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Synthesis and properties of *N*-carbazole end-capped conjugated molecules

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Abstract—A series of novel *N*-carbazole end-capped π-conjugated molecules were synthesized by a divergent approach with the use of bromination, Suzuki cross-coupling, and Ullmann reactions and their physical properties were investigated. In dilute solution, UV–vis absorption spectra displayed bathochromic shift with respect to their conjugated backbones, and photoluminescence spectra showed emission maxima in the blue region. Thermal analysis revealed that they are thermally stable semi-crystalline and amorphous materials. All molecules exhibited good electrochemical stability with high-lying HOMO energy levels and have potential applications as hole-transporting and light-emitting layers in organic light-emitting diodes or as host materials for electrophosphorescent applications.

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1. Introduction

π-Conjugated small molecules have attracted much attention in the area of organic chemistry and material science. They have some very interesting electronic and optical properties and have been investigated as advanced molecular electronic materials.[1–3] π-Conjugated thiophene-based oligomers have earlier been used as model compounds for polymers[4] and have recently attracted interest as the sole active components in devices.[5,6] The advantages of oligomers are that their physical properties can be easily tuned to the desired properties by changing the structure e.g. solubilizing chains, end-capping groups, insertion of certain groups, and different oligomer lengths. Much synthetic effort has been focused on improving physical characteristics of the oligothiophene-based compounds.[7,8] Due to its unique photo, electrical, and chemical properties, carbazole has been widely used as a functional building block or substituent in the construction of organic photoconductors,[9] non-linear optic (NLO) materials,[10] hole-transport, and light-emissive materials for OLED devices[11] and as host materials for phosphorescence applications.[12] Moreover, thermal stability and glassy state durability of organic molecules were found to be significantly improved upon incorporation of a carbazole moiety in the structure.[13] To our best knowledge, there is no report on *N*-carbazole end-capped bisthiophenyl derivatives, the synthesis and physical properties of which still remain to be explored.

In this paper, we accomplished the synthesis of novel *N*-carbazole end-capped π-conjugated bisthiophenyl derivatives, aiming at investigating how their optical, thermal, and electrochemical properties were affected by the molecular structure of the conjugated backbones.

2. Results and discussion

2.1. Synthesis and characterization

Scheme 1 shows a synthetic route to the carbazole end-capped π-conjugated molecules **CTB**, **CTC**, **CTF**, and **CT** using a divergent approach in which the desired molecules were constructed in an outward direction stepwise from the cores, end-capping with the carbazole units in the final step. Different cores of dialkoxybenzene **1**, alkylcarbazole **6**, and dialkylfluorene **11**, were used and synthesized as described in the literature. The alkyl substituents would provide good solubility to the desired products in common organic solvents. They were first treated with either Br_2 solution or *N*-bromosuccinimide (NBS) as brominating reagents to give their corresponding dibromo compounds **2**, **7**, and **11** in high yields. Attachment of thiophene units to both ends of each molecule was accomplished by coupling of the resultant dibromo compounds **2**, **7**, and **11** with

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Keywords: Carbazole end-cap; π-Conjugated molecules; Ullmann coupling; Hole-transport; Organic light-emitting diodes.

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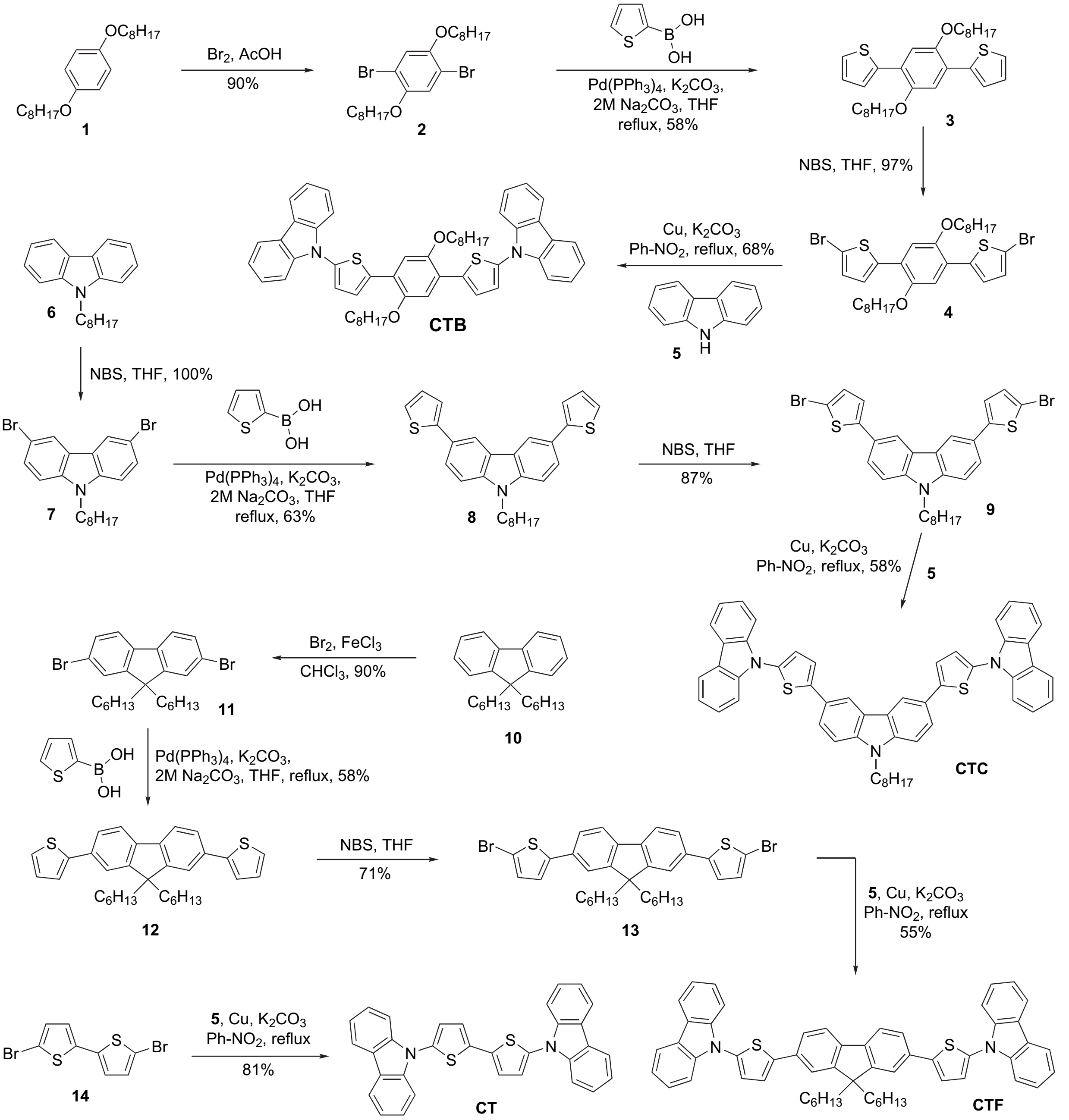

Scheme 1. Synthetic route to the target π-conjugated molecules.

