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Synthesis and photophysical properties of tetrafluorophenyl-modified carbazole oligomers

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ABSTRACT

A series of tetrafluorophenyl-modified oligo(3,6-carbazole ethynylene)s (**CfCzCf**, **CfCz2Cf**, **CfCz3Cf**, (**CfCz**)**2Cf**, and **Cf2CzCf2**) were synthesized by a Pd/Cu-catalyzed Sonogashira coupling reaction and fully characterized. Their photophysical and electronic properties as well as their thermal stabilities were investigated. It is noteworthy that these tetrafluorophenyl modified compounds showed relative thermal stabilities and low-lying HOMO levels ranging from −5.54 to −5.60 eV, which might be the promising candidates for hole-transporting materials in OLEDs.

1. Introduction

Over the past 10 years, conjugated oligomers have been subjected to important investigations in both academic and industrial laboratories[1] due to their promising applications, such as organic light-emitting diodes (OLEDs),[2] solar cells,[3] field-effect transistors (FETs),[4] and models[5] for understanding the structure–property relationships of their analogous polydisperse polymers. Development of synthetic methodology has made it possible to synthesize a variety of soluble monodisperse oligomers, which are designed to be tunable in color and/or charge injection properties through introduction of functional groups, as well as conjugated length.[6] Compared with polydispersity, the monodisperse oligomers exhibit advantages of structural uniformity, convenient purification, and easy modification.

Because of the specific optical and electrochemical properties, carbazole and its derivatives are well-known and have been widely used as functional building blocks in the fabrication of the organic photoconductors, nonlinear optical materials, and photorefractive materials.[7] Carbazole can be easily modified at its 3-, 6-, or 9-position and covalently linked to other molecular moieties.[8] It is also recognized that the introduction of carbozoles into the core structures of organic compounds can greatly improve compounds' thermal stability or glass-state durability.[9] Recently, a series of carbazole derivatives with ethynylene linkages have been fully reported,[10] as well as dibenzosilole.[11] In our previous studies, we reported a series of oligocarbazoles with ethynylene linkage, which presented good hole-transporting properties.[10] In order to obtain better understanding of oligocarbazoles and to extend application in its utility, here we wish to report a new set of oligocarbazoles, which were modified with 9-tetrafluorophenyl groups. These oligomers could be used as models to understand fluorescent structure–property relationship of their corresponding polymers and be potentially applied as hole transporting.

2. Results and discussion

2.1. Synthesis

A Pd/Cu-catalyzed Sonogashira coupling reaction was used to build ethynylene-linked molecules. Detailed experimental conditions for oligomers' formation were similar to the published method. Synthetic approach to necessary intermediates **1**–**11** was outlined in Scheme 1. Compound **1** was synthesized by Ullmann reaction between 3-iodo-9*H*-carbazole[12] and 1,2,3,4,5-pentafluoro-6-iodobenzene.[13] After treatment **1** and trimethylsilylacetylene via Sonogashira coupling and subsequent deprotection, **3** was obtained in 85% yield. Compound **5** was synthesized in a similar procedure with 65% yield and **4** was prepared according to the reported method.[14] Coupling **3** with 3 equiv of **4** in the presence of CuI/Pd$(PPh_3)_2Cl_2$/PPh_3/NEt_3 afforded intermediate (**6**)[13] in 76% yield. Sequentially, **6** was converted to **8** in 78% yield. Similarly, **9** was obtained by coupling **3** and **5** in 81% yield, which was further converted to **11** in 68% yield.

