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Synthesis and characterization of novel *N*-carbazole end-capped oligothiophene-fluorenes

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Abstract—A series of novel *N*-carbazole end-capped oligothiophene-fluorenes was synthesized using Ullmann coupling, bromination, and Suzuki coupling reactions. The optical, thermal, and electrochemical properties of these materials can be tuned by varying the conjugation length of the oligothiophene segment. The terminal carbazole and central fluorene moieties of the resulting materials are beneficial for their morphology, conjugation length, and solubility.

π-Conjugated oligothiophene molecules have attracted much attention in the area of organic chemistry and material sciences. They possess very interesting electronic and optical properties and have been investigated as advanced molecular electronic materials, including, for example, organic field effect transistors (OFETs)[1] and organic light-emitting diodes (OLEDs).[2] The advantages of oligomers are that their physical properties can be easily tuned to the desired properties by changing the structure, for example, solubilizing chains, end-capping groups, insertion of various functional groups and changing the oligomer lengths. Examples include 2-*n*-hexylfluorene,[3] diphenylamine,[4] cyclophane,[5] pyrene,[6] ethylenedithio,[7] 9,9-diphenylfluorene,[8] 2,3,4,5-tetrahydrobenzo[*b*]thiophene,[9] dimesitylboryl,[10] and bis(4-methylphenyl)aminophenyl[2] end-capped oligothiophenes, and oligothiophene-functionalized truxene,[11] tetraphenylmethane,[12] and thienyl-*S*,*S*-dioxide.[13] Due to its unique optical, electrical, and chemical properties, carbazole has been used widely as a functional building block or substituent in the construction of organic materials for optoelectronic devices.[14] Moreover, the thermal stability and glassy state durability of the organic molecules were found to be significantly improved upon incorporation of a carbazole moiety into the structure.[15] To our best knowledge, there are no reports on *N*-carbazole end-capped oligothiophene-fluorenes, whose synthesis and physical properties still remain to be explored.

In this Letter, we report our success in accomplishing the synthesis of a novel series of *N*-carbazole end-capped π-conjugated oligothiophene-fluorenes and investigate their optical, thermal, and electrochemical properties.

The synthetic strategy to the desired molecules is illustrated in Scheme 1. Dibromofluorene **1** bearing solubilizing *n*-hexyl substituents was treated with an excess of 2-thiophene boronic acid under Suzuki coupling conditions using $Pd(PPh_3)_4$ as catalyst and Na_2CO_3 as base to afford compound **2** in 58% yield. The resulting compound was chemoselectively brominated with NBS, in which only the most nucleophilic 5-positions of both thiophene rings were substituted to give the corresponding dibromo compound **3** in 71% yield. By repeating the bromination and Suzuki coupling reaction sequences, dibromo oligothiophene-fluorenes **5** and **7** were formed in good yields. Final coupling of each dibromo compound **3**, **5**, and **7** with an excess of carbazole under Ullmann coupling conditions using copper powder as catalyst and K_2CO_3 as base in nitrobenzene at reflux afforded the corresponding *N*-carbazole end-capped target oligomers **CTnF** ($n = 1$–3) in good yields. For

