Novel spiro-fluorenes from tandem radical addition for liquid crystalline monodisperse conjugated oligomers†

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3′-Nonafluorobutylmethyl-4′-methyl-spiro[cyclopentyl-9,1′]fluorenes were successfully synthesized *via* tandem radical-addition reactions between 9,9-diallylfluorenes and perfluorobutyl iodide in the presence of a radical initiator followed by reduction under mild conditions. Single crystal analysis indicates that two substituents at 3,4-positions of cyclopentane are in a maleinoid form. Accordingly, four oligo(fluorene-*co*-bithiophene)s with the same molecular length of ~10 nm (7 fluorene units and 12 thiophene units) containing one to three novel spiro-fluorene units were synthesized. The introduction of the spiro-fluorene units results in noticeable enhancement of both glass transition temperature (T_g) and clearing point temperature (T_c) of the oligomers, but has little effect on their photophysical properties. Exchanging three 9,9-dioctylfluorene units with 3′-nonafluorobutylmethyl-4′-methyl-spiro[cyclopentyl-9,1′] fluorene units results in a 37 °C enhancement of T_g and a 61 °C enhancement of T_c. All these results indicate that this new spiro-fluorene unit is an attractive building block for liquid crystalline conjugated polymers/oligomers with both high T_g and T_c.

Introduction

Monodisperse conjugated oligomers (MCOs) are characterized with well-defined and uniform chemical structures.[1] Hence, they have been extensively studied for establishing the structure–property relationship of various conjugated systems.[1–3] Of those, fluorene-based liquid crystalline MCOs have attracted particular attention in recent years due to their capability of highly ordered alignment on various substrates for preparation of high mobility organic thin-film transistors (OTFTs) and organic light-emitting diodes (OLEDs) with polarized light emission.[4–13] For example, Chen *et al.* reported several series of oligofluorenes with number of fluorene units up to 16, which exhibited chain-length dependent alignment ability. OLEDs with highly polarized light emission[9–11] and OTFTs with mobility over 10^{-2} cm^2/Vs have been realized.[13]

The morphological stability is very crucial for application of conjugated materials in optoelectronic devices, such as OLEDs.[14] That means the conjugated materials should have vitrificational capability and exhibit a glass-transition temperature (T_g) as high as possible. It was found that enhancement of both T_g and clearing point temperature (T_c) of fluorene-based polymers and oligomers could be realized by decreasing the side chain length,[8] however, which meanwhile can also induce a reduction of solubility and an increase of crystallization tendency, especially for long MCOs. Another approach normally used for increasing T_g of fluorene-based oligomers and polymers is to introduce rigid aromatic units, *e.g.*, spiro-fluorenes SF-I, SF-II, SF-III and SF-IV, as shown in Fig. 1, in the skeletons of the polymers and oligomers.[15–21] However, these spirocyclic units are usually detrimental to the liquid crystalline properties of the materials. For instance, a polymer based on a SF-I type unit exhibits a T_g of 121 °C, but neither a melting point nor a liquid crystalline–isotropic transition (clearing point) were observed.[16a] We herein report the synthesis of a new type of spiro-fluorene, *i.e.*, 3′-nonafluorobutylmethyl-4′-methyl-spiro[cyclopentyl-9,1′]fluorenes (SF-V in Fig. 1), through tandem free-radical additions. These novel spiro-fluorenes were then used to synthesize oligo (fluorene-*co*-bithiophene)s (OFbTs), a class of liquid crystalline MCOs.[22] Most importantly, it was found that the introduction of the spiro-units resulted in increased T_g and T_c. Meanwhile, this type of spiro-fluorene carrying hydrophobic substituents also makes the synthesis of amphiphilic MCOs possible.

Results and discussion

So far, spiro-fluorene derivatives have been made by either nucleophilic substitution reaction between fluorenyl carbanions and α,α′-dibromomethylbenzene derivatives[18] or nucleophilic addition of carbanions to fluorenones or cyclic ketones followed by cyclization.[16a,b,19–21] It was reported that the reactions between alkyl radicals and 1,6-heptadiene could afford five-membered cyclopentane derivatives through tandem free-radical additions, as shown in Scheme 1 with the perfluoroalkyl radical as an example.[23,24] For 9,9-diallyl-fluorene, two allyl groups together with the bridge-carbon exactly form a 1,6-heptadiene moiety. Therefore, in principle, spiro-fluorene derivatives carrying alkyl

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† Electronic supplementary information (ESI) available: Experimental procedure and characterization for all intermediates and compounds not included in experimental section, copies of H–H COSY and H–C HMQC NMR spectra of compound **4a**, and representative WAXD patterns. CCDC reference number 694714. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b811830b

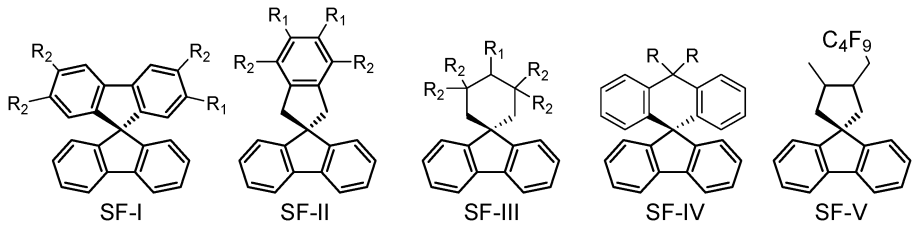
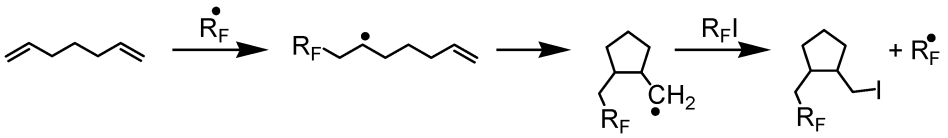


Fig. 1 Chemical structures of spiro-fluorenes which have been used to increase the glass transition temperatures (T_gs) of fluorene-based oligomers and polymers (SF-1 to SF-IV) and newly developed spiro-fluorene (SF-V).



Scheme 1 Reaction of R_FI with 1,6-heptadiene.

chains, *i.e.*, semifluoroalkyl, can be synthesized. Keep this in mind, we synthesized two novel spiro[cyclopentyl-9,1′]fluorenes, *i.e.*, 2,7-dibromo-3′-nonafluorobutylmethyl-4′-methyl-spiro[cyclopentyl-9,1′]fluorene (**4a**) and 2-bromo-3′-nonafluorobutylmethyl-4′-methyl-spiro[cyclopentyl-9,1′]fluorene (**4b**).

Scheme 2 outlines the synthesis of **4**. For compound **4a**, 2,7-dibromo-9,9-diallyl-fluorene (**2a**) was synthesized from 2,7-dibromo-fluorene (**1a**) and allyl bromide in a high yield of 91%. In the presence of azobisisobutyronitrile (AIBN), iodo-substituted spiro[cyclopentyl-9,1′]fluorene derivative **3a** was obtained through a tandem radical-addition reaction between **2a** and perfluorobutyl iodide in 89% yield. Reduction of **3a** with $NaBH_4$ under mild conditions afforded **4a** in a yield of 76% as a white solid. Similarly, compound **4b** was also synthesized in good yield.

^{1}H NMR and mass spectra of **4** confirmed the formation of the proposed spiro-structure. Compound **4a** was further analyzed by H–H COSY and H–C HMQC techniques (see Electronic Supplementary Information (ESI)†) for assignment of ^{1}H NMR peaks, as shown in Fig. 2. It is worth noting that only a double split $-CH_3$ signal appears in the ^{1}H NMR spectra of both **4a** and **4b**, indicating that only one conformer, either *cis*- or *trans*-conformer, was formed, in contrast to the reaction of 1,6-heptadiene, in which both *cis*- and *trans*-conformers were observed.[24] The single crystals of compound **4a** obtained from recrystallization are good enough for single-crystal X-ray diffraction analysis. Depicted in Fig. 3 is the ORTEP view of **4a**. The two aliphatic groups (*i.e.*, $-CH_3$ and $-CH_2C_4F_9$ at 3,4-positions of cyclopentane) are in a maleinoid form. It is noteworthy that although C15 and C16 are chiral centers, the crystals of **4a** are not optically active because **4a** consists of a 1:1 racemic mixture from the view of the whole molecule.

