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Head-to-Tail Regioregular Oligothiophene-Functionalized 9,9′-Spirobifluorene Derivatives. 1. Synthesis

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Two series of novel fully conjugated oligomers, oligothiophene-functionalized 9,9′-spirobifluorene derivatives, have been developed in this contribution. First, four 9,9′-spirobifluorene bromide derivatives (compounds **1a**−**d**) are prepared through various synthetic routes. Oligothiophene derivatives with or without substituents are synthesized through the Grignard and Suzuki coupling reactions. The Negishi coupling reactions between oligothienylzinc chloride and various 9,9′-spirobifluorene bromides with $Pd(PPh_3)_4$ as catalyst successfully produce the desired compounds, unsubstituted oligothiophene-functionalized 9,9′-spirobifluorene derivatives, compounds **2** to **4a**−**d**. Since the Negishi coupling reactions afford regioregularly head-to-tail (H−T) oligo(4-*n*-hexylthiophene)-functionalized 9,9′-spirobifluorene derivatives in poor yields, the Suzuki coupling reactions between sodium 4-*n*-hexylthienyl-2-boronate **8**, and various 9,9′-spirobifluorene-based bromides **1a**−**d** and **9**−**16** are employed to produce highly regioregular head-to-tail oligothiophene-functionalized 9,9′-spirobifluorene derivatives (compounds **5** to **7a**−**d**) in very high yields. We also investigate the effect of solvents on the Suzuki coupling reactions. The structure and purity of all compounds are verified by FT-IR, ^1H and ^{13}C NMR, MS, and elemental analysis.

Introduction

Organic oligomers and polymers with electronically conjugated backbones have attracted considerable interest in both academic research and important industrial applications due to fulfilling a pivotal role in the design and generation of new materials utilizing their unique physical and chemical properties.[1] Recently, oligo- and polythiophenes, pyrroles, pyridines, fluorenes, *p*-phenylenes, and *p*-phenylenevinylenes have been demonstrated to function as organic electronic conductors and photoconductors,[1] electroluminescent materials for light-emitting diodes (LED),[2] field-effect transistors (FET),[3] laser emitters,[4] NLO substrates,[5] and materials with high tensile strength and heat resistance.[6] Therefore, within the field of nanoengineering, some conjugated oligomers with the structural rigidity had been successfully exploited for the construction of a range of nanosized hydrocarbon molecular architectures such as rings, cages, and dendritic macromolecules.[7]

Among these approaches to create amorphous π-conjugated molecules suitable for use in photoelectronic devices, especially in electroluminescent devices, a few dedications have been contributed to spiro-type molecules.[8] Because of their attractive properties, bichromophoric spiro-type molecules have been proposed as suitable materials in the field of photoelectronic devices, including electroluminescence devices, photovoltaic cells, etc.[8] The specific, orthogonally fused structure of the spiro-type molecules entitles them the desired steric demand, which minimizes interchain contacts of the molecules and, hence, prevents crystallization. With spiro-type structures, it is also proposed the possibility to develop proconducting (nondoped or nonoxidized system, hence insulating)/σ/conducting (doped or oxidized) molecules, which may be useful for the memory, logic, and amplification computing systems due to the little communication between two branches.[9] Their ability to

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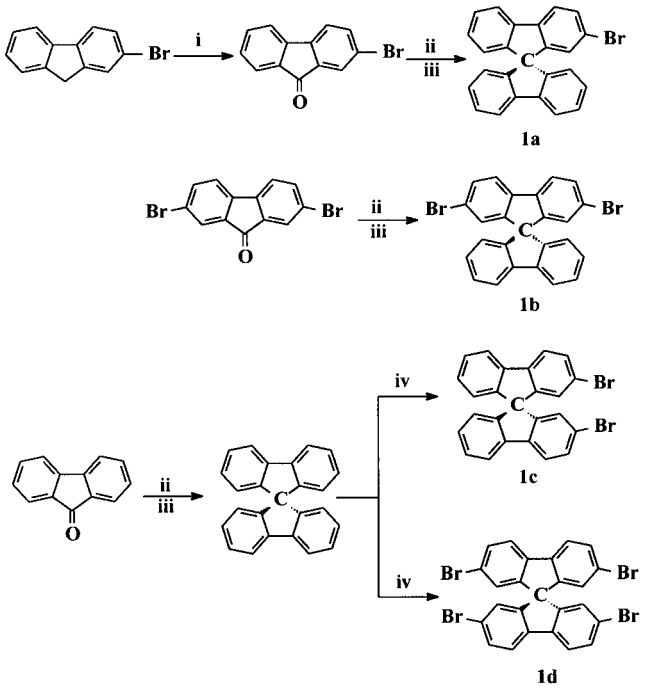
form molecular glass and to reduce the crystallization tendency of resulting molecules and consequently to prevent the crystal boundaries has been widely demonstrated.

To develop spiro-type molecules, several series of spiro-type molecules including silicon orthogonally fused oligothiophenes and silicon-fused or 9,9′-spirobifluorene-linked thiophene ethylynlene oligomers were synthesized.[8−10] Detailed studies on the convergent synthesis and electrochemical properties of these spiro-fused oligomers have been performed and illustrated their potential applications toward molecular electronic devices. On the other hand, oligomers based on 9,9′-spirobifluorene for photoelectronic device applications have been carefully investigated on the morphologic stability, electronic properties, as well as optical properties of these molecules.[8c,11] Furthermore, amplified spontaneous emission and spectral narrowing have been found among these spiro-type molecules applied as gain media in lasers at solid states.

In our previous contributions, a series of thiophene-containing conjugated polymers with their backbone modified by inserting different aromatic groups have been reported, with the aim of improving PL efficiencies and EL performance of polythiophenes.[12] The results demonstrated that this approach to the improvement of PL quantum yield and EL performance was successful. However, differential scanning calorimetry (DSC) analyses performed on the new series of polymers indicated low T_g's slightly above room temperature, which meant that the thermal stress produced during the device running or storage was likely to induce the thermally activated degradation processes. Therefore, effort should be made to enhance the morphologic stability of these thiophene-based materials, such as introducing spiro-type structures, so that better device performance might be achieved.

Herein, we reported the synthesis of two series of oilgothiophene-functionalized 9,9′-spirobifluorenes. The unsubstituted oligothiophene-functionalized 9,9′-spirobifluorenes were prepared through the Negishi coupling reactions. The Suzuki coupling reactions were also employed to prepare head-to-tail regioregular oligo(4-*n*-hexylthiophene)-functionalized 9,9′-spirobifluorenes in high yields. We also investigated the difference between these two coupling reactions. These conjugated oligomers based on 9,9′-spirobifluorene showed good thermal stability and unique optical and electrochemical properties in use as a new generation of display technologies. We will successively report these interesting properties in our subsequent contributions.

SCHEME 1. Synthetic Route to 9,9′-Spirobifluorene Bromide Derivatives[a]



[a] Reagents and conditions: (i) *n*-Bu_4NOH, pyridine, air; (ii) 2-biphenylmagnesium bromide, THF; (iii) AcOH, HCl; (iv) Br_2, $FeCl_3$, $CHCl_3$.

Results and Discussion

The synthetic approach to the starting materials, 9,9′-spirobifluorene and its bromide derivatives, is outlined in Scheme 1. 9,9′-Spirobifluorene[13] was prepared through the addition of 9-fluorenone to 2-biphenylmagnesium bromide to yield the tertiary alcohol followed by dehydration cyclization in a mixture of hydrochloride and acetic acid. Usually, the bromide derivatization of 9,9′-spirobifluorene is accomplished via electrophilic bromination. The reactions carried out using 2 equiv of bromine afforded 2,2′-dibromo-9,9′-spirobifluorene **1c** in high yield,[14] also using 4 equiv of bromine yielded 2,2′,7,7′-tetrabromo-9,9′-spirobifluorene **1d**.[15] However, reactions carried out using 1 equiv of bromine prepared 2-bromo-9,9′-spirobifluorene **1a** usually mixing with some multiple brominated compounds. Due to the similar polarity of these compounds, it resulted in difficulty of getting pure 2-bromo-9,9′-spirobifluorene **1a** in final purification upon recrystallization from ethanol or flash column chromatography. Therefore, 2-bromo-9,9′-spirobifluorene[16] **1a** was prepared between 2-bromo-9-fluorenone and 2-biphenylmagnesium bromide followed by the same procedure for the preparation of 9,9′-spirobifluorene. This approach highly yielded very pure 2-bromo-9,9′-spirobifluorene **1a** without active impurities.

For 2,7-dibromo-9,9′-spirobifluorene, it is also impossible to afford 2,7-dibromo-9,9′-spirobifluorene **1b** through

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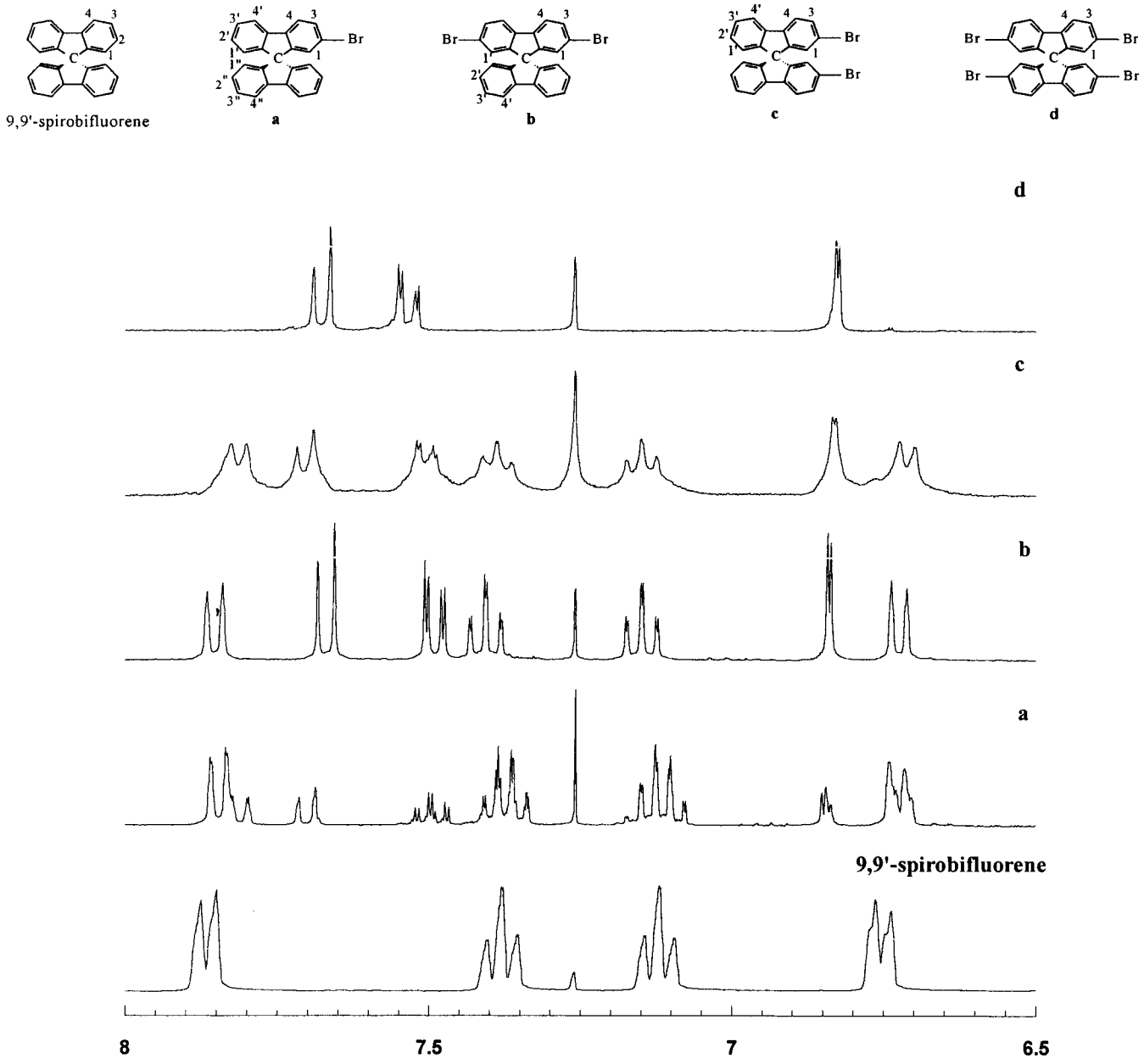

FIGURE 1. ^{1}H NMR spectra of compounds **1a**−**d** and 9,9′-spirobifluorene.

the electrophilic bromination of 9,9′-spirobifluorene, since the dibromination of 9,9′-spirobifluorene only occurred at the 2,2′-positions instead of the 2,7-positions of 9,9′-spirobifluorene. 2,7-Dibromo-9-fluorenone was employed to afford 2,7-dibromo-9,9′-spirobifluorene **1b** through the same procedure as preparing 2-bromo-9,9′-spirobifluorene. ^{1}H and ^{13}C NMR spectroscopy provided unambiguous proof of the structures for 9,9′-spirobifluorene, 2-bromo-9,9′-spirobifluorene **1a**, 2,7-dibromo-9,9′-spirobifluorene **1b**, 2,2′-dibromo-9,9′-spirobifluorene **1c**, and 2,2′,7,7′-tetrabromo-9,9′-spirobifluorene **1d**. The ^{1}H NMR spectra and chemical shift assignments are given in Figure 1 and Table 1, respectively.