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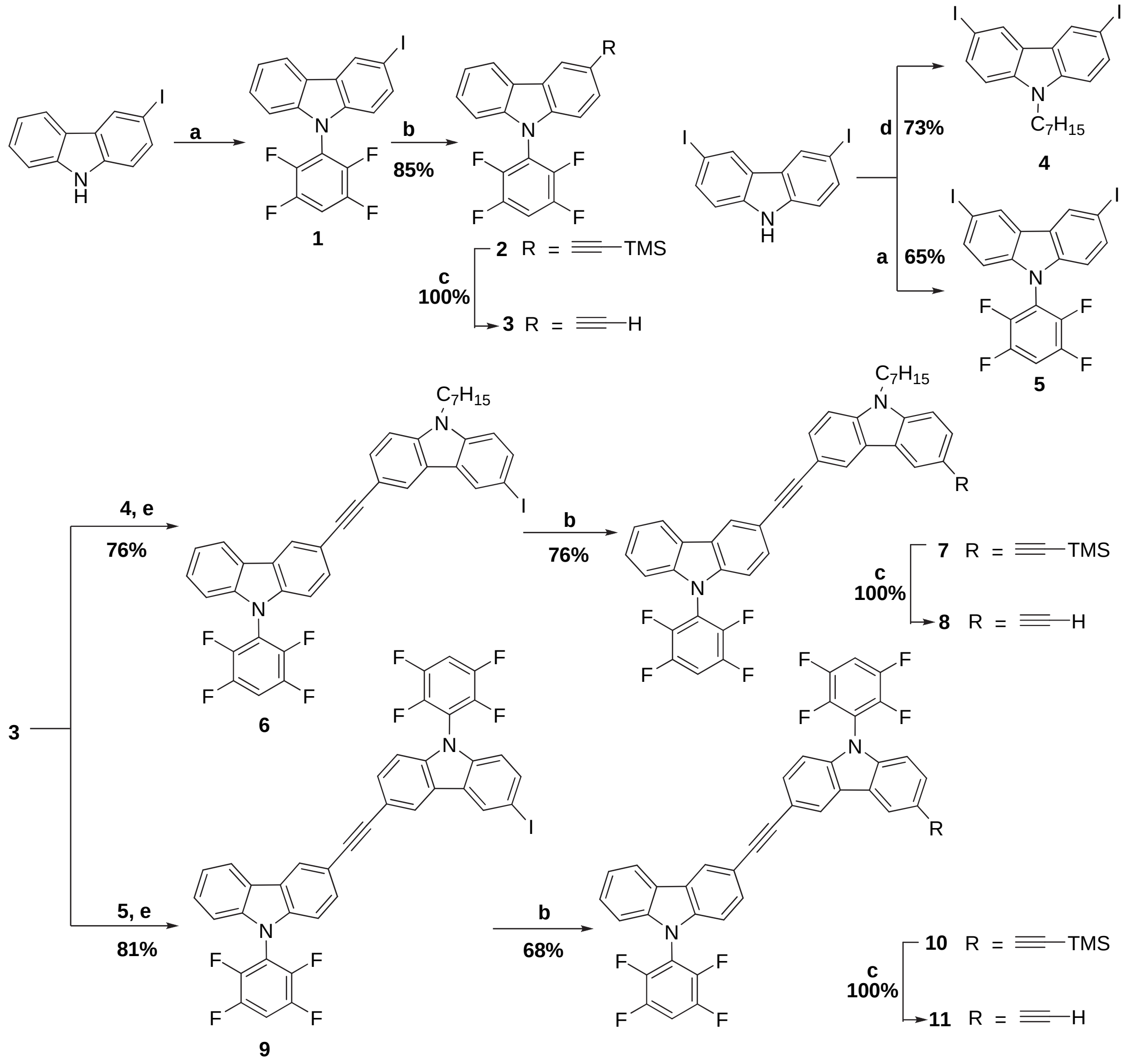


Scheme 1. (a) Iodopentafluorobenzene, Cu(powder), K_2CO_3, 18-crown-6, DMF, N_2, reflux; (b) trimethylsilylacetylene CuI, $Pd(PPh_3)_2Cl_2$, PPh_3, NEt_3, N_2, reflux; (c) K_2CO_3, *n*-Bu_4NF, methanol, THF, N_2, reflux; (d) *n*-$C_7H_{15}Br$, KOH, tetrabutylammonium hydrogen sulfate, acetone, rt; (e) CuI, $Pd(PPh_3)_2Cl_2$, PPh_3, NEt_3, N_2, reflux.

Final construction to target molecules was illustrated in Scheme 2. **CfCzCf** and **CfCz2Cf** were obtained in 53% and 55% yields, respectively. Coupling of **4** with 2 equiv of **8** led to **CfCz3Cf** in 62% yield. Similarly, (**CfCz**)**2Cf** and **Cf2CzCf2** were obtained in 53% and 46% yields, respectively. Due to the presence of the flexible *n*-heptyl substitutes, all of these synthesized oligomers were soluble in common organic solvents, such as dichloromethane (DCM) and tetrahydrofuran (THF). Attempt to obtain pure **Cf5** via coupling of **5** and **11** failed due to the soluble problem.

Structures of the target compounds were characterized by NMR, MALDI-TOF mass spectroscopy, and high resolution mass spectroscopy. Further, these compounds showed good thermal stabilities. The glass transition, melting, and decomposition temperatures of these compounds, determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) under N_2 at a heating rate of 10 °C/min, were shown in Table 1. The decomposition temperatures (T_d, 5% loss of initial weight) of these oligomers **CfCzCf**, **CfCz2Cf**, **CfCz3Cf**, (**CfCz**)**2Cf**, and **Cf2CzCf2** were 551.3 °C, 534.2 °C, 458.5 °C, 317.3 °C, and 497.2 °C, respectively.