To verify the advantages of the novel spiro-fluorene derivatives in design and synthesis of liquid crystalline MCOs, four oligo(fluorene-*co*-bithiophene)s (OFbTs), *i.e.*, **F7Th12-F1O1**, **F7Th12-F2**, **F7Th12-F3** and **F7Th12-F3O4** as shown in Fig. 4,

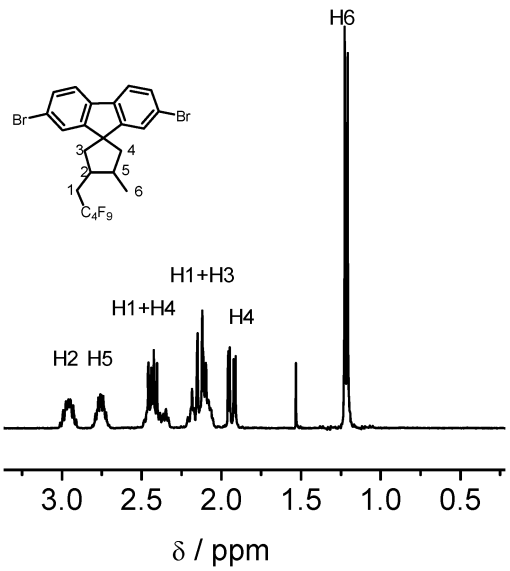
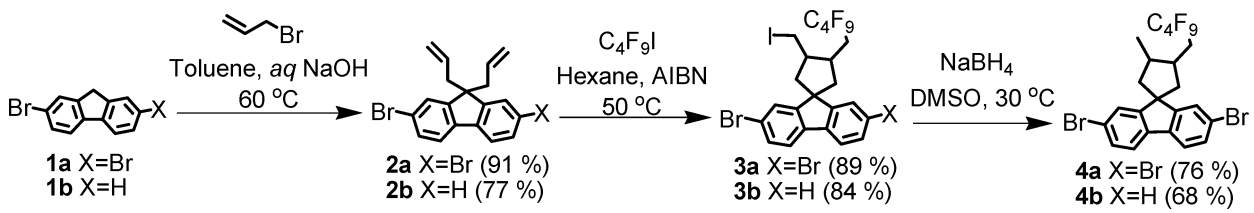


Fig. 2 ^{1}H NMR spectrum of compound **4a** (400 MHz, $CDCl_3$).



Scheme 2 Synthesis of spiro-fluorene **4**.

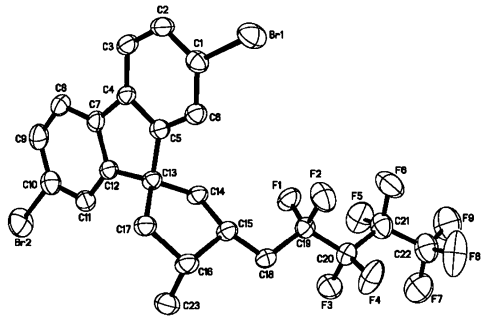


Fig. 3 ORTEP view of compound **4a**.

were synthesized, which contain 1–3 spiro[cyclopentyl-9,1′]fluorene units. Meanwhile, introduction of hydrophilic substituents in **F7Th12-F1O1** and **F7Th12-F3O4** provides the possibility to construct amphiphilic MCOs. Oligomer **F7Th12**, prepared in a previous report, is also included for comparison.[22] All molecules have the same length for easily investigating the effect of the spiro-fluorene unit on the properties of OFbTs.

Oligomers **F7Th12-F1O1**, **F7Th12-F2**, **F7Th12-F3** and **F7Th12-F3O4** were synthesized through a divergent/convergent approach as outlined in Scheme 3. A similar route has been used by us for the successful synthesis of OFbTs with molecular length up to 19.5 nm.[22] The compound 5-tributylstannyl-2,2′-bithiophene (**5**) was reacted with **4a**, 2-bromo-9,9-bis(3-(2-methoxyethoxy)propyl)-fluorene (**7**) or **4b** to afford intermediates **6**, **8a** and **9a** in yields of 81%, 75%, and 74%, respectively. The compounds **8a** and **9a** were almost quantitatively converted to organotin reagents **8b** and **9b** by treatment with *n*-BuLi and Bu_3SnCl in succession. Intermediates **11a**, **13a**, **14a**, and **15a** were then synthesized in yields of 90, 81, 84, and 79%, respectively, by Stille cross-coupling reactions. Deprotonation of **11a**, and **13–14a** with *n*-BuLi followed by treatment with Bu_3SnCl afforded corresponding organotin reagent **11b**, and **13–14b**. All these organotin reagents were directly used for the next step without any further purification. To synthesize dibromo-terminated intermediates **18** and **20**, compound **16b** was first synthesized, and then reacted with an excess of **17** and **19** to afford **18** and **20** in yields of 51 and 62%, respectively. Finally, oligomers **F7Th12-F3** and **F7Th12-F3O4** were obtained in yields of 40 and 41%, respectively. To synthesize asymmetric oligomer **F7Th12-F1O1**, compound **22** was first synthesized in a yield of 52% *via* Stille coupling of 2 equiv compound **21** and 1 equiv **11b**. Oligomer **F7Th12-F2** was also obtained as a by-product in a yield of 20%. The compound **22** was further coupled with **14b** to afford **F7Th12-F1O1** in a yield of 54%. To ensure the purity, all four oligomers were further purified by preparative gel permeation chromatography (PGPC) equipped with a size-exclusion column assembly (2H-40/3H-40) after purification by column chromatography on silica gel.

The molecular structures of all four oligomers, *i.e.*, **F7Th12-F1O1**, **F7Th12-F2**, **F7Th12-F3** and **F7Th12-F3O4**, were validated by ^{1}H NMR, ^{13}C NMR and matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectroscopic (MS) techniques in addition to elemental analysis. The molecular weights determined by MALDI-TOF mass spectrometry are in good agreement with the calculated molecular weights. Fig. 5 displays the mass spectra of **F7Th12-F1O1**, **F7Th12-F2**, **F7Th12-F3** and **F7Th12-F3O4**, and all of them