2-thiopheneboronic acid under Suzuki cross-coupling conditions. The reaction was performed using $Pd(PPh_3)_4$ as a catalyst and an aqueous solution of Na_2CO_3 as base in THF. The corresponding thiophene capped products **3**, **8**, and **12** were isolated in reasonable yields (58–63%). Individually, they were subsequently chemoselectively brominated with NBS in THF, in which only the most nucleophilic 5-positions of both terminal thiophene rings reacted to give the corresponding dibromo compounds **4**, **9**, and **13** in good yields. Then, coupling of the resulting dibromine compounds **4**, **9**, and **13** with an excess carbazole (**5**) under Ullmann amination reaction conditions in the presence of Cu-bronze as catalyst and K_2CO_3 as base, in a refluxing nitrobenzene afforded the target *N*-carbazole-capped products, **CTB**, **CTC**, and **CTF**, in 68, 58, and 55% yields, respectively. For comparison purposes, compound **CT** was also prepared using similar Ullmann coupling reaction and was isolated in 71% yield. All target molecules **CTB**, **CTC**, **CTF**, and **CT** are soluble in all common organic solvents and their structures were confirmed by IR, ^1H NMR, ^{13}C NMR, and HRMS spectrometric methods.

2.2. Optical properties

The optical properties of all π-conjugated molecules were investigated by UV–vis and photoluminescence spectroscopies in a dilute CH_2Cl_2 solution as shown in Figure 1 and summarized in Table 1. Normalized absorption spectra of **CTB**, **CTC**, **CTF**, and **CT** exhibit two major absorption bands, an absorption band at 292 nm assigned to the π–π*

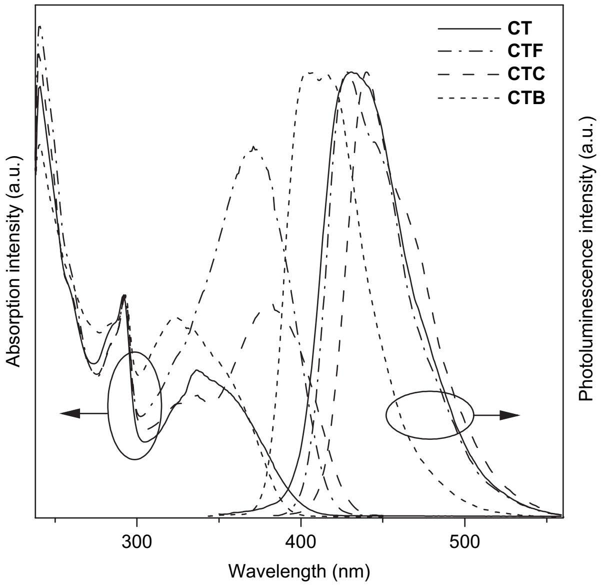

Figure 1. Optical properties of π-conjugated molecules measured in CH_2Cl_2 solution (~10^{-5} M).

electron transition of the end-capped carbazole units and a broader absorption band at longer wavelength corresponding to the π–π* transition of the entire π-conjugated backbone. Compound **CT** bearing a dithiophene unit as a core shows absorption bands at 292 and 336 nm, while compounds **CTF** and **CTB** having aromatic fluorene and phenylene units in between these two thiophene rings show a red shift of the latter band to 371 and 381 nm, respectively. This indicates that the additional fluorenyl and phenyl moieties have increased the degree of π-conjugation of the system by lowering the HOMO and LUMO energy levels of the backbones. On the other hand, it is blue shifted to 323 nm when the carbazole unit is introduced into the system in compound **CTC**. An explanation for the different electronic absorption behaviors of these compounds would be that in the case of compound **CTC**, it can be recognized as two thiophene rings being linked by a *m*-biphenyl unit, therefore there is no long-range conjugation. The conjugation segment can probably be best described as 5-(4-aminophenyl)thiophen-2-amine structure as illustrated in Figure 2. On the contrary, in compounds **CTB** and **CTF** the two thiophene rings are linked by *p*-phenyl and *p*-biphenyl units, respectively, therefore delocalization of π-electrons can extend over the whole molecule. The longest conjugation segments for compounds **CTB** and **CTF** are bisthiophenylbenzene and bisthiophenylfluorene, respectively. In fact, the absorption spectrum of **CTB** is around 10 nm red shifted with respect to that of **CTF**. This bathochromic shift is a consequence of the degree of free rotation about 1,4-positions of benzene rings in **CTB**, which is greater than that about 2,7-positions of fluorene unit in **CTF**. As a result, π-electrons can be easily delocalized along the bisthiophenylbenzene backbone of **CTB** leading to a decrease in the energy gap (Table 1) or a red shift of the absorption spectrum.

Photoluminescence spectra of π-conjugated molecules **CTB**, **CTC**, **CTF**, and **CT** are located in blue region with their emission maxima at 440, 403, 428, and 430 nm, respectively (Fig. 1 and Table 1). In fact, the introduction of the carbazole moieties at terminal of the conjugated backbone would result in a less planar molecule by means of the plane of the carbazole unit being nearly perpendicular to that of the backbone. However, in view of the absorption and photoluminescence spectra, the absorption bands and maxima of **CTF** were red shifted (~35 nm) relative to those of its corresponding bisthiophenylfluorene **12** (Fig. 3). There is a substantial red shift of the absorption and the emission maxima of bisthiophenylfluorene core upon incorporation of strong electron donating carbazole groups at both ends. This suggests that there is π-electron conjugation through the lone electron pair at the nitrogen atom of the carbazole end-caps and that π-electrons are delocalized over the entire conjugated backbone, which is attributed to the asymmetric destabilization of the HOMO and LUMO energy levels leading to the decrease of the energy gap. Moreover, upon excitation either at 292 nm attributed to the absorption of carbazole moiety or at 350 nm corresponding to the absorption of the conjugated backbone, the emission spectra obtained are identical, indicating that energy or electrons can efficiently transfer from the peripheral carbazole to the inner backbone.