2.2. Visualization and simulation

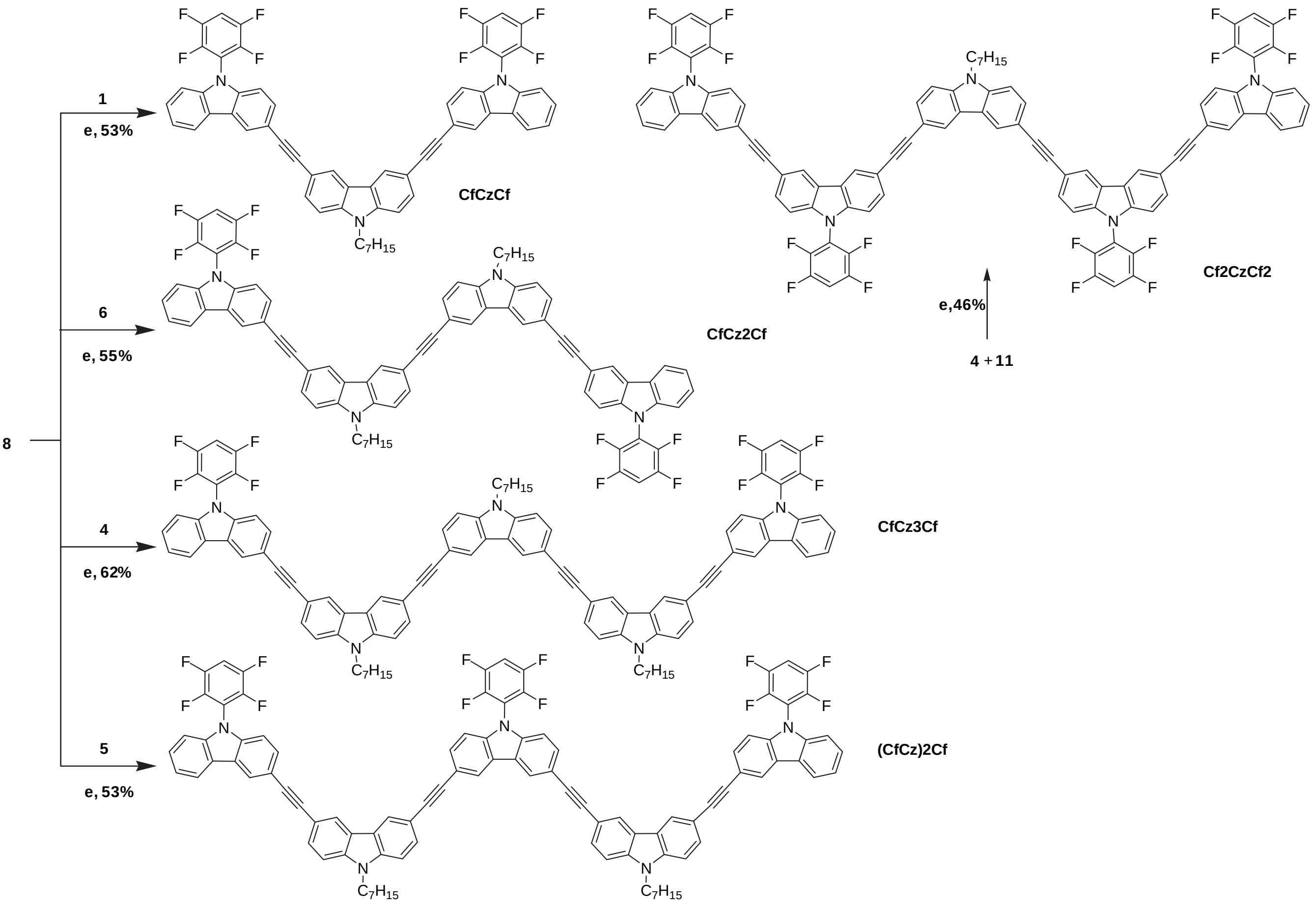
Structures of the synthesized compounds were optimized by Gaussian 03 through PM3 method, as well as the HOMO and LUMO orbitals. Figure 1 illustrated the energy-minimized structure of **Cf2CzCf2** as a representative. Others were listed in Supplementary data. It was noteworthy that each tetrafluorophenyl group was perpendicular to its carbazole matrix, which inferred that the steric hindrance could hamper the intermolecular packing of oligocarbazoles and thereafter hinder its aggregation and/or excimer formation. Similar situations were observed in the cases of other four compounds.

Figure 2 illustrated the HOMO and LUMO orbitals of **Cf2CzCf2**. Electron cloud at its ground state was mostly located at the central carbazole, while the electron cloud at its excited state was extremely centered at one of tetrafluorophenyl groups. Similar distribution of electron cloud of HOMOs and LUMOs could be observed in other four compounds (see Supplementary data). We could infer that the electron be promoted from carbazole to tetrafluorophenyl group when the molecule was excited.

2.3. Photophysical properties

The UV–vis absorption and photoluminescence of these compounds in dilute solutions (10^{-5} M) as well as their emissions in solid states were presented in Table 1.

Absorption spectra of these oligomers were complex with multiple overlapping broad bands. Figure 3a and b illustrated their



Scheme 2. (e) CuI, $Pd(PPh_3)_2Cl_2$, PPh_3, NEt_3, N_2, reflux.

Table 1
Optical and electrochemical properties of the oligomers

Compound	Abs (nm)[a]	Em. (nm)		Φ[b]	E_g[c] (eV)	E_{onset}^{ox} [d] (V)	HOMO/LUMO[e] (eV)	$T_g/T_m/T_d$[f] (°C)
	THF($\varepsilon \times 10^5$)	THF	Powder					
CfCzCf	355(0.50)	382, 400	431	0.25	3.25	1.17	−5.57/−2.32	110.4/—/551.3
CfCz2Cf	360(0.31)	382, 402	454	0.32	3.21	1.16	−5.56/−2.35	133.1/—/534.2
CfCz3Cf	363(0.77)	382, 403	441–465	0.38	3.16	1.14	−5.54/−2.38	131.1/—/458.5
(**CfCz**)**2Cf**	356(1.51)	382, 400	464	0.28	3.14	1.17	−5.57/−2.43	223.0/266.5/317.3
Cf2CzCf2	339(1.71)	380, 400	409	0.31	3.23	1.20	−5.60/−2.37	—/220.0/497.2

[a] First absorption peak;
[b] Measured in THF solutions using DPA as a standard.
[c] Determined from UV–vis absorption spectra.
[d] E_{onset}^{ox}=onset oxidation potential; Potentials vs Ag/AgCl, working electrode Pt, 0.1 M Bu_4NPF_6–THF, scan rate 100 mV/s.
[e] HOMO $= E_{onset}^{ox} + 4.4$eV; LUMO=HOMO$-E_g$ eV.
[f] Measured by DSC and TGA analysis in N_2 at heating rate of 10 °C/min.