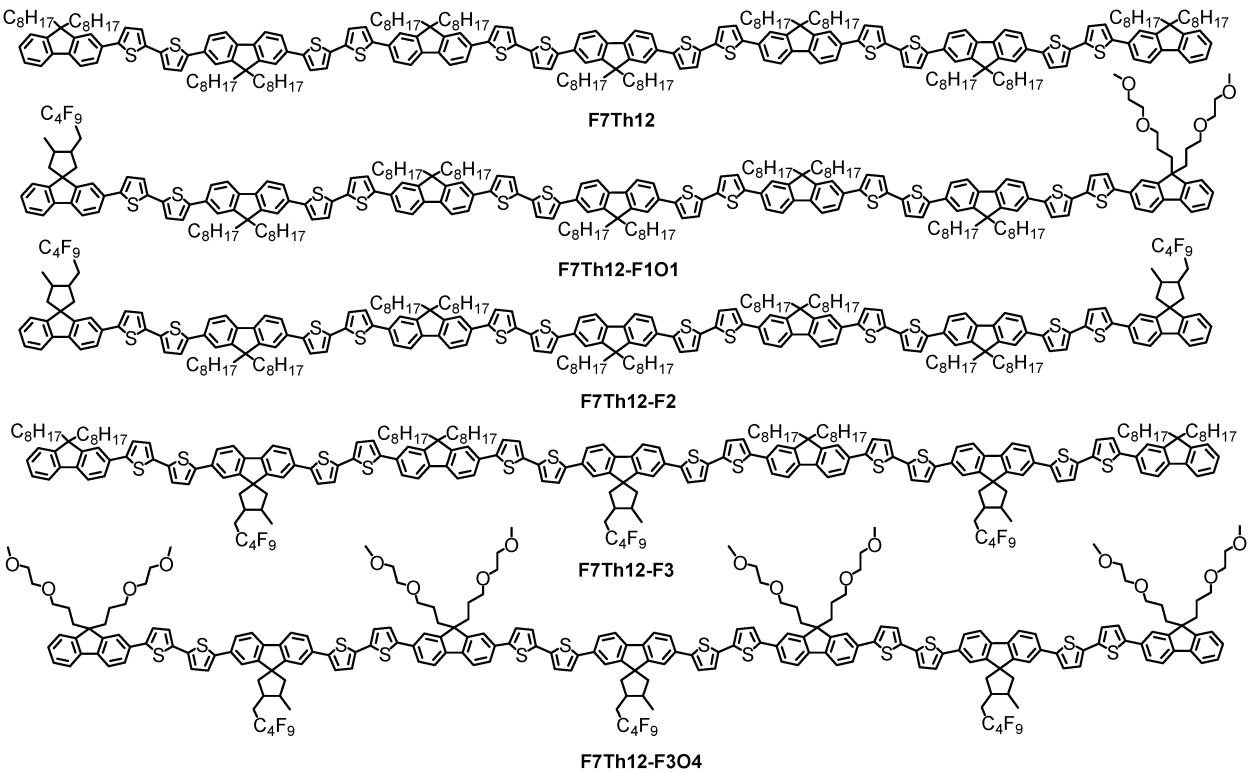
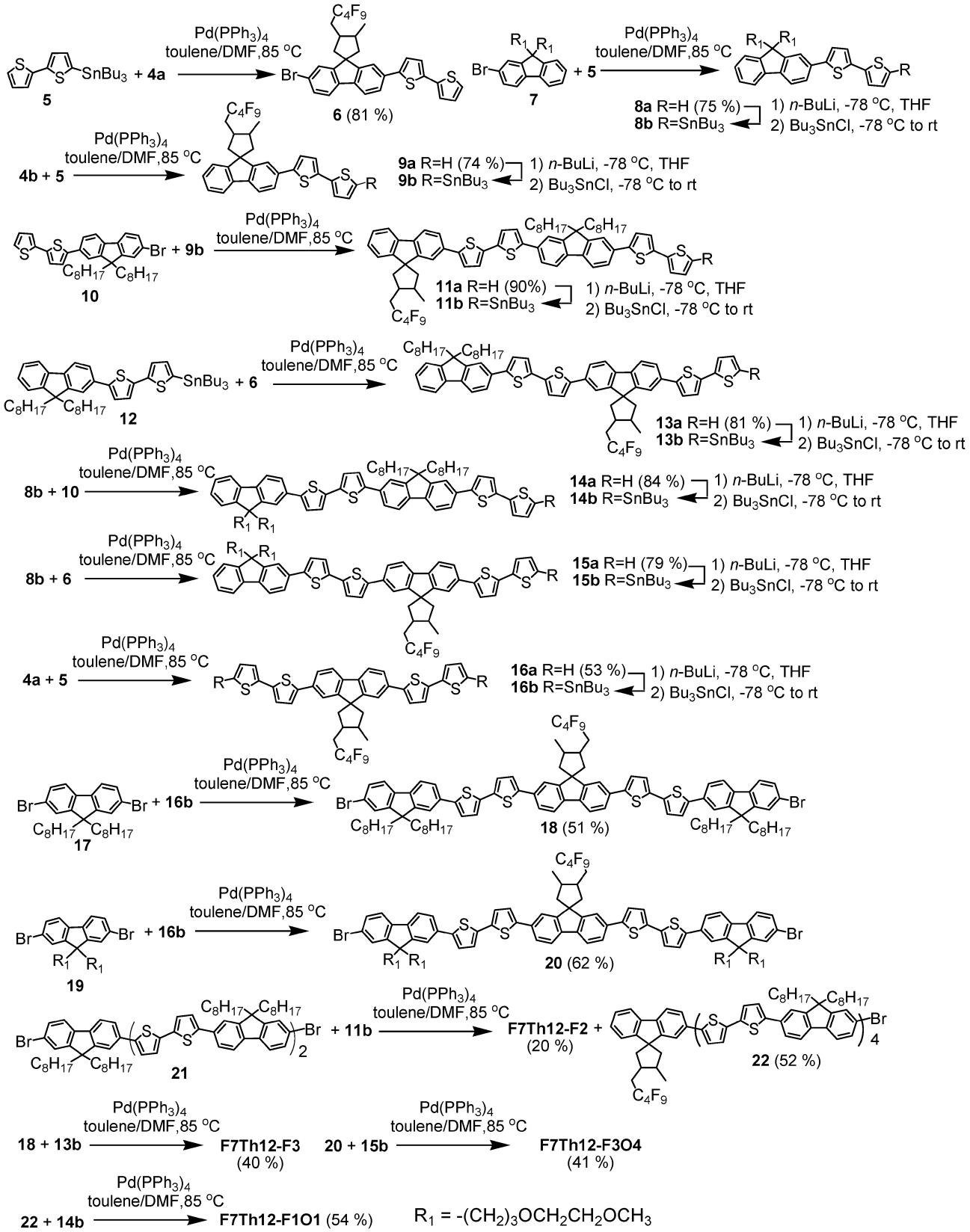


Fig. 4 Chemical structures of oligomers **F7Th12-F1O1**, **F7Th12-F2**, **F7Th12-F3** and **F7Th12-F3O4**.



Scheme 3 Synthesis route for oligomers **F7Th12-F1O1**, **F7Th12-F2**, **F7Th12-F3** and **F7Th12-F3O4**.

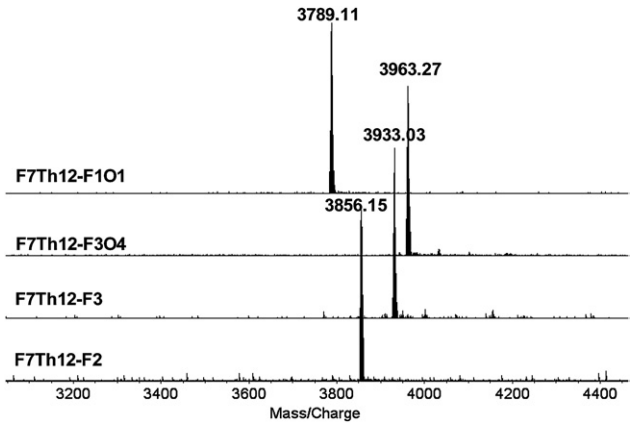


Fig. 5 MALDI-TOF-MS spectra of oligomers **F7Th12-F1O1**, **F7Th12-F2**, **F7Th12-F3** and **F7Th12-F3O4** with anthracene-1,8,9-triol as the matrix.

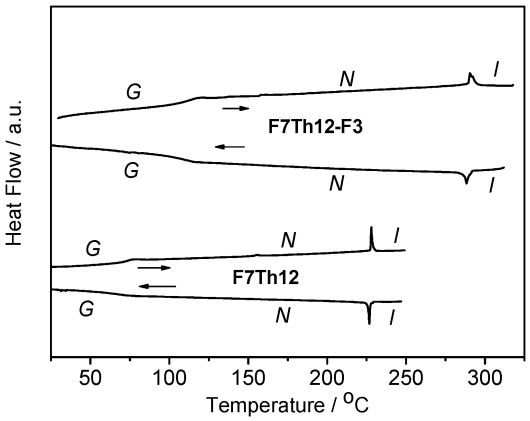


Fig. 6 The second DSC heating and cooling traces of **F7Th12** and **F7Th12-F3** under nitrogen with a heating/cooling rate of 10 °C min^{-1}, the curves of **F7Th12** have been reported in a previous paper.[22] Symbols: *G*, glassy; *N*, nematic; *I*, isotropic.

exhibit one peak corresponding to the molecular ion. They are soluble in common organic solvents, such as toluene, tetrahydrofuran (THF), methylene chloride and chloroform. However, none of them was found capable of micellization in the above solvents and more polar solvents, such as *N*,*N*-dimethylformamide (DMF), probably due to the fact that both hydrophilic and hydrophobic chains are not long enough.

Thermal properties of all four oligomers were studied by differential scanning calorimetry (DSC), polarizing optical microscopy (POM) and wide-angle X-ray diffraction (WAXD), and phase transition temperatures are summarized in Table 1. In contrast to the previously reported conjugated oligomers and polymers containing spiro-fluorene units, which are not mesomorphic,[15–21] all four newly synthesized oligomers are verified nematic liquid crystals, like their mother-oligomer **F7Th12**. Fig. 6 shows the second DSC heating and cooling traces of **F7Th12** and **F7Th12-F3** with a heating/cooling rate of 10 °C min^{-1}. **F7Th12-F3** exhibits a T_g of 113 °C and a T_c of 289 °C, which are noticeably higher than those of **F7Th12** ($T_g = 76$ °C; $T_c = 228$ °C).[22] Meanwhile, no other transitions are observed, indicative of a vitrified nature. Shown in Fig. 7 are the typical nematic textures of **F7Th12-F3** at 210 °C observed under a POM. As shown in Table 1, both T_g and T_c increase as the number of spiro-fluorene units increases. T_c of **F7Th12-F3O4** is noticeably higher than that of **F7Th12-F3** possibly due to enhanced intermolecular interaction by amphiphilic side chains. Only a diffused halo at around 20° was observed in WAXD patterns (2θ = 2–30°) at both room temperature and temperatures above T_g (as shown in ESI† with **F7Th12-F3O4** as an example), consistent with the glassy-nematic nature of the oligomers.

Fig. 7 POM image of **F7Th12-F3** at 210 °C on heating.