Nonsubstituted oligothiophene-functionalized 9,9′-spirobifluorene derivatives were one series of our designed 9,9′-spirobifluorene-based molecules. The synthetic approach to these compounds is listed in Scheme 2. Various synthetic approaches to nonsubstituted oligothiophenes are available now, such as thiophene ring formation utilizing Lawesson's reagent, cyclization of the 1,3-butadiyne,[17] intramolecular reductive coupling reaction of diketone sulfide,[18] reductive coupling reactions with an activated nickel(0) reagent of corresponding monobromide,[19] Grignard coupling reactions using Ni(0) catalyst, modified Wittig reaction, synthesis via organoboranes,[20] and so on. Due to their convenience and high yields, the Grignard coupling reactions were employed to prepare 2,2′-bithiophene **18**,[21] 2,2′:5′,2″-terthiophene

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(18) Nakayama, J.; Murabayashi, S.; Hoshino, M. *Heterocycles* **1987**, *26*, 2599.
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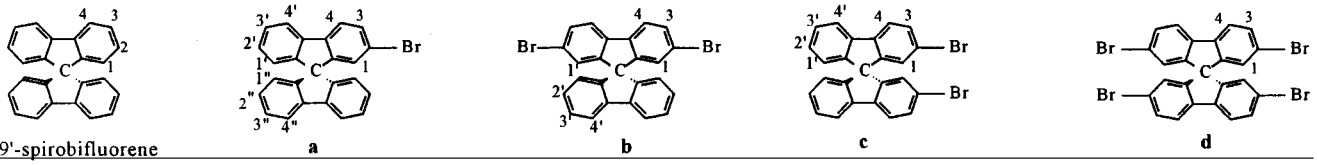
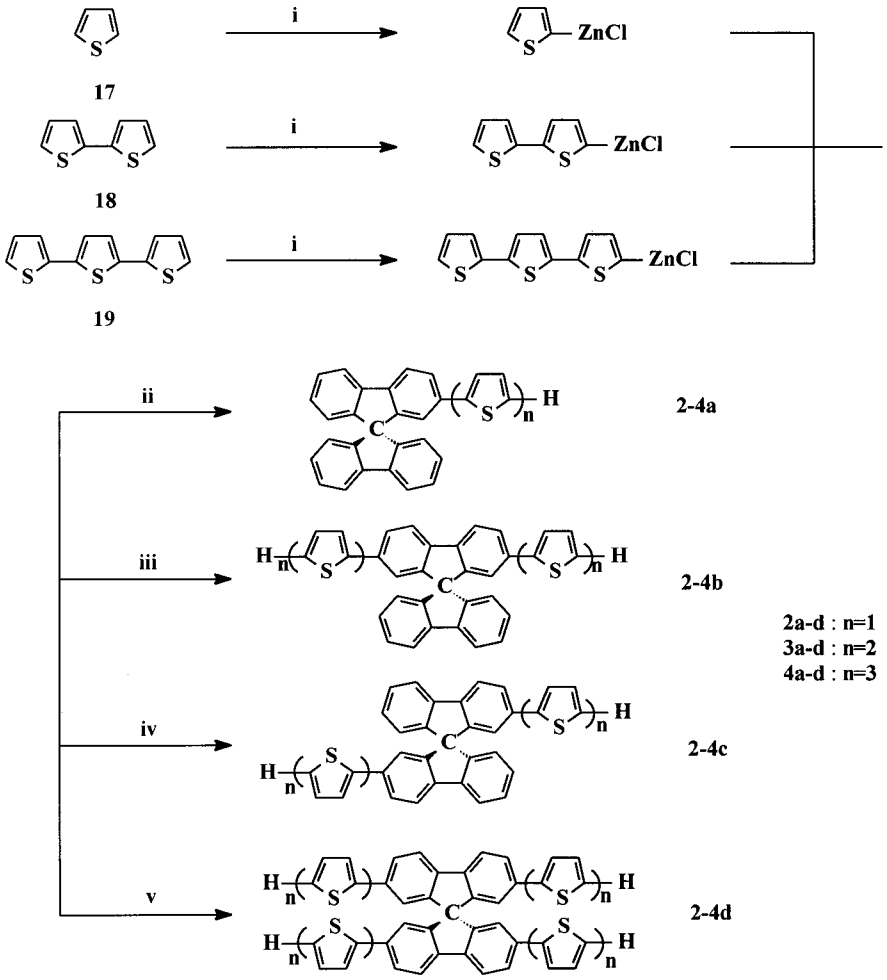
TABLE 1. Chemical Shifts and Assignments of Compounds 1a−d and 9,9′-Spirobifluorene (ppm)



9,9'-spirobifluorene **a** **b** **c** **d**

protons	9,9′-spirobifluorene	**1a**	**1b**	**1c**	**1d**
H-1	6.74−6.76 (d)	6.85 (s)	6.83−6.84 (d)	6.83−6.84 (d)	6.82−6.83 (d)
H-1′		6.71−6.74 (d)	6.71−6.74 (d)	6.70−6.73 (d)	
H-2	7.10−7.15 (t)				
H-2′		7.08−7.17 (m)	7.12−7.18 (td)	7.13−7.18 (t)	
H-2″					
H-3	7.35−7.41 (t)	7.48−7.50 (dd)	7.47−7.51 (dd)	7.49−7.52 (d)	7.52−7.55 (dd)
H-3′		7.34−7.41 (m)	7.38−7.43 (td)	7.37−7.41 (d)	
H-3″					
H-4	7.85−7.88 (d)	7.69−7.71 (d)	7.66−7.68 (d)	7.69−7.72 (d)	7.66−7.69 (d)
H-4′		7.80−7.86 (m)	7.85−7.87 (d)	7.80−7.83 (d)	
H-4″					

SCHEME 2. Synthetic Route to Nonsubstituted Oligothiophenes-Functionalized 9,9′-Spirobifluorene Derivatives[a]



[a] Reagents and conditions: (i) *n*-BuLi, TMEDA, $ZnCl_2$, THF; (ii) $Pd(PPh_3)_4$, 2-bromo-9,9′-spirobifluorene; (iii) $Pd(PPh_3)_4$, 2,7-dibromo-9,9′-spirobifluorene; (iv) $Pd(PPh_3)_4$, 2,2′-dibromo-9,9′-spirobifluorene; (v) $Pd(PPh_3)_4$, 2,2′,7,7′-dibromo-9,9′-spirobifluorene.

19[22] through utilizing 2-thienylmagnesium bromide, and 2-bromothiophene or 2,5-dirbromthiophene, respectively.

A variety of unsubstituted oligothiophenes-functionalized 9,9′-spirobifluorene compounds were prepared from the appropriate bromo-9,9′-spirobifluorene derivatives using the Negishi coupling procedures. The formation of 2-thienylbenzenes utilizing 2-thienylzinc chloride

(21) Chan, H. S. O.; Ng, S. C.; Huang, H. H.; Seow, S. H. In *Progress in Pacific Polymer Science 3*; Ghiggino, K. P., Ed.; Springer-Verlag: Berlin, Heidelberg, 1994; p 238.

and bromobenzene catalyzed by a palladium(0) catalyst was effective to prepare some compounds with certain linkage point.[12,23] The reactions occurred under mild conditions and also tolerated both electron-withdrawing and -donating groups on the benzene ring and thus were selected for synthesis of 9,9′-spirobifluorene-linked nonsubstituted oligothiophenes, including compounds **2**−**4a**, **2**−**4b**, **2**−**4c**, **2**−**4d**. The key intermediates, thienylzinc chlorides, were prepared by the lithiation of the corresponding oligothiophene followed by transmetalation reactions with anhydrous zinc chloride in THF. The subsequent Negishi coupling reactions of the corresponding 2-thienylzinc chloride and brominated 9,9′-spirobifluorenes in THF in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium(0), $Pd(PPh_3)_4$, afforded a series of nonsubstituted oligothiophene-functionalized 9,9′-spirobifluorene derivatives **2a**−**d**, **3a**−**d**, **4a**−**d**. These compounds were purified by recrystallization from $CHCl_3$/EtOH. The structure and purity of all these compounds were confirmed by ^1H and ^{13}C NMR, nominal and accurate MS, FT-IR spectra, and elemental analyses, which showed very good agreement between experimental and theoretical results for the proposed structures.

For the synthesis of head-to-tail (H−T) regioregular *n*-hexyl-substituted oligothiophene-fuctionalized 9,9′-spirobifluorene derivatives, compounds **5a**−**d**, **6a**−**d**, and **7a**−**d**, the Negishi coupling reactions between brominated 9,9′-spirobifluorene derivatives and corresponding organozincs of H−T regular oligothiophenes with *n*-hexyl substituents was also initially employed. The synthesis of H−T regioregular substituted oligothiophenes was reported in many literatures. Barbarella et al.[24] reported the synthesis of methyl-substituted regioregular bi- and terthiophenes in low yields due to high isomeric purity via successive nickel-catalyzed cross-coupling reactions. The synthesis of 3,4′,4″-trihexyl-2,2′,5′,5″-terthiphene via Pd(0)-catalyzed Stille coupling of organotin and brominated units was also reported.[25] Some groups[26] tried to protect one of the reactive α-positions in the monomers and oligomers with chloride substituents and perform stepwise growth by a monothiophene unit achieved by successive iodination. The Negishi-coupling reactions between brominated 3-*n*-octylthiophene units and organozinc derivatives also afforded H−T regioregular oligothiophenes, which were difficult to purify through the flash column chromatography or other purification methodologies. To prevent the impurities from our desired compounds, the Suzuki coupling reactions were employed to achieve the synthesis of H−T regular oligothiophenes in place of the Negishi coupling reactions.

Sodium 4-*n*-hexyl-2-thienylboronate (**8**) was prepared in high yield (up to 95%), which is quite high in comparison with the literature (36%).[27] Compound **8** coupled with corresponding head-to-tail (H−T) regular *n*-hexyl-substituted oligothiophene bromide derivatives gave 3,4′-dihexyl-2,2′-bithiophene and 3,4′,4″-trihexyl-2,2′:5′,2″-terthiophene in high yields, respectively. Highly pure products were afforded though flash column chromatography with hexane as eluent.

TABLE 2. Comparison of the Yield of the (a) Negishi and (b) Suzuki Coupling Reactions

	yield (%)			yield (%)	
compd	a	b	compd	a	b
5a	71.2	97.0	**6c**	23.8	97.5
5b	75.6	98.1	**6d**	20.5	97.5
5c	73.3	97.4	**7a**	20.7	97.5
5d	68.7	98.1	**7b**	15.1	97.4
6a	27.7	98.2	**7c**	16.0	96.8
6b	24.3	98.6	**7d**	12.9	97.8

Compounds **5a**−**d** were also prepared through the Negishi coupling reactions between 4-hexyl-2-thienylzinc chloride and compounds **1a**−**d** with $Pd(PPh_3)_4$ as catalyst. Subsequent purification by flash column chromatography afforded pure products. However, the same procedure afforded compounds **6a**−**d** and **7a**−**d** in very low yields as shown in Table 2. It indicated that the yields decreased with the increase of oligothiophenes because the 3,4′-di-*n*-hexyl-2,2′-bithiophene and 3,4′,4″-tri-*n*-hexyl-5′-2,2′:5′,2″-terthiophene were more difficult to react with *n*-butyllithium and/or zinc chloride than 3-hexylthiophene.

Due to low yields of the Negishi coupling reactions and difficult purification of desired final products, the Suzuki coupling reactions depicted in Schemes 3−5 instead of the Negishi coupling reactions were employed. The Suzuki coupling reactions with high efficiency and selectivity avoided problems of low yields in metal-catalyzed cross-coupling step,[28] and the formation of isomeric homocoupling products. Another advantage of the Suzuki coupling reactions was the mild, fast, and complete reaction conditions. Table 2 also shows the yield comparison of our final products between the Negishi and the Suzuki coupling reactions. It obviously demonstrated that the yields of the Negishi coupling reactions decreased with the increase of H−T regioregular oligothiophenes, typically within the range of 10∼30%, which was not practical for development of new materials. In contrast, the yields of the Suzuki coupling reactions were much improved, which were among the highest of organic reactions.