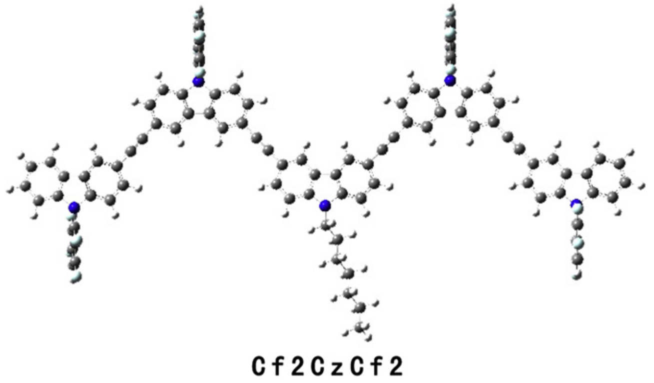


Figure 1. Energy-minimized **Cf2CzCf2** calculated by Gaussian 03 through PM3 method.

UV–vis absorption spectra with the same concentration (10^{-5} M) in THF. **CfCzCf**, **CfCz2Cf**, and **CfCz3Cf** (Fig. 3a) exhibited similar absorption patterns but different maximum absorption wavelengths, varied from 355 nm to 363 nm, increasing with the elongation of the conjugated length of these molecules.[14] With the same conjugation lengths, **CfCz3Cf**, (**CfCz**)**2Cf**, and **Cf2CzCf2** (Fig. 3b) presented the decreasing maximum absorption wavelengths as the number of tetrafluorophenyl group increased. In addition, the more tetrafluorophenyl groups attached the higher molar absorptivity (Table 1). The $\pi-\pi^*$ energy gaps (E_g, Table 1) of these oligomers were calculated from the UV–vis absorption threshold, which ranged from 3.14 eV to 3.25 eV. It is noteworthy that all of these UV–vis spectra exhibited the broad absorption peaks ranging from 230 nm to 380 nm, which indicated that these compounds could absorb light and be excited within a wide range.

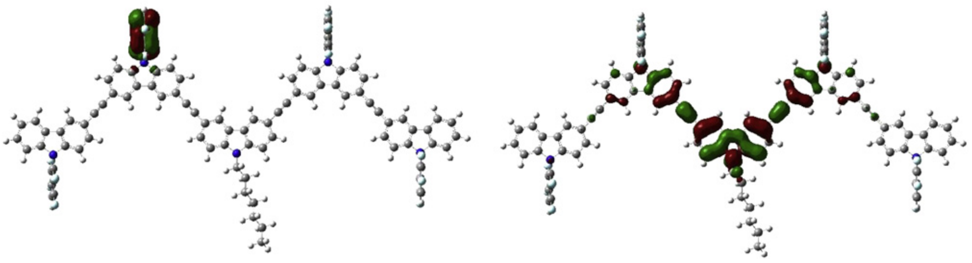


Figure 2. HOMO (left) and LUMO (right) orbitals of **Cf2CzCf2**, calculated by Gaussian 03 through PM3 method.