2.3. Electrochemical properties

In order to investigate the redox properties of these π-conjugated molecules and their HOMO and LUMO energy levels, cyclic voltammetry (CV) analysis was performed. The measurements were carried out in CH_2Cl_2 solution containing 0.1 M *n*-Bu_4NPF_6 as supporting electrolyte using three-electrode systems under an argon atmosphere. The reference electrode was Ag/Ag^+. The results are shown in Figure 4 and

Table 1. Summary of physical measurements of π-conjugated molecules

Compd	λ_{abs}[a] (nm)	λ_{lum}[b] (nm)	λ_{onset}[a] (nm)/E_g[c] (eV)	$T_g/T_c/T_m/T_d$[d] (°C)	$E_{1/2}/\Delta E$[e] (V)	HOMO[f] (eV)	LUMO[g] (eV)
CTB	292, 381	440	428/2.90	NA/116/197/430	0.95/0.335, 1.24/0.337	5.23	2.33
CTF	292, 371	428	416/2.98	85/NA/NA/425	1.07/0.153, 1.63/0.130	5.43	2.45
CTC	293, 323	403	390/3.18	98/NA/NA/427	0.95/0.244, 1.27/0.276, 1.45/0.249, 1.70/0.232	5.30	2.12
CT	291, 336	430	402/3.08	78/141/209/379	0.98/0.398, 1.24/0.337	5.24	2.16

[a] Measured in a dilute CH_2Cl_2 solution (~10^{-5} M).

[b] Excited at the absorption maxima.

[c] Estimated from the onset of absorption (E_g=1240/λ_{onset}).

[d] Obtained from DSC and TGA measurements with a heating rate of 10 °C/min under N_2.

[e] Measured using a glassy carbon electrode as a working electrode, a platinum rod as a counter electrode, and Ag/Ag^+ as a 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 under an argon atmosphere.

[f] Calculated using the empirical equation: HOMO=(4.44+E_{onset}).

[g] Calculated from LUMO=HOMO−E_g.

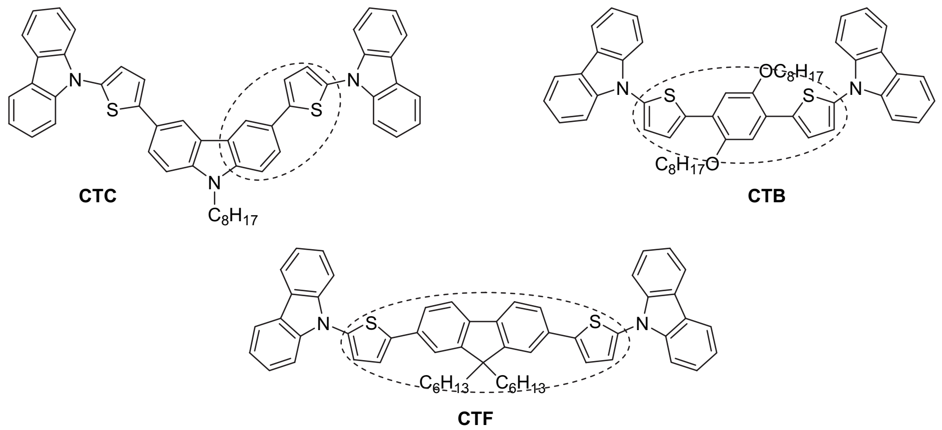

Figure 2. Chemical structures of compounds **CTB**, **CTF**, and **CTC**. The longest π-conjugation is enclosed in a dashed ellipsoid.

summarized in Table 1. In the case of compound **CTC** possessing the least conjugation length, the cyclic voltammogram showed four chemically quasi-reversible oxidation processes, while the CV curves of compounds **CTB**, **CTF**, and **CTC** exhibit two chemically quasi-reversible oxidation processes. During the successive oxidation cycles of all compounds a slight shift of the CV curves was observed indicating a weak oxidative coupling at 3,6-positions of the peripheral carbazole moieties (Fig. 5). This is usually detected in most carbazole derivatives with open 3,6-positions. However, no additional peak at lower potential on the re-reduction process (E_{pc}) due to the electropolymerization of these carbazole end-capped molecules was detected as in the case of bis{2-[4-(*N*-carbazolyl)phenyl]-1,3,4-oxadiazol-5-yl}-9,9-dihexylfluorene.[14] In all samples, no distinct reduction process was observed. The first oxidation processes can be attributed to the removal of electrons from the peripheral carbazole units and the other reversible processes corresponding to removal of electrons from the interior moieties. Their first oxidation values are slightly affected by the length and structure of the conjugated backbones, with compound **CTF** having the highest first oxidation potential of 1.07 V. However, these first potential values are slightly smaller than that of carbazole ($E_{1/2}$=1.09 V), suggesting that the incorporation of carbazole ring makes the resulting molecules more susceptible for electrochemical oxidation. The HOMO energy levels were calculated from the onset of oxidation potential (E_{onset}) according to an empirical formula, HOMO=(4.44+E_{onset}) (eV).[15] The LUMO energy levels were calculated by subtracting the HOMO energy levels with the energy band gaps estimated from the onset of UV–vis absorption. The results are tabulated in Table 1. The HOMO energy levels of these π-conjugated molecules are in the range of 5.23–5.43 eV and this greatly reduce the energy barrier for the hole injection from ITO (ϕ=4.80 eV) to the emissive Alq$_3$ (ϕ=5.80 eV). As a result, all compounds **CTB**, **CTC**, **CTF**, and **CT** showing chemically reversible oxidation processes and high-lying HOMO