We also investigated the solvent effect on the Suzuki coupling reactions, such as toluene, xylene, and THF. In our experiment, carefully degassed THF rather than two others was employed as the coupling solvent, because THF is a miscible solvent with sodium bicarbonate aqueous solution, which enabled microscale mixing of the reaction reagents possible and created more chance for molecular contact, thus led to faster and more complete

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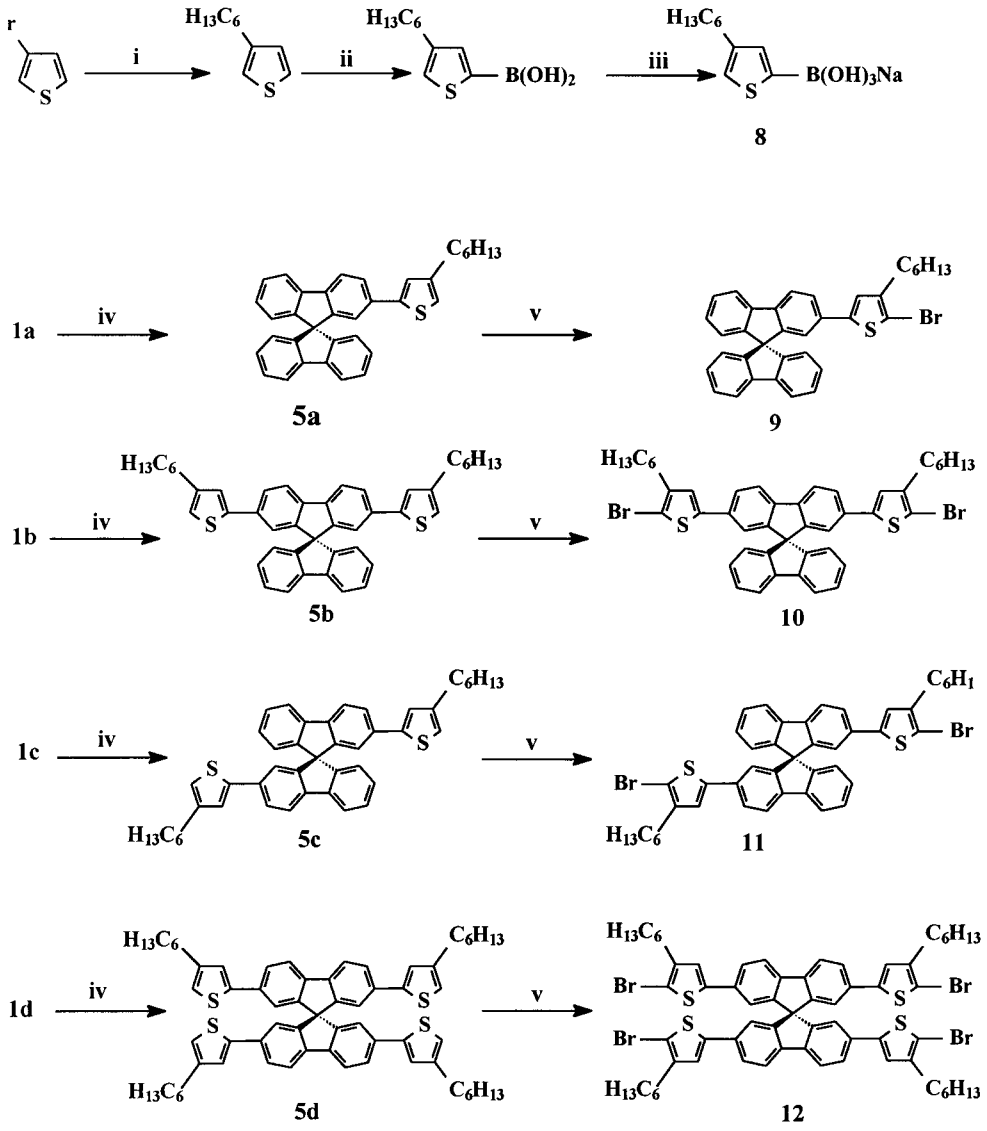
SCHEME 3. Synthetic Route to *n*-Hexyl-Substituted Oligothiophene-Functionalized 9,9′-Spirobifluorene Derivatives[a]



[a] Reagents and conditions: (i) $C_6H_{13}MgBr$, $Ni(dppp)Cl_2$, ethyl ether; (ii) LDA, $B(OCH_3)_3$, HCl; (iii) NaOH, ethyl ether; (iv) **8**, $Pd(PPh_3)_4$, THF, $NaHCO_3/H_2O$; (v) NBS, $CHCl_3$/AcOH.

coupling reactions.[29] To ensure the complete conversion of bromide to the final product, the first batch of excessive sodium 4-hexyl-2-thienylboronate (**8**) was added at the beginning of coupling reactions and followed by successive supplementary batches with reference to TLC monitoring reactions. Under reflux, it only took about 2 h to complete the coupling. The pure final products were obtained in very high yields from 96% to 99% after simple flash column chromatography purification using $CHCl_3$/hexane as eluent.

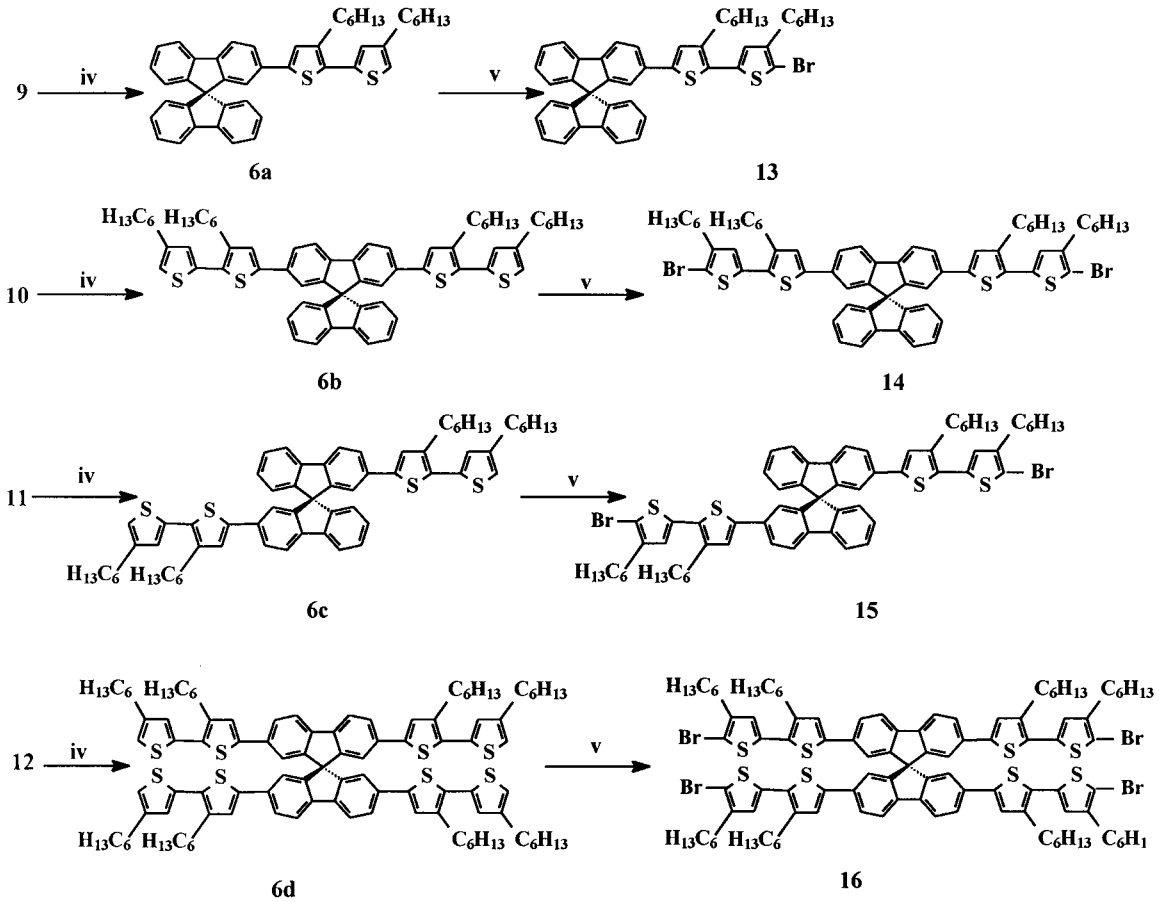
In this approach, NBS bromination of the compounds is also key step to achieve the pure final products. Strict control on stoichiometric ratios of NBS and the reaction temperature produced H−T regioregular *n*-hexyl-substituted oligothiophene functionalized 9,9′-spirobifluorene bromide derivatives (**9**−**16**) without bromination on β-position of thiophene rings. The exclusive α-position bromination avoided the analogous impurities generated, which were normally difficult to remove through normal separation methodologies.

Conclusion

In summary, two convenient approaches to oligothiophene-functionalized 9,9′-spirobifluorenes, including the Negishi and the Suzuki coupling reactions, are developed in this contribution. Four 9,9′-spirobifluorene bromide derivatives (compounds **1a**−**d**) are prepared through utilizing various starting materials. The oligothiophenes with substituents and without substituents are synthesized through the Suzuki and the Grignard coupling reactions. The preparations of oligothiophene-functionalized 9,9′-spirobifluorene are investigated. Although the coupling reactions between oligothienylzinc chloride and various 9,9′-spirobifluorene bromides with

(29) Kirschbaum, T.; Azumi, R.; Mena-Osteritz, E.; Bäuerle, P. *New J. Chem.* **1999**, *23*, 241.

SCHEME 4. Synthetic Route to *n*-Hexyl-Substituted Oligothiophene-Functionalized 9,9′-Spirobifluorene Derivatives[a]



[a] Reagents and conditions: (iv) **8**, $Pd(PPh_3)_4$, THF, $NaHCO_3/H_2O$; (v) NBS, $CHCl_3$/AcOH.

$Pd(PPh_3)_4$ as catalyst successfully produce unsubstituted oligothiophene-fuctionalized 9,9′-spirobifluorene derivatives, the Negishi coupling reactions afford pure oilgohexylthiophene functionalized 9,9′-spirobifluorenes in poor yields, indicating that the yield decreases with the increase of the number of the thiophene ring. Therefore, the Suzuki coupling reactions between oligothiopheneboronic acid derivatives and various 9,9′-spirobifluorene bromides are employed to produce the second series of head-to-tail regioregular oligothiophene modified 9,9′-spirobifluorenes in high yields. We also investigate the solvent effect on the Suzuki coupling reaction and demonstrate that THF as the solvent is much better than others, such as toluene and xylene. The structure and purity of all compounds are verified by FT-IR, ^1H and ^{13}C NMR, MS, and elemental analysis. The thermal stability and special optical and electrochemical properties of these organic conjugated materials will be reported successively in our subsequent contributions.

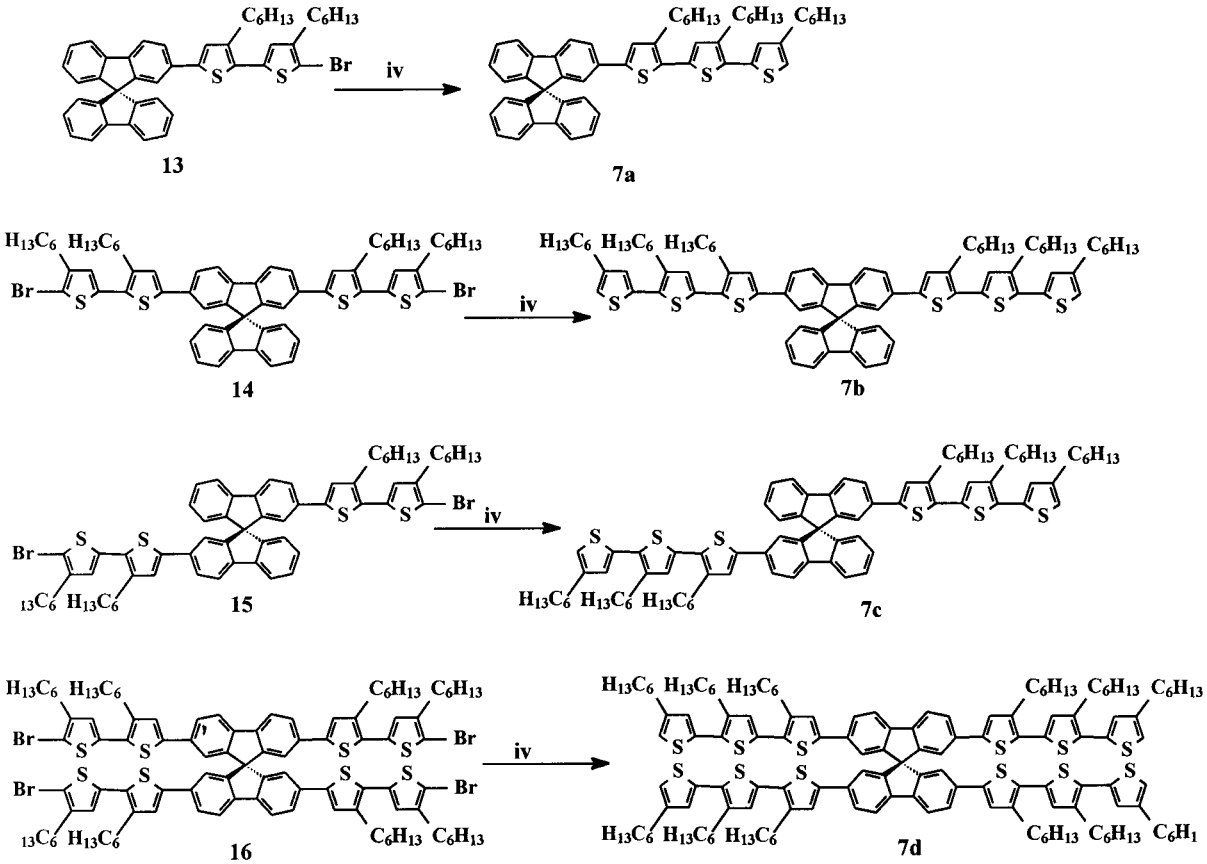
Experimental Section

Instruments and Materials. FT-IR spectra were recorded by dispersing samples in dry KBr disk pellets. ^1H (300 MHz) and ^{13}C (75.5 MHz) NMR spectra were obtained as solutions in deuterated chloroform or DMSO. TMS was used as internal reference for both monomer and polymer. Elemental analyses were obtained in the Microanalysis Lab at the National University of Singapore and in the Analytic Center at Peking University. Tetrahydrofuran were dried and distilled under argon from metal sodium powder and benzophenone ketyl. All chemicals were purchased from commercial suppliers and used as received unless otherwise stated. 2,2′-Bithiophene (**18**)[21] and 2,2′:5′.2″-terthiophene (**19**)[22] were prepared by standard procedures.

