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SYNTHESIS OF FLUORENE- AND SPIROBIFLUORENE-FUSED THIOPHENES

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Abstract – A novel synthetic route to fluorene- and spirobifluorene-fused thiophenes is explored by starting with ninhydrin. The Diels-Alder cycloaddition was employed to construct the key intermediate, 2,3-bis(hydroxymethyl)-1,4-diphenyl-fluorenone, which was further converted stepwise to the target molecules. All of dihydrothiophenes and final products are confirmed by ^{1}H NMR, ^{13}C NMR and mass spectrometry.

INTRODUCTION

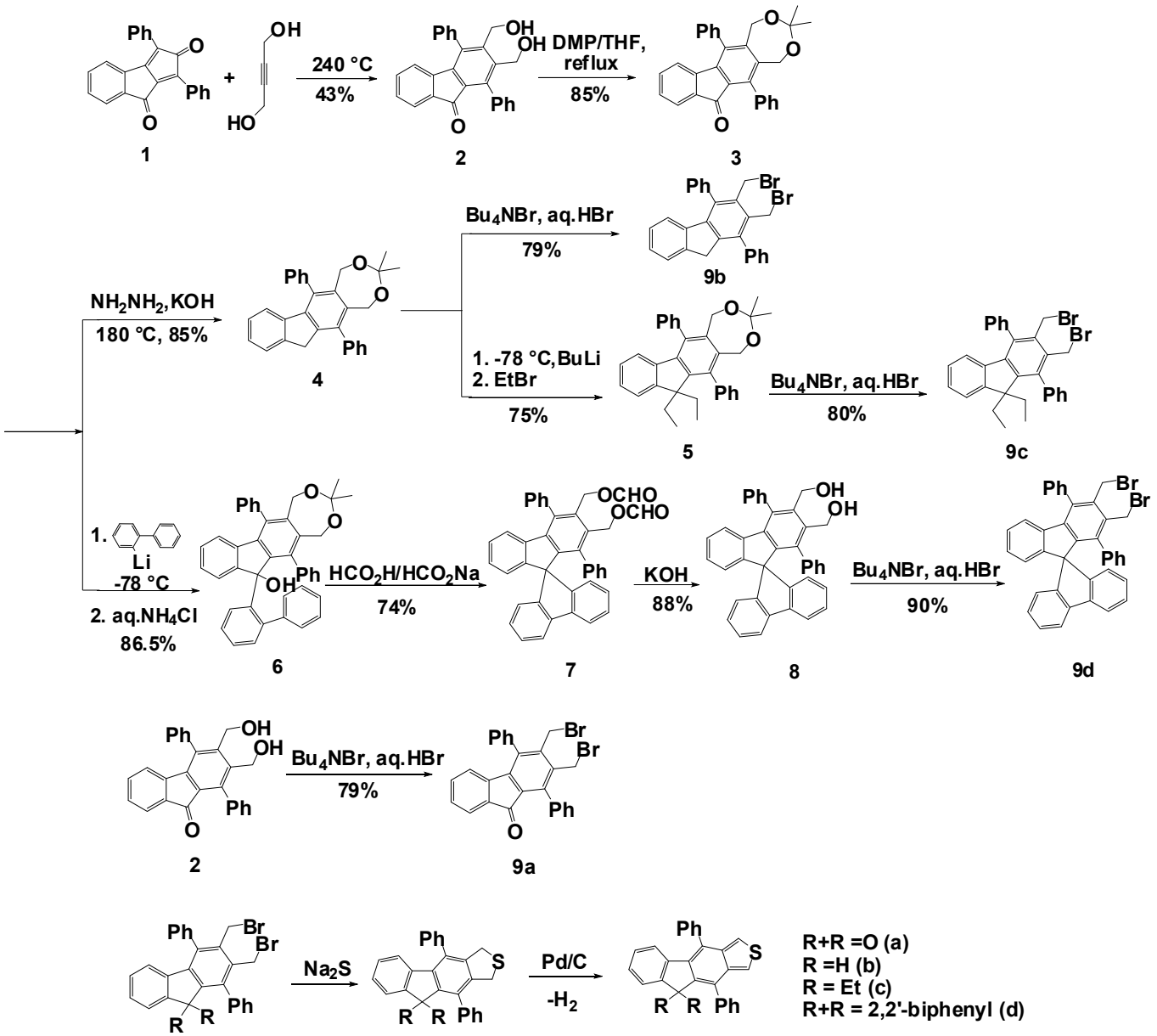
Organic π-conjugated oligomers and polymers are useful compounds as organic materials which are of interests in the fields of organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs) and organic solar cells. Heteroatom(s) are often contained or incorporated in the π-conjugated systems, and these heteroatom(s) play very important roles in the properties of the materials.[1] Heteroatom(s) cooperated polyaromatic hydrocarbons (PAHs) have attracted numerous attention due to their potentials for device fabrication. In particular, fluorene and thiophene derivatives are notable structural motifs to diverse PAHs for various applications in different materials.[2a,2b] For examples, linear- and angular-shaped polyacene-fused thiophenes have been used in the areas of organic field-effect transistors and organic photovoltaic devices.[2c,2d] Conventional multistep procedures are often employed for synthesis of chacogen-incorporated derivatives with fluorene or spirofluorene rings, which have attracted considerable attention recently in the field of organic optoelectronics, owing to their intriguing electronic properties.[3] For example, thiophene-fused indeno-spirofluorenes have been reported as promising building blocks for