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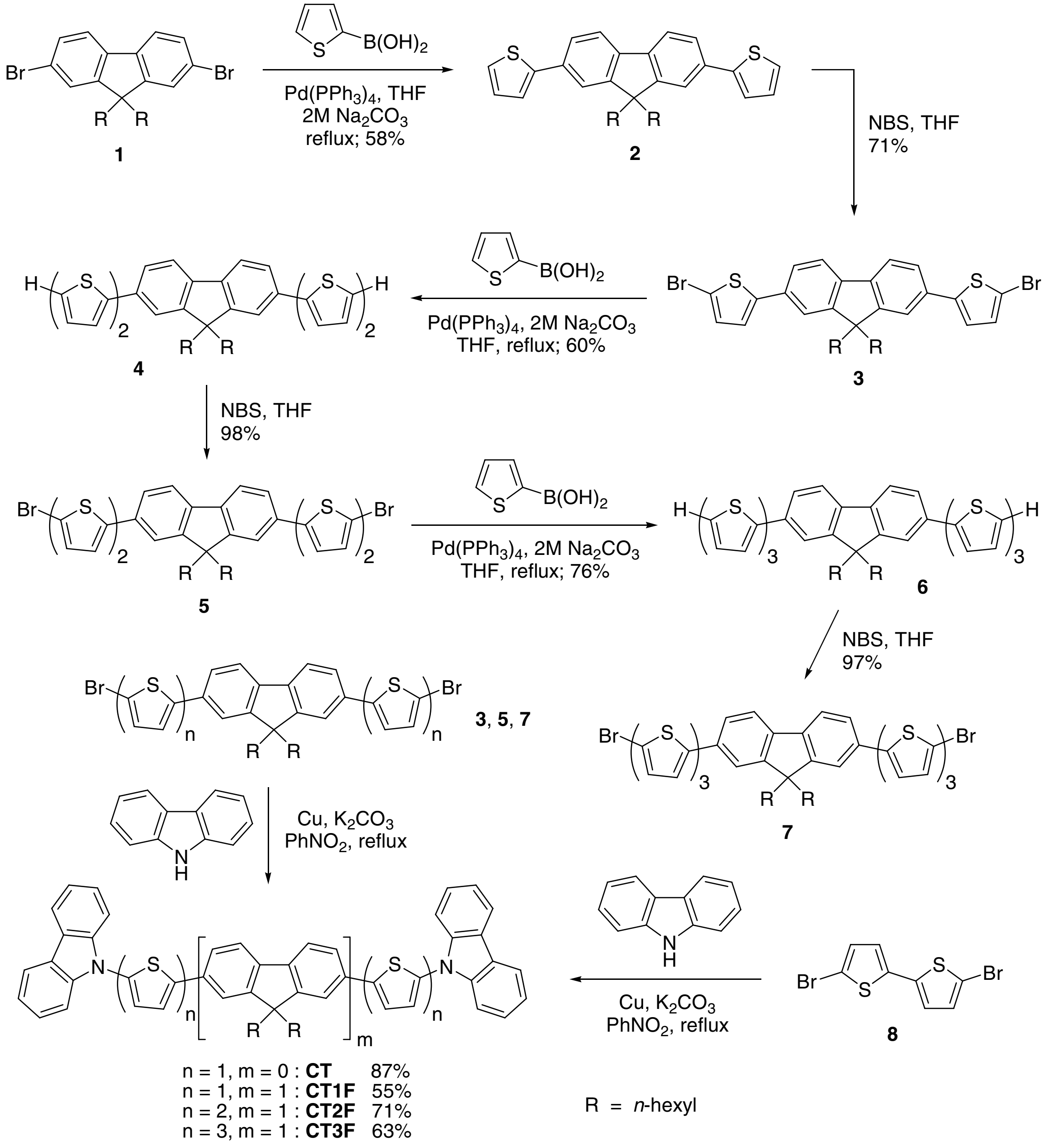

Scheme 1. Synthesis of **CT** and **CTnF** ($n = 1$–3).

comparison purposes, compound **CT** was also prepared via similar Ullmann coupling of dibromo bithiophene **8** with carbazole and was isolated in 87% yield. The chemical structures of all the oligomeric materials were confirmed by ^{1}H, ^{13}C NMR, IR, and HRMS analysis.[16] All the compounds exhibited a good solubility in organic solvents at room temperature.

The optical properties of *N*-carbazole end-capped products **CT** and **CTnF** ($n = 1$–3) in CH_2Cl_2 solution are shown in Figure 1 and summarized in Table 1. Normalized absorption spectra of all the compounds exhibited two absorption bands, a less intense absorption band at around 291 nm being assigned to the π–π^* local electron transition of the carbazole moiety and a strong absorption band at longer wavelength corresponding to the π–π^* electron transition of the entire conjugated backbone. The latter absorption band displays a perfect correlation to the conjugation length, that is the absorption intensity and absorption maxima are significantly increased and red-shifted, respectively, with increase of the conjugation length of the respective oligothiophene segment. They were also substantially red-shifted relative to the corresponding non-carbazole-capped oligothiophene-fluorenes **2**, **4**, and **6**. Such a red-shift is may be due to the incorporation of the strong electron donating carbazole groups at both ends. π-Electrons are delocalized over the entire conjugated backbone through the lone electron pair at the nitrogen atom of the carbazole, which is attributed to the asymmetric destabilization of the HOMO and LUMO energy levels leading to a decrease in the energy gap. The photoluminescence (PL) spectra of all the carbazole end-capped molecules are located in the blue to green region and their emission