2-Bromofluorenone. A solution of 2-bromofluorene (9.8 g, 0.04 mol) and tetrabutylammonium hydroxide in methanol (1 mL) in pyridine (40 mL) was vigorously stirred overnight at room temperature while a stream of air was passed over the stirred liquid through the side openings. The mixture was then acidified with acetic acid and removed of solvent by distillation under reduced pressure, the residue was poured into water, and 9.3 g of yellow crude product was obtained. Recrystallization from ethanol afforded 8.7 g (yield 84%) of the pure product. EI-MS (*m*/*z*): 260, 258 (M^+, 100). ^1H NMR ($CDCl_3$, 300 MHz) δ: 7.76−7.77 (1H, d, J = 1.8 Hz, Ar-H), 7.65−7.68 (1H, dt, J = 1.1, 7.4 Hz, Ar-H), 7.59−7.64 (1H, dd, J = 1.8 Hz, J = 8.0 Hz, Ar-H), 7.51−7.52 (1H, d, J = 1.1 Hz, Ar-H), 7.49−7.50 (1H, m, Ar-H), 7.38−7.40 (1H, d, J = 8.0 Hz, Ar-H), 7.29−7.35 (1H, m, Ar-H). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 192.2, 143.5, 142.9, 137.0, 135.7, 134.9, 133.6, 129.3, 127.4, 124.5, 122.8, 121.6, 120.3. FT-IR (λ, cm^{-1}): 3014, 1719, 1595, 1442, 1257, 1189, 759, 736, 660.

9,9′-Spirobifluorene.[13] A solution of 2-bromobiphenyl (11.65 g, 50 mmol) in 20 mL of dry diethyl ether was added to the initially charged magnesium turnings (1.26 g, 52.5 mmol) to initiate the Grignard reaction. After the reaction initiated, the solution was added dropwise in such a way that the solution gently refluxed, and the reaction mixture was then refluxed for 3 h to complete the reaction. Afterward, a solution of

SCHEME 5. Synthetic Route to *n*-Hexyl-Substituted Oligothiophene-Functionalized 9,9′-Spirobifluorene Derivatives[a]



[a] Reagents and conditions: (iv) **8**, $Pd(PPh_3)_4$, THF, $NaHCO_3/H_2O$.

fluorenone (9.9 g, 55 mmol) in diethyl ether was slowly added to the Grignard solution and the mixture was refluxed overnight. The precipitated yellow magnesium complex was collected and washed with dry ether. The solid was stirred into ice-cold saturated ammonium chloride solution, and after 2 h, the precipitate was collected and dried in a vacuum and a white solid of carbinol was obtained. The carbinol was then dissolved in boiling acetic acid (100 mL), and several drops of concentrated hydrochloric acid were added. An intermediate reaction took place and the mixture solidified. The 9,9′-spirobifluorene was filtered off and recrystallized from ethanol to give 14.2 g of colorless plates (yield: 90%). EI-MS (*m*/*z*): 316 (M^+, 100). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.85−7.88 (4H, d, J = 7.7 Hz, Ar-H), 7.35−7.41 (4H, t, J = 7.7 Hz, Ar-H), 7.10−7.15 (4H, t, J = 7.7 Hz, Ar-H), 6.74−6.76 (4H, d, J = 7.7 Hz, Ar-H). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 148.7, 141.7, 127.7, 127.6, 124.0, 119.9, 119.9. FT-IR (λ, cm^{-1}): 3062, 1474, 1448, 1281, 1152, 748, 728, 635.

2-Bromo-9,9′-spirobifluorene (1a).[16] This compound was prepared according to the procedure described for 9,9′-spirobifluorene (**1**) utilizing magnesium (0.79 g, 33 mmol), 2-bromobiphenyl (7.69 g, 33 mmol), and 2-bromofluorenone (7.77 g, 30 mmol) in dry diethyl ether. Recrystallization of the obtained white solid from $CHCl_3$/EtOH yielded 10.4 g of the pure product (yield: 88%). EI-MS (*m*/*z*): 396, 394 (M^+, 100). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.80−7.86 (3H, m, Ar-H), 7.69−7.71 (1H, d, J = 8.0 Hz, Ar-H), 7.48−7.50 (1H, dd, J = 1.6 Hz, J = 8.0 Hz, Ar-H), 7.34−7.41 (3H, m, Ar-H), 7.08−7.17 (3H, m, Ar-H), 6.85 (1H, s, Ar-H), 6.71−6.74 (3H, d, J = 7.2 Hz, Ar-H). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 150.8, 149.9, 147.9, 147.6, 141.7, 140.7, 140.6, 131.1, 130.8, 128.3, 128.2, 127.9, 127.9, 127.8, 127.7, 127.2, 124.0, 121.3, 120.1. FT-IR (λ, cm^{-1}): 3064, 1464, 1445, 1405, 1262, 823, 770, 747, 727, 634.

2,7-Dibromo-9,9′-spirobifluorene (1b).[14] This compound was prepared according to the procedure described for 9,9′-spirobifluorene (**1**) utilizing magnesium (0.77 g, 32 mmol), 2-bromobiphenyl (6.3 g, 27 mmol), and 2,7-dibromofluorenone (8.3 g, 25 mmol) in dry diethyl ether. Recrystallization of the obtained white solid from $CHCl_3$/EtOH afforded 10.0 g of the pure products (yield 86%). EI-MS (*m*/*z*): 476, 474 (M^+, 100), 472. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.85−7.87 (2H, d, J = 7.8 Hz, Ar-H), 7.66−7.68 (2H, d, J = 8.2 Hz, Ar-H), 7.47−7.51 (2H, dd, J = 1.8, 8.2 Hz, Ar-H), 7.38−7.43 (2H, td, J = 1.1, 7.5 Hz, Ar-H), 7.12−7.18 (2H, td, J = 1.1, 7.5 Hz, Ar-H), 6.83−6.84 (2H, d, J = 1.8 Hz, Ar-H), 6.71−6.74 (2H, d, J = 7.8 Hz, Ar-H). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 150.5, 147.0, 141.6, 139.6, 131.0, 128.2, 128.0, 127.3, 127.2, 123.9, 121.8, 121.3, 120.2. FT-IR (λ, cm^{-1}): 3051, 1444, 1400, 1251, 871, 809, 731, 671.

2,2′-Dibromo-9,9′-spirobifluorene (1c).[14] To a mixture of 9,9′-spirobifluorene (**1**) (6.52 g, 20.6 mmol) and 10 mg of anhydrous $FeCl_3$ as catalyst in 60 mL of chloroform was added a solution of bromine (2.24 mL, 43.6 mmol) in 10 mL of chloroform dropwise at 0 °C over 1 h. After 24 h, the mixture was washed with saturated sodium thiosulfate solution and water to remove excess bromine. The organic phase was dried over Na_2SO_4. Removal of solvents gave a white residue. Recrystallization of the white residue from $CHCl_3$/EtOH afforded 8.8 g of the pure products (yield 88%). EI-MS (*m*/*z*): 476, 474 (M^+, 100), 472. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.80−7.83 (2H, d, J = 7.7 Hz, Ar-H), 7.69−7.72 (2H, d, J = 8.2 Hz, Ar-H), 7.49−7.52 (2H, dd, J = 1.6, 8.2 Hz, Ar-H), 7.37−7.41 (2H, t, J = 7.1 Hz, Ar-H), 7.13−7.18 (2H, t, J = 7.1 Hz, Ar-H), 6.83−6.84 (2H, d, J = 1.6 Hz, Ar-H), 6.70−6.73 (2H, d, J = 7.7 Hz, Ar-H). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 149.9, 147.6, 140.6, 140.5, 131.1, 128.3, 128.1, 127.2, 127.1, 124.0, 121.5,

121.3, 120.1. FT-IR (λ, cm^{-1}): 3057, 2925, 1461, 1444, 822, 755, 727, 636.

2,2′,7,7′-Tetrabromo-9,9′-spirobifluorene (1d).[15] This compound was prepared according to the procedure described for 2,2′-dibromo-9,9′-pirobifluorene utilizing 9,9′-spirobifluorene (6.52 g, 20.6 mmol), $FeCl_3$ (10 mg), and bromine (4.45 mL, 86.6 mmol). A total of 11.3 g of the white solids was obtained (yield 87%). EI-MS (*m*/*z*): 636, 634, 632 (M^+, 100), 630, 628. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.66−7.69 (4H, d, J = 8.1 Hz, Ar-H), 7.52−7.55 (4H, dd, J = 1.7, 8.1 Hz, Ar-H), 6.82−6.83 (4H, d, J = 1.7 Hz, Ar-H). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 148.7, 139.5, 131.7, 127.3, 127.2, 122.1, 121.6. FT-IR (λ, cm^{-1}): 3057, 2906, 2852, 1595, 1450, 1411, 1396, 1250, 1060, 1006, 951, 808, 732, 672.

General Procedure for Preparation of 2-(2-Thienyl)-9,9′-spirobifluorene (2a), 2-(5,2′-Bithiophene-2-yl)-9,9′-spirobifluoene (3a), and 2-(5,2′:5′,2″-Terthiophene-2-yl)-9,9′-spirobifluoene (4a). *n*-Butyllithium (10 mL, 1.2 M solution in hexanes, 12 mmol) was added dropwise to a solution of compound **17**, **18**, or **19** (12 mmol) and tetramethylethylenediamine (TMEDA) (1.4 g, 12 mmol) in 30 mL of dry THF at 0 °C under a nitrogen atmosphere. After being stirred for 1.5 h at room temperature, the mixture was transferred to a solution of anhydrous zinc chloride (1.84 g, 13.5 mmol) in 30 mL of dry THF via a double-tipped plastic needle. The resulting mixture was refluxed for 1 h and allowed to cool to room temperature. Afterward the mixture was transferred dropwise to a solution containing 2-bromo-9,9′-spirobifluorene (2.4 g, 6 mmol) and $Pd(PPh_3)_4$ (70 mg, 0.06 mmol) in 15 mL of THF. The resulting reaction mixture was refluxed for 12 h and was quenched by being poured into saturated ammonium chloride solution. The precipitated solid was collected. The aqueous layer was extracted with chloroform three times. The separated chloroform phase was washed with water and brine and dried over anhydrous Na_2SO_4. After the solvent was removed, recrystallization of the residue from $CHCl_3$/EtOH gave the pure product.

2-(2-Thienyl)-9,9′-spirobifluorene (2a). Green crystals (yield 84%). EI-MS (*m*/*z*): 398 (M^+, 100). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.89−7.95 (4H, t, J = 8.4 Hz, Ar-H), 7.70−7.72 (1H, dd, J = 1.6, 7.6 Hz, Ar-H), 7.40−7.47 (3H, m, Ar-H), 7.14−7.20 (5H, m, Ar-H, Th-H), 7.06 (1H, s, Ar-H), 6.96−6.99 (1H, dd, J = 3.6, 5.2 Hz, Th-H), 6.84−6.87 (2H, dd, J = 0.8, 7.6 Hz, Ar-H), 6.78−6.80 (1H, d, J = 7.6 Hz, Ar-H). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 149.6, 149.2, 148.6, 144.3, 141.8, 141.3, 141.2, 134.1, 128.0, 127.9, 127.8, 125.9, 125.8, 124.6, 124.2, 124.0, 123.2, 121.4, 120.5, 120.4, 120.3, 120.1, 120.0. FT-IR (λ, cm^{-1}): 3062, 2923, 1446, 1265, 853, 820, 774, 754, 729, 699. Anal. Calcd for $C_{29}H_{18}S$: C, 87.40; H, 4.55; S, 8.04. Found: C, 87.69; H, 4.23; S, 7.71.

2-(5,2′-Bithiophene-2-yl)-9,9′-spirobifluoene (3a). Yellow crystals (yield 82%). EI-MS (*m*/*z*): 480 (M^+, 100). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.82−7.90 (4H, m, Ar-H), 7.60−7.63 (1H, dd, J = 2, 8 Hz, Ar-H), 7.34−7.41 (3H, m, Ar-H), 7.15−7.18 (2H, td, J = 1.2, 4.4 Hz, Th-H), 7.08−7.13 (3H, m, Ar-H), 7.01−7.05 (2H, m, Th-H), 6.96−6.99 (1H, dd, J = 3.6, 4.8 Hz, Th-H), 6.93−6.94 (1H, d, J = 1.6 Hz, Ar-H), 6.76−6.79 (2H, dd, J = 0.8, 7.6 Hz, Ar-H), 6.70−6.72 (1H, d, J = 7.6 Hz, Ar-H). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 149.5, 149.1, 148.4, 142.9, 141.7, 141.3, 141.0, 137.3, 136.4, 133.6, 127.9, 127.7, 125.4, 124.3, 124.2, 124.1, 124.0, 123.7, 123.4, 120.9, 120.8, 120.4, 120.0, 119.9. FT-IR (λ, cm^{-1}): 3064, 2932, 1460, 1445, 1421, 802, 775, 753, 729, 702, 636. EI-HRMS calcd for $C_{37}H_{22}S_3$ 480.1006, found 480.1004.

