SHORT COMMUNICATION



Synthesis and luminescent properties of novel organic luminescent materials based on carbazole derivatives

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Abstract

Four novel host materials C1–C4 based on carbazole derivatives have been designed, synthesized, characterized, and applied as organic light-emitting devices. This report presents a novel approach, which combines carbazole and aromatic hydrocarbons through methylene. The formed molecules exhibited twisted structures, which resulted in high glass transition temperatures (T_g), ranged from 90.4 to 148.0 °C. They also had high optical bandgaps (E_g), their optical energy bandgaps are determined by absorption edge technique as 3.22 to 3.50 eV, evaluated photo-physical properties of these synthesized novel chromophores, the optical properties such as maximum absorption and emission wavelengths (λ , nm), molar extinction coefficients (ε , cm⁻¹ M⁻¹), Stoke's shifts ($\Delta\lambda_{ST}$, nm), and quantum yields (φ_F) also studied the effect of solvent polarity on absorption and emission of these carbazole derivatives, and these compounds exhibited intense absorption bonds between 250 and 325 nm, which are attributed to the π - π * transition of the carbazole-centered units. In addition, they showed blue fluorescence in different solvents. These compounds showed bathochromic shift with the increase in the solvent polarity.

Keywords Carbazole · Methylene · $T_g \cdot E_g$ · The optical properties · Blue fluorescence

Introduction

Organic light-emitting diodes (OLEDs) have attracted extensive research attention in the few years due to its appealing commercial interest in the field of new-generation flat-panel displays, energy-saving lighting sources, and virtual reality. Numerous works have been done to push the development of OLEDs, since the first device was designed by Tang (Uoyama et al. 2012; Tang and VanSlyke 1987; Baldo et al. 1998; Yang et al. 2015). Although OLEDs technology has been successfully commercialized, there are still many

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challenges that need to be addressed, such as development, device design, and electronics. OLED remains one of the hottest areas of organic electronics.

Carbazole and its derivatives have been extensively studied over the past two decades for their particular electrical, electrochemical, and photo-physical properties and thermal stability (Zhuang et al. 2012; Tsai et al. 2009). Due to their electron-donating properties, these materials are typical hole-transporting units that can be easily modified with electron-transporting units in different positions. Therefore, it is more efficient and easier to inject both electrons and holes into the deep blue emitters. Meanwhile, there is a good balance between electrons and holes. On the other hand, the electron-rich electro-activity of carbazole-based molecular materials, which overlap in the small transitions of $n-\pi$, resulted in smaller energy exchange (Justin Thomas et al. 2001). It is reported that carbazole and its derivatives have great promise as photoelectric functional materials for their photo-physical and fluorescent properties in the blue light region (Li et al. 2012; Liang et al. 2011; Kim et al. 2006; Boudreault et al. 2009). Carbazole and its derivatives not only can be used as small molecules in fluorescent materials, but also can be designated as phosphorescent materials and thermally activated delayed fluorescence materials (Wang et al. 2011; Leyla et al. 2017; Gupta et al. 2010; Chen et al. 2006; Diaz et al. 2001). In recent years, the synthesis of carbazole derivatives and their applications become the highlight in blue light-emitting organic light-emitting diodes (Treutler and Ahlrichs 1995; Becke. 1993; Kim et al. 2010). In this report, we have designed a series of small carbazolerelated materials as organic luminescent materials and studied the concept of molecular design, optical physical properties, and thermal stability. Electrochemical properties are also discussed. Finally, the trends and development trends of carbazole organic light-emitting devices in the foreseeable future are also introduced (Li et al. 2011; Tao et al. 2008; Sasabe et al. 2009).

