Synthesis and Characterization of Monodisperse Oligo(fluorene-*co*-bithiophene)s

Xiaojie Zhang,[a] Yao Qu,[a] Laju Bu,[a] Hongkun Tian,[a] Jingping Zhang,[b] Lixiang Wang,[a] Yanhou Geng,*[a] and Fosong Wang[a]

Abstract: A series of monodisperse oligo(9,9-di-*n*-octylfluorene-*co*-bithiophene)s (OFbTs) with molecular lengths of up to 19.5 nm and molecular weights up to 7025 gmol^{-1} has been synthesized by a divergent/convergent approach involving Stille coupling reactions. Stille coupling is quite efficient in preparing this class of oligomers, and even the molecule with nine fluorene units and eight bithiophene units (**F9Th16**) can be synthesized in a yield as high as 70%. Because of easy functionalization of the thiophene ring at

its α position, no additional protecting group allowing activation for further reaction is necessary. However, the synthetic routes must be optimized to eliminate contamination of the targeting compounds with the homocoupling product of the organotin reagents. Synthesis of the longest oligomer **F13Th24** in a relative large quantity is limited by its low yield due to the pronounced

ligand-exchange side reactions of the starting materials and reaction intermediates. All oligomers longer than **F4Th6** are nematic mesomorphs and exhibit enhanced glass transition temperature and clearing point with increasing molecular length, as revealed by differential scanning calorimetry and polarizing optical microscopy. Absorption and photoluminescence (PL) measurements reveal that OFbTs are well-conjugated systems with an effective conjugation length longer than the length of **F13Th24**.

Keywords: conjugation · cross-coupling · liquid crystals · oligomers

Introduction

Monodisperse conjugated oligomers (MCOs) are characterized by well-defined and uniform structure.[1] Hence, MCOs have been extensively studied for understanding the intrinsic properties and establishing structure–properties relationships of various conjugated systems.[1–3] In recent years, they have also been intensively explored as high-performance optoelectronic materials for applications in optoelectronic devices.[4–8] Besides optical properties, thermal properties, film

[a] X. Zhang, Y. Qu, L. Bu, Dr. H. Tian, Prof. L. Wang, Prof. Y. Geng, Prof. F. Wang
State Key Laboratory of Polymer Physics and Chemistry
Changchun Institute of Applied Chemistry
Graduate School of Chinese Academy of Sciences
Chinese Academy of Sciences
5625, Renmin Street, Changchun 130022 (P. R. China)
Fax: (+86)0431-8568-5653
E-mail: yhgeng@ciac.jl.cn

[b] Prof. J. Zhang
Faculty of Chemistry
Northeast Normal University
Changchun 130024 (P. R. China)

morphology, and device performance are also dependent on chain length when the molecular weight approaches the macromolecular range.[7a,9–11] Therefore, synthesis of long-chain MCOs is important for fully exploring the relationship between molecular structure (or length) and properties, as well as for determination of effective conjugation length (ECL), since extrapolating the linear curve of energy gap against the reciprocal of the number of repeating units to estimate the ECL is not reliable for many conjugated systems.[2a,12] However, synthesis of long-chain MCOs still remains a challenge today, although several series of MCOs with molecular length exceeding 10 nm have been reported.[3,10,13–15]

The most elegant and efficient way to prepare long-chain MCOs is an iterative divergent/convergent binomial approach, in which two orthogonal protecting groups allowing selective deprotection or activation for the next chain-growth step are employed.[1b,c] This approach was first developed by Tour et al. for synthesis of oligo(arylene ethynylene)s with molecular lengths up to 12.8 nm.[1b,13] Following this approach, Schlüter et al. later synthesized oligophenylenes with up to 16 phenylene rings.[16] In a modified divergent/convergent approach, long-chain oligofluorenes (OFs),[10,17] oligothiophenes (OThs),[15b,18] oligo(arylene vi-

nylene)s,[3c,19] and oligoynes[3a,20,21] have also been synthesized. However, success of all the aforementioned syntheses relied on introduction of appropriate protecting groups. More recently, OThs with up to 96 thiophene rings, the longest MCO so far, were synthesized by controlled oxidative homocoupling of shorter OThs followed by purification by preparative gel-permeation chromatography (PGPC).[15a] Unfortunately, this method is difficult to extend to the synthesis of other MCOs.

Fluorene has become one of the most promising building blocks for construction of soluble conjugated materials, since introduction of substituents at its 9-position to endow solubility has almost no effect on the molecular conjugation. Thiophene is another important aromatic ring, especially for synthesis of high-performance semiconducting materials.[22] Its easy functionalization has generated abundant new chemistry. For example, trialkyltin and boronic acid groups can be easily introduced by deprotonation followed by treatment with organotin and organoboron reagents for efficient metal-mediated cross-coupling reactions to synthesize various conjugated molecules.[23] Thus, it is possible to avoid using protecting groups for introduction of new reactive groups, which are essential for further chain growth. The conjugated polymer composed of fluorene and bithiophene units, that is, poly(fluorene-co-bithiophene), PFbT, has proved to be one of the most promising semiconducting polymers due to its excellent stability against oxidation, capability for supramolecular organization, and high charge-carrier transport capability.[9,24] Herein we present the synthesis of a first series of oligo(fluorene-co-bithiophene)s (OFbTs) with 2–13 fluorene and 1–12 bithiophene units by means of Stille coupling. The longest oligomer has a length of about 19.5 nm and a molecular weight of 7025 g mol^{-1}, and is the longest oligoaryl so far synthesized by metal-mediated cross-coupling. The thermal and optical properties of the oligomers were also studied in detail to gain insights into this conjugated system.

Results and Discussion

Synthesis and structural characterization: Separating the target compound from reactants and by-products is a key issue in choosing synthetic routes for long-chain MCOs. In the current work, a divergent/convergent approach (Figure 1) was followed to synthesize OFbTs, that is, two building blocks A and B of certain length were first synthesized in a divergent manner and then converted to target compound ABA by Stille coupling. The reaction has two main by-products: homocoupling product AA and one-sided coupling product AB in addition to products of ligand-exchange reactions.[25] Therefore, it is important to select appropriate lengths of building blocks A and B to achieve large enough mass differences between ABA and AA/AB, so that product and by-products are separable. Choosing an appropriate solvent for Stille coupling is another key issue in the synthesis of the current oligomeric systems. We found
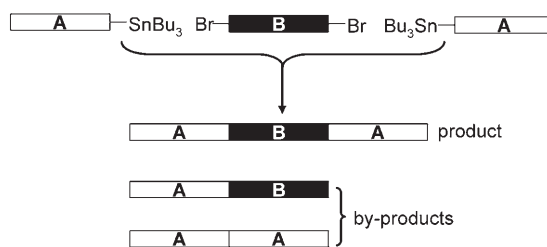

Figure 1. Divergent/convergent synthetic approach to OFbTs; the two main by-products that should have an effect on purification of the product are shown.

that reactions in toluene, which is generally used for Stille coupling, were slow and less efficient, and addition of certain amount of DMF could accelerate the reaction. Therefore, toluene/DMF with a volume ratio of 2/1 to 8/1 was used as the solvent to maintain both good solubility and high reaction rate.

The synthesis of building block A is outlined in Scheme 1. 5-Tributylstannyl-2,2′-bithiophene (**2**) was treated with 2,7-dibromo-9,9-dioctylfluorene (**1**) and 2,7-diiodo-9,9-dioctylfluorene (**3**) to afford bromo- and iodo-terminated 5-fluorenyl-2,2′-bithiophenes **5** and **7** in yields of 82 and 79%, respectively. Compound **5** was almost quantitatively converted to organotin reagent **6** by treatment with LDA and Bu₃SnCl in succession. Because of the higher reactivity of the iodo group compared to the bromo group in Stille coupling, bromo-terminated compound **8** with two fluorene and two bithiophene units was prepared in good yield by the coupling of **6** and **7**. To synthesize the final building blocks **9–12** with different lengths, 2-bromo-9,9-dioctylfluorene (**4**) was treated with **2** to give **9a** in 76% yield. Deprotonation of **9a** followed by treatment with Bu₃SnCl afforded organotin reagent **9b** quantitatively, which was further coupled with **5** to give **10a**. Reactions of the corresponding organotin reagent **10b** with **5** and **8** afforded **11a** and **12a** in yields of 79 and 71%, respectively. To ensure its purity, **12a** was further purified by PGPC after column chromatography on silica gel. Organotin reagents **11b** and **12b** were also prepared quantitatively by following the same procedure as for preparation of **9b**. Since deprotonation of thiophene units at the α position by *n*BuLi and subsequent reaction with Bu₃SnCl are both very efficient, all organotin reagents were sufficiently pure for the next reaction step without any further purification. This advantage of the thiophene unit can eliminate the limitations due to difficult introduction of appropriate protecting/reactive groups in the synthesis of long-chain conjugated oligomers.

