

Synthesis and characterization of deep blue emitters from starburst carbazole/fluorene compounds

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Abstract

A series of well-defined, highly fluorescent starburst compounds with a carbazole core and oligo(2,7-fluorene ethynylene) arms have been synthesized by Sonogashira coupling reaction and fully characterized. These conjugated compounds exhibit good solubility, high thermal stability, and excellent fluorescence quantum yields (up to 0.99). The incorporation of carbazole core interrupted the main-chain conjugation and resulted in blue-shifted absorption and emission. Moreover, deep blue light has been approached from organic light-emitting diodes (OLEDs) adopting these compounds as emitting layer.

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Keywords: Blue emitter; Starburst molecules; Photoluminescence; Electroluminescence

1. Introduction

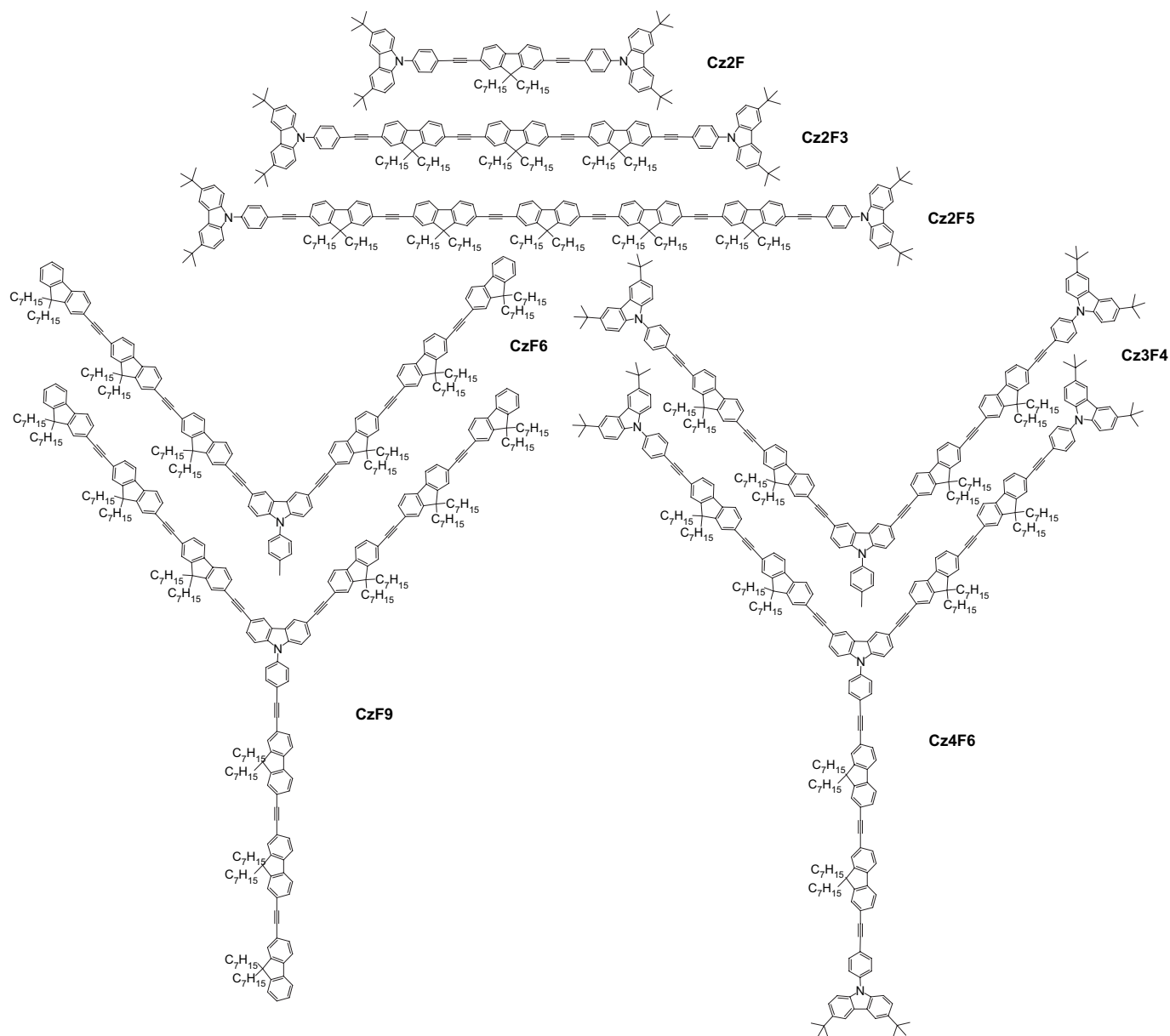
Since the development of first efficient OLEDs by Tang and VanSlyke,¹ significant attention has been paid on the production of full-color flat panel displays.^{2,3} Full-color displays based on OLEDs exhibit many attractive features, such as wide viewing angles, bright self-emission, facile color tunability, and compatibility with flexible substrates and now exist in a range of commercial applications and compete with conventional liquid-crystal displays (LCDs).^{4–7} To realize full-color OLED displays, highly efficient red-, green-, and blue-emitting materials and devices are required. However, only red and green materials and devices with sufficient efficiencies and lifetimes of commercial value have been described,^{8–11} while high-efficient, pure blue light still remains a challenge. Consequently, a great number of blue-emitting materials, such as anthracene derivatives,^{12–15} oligoquinoline,¹⁶ tetraphenylsilane,^{17,18} and diarylfluorene derivatives^{19,20} have been developed. However, most of these materials are still not

satisfactory due to their large energy gaps and low electron affinities leading to inefficient electron injection into the blue emitters.

Monodisperse oligofluorenes, first reported by Klaerner and Miller,²¹ have recently attracted much attention because of their excellent chemical, thermal, photochemical stabilities as well as the possibility of structure tuning to adjust the electronic and morphological properties of desired compounds via the substitution on the C-9 position of fluorene.^{22,23} Not only does this class of materials have great potential applications for optoelectronic materials, such as blue emitters of OLEDs,^{24,25} but also it would be very helpful to study the properties of a series of pure compounds and to have a better understanding of the structure–property relationships of their corresponding polymers. On the other hand, carbazole units hold hole-transport ability and incorporation of them could improve the hole-transport properties of materials as well as suppress the aggregation and/or excimers formation of molecules.^{26–29} In this report, carbazole units were successfully introduced into fluorene compounds through 3-, 6-, and/or 9-positions of carbazole. Thus, linear and starburst structures of molecules were obtained (Scheme 1). These synthesized compounds emitted deep blue light with high quantum yields

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Scheme 1. Chemical structures of carbazole/fluorene compounds.