Experimental

General information

The NMR spectra were recorded on a Bruker Advance 400 spectrometer at resonant frequencies of 400 MHz for ¹H and 101 MHz for ¹³C nuclei using DMSO- d_6 or CDCl₃ as the solvent. Uncorrected melting points were observed in sealed capillaries. UV-visible absorption spectroscopy was obtained on a UV-2550 UV-Vis spectrophotometer. Fourier transform infrared (FT-IR) spectra of intermediates and monomer were obtained from KBr pellets with a Nicolet NEXUS-470 FT-IR spectrometer. Differential scanning calorimetry (DSC) studies were performed using a Netzsch DSC 214, at a heating rate of 10 °C min⁻¹ from 40 to 300 °C under a nitrogen atmosphere, respectively. T_{σ} was determined from the second heating scan. The fluorescence and UV-Vis absorption spectra of solutions were measured at room temperature. The cyclic voltammetry properties were studied on a CHI 660b electrochemical workstation. Cyclic voltammetry (CV) was carried out using nitrogenpurged N,N-dimethylformamide (DMF) for the reduction and dichloromethane for the oxidation scan at room temperature with a CHI voltammetric analyzer. Tetrabutylammonium perchlorate (n-Bu₄NClO₄) (0.1 M) was used as the supporting electrolyte. The conventional three-electrode configuration consists of a platinum working electrode, a platinum wire auxiliary electrode, and a saturated calomel electrode (SCE). Cyclic voltammograms were obtained at a scan rate of 100 mV s^{-1} .

Synthesis

The starting material, arylboronic acids including phenylboronic acid (A1), [4-(diphenylamino)phenyl]boronic acid (A2), and 4-(1-naphthyl)phenylboronic acid (A3) were purchased and [4-(9*H*-carbazol-9-yl)phenyl]boronic acid (A4), was used without further purification.

Synthesis of 3,6-dibromocarbazole (2)

A mixture of carbazole (1.00 g, 6.00 mmol) and silica gel (8.00 g, 133.33 mmol) was added to CH_2Cl_2 (60 mL) at room temperature, *N*-bromosuccinimide (1.07 g, 12.00 mmol), added to the above system, the mixture was reacted for 24 h at room temperature, then filtering and evaporating off the solvent, and the residue was extracted with n-hexane/ethyl acetate (10:1, v/v) to generate a white solid. 1.71 g, yield: 88%.

Mp: 204–206 °C. ¹H NMR (400 MHz, DMSO- d_6 , δ , ppm): 11.60 (s, 1H, –NH), 8.44 (d, J=8.8 Hz, 2H), 7.54 (d, J=8.9 Hz, 2H), 7.48 (d, J=8.7 Hz, 2H). ¹³C NMR (101 MHz, DMSO- d_6 , δ , ppm): 139.3, 129.2, 123.9, 123.8, 113.8, 111.5. Anal. calcd for C₁₂H₇Br₂N: C, 44.35; H, 2.17; Br, 49.17; N, 4.31. Found: C, 44.28; H, 2.15; Br, 49.14; N, 4.29.

Synthesis of 3,6-dibromo-9-(2-bromobenzyl)-9H-carbazole (3)

3,6-dibromocarbazole (3.25 g, 10.00 mmol) was added to DMF (30 mL) at room temperature. It was stirred for 30 min and to this solution was then added 2-bromobenzyl bromide (4.30 g, 70.00 mmol) and K_2CO_3 (8.00 g, 70.00 mmol). The reaction temperature was controlled at about 60 °C. The mixture was stirred at this temperature for 5 h and then poured into distilled water (200 mL). The precipitate was collected by filtration, washed with water (3 × 100 mL), and air-dried. The product was recrystallized from ethanol to give yellow solid 3.30 g. Yield: 67%.

Mp: 225–228 °C. ¹H NMR (400 MHz, CDCl₃, δ , ppm): 8.51 (s, 2H), 7.74 (d, J=8.8 Hz, 2H), 7.60 (d, J=8.9 Hz, 2H), 7.48 (d, J=8.7 Hz, 2H), 7.21 (s, 1H), 7.12 (d, J=8.8 Hz, 2H), 5.70 (s, 2H, –CH₂). ¹³C NMR (101 MHz, DMSO- d_6 , δ , ppm): 139.7, 139.6, 135.9, 133.3, 129.9, 129.6, 128.6, 127.5, 124.1, 123.7, 122.2, 112.4, 112.2, 46.8. Anal. calcd for C₁₉H₁₂Br₃N: C, 46.19; H, 2.45; Br, 48.52; N, 2.84. Found: C, 46.16; H, 2.43; Br, 48.50; N, 2.83.