Similar reactions were used in the synthesis of building block B (Scheme 2). An excess of **1** was required to achieve reasonable yield in the preparation of dibrominated compounds **14**, **17**, and **18**. The longest B building block, **18**, was also purified by PGPC after column chromatography on silica gel.

Scheme 3 displays the synthesis of the final OFbTs oligomers. Organotin reagent **13** was coupled with **4** to
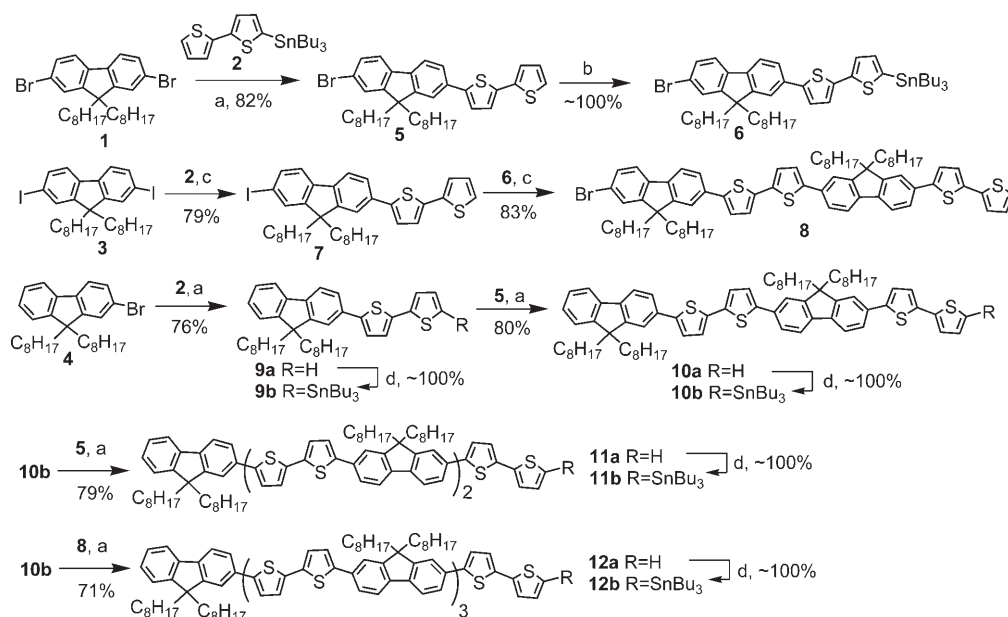
Scheme 1. Synthesis of building block A: a) toluene/DMF, [Pd(PPh₃)₄], 85 °C; b) 1) LDA, −78 °C to room temperature; 2) Bu₃SnCl, −78 °C to room temperature, THF; c) Toluene/DMF, [Pd(PPh₃)₄], 70 °C; d) 1) *n*BuLi, −78 °C; 2) Bu₃SnCl, −78 °C to room temperature, THF. LDA: lithium diisopropylamide.
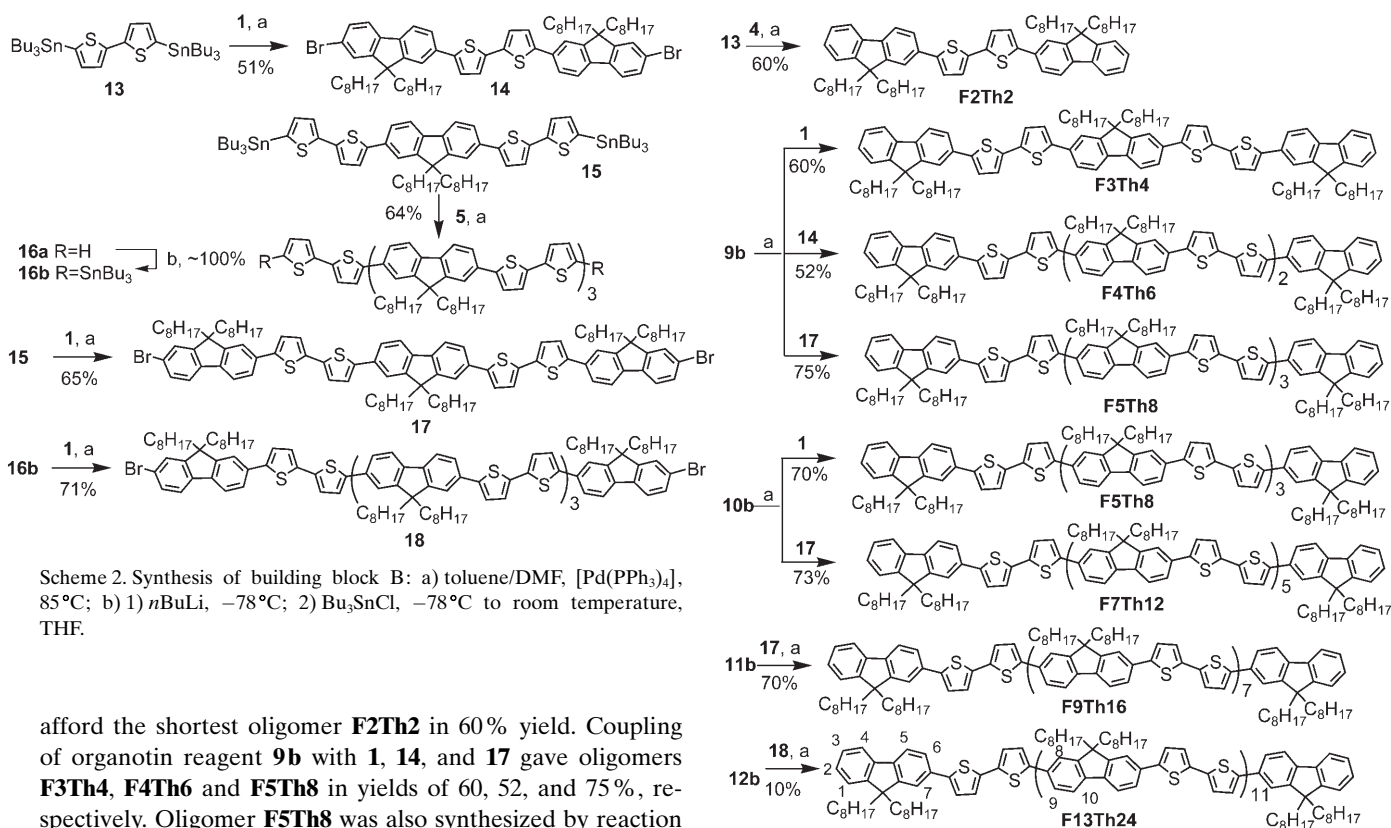
Scheme 2. Synthesis of building block B: a) toluene/DMF, [Pd(PPh₃)₄], 85 °C; b) 1) *n*BuLi, −78 °C; 2) Bu₃SnCl, −78 °C to room temperature, THF.

Scheme 3. Synthesis of OFbTs: a) toluene/DMF, [Pd(PPh₃)₄], 85 °C.

afford the shortest oligomer **F2Th2** in 60 % yield. Coupling of organotin reagent **9b** with **1**, **14**, and **17** gave oligomers **F3Th4**, **F4Th6** and **F5Th8** in yields of 60, 52, and 75 %, respectively. Oligomer **F5Th8** was also synthesized by reaction of **10b** and **1** in a 70 % yield. The yields of the Stille coupling reactions for the synthesis of **F7Th12** and **F9Th16** were still as high as 73 and 70 %, respectively, although the molecular weights of all the reactants are higher than 1600 g mol⁻¹. However, the reaction of organotin reagent **12b** and **18** gave the longest oligomer **F13Th24** in a yield of

only 10 %. This low yield is ascribed to the considerably increased amount of by-products and losses in recycling PGPC purification. Nevertheless, a sufficient quantity of

Oligomers	$M_{w,MS}$[a]	M_{calcd}	$M_{w,GPC}$[b]	$M_{w,GPC}/M_{w,MS}$	PDI[b]	T_g [°C][c]	T_m [°C][c]	T_c [°C][c]
F2Th2	941.58	942.62	1 400	1.44	1.04	NA	NA	NA
F3Th4	1495.44	1495.91	2 200	1.47	1.03	37	128	NA
F4Th6	2048.81	2048.20	3 500	1.71	1.04	53	184	NA
F5Th8	2601.07	2601.49	4 600	1.77	1.03	65	154	177
F7Th12	3708.55	3707.07	8 200	2.21	1.03	76	NA	228
F9Th16	4814.32	4812.65	11 100	2.31	1.03	88	204	258
F13Th24	7026.59	7024.80	17 700	2.52	1.09	97	236	279
PF8bT[d]	NA	NA	53 800	NA	2.83	93	239	280

[a] Measured by MALDI-TOF MS. [b] Measured by GPC with PS as standard. [c] Measured by DSC with second heating at 10°C min⁻¹. [d] From reference [27].