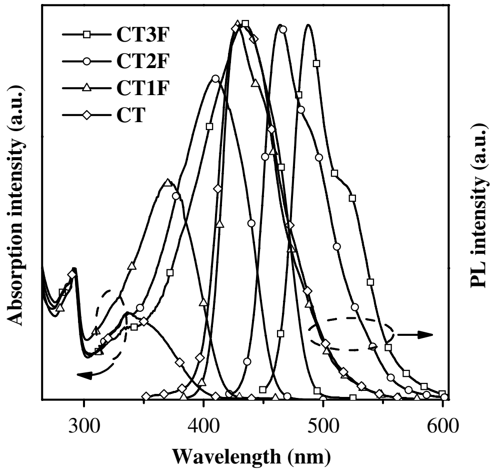

Figure 1. UV–vis absorption and photoluminescence spectra of **CT** and **CTnF** ($n = 1$–3) in dilute CH_2Cl_2 solution.

maxima were red-shifted with increasing number of thiophene units (Fig. 1 and Table 1) and were red-shifted in comparison with their corresponding non-carbazole-capped compounds. Upon excitation either at 290 nm attributed to the absorption of the carbazole moiety or at 370 nm corresponding to the absorption of the oligothiophene-fluorene cores, the emission spectra obtained were identical, indicating that energy or electrons can efficiently transfer from the peripheral carbazole to the inner backbone. Moreover, the presence of the fluorene ring at the center of the molecules not only enhanced their solubility, but also increased their π-conjugation length as can be seen from a red-shift in both absorption and PL spectra of **CT1F** with respect to those of **CT** (Fig. 1).

Cyclic voltammetry (CV) experiments were performed on all the target compounds in order to investigate their electrochemical behavior and the results are tabulated in Table 1. Compounds **CT1F** and **CT3F** display two reversible oxidation processes, while **CT** and **CT2F** show one and three reversible oxidation processes, respectively. During the successive oxidation cycles of all the compounds, a slight shift of the CV curves was observed indicating weak oxidative coupling at the 3,6-positions of the peripheral carbazole moieties. This is usually detected in most carbazole derivatives with unsubstituted 3,6-positions. The first oxidation process can be attributed to removal of electrons from the periphery of the carbazole units and the other reversible process corresponds to removal of electrons from the interior moieties. The increased conjugation length (from **CT1F** to **CF3F**) results in a decrease of the potentials of the first oxidation process. Similar behavior has been observed in cyclophane,[5] ethylenedithio,[7] and 2-*n*-hexylfluorene[3] end-capped oligothiophenes. Moreover, these first potential values were smaller than that of carbazole ($E_{1/2} = 1.09$ V), suggesting that the incorporation of carbazole makes the resulting molecules more susceptible to electrochemical oxidation. The HOMO and LUMO energy levels of the materials were determined using the onset of the first oxidation process (E_{onset}) and the energy band gaps (E_g) (Table 1). The HOMO levels of the *N*-carbazole end-capped oligomers are in the range of 5.28–5.44 eV, which match well with the work function of the indium tin oxide (ITO) ($\phi = 4.80$ eV) electrode for reducing the energy barrier for hole injection to the emissive layer such as Alq3 ($\phi = 5.80$ eV). As a result, electrochemically reversible **CT** and **CTnF** ($n = 1$–3) can also be used as hole transport and injection materials for multi-layer OLEDs.

The thermal properties of **CT** and **CTnF** ($n = 1$–3) were investigated by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) and the results are shown in Figure 2 and summarized in Table 1. All the compounds exhibited an onset of evaporation or decomposition at temperatures greater than 350 °C with no weight loss at lower temperatures. The temperatures corresponding to a 5% weight loss ($T_{5\text{d}}$) ranged from 358–487 °C. Compounds **CTnF** ($n = 1$–3) were in an amorphous state at room temperature. The glass transition temperatures (T_g) were improved from 81 °C (**CT1F**) to 93 °C (**CT3F**) with an increased number of thiophene rings. They formed stable amorphous glasses as under repeated heating cycles only a baseline shift due to T_g was observed with no exothermic peak due to crystallization or endothermic peak due to the melting point being detected at higher temperatures. In contrast, their parent oligothiophene-fluorenes **4** and **6** were crystalline materials with melting temperatures (T_m) of 120 and 200 °C, respectively. The results indicate that steric hindrance due to the terminal carbazole effectively induces the formation of a stable amorphous glass in the result-