2-(5,2′:5′,2″-Terthiophene-2-yl)-9,9′-spirobifluoene (4a). Yellow solids (yield 81%). EI-MS (*m*/*z*): 562 (M^+, 100). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.83−7.89 (4H, t, J = 8.2 Hz, Ar-H), 7.60−7.64 (1H, dd, J = 2, 7.6 Hz, Ar-H), 7.37−7.41 (3H, m, Ar-H), 7.19−7.21 (1H, d, J = 6.0 Hz, Th-H), 7.08−7.15 (3H, m, Ar-H), 6.99−7.05 (6H, m, Th-H), 6.94 (1H, s, Ar-H), 6.76−6.79 (2H, d, J = 7.6 Hz, Ar-H), 6.70−6.72 (1H, d, J = 7.2 Hz, Ar-H). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 149.5, 149.1, 148.4, 143.0, 141.7, 141.4, 141.0, 137.0, 136.1, 136.0, 133.5, 127.9, 127.8, 127.7, 127.7, 125.4, 124.3, 124.2, 124.2, 124.0, 123.9, 123.9, 123.8, 123.6, 120.9, 120.8, 120.4, 120.3, 120.0, 119.9, 119.8. FT-IR (λ, cm^{-1}): 3064, 2928, 1446, 830, 795, 752, 728, 699. Anal. Calcd for $C_{37}H_{22}S_3$: C, 78.97; H, 3.94; S, 17.09. Found: C, 78.12; H, 3.96; S, 17.30.

General Procedure for Preparation of 2,7-Bis(2-thienyl)-9,9′-spirobifluorene (2b), 2,2′-Bis(2-thienyl)-9,9′-spirobifluorene (2c), 2,7-Bis(5,2′-bithiophene-2-yl)-9,9′-spirobifluoene (3b), 2,2′-Bis(5,2′-bithiophene-2-yl)-9,9′-spirobifluoene (3c), 2,7-Bis(5,2′:5′,2″-terthiophene-2-yl)-9,9′-spirobifluoene (4b), and 2,2′-Bis(5,2′:5′,2″-terthiophene-2-yl)-9,9′-spirobifluoene (4c). Compounds **2**−**4b**, **2**−**4c** were prepared according to the procedure described for compounds **2**−**4a** utilizing *n*-Butyllithium (10 mL, 1.2 M solution in hexanes, 12 mmol), tetramethylethylenediamine (TMEDA) (1.4 g, 12 mmol), compound **17**, **18**, or **19** (12 mmol), anhydrous zinc chloride (1.84 g, 13.5 mmol), **1b** or **1c** (1.4 g, 3 mmol), and $Pd(PPh_3)_4$ (70 mg, 0.06 mmol) in dry THF. Recrystallization from $CHCl_3$/EtOH gave pure products.

2,7-Bis(2-thienyl)-9,9′-spirobifluorene (2b). Yellow solids (yield 83%). EI-MS (*m*/*z*): 480 (M^+, 100). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.87−7.90 (2H, d, J = 7.6 Hz, Ar-H), 7.82−7.84 (2H, d, J = 8.0 Hz, Ar-H), 7.62−7.65 (2H, dd, J = 1.6, 8.0 Hz, Ar-H), 7.37−7.42 (2H, td, J = 1.2, 7.3 Hz, Ar-H), 7.11−7.17 (6H, m, Ar-H, Th-H), 6.95−6.96 (2H, m, Th-H), 6.93 (2H, s, Ar-H), 6.80−6.82 (2H, d, J = 7.6 Hz, Ar-H). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 149.8, 148.2, 144.2, 141.7, 140.6, 134.0, 127.9, 127.8, 125.9, 124.5, 124.1, 123.1, 121.2, 121.1, 120.3, 120.2, 120.0. FT-IR (λ, cm^{-1}): 3062, 2923, 1467, 1447, 1271, 848, 754, 728, 637. Anal. Calcd for $C_{33}H_{20}S_2$: C, 82.47; H, 4.19; S, 13.34. Found: C, 82.11; H, 4.13; S, 13.14.

2,2′-Bis(2-thienyl)-9,9′-spirobifluorene (2c). Whitish yellow solid (yield 84%). EI-MS (*m*/*z*): 480 (M^+, 100). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.83−7.86 (4H, d, J = 8.0 Hz, Ar-H), 7.62−7.65 (2H, dd, J = 1.6, 8.0 Hz, Ar-H), 7.34−7.39 (2H, td, J = 0.8, 7.5 Hz, Ar-H), 7.07−7.15 (6H, m, Ar-H, Th-H), 6.96−6.97 (2H, d, J = 1.6 Hz, Ar-H), 6.91−6.94 (2H, dd, J = 3.6, 5.2 Hz, Th-H), 6.72−6.74 (2H, d, J = 7.6 Hz, Ar-H). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 149.2, 148.8, 144.2, 141.2, 141.1, 134.1, 128.0, 127.9, 127.8, 125.9, 124.5, 124.0, 123.1, 121.3, 120.3, 120.0. FT-IR (λ, cm^{-1}): 3067, 2954, 1461, 1420, 1273, 883, 753, 685. Anal. Calcd for $C_{33}H_{20}S_2$: C, 82.47; H, 4.19; S, 13.34. Found: C, 82.08; H, 4.18; S, 13.10.

2,7-Bis(5,2′-bithiophene-2-yl)-9,9′-spirobifluoene (3b). Yellow crystals (yield 82%). EI-MS (*m*/*z*): 644 (M^+, 100). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.88−7.91 (2H, d, J = 7.4 Hz, Ar-H), 7.82−7.84 (2H, d, J = 8.0 Hz, Ar-H), 7.61−7.64 (2H, dd, J = 1.6, 8.0 Hz, Ar-H), 7.38−7.44 (2H, td, J = 1.2, 7.6 Hz, Ar-H), 7.11−7.18 (6H, m, Ar-H, Th-H), 7.01−7.04 (4H, m, Th-H), 6.96−6.99 (2H, m, Th-H), 6.91−6.92 (2H, d, J = 2 Hz, Ar-H), 6.80−6.83 (2H, J = 7.2 Hz, Ar-H). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 149.9, 148.1, 142.8, 141.7, 140.6, 137.3, 136.5, 133.7, 128.0, 127.9, 127.7, 125.5, 124.3, 124.2, 124.1, 123.8, 123.4, 120.8, 120.7, 120.4, 120.1. FT-IR (λ, cm^{-1}): 3065, 2922, 1473, 1446, 1422, 838, 821, 798, 693. Anal. Calcd for $C_{41}H_{24}S_4$: C, 76.36; H, 3.75; S, 19.89. Found: C, 76.06; H, 3.78; S, 19.56.

2,2′-Bis(5,2′-bithiophene-2-yl)-9,9′-spirobifluoene (3c). Yellow solids (yield: 83%). EI-MS (*m*/*z*): 644 (M^+, 100). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.85−7.88 (4H, dd, J = 2, 8.0 Hz, Ar-H), 7.63−7.66 (2H, dd, J = 1.6, 8.0 Hz, Ar-H), 7.37−7.41 (2H, t, J = 7.2 Hz, Ar-H), 7.15−7.17 (2H, dd, J = 1.2, 5.2 Hz, Th-H), 7.10−7.12 (4H, m, 2Th-H, 2Ar-H), 7.05−7.06 (2H, d, J = 4 Hz, Th-H), 6.91−6.92 (2H, d, J = 3.6 Hz, Th-H), 6.96−6.98 (4H, m, 2Ar-H, 2Th-H), 6.74−6.76 (2H, J = 7.6 Hz, Ar-H). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 149.2, 148.8, 142.9, 141.3, 141.1, 137.3, 136.5, 133.7, 128.0, 127.8, 127.7, 125.5, 124.3, 124.2, 124.0, 123.8, 123.4, 121.0, 120.9, 120.4, 120.0. FT-IR (λ, cm^{-1}): 3065, 2927, 1473, 1460, 840, 796, 730, 694. EI-HRMS calcd for $C_{41}H_{24}S_4$ 644.0760, found 644.0758.

2,7-Bis(5,2′:5′,2″-terthiophene-2-yl)-9,9′-spirobifluoene (4b). Brown solids (yield: 82%). EI-MS (*m*/*z*): 808 (M^+, 100). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.89−7.92 (2H, d, J = 8.0 Hz, Ar-H), 7.82−7.85 (2H, d, J = 8.0 Hz, Ar-H), 7.61−7.63 (2H,

d, J = 8.8 Hz, Ar-H), 7.39−7.44 (2H, t, J = 7.2 Hz, Ar-H), 7.12−7.21 (6H, m, Th-H, Ar-H), 6.97−7.08 (10H, m, Th-H), 6.91 (2H, s, Ar-H), 6.80−6.82 (2H, d, J = 7.2 Hz, Ar-H). FT-IR (λ, cm^{-1}): 3100, 3063, 2927, 1473, 1445, 1423, 836, 792, 696, 638, 469. FAB-HRMS: calcd for $C_{49}H_{28}S_6$ 808.0515, found 808.0510.

2,2′-Bis(5,2′:5′,2″-terthiophene-2-yl)-9,9′-spirobifluoene (4c). Yellow solids (yield: 83%). FAB MS (m/z): 808 (M$^+$, 100). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.85−7.89 (4H, dd, J = 2.6, 7.8 Hz, Ar-H), 7.63−7.66 (2H, dd, J = 1.8, 7.8 Hz, Ar-H), 7.37−7.42 (2H, t, J = 7.4 Hz, Ar-H), 7.19−7.21 (2H, dd, J = 1.0, 5.0 Hz, Th-H), 7.13−7.15 (4H, m, Th-H, Ar-H), 6.97−7.07 (10H, m, Th-H), 6.97−6.98 (2H, d, J = 1.2 Hz, Ar-H), 6.74−6.77 (2H, d, J = 7.6 Hz, Ar-H). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 149.2, 148.8, 142.9, 141.3, 141.1, 137.0, 136.1, 136.0, 136.0, 133.7, 128.0, 127.9, 127.8, 125.5, 124.4, 124.3, 124.2, 124.0, 123.9, 123.6, 123.5, 120.9, 120.5, 120.0. FT-IR (λ, cm^{-1}): 3064, 2922, 1460, 1449, 834, 793, 756. FAB-HRMS: calcd for $C_{49}H_{28}S_6$ 808.0515, found 808.0508.

General Procedure for Preparation of 2,2′,7,7′-Tetrakis(2-thienyl)-9,9′-spirobifluorene (2d), 2,2′,7,7′-Bis(5,2′-bithiophene-2-yl)-9,9′-spirobifluoene (3d), and 2,2′,7,7′-Tetrakis(5,2′:5′,2″-terthiophene-2-yl)-9,9′-spirobifluoene (4d). Compounds **2**−**4d** were prepared according to the procedure described for compounds **2**−**4a** utilizing *n*-butyllithium (10 mL, 1.2 M solution in hexanes, 12 mmol), tetramethylethylenediamine (TMEDA) (1.4 g, 12 mmol), compound **17**, **18**, or **19** (12 mmol), anhydrous zinc chloride (1.84 g, 13.5 mmol), compound **1d** (0.95 g, 1.5 mmol), and Pd(PPh$_3$)$_4$ (70 mg, 0.06 mmol) in dry THF. Recrystallization from $CHCl_3$/EtOH gave pure products.

2,2′,7,7′-Tetrakis(2-thienyl)-9,9′-spirobifluorene (2d). Yellowish brown crystals (yield: 86%). EI-MS (m/z): 644 (M$^+$, 100).^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.85−7.88 (4H, d, J = 8.0 Hz, Ar-H), 7.65−7.68 (4H, dd, J = 1.4, 7.8 Hz, Ar-H), 7.14−7.17 (8H, m, Th-H), 7.00−7.01 (4H, d, J = 1.6 Hz, Ar-H), 6.93−6.96 (4H, t, J = 4.4 Hz, Th-H). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 149.3, 144.0, 140.5, 134.2, 127.7, 126.0, 124.6, 123.2, 121.3, 121.3, 120.4. FT-IR (λ, cm^{-1}): 3106, 2921, 1467, 1270, 1211, 813, 694. Anal. Calcd for $C_{41}H_{24}S_4$: C, 76.36; H, 3.75; S, 19.89. Found: C, 76.44; H, 3.60; S, 19.63.

2,2′,7,7′-Bis(5,2′-bithiophene-2-yl)-9,9′-spirobifluoene (3d). Brown crystals (yield: 84%). EI-MS (m/z): 972 (M$^+$, 100). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.87−7.90 (4H, d, J = 8.0 Hz, Ar-H), 7.65−7.68 (4H, dd, J = 1.6, 8.0 Hz, Ar-H), 7.15−7.17 (4H, d, J = 5.2 Hz, Th-H), 7.10−7.11 (4H, dd, J = 1.2, 3.6 Hz, Th-H), 7.06−7.08 (4H, d, J = 3.6 Hz, Th-H), 7.01−7.02 (4H, d, J = 4 Hz, Th-H), 6.98−6.99 (4H, d, J = 1.6 Hz, Ar-H), 6.95−6.98 (4H, q, J = 3.8, 5.0 Hz, Th-H). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 154.9, 149.3, 142.71, 140.6, 137.3, 136.6, 134.0, 127.7, 125.8, 124.4, 124.2, 123.9, 123.4, 120.9, 120.6. FT-IR (λ, cm^{-1}): 3100, 2922, 1473, 1420, 1269, 1203, 802, 746, 697, 473. EI-HRMS: calcd for $C_{57}H_{32}S_8$ 972.0270, found 972.0271.

2,2′,7,7′-Tetrakis(5,2′:5′,2″-terthiophene-2-yl)-9,9′-spirobifluoene (4d). Brown solids (yield: 85%). EI-MS (m/z): 1300 (M$^+$, 100). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.87−7.90 (4H, d, J = 8.0 Hz, Ar-H), 7.65−7.68 (4H, dd, J = 1.4, 7.8 Hz, Ar-H), 7.18−7.20 (4H, d, J = 5.2 Hz, Th-H), 7.12−7.13 (4H, d, J = 3.6 Hz, Th-H), 7.08−7.09 (4H, d, J = 3.6 Hz, Th-H), 6.98−7.03 (20H, m, Th-H, Ar-H), 6.98−6.99 (4H, d, J = 2.4 Hz, Ar-H), 6.95−6.97 (4H, q, J = 3.6, 4.8 Hz, Th-H). FT-IR (λ, cm^{-1}): 3100, 2965, 2853, 1473, 1458, 1263, 1045, 835, 819, 791, 692. EI-HRMS: calcd for $C_{57}H_{32}S_8$ 1299.9779, found 1299.9773.