the construction of optoelectronic materials in few cases.[4] Compounds with spiro-sp^3 carbon center have become promising candidates for optoelectronic devices due to their high energy gap and low HOMO levels.[5] The above reasons led us to initiate our efforts on the study of fluorine-based thiophenes, which are never studied in detail before and might be used as building blocks for further transformations. To our best knowledge, only one example on fluorene-fused thiophene, 1,3-bis(4-bromophenyl)-9,9-dimethyl-4,10-diphenyl-9*H*-fluoreno[2,3-*c*]thiophene, was reported so far by employing the Diels-Alder reaction of cyclopentadienones with diaroylacetylenes and subsequently treated with P_2O_5 in the presence of base,[6] and none of spirobifluorene-fused analogue has ever been reported.

As a part of our ongoing project on heteroatom-cooperated or containing fluorenes,[7] we describe here the latest progress on this type of compounds. The scope and synthetic applicability are quite versatile. The results presented here afford an alternative route to fluorene-fused thiophenes, which should allow further synthesis of a wide range of π-conjugated fluorene- and spirobifluorene-based thiophenes by functional transformation through either thienyl or fluorenyl subunit.

RESULTS AND DISCUSSION

For the preparation of fluorene-based thiophenes, 2,8-dioxo-1,3-diphenyl-2,8-dihydro-cyclopenta[*a*]-indene (indanocyclone **1**) was evaluated as building block because it has been revealed that **1** could act as a promising precursor to construct substituted fluorenes. Compounds **1** could be easily accessible by the reaction of nihydrin with 1,3-diphenylacetone under basic conditions by following literatures reported before and its recent modification.[8] We found that the Diels-Alder cycloaddition reaction between indanocyclone and 1,4-Dihydroxy-2-butyne proceeded at 240 °C in a short time (5 min) to afford 1,4-diphenyl-2,3-bis(hydroxymethyl)fluorenone (**2**) with an isolated yield of 43%. Then the two hydroxy groups of **2** were protected by reacting with 2,2-dimethoxypropane (DMP) in the presence of *p*-TsOH in THF to form **3** in excellent yield (85%), which was subsequently used in next steps. Compound **2** could easily be converted into **9a** (79%) in a refluxing mixture of 40% aq. HBr and chloroform in the presence of Bu_4NBr (TBAB). Compound **4** could be changed directly to compound **9b** (78.6%) under condition similar to that of **9a**. For the indeno analogue, **3** was firstly converted into **4** by Wolff-Kishner reduction (85%), followed by a halogen-alkali exchange to afford diethyl compound **5** (75.4%). For the spirobifluorene-based analogue, the lithium salt formed *in situ* from 2-bromobiphenyl and BuLi was used to react with **3** at -78 °C to form fluorenol **6** (86.5%), which was then converted into **7** (83%) under acidic conditions (HCO_2H/HCO_2Na). Hydrolysis of **7** under basic condition resulted in compound **8**. The bromination of **5** and **8** was readily accomplished by similar procedure for preparation of **9a** to form **9c** (80%) and **9d** (90%).



Scheme 1. Synthetic approach to the fluorene-fused thiophenes

With the four bis(bromomethyl)fluorene intermediates (**9a-9d**) in hands, our next step is to construct 2,5-dihydrothiophene ring. Generally 2,5-dihydrobenzo[*b*]isothiophene could easily be accomplished by

the reaction of 1,2-di(bromomethyl)benzene with different sulfide sources ($Na_2S·9H_2O$ or Na_2SO_3) in polar solvents or by the reaction of elemental sulfur with reduction reagent such as SmI_2.[9,10] It was found that steric congestions from substituents such as alkoxy and aryl groups at the either 3- or 3,6-positions have no strong impact on the formation of 2,5-dihydrobenzoisothiophenes.[11] All of the reactions could be proceeded as expected. Then we decided to take use of $Na_2S·9H_2O$ as a sulfide source, it was pleased to find that all of the reactions could proceed smoothly to afford fluorene-based 2,5-dihydrothiophenes (**10a-10d**) in isolated yields of 46% to 55%. Subsquently dehydrogenation of 2,5-dihydrothiophenes with palladium on charcoal led to the formation of fluorene- and spirobifluorene-fused thiophenes (**11a-11d**, yields from 37% to 46%).[12,9a]

The UV-Vis spectra of compounds **11a-11d** (Figure 1**)** were measured with maximum absorptions at 307 nm (**11a**), 281nm (**11b**), 281nm (**11c**), 277 nm (**11d**) respectively, while fluorescence emission spectra were obtained with blue emission at 442 nm (**11b**), 439 nm (**11c**), 437 nm (**11d**), however the maximum emission of **11a** appears at 515 nm, *ca.* 60 - 80 nm redshifted from those of **11b-11d** (Figure 2), which might be explained by the electron effect of fluorenyl carbonyl group in **11a**.