Table 1. Summary of the physical property measurements of **CT** and **CTnF** ($n = 1$–3)

Comp	λ_{abs}/nm (log ε)[a]	λ_{em}/nm[b]	$E_{1/2}$/V (ΔE/mV)[c]	T_g/$T_{5\text{d}}$/°C[d]	E_g/eV[e]	HOMO/eV[f]	LUMO/eV[g]
CT	291 (4.60), 336 (4.40)	431	1.05 (160)	78/400	3.10	−5.41	−2.31
CT1F	292 (4.59), 371 (4.81)	428	1.08 (140), 1.63 (98)	81/416	2.89	−5.44	−2.46
CT2F	291 (4.59), 409 (4.87)	463	0.99 (120), 1.24 (90), 1.39 (110)	89/458	2.71	−5.35	−2.64
CT3F	291 (4.59), 434 (5.05)	487	0.88 (140), 1.09 (220)	93/487	2.55	−5.28	−2.73

[a] Measured in CH_2Cl_2 solution.
[b] Excited at the absorption maxima.
[c] Performed with a three electrode system (glassy carbon as working electrode, platinum rod as counter electrode, and Ag/Ag$^+$ as reference electrode) in CH_2Cl_2 containing 0.1 M n-Bu_4NPF_6 as a supporting electrolyte at a scan rate of 50 mV/s.
[d] Obtained from DSC and TGA measurements under N_2 at a heating rate of 10 °C/min.
[e] Estimated from the onset of the absorption spectra ($E_g = 1240/\lambda_{\text{onset}}$).
[f] Calculated using the empirical equation: HOMO = $-(4.44 + E_{\text{onset}})$.
[g] Calculated from LUMO = HOMO + E_g.

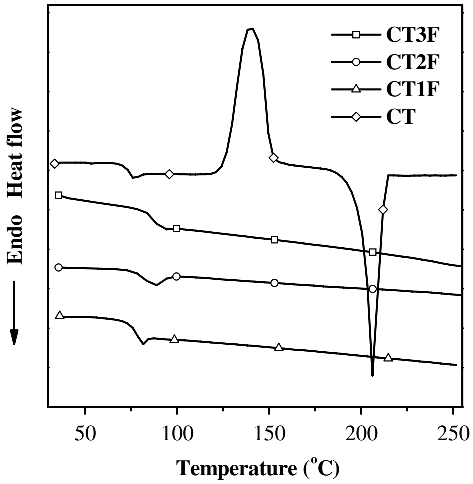

Figure 2. DSC curves (second heating) of **CT** and **CTnF** ($n = 1$–3).

ing molecules. However, compound **CT** behaves totally different. During the second heating, an endothermic phenomenon (T_g) at 78 °C was observed followed by an exothermic peak due to crystallization around 140 °C to give a crystal, which endothermically melted at 209 °C. The ability of compounds **CTnF** ($n = 1$–3) to form stable amorphous glasses and the possibility to prepare thin films from **CTnF** ($n = 1$–3) both by evaporation and by solution casting are highly desirable for applications in OLEDs.

In summary, we have presented a facile synthetic approach to a series of *N*-carbazole end-capped oligothiophene-fluorenes using a combination of bromination and Suzuki and Ullmann coupling reactions. The incorporation of the *N*-carbazole units at the terminal ends of the oligothiophene-fluorenes had significant effects on improving the morphology and electrochemical properties. The optical and thermal properties of the resulting new materials could be readily controlled by varying the conjugation of the oligothiophene segment. These materials show promise as potential hole-transporting and light-emitting layers in OLED devices.

