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Synthesis and characterization of *N*-carbazole end-capped oligofluorene-thiophenes

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Abstract—A series of novel *N*-carbazole end-capped oligofluorene-thiophenes with one, two, three, and four thiophene rings were synthesized using either palladium catalyzed cross-coupling reaction or nickel-catalyzed reductive dimerization. All the oligomers have been characterized by ^{1}H, ^{13}C NMR, FTIR, UV–vis, PL spectroscopy and mass spectrometry. It has been demonstrated that 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 fluorene moieties of the resulting materials are beneficial for their morphology, conjugation length, and solubility. These bright fluorescent, thermally and electrochemically stable compounds have potential applications as light-emitting and hole-transporting layers in organic light-emitting devices.

1. Introduction

Over the past few years, π-conjugated organic materials have been the subject of great interest due to the increasing development of potentially active components for a wide range of electronic and optoelectronic devices.[1,2] The simplicity in the modification of chemical structure, solubility, and optical properties of the organic materials makes them superior to those based on inorganic substances in both manufacturing costs of the devices and improving some technological aspects. In particular, oligothiophenes have shown excellent conductivity, electroluminescent behavior, and characteristics as advanced materials for organic field effect transistors (OFETs)[3,4] and organic light-emitting diodes (OLEDs).[5,6] With π-conjugated small molecules or oligomers, not only can they be obtained in high-purity and well-defined structures, but also their optical, electrochemical, and thermal properties can be easily tuned to the desired properties by changing the structure, e.g. solubilizing chains, end-capping groups, insertion of various functional groups, and changing the oligomer lengths. Oligothiophenes with different terminal α,α' substituents such as aldehyde,[7] diphenylamine,[8] cyclophane,[9] pyrene,[10] bis(4-methylphenyl)-aminophenyl,[11] cyclohexen,[12] ethylenedithio,[13] and phenyl[14] groups are a growing synthetic interest. Recently, a series of oligothiophenes terminated with fluorene moieties[15,16] have also been synthesized using palladium catalyzed Suzuki and Stille coupling reactions or nickel-catalyzed reductive dimerization. These materials exhibited interesting optical and electrochemical properties and have been shown to act as potential light-emitting materials in OLEDs and active components in OFETs. Carbazole has strong absorption in the near-UV region and a low redox potential. The electrochemical and spectroscopic properties of carbazole and its derivative have been extensively investigated.[17] Chemically, carbazole can be easily functionalized at its 3-,6- or 9-positions and covalently linked to other molecular moieties.[18,19] 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 molecules for use as light-emitting and hole-transporting layers in OLED devices,[20–27] as host materials for electrophosphorescent applications,[26,28] and as active components in solar cells.[29,30] 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.[31,32] To our best knowledge, there are no reports on *N*-carbazole end-capped oligofluorene-thiophenes, the synthesis and physical properties of which still remain to be explored. Therefore, in this paper, we report a successful synthesis of a series of new *N*-carbazole end-capped oligofluorene-thiophenes with one, two, three, and four thiophene rings by the use of either nickel-catalyzed reductive dimerization or palladium catalyzed cross-coupling reaction. Their basic optical, electrochemical, and thermal

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Keywords: Oligomer; Thiophene; Fluorene; Carbazole; Electrochemical property; Organic light-emitting device (OLED).

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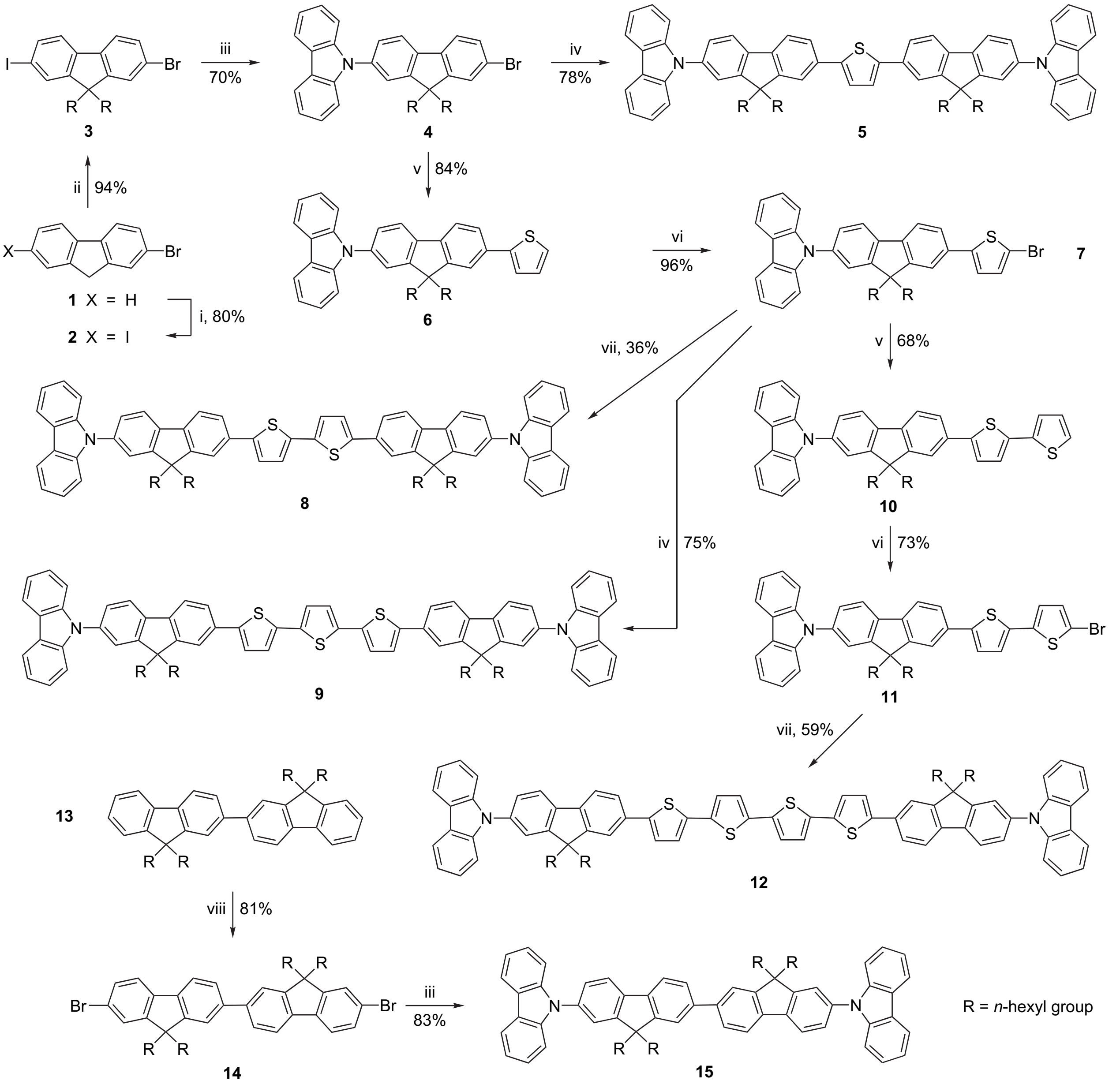
properties have been investigated with the aim of understanding the structure–physical property relationships and developing novel molecular organic materials.