General procedure for synthesis

of 9-([1,1'-biphenyl]-2-ylmethyl)-3,6-diphenyl-9H-carbazole (C1) and other final products 9-((4'-(naphthalen-1-yl)-[1,1'-biphenyl]- 2-yl)methyl)-3,6-bis(4-(naphthalen-1-yl)phenyl)-9H-carbazole (C2),4,4'-(9-((4'- (diphenylamin o)-[1,1'-biphenyl]-2-yl)methyl)-9H-carbazole-3,6- diyl) bis(*N*,*N*-diphenylaniline) (C3), 9,9'-((9-((4'-(8aH-9)^4-carbaz ol-9-yl)-[1,1'-biphenyl]-2-yl)methyl)-9H-carbazole-3,6-diyl) bis(4,1-phenylene))bis(8aH-9)^4-carbazole) (C4)

The reaction mixture containing intermediate **3** (289 mg, 1 mmol), the corresponding Phenylboronic Acid for **A1**, [4-(diphenylamino)phenyl]-boronic acid for **A2**,

4-(1-naphthyl)phenylboronic acid for A3, and [4-(9H-carbazol-9-yl)phenyl]boronic acid for A4 (1.1 mmol), toluene (10 mL), H₂O (5 mL), K₂CO₃ (2.5 mL, 5 mmol), and tetrakis- (triphenylphosphino)palladium(0) (28 mg, 0.02 mmol) was refluxed under nitrogen atmosphere for 6 h. After the reaction finished, the reaction mixture was cooled to room temperature and diluted by water (20 mL). The reaction mixture was separated into organic layer and aqueous layer, and the layer of which was extracted with dichloromethane $(3 \times 20 \text{ mL})$. After the combined organic layers were washed with brine (50 mL), dried over anhydrous magnesium sulfate, and filtered, the solvent was removed under reduced pressure. Then, the residue was isolated by column chromatography over silica using petroleum ether/ethyl acetate (10:1, v/v) as eluent and further purified by recrystallization in methanol/chloroform to give pure products as white solids.

9-([1,1'-biphenyl]-2-ylmethyl)-3,6-diphenyl-9H-carbazole (C1)

Yield: 73%. Mp: 168–170 °C. ¹H NMR (400 MHz, DMSOd₆, δ , ppm): 8.60 (s, 2H), 7.81 (d, J=7.2 Hz, 4H), 7.72 (d, J=7.5 Hz, 2H), 7.59 (t, J=7.3 Hz, 2H), 7.49 (t, J=2.0 Hz, 5H), 7.47 (d, J=7.3 Hz, 2H), 7.42 (t, 4H), 7.34 (t, J=7.5 Hz, 1H), 6.54 (d, J=7.8 Hz, 1H), 5.64 (s, 2H, –CH₂–). ¹³C NMR (101 MHz, DMSO-d₆, δ , ppm): 141.4, 141.1, 140.6, 140.5, 134.9, 132.1, 130.5, 129.7, 129.3, 129.1, 128.2, 128.0, 127.7, 127.1, 127.0, 126.0, 125.5, 123.5, 119.4, 110.1, 44.6. Anal. calcd for C₃₇H₂₇N: C, 91.51; H, 5.60; N, 2.88. Found: C, 91.48; H, 5.59; N, 2.85.

9-((4'-(naphthalen-1-yl)-[1,1'-biphenyl]-2-yl)methyl)-3,6-bi s(4-(naphthalen-1-yl)phenyl)-9H- carbazole (C2)

Yield: 77%. Mp: 264–266 °C. ¹H NMR (400 MHz, DMSOd₆, δ , ppm): 8.85 (s, 2H), 8.29 (d, J=7.2 Hz, 5H), 8.09 (d, J=9.3 Hz, 4H), 7.74 (dd, J=9.3 Hz, 3H), 7.58 (d, J=8.2 Hz, 5H), 7.53 (m, 7H), 6.91 (d, J=1.8 Hz, 1H), 5.89 (s, 2H, –CH₂–). ¹³C NMR (101 MHz, CDCl₃, δ , ppm): 133.8, 132.6, 129.5, 128.4, 128.3, 128.2, 127.7, 127.7, 126.3, 125.9, 125.5, 125.4, 109.5, 45.4. Anal. calcd for C₆₇H₄₅N: C, 93.13; H, 5.25; N, 1.62. Found: C, 93.08; H, 5.24; N, 1.59.