Acknowledgement

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16. Characterization data for compounds: **CT1F**; IR (KBr) 2925, 1556, 1492, 1449, 1228, and 749 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.79–0.84 (10H, m), 1.13–1.19 (12H, m), 2.08–2.13 (4H, m), 7.25 (2H, d, $J = 3.9$ Hz), 7.37 (4H, t, $J = 7.5$ Hz), 7.49–7.54 (6H, m), 7.62 (2H, s), 7.64 (4H, d, $J = 4.8$ Hz), 7.68 (2H, d, $J = 8.0$ Hz), 7.77 (2H, d, $J = 7.9$ Hz), and 8.16 (4H, d, $J = 7.5$ Hz); ^{13}C NMR (75 MHz, CDCl$_3$) δ 14.02, 22.61, 23.82, 29.70, 31.51, 40.47, 55.47, 110.33, 119.93, 120.27, 120.38, 120.71, 121.66, 123.63, 124.88, 125.95, 126.33, 133.07, 137.07, 140.58, 141.96, 143.37, and 151.96; HRMS-ESI *m*/*z*: [MH$^+$] calcd for $C_{57}H_{53}N_2S_2$, 829.3645; found, 829.3631. Compound **CT2F**; IR (KBr) 2925, 1555, 1492, 1444, 1226, and 746 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.74–0.82 (10H, m), 1.11–1.17 (12H, m), 2.05–2.11 (4H, m), 7.17 (2H, d, $J = 3.9$ Hz), 7.25 (2H, d, $J = 3.9$ Hz), 7.30 (2H, d, $J = 3.9$ Hz), 7.32–7.37 (6H, m), 7.46 (4H, dt, $J = 8.1$ Hz, $J = 1.2$ Hz), 7.58 (6H, d, $J = 8.1$ Hz), 7.65 (2H, dd, $J = 8.1$ Hz, $J = 1.5$ Hz), 7.73 (2H, d, $J = 7.8$ Hz), and 8.13 (4H, d, $J = 7.5$ Hz); ^{13}C NMR (75 MHz, CDCl$_3$) δ 13.99, 22.56, 23.78, 29.66, 31.46, 40.41, 55.38, 110.29, 119.88, 120.25, 120.78, 122.12, 123.63, 123.69, 124.78, 124.93, 125.64, 126.35, 132.90, 135.96, 136.01, 137.23, 140.44, 141.84, 144.44, and 151.89; HRMS-ESI *m*/*z*: [MH$^+$] calcd for $C_{65}H_{57}N_2S_4$, 993.3399; found, 993.3420. Compound **CT3F**; IR (KBr) 2925, 1553, 1491, 1447, 1226, and 746 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.74–0.82 (10H, m), 1.11–1.17 (12H, m), 2.05–2.10 (4H, m), 7.17 (6H, s), 7.25 (4H, br s), 7.35 (6H, t, $J = 7.2$ Hz), 3.50 (4H, t, $J = 7.3$ Hz), 7.57 (6H, d, $J = 7.5$ Hz), 7.61 (2H, d, $J = 8.7$ Hz), 7.71 (2H, d, $J = 7.8$ Hz), and 8.13 (4H, d, $J = 7.8$ Hz); ^{13}C NMR (75 MHz, CDCl$_3$) δ 14.00, 22.57, 23.78, 31.47, 40.43, 55.36, 110.28, 119.84, 120.26, 120.81, 122.28, 123.64, 123.72, 124.20, 124.72, 125.65, 126.36, 132.87, 135.56, 135.96, 140.42, 141.80, and 151.86; HRMS-ESI *m*/*z*: [MH$^+$] calcd for $C_{73}H_{61}N_2S_6$, 1157.3154; found, 1157.3141.
Compound **CT**; IR (KBr) 1579, 1537, 1451, 1221, 1164,799, and 744 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.18 (2H, d, $J = 3.9$ Hz), 7.30 (2H, d, $J = 3.9$ Hz), 7.36 (4H, dt, $J = 7.8$ Hz, $J = 1.0$ Hz), 7.50 (4H, dt, $J = 8.0$ Hz, $J = 1.1$ Hz), 7.58 (4H, d, $J = 8.0$ Hz), and 8.13 (4H, d, $J = 7.8$ Hz); ^{13}C NMR (75 MHz, CDCl$_3$) δ 110.24, 120.29, 120.85, 122.68, 123.67, 125.67, 126.39, 135.43, 137.84, and 141.81; HRMS-ESI *m*/*z*: [MH$^+$] calcd for $C_{32}H_{21}N_2S_2$, 497.1141; found, 497.1149.