2. Results and discussion

2.1. Synthesis and characterization

Scheme 1 illustrates the synthetic approach to the target oligomers **5**, **8**, **9**, **12**, and **15**. The *n*-hexyl substituents were introduced on the C-9 position of fluorene ring to increase the solubility. In this synthetic sequence, the key intermediate to the carbazole end-capped oligofluorene-thiophenes **5**, **8**, **9**, and **12** was 2-bromo-7-(carbazol-9-yl)-9,9-bis-*n*-hexylfluorene (**4**), the preparation of which we have reported previously. Earlier, we synthesized this compound by a Cu-mediated Ullmann condensation reaction of 2,7-dibromo-9,9-bis-*n*-hexylfluorene with 1 equiv of carbazole in moderate yield.[31] However, in this work, we used a new synthetic approach with higher overall yield to prepare the mono carbazole end-capped fluorene intermediate **4** as described in Scheme 1. Thus, 2-bromo-7-iodofluorene (**2**) was first prepared in 80% yield by a regiospecific iodination of 2-bromofluorene (**1**)[33] with I_2 and KIO_3 in a mixture of AcOH and concd H_2SO_4 at 80 °C. Dialkylation at the C-9 position of the resultant compound **2** was accomplished by generation of the fluorenyl anion with an aqueous NaOH solution in DMSO and subsequent dihexylation with 1-bromohexane in the presence of triethylbenzylammonium chloride as phase transfer catalyst at room temperature. 2-Bromo-7-iodo-9,9-bis-*n*-hexylfluorene (**3**) was obtained as



Scheme 1. The synthesis of **5**, **8**, **9**, **12**, and **15**. Reagents and conditions: (i) I_2, KIO_3, AcOH, concd H_2SO_4, 80 °C, 20 h; (ii) n-$C_6H_{13}Br$, 50% NaOH, Et_3BnNCl, DMSO, room temperature, 15 h; (iii) carbazole, Cu-bronze, K_2CO_3, nitrobenzene, reflux, 24 h; (iv) 2,5-thiophenediboronic acid, $Pd(PPh_3)_4$, 2 M Na_2CO_3, THF, reflux, 18 h; (v) 2-thiopheneboronic acid, $Pd(PPh_3)_4$, 2 M Na_2CO_3, THF, reflux, 18 h; (vi) NBS, $CHCl_3$, AcOH, room temperature, 3 h; (vii) $NiCl_2$, PPh_3, Zn powder, bpy, DMAc, reflux, 22 h; and (viii) Br_2, I_2, $CHCl_3$, room temperature, in the dark, 18 h.

a pale yellow viscous oil in good yield. Subsequently, copper-catalyzed Ullmann coupling reaction of **3** with 1 equiv of carbazole in nitrobenzene using Cu-bronze as catalyst and K_2CO_3 as base at refluxing temperature afforded the mono adduct **4** in 70% yield as a colorless solid, which co-chromatographed with, and had identical MS, ^1H and ^{13}C NMR spectra to, the authentic sample.[31] The ^1H NMR spectrum showed a characteristic doublet signal for 4-H and 5-H of the carbazole at chemical shift 8.19 ppm (J=7.8 Hz) and the non-equivalent 4′-H and 5′-H of the fluorene moiety were observed as two doublet signals at chemical shift 7.89 ppm (J=7.8 Hz) and 7.65 ppm (J=8.4 Hz), respectively. The target carbazole end-capped oligofluorene-thiophene **5** was obtained as a green-yellow solid in 78% yield in a palladium catalyzed Suzuki cross-coupling reaction between **4** and 2,7-thiophenediboronic acid in the presence of $Pd(PPh_3)_4$ as catalyst and 2 M Na_2CO_3 as base in THF at reflux. Coupling of the intermediate **4** with an excess of 2-thiopheneboronic acid under similar cross-coupling conditions afforded 2-[2-(carbazol-9-yl)-9,9-bis-*n*-hexylfluoren-7-yl]thiophene (**6**) as a pale yellow solid in good yield. Subsequently, treatment of the resulting compound **6** with NBS in $CHCl_3$/AcOH (1:1) allowed the bromo functional group to be selectively introduced at the nucleophilic 5-position of the terminal thiophene ring. 2-Bromo-5-[2-(carbazol-9-yl)-9,9-bis-*n*-hexylfluoren-7-yl]thiophene (**7**) was obtained as a light green-yellow solid in 96% yield. The oligomer **8** was attained as a yellow-green solid in 36% yield via a reductive nickel-catalyzed dimerization reaction of the bromo compound **7** with the catalytic system of $NiCl_2$, zinc powder, PPh_3, and bipyridine (bpy) in DMAc at 90 °C. Alternatively, coupling of the resulting **7** with 2,7-thiophenediboronic acid under Suzuki cross-coupling conditions afforded the target oligomer **9** as an orange-yellow solid in good yield. Further coupling of **7** with an excess of 2-thiopheneboronic acid under similar cross-coupling conditions gave 5-[2-(carbazol-9-yl)-9,9-bis-*n*-hexylfluoren-7-yl]-2,2′-bithiophene (**10**) in 68% yield, which was subsequently brominated with NBS to afford 5-bromo-5′-[2-(carbazol-9-yl)-9,9-bis-*n*-hexylfluoren-7-yl]-2,2′-bithiophene (**11**) in 73% yield. Dimerization of the resulting intermediate **11** under reductive nickel-catalyzed coupling conditions gave the desired oligomer **12** as an orange solid in 59% yield. For comparison purpose, the carbazole end-capped bifluorene **15** was prepared as described in our previous report.[31] As shown in Scheme 1, bifluorene **13**[34] was selectively brominated at the 7,7′-position with Br_2 in the presence of catalytic I_2 in $CHCl_3$ to give the dibromo compound **14** in 81% yield. Direct coupling of **14** with an excess of carbazole with the aid of a Cu-bronze/K_2CO_3 catalytic system in nitrobenzene at reflux gave 7,7′-bis(carbazol-9-yl)-2,2′-bis(9,9-bis-*n*-hexylfluorene) (**15**) as a white solid in an improved yield of 83%. Compounds **5**, **8**, **9**, **12**, and **15** are soluble in a wide variety of organic solvents including most chlorinated solvents. Their chemical structures were confirmed by HRMS, IR, ^1H and ^{13}C NMR spectroscopic methods. The ^1H NMR spectra of the carbazole end-capped oligomers **5**, **8**, **9**, **12**, and **15** showed a characteristic doublet signal of the 4-H and 5-H of the carbazole caps at chemical shift around 8.20–8.22 ppm (J=7.5–7.8 Hz) and the non-equivalent 4′-H and 5′-H of the fluorene units were observed as two doublet signals at chemical shifts around 7.77–7.90 ppm (J=7.8–8.1 Hz) and 7.91–7.97 ppm (J=7.4–8.7 Hz), respectively.

2.2. Theoretical calculation

To gain insights into the electronic properties and the geometries of the oligomers **5**, **8**, **9**, **12**, and **15**, quantum chemical calculations were performed. In our calculations, the ground state geometries of **5**, **8**, **9**, **12**, and **15** were fully optimized using density functional theory (DFT) at the B3LYP/6-31G (d,p) level, as implemented in Gaussian 03.[35] TDDFT/B3LYP calculation of lowest excitation energies was performed at the optimized geometries of the ground states. The optimized structures of all the compounds (Fig. 1) revealed that the carbazole moieties attached to both ends of the molecule are nearly perpendicular with the plane of the oligofluorene-thiophene moiety. Therefore, π-electron delocalization between those units will be negligible. However, in their HOMO orbitals (Fig. 2) the π-electrons are able to delocalize over the entire oligofluorene-thiophene backbone and end-capped carbazole moieties through the lone electron pair of the nitrogen of the carbazole. The electron density on the carbazole rings was found to decrease gradually as the number of thiophene rings in the oligomer increase. In the HOMO, the bonding orbitals locate on the bridge C=C atoms and the antibonding orbitals locate on the bridge C–C atoms. On the other hand, in the LUMO, the bonding orbitals locate on the bridge C–C atoms and the antibonding orbitals located on the bridge C=C atoms. In all cases, the HOMO is delocalized extensively over the whole π-conjugated systems via the oligofluorene-thiophene chain and carbazole terminal substituents, while the LUMO is delocalized through the oligofluorene-thiophene chain units as illustrated in Figure 2. Therefore, a significant change in charge distribution would result upon the HOMO–LUMO transition in the oligomers **5**, **8**, **9**, **12**, and **15**. The HOMO−LUMO energy differences (energy band gaps, calcd E_g) at TDDFT/B3LYP level of theory are presented in Table 1.