Solution and film absorption and photoluminescence (PL) spectra of MCOs are shown in Fig. 8. In solution, the oligomers exhibit featureless absorption spectra (Fig. 8a). In contrast, the film absorption spectra are well resolved along with a considerable bathochromic shift (Fig. 8b), indicating that the molecules adopt a more extended conformation in the solid state. Introduction of spiro-fluorene units and fluorene units carrying hydrophilic groups has almost no effect on the absorption spectra. As shown in Fig. 8c, normalized PL spectra of the MCOs

Table 1 Optical and thermal properties of oligomers **F7Th12**, **F7Th12-F1O1**, **F7Th12-F2**, **F7Th12-F3** and **F7Th12-F3O4**

			$\lambda_{max,\ abs}$ (nm)		$\lambda_{max,\ PL}$ [nm]	
Oligmers	N^a	Phase transition temperatures[b]	Solution[c]	Film	Solution[c]	Film
F7Th12[d]	0	*G* 76 °C *N* 228 °C *I*	446.5	458.0, 484.0	496.5, 529.0	509.5, 542.5
F7Th12-F1O1	1	*G* 82 °C *N* 246 °C *I*	445.5	459.0, 483.5	495.5, 529.5	510.5, 543.0
F7Th12-F2	2	*G* 96 °C *N* 253 °C *I*	446.0	459.0, 483.0	496.0, 528.5	511.0, 538.0
F7Th12-F3	3	*G* 113 °C *N* 289 °C *I*	446.0	460.0, 483.0	496.5, 529.0	513.5, 549.0
F7Th12-F3O4	3	*G* 114 °C *N* 310 °C *I*	446.5	459.5, 483.0	496.5, 529.0	516.0, 548.0

[a] The number of spiro-fluorene units. [b] Measured by DSC under nitrogen with a heating rate of 10 °C/min. [c] Measured in chloroform with a concentration of 10^{-6} mol/L. [d] Data reported in ref. 22. Symbols: *G*, glassy; *N*, nematic; *I*, isotropic.

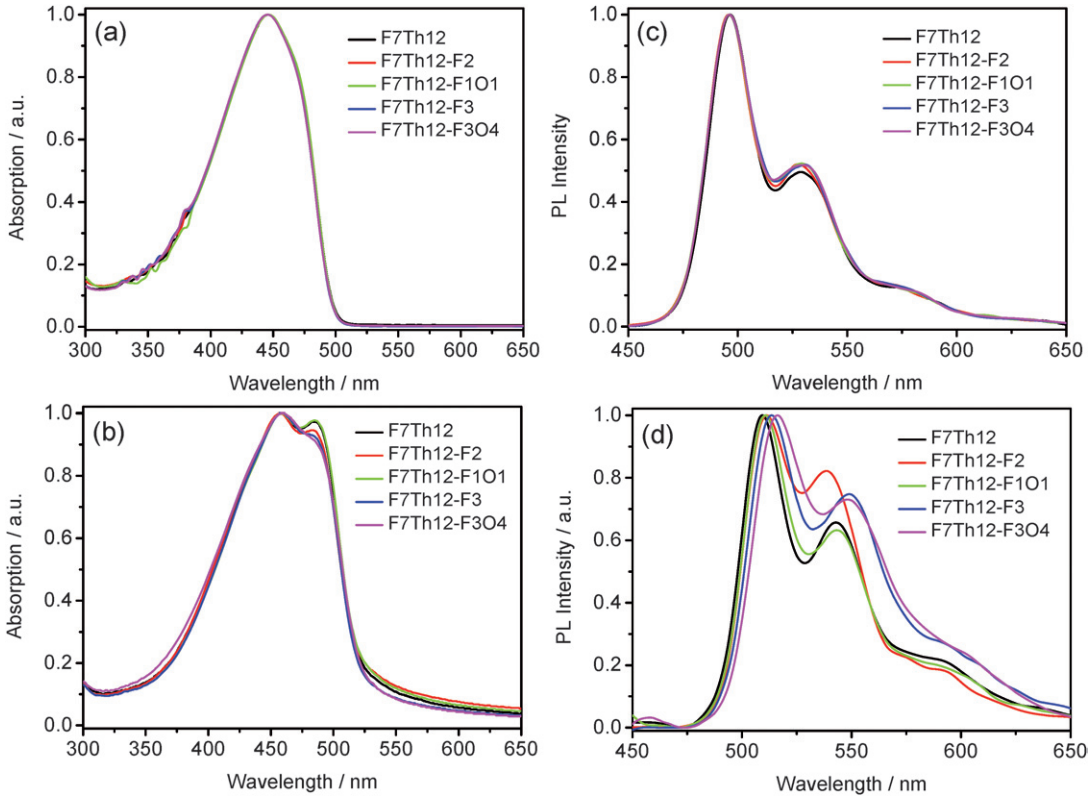


Fig. 8 Absorption (a and b) and PL (c and d) spectra of **F7Th12**, **F7Th12-F1O1**, **F7Th12-F2**, **F7Th12-F3** and **F7Th12-F3O4** in chloroform solution (a and c) and film (b and d). The concentration for solution absorption and PL measurements was 10^{-6} mol/L.

in chloroform with a concentration of 10^{-6} mol/L and the excitation wavelength at the absorption maximum are almost identical for all five OFbTs. However, the film PL spectra of the oligomers are slightly different. Introduction of both spiro-fluorene and fluorene carrying hydrophilic chains results in a red-shift of the emission maximum. For example, film PL maxima of **F7Th12-F1O1**, **F7Th12-F2**, **F7Th12-F3** and **F7Th12-F3O4** are at 509.5, 510.5, 511.0, 513.5 and 516.0 nm, respectively, as shown in Table 1 and Fig. 8d.

Conclusion

We have demonstrated an approach for synthesis of spiro-fluorene derivatives, *i.e.*, 2,7-dibromo-3′-nonafluorobutylmethyl-4′-methyl-spiro[cyclopentyl- 9,1′] fluorene and 2-bromo-3′-nonafluorobutylmethyl-4′-methyl-spiro [cyclopentyl-9,1′] fluorene. Two substituents in cyclopentyl group, $-CH_2C_4F_9$ and $-CH_3$, are in a maleinoid form as revealed by single crystal X-ray analysis. Four OFbTs comprising seven fluorene units and twelve thiophene units, *i.e.*, **F7Th12-F1O1**, **F7Th12-F2**, **F7Th12-F3** and **F7Th12-F3O4**, were synthesized, in which there were 1–3 newly developed spiro-fluorene units. It was found that the introduction of the new spiro-fluorene units into OFbTs resulted in noticeable enhancement of T_g and T_c. For example, compared to the mother compound **F7Th12**, **F7Th12-F3** containing 3 spiro-fluorene units exhibits a 37 °C enhancement of T_g and a 61 °C enhancement of T_c. This indicates that the newly developed spiro-fluorene can encourage the mesophase formation, and is an attractive building block for liquid crystalline conjugated polymers/oligomers with both high T_g and T_c.

Experimental

Materials

THF and toluene were distilled over sodium/benzophenone. DMF was distilled over CaH_2 under reduced pressure. Other reagents were obtained from commercial resources and used without further purification. Compounds **5**, **10**, **12**, **17**, and **21** were synthesized following a previous report.[22] The synthesis of **7** and **19** was reported in the ESI.† All reactions were carried out under argon.

2,7-Dibromo-9,9-diallyl-fluorene (2a). A solution of 2,7-dibromo-fluorene (**1a**, 5.00 g, 15.4 mmol), sodium hydroxide (15 g, 0.38 mmol), tetrabutylammonium bromide (0.35 g, 1.1 mmol), and allyl bromide (4.28 g, 35.0 mmol) in 30 mL of toluene and 30 mL of water was stirred for 3 h at 60 °C. The mixture was cooled to room temperature then poured into a large amount of brine for extraction with methylene chloride. The organic extracts were washed with brine before drying over $MgSO_4$. Upon evaporating off the solvent, the residue was purified by recrystallization with ethanol to afford **2a** (5.7 g, 91%) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.53–7.56 (m, 4H), 7.47–7.50 (m, 2H), 5.18–5.31 (m, 2H), 4.81–4.92 (m, 4H), 2.70 (d, $J = 7.71$ Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 151.5, 139.1, 133.0, 130.9, 127.4, 121.7, 118.9, 55.1, 43.6. Anal. Calcd. for $C_{19}H_{16}Br_2$: C,

56.47; H, 3.99. Found: C, 56.37; H, 3.75%. Molecular Mass: Calcd for $C_{19}H_{16}Br_2$: 404.14. Found: 404.10.