F13Th24 can still be obtained for general characterization. To the best of our knowledge, this oligomer is the longest monodisperse oligoaryl synthesized by means of metal-mediated cross-coupling reactions to date. Its molecular length is about 19.5 nm in the optimized chain conformation. To ensure purity, all these oligomers were further purified by PGPC with a size-exclusion column (2H-40/3H-40) after purification by column chromatography on silica gel.

The molecular structures of OFbTs were validated by ¹H NMR spectroscopy, gel-permeation chromatography (GPC), and matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry (MS), and elemental analysis. Molecular weights measured by GPC (weight-average molecular weight $M_{w,GPC}$) and MS ($M_{w,MS}$) along with calculated ones (M_{calcd}) are listed in Table 1. The $M_{w,MS}$ of all oligomers determined by means of MALDI-
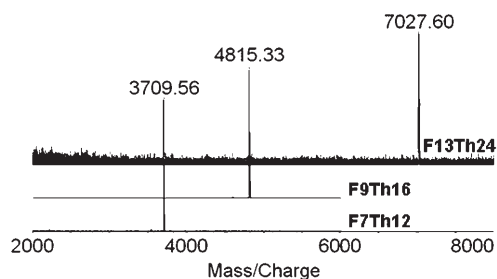

Figure 2. MALDI-TOF mass spectra ([*M*+H]⁺) of oligomers **F7Th12**, **F9Th16**, and **F13Th24** with anthracene-1,8,9-triol as matrix.

TOF MS are consistent with M_{calcd}. Figure 2 displays representative mass spectra for **F7Th12**, **F9Th16**, and **F13Th24**, all of which exhibit one peak corresponding to the molecular ion. The polydispersity indexes (PDI) of the oligomers determined by GPC are ≤1.04, except for that of **F13Th24**, consistent with their monodisperse character. The relatively large PDI of the longest oligomer **F13Th24** (1.09) is attributable to its high molecular weight, close to those of polymers, so that chain entanglement or aggregation is inevitable. In fact, NMR measurements indicate that aggregates of **F13Th24** do exist in solution. As shown in Figure 3, the ¹H NMR spectrum of **F13Th24** is featureless at 20°C, and the peaks corresponding to H4, H5, and H10 overlap with
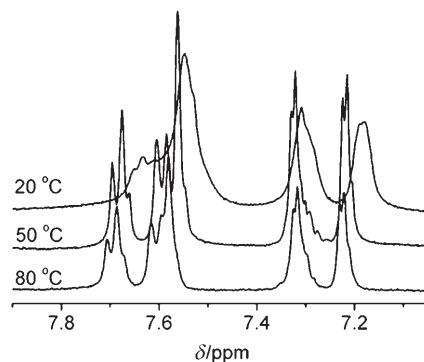

Figure 3. ¹H NMR spectrum of **F13Th24** in $C_2D_2Cl_4$ at 20°C, 50°C, and 80°C, with a concentration of 8.5×10^{-4} mol L⁻¹ (6.0 mg mL⁻¹).

those of H6–H9 (these two groups of peaks are located at 7.66–7.70 and 7.56–7.61 ppm, respectively, at 50°C). On increasing the temperature to 50 and 80°C, the spectra are shifted downfield and the aforementioned peaks become distinct. The $M_{w,GPC}$ values significantly deviate from the true molecular weight, especially for the long oligomers. For instance, $M_{w,GPC}$ of **F13Th24** is 17 700 g mol⁻¹, 2.5 times M_{calcd} (7025 g mol⁻¹). This deviation is very close to that of polyfluorenes (2.7)[26] and further corroborates the polymer character of **F13Th24**. This inflation of molecular weights in GPC measurements versus polystyrene (PS) standard is a general phenomenon for rodlike long conjugated oligomers and polymers, and it originates from different chain geometries of rigid conjugated molecules and PS, a random-coil polymer.

Homocoupling of organotin reagents is one of the main side reactions in Stille coupling.[25] Therefore, choosing building blocks A and B with appropriate length is very important for obtaining pure target compounds. We synthesized **F5Th8** by two different routes (Scheme 3). The two reactions gave products with identical ¹H NMR spectra, GPC profiles, and yield. However, MALDI-TOF MS indicated presence of traces of homocoupling product **19** (Figure 4) in **F5Th8** prepared from **10b** and **1**, which can not be detected by ¹H NMR. This by-product is very difficult to remove from the product, even with recycling PGPC, since they differ by only one fluorene unit. The presence of traces of **19** has a substantial effect on film PL spectrum of **F5Th8**, al-
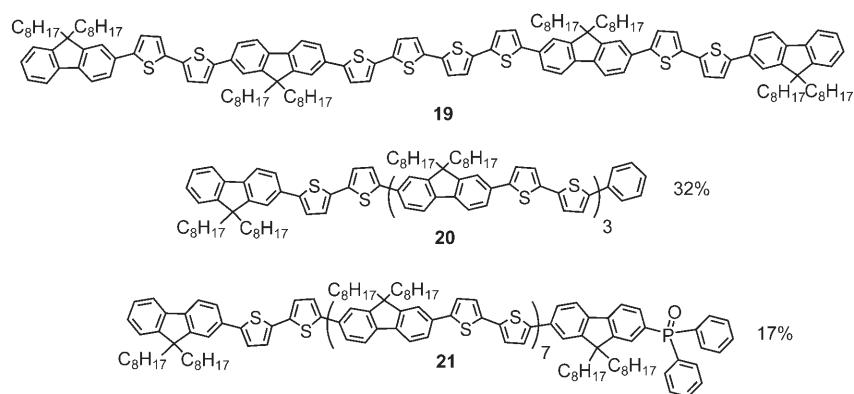
Figure 4. By-products in the preparation of **F5Th8** and **F13Th24**.

though there is no difference in absorption spectra (both solution and film) and solution PL spectra between products prepared by the two routes.

The 52–75 % yield for all the oligomers except **F13Th24** is notably high considering the high molecular weight of both reactants and products. To elucidate the reason for the low yield of **F13Th24**, two main by-products (Figure 4) with a yield of 32 and 17 %, respectively, were isolated by means of recycling PGPC. The first by-product exhibits identical retention time to **12a**, and MALDI-TOF MS indicates that the main component is compound **20**. This means that the tributyltin group can also participate in ligand-exchange reaction. The second by-product exhibits identical retention time to **F9Th16** on a size-exclusion column in the PGPC purification process, but its polarity is higher than that of **F9Th16**, as indicated by longer retention time on a silica gel column. On the basis of MALDI-TOF MS, ^{31}P NMR, and IR measurements (see Figures S4–S6 in the Supporting Information), this by-product was identified as **21**. Therefore, it originated from ligand exchange between one-sided coupling product (A-B-Br) and PPh$_3$, followed by oxidation in the workup process. This type of ligand exchange is one of the main side reactions in Pd^0-catalyzed cross-coupling reactions. Since the Stille coupling reaction between large molecules **12b** and **18** should be very slow (molecular weights of **12b** and **18** are 2502 and 2759 gmol^{-1}, respectively), these side reactions should be more pronounced than in the preparation of shorter OFbTs. Further improving the yield for the preparation of **F13Th24** and even longer oligomers by Stille coupling would rely on exploring new catalyst systems to avoid the above side reactions.