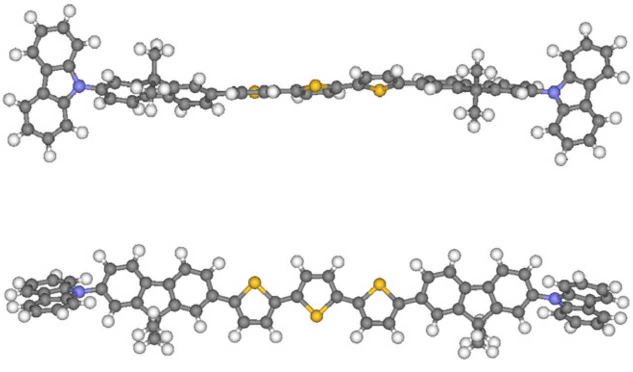


Figure 1. B3LYP/6-31G (d,p) optimized geometry of compound **9**.

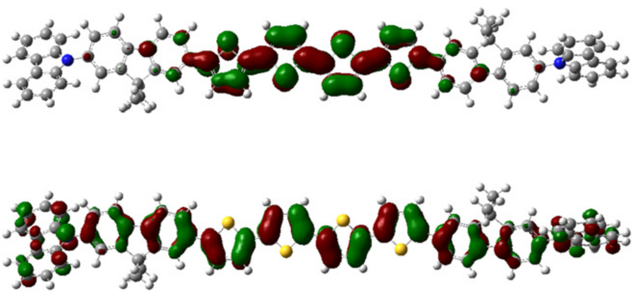


Figure 2. The HOMO (bottom) and LUMO (top) orbitals of compound **12**.

Table 1. Summary of the physical measurements of **5**, **8**, **9**, **12**, and **15**

Compd	λ_{abs} (log ε)[a] (nm/dm^3 mol^{-1} cm^{-1})	λ_{ex}[b] (nm)	E_g[c] (eV)	Calcd E_g[d] (eV)	Φ_F[e]	$E_{1/2}$ (ΔE)[f] V (mV)	$T_g/T_c/T_m/T_{5d}$[g] (°C)	HOMO[h] (eV)	LUMO[i] (eV)
5	382 (4.88), 294 (4.67)	435, 460	2.84	2.98	0.65	1.07 (94), 1.24 (82), 1.41 (140)	84/—/—/—/341	−5.34	−2.59
8	411 (4.88), 294 (4.68)	472, 499	2.63	2.78	0.35	1.00 (133), 1.20 (110), 1.37 (185)	86/*160*/224/357	−5.30	−2.67
9	430 (4.90), 337 (4.54), 294 (4.70)	498, 528	2.49	2.52	0.22	0.82 (190), 1.03 (235), 1.20 (228), 1.39 (218)	92/—/224/372	−5.22	−2.73
12	446 (4.92), 343 (4.67), 294 (4.68)	518	2.40	2.40	0.20	0.72 (213), 1.08 (342), 1.36 (250)	96/127/221/375	−5.15	−2.75
15	349 (4.90), 294 (4.63)	391, 412	3.20	3.25	>0.99	0.94 (62), 1.28 (110), 1.67 (125)	69/148/196/340	−5.29	−2.09

[a] Measured in dilute CH_2Cl_2 solution.
[b] Excited at the absorption maxima.
[c] Estimated from the onset of the absorption spectra (E_g=1240/λ_{onset}).
[d] Obtained from the TDDFT/B3LYP calculation.
[e] Determined in CH_2Cl_2 solution (A<0.1) at room temperature using quinine sulfate solution in 0.01 M H_2SO_4 (Φ_F=0.54) as a standard.[38]
[f] Measured using a three-electrode system fitted with a glassy carbon working electrode, a platinum rod counter electrode and SCE 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.
[g] Obtained from DSC and TGA measurements under N_2 at a heating rate of 10 °C/min.
[h] Calculated using the empirical equation: HOMO=−(4.44+E_{onset}).
[i] Calculated from LUMO=HOMO+E_g.

The result indicates that calcd E_g values decrease as the number of the thiophene units increases. These predicted calcd E_g values slightly deviate from those estimated from the onset of UV–vis absorption and the cyclic voltammogram (~0–0.15 eV). There are factors which may be responsible for the errors because the orbital energy difference between HOMO and LUMO is still an approximate estimation to the transition energy since the transition energy also contains significant contributions from some two-electron integrals. The real situation is that an accurate description of the lowest singlet excited state requires a linear combination of a number of excited configurations.

2.3. Optical properties

The optical properties of newly synthesized carbazole end-capped oligomers **5**, **8**, **9**, **12**, and **15** were investigated using UV–vis absorption and photoluminescence (PL) spectroscopy in dilute CH_2Cl_2 solution. The results are depicted in Figures 3 and 4 and summarized in Table 1. The absorption spectra of **5**, **8**, **9**, **12**, and **15** showed two major absorption bands, an absorption band at 294 nm assigned to the π–π* local electron transition of the end-capped carbazole units and a broader absorption band at longer wavelength corresponding to the π–π* electron transition of the entire π-conjugated backbone. The absorption maxima of the latter bands of **5**, **8**, **9**, **12**, and **15** were gradually red-shifted with the increasing number of thiophene rings as the extent of the π-conjugation system in the oligomer increases, as expected. Compounds **5**, **8**, **9**, **12**, and **15** exhibited the longest wavelength absorptions at 382, 411, 430, 446, and 349 nm, respectively, which were considerably red-shifted in comparison to those of the corresponding non-carbazole end-capped oligofluorene-thiophene (374 nm), bithiophene (404 nm), terthiophene (425 nm), quarterthiophene (442 nm),[16] and bifluorene (329 nm).[36] Such a red-shift may be due to the incorporation of the strong electron donating carbazole groups at both ends. As observed in the quantum chemical calculation results, 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. However, the participation of the carbazole substituents in the π-electrons delocalization becomes less significant as the number of the thiophene rings increases. The HOMO–LUMO energy gaps (E_g) of **5**, **8**, **9**, **12**, and **15** (Table 1),

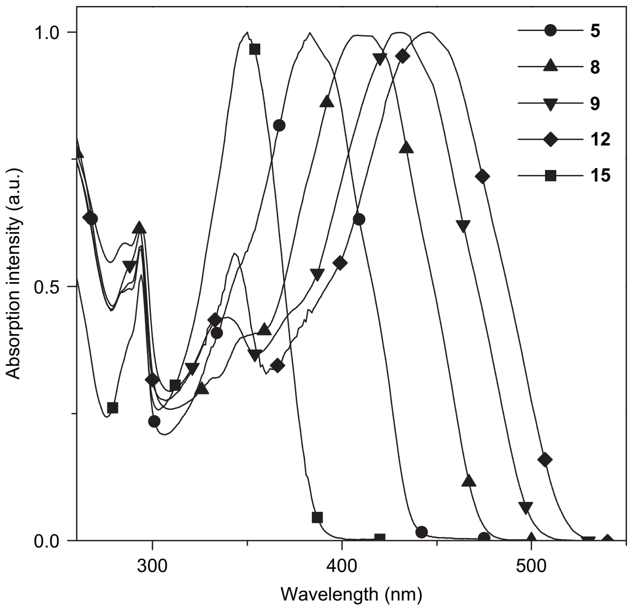


Figure 3. Normalized absorption spectra of **5**, **8**, **9**, **12**, and **15** in dilute CH_2Cl_2 solution.