4,4'-(9-((4'-(diphenylamino)-[1,1'-biphenyl]-2-yl) methyl)-9H-carbazole-3,6-diyl)bis(N,N-diphenylaniline) (C3)

Yield: 78%. Mp: 258–260 °C. ¹H NMR (400 MHz, DMSO d_6 , δ , ppm): 8.85 (s, 2H), 8.29 (d, J = 8.4 Hz, 6H), 8.09 (d, J = 8.2 Hz, 4H), 7.92 (dd, J = 7.7 Hz, 5H), 7.74 (d, J = 7.7 Hz, 6H), 7.55 (m, 19H), 7.31 (d, J = 2.0 Hz, 9H), 6.93 (d, J = 2.1 Hz, 1H), 5.89 (s, 2H, $-CH_2-$). ¹³C NMR (101 MHz, CDCl₃, δ , ppm): 141.0, 140.9, 140.7, 140.4, 139.6, 139.1, 138.2, 137.9, 134.3, 133.8, 133.7, 132.7, 132.6, 130.3, 129.5, 128.6, 128.4, 128.3, 128.1, 127.7, 127.7, 127.5, 126.8, 126.4, 126.3, 126.1, 125.9, 125.5, 125.5, 132.7, 45.5. Anal. calcd for C₇₃H₅₄N₄: C, 88.81; H, 5.51; N, 5.68. Found: C, 88.79; H, 5.50; N, 5.66.

9,9'-((9-((4'-(8aH-9λ4-carbazol-9-yl)-[1,1'-biphenyl]-2 -yl)methyl)-9H-carbazole-3,6-diyl) bis(4,1-phenylene)) bis(8aH-9λ4-carbazole) (C4)

Yield: 65%. Mp: 267–269 °C. ¹H NMR (400 MHz, DMSOd₆, δ , ppm): 8.42 (s, 2H), 8.08 (d, J=8.5 Hz, 6H), 7.79 (d, J=8.2 Hz, 4H), 7.69 (d, J=7.7 Hz, 2H), 7.68 (t, J=7.7 Hz, 8H), 7.43 (t, J=7.9 Hz, 7H), 7.35 (t, J=8.0 Hz, 8H), 7.28 (t, J=7.5 Hz, 2H), 7.21 (t, J=7.9 Hz, 8H), 7.14 (s, 1H), 5.58 (s, 2H, –CH₂–). ¹³C NMR (101 MHz, CDCl₃, δ , ppm): 139.9, 139.9, 139.8, 139.6, 139.4, 138.5, 136.1, 135.1, 133.1, 131.0, 129.5, 129.4, 127.4, 126.7, 126.3, 125.9, 125.0, 124.9, 124.5, 119.3, 119.3, 118.8, 108.8, 108.6, 44.6. Anal. calcd for C₇₃H₄₈N₄: C, 89.36; H, 4.93; N, 5.71. Found: C, 89.34; H, 4.90; N, 5.69.

Results and discussion

Synthesis

The synthetic procedure of these materials is shown in Scheme 1. All these four compounds are synthesized through a Suzuki cross-coupling reaction between 3,6-dibromo-9-(2-bromobenzyl)-9*H*-carbazole (**3**) and the corresponding carbazole-containing boronic acid. These target compounds, **C1**, **C2**, **C3**, and **C4**, were then prepared at yields of 65–78%. All these compounds could be easily purified by column chromatography and recrystallization to reach a high purity for research and applications. The structures of the newly synthesized compounds were determined by ¹H and ¹³C NMR spectroscopy and elemental analysis.

NMR and IR spectra

Figure 1 shows the ¹H NMR spectra of 2 and 3 before and after the deprotonation of the N–H group. The deprotonation of the N–H group of the compound 2 and the appearance of the –CH₂– group of the compound 3 were reacted with 2-bromobenzyl bromide. The disappearance of the signal corresponding to N–H group from the ¹H NMR spectra of solutions of the compounds indicated that the deprotonation proceeded quantitatively.