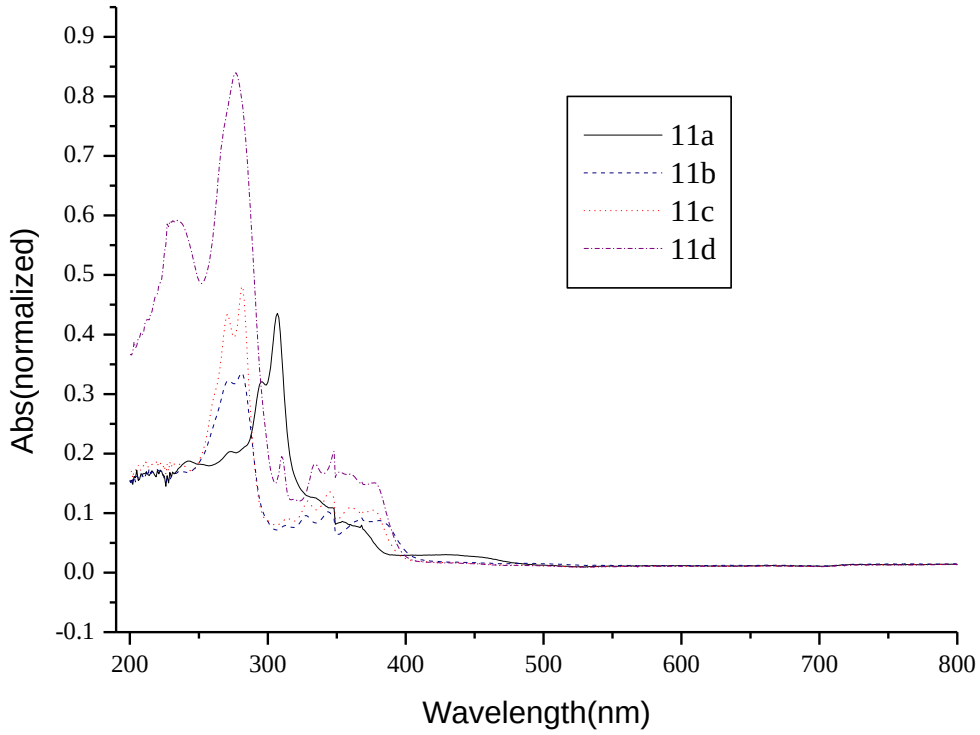


Figure1. The UV-Vis spectra of compounds **11a-11d**

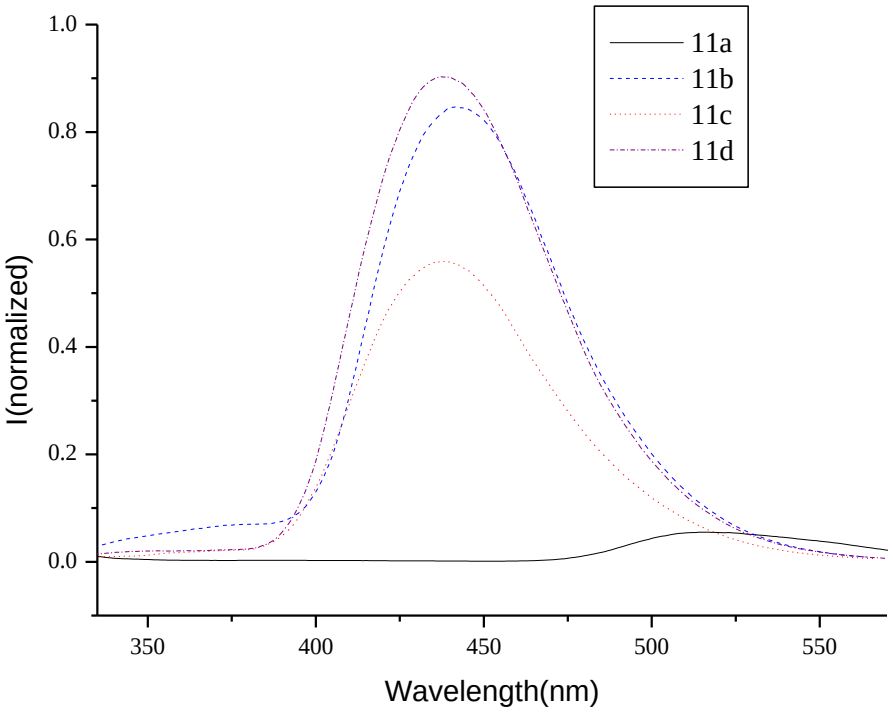


Figure 2. The fluorescence emission spectra of **11a-11d**

In conclusion, we have successfully completed novel fluorenyl and spirobifluorenyl-fused thiophenes, which could be considered as precursors for blue emission materials from primary spectrometric study. The key steps of the synthetic strategy involve the formation of 2,5-dihydrobenzoisothiophenes from bis(bromomethyl)fluorene and spirobifluorene intermediates, and dehydrogenation of fluorene-based 2,5-dihydrothiophenes with palladium on charcoal.

EXPERIMENTAL

1. Instruments and materials

All manipulations for air- and moisture-sensitive operations are conducted by using of standard Schlenk techniques. All chemicals are available from commercial sources and used without further purification. Solvents are purified according to standard methods prior to use. Melting point was measured on an X-4 micrographic melting point apparatus. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker DR × 500 spectrometer (^{1}H NMR 500 MHz, ^{13}C NMR 125 Hz). Mass spectra were measured on micOTOF II (ESI) spectrometer and Agilent 5973N mass spectrometer (EI).