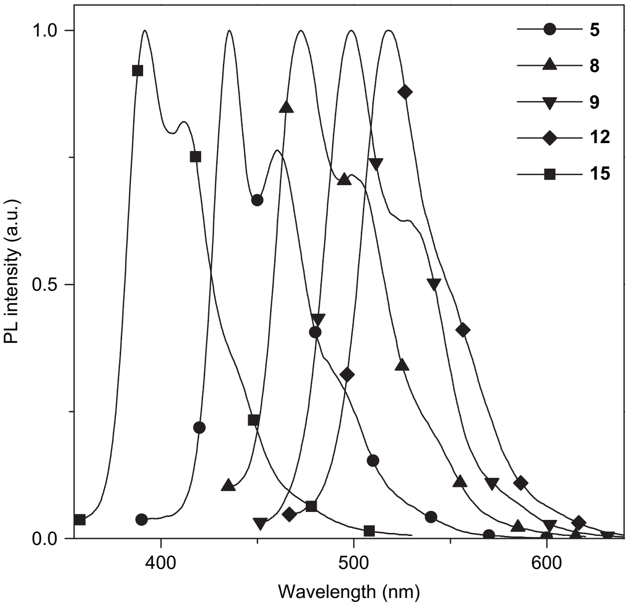


Figure 4. Normalized photoluminescence (PL) spectra of **5**, **8**, **9**, **12**, and **15** in dilute CH_2Cl_2 solution.

estimated from the onset of absorption, agree with the energy gaps obtained from the TDDFT/B3LYP calculation and decrease with the increase of the π-conjugation length of the oligofluorene-thiophene segments. All compounds **5**, **8**, **9**, **12**, and **15** in this study are highly fluorescent with the color of the fluorescence ranging from bright blue to bright yellow-orange. The quantum yields (Φ_F) of these oligomers were also determined in dilute CH_2Cl_2 solutions by comparison with the solution emission of quinine sulfate dehydrate (Φ=0.546) standard.[37,38] The fluorescence quantum yields (Φ_F) of the fluorescence for the oligomers **5**, **8**, **9**, **12**, and **15** range from 0.20 to 1.00 (Table 1). The results indicate that the fluorescence quantum yields of the oligomers decrease with the increasing number of thiophene units, as commonly observed in most cases with oligothiophene derivatives.[15,16] The PL spectra of **5**, **8**, **9**, **12**, and **15** were located in the blue to orange region, and their emission maxima were increasingly red-shifted with the increasing number of thiophene rings (Fig. 4 and Table 1), and were red-shifted (3–11 nm) in comparison with the non-carbazole end-capped compounds.[16,31] Upon excitation, either at 294 nm attributed to the absorption of the carbazole moiety, or at the absorption maxima corresponding to the absorption of the oligofluorene-thiophene cores, the emission spectra obtained were identical, indicating that energy or electrons can efficiently transfer from the peripheral carbazole to the inner backbone. The PL spectra of **5**, **8**, and **15** are characterized by a well-defined two vibronic maxima namely strong emission peak and less intense peak at longer wavelength. However, they turned into a shoulder and single peak for compounds **9** and **12**, respectively. This indicates the existence of a broad distribution of the ground and excited state molecular conformations for **9** and **12**. This is clearly supported by the Stokes' shift between the PL and absorption maxima. The Stokes' shifts of the oligomers **5**, **8**, **9**, **12**, and **15** are relatively large ranging from 50 to 72 nm and gradually increase with increasing number of thiophene units (Table 1). This indicates a noticeable change in the position of the atoms of the molecules between the ground and the excited states. This also reflects the existence of a twist in the ground state structure, whereas the excited state is more planar.

2.4. Electrochemical properties

In order to investigate the electrochemical behaviors of the target oligomers, cyclic voltammetry (CV) measurements were performed in CH_2Cl_2 containing 0.1 M n-Bu_4NPF_6 as a supporting electrolyte. The results are shown in Figure 5 and the electrochemical potentials are summarized in Table 1. Compounds **5**, **8**, **12**, and **15** demonstrated three quasi-reversible oxidation processes, while compound **9** showed four quasi-reversible oxidation processes. However, under these experimental conditions no distinct reduction process was observed in all cases. During the consecutive oxidation cycles of all the compounds, a slight shift of the CV curves was observed indicating a weak oxidative coupling at the 3,6-position of the peripheral carbazole moieties (Fig. 6). This is usually detected in most carbazoles with unsubstituted 3,6-position. The first oxidation process can be attributed to the removal of electrons from the periphery of the carbazole units and the other reversible process corresponds to removal of electrons from the interior moieties. In analogy with the spectroscopic results, the oxidation potentials progressively shifted to lower energies with increasing length of the π-conjugation system. Similar behavior has been observed in cyclophane,[9] ethylenedithio,[13] 2-n-hexylfluorene[15] end-capped oligothiophenes. The first oxidation values of **5**, **8**, **9**, **12**, and **15** were 1.07, 1.00, 0.82, 0.72, and 0.94 V, respectively, which are lower than those of the non-carbazole end-capped molecules.[16] This suggests that the incorporation of carbazole makes the resulting materials more susceptible to electrochemical oxidation. The noticeable potential differences between the first and second oxidation processes ranging from 170 to 360 mV indicate that the radical cation could efficiently delocalize the charge

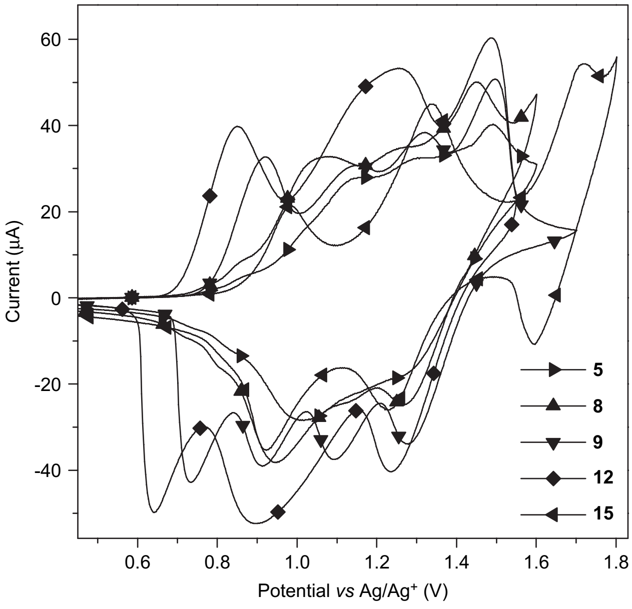


Figure 5. CV curves of **5**, **8**, **9**, **12**, and **15** in dichloromethane containing 0.1 M n-Bu_4NPF_6 at scan rate of 50 mV/s.

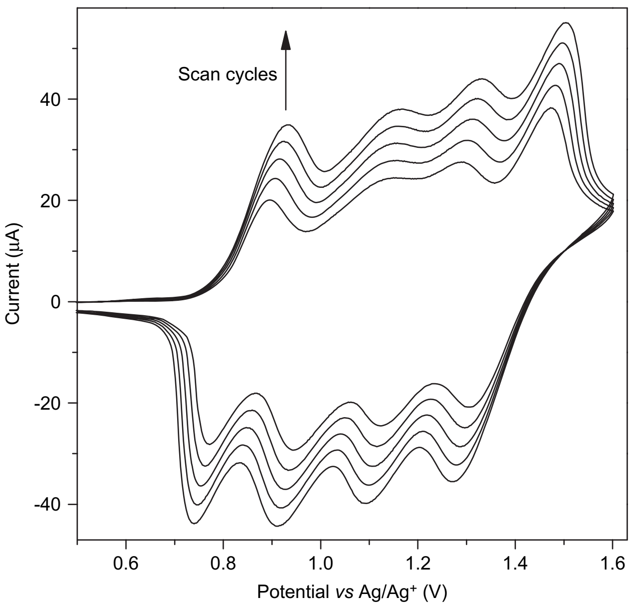


Figure 6. The consecutive CV curves of compound **9** in dichloromethane containing 0.1 M n-Bu_4NPF_6 at scan rate of 50 mV/s.