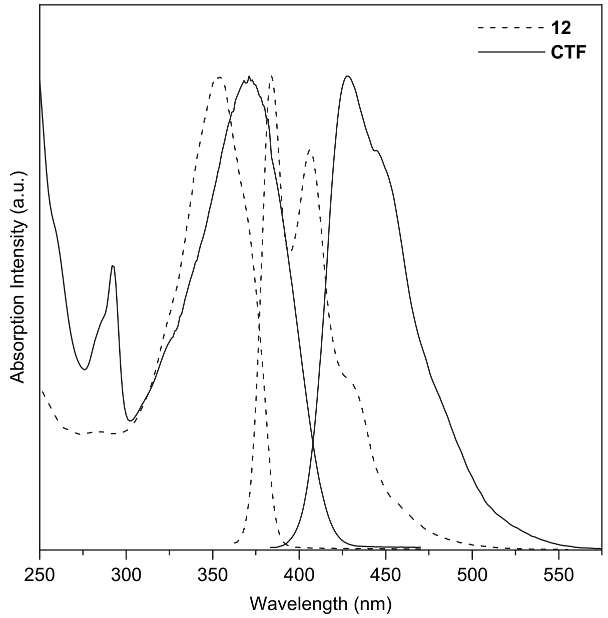

Figure 3. Absorption and photoluminescence spectra of **CTF** and **12** measured in CH$_2$Cl$_2$.

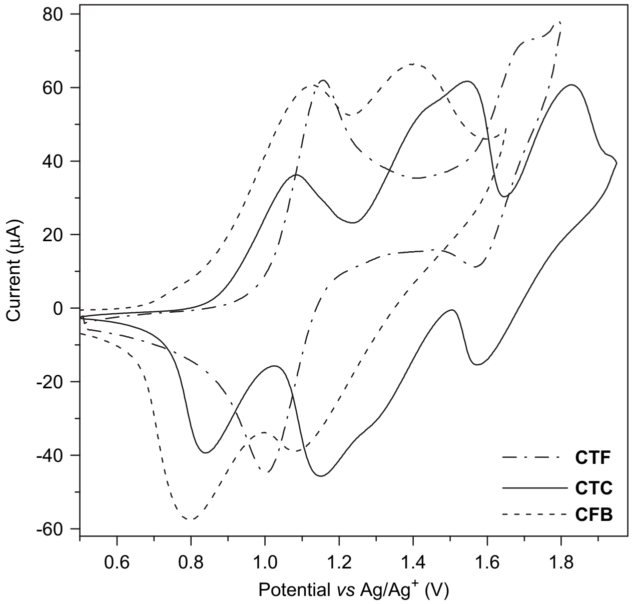

Figure 4. Cyclic voltammetry curves of compounds **CTC** and **CTB** in CH$_2$Cl$_2$ containing n-Bu$_4$NPF$_6$ electrolyte at a scan rate of 50 mV/s under an argon atmosphere.

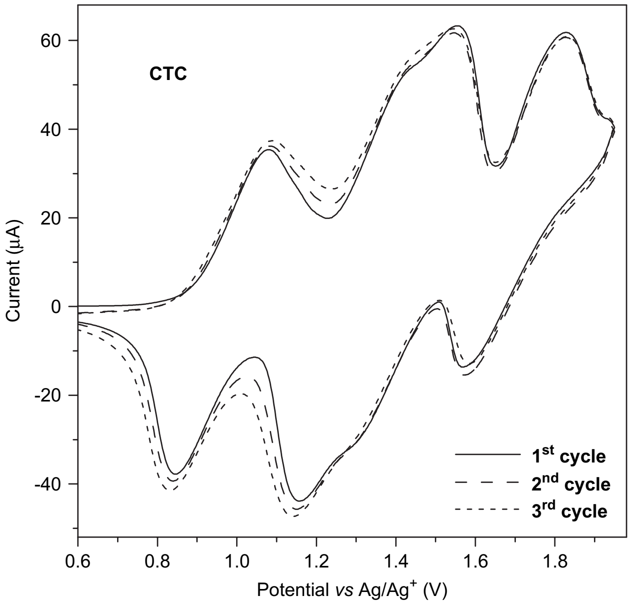

Figure 5. The successive cyclic voltammetry curves of **CTC** measured in CH_2Cl_2 at a scan rate of 50 mV/s.

energy levels can be good and stable hole-transport and injection materials for double-layer OLED. This may be a benefit arising from incorporation of the carbazole end-caps.

2.4. Thermal properties

Thermal properties of the π-conjugated molecules are shown in Figure 6 and summarized in Table 1. The results reveal that all π-conjugated molecules exhibit high thermal stability with the onset of decomposition temperatures in the range of 379–430 °C under a nitrogen atmosphere. DSC measurements show that both **CTB** and **CT** are semi-crystalline. During the first heating cycle of **CTB** and **CT**, sharp endothermic melting peaks at 197 and 209 °C, respectively, were observed. When the samples were cooled down from the melt at a cooling rate of 50 °C/min, the samples spontaneously formed a glassy state. When the amorphous glassy samples were heated again, an endothermic phenomenon at 78 °C, at which point the glassy state changed into the supercooled liquid state (T_g), was observed for compound **CT**. Then broad exothermic peaks due to the crystallization were observed in both samples around 116 and 141 °C, respectively, to give the same crystals as observed by crystallization from solution, which melted at 197 and 209 °C, respectively. Moreover, when the crystalline sample of **CTF** prepared by crystallization from a mixture of dichloromethane and methanol was heated, the endothermic peak due to melting was observed at 149 °C. This was no longer detected during the second heating scan and only an endothermic baseline shift due to glass transition was observed at 81 °C, and on further heating no peaks due to the crystallization and melting appeared. However, compound **CTC** behaves in a totally different manner. Only the glass transition at about 98 °C can be seen in repeated DSC heating cycles with no crystallization and melting peaks observed. This unique thermal behavior of **CTC** may arise from its V-shape structure. The thermal and morphological stabilities of all compounds may benefit from the presence of carbazole moieties at both ends. The ability of **CTC** and **CTF** to form a molecular glass and the possibility to prepare thin films from **CTC** and **CTF** both by evaporation and by solution casting are highly desirable for applications in OLEDs and OFETs.