2-Bromo-9,9-diallyl-fluorene (2b). The procedure for the synthesis of **2a** was followed to prepare **2b** from **1b** in a yield of 77%. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.64–7.67 (m, 1H), 7.52–7.56 (m, 2H), 7.43–7.46 (m, 1H), 7.31–7.40 (m, 3H), 5.15–5.27 (m, 2H), 4.74–4.86 (m, 4H), 2.67 (d, $J = 7.20$ Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 151.9, 149.4, 140.2, 140.1, 133.6, 130.7, 127.8, 127.7, 127.4, 124.1, 121.6, 120.3, 118.4, 54.9, 43.7. Anal. Calcd. for $C_{19}H_{17}Br$: C, 70.16; H, 5.27. Found: C, 70.32; H, 5.21%. Molecular Mass: Calcd for $C_{19}H_{17}Br$: 325.24. Found: 325.37.

2,7-Dibromo-3′-nonafluorobutylmethyl-4′-iodomethyl-spiro[cyclopentyl-9,1′]fluorene (3a). A solution of **2a** (4.00 g, 10.0 mmol), AIBN (0.38 g, 2.3 mmol), and perfluoro-4-iodobutane (8.00 g, 23.0 mmol) in 100 mL hexane was stirred for 48 h at 50 °C. The mixture was cooled to room temperature then poured into a large amount of brine for extraction with petroleum ether. The organic extracts were washed brine before drying over $MgSO_4$. Upon evaporating off the solvent, the residue was purified with column chromatography on silica gel with petroleum as the eluent to afford **3a** (6.7 g, 89%) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.44–7.54 (m, 6H), 3.43–3.48 (m, 1H), 3.27–3.33 (m, 1H), 3.03–3.07 (m, 2H), 2.40–2.59 (m, 1H), 2.12–2.38 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 155.7, 153.6, 138.1, 137.7, 131.1, 126.7, 126.5, 122.4, 122.2, 121.7, 121.6, 56.9, 46.1, 45.4, 44.9, 36.0, 31.1, 8.0. Anal. Calcd. for $C_{23}H_{16}Br_2F_9I$: C, 36.83; H, 2.15. Found: C, 37.21; H, 2.17%. Molecular Mass: Calcd for $C_{23}H_{16}Br_2F_9I$: 750.07. Found: 750.33.

2-Bromo-3′-nonafluorobutylmethyl-4′-iodomethyl-spiro[cyclopentyl-9,1′]fluorene (3b). The procedure for the synthesis of **3a** was followed to prepare **3b** from **2b** in a yield of 84%. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.63–7.69 (m, 1H), 7.53–7.58 (m, 2H), 7.45–7.49 (m, 2H), 7.33–7.39 (m, 2H), 3.44–3.50 (m, 1H), 3.28–3.37 (m, 1H), 3.08–3.12 (m, 2H), 2.43–2.59 (m, 1H), 2.17–2.38 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 156.3,153.8, 153.7, 151.7, 139.1, 138.7, 130.9, 128.7, 128.6, 127.9, 126.6, 126.5, 123.1, 121.8, 121.6, 121.5, 120.4, 120.3, 56.8, 56.7, 46.3, 46.1, 45.7, 45.4, 45.2, 44.9, 36.2, 35.9, 31.0, 8.4, 8.2. Anal. Calcd. for $C_{23}H_{17}BrF_9I$: C, 41.16; H, 2.55. Found: C, 41.38; H, 2.80%. Molecular Mass: Calcd for $C_{23}H_{17}BrF_9I$: 671.18. Found: 671.16.

2,7-Dibromo-3′-nonafluorobutylmethyl-4′-methyl-spiro[cyclopentyl-9,1′]fluorene (4a). A solution of **3a** (2.52 g, 3.36 mmol) and $NaBH_4$ (0.64 g, 16.8 mmol) in 30 mL DMSO was stirred overnight at 30 °C. The mixture was cooled to room temperature then poured into a large amount of brine for extraction with petroleum ether. The organic extracts were washed brine before drying over $MgSO_4$. Upon evaporating off the solvent, the residue was purified with column chromatography on silica gel with petroleum as the eluent and follow by recrystallization with hexane to afford **4a** (1.6 g, 76%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.57 (d, $J = 1.5$ Hz, 1H), 7.42–7.52 (m, 5H), 2.93–2.97 (m, 1H), 2.73–2.77 (m, 1H), 2.39–2.47 (m, 2H), 2.04–2.19 (m, 3H), 1.94 (dd, $J = 14.1$ Hz, $J = 4.20$ Hz, 1 H), 1.21 (d, $J = 7.20$, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 156.6, 154.5, 137.7, 137.1, 130.3, 126.4, 126.2, 121.8, 121.1, 56.8, 46.5, 45.1, 36.3, 36.1, 31.4, 31.3, 31.2, 16.8. Anal. Calcd. for $C_{23}H_{17}Br_2F_9$: C, 44.26; H, 2.75. Found: C, 44.60; H, 2.65%. Molecular Mass: Calcd for $C_{23}H_{17}Br_2F_9$: 624.17. Found: 623.98.

2-Bromo-3′-nonafluorobutylmethyl-4′-methyl-spiro[cyclopentyl-9,1′]fluorene (4b). The procedure for the synthesis of **4a** was followed to prepare **4b** from **3b** in a yield of 68%. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.63–7.67 (m, 1H), 7.52–7.59 (m, 2H), 7.40–7.49 (m, 2H), 7.32–7.35 (m, 2H), 2.93–2.97 (m, 1H), 2.73–2.77 (m, 1H), 2.39–2.47 (m, 2H), 2.04–2.19 (m, 3H), 1.94 (dd, $J = 14.1$ Hz, $J = 4.20$ Hz, 1 H), 1.21 (d, $J = 7.20$, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 157.4, 155.2, 155.0, 152.9, 139.2, 139.1, 138.6, 138.4, 130.5, 128.5, 127.5, 126.7, 126.6, 123.2, 121.7, 121.4, 120.1, 57.0, 47.1, 47.0, 45.6, 45.5, 36.8, 36.7, 36.6, 36.4, 31.8, 17.2. Anal. Calcd. for $C_{23}H_{18}BrF_9$: C, 50.66; H, 3.33. Found: C, 50.82; H, 2.95%. Molecular Mass: Calcd for $C_{23}H_{18}BrF_9$: 545.28. Found: 544.00.

2-(2,2′-Bithien-5-yl)-7-bromo-3′-nonafluorobutylmethyl-4′-methyl-spiro[cyclopentyl-9,1′]fluorene (6). In the absence of light, a solution of 5-tributylstannyl-2,2′-bithiophene (**5**, 1.82 g, 4.00 mmol), **4a** (6.74 g, 10.8 mmol), and $Pd(PPh_3)_4$ (46 mg, 0.040 mmol) in anhydrous DMF/toluene (100 ml, volume ratio = 1:4) was stirred at 85 °C for 24 h. The mixture was cooled to room temperature and then poured into a large amount of water for extraction with methylene chloride. The organic extracts were washed with KF aqueous solution and brine before drying over $MgSO_4$. Upon evaporating off the solvent, the residue was purified with column chromatography on silica gel with petroleum:chloroform (10:1) as the eluent to afford **6** (2.3 g, 81%) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.51–7.69 (m, 6H), 7.43–7.48 (m, 1H), 7.22–7.29 (m, 2H), 7.16 (dd, $J = 0.72$ Hz, $J = 3.75$ Hz, 1H), 7.01 (m, 1 H), 2.97–2.99 (m, 1H), 2.76–2.80 (m, 1H), 2.42–2.50 (m, 2H), 2.07–2.22 (m, 3H), 1.97 (dd, $J = 14.1$ Hz, $J = 4.20$ Hz, 1 H), 1.21 (d, $J = 7.20$, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 157.5, 155.9, 155.4, 153.7, 143.7, 138.7, 138.1, 137.8, 134.4, 130.7, 128.3, 126.8, 126.6, 125.4, 125.3, 125.1, 124.8, 124.2, 121.9, 121.4, 120.6, 120.3, 57.1, 47.2, 47.0, 45.6, 36.9, 36.6, 17.2, 17.1, 1.4. Anal. Calcd. for $C_{31}H_{22}BrF_9S_2$: C, 52.48; H, 3.13. Found: C, 52.42; H, 2.98%. Molecular Mass: Calcd for $C_{31}H_{22}BrF_9S_2$: 709.53. Found: 707.85.