2. Synthesis

1) 1,3-Diphenylindeno[*a*]cyclopenta-2,8-dione (indanocyclone 1) was synthesized by literature method.[8] To a solution of ninhydrin (4.86 g, 27.3 mmol) and 1,3-diphenyacetone (5.73 g, 27.3 mmol)

dissolved in hot EtOH (40 mL) was added slowly as 10% KOH in MeOH (3.5 mL). The resulting reaction mixture was heated at 75 °C for 3 h with a color changed from yellow to deep red-brown. The solid was filtered and recrystallized from toluene to afford **1** as red-brown crystals (7.43 g, 81.9%); mp 204-206 °C (lit.,[8a] mp 204-206 °C), ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.61 (dd, *J* = 7.6 Hz, *J* = 1.0 Hz, 1H), 8.23-8.19 (m, 1H), 8.08-8.07 (m, 1H), 7.76-7.73 (m, 4H), 7.52-7.48 (m, 6H).

2) 1,4-Dipheny-2,3-bis(hydroxymethyl)-9-fluorenone (2)

The mixture of **1** (4 g, 12 mmol) and 1,4-dihydroxybutyne (1.3 g, 14.3 mmol) in a 50 mL round bottom flask was heated at 240 °C for 5 min, then it was cooled to room temperature and purified by column chromatography (CH_2Cl_2 : EtOAc = 10 : 1), the resulting solid was washed with hexane to afford a yellow powder (2 g, 43%); R_f = 0.11 (PE : EtOAc = 1 : 1); mp 224-225 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ: 7.57-7.51 (m, 3H), 7.48-7.42 (m, 4H), 7.40-7.38 (m, 2H), 7.32-7.30 (m, 2H), 7.11 (t, *J* = 7.5 Hz, 1H), 7.03 (td, *J* = 7.5 Hz, *J* = 1.0 Hz, 1H), 5.98 (d, *J* = 5.0 Hz, 1H), 4.56 (d, *J* = 5.0 Hz, 4H), 2.99 (br.s, 1H), 2.67 (br.s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ: 192.53, 145.16, 143.27, 142.29, 139.56, 187.82, 137.70, 136.18, 134.67, 134.17, 130.40, 129.22, 129.12, 128.79, 128.72, 128.36, 128.10, 127.82, 123.72, 123.14, 59.75, 59.30.

3) 3,3-Dimethyl-6,12-diphenyl-1*H*-fluoreno[3,2-*e*][1,3]dioxepin-11(5*H*)-one (3)

A mixture of **2** (11.26 g, 28.7 mmol), 2,2-dimethoxypropane (3.47 g, 34.4 mmol) and *p*-TsOH 2.6 g (14.4 mmol) in THF (200 mL) was heated to reflux for 4 h. Then the mixture was poured into aq. NaOH (20%, 200 mL) and extracted with CH_2Cl_2 (3 × 50 mL), the combined organic phase was dried over anhydrous $MgSO_4$. After workup, the residue was purified by column chromatography (PE : CH_2Cl_2 = 1 : 1) to form a yellow solid (10.5 g, 85%); R_f = 0.26 (PE : CH_2Cl_2 = 1 : 1); mp 211-213 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ: 7.56-7.49 (m, 3H), 7.48-7.41 (m, 4H), 7.33-7.31 (m, 2H), 7.24-7.22 (m, 2H), 7.09 (t, *J* = 7.5 Hz, 1H), 7.03 (td, *J* = 7.5 Hz, *J* = 1.0 Hz, 1H), 5.93 (d, *J* = 5.0 Hz, 1H), 4.62 (d, *J* = 5.0 Hz, 4H), 1.39 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ: 192.59, 143.56, 143.33, 140.80, 138.95, 138.00, 137.59, 136.11, 135.05, 134.94, 133.94, 129.49, 129.34, 128.73, 128.41, 128.33, 128.31, 127.77, 123.63, 122.80, 120.13, 63.13, 62.25, 23.54.

4) 5,11-Dihydro-3,3-dimethyl-6,12-diphenyl-1*H*-fluoreno[3,2-*e*][1,3]dioxepine (4)

To a suspension of **3** (6.48 g, 15 mmol) in diethylene glycol (150 mL) was added hydrazine hydrate 13.5 mL (85%, 202 mmol), then the mixture was heated at 180 °C and maintained for 2 h. After cooling to room temperature, solid KOH (1.3 g, 22.5 mmol) was added, and it was again heated to 180 °C till the color turned to be white. The cooled mixture was poured into ice-cold water (200 mL) and extracted with CH_2Cl_2 (3 × 50 mL), the organic phase was dried over $MgSO_4$. After workup, the residue was recrystallized from EtOH to afford a white solid (5.2 g, 83%), R_f = 0.25 (PE : CH_2Cl_2 = 2 : 1); mp 173-175 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ: 7.55-7.47 (m, 5H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.34 (d, *J* = 7.0 Hz, 3H), 7.31 (d, *J* = 7.0 Hz, 2H), 7.11 (t, *J* = 7.2 Hz, 1H), 6.94 (t, *J* = 7.8 Hz, 1H), 6.22 (d, *J* = 7.6 Hz, 1H),

4.73 (d, J = 9.0 Hz, 4H), 3.57 (s, 2H), 1.42 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ:143.99, 141.59, 141.06, 139.26, 139.19, 137.68, 136.52, 135.25, 134.25, 134.17, 129.18, 129.09, 128.87, 128.74, 127.69, 127.36, 126.24, 126.09, 124.52, 122.67, 102.01, 36.52, 23.73.