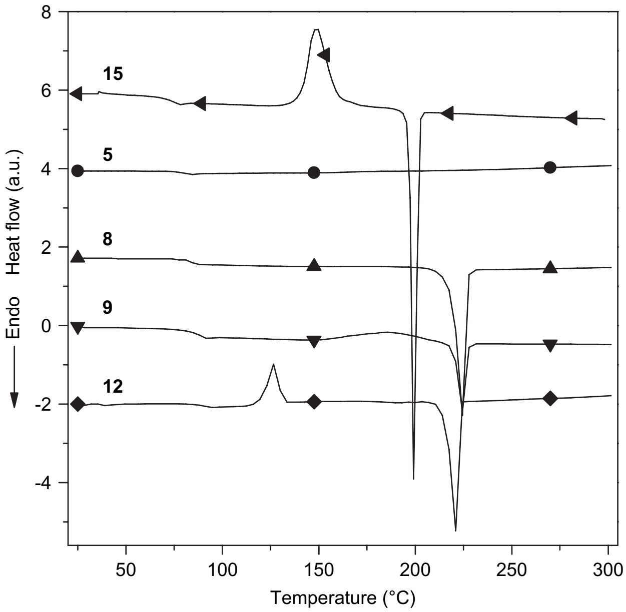


Figure 7. DSC thermograms (second heating) of **5**, **8**, **9**, **12**, and **15** at a heating rate of 10 °C/min.

along the oligofluorene-thiophene backbone to the carbazole end-caps. These results are consistent with the increasing red shifts in the absorption and PL spectra. The increasing π-conjugation length is due to the extent of delocalization of the π-electron system along the backbone. The HOMO and LUMO energy levels of the oligomers were calculated from the oxidation onset potentials (E_{onset}) and energy gaps (E_g) and the results are summarized in Table 1. The HOMO levels of these oligothiophenes are in the range of −5.34 to −5.15 eV, which match well with the work functions of the gold (Au) or indium tin oxide (ITO) electrodes, favoring the injection and transport of holes.

2.5. Thermal properties

For optoelectronic applications, the thermal stability of organic materials is crucial for device stability and lifetime. The degradation of organic optoelectronic devices depends on morphological changes resulting from the thermal stability of the amorphous organic layer. Morphological change might be promoted by rapid molecular motion near the glass transition temperature (T_g). The thermal properties of newly synthesized oligomers **5**, **8**, **9**, **12**, and **15** were investigated by thermalgravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA and DSC results are shown in Figure 7 and summarized in Table 1. The TGA data revealed that all the materials **5**, **8**, **9**, **12**, and **15** were thermally stable materials, with the onset of evaporation or decomposition temperatures above 340 °C under nitrogen. The temperatures corresponding to 5% weight loss (T_{5d}) range from 340 to 375 °C. As expected, the increase in the number of thiophene rings results in increase of the phase transition temperature. The DSC curves of the semi-crystalline compounds **8** and **9** showed endothermic baseline shifts at 86 and 92 °C, respectively, at which point the glassy state changed into the supercooled liquid state (T_g), followed by the endothermic melting peaks (T_m) at 224 °C. While the DSC curves of the semi-crystalline compounds **12** and **15** exhibited endothermic baseline shifts due to glass transitions at 96 and 69 °C, respectively. Then broad exothermic peaks due to the crystallization were observed around 126 and 148 °C, respectively, to give the same crystals as observed by crystallization from solution, which melted at 221 and 196 °C, respectively. However, compound **5** behaved in a totally different manner. Only the glass transition at about 84 °C can be seen in repeated DSC heating cycles with no crystallization and melting peaks observed. The thermal and morphological stabilities of all compounds may benefit from the presence of carbazole moieties at both ends. The ability of all the compounds to form a molecular glass and the possibility to prepare thin films from these materials both by evaporation and by solution casting is highly desirable for applications in OLEDs and OFETs.

3. Conclusion

We have presented the synthesis of a series of new *N*-carbazole end-capped oligofluorene-thiophenes with one, two, three, and four thiophene units via a nickel-catalyzed reductive or palladium catalyzed coupling reactions of the corresponding bromo oligofluorene-thiophenes and their properties were investigated. The presence of carbazole and 9,9-bis-*n*-hexylfluorene rings at both ends of the oligomers has a significant effect on improving the material solubility and thermal stability. The optical and electrochemical investigations reveal an electronic connection between the carbazole moieties and the oligofluorene-thiophene chains. The thermal properties of these materials are enhanced with the increasing number of thiophene rings. These high lying HOMO level oligothiophene derivatives display a bright fluorescence and should be promising light-emitting or hole-transporting layers for OLED devices. The performance of OLEDs using these materials as light-emitting and hole-transporting layers is under investigation and will be reported in the future.

4. Experimental

4.1. General procedures

Tetrahydrofuran (THF) was refluxed with sodium and benzophenone and distilled. Nitrobenzene was distilled from calcium hydride under high vacuum prior to use. Dichloromethane for cyclic voltammetry (CV) measurements was washed with concd H_2SO_4 and distilled twice from calcium hydride. All reagents and solvents were purchased from Aldrich, Acros, Fluka or Thai Suppliers and used as received unless otherwise stated. ^1H and ^{13}C NMR spectra were recorded on a Brüker AVANCE 300 MHz spectrometer using $CDCl_3$ as solvent in all cases. IR spectra were measured on a Perkin–Elmer FTIR spectroscopy spectrum RXI spectrometer as KBr disc. UV–vis absorption and photoluminescence (PL) spectra were recorded as a dilute solution in spectroscopic grade CH_2Cl_2 on a Perkin–Elmer UV Lambda 25 and Perkin–Elmer LS 50B Luminescence Spectrometer, respectively. The fluorescence quantum yields (Φ) were determined by comparison with a fluorescence standard of known fluorescence quantum yield value according to the following equation;[37,38]

$$\Phi_X = \Phi_{ST}\left(\frac{Slope_X}{Slope_{ST}}\right)\left(\frac{\eta_X^2}{\eta_{ST}^2}\right)$$

Where the subscripts X refer to the unknown samples and ST refers to the standard quinine sulfate solution in 0.01 M H_2SO_4, whose fluorescence quantum yield is known to be 0.54.[30,31] Φ is the fluorescence quantum yield, *Slope* is the slope from the plot of integrated fluorescence intensity versus absorbance, and η is the refractive index of the solvent. The refractive indexes of the solvents were taken as 1.424 and 1.333 for CH_2Cl_2 and 0.01 M H_2SO_4, respectively. Melting points were measured using an Electrothermal IA 9100 series of digital melting point instrument and are uncorrected. Differential scanning calorimetric (DSC) analysis was performed on a METTLER DSC823e thermal analyzer using a heating rate of 10 °C/min and a cooling rate of 50 °C/min under a nitrogen flow. Samples were scanned from 25 to 350 °C and then rapidly cooled to 25 °C and scanned for the second time at the same heating rate to 350 °C. Thermogravimetric analysis (TGA) was carried out on a METTLER TGA851 thermal analyzer at a heating rate of 10 °C/min under nitrogen flow. Cyclic voltammetry (CV) measurements were carried out under an inert argon atmosphere with an Autolab potentiostat PGSTAT 12 using a three-electrode system fitted with a platinum rod counter electrode, a glassy carbon working electrode and a Ag/Ag^+ reference electrode. The solvent in all the experiments was dichloromethane and the supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate (n-Bu_4NPF_6). The concentrations of the oligothiophene derivatives were 0.9–1.0 mM and the scan rate was 50 mV/s. The $E_{1/2}$ values were determined as $(E_p^a+E_p^c)/2$, where E_p^a and E_p^c are the anodic and cathodic peak potentials, respectively. High resolution mass spectrometry (HRMS) analysis was performed by Mass Spectrometry Unit, Chulabhorn Research Institute (CRI) of Thailand using a Micro TOF Brüker.