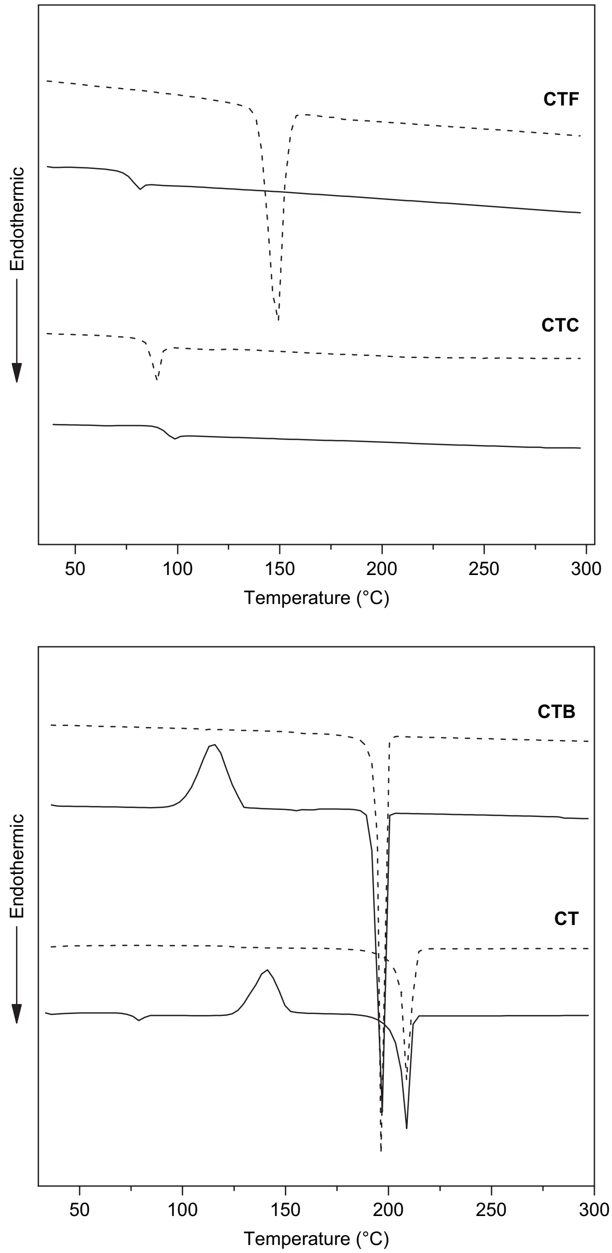

Figure 6. DCS traces of π-conjugated molecules measured under nitrogen atmosphere at heating rate of 10 °C/min: first heating (dotted lines) and second heating (solid lines).

3. Conclusions

The properties of novel *N*-carbazole end-capped π-conjugated molecules prepared by a divergent approach using a combination of bromination, Suzuki cross-coupling, and Ullmann coupling reactions were investigated. Their optical, thermal, and electrochemical properties are strongly influenced by molecular structure of the inner conjugated backbone. All molecules exhibit good electrochemical reversibility and have the potential to be good hole-transporting and light-emitting layers in organic light-emitting diodes or as host materials for electrophosphorescent applications. Attachment of carbazole via its *N*-position might be an effective way to make amorphous materials with low oxidation potential for optoelectronic applications by forming dicarbazole end-capped or carbazole dendritic structures with other fluorescent or non-fluorescent backbones.

4. Experimental

4.1. General procedures

Tetrahydrofuran (THF) was refluxed with sodium and benzophenone, and distilled. Nitrobenzene and $CHCl_3$ were distilled from CaH_2 prior to use. CH_2Cl_2 for cyclic voltammetry analysis was washed with concd H_2SO_4 and distilled twice from CaH_2. 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 with TMS as an internal reference using $CDCl_3$ as solvent in all cases. IR spectra were measured on a Perkin–Elmer FT-IR spectroscopy spectrum RXI spectrometer as KBr disc. UV–vis spectra were recorded as a dilute solution in spectroscopic grade CH_2Cl_2 on a Perkin–Elmer UV Lambda 25 spectrometer. Photoluminescence spectra were recorded with a Perkin–Elmer LS 50B Luminescence Spectrometer as a dilute solution in spectroscopic grade CH_2Cl_2. Differential scanning calorimetry (DSC) analysis was performed on a METTLER DSC823e thermal analyzer under N_2 atmosphere. Samples were scanned from 25 to 430 °C at a heating rate of 10 °C/min then rapidly cooled to 25 °C and heated at the same heating rate to 430 °C. Thermogravimetric analysis (TGA) was carried out on a Seiko EXSTAR 6000 TG/DTA 6300 thermal analyzer at heating rate of 10 °C/min under N_2 atmosphere. 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 was CH_2Cl_2 with n-Bu_4NPF_6 (0.1 M) as a supporting electrolyte. The concentration of the samples was 0.9–1.0 mM and the scan rate was 50 mV/s. High resolution mass spectrometry (HRMS) analysis was performed by Mass Spectrometry Unit, Chulabhorn Research Institute (CRI) of Thailand using a Micro TOF Brüker. The synthesis of compounds 1,4-bis(2-ethylhexyloxy)benzene (**1**), 1,4-dibromo-2,5-bis(2-ethylhexyloxy)benzene (**2**),[16] 9-(2-ethylhexylcarbazole) (**6**), 3,6-dibromo-9-(2-ethylhexyl)carbazole (**7**),[17] 9,9-bis-*n*-hexylfluorene (**10**), and 2,7-dibromo-9,9-bis-*n*-hexylfluorene (**11**)[18] was performed according to or slightly modified literature procedures.