Sodium 4-Hexyl-2-thienylboronate (8).[27] *n*-Butyllithium (100 mL, 1.2 M solution in hexanes, 120 mmol) was added dropwise to a solution of diisopropylamine (12.1 g, 120 mmol) in anhydrous THF at 0 °C under a nitrogen atmosphere. The mixture was stirred for 0.5 h and then cooled to −78 °C. To the mixture was added a solution of 3-hexylthiophene (20.2 g, 120 mmol) in dry THF. The resulting mixture was stirred for 1 h at −78 °C and allowed to warm to room temperature over 2 h. After the mixture was cooled to −78 °C, trimethylborate (40.1 mL, 360 mmol) was slowly added. The mixture was allowed to come to room temperature overnight and was hydrolyzed with aqueous HCl solution. After extraction with diethyl ether, the organic phase was dried over Na_2SO_4 and stirred with sodium hydroxide. The resulting precipitate was filtered off and washed with diethyl ether to get 28.6 g of sodium 4-hexyl-2-thienylboronate as a white porous solid (yield 95%). ^{1}H NMR (D_2O, 300 MHz) δ: 6.96 (1H, s, Th-H), 6.93 (1H, s, Th-H), 2.58−2.63 (2H, t, J = 7.4 Hz, CH_2), 1.58−1.61 (2H, m, CH_2), 1.30−1.32 (6H, m, CH_2), 0.85−0.89 (3H, t, J = 6.6 Hz, CH_3).

General Procedure for Preparation of 2-(4-Hexylthienyl)-9,9′-spirobifluorene (5a), 2-(3,4′-Dihexyl-5,2′-bithiophene-2-yl)-9,9′-spirobifluoene (6a), and 2-(3,4′,4″-Trihexyl-5,2′:5′,2″-terthiophene-2-yl)-9,9′-spirobifluoene (7a). To a degassed mixture of Pd(PPh$_3$)$_4$ (70 mg, 0.06 mmol) and compound **1a**, **9**, or **13** (2 mmol) in THF were added compound **8** and a saturated aqueous solution of $NaHCO_3$ (1.0 g, 4 mmol). The mixture was refluxed for 2 h, poured into a saturated solution of ammonium chloride, and extracted with ethyl acetate three times. The combined extracts were washed with brine and dried over Na_2SO_4. After the solvent was removed by rotary evaporation, the remaining oil was purified by flash chromatography (silica gel, $CHCl_3$/hexane 1:25) to yield pure products.

2-(4-Hexylthienyl)-9,9′-spirobifluorene (5a). Light yellow crystals (yield 97%). EI-MS (m/z): 482 (M$^+$, 100). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.82−7.89 (4H, m, Ar-H), 7.60−7.63 (1H, dd, J = 1.8, 7.8 Hz, Ar-H), 7.34−7.42 (3H, m, Ar-H), 7.07−7.15 (3H, m, Th-H), 6.96−6.97 (1H, d, J = 1.6 Hz, Ar-H), 6.94−6.95 (1H, d, J = 1.2 Hz, Th-H), 6.76−6.79 (3H, m, Ar-H, Th-H), 6.69−6.72 (1H, d, J = 7.6 Hz, Ar-H), 2.48−2.53 (2H, t, J = 7.6 Hz, CH_2), 1.51−1.58 (2H, m, CH_2), 1.25−1.32 (6H, m, CH_2), 0.85−0.89 (3H, t, J = 6.8 Hz, CH_3). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 149.3, 149.1, 148.5, 144.1, 143.7, 141.7, 141.2, 141.0, 134.3, 127.8, 127.7, 127.6, 125.6, 124.5, 124.1, 123.9, 121.0, 120.2, 120.0, 119.9, 119.2, 31.5, 30.5, 30.2, 28.9, 22.5, 14.0. FT-IR (λ, cm^{-1}): 3057, 2960, 1463, 1446, 1421, 827, 776, 750, 727, 636. Anal. Calcd for $C_{35}H_{30}S$: C, 87.09; H, 6.26; S, 6.64. Found: C, 86.90; H, 6.13; S, 6.31.

2-(3,4′-Dihexyl-5,2′-bithiophene-2-yl)-9,9′-spirobifluoene (6a). Yellow crystals (yield 98%). EI-MS (m/z): 648 (M$^+$, 100). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.83−7.90 (4H, m, Ar-H), 7.61−7.64 (1H, dd, J = 1.6, 8.0 Hz, Ar-H), 7.34−7.42 (3H, m, Ar-H), 7.08−7.16 (3H, m, Ar-H), 6.97 (1H, s, Th-H), 6.95−6.96 (1H, d, J = 1.6 Hz, Ar-H), 6.91−6.92 (1H, d, J = 1.2 Hz, Th-H), 6.85−6.86 (1H, d, J = 1.2 Hz, Th-H), 6.78−6.80 (2H, d, J = 7.6 Hz, Ar-H), 6.70−6.73 (1H, d, J = 7.6 Hz, Ar-H), 2.64−2.70 (2H, t, J = 7.8 Hz, CH_2), 2.56−2.61 (2H, t, J = 7.8 Hz, CH_2), 1.52−1.63 (4H, m, CH_2), 1.24−1.33 (12H, m, CH_2), 0.85−0.96 (6H, m, CH_3). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 149.4, 149.1, 148.5, 143.5, 141.7, 141.3, 141.2, 141.1, 140.1, 135.7, 133.8, 130.4, 127.9, 127.8, 127.7, 126.9, 126.0, 125.4, 124.1, 123.9, 120.8, 120.3, 120.0, 119.9, 119.7, 31.6, 31.5, 30.5, 30.4, 30.3, 29.3, 29.2, 28.9, 22.5, 14.0, 13.9. FT-IR (λ, cm^{-1}): 3089, 2923, 1459, 823, 750, 728, 636. Anal. Calcd for $C_{45}H_{44}S_2$: C, 83.29; H, 6.83; S, 9.88. Found: C, 83.00; H, 6.77; S, 9.79.

2-(3,4′,4″-Trihexyl-5,2′:5′,2″-terthiophene-2-yl)-9,9′-spirobifluoene (7a). Brown solid (yield 97%). EI-MS (m/z): 814 (M$^+$, 100). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.84−7.91 (4H, m, Ar-H), 7.62−7.65 (1H, d, J = 8.0 Hz, Ar-H), 7.35−7.43 (3H, m, Ar-H), 7.09−7.17 (3H, m, Ar-H), 6.97−6.99 (3H, m, Th-H), 6.93 (1H, s, Ar-H), 6.89 (1H, s, Th-H), 6.79−6.82 (2H, d, J = 7.6 Hz, Ar-H), 6.71−6.74 (1H, d, J = 7.6 Hz, Ar-H), 2.69−2.77 (4H, m, CH_2), 2.59−2.65 (2H, t, J = 7.8 Hz, CH_2), 1.55−1.67 (6H, m, CH_2), 1.31−1.35 (18H, m, CH_2), 0.88−0.92 (9H, m, CH_3). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 149.4, 149.1, 148.5, 143.5, 141.7, 141.4, 141.2, 141.1, 140.3, 139.5, 135.5, 133.8, 133.7, 130.7, 130.0, 128.2, 127.9, 127.8, 127.7, 127.0, 126.2, 125.4, 124.9, 124.1, 123.9, 120.8, 120.3, 120.0, 119.9, 119.7, 31.7, 31.6, 31.5, 30.5, 30.4, 30.3, 29.5, 29.2, 28.9, 22.5, 14.0. FT-IR (λ, cm^{-1}): 3062, 2953, 1458, 1420, 825, 751, 728, 636. Anal. Calcd for $C_{55}H_{58}S_3$: C, 81.03; H, 7.17; S, 11.80. Found: C, 80.87; H, 7.32; S, 11.86.

General Procedure for Preparation of 2-(5-Bromo-4-hexylthienyl)-9,9′-spirobifluorene (9) and 2-(5′-Bromo-3,4′-dihexyl-5,2′-bithiophene-2-yl)-9,9′-spirobifluoene (13). *N*-Bromosuccinimide (0.356 g, 2.05 mmol) was added slowly in portions to a solution of compound **5a** or **6a** (2 mmol) in 25 mL of acetic acid and chloroform (1:1) at 0 °C. The mixture was stirred overnight at room temperature, poured into water, and then extracted with chloroform. The combined organic layers were washed with saturated $NaHCO_3$ and brine and were dried over Na_2SO_4. After the solvent was removed by rotary evaporation, the remaining solid was recrystallized from $CHCl_3$/EtOH to give pure products.

2-(5-Bromo-4-hexylthienyl)-9,9′-spirobifluorene (9). Brown crystals (yield 95%). EI-MS (*m*/*z*): 562, 560 (M^+, 100). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.82−7.90 (4H, m, Ar-H), 7.52−7.55 (1H, dd, J = 1.6, 8.0 Hz, Ar-H), 7.35−7.43 (3H, m, Ar-H), 7.09−7.16 (3H, m, Ar-H), 6.89−6.90 (1H, d, J = 1.6 Hz, Ar-H), 6.83 (1H, s, Th-H), 6.77−6.79 (2H, d, J = 7.6 Hz, Ar-H), 6.71−6.74 (1H, d, J = 7.6 Hz, Ar-H), 2.45−2.50 (2H, t, J = 7.6 Hz, CH_2), 1.49−1.56 (4H, m, CH_2), 1.28−1.34 (6H, m, CH_2), 0.86−0.91 (3H, t, J = 6.6 Hz, CH_3). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 149.5, 149.1, 148.4, 143.5, 143.0, 141.7, 141.4, 141.0, 133.4, 127.9, 127.8, 127.7, 125.3, 124.1, 123.9, 120.7, 120.4, 120.0, 119.9, 112.0, 107.8, 31.5, 29.6, 29.5, 28.8, 22.5, 14.0. FT-IR (λ, cm^{-1}): 3057, 2927, 1448, 824, 754, 730, 636. Anal. Calcd for $C_{35}H_{29}BrS$: C, 74.86; H, 5.21; S, 5.71, Br, 14.23. Found: C, 74.87; H, 5.41; S, 5.36; Br, 14.49.

2-(5′-Bromo-3,4′-dihexyl-5,2′-bithiophene-2-yl)-9,9′-spirobifluoene (13). Yellow crystals (yield 94%). EI-MS (*m*/*z*): 728, 726 (M^+, 100). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.82−7.90 (4H, m, Ar-H), 7.59−7.62 (1H, dd, J = 1.6, 8.0 Hz, Ar-H), 7.34−7.42 (3H, m, Ar-H), 7.08−7.15 (3H, m, Ar-H), 6.95 (1H, s, Th-H), 6.92−6.93 (1H, d, J = 0.8 Hz, Ar-H), 6.77−6.79 (2H, d, J = 7.6 Hz, Ar-H), 6.76 (1H, s, Th-H), 6.70−6.72 (1H, d, J = 7.2 Hz, Ar-H), 2.59−2.64 (2H, t, J = 7.8 Hz, CH_2), 2.51−2.56 (2H, t, J = 7.6 Hz, CH_2), 1.53−1.58 (4H, m, CH_2), 1.22−1.37 (12H, m, CH_2), 0.84−0.92 (6H, m, CH_3). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 149.4, 149.1, 148.4, 142.3, 141.9, 141.7, 141.4, 141.0, 140.6, 135.6, 133.5, 129.3, 127.8, 127.7, 126.4, 126.0, 125.4, 124.1, 123.9, 120.9, 120.3, 120.0, 119.9, 108.3, 31.5, 30.5, 29.5, 29.4, 29.3, 29.1, 28.8, 22.5, 14.0, 13.9. FT-IR (λ, cm^{-1}): 3057, 2957, 1459, 1446, 825, 753, 734, 637. Anal. Calcd for $C_{45}H_{43}BrS_2$: C, 74.26; H, 5.95; Br, 10.98; S, 8.81. Found: C, 74.07; H, 5.87; Br, 11.32; S, 8.73.

General procedure for preparation of 2,7-Bis(4-hexylthienyl)-9,9′-spirobifluorene (5b), 2,2′-Bis(4-hexylthienyl)-9,9′-spirobifluorene (5c), 2,7-Bis(3,4′-dihexyl-5,2′-bithiophene-2-yl)-9,9′-spirobifluoene (6b), 2,2′-Bis(3,4′-dihexyl-5,2′-bithiophene-2-yl)-9,9′-spirobifluoene (6c), 2,7-Bis(3,4′,4″-trihexyl-5,2′:5′,2″-terthiophene-2-yl)-9,9′-spirobifluoene (7b), and 2,2-Bis(3,4′,4″-trihexyl-5,2′:5′,2″-terthiophene-2-yl)-9,9′-spirobifluoene (7c). These compounds were prepared according to the procedure described for compounds **5**−**7a** and $Pd(PPh_3)_4$ (70 mg, 0.06 mmol), compound **1b**, **1c**, **10**, **11**, **14**, or **15** (2 mmol) in THF, compound **8** (2.0 g, 8 mmol) and $NaHCO_3$ (20 mL). Pure products were obtained through flash chromatography (silica gel, $CHCl_3$/hexane 1:25).