5) 1,4-Diphenyl-2,3-bis(bromomethyl)-9-fluorenone (9a)

To a solution of compound **2** (2.1 g, 5 mmol) in $CHCl_3$ (50 mL) were added Bu_4NBr (0.6 g, 2 mmol), aq. HBr (40%, 10 mL) and conc. H_2SO_4 (1 mL), and the mixture was heated at 60 °C for 72 h and poured into water (200 mL). It was then extracted with CH_2Cl_2 (3 × 50 mL) and the organic phase was dried over $MgSO_4$. After workup, the crude product was isolated by column chromatography (CH_2Cl_2 : PE = 1 : 1) to get a yellow solid (2.2 g, 79%), R_f = 0.68 (CH_2Cl_2 : PE = 2 : 3); mp 191-193 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ: 7.62-7.61 (m, 3H), 7.55-7.53 (m, 3H), 7.50-7.47 (m, 3H), 7.42-7.40 (m, 2H), 7.15 (t, J = 7.5 Hz, 1H), 7.09 (t, J = 7.5 Hz, 1H), 5.95 (d, J = 7.5 Hz, 1H), 4.52 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ:191.96, 143.22, 142.86, 142.12, 141.83, 138.20, 136.90, 136.57, 135.19, 134.59,134.36, 131.16, 129.36, 129.13, 128.98, 128.86, 128.52, 128.23, 123.91, 123.28, 27.49, 27.19.

6) 9-Oxo-4,10-diphenylfluoreno[2,3-*c*]-2,5-dihydrothiophene (10a)

A mixture of $Na_2S{\cdot}9H_2O$ (1.5 g, 6.2 mmol) and THF solution in EtOH (V_{THF} : V_{EtOH} = 1 : 5, 36 mL) in a three-necked flask was heated to reflux under nitrogen, then a solution of **9a** (2 g, 3.86 mmol) in THF (20 mL) was added slowly and the heating was continued for 3 h. It was stirred at room temperature overnight before being poured into water and extracted with CH_2Cl_2. The organic phase was dried over $MgSO_4$. After workup, the crude product was purified by column chromatography (CH_2Cl_2 : PE = 3 : 2) to obtain a yellow solid (0.7 g, 46%); R_f = 0.59 (CH_2Cl_2 : PE = 3 : 2); mp 270-272 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ: 7.58-7.53 (m, 3H), 7.50-7.44 (m, 4H), 7.40-7.38 (m, 2H), 7.34-7.32 (m, 2H), 7.15-7.08 (m, 2H), 6.24 (d, J = 7.3 Hz, 1H), 4.04-4.00 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ: 192.14, 146.59, 143.05, 141.67, 141.03, 137.68, 137.44, 136.22, 135.06, 133.91, 133.63, 130.21, 129.21, 128.40, 128.28, 128.24, 128.08, 127.82, 123.64, 122.60, 37.85, 37.30. MS (EI): m/z = 390 [M^+].

7) 9-Oxo-4,10-diphenylfluoreno[2,3-*c*]thiophene (11a)

A 100 mL three-necked round bottom flask were charged with **10a** (0.7 g, 1.80 mmol); wet Pd/C (10%) 0.5 g (containing *ca.* 30% water) and xylenes (20 mL) and the mixture was heated to reflux for 48 h under nitrogen. After completion, the mixture was filtered through a kieselguhr pad, the filtrate was evaporated and the crude product was purified by column chromatography (CH_2Cl_2 : PE = 1 : 1) to afford a light yellow solid (0.26 g, 37%); R_f = 0.50 (PE : CH_2Cl_2 = 2 : 3); mp 265-267 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ: 7.65-7.53 (m, 12H), 7.22-7.20 (m, 3H), 6.61 (d, J = 6.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ: 191.67, 143.99, 141.62, 139.65, 137.75, 137.60, 137.03, 135.61, 134.13, 132.02, 129.31, 129.29, 128.42, 128.38, 128.09, 127.35, 124.73, 123.78, 123.65, 119.59. MS (EI): m/z = 388 [M^+].

8) 1,4-Diphenyl-2,3-bis(bromomethyl)-9-fluorene (9b)

9b was prepared essentially the same procedure for **9a** by employing **4** (1.9 g, 4.5 mmol), $CHCl_3$ (50 mL),

Bu_4NBr (0.6 g, 2 mmol), aq. HBr (10 mL, 40%) and conc. H_2SO_4 (0.8 mL), and it was isolated (PE : CH_2Cl_2 = 3 : 1) as a white solid (1.8 g, 78.6%); R_f = 0.65 (PE : CH_2Cl_2 = 3 : 1); mp 180-182 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ: 7.62-7.55 (m, 5H), 7.50-7.49 (m, 5H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.17 (t, *J* = 7.4 Hz, 1H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.22 (d, *J* = 7.9 Hz, 1H), 4.68 (s, 4H), 3.63 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ: 144.03, 143.81, 140.97, 140.41, 140.11, 138.27, 138.04, 137.82, 134.49, 132.89, 129.21, 129.08, 128.90, 128.70, 128.26, 127.92, 126.91, 126.52, 124.56, 123.14, 37.17, 29.52, 28.87.