4.2. Synthetic procedures

4.2.1. Synthesis of 1,4-bis(thiophen-2-yl)-2,5-bis(2-ethylhexyloxy)benzene (3). A mixture of **2** (4.95 g, 10.05 mmol), 2-thiopheneboronic acid (2.83 g, 22.10 mmol), $Pd(PPh_3)_4$ (0.2 g, 0.17 mmol), and 2 M Na_2CO_3 aqueous solution (23 ml, 46 mmol) in THF (35 ml) was stirred at reflux under N_2 atmosphere for 24 h. CH_2Cl_2 (150 ml) and water (150 ml) were added. The organic phase was separated, washed with water (100 ml), brine solution (100 ml), dried over anhydrous Na_2SO_4, filtered, and the solvents removed to dryness. Purification by column chromatography using silica gel eluting with hexane gave yellow-green solids. Yield was 2.91 g, (58%); IR (KBr) 2956, 1494, 1436, 1213, 1037, 826, and 689 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.95–1.00 (12H, m), 1.34–1.65 (16H, m), 1.82–1.88 (2H, m), 3.99 (4H, d, J=5.4 Hz), 7.12 (2H, dd, J=5.2 Hz, J=3.6 Hz), 7.28 (2H, s), 7.36 (2H, d, J=5.2 Hz), and 7.54 (2H, d, J=3.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.19, 14.08, 23.05, 24.06, 29.14, 30.66, 39.66, 71.89, 112.79, 122.95, 125.26, 125.56, 126.67, 139.38, and 149.40; HRMS-ESI *m/z*: [MH^+] calcd for $C_{30}H_{43}O_2S_2$, 499.2699; found, 499.2703.

4.2.2. Synthesis of 1,4-bis(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyloxy)benzene (4). *N*-Bromosuccinimide (0.93 g, 5.25 mmol) was added in small portions to a solution of **3** (1.20 g, 2.60 mmol) in THF (50 ml). The mixture was stirred at room temperature under N_2 atmosphere for 1 h. Water (100 ml) and CH_2Cl_2 (100 ml) were added. The organic phase was separated, washed with water (100 ml), brine solution (100 ml), dried over anhydrous Na_2SO_4, filtered and the solvents removed to dryness. Purification by column chromatography using silica gel eluting with hexane gave yellow solids. Yield was 1.63 g (97%); IR (KBr) 2956, 1494, 1436, 1213, 1037, 826 and 689 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.91–1.00 (14H, m), 1.30–1.63 (16H, m), 1.84–1.90 (2H, m), 3.97 (4H, d, J=5.7 Hz), 7.05 (2H, d, J=4.0 Hz), 7.18 (2H, s), and 7.26 (2H, d, J=4.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.17, 14.08, 23.04, 24.04, 29.15, 30.68, 39.58, 72.12, 111.46, 113.01, 122.47, 124.78, 129.30, 140.43, and 149.17; HRMS-ESI *m/z*: [MH^+] calcd for $C_{30}H_{41}O_2S_2Br_2$, 655.0909; found, 655.0904.

4.2.3. Synthesis of 1,4-bis[5-(carbazol-9-yl)thiophene-2-yl]-2,5-bis(2-ethylhexyloxy)benzene (CTB). A mixture of **4** (1.36 g, 2.07 mmol), carbazole (1.04 g, 6.21 mmol), K_2CO_3 (1.16 g, 8.41 mmol), and Cu-bronze (0.13 g, 2.07 mmol) in nitrobenzene (20 ml) was stirred at reflux under N_2 atmosphere for 18 h. After removal of the solvent in vacuo, ammonia solution (50 ml) was added and the mixture was left to stand for 2 h. CH_2Cl_2 (150 ml) and water (100 ml) were added. The organic phase was separated, washed with water (100 ml×2), brine solution (100 ml), dried over anhydrous Na_2SO_4, filtered, and the solvent removed to dryness. Purification by column chromatography using silica gel eluting with a mixture of CH_2Cl_2 and hexane followed by recrystallization with hexane afforded white solids. Yield was 1.17 g (68%); IR (KBr) 2915, 1553, 1509, 1443, 1207, 1026, 750, and 639 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.78 (6H, t, J=6.9 Hz), 0.96 (6H, t, J=7.5 Hz), 1.26–1.65 (20 H, m), 1.86–1.90 (2H, m), 4.07 (4H, d, J=5.7 Hz), 7.24 (2H, d, J=3.9 Hz), 7.32–7.37 (6H, m), 7.46–7.52 (4H, m), 7.61 (6H, d, J=8.1 Hz), and 8.14 (4H, d, J=7.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.21, 14.02, 23.03, 24.07, 29.10, 30.71, 39.63, 72.09, 110.36, 112.02, 120.18, 120.54, 123.56, 123.96, 124.28, 126.23, 137.25, 141.92, and 149.54; HRMS-ESI *m/z*: [MH^+] calcd for $C_{54}H_{57}N_2O_2S_2$, 829.3856; found, 829.3839.

4.2.4. Synthesis of 3,6-bis(thiophen-2-yl)-9-(2-ethylhexyl)carbazole (8). A mixture of **7** (5.20 g, 11.89 mmol), 2-thiopheneboronic acid (3.35 g, 26.17 mmol), $Pd(PPh_3)_4$ (0.2 g, 0.17 mmol), and 2 M Na_2CO_3 aqueous solution (23 ml, 46 mmol) in THF (35 ml) was stirred at reflux under N_2 atmosphere for 24 h. Water (150 ml) and CH_2Cl_2 (150 ml) were added. The organic phase was separated, washed with water (150 ml), brine solution (100 ml), dried over anhydrous Na_2SO_4, filtered, and the solvents removed to dryness. Purification by column chromatography using silica gel eluting with hexane gave light green solids. Yield was 3.32 g (63%); IR (KBr) 2955, 1601, 1484, 1291, 1221, 850, and 681 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.88–0.98 (6H, m), 1.27–1.47 (8H, m), 2.07–2.11 (1H, m), 4.16 (2H, dd, J=7.8 Hz, J=1.8 Hz), 7.14 (2H, dd, J=5.1 Hz, J=3.6 Hz), 7.29 (2H, dd, J=5.1 Hz, J=1.2 Hz), 7.38–7.40 (4H, m), 7.75 (2H, dd, J=8.4 Hz, J=1.8 Hz), and 8.36 (2H, d, J=1.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.91, 14.03, 23.04, 24.43, 28.84, 31.04, 39.47, 47.63, 109.46, 117.94, 122.12, 123.20, 123.71, 124.59, 125.92, 128.00, 140.91, and 145.67; HRMS-ESI m/z: [MH^+] calcd for $C_{28}H_{30}NS_2$, 444.1814; found, 444.1817.