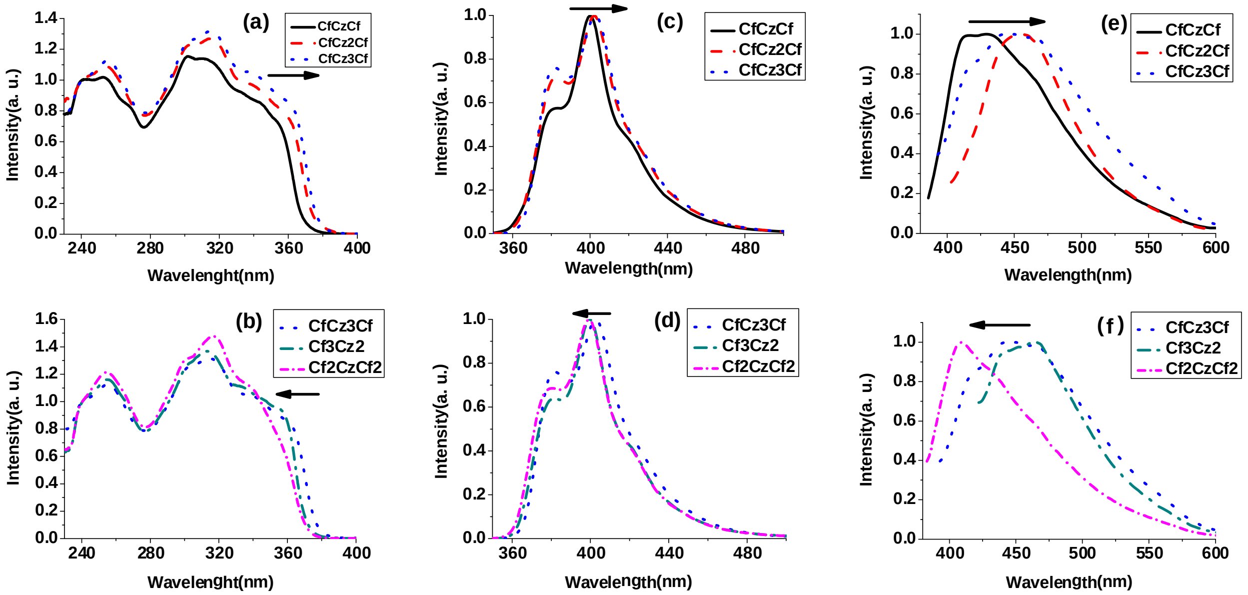


Figure 3. UV–vis absorption spectra (a and b), PL emission spectra in THF (c and d), and solid state (e and f).

Figure 3c and d presented the photoluminescence (PL) emission spectra of these oligomers excited at about 360 nm. These compounds showed blue PL emissions with the maximum emission peaks at about 400 nm and shoulder peaks at 382 nm in THF solutions. Stokes shifts were 27 nm, 22 nm, and 19 nm for **CfCzCf**, **CfCz2Cf**, and **CfCz3Cf**, respectively. The more tetrafluorophenyl groups attached the larger Stokes shift. As for **Cf2CzCf2**, Stokes shift was determined up to 41 nm in THF, which indicated that the conformational variation between the twisty ground state and planar excited state was the largest.[15] PL quantum yield was measured in the range of 0.25–0.38 in degassed THF solutions using 9,10-diphenylanthracene (DPA, Φ=0.95)[16] as a standard. The relatively low quantum yield might be due to the decentralization of excitons caused by the strong electron withdrawing moiety.[17] Figure 3e and f illustrated the PL emission spectra of their solid states. It was obvious that the emission in solid state was red-shifted greatly except **Cf2CzCf2**. Moreover, the full width at half emission maximum at solid state was much wider than that in solutions.

Solvent effect was investigated in solutions of cyclohexane, THF, and DCM. The representative spectrum of **Cf2CzCf2** is shown in Figure 4. The emission wavelength was red-shifted slightly with the increment of solvent polarity. The emission of **Cf2CzCf2** at solid state was red-shifted 9 nm with respect to that in solutions (Table 1). It inferred that the conformation of **Cf2CzCf2** at solid state was similar to that in THF. Four 2,3,5,6-tetrafluorophenyls not only restrained delocalization of the lone electron pair of the nitrogen atoms[18] but also decreased the intermolecular interaction in solid state due to their strong steric hindrance.

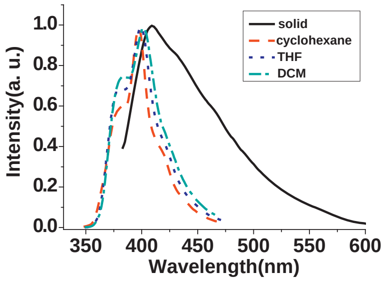


Figure 4. PL emission spectra of **Cf2CzCf2** in cyclohexane, THF, DCM, and solid state.

In order to understand the broaden emission spectrum in film, emission of **Cf2CzCf2** in THF with different concentrations was investigated (Fig. 5). In diluted solution (10^{-7} M) the emission spectra have two peaks: shoulder peak at 382 nm and major peak at 400 nm. As the concentration of **Cf2CzCf2** increased, the

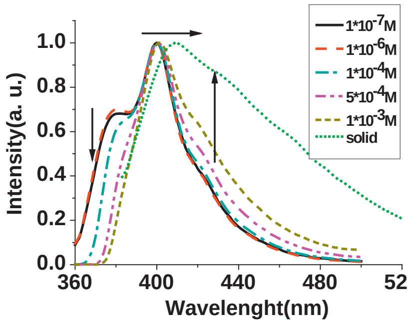


Figure 5. PL emission spectra of **Cf2CzCf2** in THF with different concentrations.

emission peak was slightly red-shifted while the relative intensity of the shoulder peak decreased. Finally, this shoulder peak disappeared when the concentration was up to 1×10^{-3} M. It indicated that **Cf2CzCf2** displayed a highly structured emission in diluted solution. While at higher concentrations, restricted rotation of tetrafluorophenyl made the formation of intermolecular $\pi-\pi$ stacking of backbone possible, and the profile of the emission became structureless and broadish.

2.4. Cyclic voltammetric studies

The electronic properties of these compounds were investigated by cyclic voltammetry at room temperature and the results were listed in the Table 1. Figure 6 shows cyclic voltammograms (CVs) of these compounds. All these oligomers displayed an irreversible reduction peak, which might be due to the nature of the electron withdrawing of tetrafluorophenyl groups, as well as an irreversible oxidation peak, which might be attributed to the nature of the electron donating of carbazole segment. According to CVs and UV–vis absorptions, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels were estimated (Table 1). The HOMO energy levels ranged from −5.54 eV to −5.60 eV with a steady increment as the number of tetrafluorophenyl units rose up. Furthermore, the HOMO and LUMO energy levels of these oligomers were comparable to those of widely used hole-transporting materials (NPB: HOMO, −5.2 eV; LUMO, −2.2 eV),[19] and therefore, these compounds might be used for hole-transporting materials in OLEDs.