2,7-Bis(4-hexylthienyl)-9,9′-spirobifluorene (5b). Yellow crystals (yield 98%). EI-MS (*m*/*e*): 648 (M^+, 100). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.89−7.91 (2H, d, J = 7.6 Hz, Ar-H), 7.80−7.82 (2H, d, J = 8.0 Hz, Ar-H), 7.62−7.65 (2H, dd, J = 1.6, 8.0 Hz, Ar-H), 7.37−7.42 (2H, td, J = 1.1, 7.4 Hz, Ar-H), 7.11−7.17 (2H, td, J = 1.1 , 7.4 Hz, Ar-H), 6.95−6.96 (2H, d, J = 1.2 Hz, Th-H), 6.90−6.91 (2H, d, J = 0.8 Hz, Ar-H), 6.80−6.83 (2H, dd, J = 0.8, 7.6 Hz, Ar-H), 6.76 (2H, s, Th-H), 2.48−2.53 (4H, t, J = 7.6 Hz, CH_2), 1.53−1.58 (4H, m, CH_2), 1.23−1.32 (12H, m, CH_2), 0.85−0.89 (6H, t, J = 6.6 Hz, CH_3). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 149.7, 148.4, 144.1, 143.7, 141.7, 140.5, 134.2, 127.9, 127.7, 125.7, 124.5, 124.2, 120.9, 120.2, 120.0, 119.3, 31.5, 30.5, 30.3, 28.9, 22.5, 14.0. FT-IR (λ, cm^{-1}): 3057, 2953, 1475, 867, 816, 755, 732, 638. Anal. Calcd for $C_{45}H_{44}S_2$: C, 83.29; H, 6.83; S, 9.88. Found: C, 82.99; H, 6.71; S, 9.60.

2,2′-Bis(4-hexylthienyl)-9,9′-spirobifluorene (5c). Yellow crystals (yield 97%). EI-MS (*m*/*z*): 648 (M^+, 100). ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 7.84−7.88 (4H, d, J = 7.9 Hz, Ar-H), 7.62−7.67 (2H, q, J = 1.6, 9.9 Hz, Ar-H), 7.35−7.43 (2H, t, J = 7.3 Hz, Ar-H), 7.08−7.16 (2H, t, J = 7.6 Hz, Ar-H), 6.98 (2H, s, Th-H), 6.95−6.98 (2H, m, Ar-H), 6.73−6.80 (2H, d, J = 7.6 Hz, Ar-H), 6.77 (2H, s, Th-H), 2.46−2.54 (4H, t, J = 7.3 Hz, CH_2), 1.61−1.71 (4H, m, CH_2), 1.27−1.43 (12H, m, CH_2), 0.83−0.89 (6H, t, J = 6.3 Hz, CH_3). ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 149.16, 148.92, 144.20, 141.23, 141.08, 134.40, 127.88, 127.80, 127.74, 125.73, 124.63, 124.07, 121.17, 120.39, 119.99, 119.33, 31.62, 30.57, 30.40, 28.97, 22.58, 14.08. FT-IR (λ, cm^{-1}): 3094, 2960, 2925, 1465, 823, 770, 754, 729, 641. Anal. Calcd for $C_{45}H_{44}S_2$: C, 83.29; H, 6.83; S, 9.88. Found: C, 82.97; H, 6.69; S, 10.01.

2,7-Bis(3,4′-dihexyl-5,2′-bithiophene-2-yl)-9,9′-spirobifluoene (6b). Brown solids (yield 99%). EI-MS (*m*/*z*): 980 (M^+, 100). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.90−7.92 (2H, d, J = 8.0 Hz, Ar-H), 7.80−7.83 (2H, d, J = 8.0 Hz, Ar-H), 7.60−7.62 (2H, dd, J = 1.6, 8.0 Hz, Ar-H), 7.39−7.44 (2H, t, J = 7.2 Hz, Ar-H), 7.12−7.17 (2H, t, J = 7.2 Hz, Ar-H), 6.94 (2H, s, Th-H), 6.90−6.91 (4H, m, Ar-H, Th-H), 6.81−6.85 (4H, m, Ar-H, Th-H), 2.63−2.69 (4H, t, J = 8.0 Hz, CH_2), 2.55−2.60 (4H, t, J = 8.0 Hz, CH_2), 1.53−1.59 (8H, m, CH_2), 1.27−1.32 (24H, m, CH_2), 0.84−0.89 (12H, m, CH_3). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 149.8, 148.3, 143.5, 141.7, 141.3, 140.6, 140.1, 135.7, 133.8, 130.5, 128.0, 127.8, 126.9, 126.0, 125.4, 124.2, 120.7, 120.3, 120.0, 119.7, 31.6, 31.5, 30.5, 30.4, 30.3, 29.3, 29.1, 28.9, 22.5, 14.0, 13.9. FT-IR (λ, cm^{-1}): 3062, 2953, 1447, 816, 757, 735, 639. Anal. Calcd for $C_{65}H_{72}S_4$: C, 79.54; H, 7.39; S, 13.07. Found: C, 79.48; H, 7.52; S, 13.35.

2,2′-Bis(3,4′-dihexyl-5,2′-bithiophene-2-yl)-9,9′-spirobifluoene (6c). Brown solids (yield 97%). EI-MS (*m*/*z*): 980 (M^+, 100). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.84−7.86 (4H, d, J = 7.6 Hz, Ar-H), 7.61−7.64 (2H, dd, J = 1.6, 8.0 Hz, Ar-H), 7.35−7.40 (2H, td, J = 1.0, 7.6 Hz, Ar-H), 7.08−7.13 (2H, td, J = 1.0, 7.4 Hz, Ar-H), 6.96 (4H, s, Th-H), 6.88−6.89 (2H, d, J = 1.2 Hz, Ar-H), 6.83 (2H, s, Th-H), 6.72−6.75 (2H, J = 7.2 Hz, Ar-H), 2.62−2.67 (4H, t, J = 7.8 Hz, CH_2), 2.53−2.58 (4H, t, J = 7.6 Hz, CH_2), 1.53−1.58 (8H, m, CH_2), 1.24−1.31 (24H, m, CH_2), 0.82−0.90 (12H, m, CH_3). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 149.2, 148.9, 143.5, 141.3, 141.2, 141.1, 140.1, 135.7, 133.8, 130.4, 127.9, 127.8, 126.9, 126.1, 125.5, 124.0, 120.9, 120.4, 119.9, 119.7, 31.6, 31.5, 30.5, 30.4, 30.3, 29.3, 29.1, 28.9, 22.5, 14.0, 13.9. FT-IR (λ, cm^{-1}): 3068, 2924, 1458, 1443, 1415, 851, 825, 754, 729. Anal. Calcd for $C_{65}H_{72}S_4$: C, 79.54; H, 7.39; S, 13.07. Found: C, 79.42; H, 7.71; S, 12.89.

2,7-Bis(3,4′,4″-trihexyl-5,2′:5′,2″-terthiophene-2-yl)-9,9′-spirobifluoene (7b). Brown solids (yield 97%). EI-MS (*m*/*z*): 1313 (M^+, 100). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.92−7.94 (2H, d, J = 7.6 Hz, Ar-H), 7.81−7.84 (2H, d, J = 8.0 Hz, Ar-H), 7.61−7.64 (2H, dd, J = 1.6, 8.0 Hz, Ar-H), 7.41−7.46 (2H, t, J = 7.2 Hz, Ar-H), 7.14−7.19 (2H, t, J = 7.4 Hz, Ar-H), 6.98 (2H, s, Th-H), 6.96−6.97 (2H, d, J = 1.6 Hz, Ar-H), 6.92 (4H, s, Th-H), 6.89 (2H, s, Th-H), 6.83−6.86 (2H, d, J = 7.6 Hz, Ar-H), 2.67−2.76 (8H, m, Ar-H), 2.59−2.64 (4H, t, J = 7.8 Hz, CH_2), 1.57−1.70 (12H, m, CH_2), 1.24−1.34 (36H, m, CH_2), 0.87−0.96 (18H, m, CH_3). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 149.8, 148.3, 143.5, 141.7, 141.4, 140.6, 140.3, 139.4, 133.7, 133.6, 130.7, 130.1, 128.2, 128.0, 127.8, 127.0, 126.2, 125.5, 124.9, 124.2, 120.7, 120.3, 120.0, 119.9, 119.7, 31.6, 31.5, 31.4, 30.5, 30.4, 30.3, 30.2, 29.5, 29.2, 29.1, 28.9, 22.5, 20.9, 14.1, 13.9. FT-IR (λ, cm^{-1}): 3057, 2954, 1475, 1446, 1420, 1375, 816, 757, 735, 639. Anal. Calcd for $C_{85}H_{100}S_6$: C, 77.69; H, 7.67; S, 14.64. Found: C, 77.76; H, 8.02; S, 14.33.

2,2′-Bis(3,4′,4″-trihexyl-5,2′:5′,2″-terthiophene-2-yl)-9,9′-spirobifluoene (7c). Brown solids (yield: 97%). EI-MS (*m*/*z*): 1313 (M^+, 100). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.88−7.91 (4H, d, J = 7.6 Hz, Ar-H), 7.67−7.70 (2H, dd, J = 1.4, 7.8 Hz, Ar-H), 7.39−7.44 (2H, t, J = 7.4 Hz, Ar-H), 7.13−7.18 (2H, t, J = 7.4 Hz, Ar-H), 7.03−7.06 (4H, m, Th-H), 7.00−7.01 (2H, d, J = 1.2 Hz, Ar-H), 6.95−6.97 (2H, m, Th-H), 6.91 (2H, s, Th-H), 6.76−6.81 (2H, d, J = 7.2 Hz, Ar-H), 2.61−2.80 (12H,

m, CH_2), 1.63−1.69 (12H, m, CH_2), 1.29−1.41 (36H, m, CH_2), 0.87−0.95 (12H, m, CH_3). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 149.2, 148.9, 143.5, 141.3, 141.2, 141.1, 140.3, 139.5, 135.5, 133.8, 133.7, 130.7, 130.1, 128.2, 127.9, 127.8, 127.0, 126.2, 125.5, 124.0, 120.9, 120.4, 120.0, 119.9, 31.6, 31.5, 31.4, 30.5, 30.4, 30.3, 29.5, 29.2, 29.1, 28.9, 22.5, 14.0, 13.9. FT-IR (λ, cm^{-1}): 3052, 2954, 1458, 825, 770, 754, 730. Anal. Calcd for $C_{85}H_{100}S_6$: C, 77.69; H, 7.67; S, 14.64. Found: C, 77.39; H, 7.56; S, 14.41.

General Procedure for Preparation of 2,7-Bis(5-bromo-4-hexylthienyl)-9,9″-spirobifluorene (10), 2,2′-Bis(5-bromo-4-hexylthienyl)-9,9′-spirobifluorene (11), 2,7-Bis(5′-bromo-3,4′-dihexyl-5,2′-bithiophene-2-yl)-9,9′-spirobifluoene (14), and 2,2′-Bis(5′-bromo-3,4′-dihexyl-5,2′-bithiophene-2-yl)-9,9′-spirobifluoene (15). These compounds were prepared according to the procedure described for compounds **9** and **13** utilizing *N*-bromosuccinimide (0.72 g, 4.05 mmol), compound **5b**, **5c**, **6b**, or **6c** (2 mmol) in acetic acid and chloroform (1:1). Recrystallization from $CHCl_3$/EtOH gave pure products.

2,7-Bis(5-bromo-4-hexylthienyl)-9,9′-spirobifluorene (10). Lightly pink crystals (yield 96%). EI-MS (*m*/*z*): 808, 806 (100), 804 (M^+). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.88−7.90 (2H, d, J = 7.6 Hz, Ar-H), 7.79−7.81 (2H, d, J = 7.6 Hz, Ar-H), 7.49−7.52 (2H, dd, J = 1.6, 8.0 Hz, Ar-H), 7.39−7.44 (2H, t, J = 7.4 Hz, Ar-H), 7.11−7.16 (2H, t, J = 7.4 Hz, Ar-H), 6.81−6.82 (2H, d, J = 1.6 Hz, Ar-H), 6.80 (2H, s, Th-H), 6.77−6.80 (2H, d, J = 7.6 Hz, Ar-H), 2.43−2.48 (4H, t, J = 7.8 Hz, CH_2), 1.47−1.55 (4H, m, CH_2), 1.23−1.31 (12H, m, CH_2), 0.84−0.88 (6H, t, J = 6.6 Hz, CH_3). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 149.9, 148.0, 143.3, 143.0, 141.7, 140.7, 133.6, 128.0, 127.9, 125.4, 124.1, 124.0, 120.6, 120.4, 120.1, 112.1, 108.0, 31.5, 29.6, 29.5, 28.8, 22.5, 14.0. FT-IR (λ, cm^{-1}): 3040, 2948, 1473, 1447, 1421, 1257, 808, 752, 731, 638. Anal. Calcd for $C_{45}H_{42}Br_2S_2$: C, 67.00; H, 5.25; Br, 19.81; S, 7.95. Found: C, 66.89; H, 5.28; Br, 19.30; S, 7.75.