2-(2,2′-Bithien-5-yl)-9,9-bis(3-(2-methoxyethoxy)propyl)-fluorene (8a). The procedure for the synthesis of **6** was followed to prepare **8a** from **7** and **5** in a yield of 75%. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.65 (d, $J = 7.80$ Hz, 2H), 7.56 (d, $J = 8.79$ Hz, 2H), 7.25–7.35 (m, 4H), 7.21–7.22 (m, 2H), 7.16 (d, $J = 3.78$ Hz, 1H), 7.03 (m, 1H), 3.45–3.50 (m, 4H), 3.39–3.42 (m, 4H), 3.41 (s, 6H), 3.17–3.20 (m, 4H), 2.04–2.09 (m, 4H), 0.91–1.01 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 151.2, 150.4, 144.1, 141.3, 141.1, 137.9, 136.8, 133.5, 128.3, 127.8, 127.6, 125.3, 125.0, 124.7, 124.0, 123.9, 123.4, 120.7, 120.3, 72.3, 71.8, 70.1, 59.4, 55.0, 36.9, 24.5. Anal. Calcd. for $C_{33}H_{38}O_4S_2$: C, 70.43; H, 6.81. Found: C, 70.47; H, 6.67%. Molecular Mass: Calcd for $C_{33}H_{38}O_4S_2$: 562.78. Found: 562.19.

2-(2,2′-Bithien-5′-tributylstannyl-5-yl)-9,9-bis(3-(2-methoxyethoxy)propyl)-fluorene (8b). Under an argon atmosphere,

a solution of **8a** (1.13 g, 2.00 mmol) in anhydrous THF (20 ml) was added to *n*-BuLi (2.50 M in hexane, 0.88 ml, 2.2 mmol) at −78 °C. The reaction mixture was stirred at −78 °C for 60 min before tributyltin chloride (0.75 g, 0.63 ml, 2.3 mmol) was added dropwise. The mixture was warmed to room temperature, stirred overnight and then poured into a large amount of water for extraction with petroleum ether. The organic extracts were washed with KF aqueous solution and brine and dried over $MgSO_4$. Upon evaporating off the solvent, the crude product **8b** was obtained, which was used in the next step without further purification. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.65 (d, $J = 7.50$ Hz, 2H), 7.56 (d, $J = 9.33$ Hz, 2H), 7.26–7.35 (m, 4H), 7.16 (d, $J = 3.75$ Hz, 1H), 7.04 (d, $J = 3.36$ Hz, 1H), 3.45–3.50 (m, 5H), 3.39–3.42 (m, 4H), 3.41 (s, 6H), 3.17–3.20 (m, 4H), 2.04–2.09 (m, 4H), 1.57–1.59 (m, 6H), 1.32–1.39 (m, 6H), 1.10–1.15 (m, 6H), 0.91–1.01 (m, 13H).

2-(2,2′-Bithien-5-yl)-3′-nonafluorobutylmethyl-4′-methyl-spiro-[cyclopentyl-9,1′]fluorene (9a). The procedure for the synthesis of **6** was followed to prepare **9a** from **4b** and **5** in a yield of 74%. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.66–7.69 (m, 2H), 7.56–7.65 (m, 2H), 7.42–7.51 (m, 1H), 7.32–7.37 (m, 2H), 7.21–7.26 (m, 3H), 7.16 (d, $J = 3.69$ Hz, 1H), 7.03 (m, 1 H), 3.03–3.06 (m, 1H), 2.82–2.86 (m, 1H), 2.42–2.50 (m, 2H), 2.07–2.22 (m, 3H), 1.97 (dd, $J = 14.1$ Hz, $J = 4.20$ Hz, 1 H), 1.23 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 156.4, 155.6, 154.0, 153.4, 144.0, 139.9, 139.0, 137.9, 137.0, 134.0, 128.3, 127.5, 125.2, 124.8, 124.0, 123.3, 123.2, 120.5, 120.4, 120.2, 120.1, 56.9, 47.2, 45.8, 37.0, 36.9, 36.5, 31.8, 17.2, 17.1. Anal. Calcd. for $C_{31}H_{23}F_9S_2$: C, 59.04; H, 3.68. Found: C, 59.09; H, 3.27%. Molecular Mass: Calcd for $C_{31}H_{23}F_9S_2$: 630.63. Found: 630.04.

2-(2,2′-Bithien-5′-tributylstannyl-5-yl)-3′-nonafluorobutylmethyl-4′-methyl-spiro[cyclopentyl-9,1′]fluorene(9b). The procedure for the synthesis of **8b** was followed to prepare **9b** from **9a**. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.66–7.69 (m, 2H), 7.56–7.65 (m, 2H), 7.42–7.51 (m, 1H), 7.30–7.34 (m, 3H), 7.21–7.26 (m, 1H), 7.17 (d, $J = 3.84$ Hz, 1H), 7.05 (d, $J = 3.36$ Hz, 1H), 3.30–3.06 (m, 1H), 2.79–2.81 (m, 1H), 2.47–2.50 (m, 2H), 2.10–2.25 (m, 4H), 1.11–1.60 (m, 21H), 0.82–0.94 (m, 9H).

Compound 11a. The procedure for the synthesis of **6** was followed to prepare **11a** from **9b** and **10** in a yield of 90%. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.55–7.71 (m, 10H), 7.42–7.52 (m, 1H), 7.30–7.38 (m, 5H), 7.22–7.25 (m, 4H), 7.18 (d, $J = 3.78$ Hz, 1H), 7.03 (m, 1 H), 3.06–3.08 (m, 1H), 2.80–2.81 (m, 1H), 2.40–2.48 (m, 2H), 2.17–2.22 (m, 3H), 2.02–2.06(m, 5H), 1.07–1.53 (m, 23H), 0.70–0.92 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 155.6, 154.9, 153.3, 152.7, 151.5, 143.5, 143.2, 140.0, 139.9, 139.1, 138.9, 138.5, 138.2, 137.2, 136.3, 136.1, 133.2, 132.6, 127.5, 126.8, 124.5, 124.3, 124.1, 124.0, 123.3, 123.2, 119.8, 119.7, 119.4, 56.2, 55.0, 46.5, 45.0, 40.0, 36.1, 31.4, 29.6, 28.8, 23.4, 22.2, 13.7. Anal. Calcd. for $C_{68}H_{67}F_9S_4$: C, 69.01; H, 5.71. Found: C, 69.02; H, 5.46%. Molecular Mass: Calcd for $C_{68}H_{67}F_9S_4$: 1183.51. Found: 1181.86.

Compound 11b. The procedure for the synthesis of **8b** was followed to prepare **11b** from **11a**. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.55–7.71 (m, 10H), 7.42–7.52 (m, 1H), 7.30–7.38 (m, 6H), 7.20–7.23 (m, 2H), 7.17 (d, $J = 3.75$ Hz, 1H), 7.08 (d, $J = 3.36$ Hz, 1 H), 3.06–3.08 (m, 1H), 2.80–2.81 (m, 1H), 2.40–2.48 (m, 2H), 2.17–2.22 (m, 3H), 2.02–2.06(m, 5H), 0.78–1.62 (m, 60H).

Compound 13a. The procedure for the synthesis of **6** was followed to prepare **13a** from **12** and **6** in a yield of 81%. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.55–7.71 (m, 10H), 7.42–7.52 (m, 1H), 7.30–7.38 (m, 5H), 7.22–7.25 (m, 4H), 7.18 (d, $J = 3.78$ Hz, 1H), 7.03 (m, 1 H), 3.06–3.08 (m, 1H), 2.80–2.81 (m, 1H), 2.40–2.48 (m, 2H), 2.17–2.22 (m, 3H), 2.02–2.06(m, 5H), 1.07–1.53 (m, 23H), 0.70–0.92 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 156.5, 154.3, 152.0, 151.3, 144.5, 143.9, 141.3, 141.0, 139.3, 138.6, 137.8, 137.3, 137.2, 136.7, 134.1, 133.2, 128.3, 127.6, 127.3, 125.3, 125.1, 124.9, 124.8, 124.2, 124.1, 123.3, 120.6, 120.5, 120.4, 120.2, 120.1, 57.0, 55.6, 40.8, 37.0, 32.2, 30.4, 29.6, 24.2, 23.0, 17.2, 14.4. Anal. Calcd. for $C_{68}H_{67}F_9S_4$: C, 69.01; H, 5.71. Found: C, 69.02; H, 5.46%. Molecular Mass: Calcd for $C_{68}H_{67}F_9S_4$: 1183.51. Found: 1181.86.

Compound 13b. The procedure for the synthesis of **8b** was followed to prepare **13b** from **13a**. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.55–7.70 (m, 10H), 7.25–7.35 (m, 7H), 7.21–7.23 (m, 2H), 7.17 (m, 1H), 7.08 (d, $J = 2.67$ Hz, 1 H), 3.06–3.08 (m, 1H), 2.80–2.81 (m, 1H), 2.40–2.48 (m, 2H), 2.17–2.22 (m, 3H), 2.02–2.06(m, 5H), 1.56–1.62 (m, 6H), 1.30–1.39 (m, 6H), 1.05–1.16 (m, 29H), 0.91–0.93(m, 9H), 0.78–0.82 (m, 6H), 0.65 (m, 4H).