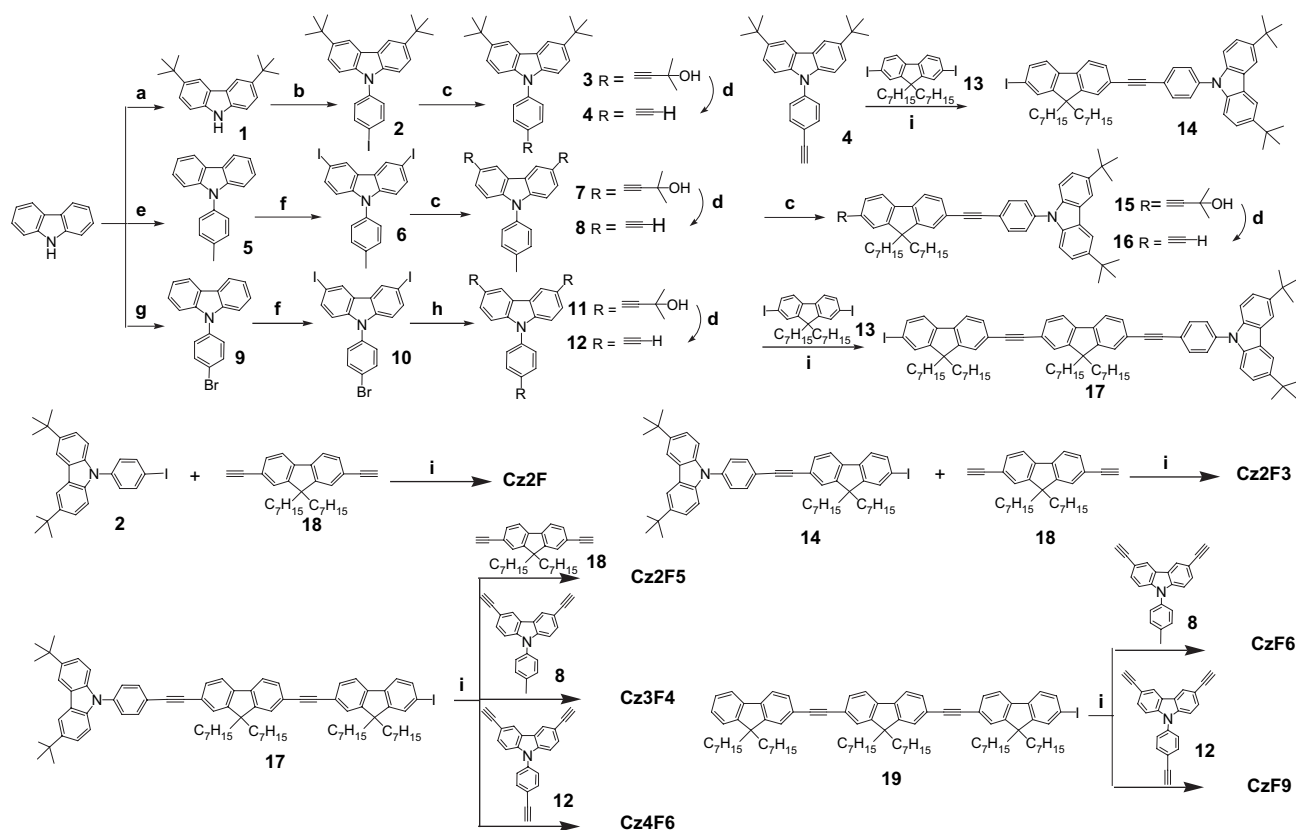
and their applications in blue OLEDs were investigated accordingly.

2. Results and discussion

2.1. Synthesis

Structures of these well-defined, carbazole end-capped and/or centered fluorene compounds are illustrated in Scheme 1. A Pd/Cu-catalyzed Sonogashira coupling reaction was used as a key reaction to construct these triple-bond-linked compounds. Scheme 2 illustrates the synthetic routes to intermediates and final compounds. Our synthetic strategy started from commercially available compounds carbazole and fluorene. The carbazole derivatives **1**–**8**^{30,31} and **9** and **10**³² were synthesized according to the reference methods. Compound 3,6-

diethynyl-9-(4-ethynylphenyl)-9*H*-carbazole (**12**), which served as a core of starburst molecules, was prepared by coupling **10** with 3-methyl-1-butyne-3-ol, and subsequently by deprotection. Fluorene derivatives **13** and **18**³³ were used to construct the main chain of these conjugated molecules. Pd/Cu-catalyzed coupling of **4** with an excess amount of **13** yielded intermediate **14**, which could be coupled with 3-methyl-1-butyne-3-ol in the presence of Pd/Cu catalyst and subsequently base-promoted deprotection to provide compound **16**. Recoupling of **16** with an excess amount of **13** afforded **17**, which served as arms of starburst compounds. Similar procedures were performed to obtain **19**.³³ Coupling of 2,7-diethynyl-9,9-diheptyl-9*H*-fluorene (**18**) with 2 equiv of **2**, **14**, and **17** offered linear compounds **Cz2F**, **Cz2F3**, and **Cz2F5** in moderate yields of 86, 78, and 72% after separation, respectively. Furthermore, treatment of 3,6-diethynyl-9-*p*-tolyl-9*H*-



Scheme 2. Conditions: (a) $(\text{CH}_3)_3\text{CCl}$, AlCl_3 , CH_2Cl_2 ; (b) K_2CO_3 , Cu, 18-crown-6, 1,4-diiodobenzene, DMF, N_2 , 170°C ; (c) 3-methyl-1-butyn-3-ol, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, PPh_3 , CuI, NEt_3 , reflux; (d) KOH, 2-propanol, reflux; (e) K_2CO_3 , Cu, 18-crown-6, 1-iodo-4-methylbenzene, DMF, N_2 , 170°C ; (f) KI, KIO_3 , acetic acid, 80°C ; (g) K_2CO_3 , Cu, 18-crown-6, 1-bromo-4-iodobenzene, DMF, N_2 , 170°C ; (h) 3-methyl-1-butyn-3-ol, $\text{Pd}(\text{Ph}_3\text{P})_4$, Ph_3P , CuI, diisopropylamine, N_2 , reflux; (i) $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, PPh_3 , CuI, NEt_3 , reflux.

carbazole (8) with 2 equiv of **19** and **17** provided **Cz6F**, and **Cz3F4** in 69 and 65% yields, respectively. Finally, **CzF9** and **Cz4F6** were synthesized by the reactions of 3,6-diethynyl-9-(4-ethynylphenyl)-9H-carbazole (**12**) with 3 equiv of **19** and **17**, respectively, in the presence of Pd/Cu catalyst.

All compounds appeared to be yellow powder after dried in vacuum. Structures of the target compounds were characterized by NMR, MALDI-TOF mass spectroscopy, and element analysis. These compounds exhibited excellent solubility in common organic solvents, such as CH_2Cl_2 , CHCl_3 , THF, toluene, and even cyclohexane, which was ascribed to the existence of *n*-heptyl and *tert*-butyl substituents. Existence of alkyl substituents not only benefited the easier preparation and purification of compounds, but also helped the device fabrication via simple spin-coating. Further, these compounds showed good thermal stabilities, and their decomposition temperatures (T_d , 5% loss of initial weight) were above 400°C examined by thermogravimetric analysis (TGA) in N_2 at a heating rate of $20^\circ\text{C min}^{-1}$. The melting and glass transition temperatures were not clearly observed by differential scanning calorimetry (DSC).

2.2. Visualization and simulation

Structures of the synthesized compounds were optimized by PM3 method. Figure 1 illustrates the energy-minimized

structures of compounds. Although the chains of all molecules were composed of fluorene units, the arrangement of fluorene units was quite interesting. **Cz2F3** and **Cz2F5**, end-capped with carbazole units, have rod-like structures and the fluorene units arranged alternatively in two different directions in backbones, which was in a good accordance with the arrangement of fluorene in its homopolymer. However, both **Cz6F** and **Cz3F4**, with V-shaped structures, presented the arrangement of fluorene in one direction. This phenomenon could also be observed in the propeller-like structures of **CzF9** and **Cz4F6**. From Figure 1, we inferred that it was much easier for small and linear molecule **Cz2F** to form close molecular packing than other compounds. The multiflexibility of the free rotation along the molecular chain and the steric hindrance arising from the centered carbazole hampered the close packing of the aromatic rings and thereafter hindered the aggregation and/or excimer formation.

2.3. Photophysical properties

The photophysical properties of these compounds were examined by UV–vis and fluorescence spectroscopy in dichloromethane solutions and in thin neat films as well. Figure 2 shows the normalized UV–vis absorption spectra. In dilute dichloromethane solutions, all the compounds exhibited structureless absorption bands arising from the π – π^* transition

