after adding distilled water.

General procedure for the synthesis of compounds pbc2, p2bc2, pbt2, p2bt2, and 3

The target compounds (**pbc2**, **p2bc2**, **pbt2**, and **p2bt2**) and the intermediate (3) were synthesized by a Wittig–Horner reaction (1 or 2) with the respective diphosphonates in essentially similar procedures. An illustrative example is provided for **pbc2**.

A solution of compound 1 (5.2 g, 10 mmol) and tetraethyl-1,4phenylenebis(methylene) diphosphonate (1.9 g, 5 mmol) in anhydrous tetrahydrofuran (THF) (50 mL) was stirred under an argon atmosphere at room temperature. Potassium *tert*-butoxide (1.1 g, 10 mmol) was quickly added and the mixture was stirred continuously for 5 h at room temperature. The reaction mixture was precipitated in ethanol. The crude product was collected, and then washed with ethanol three times. Then the crude product was purified on a silica gel column by eluting with dichloromethane (DCM)/*n*-hexane (3 : 1, v/v) to yield **pbc2** as a light-green powder (4.8 g, yield 87%).

pbc2. ¹H NMR (300 MHz, CDCl₃) δ : 7.07 (s, 4 H, =C-Ph-H), 7.19 (s, 2 H, >C=CH-), 7.31 (dd, 8 H, carbazole-H, Ph-H), 7.39– 7.70 (m, 32 H, carbazole-H, Ph-H), 8.175 (dd, 8 H, carbazole-H); ¹³C NMR (75 MHz, CDCl₃) δ : 141.70, 141.09, 140.65, 140.58, 139.06, 137.20, 137.14, 135.96, 131.84, 129.42, 128.84, 127.31,

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126.75, 125.88, 123.45, 120.31, 120.01, 109.79, 109.64; MS (FAB), *m*/*z*: 1094 ([M + H]⁺, calcd for $C_{82}H_{54}N_4$, 1095); Anal. Calc. for $C_{82}H_{54}N_4$: C, 89.92; H, 4.97; N, 5.12. Found: C, 90.12; H, 4.88; N, 5.23%.

p2bc2. ¹H NMR (300 MHz, CDCl₃) & 7.245 (d, 2 H, >C=CH-), 7.28–7.35 (m, 10 H), 7.43–7.48 (m, 8 H), 7.52–7.55 (m, 12 H), 7.58–7.72 (m, 16 H), 8.175(dd, 8 H, carbazole-H); ¹³C NMR (75 MHz, CDCl₃) & 141.78, 141.00, 140.66, 140.61, 139.07, 138.96, 137.17, 137.12, 136.185, 131.90, 128.86, 127.29, 126.75, 126.46, 125.91, 123.45, 120.31, 120.03, 109.80, 109.69; MS (FAB), *m*/*z*: 1171 ([M + H]⁺, calcd for C₈₈H₅₈N₄, 1170); Anal. Calc. for C₈₈H₅₈N₄: C, 90.23; H, 4.99; N, 4.78. Found: C, 90.04; H, 4.70; N, 5.01%.

pbt2. ¹H NMR (300 MHz, CDCl₃) δ : 1.47, 1.50 (d, 72 H, t-Bu-H), 7.03 (s, 4 H, =-Ph-H), 7.15 (s, 2 H, >C=CH-), 7.425 (s, 8 H, carbazole-H, Ph-H), 7.46–7.48 (m, 6 H, carbazole-H, Ph-H), 7.50–7.67 (m, 18 H, carbazole-H, Ph-H), 8.15 (s, 8 H, carbazole-H); ¹³C NMR (75 MHz, CDCl₃) δ : 143.025, 141.32, 141.28, 139.12, 139.06, 138.72, 137.78, 137.70, 136.06, 131.78, 129.48, 128.79, 128.70, 127.00, 126.38, 123.65, 123.62, 123.51, 116.27, 109.32, 109.21, 34.74, 32.00; MS (FAB), *m*/*z*: 1543 ([M]⁺, calcd for C₁₁₄H₁₁₈N₄, 1543); Anal. Calc. for C₁₁₄H₁₁₈N₄: C, 88.67; H, 7.70; N, 3.63. Found: C, 88.62; H, 7.84; N, 3.55%.