4.2.5. Synthesis of 3,6-bis(5-bromothiophen-2-yl)-9-(2-ethylhexyl)carbazole (9). *N*-Bromosuccinimide (2.96 g, 16.67 mmol) was added in small portions to a solution of **8** (3.7 g, 8.33 mmol) in THF (70 ml). The mixture was stirred at room temperature under N_2 for 1 h. Water (100 ml) and CH_2Cl_2 (150 ml) were added. The organic phase was separated, washed with water (100 ml), brine solution (100 ml), dried over anhydrous Na_2SO_4, filtered, and the solvents removed to dryness. Purification by column chromatography using silica gel eluting with hexane gave gray solids. Yield was 4.36 g (87%); IR (KBr) 2955, 1601, 1484, 1291, 1221, 850, and 681 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.88–0.96 (6H, m), 1.26–1.45 (8H, m), 2.03–2.06 (1H, m), 4.09 (2H, dd, J=7.8 Hz, J=2.1 Hz), 7.08 (4H, AA′BB′, J=5.7 Hz, J=3.9 Hz), 7.32 (2H, d, J=8.4 Hz), 7.61 (2H, dd, J=8.4 Hz, J=1.5 Hz), and 8.18 (2H, d, J=1.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.89, 14.03, 23.04, 24.41, 28.82, 31.02, 39.46, 47.61, 109.61, 109.97, 117.60, 122.18, 123.07, 124.24, 125.22, 130.83, 141.01, and 147.08; HRMS-ESI m/z: [MH^+] calcd for $C_{28}H_{28}Br_2NS_2$, 600.0024; found, 600.0025.

4.2.6. Synthesis of 3,6-bis[5-(carbazol-9-yl)thiophen-2-yl]-9-(2-ethylhexyl)carbazole (CTC). A mixture of **9** (2.00 g, 3.33 mmol), carbazole (1.67 g, 9.99 mmol), K_2CO_3 (1.87 g, 13.52 mmol), and Cu-bronze (0.21 g, 3.33 mmol) in nitrobenzene (20 ml) was stirred at reflux under N_2 for 18 h. After removal of the solvent in vacuo, ammonia solution (50 ml) was added and the mixture was allowed to stand for 2 h. CH_2Cl_2 (150 ml) and water (100 ml) were added. The organic phase was separated, washed with water (100 ml×2), brine solution (100 ml), dried over anhydrous Na_2SO_4, filtered, and the solvent removed to dryness. Purification by column chromatography using silica gel eluting with a mixture of CH_2Cl_2 and hexane followed by recrystallization with a mixture of CH_2Cl_2 and MeOH afforded light yellow solids. Yield was 1.80 g (58%); IR (KBr) 2925, 1555, 1503, 1444, 1226, 795, and 747 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.91 (3H, t, J=7.2 Hz), 0.98 (3H, t, J=7.5 Hz), 1.29–1.48 (8H, m), 2.12–2.15 (1H, m), 4.23 (2H, d, J=7.2 Hz), 7.23 (2H, d, J=3.9 Hz), 7.35 (4H, t, J=7.4 Hz), 7.44–7.52 (8H, m), 7.61 (4H, d, J=8.5 Hz), 7.80 (2H, dd, J=8.5 Hz, J=1.7 Hz), 8.14 (4H, d, J=7.4 Hz), and 8.44 (2H, d, J=1.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.94, 14.03, 23.04, 24.46, 28.84, 31.06, 39.51, 47.74, 109.75, 110.37, 117.89, 120.20, 120.57, 120.75, 123.27, 123.53, 124.48, 125.67, 126.00, 126.27, 136.64, 141.20, 142.03, and 144.00; HRMS-ESI m/z: [MH^+] calcd for $C_{52}H_{44}N_3S_2$, 774.2971; found, 774.2966.

4.2.7. Synthesis of 2,7-bis(thiophen-2-yl)-9,9-bis-*n*-hexylfluorene (12). A mixture of **11** (5.0 g, 10.16 mmol), 2-thiopheneboronic acid (2.58 g, 20.23 mmol), $Pd(PPh_3)_4$ (0.01 g, 0.01 mmol), and 2 M Na_2CO_3 aqueous solution (33 ml, 46 mmol) in THF (50 ml) was stirred at reflux under N_2 atmosphere for 24 h. CH_2Cl_2 (200 ml) and water (150 ml) were added. The organic phase was separated, washed with water (100 ml), brine solution (100 ml), dried over anhydrous Na_2CO_3, filtered, and the solvents removed to dryness. Purification by column chromatography using silica gel eluting with hexane gave yellow-green solids. Yield was 2.94 g (58%); IR (KBr) 2927, 1467, 1214, 1053, 809, and 691 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.68–0.79 (10H, m), 1.07–1.16 (12H, m), 2.01–2.07 (4H, m), 7.13 (2H, dd, J=4.8 Hz, J=3.6 Hz), 7.31 (2H, dd, J=5.1 Hz, J=0.9 Hz), 7.40 (2H, dd, J=4.2 Hz, J=0.9 Hz), 7.58 (2H, s), 7.64 (2H, dd, J=7.8 Hz, J=1.5 Hz), and 7.69 (2H, d, J=7.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) 13.98, 22.56, 23.72, 29.66, 31.45, 40.43, 55.28, 120.07, 120.16, 122.89, 124.53, 124.98, 128.06, 133.26, 140.21, 145.17, and 151.70; HRMS-ESI m/z: [MH^+] calcd for $C_{33}H_{39}S_2$, 499.2488; found, 499.2487.

4.2.8. Synthesis of 2,7-bis(5-bromothiophen-2-yl)-9,9-di-*n*-hexylfluorene (13). *N*-Bromosuccinimide (0.712 g, 4.00 mmol) was added in small portions to a solution of **12** (1.0 g, 2.00 mmol) in THF (50 ml). The mixture was stirred at room temperature under N_2 for 1 h. Water (100 ml) and CH_2Cl_2 (100 ml) were added. The organic phase was separated, washed with water (100 ml), brine solution (100 ml), dried over anhydrous Na_2SO_4, filtered, and the solvents removed to dryness. Purification by column chromatography using silica gel eluting with hexane gave yellow-green solids. Yield was 0.93 g (71%); ^1H NMR (300 MHz, $CDCl_3$) δ 0.65–0.70 (4H, m), 0.75–0.80 (6H, m), 1.08–1.28 (14H, m), 1.98–2.04 (4H, m), 7.08 (2H, d, J=3.9 Hz), 7.15 (2H, d, J=3.9 Hz), 7.47 (2H, d, J=1.2 Hz), 7.50 (2H, dd, J=6.6 Hz, J=1.5 Hz), and 7.68 (2H, d, J=7.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.95, 22.53, 23.72, 29.61, 31.41, 40.34, 55.33, 119.84, 120.84, 123.05, 124.70, 130.87, 132.65, 140.41, 146.55, and 151.85; HRMS-ESI m/z: [MH^+] calcd for $C_{33}H_{37}Br_2S_2$, 657.0639; found, 657.0643.