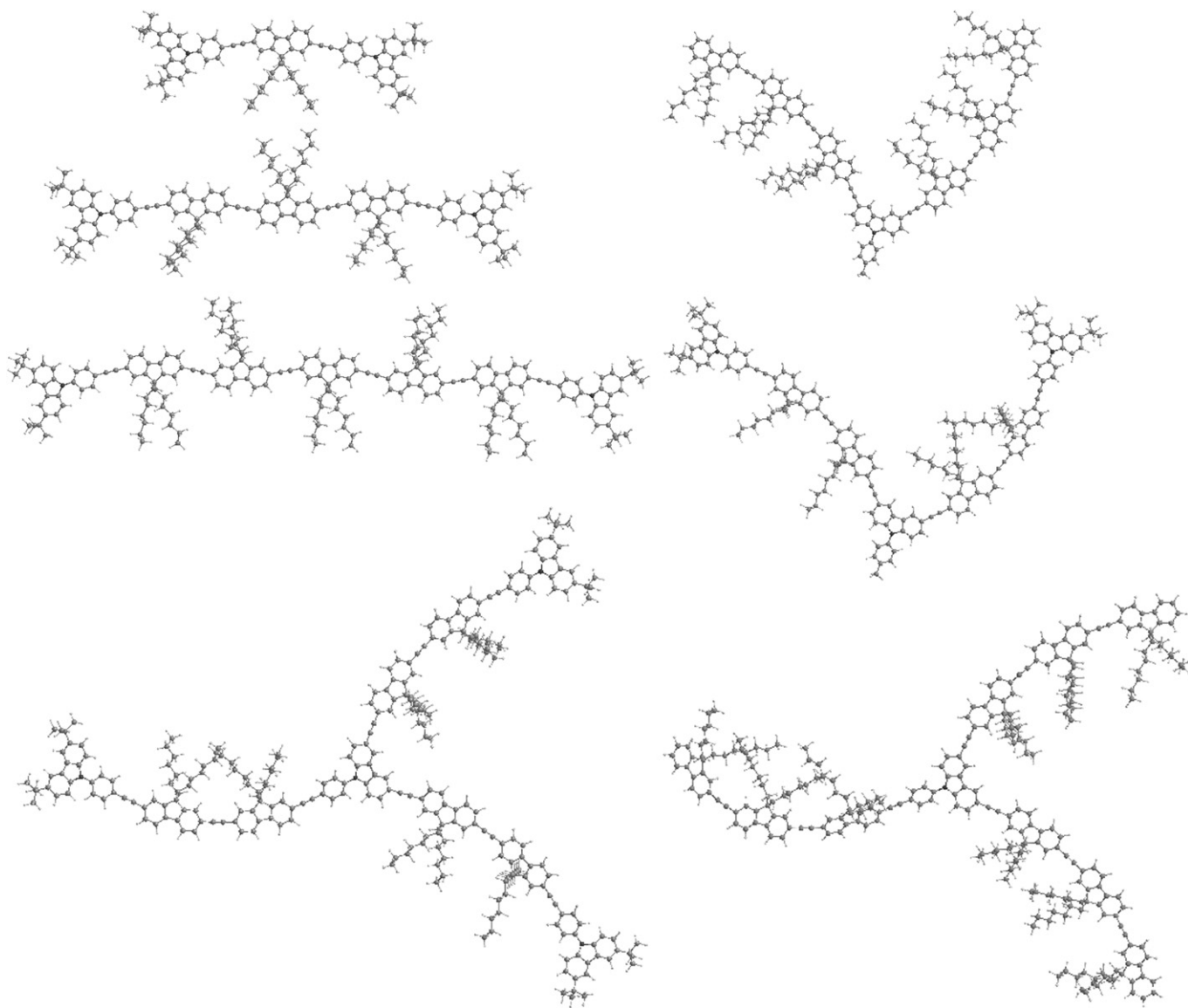


Figure 1. Energy-minimized structures of compounds calculated by PM3.

of the molecular chain. The maximum absorption peaks of linear compounds (**Cz2F**, **Cz2F3**, and **Cz2F5**) bathochromically shifted with the increase of molecular length. The V-shaped and the starburst compounds exhibited almost identical absorption bands with maximum absorption peaks at about 400 nm. The carbazole at the center of the molecules interrupted the main-chain conjugation³⁴ and resulted in relatively short absorption wavelength with respect to that of **Cz2F5**. In thin neat films, the absorption spectra of these compounds were quite similar to those in solutions except for slightly red shifts (1–5 nm), which indicated that these compounds exhibited very similar conformations in both solution and solid states. The π – π^* energy gaps (E_g , Table 1) of these compounds were calculated from the UV–vis absorption thresholds. The E_g s increased progressively with the decrease of the chain length. The E_g s of the V-shaped and the starburst compounds were 2.97 eV, which were higher than that of **Cz2F5**. This was also attributed to the different conjugation

degree of molecules with or without centered carbazole core, which could result in different energy levels.³⁵ From Table 1, it was observed that the molar absorption coefficient became larger with the increase of the conjugation length or the number of arms. Moreover, carbazole end-capped compounds seemed to have relatively larger molar absorption coefficient compared with those of similar molecules without carbazole cappers.

Figure 3 displays the emission spectra of compounds in dilute CH_2Cl_2 solutions and in thin neat films as well, excited at 380 nm. **Cz2F3** and **Cz2F5** showed narrow emission spectra with a full width at half emission maximum (fwhm) of 14 nm and emission peaks located at 417 and 421 nm, respectively. Expectably, the shortest compound (**Cz2F**) exhibited a red-shifted, broad emission peak at 422 nm with a fwhm of 65 nm, which was ascribed the excimers formation as we assumed above. Much energy loss observed from the largest Stokes shift (52 nm) was well evident. In view of

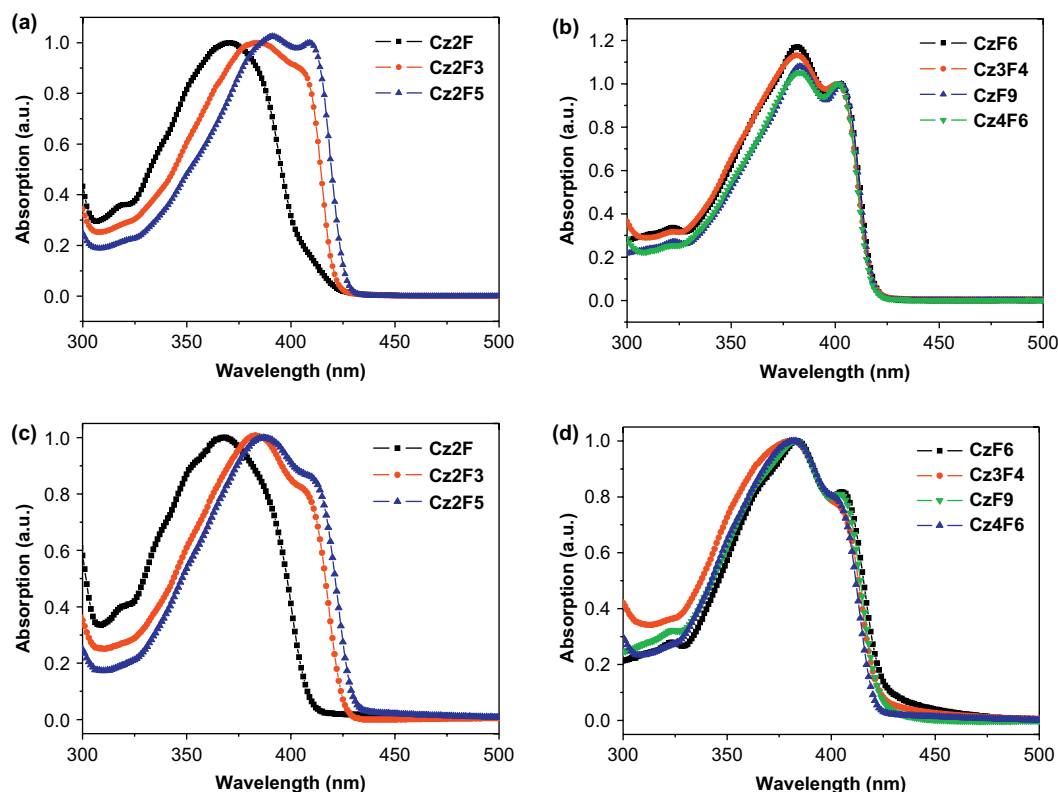


Figure 2. Absorption spectra of compounds in dilute CH₂Cl₂ solutions (a), (b), and in thin neat films (c), (d).

carbazole-centered molecules, their emission spectra were almost the same. Main emission peaks were located at about 415 nm with shoulder peaks at about 440 nm, which were close to those of reported polyfluorenes (415 and 439 nm).³⁶ Similar to the observation in solutions, **Cz2F** exhibited broad, red-shifted emission in thin neat film due to the excimer formation. Emission spectra in thin neat films of other compounds were resembled to those in solutions except for slight red shifts (≤ 6 nm).