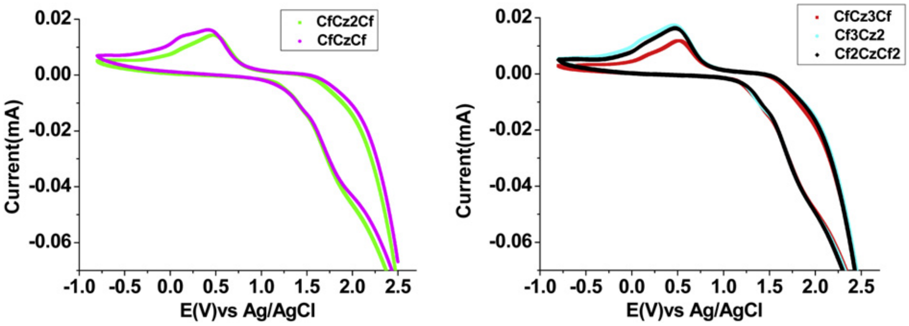


Figure 6. Cyclic voltammograms of oligomers (0.25 mM) in 0.1 M Bu_4NPF_6–CH_2Cl_2, scan rate 100 mV/s.

3. Conclusions

In summary, we had successfully synthesized and fully characterized a series of novel compounds with well-controlled, alternative alkyl carbazole and tetrafluorophenyl carbazole structures. It was obvious that the introduction of tetrafluorophenyl moiety influenced the emissions no matter in solutions or in solids. These synthesized compounds might be used as models to study structure–property relationship for their corresponding polymers or applied in optoelectronic devices directly. Further study will be focused on their applications in devices.

4. Experimental

4.1. General

^{1}H and ^{13}C NMR spectra were obtained on a Bruker AVANCE DMX400 spectrometer operating in the FT mode. Five percent w/v solutions in chloroform-*d* were used to obtain NMR spectra. TMS was used as an internal standard. IonSpec HiResMALDI was used to obtain mass spectra. 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. Cyclic voltammetric measurements were performed with CHI660A electrochemical work station, using Pt working electrode, an auxiliary Pt electrode, and an Ag/AgCl reference electrode. The solvents were distilled before used. Commercially available reagents were used without further purification unless otherwise.

4.2. General procedure for the synthesis of compounds 9, CfCzCf, CfCz2Cf, CfCz3Cf, (CfCz)2Cf, and Cf2CzCf2

These compounds were obtained following an essentially similar procedure. An illustrative example is provided for **9**.

Compound **9**: **3** (339 mg, 1 mmol), **5** (1707 mg, 3 mmol), cuprous iodide (10 mg, 0.05 mmol), dichlorobis(triphenylphosphine) palladium(II) (3.5 mg, 0.005 mmol), triphenylphosphine (5 mg, 0.02 mmol), 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 filtration was evaporated under reduced pressure. The residue was purified through column chromatography (silica gel, hexane/methylene chloride as eluent).

*4.2.1. Compound **9***. Yield 82%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, J=1.3 Hz, 1H), 8.39 (s, 1H), 8.32 (s, 1H), 8.18 (d, J=7.6 Hz, 1H), 7.81–7.62 (m, 3H), 7.51 (t, J=7.6 Hz, 1H), 7.43–7.28 (m, 3H), 7.18 (dd, J=16.9, 8.2 Hz, 3H), 6.96 (d, J=8.6 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$) δ 147.93–147.65 (m), 145.32–144.93 (m), 142.47 (d, J_{CF}=16.2 Hz), 140.20, 139.45, 139.34, 139.22, 135.20, 130.66, 130.00, 129.62, 126.96, 125.99, 124.18, 124.02, 123.95, 123.57, 122.84, 121.60, 120.71, 116.99–116.13 (m), 111.93, 110.06, 109.95, 106.34 (q, J_{CF}=23.1 Hz), 89.24, 88.52, 77.35, 77.04, 76.72.

*4.2.2. Compound **CfCzCf***. Yield 53% ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J=11.5 Hz, 4H), 8.15 (d, J=7.7 Hz, 2H), 7.69 (t, J=7.6 Hz, 4H), 7.47 (t, J=7.6 Hz, 2H), 7.40–7.24 (m, 6H), 7.15 (t, J=7.8 Hz, 4H), 4.25 (t, J=6.8 Hz, 2H), 1.92–1.76 (m, 2H), 1.33 (s, 4H), 1.26 (s, 4H), 0.86 (t, J=6.8 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$) δ 147.90–147.78 (m), 145.29–144.95 (m), 142.52 (d, J_{CF}=16.6 Hz), 140.34, 140.23, 139.23, 130.02, 129.65, 126.89, 124.19, 124.04, 123.84, 123.66, 122.56, 121.56, 120.71, 117.08 (t, J_{CF}=13.9 Hz), 116.63, 114.13, 109.90, 109.02, 106.13 (t, J_{CF}=22.6 Hz), 89.49, 88.37, 77.36, 77.04, 76.72, 43.32, 31.72, 29.05, 28.99, 27.24, 22.58, 14.06 ppm; MS (MALDI) (*m*/*z*): 393.3 (M^+). HRMS: calcd for $C_{59}H_{37}F_8N_3$ [M^+] (*m*/*z*) 939.2860, found 939.2854.