Compound 14a. The procedure for the synthesis of **6** was followed to prepare **14a** from **8b** and **10** in a yield of 84%. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.66–7.70 (m, 4H), 7.55–7.62 (m, 6H), 7.29–7.41 (m, 6H), 7.21–7.24 (m, 4H), 7.17 (d, $J = 3.75$ Hz, 1H), 7.04 (m, 1 H), 3.44–3.55 (m, 8H), 3.33 (s, 6H), 3.17–3.19 (m, 4H), 2.02–2.10(m, 8H), 0.97–1.17 (m, 24H), 0.76–0.79 (m, 6H), 0.65 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 152.2, 144.2, 144.1, 140.7, 136.9, 133.4, 128.3, 127.6, 125.2, 125.1, 124.8, 124.7, 124.1, 124.0, 123.4, 120.7, 120.6, 120.3, 120.2, 72.3, 71.8, 70.1, 59.4, 55.7, 54.9, 40.8, 36.9, 32.2, 30.4, 29.6, 24.5, 24.2, 23.0, 14.4. Anal. Calcd. for $C_{70}H_{82}O_4S_4$: C, 75.36; H, 7.41. Found: C, 74.97; H, 7.21%. Molecular Mass: Calcd for $C_{70}H_{82}O_4S_4$: 1115.66. Found: 1113.86.

Compound 14b. The procedure for the synthesis of **8b** was followed to prepare **14b** from **14a**. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.66–7.71 (m, 4H), 7.54–7.62 (m, 6H), 7.29–7.34 (m, 7H), 7.16–7.22 (m, 3H), 7.09 (d, $J = 3.36$ Hz, 1H), 3.35–3.54 (m, 8H), 3.31 (s, 6H), 3.17–3.21 (m, 4H), 2.02–2.10(m, 8H), 0.65–1.60 (m, 61H).

Compound 15a. The procedure for the synthesis of **6** was followed to prepare **15a** from **8b** and **6** in a yield of 79%. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.56–7.69 (m, 10H), 7.26–7.34 (m, 6H), 7.21–7.24 (m, 4H), 7.17 (d, $J = 3.69$ Hz, 1H), 7.04 (m, 1 H), 3.44–3.54 (m, 8H), 3.31 (s, 6H), 3.17–3.21 (m, 4H), 3.06–3.08 (m, 1H), 2.82–2.87 (m, 1H), 2.40–2.60 (m, 2H), 2.20–2.35 (m, 3H), 2.02–2.10(m, 5H), 1.29–1.33 (m, 3H), 0.95–1.01 (m, 4H). Anal. Calcd. for $C_{64}H_{59}F_9O_4S_4$: C, 64.52; H, 4.99. Found: C, 64.42; H, 4.37%. Molecular Mass: Calcd for $C_{64}H_{59}F_9O_4S_4$: 1191.40. Found: 1189.78.

Compound 15b. The procedure for the synthesis of **8b** was followed to prepare **15b** from **15a**. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.56–7.70 (m, 10H), 7.26–7.34 (m, 7H), 7.17–7.23 (m, 3H), 7.09 (d, $J = 3.33$ Hz, 1H), 3.44–3.55 (m, 8H), 3.32 (s, 6H), 3.17–3.21 (m, 4H), 3.06–3.08 (m, 1H), 2.82–2.87 (m, 1H), 2.40–2.60 (m, 2H), 2.20–2.35 (m, 3H), 2.02–2.10(m, 5H), 1.55–1.59 (m, 6H), 1.26–1.37 (m, 9H), 1.16 (m, 6H), 0.85–1.01 (m, 13H).

2,7-Bis(2,2′-bithien-5-yl)-3′-nonafluorobutylmethyl-4′-methyl-spiro[cyclopentyl-9,1′]fluorene (16a). The procedure for the synthesis of **6** was followed to prepare **16a** from **4a** and **5** in a yield of 53%. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.56–7.69 (m, 6H), 7.26–7.27 (m, 2H), 7.22–7.24 (m, 4H), 7.17 (d, $J = 3.69$ Hz, 2H), 7.03 (m, 2H), 3.10 (m, 1H), 2.84–2.85 (m, 1H), 2.49–2.54 (m, 2H), 2.21–2.31 (m, 3H), 2.02 (dd, $J = 15.6$ Hz, $J = 4.50$ Hz, 1 H), 1.28 (d, $J = 7.50$, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 156.5, 154.3, 143.9, 139.3, 138.6, 137.8, 137.1, 134.1, 128.3, 125.3, 125.1, 124.8, 124.1, 120.6, 120.5, 120.3, 57.0, 47.3, 45.8, 37.0, 36.7, 31.8, 17.2. Anal. Calcd. for $C_{39}H_{27}F_9S_4$: C, 58.93; H, 3.42. Found: C, 59.05; H, 3.06%. Molecular Mass: Calcd for $C_{39}H_{27}F_9S_4$: 794.88. Found: 793.89.

2,7-Bis(2,2′-Bithien-5′-tributylstannyl-5-yl)-3′-nonafluorobutyl-methyl-4′-methyl-spiro[cyclopentyl-9,1′]fluorene (16b). Under an argon atmosphere, a solution of **16a** (812 mg, 1.02 mmol) in anhydrous THF (15 ml) was added to *n*-BuLi (2.50 M in hexane, 1.0 ml, 2.5 mmol) at −78 °C. The reaction mixture was stirred at −78 °C for 30 min and at room temperature for another 30 min before tributyltin chloride (0.85 g, 0.71 ml, 2.6 mmol) was added dropwise at −78 °C. The mixture was warmed to room temperature, stirred overnight and then poured into a large amount of water for extraction with petroleum ether. The organic extracts were washed with KF aqueous solution and brine and dried over $MgSO_4$. Upon evaporating off the solvent, the crude product of **16b** was obtained. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.56–7.68 (m, 6H), 7.33–7.34 (d, $J = 3.18$ Hz, 2H), 7.26–7.27 (m, 2H), 7.17 (d, $J = 3.36$ Hz, 1H), 7.03 (d, $J = 3.36$ Hz, 1H), 3.10 (m, 1H), 2.84–2.85 (m, 1H), 2.49–2.54 (m, 2H), 2.21–2.31 (m, 3H), 2.02 (dd, $J = 15.6$ Hz, $J = 4.50$ Hz, 1 H), 1.56–1.64(m, 12H), 1.28 (m, 15H), 1.10–1.16 (m, 12H), 0.89–0.94 (m, 18H).

Compound 18. The procedure for the synthesis of **6** was followed to prepare **18** from **16b** and **17** (20 equiv of **16b**) in a yield of 51%. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.69–7.72 (m, 4H), 7.61–7.66 (m, 4H), 7.54–7.58 (m, 6H), 7.46–7.48 (m, 4H), 7.31–7.34 (m, 4H), 7.23–7.24 (m, 4H), 3.06–3.08 (m, 1H), 2.87 (m, 1H), 2.49–2.54 (m, 2H), 2.21–2.31 (m, 3H), 2.00–2.05 (m, 9H), 1.17–1.29 (m, 43H), 0.80–0.89 (m, 18H), 0.68–0.70 (m, 12H). Anal. Calcd. for $C_{97}H_{105}Br_2F_9S_4$: C, 67.35; H, 6.12. Found: C, 66.98; H, 5.97%. Molecular Mass: Calcd for $C_{97}H_{105}Br_2F_9S_4$: 1729.93. Found: 1727.86.

Compound 20. The procedure for the synthesis of **6** was followed to prepare **20** from **16b** and **19** (8 equiv of **16b**) in a yield of 62%. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.67–7.71 (m, 4H), 7.59–7.65 (m, 4H), 7.51–7.54 (m, 6H), 7.43–7.47 (m, 4H), 7.29–7.31 (d, $J = 3.72$ Hz, 4H), 7.21–7.25 (d, $J = 3.72$ Hz, 4H), 3.44–3.54 (m, 16H), 3.31 (s, 12H), 3.17–3.21 (m, 8H), 3.06–3.08 (m, 1H), 2.82–2.87 (m, 1H), 2.40–2.60 (m, 2H), 2.20–2.35 (m, 3H), 2.02–2.10(m, 9H), 1.29–1.33 (m, 3H), 0.95–1.01 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 156.5, 154.3, 152.7, 150.9, 143.9, 140.2, 140.1, 139.3, 138.7, 137.1, 137.0, 134.1, 133.9, 132.6, 132.4, 130.8, 129.0, 128.8, 126.7, 125.4, 125.3, 125.0, 124.3, 124.2, 121.8, 121.6, 120.8, 120.6, 120.4, 120.2, 72.3, 71.6, 70.2, 59.4, 55.3, 36.7, 24.5, 17.2. Anal. Calcd. for $C_{89}H_{89}Br_2F_9O_8S_4$: C, 61.23; H, 5.14. Found: C, 61.42; H, 5.37%. Molecular Mass: Calcd for $C_{89}H_{89}Br_2F_9O_8S_4$: 1745.71. Found: 1743.70.