4.2.9. Synthesis of 2,7-bis[5-(carbazol-9-yl)thiophen-2-yl]-9,9-di-*n*-hexylfluorene (CTF). A mixture of **13** (1.48 g, 2.24 mmol), carbazole (1.12 g, 6.71 mmol), K_2CO_3 (1.25 g, 9.08 mmol), and Cu-bronze (0.14 g, 2.24 mmol) in nitrobenzene (20 ml) was stirred at reflux under N_2 atmosphere for 20 h. After removal of the solvent in vacuo, ammonia solution (30 ml) was added and the mixture was left to stand for 2 h. CH_2Cl_2 (150 ml) and water (200 ml) were added. The organic phase was separated, washed with water (100 ml×2), brine solution (100 ml), dried over anhydrous Na_2SO_4, filtered, and the solvents removed to dryness. Purification by column chromatography using silica gel eluting with a mixture of CH_2Cl_2 and hexane followed by recrystallization with a mixture of CH_2Cl_2 and MeOH afforded light yellow solids. Yield was 1.02 g (55%); IR (KBr) 2925, 1555, 1492, 1444, 1226, 797, and 746 cm^{-1}; ^1H 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.

4.2.10. Synthesis of 5,5′-bis(carbazol-9-yl)(bithiophen-2,2′-yl) (CT). A mixture of **14** (1.00 g, 3.08 mmol), carbazole (0.94 g, 5.62 mmol), copper-bronze (0.14 g, 2.30 mmol), and K_2CO_3 (1.49 g, 10.57 mmol) in nitrobenzene (30 cm^3) was stirred at reflux under N_2 for 24 h. After removal of the solvent in vacuo, ammonia solution (30 ml) was added and the mixture was left to stand for 2 h. CH_2Cl_2 (100 ml) and water (100 ml) were added. The organic phase was separated, washed with water (100 ml×2), brine solution (100 ml), dried over anhydrous Na_2SO_4, filtered, and the solvents removed to dryness. Purification by column chromatography using silica gel eluting with a mixture of CH_2Cl_2 and hexane followed by recrystallization with a mixture of CH_2Cl_2 and MeOH afforded yellow solids. Yield was 1.24 g (81%); IR (KBr) 1579, 1537, 1451, 1221, 1164, 799, and 744 cm^{-1}; ^1H 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.

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References and notes

1. Brunner, K.; Van Dijken, A.; Börner, H.; Bastiaansen, J. J. A. M.; Kiggen, N. M. M.; Langeveld, B. M. W. *J. Am. Chem. Soc.* **2004**, *126*, 6035–6042.
2. Schon, J. H.; Kloc, C.; Bucher, E.; Batlogg, B. *Nature* **2000**, *403*, 408–410.
3. Mitschke, U.; BaÈuerle, P. *J. Mater. Chem.* **2000**, *10*, 1471–1507.
4. Nakanishi, H.; Aso, Y.; Otsubo, T. *Synth. Met.* **1999**, *101*, 604–605.
5. Noda, T.; Ogawa, H.; Noma, N.; Shirota, Y. *J. Mater. Chem.* **1999**, *9*, 2177–2181.
6. Otsubo, T.; Aso, Y.; Takimiya, K. *J. Mater. Chem.* **2002**, *12*, 2565–2575.
7. Wong, K.-T.; Hung, T. H.; Kao, S. C.; Chou, C. H.; Su, Y. O. *Chem. Commun.* **2001**, 1628–1629.
8. Pei, J.; Wang, J.-L.; Cao, X.-Y.; Zhou, X.-H.; Zhang, W.-B. *J. Am. Chem. Soc.* **2003**, *125*, 9944–9945.
9. Grazulevicius, J. V.; Strohriegl, P.; Pielichowski, J.; Pielichowski, K. *Prog. Polym. Sci.* **2003**, *28*, 1297–1353.
10. Kotler, Z.; Segal, J.; Sigalov, M.; Ben-Asuly, A.; Khodorkovsky, V. *Synth. Met.* **2000**, *115*, 269–273.
11. Kundu, P.; Thomas, K. R. J.; Lin, J. T.; Tao, Y.-T.; Chien, C.-H. *Adv. Funct. Mater.* **2003**, *13*, 445–452.
12. Van Dijken, A.; Bastiaansen, J. J. A. M.; Kiggen, N. M. M.; Langeveld, B. M. W.; Rothe, C.; Monkman, A.; Bach, I.; Stossel, P.; Brunner, K. *J. Am. Chem. Soc.* **2004**, *126*, 7718–7727.
13. Koene, B. E.; Loy, D. E.; Thompson, M. E. *Chem. Mater.* **1998**, *10*, 2235–2250.
14. Kamtekar, K. T.; Wang, C.; Bettington, S.; Batsanov, A. S.; Perepichka, I. F.; Bryce, M. R.; Ahn, J. H.; Rabinal, M.; Petty, M. C. *J. Mater. Chem.* **2006**, *16*, 3823–3835.
15. Meng, H.; Zheng, J.; Lovinger, A. J.; Wang, B.-C.; Van Patten, P. G.; Bao, Z. *Chem. Mater.* **2003**, *15*, 1778–1787.
16. Weder, C.; Wrighton, K. S. *Macromolecules* **1996**, *29*, 5157–5165.
17. Kim, J. J.; Kim, K.-S.; Baek, S.; Kim, H. C.; Ree, M. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 1173–1183.
18. Lee, S. H.; Tsutsui, T. *Thin Solid Films* **2000**, *363*, 76–80.