Thermotropic properties: Differential scanning calorimetry (DSC) and polarizing optical microscopy (POM) were employed to determine phase transition temperatures (Table 1). Oligomers longer than **F4Th6** are all nematic mesomorphs, consistent with the fact that of poly(9,9-dioctyl-fluorene-co-bithiophene), **PF8bT**, is nematic liquid crystalline.[24c] Figure 5 shows the DSC second heating traces of **F4Th6**, **F5Th8**, **F7Th12**, **F9Th16**, and **F13Th24** with a heating rate of 10 °C min^{-1}. Oligomer **F4Th6** exhibits a exother-

mal crystallization peak at 98 °C, an endothermal crystal melting peak at 184 °C, and a glass transition at 53 °C, while **F5Th8** shows an additional peak at 177 °C, above the melting point (T_m) of 154 °C, corresponding to the clearing point (T_c) of the nematic mesophase. The typical nematic textures, for example, the threaded textures shown in Figure 6, can be observed by hot-stage POM of a micrometer-thick film on a
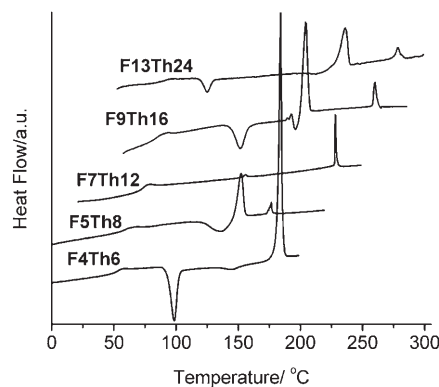

Figure 5. The DSC second heating traces of OFbTs with a heating rate of 10 °C min^{-1}.

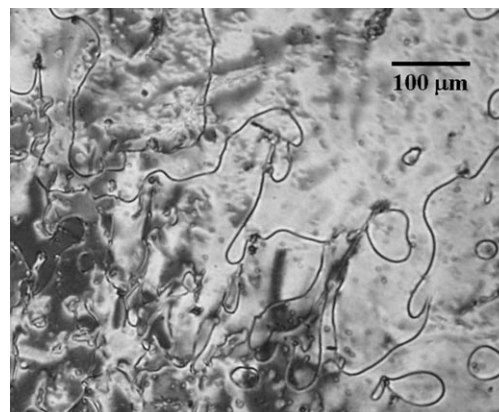

Figure 6. Nematic threaded textures of **F5Th8** at 170 °C on heating.

glass slide with a cover slip. Both glass transition temperature (T_g) and T_c increase with increasing molecular weight, and are 97 and 279 °C for **F13Th24**, respectively. These values are very close to those of **PF8bT** with a $M_{w,GPC}$ of 53 800 (PDI = 2.83),[27] as shown in Table 1. However, one cannot conclude that these parameters have attained saturation for **F13Th24**, because the polymer contains a considerable amount of molecules smaller than **F13Th24**, which can serve as plasticizers to reduce T_g and T_c. In a previous study
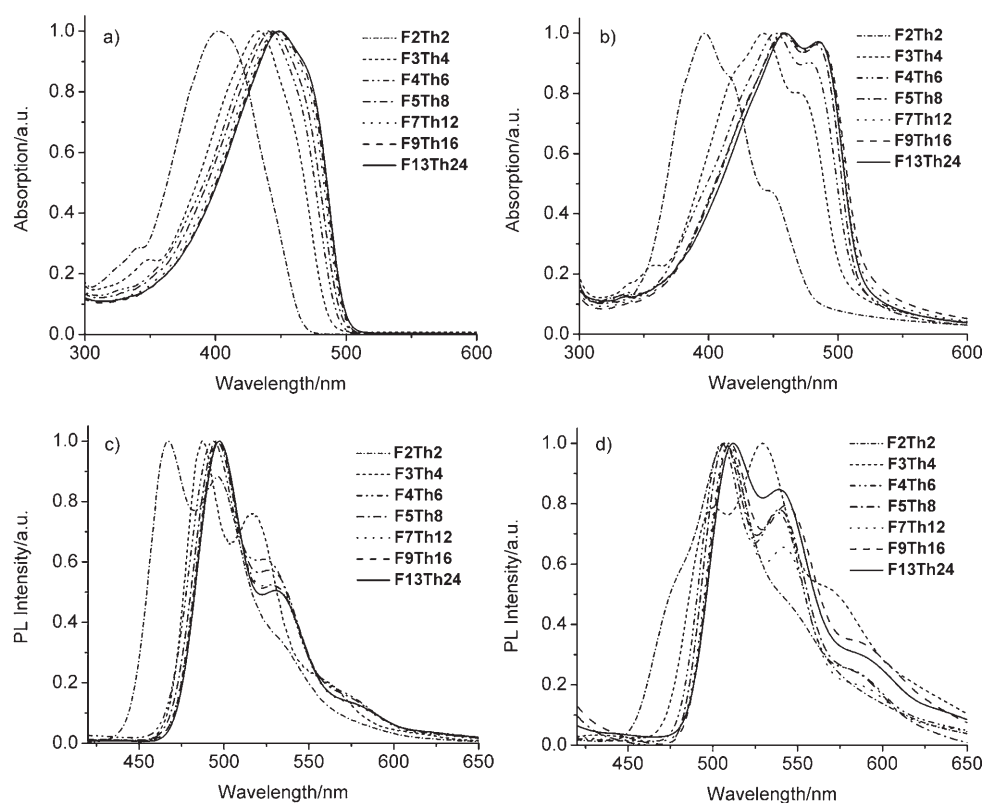
Figure 7. Absorption (a and b) and PL (c and d) spectra of OFbTs in chloroform solution (a and c) and film state (b and d). The concentrations for absorption and PL measurements were 10^{-5} and 10^{-6} mol L^{-1}, respectively.

on oligofluorenes by Wegner et al., both T_g and T_c of the corresponding polyfluorene were estimated by extrapolation of $T \sim n^{-1}$.[15b] Following this method, T_g and T_c of **PF8bT** with an infinite number of repeating unit are estimated to be 104 and 332 °C, respectively.

Optical properties: Absorption and photoluminescence (PL) spectra in solutions and films of OFbTs are shown in Figure 7, and the related data are collected in Table 2. In solution, the oligomers exhibit unstructured absorption bands (Figure 7 a). In contrast, the film absorption spectra are well resolved and exhibit a considerable bathochromic shift (Figure 7 b), that is, the molecules adopt a more extended con-

formation in the solid state. The absorption maximum is red-shifted with increasing molecular length. The plot of the wavenumber of maximum absorption ($\tilde{\nu}_{max}$) versus n^{-1} in solution is shown in Figure 8. For the short oligomers, the plot shows a linear correlation of wavenumber with n^{-1}, but for the long oligomers deviation from linearity occurs due to saturation, and the completely saturated point of the red shift is defined as the ECL. From Table 2, it is clear that the current oligomers continue to exhibit red shifts of their absorption spectra up to **F13Th24**. Considering that **F13Th24** already has 13 fluorene and 12 bithiophene units, the ECL of the current oligomeric system is quite long. Previously, Chen et al. found that the absorption spectra of chiral OFs

Table 2. Absorption ($\lambda_{max,abs}$) and PL ($\lambda_{max,PL}$) maxima of OFbTs in chloroform solution and film state, and energy levels of OFbTs.

Oligomer	$\lambda_{max,abs}$ [nm]		$\lambda_{max,PL}$ [nm]		ΔE[b] [eV]	HOMO[c] [eV]
	Solution[a]	Film	Solution[a]	Film		
F2Th2	402.5	397.0, 450.0	467.0, 496.5	476.0, 507.0, 548.0	2.66	−5.32
F3Th4	433.0	442.5, 472.0	487.0, 516.5	500.5, 530.0, 570.5	2.55	−5.27
F4Th6	440.0	452.0, 478.0	493.5, 523.5	505.5, 538.5, 573.0	2.52	−5.25
F5Th8	443.0	457.0, 483.0	495.5, 527.0	507.0, 539.5, 576.5	2.50	−5.25
F7Th12	446.5	458.0, 485.0	496.5, 528.0	509.5, 542.0, 582.0	2.49	−5.24
F9Th16	448.0	458.0, 486.0	497.0, 529.0	510.0, 543.0, 586.0	2.49	−5.24
F13Th24	448.5	459.5, 484.5	497.5, 530.5	512.0, 539.0, 588.0	2.48	NA
PF8bT[d]	452.0	458.0, 479.0	495.0, 530.0	511.0, 537.0, 577.0	NA	NA

[a] Measured in chloroform at a concentration of 10^{-5} and 10^{-6} mol L^{-1} for absorption and PL, respectively. [b] Band gap calculated from absorption edge. [c] Measured by cyclic voltammetry. [d] From reference [27].
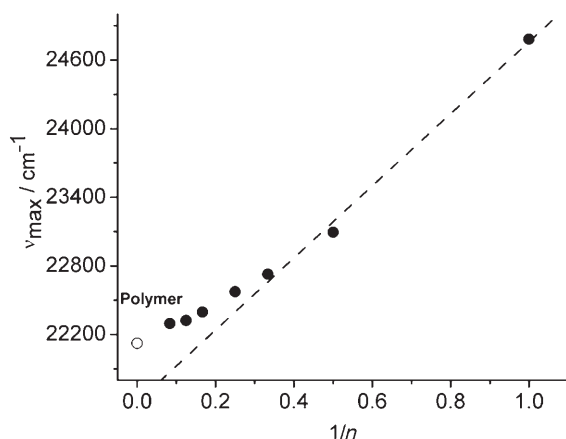
Figure 8. Plot of ν_{max} versus reciprocal number of repeat units n.