The synthesized compounds were highly fluorescent in solutions and in solid states. Quantum yields were measured in degassed cyclohexanes using the standard of 9,10-diphenylanthracene (DPA, $\Phi=0.95$ in cyclohexane).^{37–39} Those of linear ones were measured in the range of 0.74–0.96, which

increased as the chain lengths elongated. These findings were much better than those of oligo(2,7-fluorene ethynylene)s without carbazole participation (0.49–0.63).³³ Remarkably, high quantum yields (0.97–0.99) were observed for those starburst compounds with centered carbazole core, which were higher than those of compounds with similar efficient conjugation length.³⁴ For example, the quantum yield of **Cz4F6** was 0.99, while those of **Cz2F** and **Cz2F3** were 0.74 and 0.89, respectively. Similar phenomena have been reported by Yamaguchi et al.,⁴⁰ which was ascribed to an extension of the π conjugation between the arms of starburst molecules. From higher PL quantum yields as well as larger molar absorption coefficient of starburst compounds, we inferred that the insertion of carbazole core into the molecular backbone

Table 1
Photophysical properties of compounds

Compound	$\lambda_{\text{Abs.}}$ (nm)		$\lambda_{\text{Em.}}$ ^b (nm)		Φ^c (nm)	fwhm ^d (nm)	Stokes shift (nm)	E_g^e (eV)	T_d (°C)
	CH ₂ Cl ₂ ($\times 10^5$) ^a	Film	CH ₂ Cl ₂	Film					
Cz2F	370 (0.97)	369	422	411, 447	0.74	65	52	3.02	413
Cz2F3	385 (2.20), 401 (1.97)	383, 406	417, 447	423, 448	0.89	14	16	2.93	420
Cz2F5	391 (3.45), 409 (3.32)	387, 410	421, 446	427, 452	0.96	14	12	2.90	419
CzF6	381 (3.10), 402 (2.63)	381, 405	415, 440	419, 446	0.97	16	13	2.97	415
CzF9	382 (4.56), 401 (4.09)	383, 404	415, 439	420, 444	0.99	16	14	2.97	411
Cz3F4	382 (4.26), 400 (3.95)	382, 404	415, 440	421, 444	0.98	20	15	2.97	421
Cz4F6	382 (5.64), 400 (5.25)	383, 402	414, 439	419, 443	0.99	16	14	2.97	416

^a Molar absorption coefficient (ϵ): M⁻¹ cm⁻¹.

^b Excited at 380 nm.

^c Measured in cyclohexane solutions using DPA as a standard.

^d Full width at half emission maximum in dilute CH₂Cl₂ solutions ($\sim 10^{-6}$ M).

^e Determined from UV–vis absorption spectra.

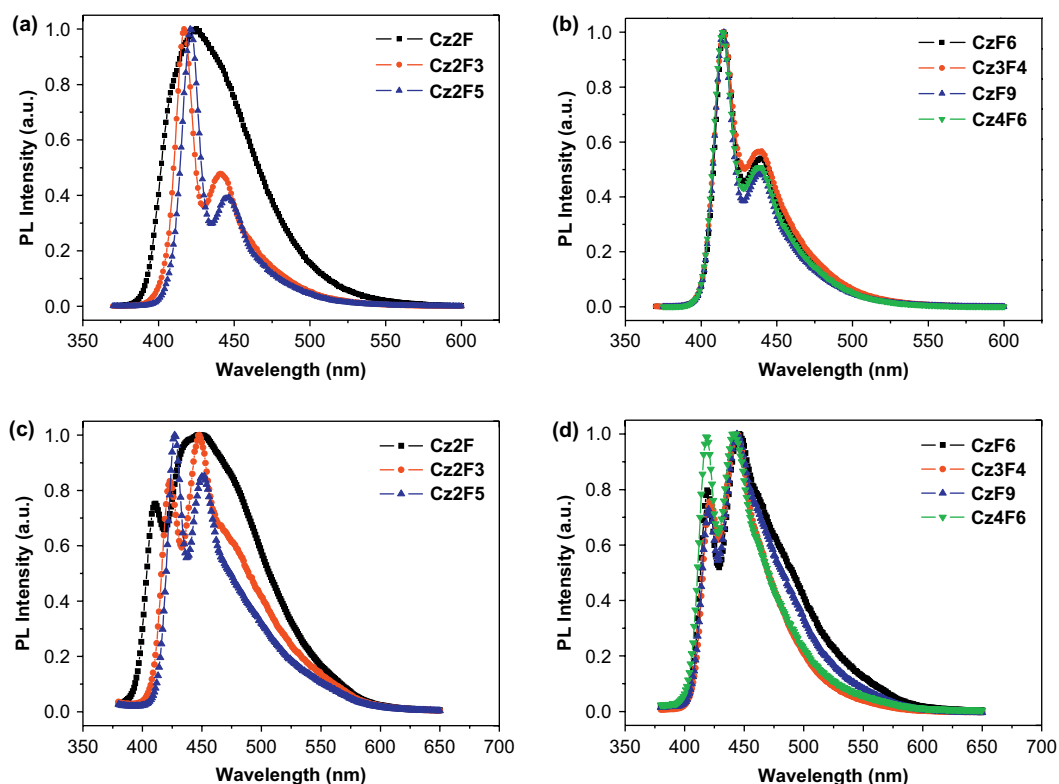


Figure 3. PL spectra of compounds in dilute CH_2Cl_2 solutions (a), (b), and in thin neat films (c), (d).

might not interrupt the main-chain conjugation completely, and a weak π conjugation still occurred between arms.

2.4. Electroluminescence properties

To investigate the EL properties of these compounds, devices with the configurations of indium tin oxides (ITO)/poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS) (30 nm)/compounds (50 nm)/1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene (TPBI) (20 nm)/Al (100 nm), were fabricated. PEDOT:PSS were used as a hole-injection layer, TPBI was adopted as an electron-transporting and hole-blocking layer, and the synthesized compounds functioned as light-emitting layers. EL spectra as well as current density–voltage–brightness characteristics were measured under ambient conditions. Figures 4–6 illustrate the normalized EL spectra and current

density–voltage–brightness characteristic curves and Table 2 summarizes the performance of devices based on these compounds. The EL spectra were similar to PL spectra in thin neat films, which indicated the same radiative decay process of singlet excitons.^{41,42} In view of linear compounds, **Cz2F** and **Cz2F3** showed broad emission peaks with additional emissions around 500 nm. This could be ascribed to the enhanced excimer formation of these short chains that were prone to align under electric fields.^{43,44} **Cz2F5**, with longer chain length, exhibited EL emission peaks at 428 and 452 nm with a fwhm of 75 nm. No excimer emission was observed in this case. Further, compounds with a carbazole core, except for **Cz4F6** whose EL emission was unstable, exhibited similar narrow emission with fwhms in the range of 72–89 nm. The preliminary results demonstrated that deep blue light could be approached from the devices based on **Cz2F5** and carbazole-centered compounds

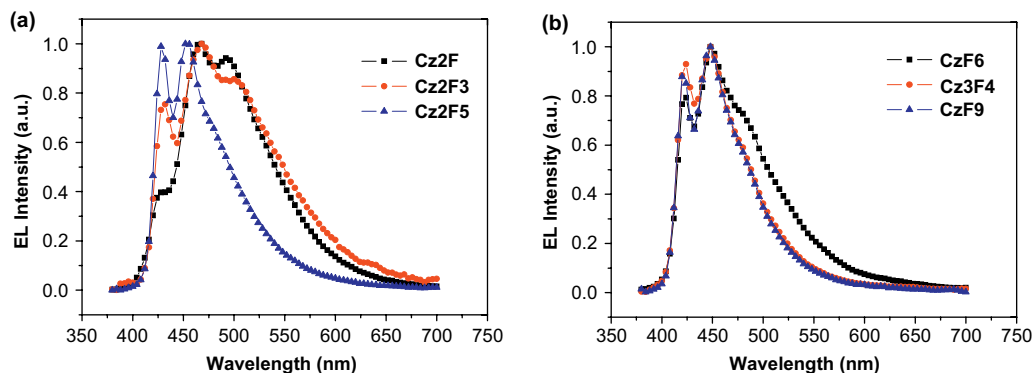


Figure 4. EL spectra of compounds in devices: ITO/PEDOT:PSS/compounds/TPBI/Al.