Scheme 1 Synthesis of compounds C1-C4



Fig. 1 H NMR spectra of the DMSO-d₆ solutions of before and after the deprotonation of the N-H group

Figure 2 shows the IR spectra of C1–C4 and the FT-IR spectra of carbazole derivatives C1–C4 presented the characteristics absorption of C–H stretching located at $3068-3028 \text{ cm}^{-1}$, $2961-2905 \text{ cm}^{-1}$. The C=C stretching located at $1603-1586 \text{ cm}^{-1}$, the bending vibration of

 $-CH_2$ - bond located at 1486–1469 cm⁻¹, and C-H outplane bending vibration located at 900–650 cm⁻¹, respectively. All spectral data are consistent with the expected structure.



Fig. 2 IR spectra of C1-C4



Fig. 3 DSC curves of C1–C4. (DSC traces at the second heating cycle heating rate $10 \,^{\circ}$ C min⁻¹, nitrogen atmosphere

Thermal properties

The thermal and morphological stabilities of these compounds were investigated by differential scanning calorimetry (DSC), as shown in Fig. 3. When the supercooled isotropic sample of each compound was reheated for the second time, a glass transition was detected with glass transition temperatures (T_g) of 90.4, 129.1, and 109.6–148.0 °C for C1, C2, C3, and C4 (Table 1), in order of decreasing twisting resistance and increasing molecular weight. All of these host materials exhibited a T_g higher than the widely used main material, mCP ($T_g = 60$ °C), indicating improved amorphous stability. Its morphological stability is the result of the introduction of methylene. These morphologies and thermal stability are desirable for host materials, because they inhibit aggregation and phase separation and ensure the amorphous nature of the solid film state.

Photo-physical properties

The electronic absorption and photoluminescence (PL) spectra of these compounds in CH₂Cl₂ solution at room temperature are presented in Fig. 4. The wavelength of maximum absorption of C1, C2, C3, and C4 in dilute CH₂Cl₂ solutions $(1 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1})$ was observed at 247, 318, 293, and 264 nm, respectively, due to the carbazole-centered $\pi - \pi^*$ transition of the unit. The weak absorption in the range of 326–348 nm for C1, which is typically observed in carbazole-containing molecules, can be attributed to $n-\pi^*$ transitions of the lone-pair electrons to the entire conjugated backbone around the carbazole unit. In contrast to this molecule, the absorption of C2, C3, and C4 covering the range of 280–370 nm is much stronger. Because of the π -conjugation enhancement of the phenyl ring in this molecule, the $\pi - \pi^*$ transition energy is reduced to lower than that of $n-\pi^*$ transition energy and dominates the absorption spectrum. Their optical energy bandgaps were determined by absorption edge technique as 3.33, 3.22, 3.32, and 3.50 eV, respectively. Upon optical emission at the absorption maxima, C1, C2, C3, and C4 emit purple-blue fluorescence with emission peaks at 383, 413, 388, and 408 nm, respectively. The large red shift of from C1 to C2, C4 is understandable, because the π -conjugation expansion and asymmetry of the molecule must result in a lower energy S1-excited state.

It should be noted that the emission maximum of C2 shows a relatively large blue shift of about 20 nm as compared to the other two molecules C1, C3. (Table 2) Then, as shown in Table 3, the larger Stokes shift value of C2 observed in dichloromethane is 69 nm. The quantum yield of the carbazole derivative was calculated and its fluorescence quantum yield was measured by quinine sulfate with a quantum yield at $\lambda_{ex} = 285$ nm. The quantum yield (Φ_F) was determined by the following formula:

$$\boldsymbol{\Phi}_{\mathrm{F}} = \boldsymbol{\Phi}_{\mathrm{std}} \times \left(FA_{\mathrm{std}}n^2 \right) / \left(F_{\mathrm{std}}An_{\mathrm{std}}^2 \right).$$

F and F_{std} refer to the area under the fluorescence emission curve for samples and standards; *A* and A_{std} refer to the absorbance of each sample and standard at the excitation wavelength; and *n* and n_{std} refer to the refractive index of the solvent used for the sample and standard.