Figure 9. Cyclic voltammograms of OFbTs ($10^{-3}\,\mathrm{mol\,L^{-1}}$) in CH_2Cl_2/Bu_4NPF_6 ($0.1\,\mathrm{mol\,L^{-1}}$) at a scan rate of $50\,\mathrm{mV\,s^{-1}}$.

remained bathochromic up to 16 fluorene units. Otsubo et al. also reported that the ECL of OThs could exceed 96 repeat units. With the polymer counterpart ($M_{w,GPC}=53\,800$) as reference, the ECL of OFbTs should be longer than 20 nm.

Normalized PL spectra of the OFbTs in chloroform with a concentration of $10^{-6}\,\mathrm{mol\,L^{-1}}$ and excitation wavelength at the absorption maximum are shown in Figure 7c, and the emission maxima are listed in Table 2. Three distinct fluorescence maxima, which can be assigned to the 0–0, 0–1, and 0–2 intrachain singlet transitions, are observed. Like the absorption spectra, the PL spectra are also red-shifted with increasing molecular length. Moreover, the relative intensity of the three emission peaks changes with the number of repeating units (n), and that of the 0–0 transition increases with increasing n, while those of the 0–1 and 0–2 transition decrease. This may be related to increased intrachain coupling interaction with increasing molecular length. Figure 7d shows the normalized film PL spectra of the oligomers on a quartz substrate with excitation wavelength at the absorption maxima, and the data are also listed in Table 2. Similar to the absorption spectra, film PL spectra exhibit noteworthy red shifts in comparison with solution spectra.

To obtain the HOMO and LUMO energy levels, the cyclic voltammograms (CV) of OFbTs were recorded in a general three-electrode electrochemical cell. As shown in Figure 9, all oligomers except **F13Th24**, the solubility of which in CH_2Cl_2 is too low to do CV measurements, exhibit reversible or quasireversible redox process in the positive potential region. With increasing chain length, the number of stable redox states increases, and the potential difference between adjacent redox states decreases. This phenomenon has been observed in regioregular oligo(3-alkylthiophene)s.[18b] From the oxidation onset, the HOMO energy level was estimated to be -5.32 eV for **F2Th2** and levels off at -5.24 eV as the molecular length increases. Although we did not observe redox processes in the negative potential region, the LUMO energy level of the oligomers can be estimated as the sum of HOMO and energy gap (ΔE), which is calculated from the absorption edge of the oligomers.
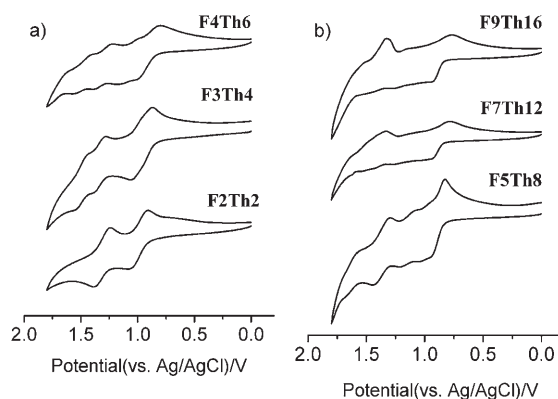
Conclusion

By taking advantage of the reactivity of thiophene at the α position, which allows a tributyltin group for chain growth to be easily introduced in high yield, we have synthesized the first series of monodisperse conjugated oligomers based on fluorene–bithiophene repeating units by means of Stille coupling without introducing additional protecting groups. There are 13 fluorene units and 12 bithiophene units in the longest oligomer, **F13Th24**, its molecular weight is as high as $7025\,\mathrm{g\,mol^{-1}}$, and its chain length is about 19.5 nm. All oligomers shorter than **F13Th24** can be prepared in high yield. Pronounced ligand-exchange side reactions are the main reason for the low yield of **F13Th24**.

Studies by DSC and POM revealed that all oligomers longer than **F3Th4** are nematic mesomorphs, and T_g and T_c increase as molecular length increases. The T_g and T_c values of **F13Th24** are very close to those of the polymer analogue with an $M_{w,GPC}$ of $53\,800\,\mathrm{g\,mol^{-1}}$ (versus PS standard), that is, it should have macromolecular features. Absorption spectra revealed that the absorption maximum of the oligomers is red-shifted with increasing molecular length and not saturated until **F13Th24**, that is, OFbTs are well-conjugated molecules.

Experimental Section

1,8,9-triol as matrix. GPC measurements were conducted on a Water 510 system using polystyrene as standard and THF as eluent. Differential scanning calorimetry (DSC) measurements were performed on TA Q100 thermal analyzer at a heating rate of 10°C min^{-1}. UV/Vis absorption and PL spectra were recorded on a Perkin Elmer Lambda 35 UV/Vis Spectrometer and a Perkin Elmer LS 50B Luminescence Spectrometer. All films for absorption and PL measurement were spin-coated from chloroform solution at 1000–2500 rpm for 30 s with a concentration of 6–7 mg mL^{-1}. Cyclic voltammetry (CV) was performed on a CHI660a electrochemical analyzer with a three-electrode cell in a solution of 0.1 mol L^{-1} tetrabutylammonium hexafluorophosphate in anhydrous CH$_2$Cl$_2$ at a scan rate of 50 mV s^{-1}. A Pt electrode with a diameter of 2 mm, a Pt wire, and an Ag/AgCl electrode were used as the working, counter-, and reference electrodes, respectively. The potential was calibrated against the ferrocene/ferrocenium couple (0.44 V vs Ag/AgCl in CH$_2$Cl$_2$). HOMO energy levels were estimated by the equation: HOMO $= -(4.36 + E_{ox}^{onset})$.[31] The structure of **F13Th24** was optimized with the aid of the Windows version of the Gaussian 98 package.[32] B3LYP[33] and PBE0[34] approaches (respectively coupled to 6-31G*[35] and 6-31G**[35] basis sets) were used respectively for the fluorene and thiophene residues of the repeating unit; the rest of the oligomer unit was treated with AM1.[36]

2-(2,2′-Bithien-5-yl)-7-bromo-9,9-dioctylfluorene (5): In the absence of light, a solution of 5-tributylstannyl-2,2′-bithiophene (**2**, 3.60 g, 7.90 mmol), 2,7-dibromo-9,9-dioctylfluorene (**1**, 8.01 g, 14.6 mmol), and [Pd(PPh$_3$)$_4$] (185 mg, 0.160 mmol) in anhydrous DMF/toluene (100 mL, 1/4) was stirred for 24 h at 85°C. 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 aqueous KF solution and brine and then dried over MgSO$_4$. After evaporating the solvent, the residue was purified by column chromatography on silica gel with petroleum as eluent to afford **5** (4.12 g, 82%) as a light yellow solid. ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.64$ (d, $J = 7.95$ Hz, 1H), 7.58 (d, $J = 1.59$ Hz, 1H), 7.50–7.56 (m, 2H), 7.42–7.45 (m, 2H), 7.27 (d, $J = 3.75$ Hz, 1H), 7.20–7.23 (m, 2H), 7.16 (d, $J = 3.60$ Hz, 1H), 7.03 (dd, $J = 3.73$, 4.95 Hz, 1H), 1.92–1.98 (m, 4H), 1.04–1.19 (m, 20H), 0.77–0.81 (m, 6H), 0.62 ppm (m, 4H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 153.1$, 151.2, 143.6, 139.7, 139.6, 137.5, 136.6, 133.3, 130.0, 127.9, 126.2, 124.7, 124.6, 124.4, 123.6, 121.2, 121.0, 120.2, 119.8, 55.5, 40.2, 31.8, 29.9, 29.2, 23.7, 22.6, 14.0 ppm; MS (MALDI-TOF, reflectron mode): m/z (%): 634.16 (100) [M+H]$^+$; elemental analysis (%) calcd for C$_{37}$H$_{45}$BrS$_2$ (634.21): C 70.12, H 7.16; found: C 70.30, H 7.21.