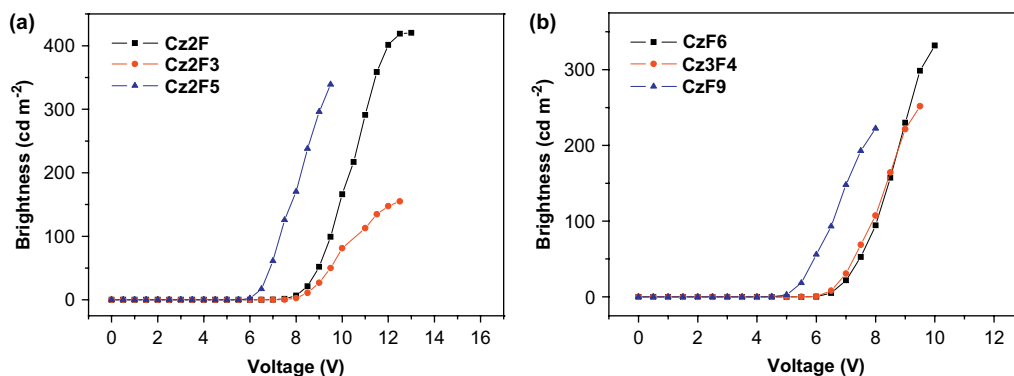


Figure 5. Brightness–voltage diagrams for device: ITO/PEDOT:PSS/compounds/TPBI/Al.

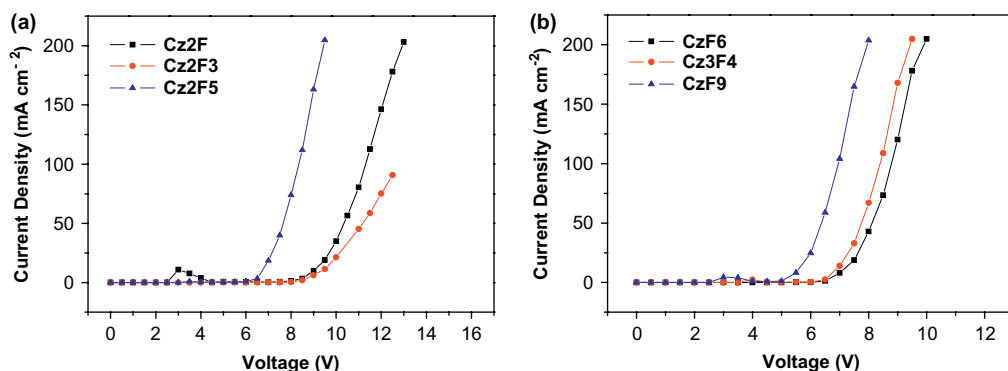


Figure 6. Current density–voltage diagrams for devices: ITO/PEDOT:PSS/compounds/TPBI/Al.

Table 2
Summary of device performances

Compound	EL (nm)	fwhm (nm)	$\eta_{\max, \text{ext}}$ (%)	$\eta_{\max, \text{L}}$ (cd A ⁻¹)	Turn-on voltage (V)	Brightness _{max} (cd m ⁻² , V)
Cz2F	468, 492	98	0.34	0.63	7.4	421, 13
Cz2F3	432, 468, 502	126	0.40	0.76	7.6	155, 12.5
Cz2F5	428, 452	75	0.44	0.52	5.2	296, 9.0
CzF6	424, 448	89	0.30	0.39	6.1	230, 9.0
Cz3F4	424, 448	72	0.31	0.34	6.1	221, 9.0
CzF9	420, 448	72	0.21	0.23	4.2	222, 8.0

(Cz3F4 and CzF9). Introduction of carbazole units into molecular backbone led to the color-stable, blue-shifted emission by suppressing excimers formation.

3. Conclusions

In summary, we had successfully synthesized and fully characterized a series of well-defined, highly fluorescent compounds with a carbazole core and oligo(2,7-fluorene ethynylene) arms. Addition of carbazole units significantly increased the fluorescence quantum yields in comparison with those of oligo(2,7-fluorene ethynylene)s, especially for carbazole-centered compounds. Moreover, participation of carbazole interrupted the conjugation and resulted in blue-shifted absorption and emission. Furthermore, deep blue light had been approached from OLEDs based on these compounds as emitters.

4. Experimental section

4.1. General information

¹H and ¹³C NMR spectra were obtained on a Bruker AVANCE DMX500 spectrometer operating in the FT mode. Solutions in chloroform-*d* (5% w/v) were used to obtain NMR spectra. TMS was used as an internal standard. Mass spectroscopic (MS) measurements were carried using matrix-assisted laser desorption–ionization time-of-flight (MALDI-TOF) technique. Fluorescence measurements were made with a RF-5301PC spectrofluorometer (Shimadzu, Kyoto, Japan) equipped with a xenon lamp. UV–vis absorption spectra were recorded on Shimadzu UV-2450 spectrophotometer. NETZSCH STA 409 PG/PC was used to measure the thermal performances of the compounds. The solvents were distilled before used. Commercially available reagents were used without further purification.

4.2. 3,6-Diethynyl-9-(4-ethynyl-phenyl)-9H-carbazole (12)

Compound **10** (2.87 g, 5 mmol), 3-methyl-1-butyn-3-ol (1.68 g, 20 mmol), cuprous iodide (20 mg, 0.1 mmol), Pd(Ph₃P)₄ (11.5 mg, 0.01 mmol), triphenylphosphine (10.5 mg, 0.04 mmol), and dry diisopropylamine (150 mL) were placed in a 250 mL round bottle flask equipped with a Teflon covered magnetic stir bar. After the solution was purged with nitrogen for half an

hour, it was refluxed under nitrogen for 12 h. The reaction mixture was filtered and the filtrate was evaporated under reduced pressure. Compound **11** was obtained through column chromatography (silica gel, hexane/ethyl acetate as eluent). Then **11**, potassium hydroxide (2.0 g, 35 mmol), and 2-propanol (150 mL) were placed in 250 mL round bottle flask equipped with a Teflon covered magnetic stir bar. After the resulting mixture was refluxed for 3 h under N₂, it was cooled to room temperature. Solution was poured into water and extracted by CH₂Cl₂. After washing by water and drying by MgSO₄, the solvent was then removed, and the residue was purified through column chromatography (silica gel, hexane/dichloromethane as eluent). In this way, 1.2 g (72 % total yield) of **12** was obtained. ¹H NMR δ CDCl₃: 3.10 (s, 2H), 3.20 (s, 1H), 7.32 (d, 2H, *J*=8.5 Hz), 7.50 (d, 2H, *J*=8.5 Hz), 7.55 (dd, 2H, *J*₁=8.5 Hz, *J*₂=1.5 Hz), 7.73 (d, 2H, *J*=8.5 Hz), 8.26 (d, 2H, *J*=1.0 Hz) ppm; ¹³C NMR δ CDCl₃: 76.17, 78.83, 82.83, 84.58, 110.18, 114.50, 122.20, 123.16, 124.99, 127.04, 130.80, 134.10, 137.30, 141.03 ppm; MS (EI) (*m/z*): 315 (M⁺). Anal. Calcd for C₂₄H₁₃N: C, 91.40; H, 4.15; N, 4.44. Found: C, 91.41; H, 4.13; N, 4.38.