9) 4,10-Diphenylfluoreno[2,3-*c*]-2,5-dihydrothiophene (10b)

10b was prepared essentially the same as for **10a** by employing $Na_2S·9H_2O$ (0.3 g, 1.2 mmol), THF in EtOH (18 mL), **10a** (0.4 g, 0.8 mmol) in THF (20 mL), and purified (PE : CH_2Cl_2 = 3 : 1) as a white solid (0.15 g, 50%); R_f = 0.48 (PE : CH_2Cl_2 = 4 : 1); mp 163-165 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ: 7.56-7.53 (m, 2H), 7.51-7.48 (m, 3H), 7.44-7.39 (m, 6H), 7.15 (t, *J* = 7.2 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.51 (d, *J* = 7.9 Hz, 1H), 4.16 (s, 2H), 4.07 (s, 2H), 3.71 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ: 144.17, 141.79, 141.24, 139.41, 139.16, 138.56, 137.36, 134.94, 132.98, 129.10, 128.71, 128.53, 127.80, 127.53, 126.31, 126.27, 124.67, 122.64, 37.77, 37.72, 36.07. MS (EI): m/z = 376 [M^+].

10) 4,10-Diphenyl-9*H*-fluoreno[2,3-*c*]thiophene (11b)

11b was prepared essentially the same as for **11a** by employing **10b** (0.15 g, 0.4 mmol); wet Pd/C (10%) 0.06 g and xylenes (15 mL), and it was isolated (CH_2Cl_2 : PE = 5 : 1) as a solid (0.06 g, 40%); R_f = 0.68 (PE : CH_2Cl_2 = 4 : 1); mp 165-167 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ: 7.62-7.59 (m, 4H), 7.57-7.54 (m, 5H), 7.48-7.46 (m, 1H), 7.43-7.42 (m, 1H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.28-7.27 (m, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.01 (t, *J* = 7.7 Hz, 1H), 6.71 (d, *J* = 7.9 Hz, 1H), 3.94 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ: 144.31, 140.75, 138.96, 129.63, 129.29, 129.08, 128.68, 127.82, 127.47, 127.16, 126.41, 124.85, 123.64, 117.05, 115.09, 30.89. MS (EI): m/z = 374 [M^+].

11) 11,11-Diethyl-5,11-dihydro-3,3-dimethyl-6,12-diphenyl-1*H*-fluoreno[3,2-*e*][1,3]dioxepine (5)

To a solution of **4** (2.22 g, 5.3 mmol) in THF (50 mL) at -78 °C under nitrogen was added BuLi (3.2 mL, 2.5 M, 7.9 mmol) and the stirring continued for 30 min, then ethyl bromide (0.63 mL, 7.9 mmol) was added. After addition, the mixture was allowed to warm to room temperature and stirred for 1 h. The above procedure was exactly repeated once and then the reaction was quenched with saturated aq. NH_4Cl and extracted with CH_2Cl_2 (3 × 50 mL). After workup, the crude product was purified by column chromatography (PE : CH_2Cl_2 = 3 : 1) and further washed with EtOH to afford **5** as a white solid (1.9 g, 75.4%), R_f = 0.33 (PE : CH_2Cl_2 = 2 : 1); mp 181-182 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ: 7.54-7.49 (m, 3H), 7.46-7.42 (m, 3H), 7.33 (d, *J* = 7. 0Hz, 2H), 7.28 (d, *J* = 6.5 Hz, 2H), 7.11 (t, *J* = 7.0 Hz, 2H), 6.87-6.85 (m, 1H), 6.05 (d, *J* = 8.0 Hz, 1H), 4.68 (s, 2H), 4.51 (s, 2H), 1.63 (q, *J* = 7.0 Hz, 4H), 1.39 (s, 6H), 0.25 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ: 151.12, 143.25, 141.01, 139.46, 138.64, 138.44, 136.36, 135.12, 135.00, 134.33, 129.21, 129.17, 129.09, 128.13, 127.62, 127.47, 126.56, 126.09, 122.24, 121.43, 101.90, 63.08, 62.86, 57.43, 31.90, 23.66, 8.27.