2-(2,2′-Bithien-5′-tributylstannyl-5-yl)-7-bromo-9,9-dioctylfluorene (6): Under an argon atmosphere, nBuLi (2.50 M in hexane, 0.64 mL, 1.6 mmol) was added dropwise to a stirred solution of diisopropylamine (0.23 mL, 1.6 mmol) in dry THF (10 mL) at -78°C. The mixture was warmed to 0°C, stirred for 5 min, and then cooled to -78°C, after which **5** (1.00 g, 1.60 mmol) in dry THF (10 mL) was added dropwise. The reaction mixture was stirred at -78°C for a further 60 min, and then tributyltin chloride (0.52 g, 0.43 mL, 1.60 mmol) was added in one portion. 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 extract was washed with aqueous Na$_2$CO$_3$ solution and brine and then dried over MgSO$_4$. After the solvent was evaporated, the crude product **6** was used for the next step without further purification. ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.68$ (d, $J = 7.89$ Hz, 1H), 7.63 (d, $J = 1.26$ Hz, 1H), 7.55–7.60 (m, 2H), 7.48–7.50 (m, 2H), 7.37 (d, $J = 3.3$ Hz, 1H), 7.32 (d, $J = 3.72$ Hz, 1H), 7.21 (d, $J = 3.75$ Hz, 1H), 7.13 (d, $J = 3.30$ Hz, 1H), 1.99–2.01 (m, 4H), 1.60–1.64 (m, 6H), 1.36–1.44 (m, 6H), 1.09–1.23 (m, 26H), 0.93–0.98 (m, 9H), 0.82–0.87 (m, 6H), 0.63 ppm (m, 4H).

2-(2,2′-Bithien-5-yl)-7-iodo-9,9-dioctylfluorene (7): In the absence of light, a solution of 5-tributylstannyl-2,2′-bithiophene (1.00 g, 2.20 mmol), 2,7-diiodo-9,9-dioctyl-fluorene (3.99 g, 6.20 mmol), and [Pd(PPh$_3$)$_4$] (25 mg, 0.021 mmol) in anhydrous DMF/toluene (50 mL, 1/4) was stirred for 24 h at 70°C. 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 aqueous KF solution and

brine and then dried over MgSO$_4$. After the solvent was evaporated, the residue was purified by column chromatography on silica gel with petroleum as eluent to afford **7** (1.21 g, 79%) as a light yellow solid. ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.68$–7.71 (m, 3H), 7.62 (dd, $J = 7.92$, 1.32 Hz, 1H), 7.55 (s, 1H), 7.47 (d, $J = 8.34$ Hz, 1H), 7.32 (d, $J = 3.75$ Hz, 1H), 7.26–7.28 (m, 2H), 7.21 (d, $J = 3.78$ Hz, 1H), 7.08 (dd, $J = 3.77$, 4.92 Hz, 1H), 1.94–2.07 (m, 4H), 1.10–1.31 (m, 20H), 0.83–0.92 (m, 6H), 0.68 ppm (m, 4H); ^{13}C NMR (100 MHz, CDCl$_3$, 25°C): $\delta = 153.3$, 151.0, 143.6, 140.2, 139.8, 137.5, 136.6, 135.9, 133.5, 132.1, 127.9, 124.7, 124.6, 124.4, 123.7, 123.6, 121.4, 119.7, 92.6, 55.43, 40.2, 31.8, 29.9, 29.2, 29.1, 23.7, 22.6, 14.1 ppm; MALDI-TOF MS (reflectron mode): m/z (%): 680.15 (100) [M+H]$^+$; elemental analysis (%) calcd for C$_{37}$H$_{45}$IS$_2$ (680.20): C 65.28, H 6.66; found: C 65.36, H 6.57.

2-{5′-[7-(2,2′-Bithien-5-yl)-9,9-dioctylfluoren-2-yl]-2,2′-bithien-5-yl}-7-bromo-9,9-dioctylfluorene (8): In the absence of light, a solution of **6** (1.46 g, 1.58 mmol), **7** (1.64 g, 2.41 mmol), and [Pd(PPh$_3$)$_4$] (20 mg, 0.02 mmol) in anhydrous DMF/toluene (24 mL, 1/4) was stirred for 24 h at 70°C. The mixture was cooled to room temperature then poured into a large amount of water for extraction with chloroform. The organic extracts were washed with aqueous KF solution and brine and then dried over MgSO$_4$. After the solvent was evaporated, the residue was purified by column chromatography on silica gel with petroleum/chloroform (10/1) as eluent to afford **4** (1.57 g, 83%) as a yellow solid. ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.74$ (d, $J = 1.41$ Hz, 1H), 7.72 (s, 1H), 7.69 (s, 1H), 7.62–7.66 (m, 3H), 7.58–7.60 (m, 4H), 7.48–7.51 (m, 2H), 7.33–7.37 (m, 3H), 7.26–7.28 (m, 4H), 7.22 (d, $J = 3.75$ Hz, 1H), 7.08 (dd, $J = 3.87$, 4.80 Hz, 1H), 1.98–2.10 (m, 8H), 1.15–1.26 (m, 40H), 0.81–0.96 (m, 12H), 0.72 ppm (m, 8H); MS (MALDI-TOF, reflectron mode): m/z (%): 1186.48 (100) [M+H]$^+$; elemental analysis (%) calcd for C$_{74}$H$_{89}$BrS$_4$ (1186.50): C 74.90, H 7.56; found C 74.60, H 7.53.

2-(2,2′-Bithien-5-yl)-9,9-dioctylfluorene (9a): In the absence of light, a solution of **2** (4.55 g, 10.0 mmol), 2-bromo-9,9-dioctylfluorene (**4**, 4.93 g, 10.5 mmol), and [Pd(PPh$_3$)$_4$] (115 mg, 0.100 mmol) in anhydrous DMF/toluene (90 mL, 1/4) was stirred for 24 h at 85°C. 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 aqueous KF solution and brine and then dried over MgSO$_4$. After the solvent was evaporated, the residue was purified by column chromatography on silica gel with petroleum as eluent to afford **9a** (4.21 g, 76%) as a light green solid. ^{1}H NMR (300 MHz, CDCl$_3$, 25°C, TMS): $\delta = 7.71$–7.74 (m, 2H), 7.58–7.63 (m, 2H), 7.35–7.38 (m, 4H), 7.32 (d, $J = 3.75$ Hz, 1H), 7.25–7.27 (m, 1H), 7.21 (d, $J = 3.72$ Hz, 1H), 7.07–7.09 (m, 1H), 2.02–2.05 (m, 4H), 1.09–1.36 (m, 20H), 0.81–0.86 (m, 6H), 0.68 ppm (m, 4H); ^{13}C NMR (100 MHz, CDCl$_3$, 25°C): $\delta = 151.6$, 150.9, 144.0, 140.9, 140.6, 137.6, 136.3, 132.8, 127.8, 127.1, 126.8, 124.6, 124.5, 124.3, 123.5, 123.4, 122.9, 120.0, 119.8, 119.7, 55.2, 40.4, 31.8, 30.0, 29.2, 23.7, 22.6, 14.0 ppm; MS (MALDI-TOF, reflectron mode): m/z (%): 554.32 (100) [M+H]$^+$; elemental analysis (%) calcd for C$_{37}$H$_{46}$S$_2$ (554.30): C 80.09, H 8.36; found: C 80.28, H 8.46.

2-(-5′-Tributylstannyl-2,2′-bithien-5-yl)-9,9-dioctylfluorene (9b): Under an argon atmosphere, nBuLi (2.50 M in hexane, 0.80 mL, 2.0 mmol) was added to a solution of **9a** (1.0 g, 1.8 mmol) in anhydrous THF (18 mL) at -78°C. The reaction mixture was stirred at -78°C for 60 min and then tributyltin chloride (0.67 g, 0.57 mL, 2.0 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 aqueous Na$_2$CO$_3$ solution and brine and dried over MgSO$_4$. After the solvent was evaporated, crude **9b** was obtained. ^{1}H NMR (300 MHz, CDCl$_3$, 25°C, TMS): $\delta = 7.67$–7.70 (m, 2H), 7.54–7.60 (m, 2H), 7.31–7.36 (m, 4H), 7.28 (d, $J = 3.72$ Hz, 1H), 7.17 (d, $J = 3.72$ Hz, 1H), 7.09 (d, $J = 3.42$ Hz, 1H), 1.95–1.98 (m, 4H), 1.51–1.60 (m, 6H), 1.33–1.40 (m, 6H), 1.05–1.16 (m, 26H), 0.87–0.94 (m, 9H), 0.77–0.82 (m, 6H), 0.64 ppm (m, 4H).