4.3. 3,6-Di-*tert*-butyl-9-[4-(9,9-diheptyl-7-iodo-9H-fluoren-2-ylethynyl)-phenyl]-9H-carbazole (**14**)

Compound **4** (379 mg, 1 mmol), **13** (1842 mg, 3 mmol), cuprous iodide (10 mg, 0.05 mmol), Pd(PPh₃)₂Cl₂ (3.5 mg, 0.005 mmol), triphenylphosphine (5 mg, 0.02 mmol), and dry triethylamine (150 mL) were placed in a 250 mL round bottle flask equipped with a Teflon covered magnetic stir bar. After the solution was purged with nitrogen for half an hour, it was refluxed under nitrogen for 4 h. The reaction mixture was filtered and the filtrate was evaporated under reduced pressure. The residue was purified through column chromatography (silica gel, hexane/dichloromethane as eluent). In this way, 623 mg (72 % yield) of **14** was obtained. ¹H NMR δ CDCl₃: 0.62 (br, 4H), 0.80 (t, 6H, *J*=7.5 Hz), 1.06–1.07 (m, 12H), 1.16–1.20 (m, 4H), 1.47 (s, 18H), 1.95–2.00 (m, 4H), 7.34 (d, 2H, *J*=6.5 Hz), 7.39 (d, 2H, *J*=8.0 Hz), 7.47–7.49 (m, 2H), 7.55–7.58 (m, 4H), 7.65–7.70 (m, 2H), 7.75–7.77 (m, 2H), 8.14 (d, 2H, *J*=1.5 Hz) ppm; ¹³C NMR δ CDCl₃: 14.28, 22.82, 24.00, 29.21, 30.26, 32.04, 32.23, 34.99, 40.61, 55.40, 89.02, 91.57, 93.42, 109.46, 116.54, 119.92, 120.08, 120.27, 121.93, 123.16, 123.81, 123.96, 126.25, 126.65, 127.14, 127.81, 130.89, 132.37, 133.20, 136.26, 139.12, 141.87, 143.44, 151.30, 153.67 ppm; MS (MALDI-TOF) (*m/z*): 739.7 (M⁺–I). Anal. Calcd for C₅₅H₆₄IN: C, 76.28; H, 7.45; I, 14.65; N, 1.62. Found: C, 76.25; H, 7.49; N, 1.58.

4.4. 3,6-Di-*tert*-butyl-9-[4-(7-ethynyl-9,9-diheptyl-9H-fluoren-2-ylethynyl)-phenyl]-9H-carbazole (**16**)

Compound **14** (866 mg, 1 mmol), 3-methyl-1-butyne-3-ol (168 mg, 2 mmol), cuprous iodide (10 mg, 0.05 mmol), Pd(PPh₃)₂Cl₂ (3.5 mg, 0.005 mmol), triphenylphosphine (5 mg,

0.02 mmol), and dry triethylamine (150 mL) were placed in a 250 mL round bottle flask equipped with a Teflon covered magnetic stir bar. After the solution was purged with nitrogen for half an hour, it was refluxed under nitrogen for 12 h. The reaction mixture was filtered and the filtrate was evaporated under reduced pressure. The residue was purified through column chromatography (silica gel, hexane/dichloromethane/ethyl acetate as eluent) to afford **15**. Then **15**, potassium hydroxide (2.0 g, 35 mmol), and 2-propanol (150 mL) were placed in 250 mL round bottle flask equipped with a Teflon covered magnetic stir bar. After the resulting mixture was refluxed for 3 h under N₂, it was cooled to room temperature. Solution was poured into water and extracted by CH₂Cl₂. After washing by water and drying by MgSO₄, the solvent was then removed, and the residue was purified through column chromatography (silica gel, hexane/dichloromethane as eluent). Yield 62%. ¹H NMR δ CDCl₃: 0.61–0.62 (m, 4H), 0.81(t, 6H, *J*=7.5 Hz), 1.06 (br, 12H), 1.17–1.21 (m, 4H), 1.47 (s, 18H), 1.96–1.99 (m, 4H), 3.15 (s, 1H), 7.39 (d, 2H, *J*=9.0 Hz), 7.47–7.50 (m, 4H), 7.54–7.58 (m, 4H), 7.65 (d, 1H, *J*=7.5 Hz), 7.68 (d, 1H, *J*=8.0 Hz), 7.76 (d, 2H, *J*=8.5 Hz), 8.14 (d, 2H, *J*=1.0 Hz) ppm; ¹³C NMR δ CDCl₃: 14.29, 22.83, 23.99, 29.22, 30.23, 32.05, 32.25, 35.01, 40.55, 55.52, 77.57, 84.85, 89.48, 91.38, 109.47, 116.56, 120.19, 120.36, 121.02, 121.97, 122.20, 123.86, 123.98, 126.29, 126.67, 128.82, 131.07, 131.54, 133.23, 138.36, 139.17, 140.93, 141.40, 143.47, 151.32, 151.45 ppm; MS (MALDI-TOF) (*m/z*): 763.9 (M⁺). Anal. Calcd for C₅₇H₆₅N: C, 89.59; H, 8.57; N, 1.83. Found: C, 89.60; H, 8.55; N, 1.80.

4.5. 3,6-Di-*tert*-butyl-9-[4-[7-(9,9-diheptyl-7-iodo-9H-fluoren-2-ylethynyl)-9,9-diheptyl-9H-fluoren-2-ylethynyl]-phenyl]-9H-carbazole (**17**)

The procedure is analogous to that described for **14**. Yield 58%. ¹H NMR δ CDCl₃: 0.62 (br, 8H), 0.80–0.83 (m, 12H), 1.06–1.07 (m, 24H), 1.17–1.21 (m, 8H), 1.47 (s, 18H), 1.93–1.97 (m, 4H), 2.00–2.03 (m, 4H), 7.39–7.45 (m, 3H), 7.48 (dd, 2H, *J*₁=8.5 Hz, *J*₂=1.5 Hz), 7.53–7.59 (m, 8H), 7.65–7.71 (m, 5H), 7.77 (d, 2H, *J*=8.5 Hz), 8.15 (d, 2H, *J*=1.5 Hz) ppm; ¹³C NMR δ CDCl₃: 22.84, 23.94, 24.02, 29.20, 29.28, 30.19, 30.28, 32.05, 32.09, 32.25, 35.00, 40.54, 40.70, 55.54, 55.67, 89.47, 90.97, 91.03, 91.43, 93.37, 109.46, 116.55, 120.09, 120.27, 120.31, 121.92, 121.96, 122.02, 122.27, 122.43, 123.98, 126.13, 126.20, 126.52, 126.66, 131.01, 131.07, 132.34, 133.22, 136.25, 138.32, 139.14, 140.35, 140.61, 140.92, 141.13, 143.44, 150.49, 151.41, 153.64 ppm; MS (MALDI-TOF) (*m/z*): 1250.1 (M⁺). Anal. Calcd for C₈₄H₁₀₀IN: C, 80.67; H, 8.06; I, 10.15; N, 1.12. Found: C, 80.70; H, 8.10; N, 1.10.

4.6. 2-((9,9-Diheptyl-7-iodo-9H-fluoren-2-yl)ethynyl)-7-((9,9-diheptyl-9H-fluoren-2-yl)ethynyl)-9,9-diheptyl-9H-fluorene (**19**)

The procedure is analogous to that described for **17**. Yield 77%. ¹H NMR δ CDCl₃: 0.61 (br, 12H), 0.78–0.83 (m, 18H),

1.06 (br, 36H), 1.17–1.18 (m, 12H), 1.94–2.02 (m, 12H), 7.33–7.34 (m, 3H), 7.44 (d, 1H, $J=8.0$ Hz), 7.52–7.58 (m, 8H), 7.66–7.71 (m, 7H) ppm; ^{13}C NMR δ CDCl_3 : 14.29, 14.31, 22.83, 23.92, 23.98, 29.20, 29.24, 29.28, 30.18, 30.26, 32.04, 32.08, 40.54, 40.69, 40.75, 55.38, 55.50, 55.65, 90.60, 90.91, 91.05, 91.18, 93.38, 119.91, 120.08, 120.24, 121.63, 121.91, 122.12, 122.35, 122.41, 123.10, 126.10, 126.15, 127.11, 127.76, 130.81, 130.96, 132.30, 136.23, 140.33, 140.58, 140.65, 140.83, 141.00, 141.69, 150.45, 151.02, 151.24, 151.31, 151.34, 153.62 ppm; MS (MALDI-TOF) (m/z): 1256.9 (M^+). Anal. Calcd for $\text{C}_{85}\text{H}_{109}\text{I}$: C, 81.17; H, 8.74; I, 10.09. Found: C, 81.19; H, 8.71.