In addition, C2 in dichloromethane exhibited the highest quantum yield value of 0.63 (Table 3), and other compounds also showed larger values. Because they have strong fluorescence, electron-donating groups can increase the fluorescence intensity.

Table 1Physical data of C1,C2, C3, and C4

Compounds	$\lambda_{abs} (nm)^a$	$\lambda_{\max}^{em} (nm)^{a}$	$E_{\rm g} ({\rm eV})^{\rm b}$	HOMO/LUMO (eV) ^c	T _g °C
C1	233	383	3.33	-5.58/-2.22	90.4
	262				
C2	301	416	3.22	-5.38/-2.16	129.1
	233				
	318				
C3	232	388	3.32	-5.37/-2.05	109.6
	293				
	313				
C4	233	408	3.51	-5.51/-2.01	148
	264				
	301				

^aAbsorption and fluorescence wavelengths in dilute dichloromethane solutions

^bThe optical bandgap, calculated by the absorption edge technique

^cDetermined using electrochemical potentials and optical bandgaps



Fig.4 UV–Vis absorption and PL spectra of C1–C4 in dilute CH2Cl2 solutions at 293 K $\,$

Table 2 Photo-physical properties of the C1–C4 in different solvents

Solvents	C1 $\lambda_{\max}^{em/nm}$	C2 $\lambda_{\max}^{em/nm}$	C3 $\lambda_{\max}^{em/nm}$	C4 $\lambda_{\max}^{em_{/nm}}$
Ethyl Acetate	390	415	391	401
THF	392	416	398	409
Dichloromethane	383	416	388	408
Acetone	386	415	393	416
Ethanol	413	421	386	417
DMF	396	420	398	427

Effect of solvent polarity on fluorescence emission

The effect of solvent polarity on the fluorescence properties of the carbazole derivatives was also studied. They show the longest wavelength absorption maxima in DMF. **C1** emits at 390 nm in ethyl acetate and at 396 nm in DMF, **C2** emits at 415 nm in ethyl acetate and at 420 nm in DMF, and **C3** emits at 391 nm in ethyl acetate and at 398 nm in DMF. These compounds show a red shift as the solvent polarity increases, indicating that the maximum absorption is strongly influenced by the solvent polarity of all compounds (Table 2). The compound **C4** emits at around 415 nm in most of the listed solvents, but it has red shifted emission in DMF (427 nm), due to the π -conjugation of the molecule increases.

Emission spectra were recorded by exciting the 1×10^{-6} M solutions at their maximum absorption wavelengths, and for excitation spectra, their maximum emission wavelengths were used. The emission characteristics of these carbazole derivatives were also studied and the results obtained are summarized in Table 2. Figures 5, 6, 7, and 8 represent the emission overlay spectra of C1–C4. The emission of C1 and C3 in majority of the solvents lies in the range 390–400 nm, the emission of C2 in majority of the solvents lies in the range 415–420 nm, and the emission of C4 in majority of ethyl acetate, THF, and dichloromethane lies in the range 415–420 nm, but in DMF, a large red shift is observed at 427 nm.

Electrochemical properties

The electrochemical properties of these compounds were measured by cyclic voltammetry (CV) measurements in deoxygenated (DCM) and dimethylformamide (DMF) solutions containing 0.1 M tetrabutylammonium perchlorate (n-Bu₄NClO₄) as the supporting electrolyte. The cyclic voltammograms is shown in Fig. 9. During the anodic scanning in DCM solution, each compound underwent a quasi-reversible oxidation process that should be assigned to the oxidation of the electron-donating carbazole ring in each molecule. The additional reduction wave

Table 3 Absorption and fluorescence emission data for compounds **C1–C4** maximum absorption wavelengths ($\lambda_{\max}^{em/am}$), maximum emission wavelengths ($\lambda_{\max}^{em/am}$), maximum excitation wavelengths ($\lambda_{\max}^{em/am}$),

molar extinction coefficients (ε , 1 mol⁻¹ cm⁻¹), Stokes' shifts, $\Delta\lambda$ (nm), in dichloromethane for 1×10^{-6} M