Oligomer F7Th12-F3. In the absence of light, a solution of **13b** (0.81 g, 0.55 mmol), **18** (0.39 g, 0.23 mmol), and $Pd(PPh_3)_4$ (5 mg, 0.004 mmol) in anhydrous DMF/toluene (100 ml, volume ratio = 1:4) was stirred at 85 °C for 24 h. The mixture was cooled to room temperature and then poured into a large amount of water for extraction with methylene chloride. The organic extracts were washed with KF aqueous solution and brine before being dried over $MgSO_4$. Upon evaporating off the solvent, the residue was purified with column chromatography on silica gel with petroleum:chloroform (4:1) as the eluent. Further purification with PGPC afforded **F7Th12-F3** (0.40 g, 40%) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.53–7.66 (m, 38H), 7.26–7.31 (m, 18H), 7.15–7.20 (m, 12H), 3.02–3.04 (m, 3H), 2.79–2.80 (m, 3H), 2.40–2.48 (m, 6H), 2.18–2.32 (m, 9H), 2.02–2.10(m, 19H), 1.25–1.26 (m, 9H), 1.02–1.15 (m, 80H), 0.77–0.83 (m, 24H), 0.71 (m, 16H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 156.1, 154.0, 151.9, 151.7, 151.0, 143.7, 143.2, 140.9, 140.6, 140.2, 138.9, 138.2, 136.8, 136.7, 136.4, 136.3, 133.6, 132.8, 127.2, 127.1, 127.0, 126.9, 125.0, 124.8, 124.7, 124.6, 124.1, 123.8, 122.9, 120.6, 120.3, 119.8, 119.6, 119.4, 119.1, 55.6, 55.2, 31.9, 31.8, 30.0, 29.2, 22.6, 16.7, 14.0. Anal. Calcd. for $C_{233}H_{237}F_{27}S_{12}$: C, 71.12; H, 6.07. Found: C, 71.03; H, 6.24%. Molecular Mass: Calcd for $C_{233}H_{237}F_{27}S_{12}$: 3933.48. Found: 3933.03.

Oligomer F7Th12-F3O4. The procedure for the synthesis of **F7Th12-F3** was followed to prepare **F7Th12-F3O4** from **15b** and **20** in a yield of 41%. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.56–7.70 (m, 38H), 7.28–7.35 (m, 18H), 7.21–7.22 (m, 12H),, 3.44–3.54 (m, 32H), 3.31 (s, 24H), 3.17–3.21 (m, 16H), 3.06–3.08 (m, 3H), 2.82–2.87 (m, 3H), 2.40–2.60 (m, 6H), 2.20–2.35 (m, 9H), 2.02–2.10(m, 19H), 1.29–1.33 (m, 9H), 0.95–1.01 (m, 16H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 156.2, 154.0, 151.1, 150.9, 150.1, 143.7, 143.5, 143.3, 143.2, 141.0, 140.7, 140.3, 138.9, 138.3, 136.7, 136.5, 136.3, 133.6, 133.0, 127.2, 125.1, 124.9, 124.7, 124.0, 123.9, 123.0, 120.6, 120.4, 119.9, 119.8, 119.7, 119.5, 71.9, 71.4, 71.3, 69.7, 69.6, 59.0, 56.7, 54.8, 54.6, 36.6, 36.5, 24.2, 16.8. Anal. Calcd. for $C_{217}H_{205}F_{27}O_{16}S_{12}$: C, 65.71; H, 5.21. Found: C, 65.49; H, 5.02%. Molecular Mass: Calcd for $C_{217}H_{205}F_{27}O_{16}S_{12}$: 3965.15. Found: 3963.27.

Compound 22. The procedure for the synthesis of **6** was followed to prepare **22** from **11b** and **21** (1 equiv of **11b**) in a yield of 52%. Oligomer **F7Th12-F2** was also obtained in a yield of 20%. **22**: ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.68–7.71 (m, 10H), 7.53–7.65 (m, 16H), 7.43–7.50 (m, 3H), 7.29–7.38 (m, 10H), 7.22–7.24 (m, 8H), 3.06–3.08 (m, 1H), 2.82–2.87 (m, 1H), 2.40–2.60 (m, 2H), 2.20–2.35 (m, 3H), 2.02–2.10(m, 17H), 1.29–1.33 (m, 83H), 0.77–0.83 (m, 24H), 0.71 (m, 16H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 152.2, 144.2, 140.7, 137.0, 133.4, 125.2, 124.9,

124.2, 124.1, 120.8, 120.1, 120.0, 55.8, 40.8, 32.2, 30.4, 29.6, 24.3, 23.0, 14.4. Anal. Calcd. for $C_{171}H_{194}BrF_9S_8$: C, 74.50; H, 7.09. Found: C, 74.44; H, 7.12%. Molecular Mass: Calcd for $C_{171}H_{194}BrF_9S_8$: 2756.78. Found: 2753.69. **F7Th12-F2**: ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.56–7.71 (m, 38H), 7.43–7.52 (m, 2H), 7.33–7.35 (m, 12H), 7.29–7.31 (m, 4H), 7.21–7.24 (m, 12H), 3.02–3.04 (m, 2H), 2.79–2.80 (m, 2H), 2.40–2.48 (m, 4H), 2.18–2.32 (m, 6H), 2.02–2.10(m, 22H), 1.01–1.30 (m, 106H), 0.77–0.83 (m, 30H), 0.71 (m, 20H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 152.2, 144.1, 140.7, 136.9, 133.3, 125.2, 125.0, 124.3, 120.9, 119.9, 55.9, 32.2, 30.4, 29.6, 23.0, 14.5. Anal. Calcd. for $C_{239}H_{260}F_{18}S_{12}$: C, 74.38; H, 6.79. Found: C, 74.48; H, 6.79%. Molecular Mass: Calcd for $C_{239}H_{260}F_{18}S_{12}$: 3857.68. Found: 3856.15.

Oligomer F7Th12-F1O1. The procedure for the synthesis of **22** was followed to prepare **F7Th12-F1O1** from **22** and **14b** in a yield of 54%. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.53–7.66 (m, 38H), 7.43–7.52 (m, 1H), 7.33–7.35 (m, 12H), 7.29–7.31 (m, 5H), 7.21–7.24 (m, 12H), 3.35–3.55 (m, 8H), 3.31 (s, 6H), 3.17–3.22 (m, 4H), 3.02–3.04 (m, 1H), 2.79–2.80 (m, 1H), 2.40–2.48 (m, 2H), 2.18–2.32 (m, 3H), 2.02–2.10(m, 25H), 1.01–1.30 (m, 107H), 0.77–0.83 (m, 30H), 0.71 (m, 20H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 152.2, 144.2, 140.7, 137.0, 133.4, 125.1, 124.9, 124.1, 120.7, 120.1, 72.3, 71.8, 70.1, 59.4, 55.8, 40.8, 32.2, 30.4, 29.6, 24.2, 23.0, 14.4. Anal. Calcd. for $C_{241}H_{275}F_9O_4S_{12}$: C, 76.34; H, 7.31. Found: C, 76.09; H, 7.32%. Molecular Mass: Calcd for $C_{241}H_{275}F_9O_4S_{12}$: 3789.79. Found: 3789.11.

General information. Nuclear magnetic resonance spectra were taken on Bruker 300- or 400-MHz spectrometers. Chemical shifts are reported relative to internal tetramethylsilane. Mass spectra were acquired on a Kratos AXIMA-CFR mass spectrometer with anthracene-1,8,9-triol as the matrix (10 mg/ml in chloroform, sample/matrix = 500:1; laser: 337 nm). PGPC purification was carried out using a JAI LC-9104 recycling preparative gel permeation chromatograph (JAIGEL 2H/3H column assembly) with toluene as the eluent. Elemental analysis was carried out on a FlashEA1112 elemental analysis system. DSC measurements were performed on TA Q100 thermal analyzer at a heating/cooling rate of 10 °C min^{-1}. WAXD was carried out on a D\Max 2500V X-ray diffractometer. UV/Vis absorption and PL spectra were recorded on a Perkin Elmer Lambda 35 UV/Vis Spectrometer and a PerkinElmer LS 50B Luminescence Spectrometer, respectively.

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