2,2′-Bis(5-bromo-4-hexylthienyl)-9,9′-spirobifluorene (11). White crystals (yield 96%). EI-MS (*m*/*z*): 808, 806 (100), 804 (M^+). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.82−7.86 (4H, dd, J = 2.6, 7.8 Hz, Ar-H), 7.79−7.81 (2H, dd, J = 2.0, 8.0 Hz, Ar-H), 7.39−7.44 (2H, td, J = 1.1, 7.5 Hz, Ar-H), 7.11−7.16 (2H, td, J = 1.1, 7.5 Hz, Ar-H), 6.86−6.87 (2H, d, J = 1.2 Hz, Ar-H), 6.81 (2H, s, Th-H), 6.71−6.74 (2H, d, J = 7.6 Hz, Ar-H), 2.43−2.48 (4H, t, J = 7.6 Hz, CH_2), 1.46−1.54 (4H, m, CH_2), 1.24−1.28 (12H, m, CH_2), 0.83−0.89 (6H, m, CH_3). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 149.2, 148.7, 143.4, 143.0, 141.4, 141.0, 133.5, 128.0, 127.9, 125.4, 124.1, 124.0, 120.7, 120.5, 120.0, 108.0, 31.5, 29.6, 29.5, 28.8, 22.5, 14.0. FT-IR (λ, cm^{-1}): 3057, 2950, 1491, 1459, 1438, 820, 770, 754, 729. Anal. Calcd for $C_{45}H_{42}Br_2S_2$: C, 67.00; H, 5.25; Br, 19.81; S, 7.95. Found: C, 66.62; H, 5.18; Br, 20.03; S, 7.67.

2,7-Bis(5′-bromo-3,4′-dihexyl-5,2′-bithiophene-2-yl)-9,9′-spirobifluoene (14). Yellow crystals (yield 96%). EI-MS (*m*/*z*): 1140, 1138 (100), 1136 (M^+). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.90−7.92 (2H, d, J = 7.6 Hz, Ar-H), 7.80−7.83 (2H, d, J = 8.0 Hz, Ar-H), 7.58−7.61 (2H, dd, J = 1.8, 7.8 Hz, Ar-H), 7.39−7.44 (2H, td, J = 0.9, 7.5 Hz, Ar-H), 7.12−7.17 (2H, td, J = 1.1, 7.5 Hz, Ar-H), 6.94 (2H, s, Th-H), 6.88−6.89 (2H, d, J = 1.2 Hz, Ar-H), 6.80−6.83 (2H, d, J = 7.6 Hz, Ar-H), 6.75 (2H, s, Th-H), 2.59−2.64 (4H, t, J = 7.8 Hz, CH_2), 2.50−2.55 (4H, t, J = 7.6 Hz, CH_2), 1.51−1.58 (8H, m, CH_2), 1.28−1.32 (24H, m, CH_2), 0.84−0.92 (12H, m, CH_3). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 149.8, 148.2, 142.3, 141.8, 141.7, 140.6, 135.5, 133.6, 129.4, 128.0, 127.8, 126.4, 126.0, 125.5, 124.2, 120.7, 120.3, 120.0, 108.3, 31.5, 30.5, 29.5, 29.4, 29.3, 29.1, 28.8, 22.5, 14.0, 13.9. FT-IR (λ, cm^{-1}): 3067, 2924, 1508, 1077, 812, 733, 668. Anal. Calcd for $C_{65}H_{70}Br_2S_4$: C, 68.52; H, 6.19; Br, 14.03; S, 11.26. Found: C, 68.40; H, 6.09; Br, 14.38; S, 11.03.

2,2′-Bis(5′-bromo-3,4′-dihexyl-5,2′-bithiophene-2-yl)-9,9′-spirobifluoene (15). Brown solids (yield 97%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.86−7.89 (4H, d, J = 8.0 Hz, Ar-H), 7.63−7.66 (2H, dd, J = 1.6, 8.0 Hz, Ar-H), 7.38−7.42 (2H, t, J = 7.4 Hz, Ar-H), 7.11−7.16 (2H, t, J = 7.4 Hz, Ar-H), 7.00 (2H, s, Ar-H), 6.99 (2H, s, Th-H), 6.76−6.78 (4H, m, 2Ar-H, 2Th-H), 2.61−2.67 (4H, t, J = 7.8 Hz, CH_2), 2.52−2.57 (4H, t, J = 7.6 Hz, CH_2), 1.51−1.58 (8H, m, CH_2), 1.28−1.34 (24H, m, CH_2), 0.86−0.93 (12H, m, CH_3). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 149.2, 148.9, 143.0, 142.3, 141.9, 141.4, 141.1, 140.7, 135.6, 133.7, 129.5, 128.0, 127.9, 126.4, 126.1, 125.6, 124.1, 121.0, 120.5, 120.0, 108.4, 31.6, 30.6, 30.3, 29.6, 29.5, 29.4, 29.3, 29.2, 29.0, 28.9, 22.5, 14.1, 14.0. FT-IR (λ, cm^{-1}): 3057, 2923, 1459, 1448, 1410, 823, 770, 754, 729. Anal. Calcd for $C_{65}H_{70}Br_2S_4$: C, 68.52; H, 6.19; Br, 14.03; S, 11.26. Found: C, 68.67; H, 6.54; Br, 14.35; S, 11.24.

General Procedure for Preparation of 2,2′7,7′-Tetrakis(4-hexylthienyl)-9,9′-spirobifluorene (5d), 2,2′,7,7′-Tetrakis(3,4′-dihexyl-5,2′-bithiophene-2-yl)-9,9′-spirobifluoene (6d), and 2,2′,7,7′-Tetrakis(3,4′,4″-trihexyl-5,2′:5′,2″-terthiophene-2-yl)-9,9′-spirobifluoene (7d). These compounds were prepared according to the procedure described for compounds **5**−**7a** utilizing $Pd(PPh_3)_4$ (70 mg, 0.06 mmol), compound **1d**, **12**, or **16** (1 mmol) in 30 mL of THF, compound **8** (2.0 g, 8 mmol), and $NaHCO_3$ (20 mL). Pure products were obtained through chromatography (silica gel, $CHCl_3$/hexane 1:25).

2,2′7,7′-Tetrakis(4-hexylthienyl)-9,9′-spirobifluorene (5d). Yellow crystals (yield 98%). EI-MS (*m*/*z*): 980 (M^+, 100). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.83−7.86 (4H, d, J = 8.0 Hz, Ar-H), 7.62−7.65 (4H, dd, J = 1.8, 7.8 Hz, Ar-H), 6.96−6.98 (8H, m, 4Ar-H, 1 Th-H), 6.75 (4H, s, Th-H), 2.46−2.51 (8H, t, J = 7.6 Hz, CH_2), 1.49−1.56 (8H, m, CH_2), 1.24−1.29 (24H, m, CH_2), 0.82−0.87 (12H, t, J = 6.6 Hz, CH_3). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 149.3, 144.1, 143.6, 140.5, 134.4, 125.8, 124.6, 121.1, 120.3, 119.3, 31.5, 30.4, 30.3, 28.9, 22.5, 13.9. FT-IR (λ, cm^{-1}): 3090, 2952, 1475, 1421, 1259, 1199, 816, 733, 630. Anal. Calcd for $C_{65}H_{72}S_4$: C, 79.54; H, 7.39; S, 13.07. Found: C, 79.32; H, 7.31; S, 12.68.

2,2′,7,7′-Tetrakis(3,4′-dihexyl-5,2′-bithiophene-2-yl)-9,9′-spirobifluoene (6d). Brown solids (yield 98%). EI-MS (*m*/*z*): 1645, 1312 (100). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.86−7.89 (4H, d, J = 8.0 Hz, Ar-H), 7.64−7.67 (4H, dd, J = 1.6, 8.0 Hz, Ar-H), 6.99 (4H, s, Th-H), 6.97−6.98 (4H, d, J = 1.6 Hz, Ar-H), 6.90−6.91 (4H, d, J = 1.6 Hz, Th-H), 6.83−6.84 (4H, d, J = 1.2 Hz, Th-H), 2.63−2.68 (8H, t, J = 7.8 Hz, CH_2), 2.54−2.59 (8H, t, J = 7.6 Hz, CH_2), 1.53−1.63 (16H, m, CH_2), 1.25−1.31 (48H, m, CH_2), 0.82−0.91 (24H, m, CH_3). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 149.3, 143.5, 141.2, 140.6, 140.2, 135.7, 134.0, 130.5, 126.9, 126.2, 125.6, 120.9, 120.4, 119.7, 119.7, 31.6, 31.5, 30.5, 30.4, 30.3, 30.2, 29.3, 29.2, 28.9, 22.5, 14.0, 13.9. FT-IR (λ, cm^{-1}): 3094, 2954, 1458, 857, 729. Anal. Calcd for $C_{105}H_{128}S_8$: C, 76.59; H, 7.84; S, 15.58. Found: C, 76.72; H, 8.24; S, 15.10.

2,2′,7,7′-Tetrakis(3,4′,4″-trihexyl-5,2′:5′,2″-terthiophene-2-yl)-9,9′-spirobifluoene (7d). Brown solids (yield 98%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.87−7.90 (4H, d, J = 8.0 Hz, Ar-H), 7.64−7.67 (4H, d, J = 8.0 Hz, Ar-H), 7.00 (4H, s, Th-H), 6.98 (4H, s, Th-H), 6.93−6.94 (4H, d, J = 1.2 Hz, Ar-H), 6.87 (4H, s, Th-H), 6.84 (4H, s, Th-H), 2.66−2.74 (16H, m, CH_2), 2.57−2.62 (8H, t, J = 7.6 Hz, CH_2), 1.58−1.68 (24H, m, CH_2), 1.29−1.33 (72H, m, CH_2), 0.84−0.92 (36H, m, CH_3). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 149.3, 143.5, 141.2, 141.1, 140.6, 140.3, 139.4, 135.4, 133.9, 133.7, 130.7, 130.2, 128.2, 127.0, 126.3, 125.6, 120.9, 120.4, 119.8, 31.6, 31.5, 31.4, 30.5, 30.4, 30.3, 29.4, 29.2, 29.1, 28.9, 22.5, 14.0. FT-IR (λ, cm^{-1}): 2954, 2926, 2854, 1458, 816, 726. Anal. Calcd for $C_{145}H_{184}S_{12}$: C, 75.34; H, 8.02; S, 16.64. Found: C, 75.36; H, 7.61; S, 16.24.

General Procedure for Preparation of 2,2′,7,7′-Tetrakis(5-bromo-4-hexylthienyl)-9,9′-spirobifluorene (8) and 2,2′,7,7′-Tetrakis(5′-bromo-3,4′-dihexyl-5,2′-bithiophene-2-yl)-9,9′-spirobifluoene (12). These compounds were prepared according to the procedure described for compounds **9** and **13** utilizing *N*-bromosuccinimide (0.72 g, 4.05 mmol), compound **5d** or **6d** (1 mmol) in acetic acid, and chloroform (1:1). Recrystallization from $CHCl_3$/EtOH gave pure products.

2,2′,7,7′-Tetrakis(5-bromo-4-hexylthienyl)-9,9′-spirobifluorene (12). Yellow crystals (yield 96%). EI-MS (*m*/*z*): 1300, 1298, 1296 (100), 1294, 1292 (M^+). ^{1}H NMR ($CDCl_3$, 300 MHz)

δ: 7.83−7.85 (4H, d, J = 8.0 Hz, Ar-H), 7.53−7.56 (4H, d, J = 7.8 Hz, Ar-H), 6.86 (4H, m, Ar-H), 6.83 (4H, s, Th-H), 2.42−2.47 (8H, t, J = 7.6 Hz, CH_2), 1.45−1.53 (8H, m, CH_2), 0.82−0.87 (12H, t, J = 6.4 Hz, CH_3). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 149.2, 143.1, 143.0, 140.6, 133.8, 125.6, 124.1, 120.7, 120.6, 112.1, 108.1, 31.5, 29.6, 28.8, 22.5, 14.0. FT-IR (λ, cm^{-1}): 3046, 2923, 2852, 1475, 1416, 812, 733. Anal. Calcd for $C_{65}H_{68}Br_4S_4$: C, 60.19; H, 5.28; Br, 24.64; S, 9.89. Found: C, 60.59; H, 5.21; Br, 24.29; S, 9.76.

2,2′,7,7′-Tetrakis(5′-bromo-3,4′-dihexyl-5,2′-bithiophene-2-yl)-9,9′-spirobifluoene (16). Brown solids (yield 95%). EI-MS (m/z): 1964, 1962, 1960, 1958, 1956 (M^+), 1794 (100). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.85−7.88 (4H, d, J = 8.0 Hz, Ar-H), 7.62−7.65 (4H, dd, J = 1.6, 8.0 Hz, Ar-H), 6.96 (4H, s, Th-H), 6.93−6.94 (4H, d, J = 1.6 Hz, Ar-H), 6.74 (4H, s, Th-H), 2.57−2.63 (8H, t, J = 7.8 Hz, CH_2), 2.48−2.53 (8H, t, J = 7.6 Hz, CH_2), 1.47−1.55 (16H, m, CH_2), 1.24−1.35 (48H, m, CH_2), 0.82−0.90 (24H, m, CH_3). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 149.3, 143.3, 141.7, 140.7, 140.6, 135.5, 133.8, 129.5, 126.4, 126.1, 125.7, 120.9, 120.5, 108.4, 31.5, 30.5, 29.5, 29.4, 29.3, 29.1, 28.8, 22.5, 14.0, 13.9. FT-IR (λ, cm^{-1}): 3046, 2955, 2853, 1458, 814. Anal. Calcd for $C_{105}H_{124}Br_4S_8$: C, 64.27; H, 6.37; Br, 16.29; S, 13.07. Found: C, 64.12; H, 6.61; Br, 16.36; S, 13.08.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra for compounds **2a**−**d**, **3a**−**d**, **4a**−**d**, **5a**−**d**, **6a**−**d**, **7a**−**d**, and **9**−**16**. This material is available free of charge via the Internet at http://pubs.acs.org.

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