Compounds	$\lambda_{\max}^{abs/nm}$	$\lambda_{\max}^{em/nm}$	$\lambda_{\max}^{em/nm}$	$\Delta\lambda/nm$	$\epsilon_{\rm max}$	φ
C1	262	383	332	51	20439	0.3651
C2	318	416	347	69	35600	0.6342
C3	313	388	329	59	109600	0.5148
C4	301	408	350	58	32740	0.6203



Fig. 5 Emission spectra of C1 in different solvents



Fig. 6 Emission spectra of C2 in different solvents

of 0.80–1.00 eV was detected for each compound in the reduction process. For nonprotected carbazole derivatives at 3,6 sites, this additional reduction peak was frequently observed in the previous reports (Gong et al. 2012; Deng et al. 2012). No reduction wave was detected for all these compounds during the cathodic scan to -2.0 V. The HOMO



Fig. 7 Emission spectra of C2 in different solvents



Fig. 8 Emission spectra of C2 in different solvents

energies were determined from the onset potential of the first oxidation wave (E_{ox}^{onset}) according to the formula of $E_{HOMO} = -(E_{ox}^{onset} + 4.4)$ as ca. -5.58, -5.38, -5.37, and -5.51 eV, respectively. The almost identical HOMO levels of these molecules are reasonable, since the carbazole ring stands for the exclusive and the common hole-transporting



Fig. 9 Cyclic voltammograms of C1–C4 measured in DCM (anodic) and DMF (cathodic) at a scan rate of 100 mV $\rm s^{-1}$

group in all these molecules. The HOMO energy levels of these compounds are close to the HOMO levels of the widely used hole transport material 1,1-bis[(di-4-tolylamino) phenyl]cyclohexane (TAPC, 5.50 eV), indicating small hole injection barrier from TAPC to the emitting layer when these compounds are used as the hosts in emitting layer. During the cathodic scan in DMF solution, each compound detected an irreversible reduction signal with a very similar onset potential. The LUMO energies were calculated from the HOMO energies and the optical bandgaps (E_{o}) , according to the formula of $E_{\text{LUMO}} = (E_{\text{HOMO}} + E_{\text{g}})$ as ca. -2.22, -2.16, -2.05, and -2.01 eV, respectively. In addition, E_{a} was determined as the onset potential difference between the first oxidation and reduction waves multiplied by the electron charge (e) for each compound as 3.20, 3.09, 3.13, and 3.30 eV. All of these electrochemical and electronic data are listed in Table 1.

Conclusion

In summary, four novel carbazole-based materials, C1–C4, have been developed by combing carbazole with aromatic hydrocarbons via the ortho-position of *N*-phenyl, and their structures were identified using FT-IR, ¹H NMR, and ¹³C NMR spectroscopic techniques. Special linking modes resulted in significantly different properties of these materials. The UV–Vis and fluorescence spectra properties of carbazole derivatives were measured for 1×10^{-6} M in ethyl acetate, THF, dichloromethane, acetone, ethanol, and DMF solutions. C2 has the longest absorption maxima at 318 nm in dichloromethane and C1–C4 showed a bathochromic shift with the increase in the solvent polarity and these

compounds have the longest emission maxima in DMF. All derivatives displayed large Stokes' shift values and excellent photostabilities. Thus, the maximum Stokes shift value of C2 observed in dichloromethane is 69 nm. In addition, C2 also exhibited the highest quantum yield value of 0.69 in dichloromethane. These materials can be applied as organic light-emitting devices due to their excellent thermal and morphological stability, suitable energy levels, and holetransporting capabilities The formed molecules exhibited twisted structure, which resulted in high glass transition temperatures (T_{a}) , ranged from 90.4 to 148.0 °C. They also have high optical bandgaps (E_g) , whose optical energy bandgaps are determined by the absorption edge technique to be 3.33, 3.22, 3.32, and 3.50 eV, respectively. Therefore, our research may promote the development of general-purpose hole-transporting materials for OLEDs. They also had high optical bandgaps (E_{α}) , whose optical energy bandgaps are determined by the absorption edge technique as 3.33, 3.22, 3.32, and 3.50 eV, respectively. Therefore, our research may promote the development of the universal hole-transporting materials for the development of OLEDs.

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