4.1.1. 2-Bromo-7-iodo-fluorene (2). To a solution of compound **1**[33] (8.00 g, 32.64 mmol) in a mixture of acetic acid (350 ml) and 20% H_2SO_4 (32 ml) was added KIO_3 (1.40 g, 6.53 mmol) followed by I_2 (4.47 g, 17.63 mmol). The reaction mixture was stirred at 80 °C for 20 h. After being cooled to room temperature water (400 ml) was added. The mixture was extracted with CH_2Cl_2 (150 ml×3). The combined organic phases were washed with water (150 ml×2), dilute $NaHCO_3$ solution (100 ml), and brine solution (100 ml), dried over anhydrous Na_2SO_4, filtered, and the solvent was removed to dryness. Purification by recrystallization with a mixture of CH_2Cl_2 and methanol gave white solids (9.73 g, 80%): ^1H NMR (300 MHz, $CDCl_3$) δ 3.87 (2H, s), 7.50–7.54 (2H, m), 7.61 (1H, d, J=8.4 Hz), 7.68 (1H, s), 7.71 (1H, d, J=8.1 Hz), and 7.90 (1H, s).[39,40]

4.1.2. 2-Bromo-7-iodo-9,9-bis-*n*-hexylfluorene (3). To a solution of compound **2** (2.94 g, 7.92 mmol) in DMSO (30 ml) was added triethylbenzylammonium chloride (0.5 g) followed by 50% NaOH aqueous solution (3 ml). n-Bromohexane (3.27 g, 19.80 mmol) was added. The reaction mixture was stirred at room temperature for 15 h. Water (100 ml) was added and the mixture was extracted with ethyl acetate (50 ml×3). The combined organic phases were washed with a dilute HCl solution (50 ml×2), water (100 ml), and brine solution (50 ml), dried over anhydrous Na_2SO_4, filtered and the solvents were removed to dryness. Purification by column chromatography over silica gel eluting with hexane gave a pale yellow viscous oil (4.00 g, 94%): ^1H NMR (300 MHz, $CDCl_3$) δ 0.60 (4H, br s), 0.80 (6H, t, J=6.9 Hz), 1.06–1.18 (12H, m), 1.90–1.95 (4H, m), 7.41 (1H, d, J=8.4 Hz), 7.46–7.48 (2H, m), 7.53 (1H, d, J=8.4 Hz), and 7.66–7.67 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.00, 22.57, 23.65, 29.57, 31.44, 40.15, 55.62, 92.97, 121.13, 121.17, 121.46, 121.63, 126.14, 126.20, 130.14, 132.10, 136.05, 139.14, 139.70, 152.36, and 152.73; HRMSESI m/z: $[M^+]$ calcd for $C_{25}H_{32}BrI$, 538.0727; found, 538.0725.

4.1.3. 2-Bromo-7-(carbazol-9-yl)-9,9-bis-*n*-hexylfluorene (4). A mixture of compound **3** (12.63 g, 23.42 mmol), carbazole (3.92 g, 23.42 mmol), Cu-bronze (0.59 g, 9.37 mmol), and K_2CO_3 (7.45 g, 53.87 mmol) in freshly distilled nitrobenzene (237 ml) was stirred at reflux under N_2 for 24 h. The solvent was removed under reduced pressure. Ammonia solution (100 ml) was added and remained for 15 h. Water (100 ml) was added and the mixture was extracted with CH_2Cl_2 (100 ml×3). The combined organic phases were washed with water (100 ml×2), and brine solution (100 ml), dried over anhydrous Na_2SO_4, filtered, and the solvent were removed to dryness. Purification by column chromatography over silica gel eluting with hexane afforded colorless solids (10.25 g, 70%): mp 62–64 °C; IR (KBr) 3022, 2931, 1598, 1496, 1454, 1221, 817, and 744 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.74–0.84 (10H, m), 1.14–1.22 (12H, m), 1.98–2.03 (4H, m), 7.31–7.36 (2H, m), 7.45 (4H, d, J=3.0 Hz), 7.53–7.58 (4H, m), 7.65 (1H, d, J=8.4 Hz), 7.89 (1H, d, J=7.8 Hz), and 8.19 (2H, d, J=7.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.00, 22.54, 23.85, 29.57, 29.64, 31.50, 40.20, 55.72, 109.73, 119.83, 119.94, 120.40, 120.95, 121.24, 121.46, 121.82, 123.42, 125.94, 126.31, 130.25, 136.81, 139.33, 141.00, 152.25, and 153.25; HRMSESI m/z: $[MH^+]$ calcd for $C_{37}H_{41}NBr$, 578.2417; found, 578.2415.

4.1.4. 2,5-Bis[2-(carbazol-9-yl)-9,9-bis-*n*-hexylfluoren-7-yl]thiophene (5). A mixture of compound **4** (2.04 g, 4.06 mmol), 2,5-thiophenediboronic acid (0.27 g, 1.60 mmol), $Pd(PPh_3)_4$ (0.17 g, 0.15 mmol), and 2 M Na_2CO_3 aqueous solution (17 ml, 34 mmol) in THF (25 ml) was degassed with N_2 for 5 min. The reaction mixture was stirred at reflux under N_2 for 18 h. After being cooled to room temperature, water (50 ml) was added and extracted with CH_2Cl_2 (50 ml×2). The combined organic phases were washed with water (50 ml), and brine solution (50 ml), dried over anhydrous Na_2SO_4, filtered, and the solvents were removed to dryness. Purification by column chromatography over silica gel eluting with a mixture of CH_2Cl_2 and hexane (1:4) followed by recrystallization from a mixture of CH_2Cl_2 and methanol afforded green-yellow solids (1.34 g, 78%): mp 88 °C; IR (KBr) 3045, 2925, 1555, 1492, 1444, 1333, 1226, 1607, 797, and 746 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.80–0.84 (20H, m), 1.15–1.23 (24H, m), 2.06–2.12 (8H, m), 7.31–7.37 (4H, m), 7.43–7.48 (10H, m), 7.55–7.60 (4H, m), 7.69 (2H, s), 7.74 (2H, dd, J=8.2 Hz, J=1.5 Hz), 7.81 (2H, d, J=7.8 Hz), 7.93 (2H, d, J=8.5 Hz), and 8.20 (4H, d, J=7.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.04, 22.57, 23.92, 29.65, 31.53, 40.37, 55.56, 109.81, 119.90, 120.40, 120.85, 121.81, 123.39, 124.09, 124.80, 125.93, 133.52, 136.46, 139.94, 141.05, 144.09, 151.93, and 152.77; HRMSESI *m/z*: [MH^+] calcd for $C_{78}H_{83}N_2S$, 1079.6271; found, 1079.6261.

4.1.5. 2-[2-(Carbazol-9-yl)-9,9-bis-*n*-hexylfluoren-7-yl]thiophene (6). A mixture of compound **4** (5.52 g, 9.54 mmol), 2-thiopheneboronic acid (1.32 g, 10.30 mmol), $Pd(PPh_3)_4$ (0.08 g, 0.07 mmol), and 2 M Na_2CO_3 aqueous solution (40 ml, 80.00 mmol) in THF (60 ml) was degassed with N_2 for 5 min. The reaction mixture was stirred at reflux under N_2 for 18 h. After being cooled to room temperature water (100 ml) was added. The mixture was extracted with CH_2Cl_2 (100 ml×2), washed with water (100 ml), and brine solution (50 ml), dried over anhydrous Na_2SO_4, filtered, and the solvents were removed to dryness. Purification by column chromatography over silica gel eluting with a mixture of CH_2Cl_2 and hexane (1:4) afforded pale yellow solids (4.65 g, 84%): mp 122–124 °C; IR (KBr) 2923, 1596, 1495, 1451, 1334, 1231, 815, and 747 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.78–0.83 (10H, m), 1.13–1.21 (12H, m), 2.03–2.08 (4H, m), 7.15 and 7.16 (1H, AA′BB′, J=3.6 Hz), 7.31–7.36 (3H, m), 7.42–7.48 (5H, m), 7.55–7.58 (2H, m), 7.64 (1H, s), 7.67 (1H, dd, J=8.1 Hz, J=1.8 Hz), 7.78 (1H, d, J=7.8 Hz), 7.91 (1H, d, J=8.7 Hz), and 8.19 (2H, d, J=7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.01, 22.55, 23.89, 29.62, 31.50, 40.33, 55.51, 109.80, 119.87, 120.25, 120.28, 120.38, 120.82, 121.80, 123.06, 123.37, 124.70, 125.15, 125.84, 125.91, 128.11, 133.59, 136.40, 139.84, 139.96, 141.05, 145.01, 151.84, and 152.75; HRMSESI *m/z*: [MH^+] calcd for $C_{41}H_{44}NS$, 582.3189; found, 582.3190.