*4.2.3. Compound **CfCz2Cf***. Yield 55%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J=10.3 Hz, 6H), 8.14 (d, J=7.7 Hz, 2H), 7.70 (dd, J=13.3, 7.3 Hz, 6H), 7.46 (t, J=7.7 Hz, 2H), 7.39–7.24 (m, 8H), 7.14 (t, J=7.9 Hz, 4H), 4.25 (t, J=7.0 Hz, 4H), 1.92–1.78 (m, 4H), 1.34 (s, 8H), 1.25 (s, 8H), 0.86 (t, J=6.6 Hz, 6H) ppm; ^{13}C NMR (CDCl$_3$) δ 147.94–147.66 (m), 145.70–144.67 (m), 142.50 (d, J_{CF}=15.7 Hz), 140.32, 140.23, 140.21, 139.21, 130.03, 129.66, 129.60, 126.88, 124.18, 124.04, 123.95, 123.83, 123.66, 122.57, 122.54, 121.56, 120.72, 117.07 (t, J_{CF}=14.4 Hz), 116.64, 114.40, 114.05, 109.91, 109.00, 106.13 (t, J_{CF}=22.6 Hz), 89.55, 88.95, 88.35, 77.37, 77.05, 76.74, 43.30, 31.74, 29.06, 29.00, 27.25, 22.60, 14.08. ppm; MS (MALDI) (*m*/*z*): 1226.5 (M$^+$). HRMS: calcd for $C_{80}H_{58}F_8N_4$ [M$^+$] (*m*/*z*) 1226.4534, found 1226.4528.

4.2.4. Compound ***CfCz3Cf****.* Yield 62%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.35 (s, 8H), 8.13 (d, J=7.7 Hz, 2H), 7.69 (dd, J=17.4, 8.7 Hz, 8H), 7.46 (t, J=7.6 Hz, 2H), 7.40–7.25 (m, 10H), 7.14 (t, J=8.3 Hz, 4H), 4.26 (t, J=6.6 Hz, 6H), 1.85 (d, J=6.5 Hz, 6H), 1.34 (s, 12H), 1.25 (s, 12H), 0.86 (t, J=6.1 Hz, 9H) ppm; ^{13}C NMR δ 147.91–147.58 (m), 145.25–144.87 (m), 142.48 (d, J_{CF}=13.1 Hz), 140.30, 140.22, 140.18, 139.18, 129.99, 129.67, 129.58, 126.83, 124.15, 124.03, 123.93, 123.80, 123.64, 122.56, 122.52, 121.52, 120.70, 117.39–116.77 (m), 116.61, 114.41, 114.32, 114.03, 109.87, 108.95, 106.09 (t, J_{CF}=22.9 Hz), 89.51, 88.94, 88.87, 88.32, 43.30, 31.72, 29.04, 28.99, 27.24, 22.57, 14.06 ppm; MS (MALDI) (*m*/*z*): 1513.6 (M$^+$). HRMS: calcd for $C_{101}H_{79}F_8N_5$ [M$^+$] (*m*/*z*) 1513.6208, found 1513.6202.

*4.2.5. Compound (****CfCz****)****2Cf****.* Yield 53%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.38 (d, J=9.3 Hz, 8H), 8.14 (d, J=7.7 Hz, 2H), 7.70 (dd, J=18.3, 10.5 Hz, 8H), 7.47 (t, J=7.6 Hz, 2H), 7.42–7.26 (m, 9H), 7.15 (t, J=8.6 Hz, 6H), 4.30 (t, J=6.8 Hz, 4H), 1.93–1.80 (m, 4H), 1.36 (s, 8H), 1.26 (s, 8H), 0.87 (t, J=6.3 Hz, 6H) ppm; ^{13}C NMR (CDCl$_3$) δ 147.86–147.79 (m), 145.40–144.92 (m), 142.48 (d, J_{CF}=11.2 Hz), 140.37, 140.33, 140.20, 139.56, 139.20, 130.40, 129.99, 129.69, 126.84, 124.16, 124.07, 123.96, 123.81, 123.64, 122.56, 121.52, 120.69, 117.08–117.01 (m), 116.58, 114.13, 114.04, 110.04, 109.88, 109.02, 106.09 (t, J_{CF}=22.6 Hz), 89.69, 89.43, 88.35, 88.19, 43.34, 31.70, 29.03, 28.98, 27.23, 22.56, 14.03 ppm; MS (MALDI) (*m*/*z*): 1563.5 (M$^+$). HRMS: calcd for $C_{100}H_{65}F_{12}N_5$ [M$^+$] (*m*/*z*) 1563.5048, found 1563.5043.