2-[5′-[7-(2,2′-Bithien-5-yl)-9,9-dioctylfluoren-2-yl]-2,2′-bithien-5-yl}-9,9-dioctylfluorene (10a): The procedure for the synthesis of **9a** was followed to prepare **10a** from **9b** and **5** as a yellow solid in a yield of 80%. ^{1}H NMR (300 MHz, CDCl$_3$, 25°C, TMS): $\delta = 7.68$–7.72 (m, 4H), 7.59–7.63 (m, 3H), 7.56 (m, 3H), 7.32–7.36 (m, 5H), 7.30 (d, $J = 3.93$ Hz, 1H),

7.22–7.24 (m, 4H), 7.18 (d, $J = 3.75$ Hz, 1H), 7.05 (dd, $J = 3.87$ Hz, $J = 4.8$ Hz, 1H), 1.97–2.06 (m, 8H), 1.08–1.26 (m, 40H), 0.77–0.83 (m, 12H), 0.69 ppm (m, 8H); MS (MALDI-TOF, reflectron mode): m/z (%): 1106.61 (100) $[M+H]^+$; elemental analysis (%) calcd for $C_{74}H_{90}S_4$ (1106.59): C 80.23, H 8.19; found: C 80.00, H 8.24.

2-{5′-[7-(5′-Tributylstannyl-2,2′-bithien-5-yl)-9,9-dioctylfluoren-2-yl]-2,2′-bithien-5-yl}-9,9-dioctylfluorene (10b): The procedure for the synthesis of **9b** from **9a** was followed to prepare **10b** from **10a**. ^{1}H NMR (300 MHz, CDCl$_3$, 25°C, TMS): $\delta = 7.71–7.75$ (m, 4H), 7.60–7.66 (m, 6H), 7.32–7.41 (m, 6H), 7.26–7.27 (d, $J = 3.72$ Hz, 3H), 7.22 (d, $J = 3.78$ Hz, 1H), 7.10 (d, $J = 3.36$ Hz, 1H), 2.01–2.07 (m, 8H), 1.62–1.65 (m, 6H), 1.39 (m, 6H), 1.10–1.20 (m, 46H), 0.82–0.99 (m, 21H), 0.70 ppm (m, 8H).

Compound 11a: The procedure for the synthesis of **9a** was followed to prepare **11a** from **10b** and **5** as a yellow solid in a yield of 79%. ^{1}H NMR (300 MHz, CDCl$_3$, 25°C, TMS): $\delta = 7.73–7.75$ (m, 6H), 7.60–7.67 (m, 10H), 7.32–7.41 (m, 8H), 7.26–7.28 (m, 6H), 7.22–7.23 (d, $J = 3.69$ Hz, 1H), 7.09 (dd, $J = 3.11$, 4.8 Hz, 1H), 2.01–2.21 (m, 8H), 1.12–1.24 (m, 60H), 0.81–0.89 (m, 18H), 0.72 ppm (m, 12H); MS (MALDI-TOF, reflectron mode): m/z (%): 1659.87 (100) $[M+H]^+$; elemental analysis (%) calcd for $C_{111}H_{134}S_6$ (1659.88): C 80.28, H 8.13; found: C 80.01, H 8.24.

Compound 11b: The procedure for the synthesis of **9b** was followed to prepare **11b** from **11a**. ^{1}H NMR (300 MHz, CDCl$_3$, 25°C, TMS): $\delta = 7.71–7.75$ (m, 6H), 7.60–7.67 (m, 10H), 7.34–7.39 (m, 8H), 7.27–7.28 (m, 5H), 7.22 (d, $J = 3.16$ Hz, 1H), 7.13 (d, $J = 3.36$ Hz, 1H), 2.01–2.06 (m, 12H), 1.61–1.64 (m, 6H), 1.36–1.41 (m, 6H), 1.12–1.20 (m, 66H), 0.93–0.98 (m, 9H), 0.91–0.87 (m, 18H), 0.70 ppm (m, 12H).

Compound 12a: The procedure for the synthesis of **9a** was followed to prepare **12a** from **10b** and **8** as a yellow solid in a yield of 71%. ^{1}H NMR (300 MHz, CDCl$_3$, 25°C, TMS): $\delta = 7.73–7.76$ (m, 8H), 7.61–7.67 (m, 14H), 7.34–7.38 (m, 10H), 7.26–7.28 (m, 8H), 7.22 (d, $J = 3.75$ Hz, 1H), 7.09 (m, 1H), 2.06 (m, 16H), 1.13–1.24 (m, 80H), 0.82–0.86 (m, 24H), 0.75 ppm (m, 16H); MS (MALDI-TOF, reflectron mode): m/z (%): 2213.03 (100) $[M+H]^+$; elemental analysis (%) calcd for $C_{148}H_{178}S_8$ (2212.17): C 80.31, H 8.11; found: C 80.02, H 8.00.

Compound 12b: The procedure for the synthesis of **9b** was followed to prepare **12b** from **12a**. ^{1}H NMR (300 MHz, CDCl$_3$, 25°C, TMS): $\delta = 7.73–7.76$ (m, 8H), 7.61–7.67 (m, 14H), 7.34–7.38 (m, 10H), 7.26–7.28 (m, 8H), 7.22 (d, $J = 3.75$ Hz, 1H), 7.09 (m, 1H), 2.06 (m, 16H), 1.13–1.24 (m, 80H), 0.82–0.86 (m, 24H), 0.75 ppm (m, 16H).

5,5′-Bis(7-bromo-9,9-dioctylfluoren-2-yl)-2,2′-bithiophene (14): In the absence of light, a solution of 5,5′-bis(tributylstannyl)-2,2′-bithiophene (**13**, 0.74 g, 1.0 mmol), **1** (4.06 g, 7.39 mmol), and [Pd(PPh$_3$)$_4$] (23 mg, 0.020 mmol) in anhydrous DMF/toluene (15 mL, 1/4) was stirred for 24 h at 85°C. The mixture was cooled to room temperature and then poured into a large amount of water for extraction with chloroform. The organic extracts were washed with aqueous KF solution and brine and then dried over MgSO$_4$. After the solvent was evaporated, the residue was purified by column chromatography on silica gel with petroleum as eluent to afford **14** (0.56 g, 51%) as a yellow solid. ^{1}H NMR (300 MHz, CDCl$_3$, 25°C, TMS): $\delta = 7.69–7.72$ (m, 2H), 7.57–7.65 (m, 6H), 7.49–7.51 (m, 4H), 7.35–7.37 (d, $J = 3.81$ Hz, 4H), 7.25–7.27 (d, $J = 3.72$ Hz, 4H), 2.00–2.02 (m, 8H), 1.10–1.23 (m, 40H), 0.83–0.87 (m, 12H), 0.68–0.70 ppm (m, 8H); MS (MALDI-TOF, reflectron mode): m/z (%): 1100.29 (100) $[M+H]^+$; elemental analysis (%) calcd for $C_{66}H_{84}Br_2S_2$ (1100.44): C 71.98, H 7.69; found: C 72.12, H 7.77.

Compound 16a: The procedure for the synthesis of **10a** was followed to prepare **16a** from **15** and **5** as a yellow solid in a yield of 64%. ^{1}H NMR (300 MHz, CDCl$_3$, 25°C, TMS): $\delta = 7.68–7.71$ (m, 6H), 7.56–7.63 (m, 12H), 7.33–7.35 (m, 4H), 7.31 (d, $J = 3.78$ Hz, 2H), 7.23–7.25 (m, 8H), 7.19 (d, $J = 3.72$ Hz, 2H), 7.50 (dd, $J = 4.86$, 3.84 Hz, 2H), 2.00–2.03 (m, 12H), 1.08–1.30 (m, 60H), 0.77–0.82 (m, 18H), 0.69–0.71 ppm (m, 12H); found: C 78.08, H 7.73; MS (MALDI-TOF, reflectron mode): m/z (%): 1823.73 (100) $[M+H]^+$; elemental analysis (%) calcd for $C_{119}H_{138}S_8$ (1823.86): C 78.32, H 7.62.

Compound 16b: The procedure for the synthesis of **10b** was followed to prepare **16b** from **16a** as a brown solid. ^{1}H NMR (300 MHz, CDCl$_3$,

25°C, TMS): $\delta = 7.71–7.76$ (m, 6H), 7.60–7.67 (m, 12H), 7.37–7.39 (m, 4H), 7.34 (d, $J = 3.81$ Hz, 2H), 7.27–7.28 (m, 4H), 7.22 (d, $J = 3.72$ Hz, 2H), 7.13 (d, $J = 3.33$ Hz, 2H), 2.03–2.07 (m, 12H), 1.58–1.72 (m, 12H), 1.36–1.41 (m, 12H), 1.12–1.20 (m, 72H), 0.93–0.98 (m, 18H), 0.83–0.86 (m, 18H), 0.80–0.81 ppm (m, 12H).