p2bt2. ¹H NMR (300 MHz, CDCl₃) δ : 1.50 (d, 72 H, t-Bu-H), 7.23 (d, 2 H, >C=CH-), 7.44–7.68 (m, 40 H, carbazole-H, Ph-H), 8.16(s, 8 H, carbazole-H); ¹³C NMR (75 MHz, CDCl₃) δ : 142.90, 141.34, 141.20, 139.035, 138.975, 138.58, 137.67, 137.62, 131.79, 130.05, 128.76, 128.59, 126.83, 126.49, 126.30, 123.56, 123.46, 116.22, 109.27, 109.21, 34.83, 32.11; MS (FAB), *m/z*: 1620 ([M + H]⁺, calcd for C₁₂₀H₁₂₂N₄, 1619); Anal. Calc. for C₁₂₀H₁₂₂N₄: C, 88.95; H, 7.59; N, 3.46. Found: C, 89.04; H, 7.71; N, 3.52%.

Compound 3. 87% yield. ¹H NMR (300 MHz, CDCl₃) δ : 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. Calc. for C₄₄H₂₉N₂Br: C 79.40, H 4.39, Br 12.00, N 4.21; found: C 79.42, H 4.42, N 4.16%.

General procedure for the synthesis of compounds p3bc2 and p4bc2

Aqueous K₂CO₃ solution (2 M, 3 mL) was added to a solution of **3** (1.33 g, 2 mmol) and diboric acid (1 mmol) in toluene (20 mL), and the mixture was stirred for 30 min under an argon atmosphere. Then, the Pd(PPh₃)₄ catalyst (0.05 g) was added all to the mixture, which was then stirred at 90 °C for 24 h. After cooling to room temperature, the product was precipitated in ethanol and further purified by silica gel column chromatography using DCM/n-hexane (3 : 1, v/v) as the eluent to obtain pure products **p3bc2** and **p4bc2**.

p3bc2. ¹H NMR (300 MHz, CDCl₃) δ : 7.25 (s, 2 H, >C=CH-), 7.30–7.36 (m, 10 H), 7.44–7.73 (m, 42 H), 8.19(dd, 8 H, carbazole-H); ¹³C NMR (75 MHz, CDCl₃) δ : 141.79, 141.00, 140.67, 139.36, 139.12, 137.18, 137.13, 136.155, 131.925, 130.11, 128.865, 127.32, 127.19, 126.77, 126.77, 126.56, 125.91, 123.47, 120.33, 120.04, 109.80, 109.73; MS (FAB), m/z: 1247 ([M]⁺, calcd for C₉₄H₆₂N₄, 1247); Anal. Calc. for C₉₄H₆₂N₄: C, 90.50; H, 5.01; N, 4.49. Found: C, 90.34; H, 4.85; N, 4.63%.

p4bc2. ¹H NMR (300 MHz, CDCl₃) δ: 7.27 (d, 2 H, >C=CH-), 7.31–7.37 (m, 10 H), 7.44–7.77 (m, 46 H), 8.19(dd, 8 H, carbazole-H); ¹³C NMR (75 MHz, CDCl₃) δ: 141.79, 140.99, 140.66, 139.97, 139.515, 139.35, 139.18, 139.12, 137.17, 136.14, 131.93, 128.94, 128.87, 127.31, 127.22, 126.77, 126.58, 125.92, 123.47, 120.33, 120.03, 109.81, 109.71; MS (FAB), *m*/*z*: 1324 ([M + H]⁺, calcd for C₁₀₀H₆₆N₄, 1323); Anal. Calc. for C₁₀₀H₆₆N₄: C, 90.74; H, 5.03; N, 4.23. Found: C, 90.62; H, 5.17; N, 4.36%.

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