4.2.6. Compound ***Cf2CzCf2****.* Yield 46%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.37 (s, 8H), 8.14 (d, J=7.7 Hz, 2H), 7.77–7.61 (m, 8H), 7.46 (t, J=7.7 Hz, 2H), 7.34 (m, 8H), 7.15 (d, J=7.8 Hz, 8H), 4.28 (s, 2H), 1.87 (s, 2H), 1.35 (s, 4H), 1.26 (s, 4H), 0.87 (t, J=6.1 Hz, 3H) ppm; ^{13}C NMR (CDCl$_3$) δ 147.88–47.76 (m), 145.35–145.08 (m), 142.46 (d, J_{CF}=13.7 Hz), 140.37, 140.20, 139.63, 139.55, 139.32, 130.43, 130.37, 130.03, 129.68, 126.90, 124.17, 124.05, 123.94, 123.80, 123.75, 123.60, 122.56, 121.57, 120.71, 116.93 (d, J_{CF}=32.0 Hz), 116.23, 114.04, 110.07, 109.91, 109.03, 106.25 (q, J_{CF}=22.5 Hz), 89.74, 89.14, 88.72, 88.19, 43.31, 31.72, 29.04, 28.99, 27.24, 22.58, 14.06 ppm; MS (MALDI) (*m*/*z*): 1614.4 (M$^+$). HRMS: calcd for $C_{99}H_{51}F_{16}N_5$ [M$^+$] (*m*/*z*) 1613.3889, found 1613.3883.

4.3. General procedure for the synthesis of the compounds 8 and 11

Both compounds were obtained following an essentially similar procedure. An illustrative example is provided for **8**.

Compound **8**: **6** (729 mg, 1 mmol), trimethylsilylacetylene (196 mg, 2 mmol), cuprous iodide (10 mg, 0.05 mmol), dichlorobis (triphenylphosphine)palladium (II) (3.5 mg, 0.005 mmol), triphenylphosphine (5 mg, 0.02 mmol), 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 filtration was evaporated under reduced pressure. The residue was purified through column chromatography (silica gel, hexane/methylene chloride as eluent) to get **7**. Then **7**, *n*-Bu$_4$NF (287 mg), K_2CO_3 (500 mg), methanol (50 mL), and THF (50 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 solvent was then removed and the crude product was purified by column chromatography (silica gel, hexane/methylene chloride as eluent) to afford **8** (488 mg, in 81% total yield).

4.3.1. Compound ***8****.* ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.37 (d, J=1.1 Hz, 1H), 8.31 (d, J=1.2 Hz, 1H), 8.26 (d, J=1.2 Hz, 1H), 8.16 (d, J=7.6 Hz, 1H), 7.69 (ddd, J=9.9, 8.6, 1.5 Hz, 2H), 7.61 (dd, J=8.5, 1.5 Hz, 1H), 7.52–7.46 (m, 1H), 7.41–7.29 (m, 4H), 7.15 (t, J=8.3 Hz, 2H), 4.28 (t, J=7.2 Hz, 2H), 3.09 (s, 1H), 1.92–1.80 (m, 2H), 1.41–1.30 (m, 4H), 1.25 (m, 4H), 0.86 (t, J=6.9 Hz, 3H) ppm; ^{13}C NMR (CDCl$_3$) δ 148.34–147.35 (m), 145.48–145.43 (m), 142.86–142.21 (m) 140.64, 140.28, 139.24, 130.00, 129.73, 126.87, 124.77, 123.91, 122.39, 121.54, 120.68, 117.45–116.79 (m), 116.54, 114.25, 112.53, 109.89, 108.95, 106.13 (t, J_{CF}=22.6 Hz), 89.32, 88.39, 84.85, 75.36, 43.30, 31.66, 28.95, 27.19, 22.53, 14.00 ppm; MS (MALDI) (*m*/*z*): 626.2 (M$^+$). HRMS: calcd for $C_{41}H_{30}F_4N_2$ [M$^+$] (*m*/*z*) 626.2345, found 626.2340.

4.3.2. Compound ***11****.* Yield 68%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.37 (s, 1H), 8.33 (s, 1H), 8.29 (s, 1H), 8.15 (d, J=7.7 Hz, 1H), 7.68 (ddd, J=8.4, 4.8, 1.4 Hz, 2H), 7.60 (dd, J=8.5, 1.3 Hz, 1H), 7.48 (t, J=7.7 Hz, 1H), 7.41–7.25 (m, 3H), 7.20–7.07 (m, 4H), 3.11 (s, 1H) ppm; ^{13}C NMR (CDCl$_3$) δ 147.94–147.66 (m), 145.45–144.98 (m), 142.45 (t, J_{CF}=12.3 Hz), 140.21, 140.01, 139.63, 139.35, 130.85, 130.54, 130.02, 126.96, 124.84, 124.18, 124.02, 123.97, 123.61, 123.58, 123.56, 121.60, 120.72, 116.97–116.79 (m), 116.14, 115.19, 110.11, 110.05, 109.96, 106.35 (d t, J_{CF}=32.0, 22.6 Hz), 89.22, 88.58, 84.06, 77.35, 77.03, 76.72, 76.28 ppm; MS (MALDI) (*m*/*z*): 676.1 (M$^+$). HRMS: calcd for $C_{40}H_{16}F_8N_2$ [M$^+$] (*m*/*z*) 676.1186, found 676.1180.

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Supplementary data

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