Compound 17: The procedure for the synthesis of **14** was followed to prepare **17** from **15** and **1** as a yellow solid in a yield of 65%. ^{1}H NMR (300 MHz, CDCl$_3$, 25°C, TMS): $\delta = 7.69–7.75$ (m, 4H), 7.63–7.67 (m, 4H), 7.58–7.61 (m, 6H), 7.48–7.51 (m, 4H), 7.36–7.38 (m, 4H), 7.26–7.28 (m, 4H), 2.00–2.05 (m, 12H), 1.17–1.29 (m, 60H), 0.81–0.92 (m, 18H), 0.68–0.70 ppm (m, 12H); MS (MALDI-TOF, reflectron mode): m/z (%): 1652.55 (100) $[M+H]^+$; elemental analysis (%) calcd for $C_{103}H_{128}Br_2S_4$ (1653.73): C 74.79, H 7.80; found: C 74.70, H 7.85.

Compound 18: The procedure for the synthesis of **14** was followed to prepare **18** from **16b** and **1** as orange solid in a yield of 71%. ^{1}H NMR (300 MHz, CDCl$_3$, 25°C, TMS): $\delta = 7.67–7.76$ (m, 10H), 7.58–7.64 (m, 16H), 7.49–7.51 (m, 4H), 7.36–7.39 (m, 8H), 7.27–7.28 (m, 8H), 2.00–2.05 (m, 20H), 1.13–1.31 (m, 100H), 0.82–0.85 (m, 30H), 0.70–0.80 ppm (m, 20H); MS (MALDI-TOF, reflectron mode): m/z (%): 2759.14 (100) $[M+H]^+$; elemental analysis (%) calcd for $C_{177}H_{216}Br_2S_8$ (2758.30): C 77.03, H 7.89; found: C 76.79, H 7.98.

5,5′-Bis(9,9′-dioctylfluoren-2-yl)-2,2′-bithiophene (F2Th2): In the absence of light, a solution of **13** (0.74 g, 1.0 mmol), **4** (0.94 g, 2.0 mmol), and [Pd(PPh$_3$)$_4$] (23 mg, 0.020 mmol) in anhydrous DMF/toluene (15 mL, 1/2) was stirred for 24 h at 85°C. 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 aqueous KF solution and brine and then dried over MgSO$_4$. After the solvent was evaporated, the residue was purified by column chromatography on silica gel with petroleum as eluent to afford **F2Th2** (560 mg, 60%) as a light yellow solid. ^{1}H NMR (300 MHz, CDCl$_3$, 25°C, TMS): $\delta = 7.73–7.75$ (m, 4H), 7.63 (d, $J = 7.89$ Hz, 2H), 7.60 (s, 2H), 7.33–7.41 (m, 8H), 7.26 (d, $J = 3.81$ Hz, 2H), 2.01–2.06 (m, 8H), 1.10–1.30 (m, 40H), 0.82–0.89 (m, 12H), 0.69–0.71 ppm (m, 8H); MS (MALDI-TOF, reflectron mode): m/z (%): 942.59 (100) $[M+H]^+$; elemental analysis (%) calcd for $C_{66}H_{86}S_2$ (942.62): C 84.02, H 9.19; found: C 83.86, H 9.25.

General procedure for preparation of other OFbTs: In the absence of light, a mixture of dibromide **1**, **14**, **17**, or **18** (1.0 equiv), organotin reagent **9b**–**12b** (2.2 equiv) and [Pd(PPh$_3$)$_4$] in anhydrous DMF/toluene (1/4) was stirred for 24 h at 85°C. The mixture was cooled to room temperature and then poured into a large amount of water for extraction with chloroform. The organic extracts were washed with aqueous KF solution and brine and then dried over MgSO$_4$. After the solvent was evaporated, the residue was purified by column chromatography on silica gel with petroleum: chloroform (from 10:1 to 2:1) as eluent to afford the corresponding oligomers. The crude products were further purified with PGPC and toluene as eluent.

2,7-Bis[5′-(9,9-dioctylfluoren-2-yl)-2,2′-bithien-5-yl]-9,9-dioctylfluorene (F3Th4): Yellow solid in a yield of 60%. ^{1}H NMR (300 MHz, CDCl$_3$, 25°C, TMS): $\delta = 7.69–7.72$ (m, 6H), 7.59–7.63 (m, 4H), 7.56 (s, 4H), 7.32–7.36 (m, 10H), 7.23 (d, $J = 3.75$ Hz, 4H), 1.97–2.02 (m, 12H), 1.06–1.20 (m, 60H), 0.78–0.83 (m, 18H), 0.67–0.68 ppm (m, 12H); MS (MALDI-TOF, reflectron mode): m/z (%): 1496.45 (100) $[M+H]^+$; elemental analysis (%) calcd for $C_{103}H_{130}S_4$ (1495.91): C 82.67, H 8.76; found: C 82.78, H 8.93.

Oligomer F4Th6: Yellow solid in a yield of 52%. ^{1}H NMR (300 MHz, CDCl$_3$, 25°C, TMS): $\delta = 7.70–7.72$ (m, 8H), 7.57–7.64 (m, 12H), 7.33–7.35 (m, 12H), 7.23–7.25 (m, 6H), 1.98–2.03 (m, 16H), 1.09–1.26 (m, 80H), 0.79–0.84 (m, 24H), 0.69–0.70 ppm (m, 16H); MS (MALDI-TOF, reflectron mode): m/z (%): 2049.82 (100) $[M+H]^+$; elemental analysis (%) calcd for $C_{140}H_{174}S_6$ (2048.20): C 82.05, H 8.56; found: C 81.99, H 8.55.

Oligomer F5Th8: Yellow solid in a yield of 75%. ^{1}H NMR (300 MHz, CDCl$_3$, 25°C, TMS): $\delta = 7.69–7.72$ (m, 10H), 7.57–7.64 (m, 16H), 7.32–7.35 (m, 14H), 7.23–7.25 (m, 8H), 1.97–2.03 (m, 20H), 1.09–1.25 (m, 100H), 0.78–0.83 (m, 30H), 0.69–0.70 ppm (m, 20H); MS (MALDI-TOF, reflectron mode): m/z (%): 2602.08 (100) $[M+H]^+$; elemental analysis

(%) calcd for $C_{177}H_{218}S_8$ (2601.49): C 81.70, H 8.44; found: C 81.64, H 8.60.

Oligomer F7Th12: Yellow solid in a yield of 73%. ¹H NMR (300 MHz, CDCl₃, 25°C, TMS): $\delta = 7.69–7.71$ (m, 14H), 7.58–7.63 (m, 24H), 7.32–7.35 (m, 18H), 7.23–7.25 (m, 12H), 1.98–2.03 (m, 28H), 1.10–1.25 (m, 140H), 0.77–0.86 (m, 42H), 0.70–0.71 ppm (m, 28H); MS (MALDI-TOF, reflectron mode): *m/z*(%): 3709.56 (100%) [*M*+H]⁺; elemental analysis (%) calcd for $C_{251}H_{306}S_{12}$ (3707.07): C 81.30, H 8.32; found: C 81.17, H 8.24.

Oligomer F9Th16: Yellow solid in a yield of 73%. ¹H NMR (300 MHz, CDCl₃, 25°C, TMS): $\delta = 7.68–7.72$ (m, 18H), 7.59–7.62 (m, 32H), 7.34–7.35 (m, 22H), 7.23–7.24 (m, 16H), 2.00–2.03 (m, 36H), 1.09–1.24 (m, 180H), 0.79–0.87 (m, 54H), 0.70–0.72 ppm (m, 36H); MS (MALDI-TOF, reflectron mode): *m/z* (%): 4815.33 (100) [*M*+H]⁺; elemental analysis (%) calcd for $C_{325}H_{394}S_{16}$ (4812.65): C 81.09, H 8.25; found: C 81.20, H 8.31.

Oligomer F13Th24: Yellow solid in a yield of 10%. ¹H NMR (400 MHz, $C_2D_2Cl_4$, 50°C): $\delta = 7.66–7.70$ (m, 26H), 7.56–7.61 (m, 48H), 7.28–7.32 (m, 30H), 7.22–7.23 (m, 24H), 1.97–2.03 (m, 52H), 1.09–1.20 (m, 260H), 0.70–0.81 ppm (m, 260H); MS (MALDI-TOF, reflectron mode): *m/z* (%): 7027.60 (100) [*M*+H]⁺; elemental analysis (%) calcd for $C_{473}H_{570}S_{24}$ (7024.80): C 80.87, H 8.18; found: C 80.67, H 8.04.

Acknowledgements

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