4.1.6. 2-Bromo-5-[2-(carbazol-9-yl)-9,9-bis-*n*-hexylfluoren-7-yl]thiophene (7). A solution of compound **6** (2.40 g, 4.12 mmol) in a mixture of $CHCl_3$ (20 ml) and acetic acid (20 ml) was degassed with N_2 for 5 min. NBS (0.73 g, 4.14 mmol) was added. The reaction mixture was stirred at room temperature under N_2 for 3 h. Water was added and the mixture was extracted with CH_2Cl_2 (50 ml×2). The combined organic phases were washed with water (100 ml), a dilute $NaHCO_3$ aqueous solution (50 ml), and brine solution (50 ml), dried over anhydrous Na_2SO_4, filtered, and the solvents were removed to dryness. Purification by column chromatography over silica gel eluting with a mixture of CH_2Cl_2 and hexane (1:5) gave light green-yellow solids (2.61 g, 96%): mp 116–118 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 0.78–0.83 (20H, m), 1.13–1.21 (24H, m), 2.01–2.07 (8H, m), 7.09 (2H, d, J=3.9 Hz), 7.17 (2H, d, J=3.9 Hz), 7.31–7.36 (4H, m), 7.40–7.50 (8H, m), 7.51–7.59 (8H, m), 7.77 (2H, d, J=8.1 Hz), 7.91 (2H, d, J=8.4 Hz), and 8.19 (4H, d, J=7.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.00, 22.54, 23.89, 29.60, 31.49, 40.29, 55.54, 109.78, 111.22, 119.91, 120.39, 120.92, 121.81, 123.16, 123.40, 124.83, 125.89, 125.92, 130.90, 132.79, 136.61, 139.74, 140.26, 141.03, 146.46, 151.98, and 152.77; HRMSESI *m/z*: [MH^+] calcd for $C_{41}H_{43}BrNS$, 660.2294; found, 660.2277.

4.1.7. 5,5′-Bis[2-(carbazol-9-yl)-9,9-bis-*n*-hexylfluoren-7-yl]-2,2′-bithiophene (8). A mixture of compound **7** (1.00 g, 1.51 mmol), $NiCl_2$ (1.17 g, 9.06 mmol), Zn powder (0.18 g, 2.72 mmol), PPh_3 (0.24 g, 0.91 mmol), bipyridine (bpy) (0.09 g, 0.60 mmol) in DMAc (12 ml) was degassed with N_2 for 10 min. The reaction mixture was stirred at reflux under N_2 for 22 h. Water (50 ml) was added and the mixture was extracted with CH_2Cl_2 (50 ml×2). The combined organic phases were washed with water (50 ml) and brine solution (50 ml), dried over anhydrous Na_2SO_4, filtered, and the solvent was removed to dryness. Purification by column chromatography over silica gel eluting with a mixture of CH_2Cl_2 and hexane (1:4) followed by recrystallization with a mixture of CH_2Cl_2 and methanol afforded yellow-green solids (0.48 g, 36%): mp 218–220 °C; IR (KBr) 3045, 2926, 1553, 1478, 1492, 1311, 1227, 1161, 798, and 721 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.97–0.83 (20H, m), 1.15–1.27 (24H, m), 2.04–2.10 (8H, m), 7.28–7.33 (6H, m), 7.35 (2H, d, J=2.7 Hz), 7.39–7.47 (8H, m), 7.56 (4H, d, J=6.9 Hz), 7.64 (2H, s), 7.68 (2H, d, J=8.7 Hz), 7.80 (2H, d, J=7.8 Hz), 7.92 (2H, d, J=8.7 Hz), and 8.19 (4H, d, J=7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.03, 22.56, 23.91, 29.64, 31.52, 40.36, 55.54, 109.80, 119.89, 120.38, 120.87, 121.80, 123.38, 123.85, 124.54, 124.79, 125.92, 133.19, 136.49, 136.64, 139.87, 140.04, 141.03, 143.72, 151.94, and 152.77; HRMSESI *m/z*: [MH^+] calcd for $C_{82}H_{85}N_2S_2$, 1161.6149; found, 1161.6135.

4.1.8. 5,5″-Bis[2-(carbazol-9-yl)-9,9-bis-*n*-hexylfluoren-7-yl]-2,2′;5′,2″-terthiophene (9). A mixture of compound **7** (2.50 g, 3.78 mmol), 2,5-thiophenediboronic acid (0.28 g, 1.65 mmol), $Pd(PPh_3)_4$ (0.10 g, 0.09 mmol), and 2 M Na_2CO_3 aqueous solution (15 ml, 30 mmol) in THF was degassed with N_2 for 5 min. The reaction mixture was stirred at reflux under N_2 for 16 h. After being cooled to room temperature water (50 ml) was added and extracted with CH_2Cl_2 (50 ml×2). The combined organic phases were washed with water (50 ml) and brine solution (50 ml), dried over anhydrous Na_2SO_4, filtered, and the solvents were removed to dryness. Purification by column chromatography over silica gel eluting with a mixture of CH_2Cl_2 and hexane (1:4) followed by recrystallization with a mixture of CH_2Cl_2 and methanol afforded orange-yellow solids (1.53 g, 75%): mp 210–212 °C; IR (KBr) 3044, 2920, 1596, 1555, 1478, 1448, 1311, 1228, 1161, 820, and 747 cm^{-1}; ^1H NMR

(300 MHz, $CDCl_3$) δ 0.79–0.83 (20H, m), 1.15–1.28 (24H, m), 2.04–2.10 (8H, m), 7.21 (2H, s), 7.24 (2H, d, *J*=3.6 Hz), 7.31–7.39 (6H, m), 7.43–7.47 (8H, m), 7.56 (4H, d, *J*=6.9 Hz), 7.63 (2H, s), 7.67 (2H, d, *J*=8.7 Hz), 7.79 (2H, d, *J*=8.1 Hz), 7.92 (2H, d, *J*=8.4 Hz), and 8.19 (4H, d, *J*=7.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.00, 22.55, 23.92, 29.63, 31.51, 40.34, 55.55, 109.80, 119.90, 120.38, 120.87, 121.83, 123.40, 123.85, 124.31, 124.67, 124.83, 125.92, 133.15, 136.27, 136.53, 139.87, 140.09, 141.06, 143.93, 151.96, and 152.79; HRMSESI *m*/*z*: [MH^+] calcd for $C_{86}H_{87}N_2S_3$, 1243.6026; found, 1243.5993.

4.1.9. 5-[2-(Carbazol-9-yl)-9,9-bis-*n*-hexylfluoren-7-yl]-2,2′-bithiophene (10). A mixture of compound **7** (2.85 g, 4.31 mmol), 2-thiopheneboronic acid (0.59 g, 4.65 mmol), $Pd(PPh_3)_4$ (0.03 g, 0.03 mmol), and 2 M Na_2CO_3 aqueous solution (20 ml, 40.00 mmol) in THF (30 ml) was degassed with N_2 for 5 min. The reaction mixture was stirred at reflux under N_2 for 18 h. After being cooled to room temperature water (100 ml) was added. The mixture was extracted with CH_2Cl_2 (50 ml×2), washed with water (100 ml) and brine solution (50 ml), dried over anhydrous Na_2SO_4, filtered, and the solvents were removed to dryness. Purification by column chromatography over silica gel eluting with a mixture of CH_2Cl_2 and hexane (1:4) afforded pale yellow solids (1.94 g, 68%): mp 110–114 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 0.78–0.83 (10H, m), 1.14–1.21 (12H, m), 2.03–2.09 (4H, m), 7.08 (1H, t, *J*=4.3 Hz), 7.22 (1H, d, *J*=3.1 Hz), 7.26 (2H, d, *J*=4.8 Hz), 7.31–7.36 (3H, m), 7.43–7.51 (4H, m), 7.56 (2H, d, *J*=6.9 Hz), 7.62 (1H, s), 7.66 (1H, d, *J*=7.8 Hz), 7.78 (1H, d, *J*=7.8 Hz), 7.91 (1H, d, *J*=8.4 Hz), and 8.19 (2H, d, *J*=7.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.01, 22.55, 23.90, 29.63, 31.51, 40.33, 55.54, 109.80, 119.89, 120.34, 120.38, 120.57, 120.84, 121.81, 123.39, 123.63, 123.70, 124.41, 124.68, 124.81, 125.87, 125.92, 127.91, 133.24, 126.48, 136.61, 137.50, 139.90, 139.99, 141.05, 143.70, 151.92, and 152.78; HRMSESI *m*/*z*: [MH^+] calcd for $C_{45}H_{46}NS_2$, 664.3066; found, 664.3049.