4.7. General procedure for the synthesis of the compounds (**Cz2F**, **Cz2F3**, **Cz2F5**, **CzF6**, **Cz3F4**, **CzF9**, and **Cz4F6**)

These compounds were obtained following an essentially similar procedure. An illustrative example is provided for **Cz2F**: 3,6-di-*tert*-butyl-9-(4-iodophenyl)-9H-carbazole (**2**) (962 mg, 2 mmol), 2,7-diethynyl-9,9-diheptyl-9H-fluorene (**18**) (410 mg, 1 mmol), cuprous iodide (10 mg, 0.05 mmol), dichlorobis(triphenylphosphine)palladium (II) (3.5 mg, 0.005 mmol), triphenylphosphine (5 mg, 0.02 mmol), and dry triethylamine (100 mL) were placed in a 150 mL round bottle flask equipped with a Teflon covered magnetic stir bar. After the solution was purged with nitrogen for half an hour, it was refluxed under nitrogen for 4 h. The reaction mixture was filtered and the filtrate was evaporated under reduced pressure. The residue was purified through column chromatography (silica gel, hexane/dichloromethane as eluent) to get **Cz2F** (960 mg, 86% yield).

4.7.1. 9,9'-(4,4'-(9,9-Diheptyl-9H-fluorene-2,7-diyl)bis(ethyne-2,1-diyl)bis(4,1-phenylene))bis(3,6-di-*tert*-butyl-9H-carbazole) (**Cz2F**)

Yield 86%. ^1H NMR δ CDCl_3 : 0.67 (br, 4H), 0.82 (t, 6H, $J=7.5$ Hz), 1.10 (br, 12H), 1.18–1.22 (m, 4H), 1.47 (s, 36H), 2.01–2.05 (m, 4H), 7.40 (d, 4H, $J=8$ Hz), 7.48 (dd, 4H, $J_1=8.5$ Hz, $J_2=2$ Hz), 7.57–7.59 (m, 8H), 7.71 (d, 2H, $J=7.5$ Hz), 7.78 (d, 4H, $J=8.5$ Hz), 8.14 (d, 4H, $J=1.5$ Hz) ppm; ^{13}C NMR δ CDCl_3 : 14.30, 22.85, 24.05, 29.26, 30.28, 32.08, 32.26, 35.02, 40.65, 55.58, 89.50, 91.44, 109.48, 116.56, 120.33, 122.01, 122.12, 123.87, 123.99, 126.32, 126.70, 131.10, 133.25, 138.38, 139.19, 141.10, 143.48, 151.48 ppm; MS (MALDI-TOF) (m/z): 1117.7 (M^+). Anal. Calcd for $\text{C}_{83}\text{H}_{92}\text{N}_2$: C, 89.20; H, 8.30; N, 2.51. Found: C, 89.19; H, 8.41; N, 2.50.

4.7.2. 9,9'-(4,4'-(7,7'-(9,9-Diheptyl-9H-fluorene-2,7-diyl)bis(ethyne-2,1-diyl)bis(9,9-diheptyl-9H-fluorene-7,2-diyl)bis(ethyne-2,1-diyl)bis(4,1-phenylene))bis(3,6-di-*tert*-butyl-9H-carbazole) (**Cz2F3**)

Yield 78%. ^1H NMR δ CDCl_3 : 0.65 (br, 12H), 0.82 (t, 18H, $J=7.5$ Hz), 1.08 (br, 36H), 1.18–1.21 (m, 12H), 1.47 (s, 36H), 2.02 (br, 12H), 7.40 (d, 4H, $J=9.0$ Hz), 7.48 (dd, 4H, $J_1=8.5$ Hz, $J_2=2.0$ Hz), 7.57–7.59 (m, 16H), 7.69–7.71 (m, 6H), 7.77 (d, 4H, $J=8.0$ Hz), 8.15 (d, 4H, $J=1.0$ Hz) ppm;

^{13}C NMR δ CDCl_3 : 14.29, 22.85, 24.04, 29.28, 30.29, 32.09, 32.26, 35.01, 40.71, 55.57, 89.48, 91.08, 91.12, 91.47, 109.47, 116.57, 120.27, 122.01, 122.04, 122.29, 122.35, 123.86, 123.99, 126.23, 126.27, 126.68, 131.03, 131.09, 133.23, 138.35, 139.17, 140.93, 140.99, 141.16, 143.47, 151.43 ppm; MS (MALDI-TOF) (m/z): 1886.3 (M^+). Anal. Calcd for $\text{C}_{141}\text{H}_{164}\text{N}_2$: C, 89.75; H, 8.76; N, 1.48. Found: C, 89.75; H, 8.75; N, 1.47.

4.7.3. 9,9'-(4,4'-(7,7'-(9,9-Diheptyl-9H-fluorene-2,7-diyl)bis(ethyne-2,1-diyl)bis(9,9-diheptyl-9H-fluorene-7,2-diyl)bis(ethyne-2,1-diyl)bis(9,9-diheptyl-9H-fluorene-7,2-diyl)bis(ethyne-2,1-diyl)bis(4,1-phenylene))bis(3,6-di-*tert*-butyl-9H-carbazole) (**Cz2F5**)

Yield 72 %. ^1H NMR δ CDCl_3 : 0.64 (br, 20H), 0.80–0.83 (m, 30H), 1.08 (br, 60H), 1.18–1.20 (m, 20H), 1.47 (s, 36H), 2.02 (br, 20H), 7.40 (d, 4H, $J=8.5$ Hz), 7.49 (dd, 4H, $J_1=8.5$ Hz, $J_2=2.0$ Hz), 7.56–7.59 (m, 24H), 7.70–7.72 (m, 10H), 7.78 (d, 4H, $J=8.5$ Hz), 8.15 (d, 4H, $J=1.5$ Hz) ppm; ^{13}C NMR δ CDCl_3 : 14.29, 22.84, 24.01, 29.29, 30.28, 32.08, 32.24, 35.00, 40.69, 40.76, 55.53, 75.90, 85.95, 89.45, 91.07, 91.43, 116.54, 120.27, 120.30, 121.95, 121.99, 122.23, 122.29, 123.81, 123.97, 126.17, 126.65, 131.01, 131.06, 133.22, 138.30, 139.12, 140.90, 140.96, 141.13, 143.43, 151.36, 151.40 ppm; MS (MALDI-TOF) (m/z): 2656.3 (M^+). Anal. Calcd for $\text{C}_{199}\text{H}_{236}\text{N}_2$: C, 89.99; H, 8.96; N, 1.05. Found: C, 90.00; H, 9.00; N, 0.99.

4.7.4. 3,6-Bis((7-((9,9-diheptyl-9H-fluorene-2-yl)ethynyl)-9,9-diheptyl-9H-fluorene-2-yl)ethynyl)-9,9-diheptyl-9H-fluorene-2-yl)ethynyl)-9-*p*-tolyl-9H-carbazole (**CzF6**)

Yield 69%. ^1H NMR δ CDCl_3 : 0.63–0.64 (m, 24H), 0.78–0.83 (m, 36H), 1.05–1.08 (m, 72H), 1.15–1.20 (m, 24H), 1.98–2.03 (m, 24H), 2.51 (s, 3H), 7.33–7.37 (m, 8H), 7.45 (d, 4H, $J=2.5$ Hz), 7.55–7.61 (m, 20H), 7.65 (dd, 2H, $J_1=8.0$ Hz, $J_2=1.5$ Hz), 7.69–7.71 (m, 12H), 8.38 (d, 2H, $J=1.0$ Hz) ppm; ^{13}C NMR δ CDCl_3 : 14.28, 21.54, 22.82, 22.85, 24.02, 29.24, 29.29, 30.28, 30.30, 32.06, 32.09, 40.69, 40.76, 55.41, 55.54, 89.39, 90.64, 91.02, 91.11, 91.13, 91.18, 110.44, 115.21, 119.91, 120.24, 121.64, 122.12, 122.26, 122.37, 122.68, 123.13, 123.19, 124.28, 126.13, 126.19, 127.13, 127.17, 127.76, 130.22, 130.84, 130.92, 130.98, 134.42, 138.38, 140.67, 140.70, 140.88, 140.99, 141.09, 141.36, 141.71, 151.05, 151.28, 151.38 ppm; MS (MALDI-TOF) (m/z): 2564.5 (M^+). Anal. Calcd for $\text{C}_{193}\text{H}_{231}\text{N}$: C, 90.38; H, 9.08; N, 0.55. Found: C, 90.35; H, 9.08; N, 0.65.