12) 1,4-Diphenyl-2,3-bis(bromomethyl)-9,9-diethylfluorene (9c)

9c was prepared essentially the same as **9a** by employing **5** (1.9 g, 4.0 mmol), $CHCl_3$ (50 mL), Bu_4NBr (0.68 g , 2.25 mmol), aq. HBr (40%, 12.5 mL) and conc. H_2SO_4 (1 mL), and it was purified (PE : CH_2Cl_2 = 4 : 1) as a white solid (1.8 g, 80%); R_f = 0.65 (PE : CH_2Cl_2 = 3 : 1); mp 181-183 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ: 7.56-7.48(m, 8H), 7.48-7.40 (m, 2H), 7.18-7.13 (m, 2H), 6.90 (t, *J* = 7.0 Hz, 1H), 6.05 (d, *J* = 8.0 Hz, 1H), 4.60 (s, 2H), 4.49 (s, 2H), 1.67-1.63 (m, 4H), 0.25 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ: 151.20, 146.23, 141.23, 140.29, 139.83, 138.19, 137.59, 137.04, 134.34, 133.99, 129.36, 128.97, 128.12, 128.00, 127.78, 127.34, 126.35, 122.74, 121.50, 57.91, 31.76, 29.36, 28.88, 8.28.

13) 4,10-Diphenyl-9,9-diethylfluoreno[2,3-*c*]-2,5-dihyrothiophene (10c)

This is prepared similar to **10a** by using of $Na_2S{\cdot}9H_2O$ (1.2 g, 4.8 mmol), THF in EtOH (24 mL) and **9c** (1.8 g, 3.2 mmol) in THF (10 mL) and, It was purified (CH_2Cl_2 : PE = 1 : 3) as a white solid (0.76 g, 55%), R_f = 0.63 (PE : CH_2Cl_2 = 4 : 1), mp 131-133 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ: 7.55-7.48 (m, 3H), 7.46-7.43 (m, 3H), 7.40-7.39 (m, 2H),7.32-7.30 (m, 2H), 7.16-7.15 (m, 2H), 6.94-6.91 (m, 1H), 6.36 (d, *J* = 7.9 Hz, 1H), 4.05 (s, 2H), 3.90 (s, 2H), 1.72 (q, *J* = 7.3 Hz , 4H), 0.30 (t, *J* = 7.7 Hz , 6H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ: 151.17, 144.57, 140.77, 139.71, 139.27, 139.20, 138.69, 138.41, 135.14, 132.85, 129.05, 128.78, 128.47, 128.18, 127.69, 127.51, 126.69, 126.17, 122.18, 121.65, 57.10, 38.28, 37.95, 32.03, 8.33. MS (EI): m/z = 403 $[M\text{-}CH_2CH_3]^+$

14) 4,10-Diphenyl-9,9-diethylfluoreno[2,3-*c*]thiophene (11c)

This is prepared similar to **11a** by employing **10c** (0.6 g, 1.38 mmol); wet Pd/C (10%) 0.2 g and xylenes (15 mL). It was purified (CH_2Cl_2 : PE = 1 : 5) as a solid (0.27 g, 46%); R_f = 0.79 (PE : CH_2Cl_2 = 4 : 1); mp 133-135 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ: 7.61-7.58 (m, 2H), 7.55-7.47 (m, 6H), 7.45-7.43 (m, 2H),7.21-7.14 (m, 3H), 6.96-6.92 (m, 2H), 6.58 (d, *J* = 7.9 Hz, 1H), 1.82-1.76 (m, 2H), 1.75-1.70 (m, 2H), 0.42 (t, *J* = 7.3 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ: 151.16, 141.06, 140.74, 140.31, 139.21, 136.16, 129.72, 129.63, 129.40, 129.09, 127.99, 127.74, 127.54, 127.46, 126.32, 123.08, 122.00, 116.46, 56.19, 33.19, 8.64. MS (EI): m/z = 401 $[M\text{-}CH_2CH_3]^+$.

15) 11-Hydroxyl-11-(2'-biphenyl)-5,11-dihydro-3,3-dimethyl-6,12-diphenyl-1*H*-fluoreno[3,2-*e*][1,3]-dioxepine (6)

Under nitrogen, to a solution of 2-bromobiphenyl (2 g, 8.6 mmol) in THF (15 mL) cooled to -78 °C was added dropwise BuLi (3.44 mL, 2.5 M in hexane, 8.6 mmol). Then a solution of **3** (2.3 g, 5.75 mmol) in THF (15 mL) was added slowly and the mixture was kept for 1 h and warmed gradually to room temperature, and the stirring was continued for another 1 h at room temperature and the reaction was quenched with saturated aq. NH_4Cl (50 mL). The mixture was extracted with CH_2Cl_2 (3 × 20 mL), the organic phase was dried over $MgSO_4$. After filtered, the filtration was evaporated and the residue was subjected to column chromatography (PE : CH_2Cl_2 = 1 : 1), the product was further washed with hexane to afford **6** (2.7 g, 86.5%); R_f = 0.15 (PE : CH_2Cl_2 = 1 : 2), mp 257-259 °C. ^{1}H NMR ($CDCl_3$, 500 MHz,

ppm) δ: 7.45-7.43 (m, 1H), 7.41-7.28 (m, 3H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.27 (d, *J* = 7.0 Hz , 1H), 7.23 (t, *J* = 7.0 Hz, 1H), 7.17-7.13 (m, 2H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.02-6.97 (m, 5H), 6.88 (d, *J* = 7.0 Hz, 1H), 6.77 (d, *J* = 6.5Hz, 2H), 6.52-6.49 (m, 3H), 5.83 (s, 1H), 5.60 (d, *J* = 8.0 Hz, 1H), 4.63-4.43 (m, 4H), 2.34 (s, 1H), 1.41 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ: 151.21, 145.87, 141.00, 137.34, 136.63, 130.90, 129.13, 129.05, 128.67, 128.57, 128.13, 127.90, 127.84, 127.64, 127.37, 126.89, 126.73, 125.96, 125.70, 125.40, 123.95, 122.94, 101.92, 82.14, 62.81, 62.78, 23.85, 23.63.