4.1.10. 5-Bromo-5′-[2-(carbazol-9-yl)-9,9-bis-*n*-hexylfluoren-7-yl]-2,2′-bithiophene (11). A solution of compound **10** (1.19 g, 1.79 mmol) in a mixture of $CHCl_3$ (40 ml) and acetic acid (40 ml) was degassed with N_2 for 5 min NBS (0.30 g, 1.71 mmol) was added. The reaction mixture was stirred at room temperature under N_2 for 3 h. Water (50 ml) was added and the mixture was extracted with CH_2Cl_2 (50 ml×2). The combined organic phases were washed with water (100 ml), a dilute $NaHCO_3$ aqueous solution (50 ml), and brine solution (50 ml), dried over anhydrous Na_2SO_4, filtered, and the solvents were removed to dryness. Purification by column chromatography over silica gel eluting with a mixture of CH_2Cl_2 and hexane (1:6) gave yellow solids (1.05 g, 73%): mp 104–105 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 0.78–0.83 (10H, m), 1.13–1.28 (12H, m), 2.03–2.08 (4H, m), 7.01 and 7.04 (2H, AA′BB′, *J*=3.9 Hz), 7.15 (1H, d, *J*=3.9 Hz), 7.31–7.36 (3H, m), 7.42–7.47 (4H, m), 7.56 (1H, s), 7.58 (1H, d, *J*=6.6 Hz), 7.64 (1H, d, *J*=7.8 Hz), 7.78 (1H, d, *J*=6.6 Hz), 7.91 (1H, d, *J*=8.7 Hz), and 8.19 (2H, d, *J*=7.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.01, 22.55, 23.90, 29.62, 31.50, 40.32, 55.55, 109.79, 110.95, 119.91, 120.39, 120.89, 121.81, 123.39, 123.65, 123.72, 124.88, 124.93, 125.88, 125.93, 130.73, 132.99, 135.46, 138.98, 139.81, 140.18, 141.03, 144.24, 151.95, and 152.78; HRMSESI *m*/*z*: [MH^+] calcd for $C_{45}H_{45}BrNS_2$, 742.2171; found, 742.2152.

4.1.11. 5,5‴-Bis[2-(carbazol-9-yl)-9,9-bis-*n*-hexylfluoren-7-yl]-2,2′;5′,2″;5″,2‴-quaterthiophene (12). A mixture of compound **11** (0.225 g, 0.30 mmol), $NiCl_2$ (0.23 g, 1.80 mmol), Zn powder (0.035 g, 0.54 mmol), PPh_3 (0.05 g, 0.18 mmol), bipyridine (bpy) (0.02 g, 0.12 mmol) in DMAc (5 ml) was degassed with N_2 for 10 min. The reaction mixture was stirred at reflux under N_2 for 24 h. Water (50 ml) was added and the mixture was extracted with CH_2Cl_2 (50 ml×2). The combined organic phases were washed with water (50 ml) and brine solution (50 ml), dried over anhydrous Na_2SO_4, filtered, and the solvent was removed to dryness. Purification by column chromatography over silica gel eluting with a mixture of CH_2Cl_2 and hexane (1:5) followed by recrystallization with a mixture of CH_2Cl_2 and methanol afforded orange solids (0.12 g, 59%): mp 206–208 °C; IR (KBr) 3047, 2928, 1596, 1555, 1492, 1448, 1311, 1230, 1160, 797, and 746 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.80–0.85 (20H, m), 1.16–1.21 (24H, m), 2.05–2.11 (8H, m), 7.16, and 7.18 (4H, AA′BB′, *J*=3.6 Hz), 7.23 (2H, d, *J*=3.6 Hz), 7.32–7.34 (6H, m), 7.44–7.49 (8H, m), 7.58–7.59 (4H, m), 7.65 (2H, s), 7.66 (2H, d, *J*=8.1 Hz), 7.78 (2H, d, *J*=7.8 Hz), 7.92 (2H, d, *J*=8.4 Hz), 8.21 (4H, d, *J*=7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.06, 22.59, 23.94, 29.66, 31.54, 40.36, 55.56, 109.82, 119.87, 119.92, 120.42, 120.90, 121.81, 123.41, 123.87, 124.32, 124.44, 124.74, 124.84, 125.88, 125.95, 133.12, 135.88, 136.18, 136.43, 136.52, 139.86, 140.10, 141.04, 143.95, 151.96, and 152.79; HRMSESI *m*/*z*: [MH^+] calcd for $C_{90}H_{89}N_2S_4$, 1325.5903; found, 1325.5865.

4.1.12. 7,7′-Dibromo-2,2′-bis(9,9-bis-*n*-hexylfluorene) (14). A solution of compound **13** (1.91 g, 2.86 mmol) and iodine (12 mg) in $CHCl_3$ (50 ml) was cooled to 0 °C in an ice water bath. Bromine (0.32 ml, 6.26 mmol) was added. The reaction mixture was stirred at room temperature in the dark for 18 h. A $Na_2S_2O_3$ aqueous solution was added and the mixture was extracted with $CHCl_3$ (50 ml×2). The combined organic phases were washed with water (50 ml×2) and brine solution (50 ml), dried over anhydrous Na_2SO_4, filtered, and the solvent was removed to dryness. Purification by column chromatography over silica gel eluting with hexane gave white solid (1.90 g, 80%): ^1H NMR (300 MHz, $CDCl_3$) δ 0.77–0.82 (12H, m), 0.57–0.62 (8H, m), 1.07–1.15 (24H, m), 1.90–1.95 (8H, m), 7.47 (4H, d, *J*=1.5 Hz), 7.56–7.61 (6H, m), 7.74 (2H, d, *J*=1.5 Hz).[29]

4.1.13. 7,7′-Bis(carbazol-9-yl)-2,2′-bis(9,9-bis-*n*-hexylfluorene) (15). A mixture of compound **14** (0.10 g, 0.13 mmol), carbazole (0.05 g, 0.33 mmol), Cu-bronze (4 mg, 0.06 mmol), and K_2CO_3 (0.07 g, 0.53 mmol) in a freshly distilled nitrobenzene (10 ml) was stirred at reflux under N_2 for 16 h. After being cooled to room temperature the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (50 ml) and water (50 ml), and the mixture was extracted with CH_2Cl_2 (50 ml×2). The combined organic phases were washed with water (50 ml×2) and brined solution (50 ml), dried over anhydrous Na_2SO_4, filtered, and the solvents were removed to dryness. Purification by column chromatography over silica gel eluting with a mixture of CH_2Cl_2 and hexane (1:4) followed by recrystallization with a mixture of CH_2Cl_2 and methanol afforded white solids (0.10 g, 83%): mp 196 °C; IR (KBr) 3057, 2926, 1597, 1495, 1463, 1334, 1230, 818, and 749 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.83 (12H, t, J=7.2 Hz), 0.87–0.92 (8H, m), 1.17–1.22 (24H, m), 2.07–2.18 (8H, m), 7.32–7.37 (4H, m), 7.44–7.51 (8H, m), 7.59–7.61 (4H, m), 7.72 (2H, s), 7.75 (2H, d, J=8.1 Hz), 7.90 (2H, d, J=7.8 Hz), 7.97 (2H, d, J=7.4 Hz), and 8.20 (4H, d, J=7.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.02, 22.55, 23.96, 29.64, 31.52, 40.32, 55.57, 109.83, 119.88, 120.18, 120.39, 120.87, 121.51, 121.89, 123.39, 125.86, 125.92, 126.40, 139.64, 140.10, 140.74, 141.09, 151.86, and 152.87; HRMSESI *m/z*: [MH^+] calcd for $C_{74}H_{81}N_2$, 997.6394; found, 997.6409.

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