4.7.5. 9,9'-(4,4'-(7,7'-(9-*p*-Tolyl-9H-carbazole-3,6-diyl)bis(ethyne-2,1-diyl)bis(9,9-diheptyl-9H-fluorene-7,2-diyl)bis(ethyne-2,1-diyl)bis(9,9-diheptyl-9H-fluorene-7,2-diyl)bis(ethyne-2,1-diyl)bis(4,1-phenylene))bis(3,6-di-*tert*-butyl-9H-carbazole) (**Cz3F4**)

Yield 65%. ^1H NMR δ CDCl_3 : 0.65 (br, 16H), 0.82 (t, 24H, $J=7.5$ Hz), 1.08 (br, 48H), 1.18–1.22 (m, 16H), 1.47 (s, 36H), 2.02–2.04 (m, 16H), 2.52 (s, 3H), 7.36–7.41 (m, 6H), 7.45–

7.50 (m, 8H), 7.56–7.60 (m, 20H), 7.65 (dd, 2H, $J_1=8.5$ Hz, $J_2=2.0$ Hz), 7.71 (d, 8H, $J=7.5$ Hz), 7.78 (d, 4H, $J=8.5$ Hz), 8.14 (d, 4H, $J=1.5$ Hz), 8.38 (s, 2H) ppm; ^{13}C NMR δ CDCl_3 : 14.30, 21.54, 22.85, 24.03, 29.28, 29.30, 30.29, 30.32, 32.10, 32.25, 35.01, 40.70, 40.77, 55.54, 55.55, 89.39, 89.45, 90.98, 91.14, 91.46, 109.46, 110.45, 115.20, 116.55, 120.22, 120.25, 120.28, 120.31, 121.99, 122.11, 122.37, 122.69, 123.19, 123.84, 123.98, 124.29, 126.11, 126.19, 126.22, 126.26, 126.67, 127.17, 130.23, 130.92, 131.02, 131.08, 133.23, 134.42, 138.32, 138.39, 139.15, 140.66, 140.89, 141.11, 141.16, 141.36, 143.45, 151.38, 151.42 ppm; MS (MALDI-TPF) (m/z): 2549.4 (M^+). Anal. Calcd for $\text{C}_{191}\text{H}_{213}\text{N}_3$: C, 89.94; H, 8.42; N, 1.65. Found: C, 89.98; H, 8.39; N, 1.45.

4.7.6. 3,6-Bis((7-((9,9-diheptyl-9H-fluoren-2-yl)ethynyl)-9,9-diheptyl-9H-fluoren-2-yl)ethynyl)-9,9-diheptyl-9H-fluoren-2-yl)ethynyl)-9,9-diheptyl-9H-fluoren-2-yl)ethynyl)-9,9-diheptyl-9H-fluoren-2-yl)ethynyl)phenyl)-9H-carbazole (CzF9)

Yield 58%. ^1H NMR δ CDCl_3 : 0.65 (br, 36H), 0.80–0.85 (m, 54H), 1.07–1.10 (m, 108H), 1.17–1.22 (m, 36H), 1.98–2.04 (m, 36H), 7.33–7.37 (m, 10H), 7.47 (d, 2H, $J=8.0$ Hz), 7.57–7.63 (m, 30H), 7.69–7.74 (m, 21H), 7.86 (d, 2H, $J=8.5$ Hz), 8.42 (s, 2H) ppm; ^{13}C NMR δ CDCl_3 : 14.27, 22.80, 22.84, 23.97, 29.22, 29.28, 30.26, 30.27, 32.04, 32.08, 40.67, 40.75, 55.37, 55.50, 90.60, 90.91, 90.98, 91.01, 91.06, 91.15, 110.38, 115.69, 119.90, 120.22, 121.62, 122.12, 122.18, 122.31, 122.52, 123.10, 126.10, 126.14, 126.19, 127.10, 127.75, 130.80, 130.90, 130.96, 133.45, 140.65, 140.72, 140.80, 140.85, 140.96, 141.01, 141.67, 151.00, 151.23, 151.34 ppm; MS (MALDI-TOF) (m/z): 3704.5 (M^+). Anal. Calcd for $\text{C}_{279}\text{H}_{337}\text{N}$: C, 90.45; H, 9.17; N, 0.38. Found: C, 90.44; H, 9.13; N, 0.42.

4.7.7. 9,9'-(4,4'-(7,7'-(7,7'-(9,9-diheptyl-9H-fluoren-2-yl)ethynyl)-9,9-diheptyl-9H-fluoren-2-yl)ethynyl)phenyl)ethynyl)-9,9-diheptyl-9H-fluoren-2-yl)ethynyl)phenyl)-9H-carbazole-3,6-diyl)bis(ethyne-2,1-diyl)bis(9,9-diheptyl-9H-fluorene-7,2-diyl)bis(ethyne-2,1-diyl)bis(9,9-diheptyl-9H-fluorene-7,2-diyl)bis(ethyne-2,1-diyl)bis(4,1-phenylene))bis(3,6-di-tert-butyl-9H-carbazole) (Cz4F6)

Yield 50%. ^1H NMR δ CDCl_3 : 0.65 (br, 24H), 0.81–0.84 (m, 36H), 1.09 (m, 72H), 1.18–1.21 (m, 24H), 2.04 (br, 24H), 7.41 (d, 6H, $J=8.5$ Hz), 7.45 (d, 2H, $J=8.5$ Hz), 7.49 (dd, 6H, $J_1=8.5$ Hz, $J_2=1.5$ Hz), 7.56–7.61 (m, 34H), 7.68–7.72 (m, 12H), 7.78 (d, 6H, $J=8.0$ Hz), 7.85 (d, 2H, $J=8.5$ Hz), 8.15 (s, 6H), 8.40 (s, 2H) ppm; ^{13}C NMR δ CDCl_3 : 14.31, 22.84, 24.01, 29.27, 30.28, 30.30, 32.08, 32.23, 34.98, 40.69, 46.42, 55.52, 89.43, 90.91, 90.99, 91.12, 91.41, 109.44, 115.69, 116.54, 120.27, 120.30, 121.92, 121.96, 122.10, 122.30, 122.54, 123.47, 123.79, 123.97, 126.09, 126.19, 126.22, 126.62, 130.90, 130.99, 131.05, 133.20, 138.28, 139.09, 140.72, 140.81, 140.87, 140.91, 141.04, 141.12, 141.33, 143.42, 151.37 ppm; MS

(MALDI-TOF) (m/z): 3683.2 (M^+). Anal. Calcd for $\text{C}_{276}\text{H}_{310}\text{N}_4$: C, 90.00; H, 8.48; N, 1.52. Found: C, 89.97; H, 8.50; N, 1.72.

4.8. Fabrication and characterization of OLEDs

All the devices were fabricated on bare ITO substrates that were cleaned by detergent, deionized water, acetone, and ethanol. Poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS) was spin-coated on ITO glass, and was baked under 100 °C for 2 h. Compounds **Cz2F**, **Cz2F3**, **Cz2F5**, **CzF6**, **Cz3F4**, **CzF9**, and **Cz4F6** were spin-coated onto PEDOT–PSS layer from their toluene solutions. Films of 1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene (TPBI) and Al cathodes were formed by vacuum deposition under a pressure of 3×10^{-4} Pa. The deposition rate for TPBI and Al cathode layers was 1 and 5 Å s $^{-1}$, respectively. The thickness of the thin films was monitored by a quartz crystal oscillator placed near the substrates and was calibrated ex situ by an Ambios Technology XP-2 surface profilometer. EL spectra were recorded with a Photo Research PR-650 spectrophotometer. Current–voltage characteristics were measured with a Hewlett-Packard 4140B semiconductor parameter analyzer. A Newport 2835-C multifunction optical meter was used to measure the luminescence output.

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Supplementary data

Supplementary data and representative spectra associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.12.059.

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