16) 1,4-Diphenyl-2,3-bis(dimethylene formate)-9,9'-spirobifluorene (7)

A suspension of **6** (2.7 g, 4.6 mmol) and HCO_2Na (1.75 g, 25 mmol) in HCO_2H (150 mL) was refluxed for 24 h before being poured into ice-water (500 mL). It was then extracted with CH_2Cl_2 (3 × 50 mL) and washed with water to neutral, the organic phase was dried over $MgSO_4$. After workup, the residue was recrystallized from EtOH to afford a white solid (2 g, 74%); R_f = 0.25 (PE : CH_2Cl_2 = 1 : 2); mp 150-152 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ: 7.98 (s, 1H), 7.79 (s, 1H), 6.64-6.59 (m, 3H), 7.53 (d, *J* = 7.5 Hz, 2H), 7.32 (d, *J* = 7.5 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 2H), 7.07 (t, *J* = 7.5 Hz, 2H), 6.95-6.93 (m, 2H), 6.88 (t, *J* = 7.5 Hz, 1H), 6.79 (d, *J* = 7.5 Hz, 2H), 6.62 (t, *J* = 7.8 Hz, 2H), 6.49-6.47 (m, 1H), 6.27-6.26 (m, 1H), 6.07 (d, *J* = 7.0 Hz, 2H), 5.15 (s, 2H), 4.85 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ: 178.04, 160.14, 159.99, 149.98, 147.60, 147.45, 142.06, 141.66, 140.23, 138.46, 138.07, 134.58, 132.86, 132.38, 129.43, 129.13, 128.78, 128.37, 128.04, 127.28, 127.21, 127.17, 126.60, 125.95, 123.63, 123.52, 123.29, 119.90, 65.64, 60.35, 60.32.

17) 1,4-Diphenyl-2,3-bis(hydroxymethyl)-9,9'-spirobifluorene (8)

To a solution of **7** (2 g, 3.45 mmol) in THF (50 mL) was added aq. KOH (10%, 10 mL), the mixture was stirred for 30 min and poured into water. It was then extracted with CH_2Cl_2 (3 × 50 mL) and the organic phase was washed with water for three times before subjected to be dried over $MgSO_4$. After workup, the residue was recrystallized from hexane to afford a white powder (1.6 g, 88%), R_f = 0.45 (PE : EtOAc = 1 : 1); mp 279-280 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ: 7.64-7.55 (m, 5H), 7.44 (d, *J* = 5.0 Hz, 2H), 7.20 (t, *J* = 7.5 Hz, 2H), 7.06 (t, *J* = 7.3 Hz, 2H), 6.92-6.82 (m, 3H), 6.79 (d, *J* = 7.5 Hz, 2H), 6.64 (t, *J* = 7.5 Hz, 2H), 6.47 (d, *J* = 7.0 Hz, 1H), 6.28 (d, *J* = 7.0 Hz, 1H) 6.10 (d, *J* = 7.5 Hz, 2H), 4.64 (s, 2H), 4.35 (s, 2H), 2.97 (br.s, 1H), 2.45 (br.s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ: 149.91, 148.06, 145.84, 142.03, 140.82, 139.99, 139.11, 138.32, 137.14, 135.75, 129.57, 129.05, 128.82, 127.94, 127.52, 127.16, 127.12, 127.01, 126.61, 125.59, 123.69, 123.40, 123.10, 119.81, 107.95, 65.64, 59.99, 59.91.

18) 1,4-Diphenyl-2,3-bis(bromomethyl)-9,9'-spirobifluorene (9d)

This is prepared essentially similar to **9a** by employing **8** (1.6 g, 3.0 mmol), $CHCl_3$ (50 mL), Bu_4NBr (0.6 g, 2 mmol), aq. HBr (40%, 8 mL) and conc. H_2SO_4 (0.6 mL), and it was isolated (CH_2Cl_2 : PE = 1 : 3) as a white solid (1.8 g, 90%), R_f = 0.75 (CH_2Cl_2 : PE = 1 : 3); mp 145-148 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ: 7.69-7.62 (m, 5H), 7.33 (d, *J* = 7.5 Hz, 2H), 7.21 (t, *J* = 7.5 Hz, 2H), 7.09 (t, *J* = 7.4 Hz, 2H), 6.94-6.91 (m, 3H), 6.81 (d, *J* = 7.5 Hz, 2H), 6.68 (t, *J* = 7.5 Hz, 2H), 6.48-6.46 (m, 1H), 6.23-6.20 (m,

1H), 6.17 (d, *J* = 7.1 Hz, 2H), 4.65 (s, 2H), 4.37 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ: 159.96, 147.65, 142.02, 140.96, 140.28, 137.93, 135.25, 134.72, 134.40, 129.41, 129.13, 128.84, 128.40, 127.94, 127.25, 127.23, 127.16, 126.58, 125.97, 123.71, 123.47, 123.19, 119.85, 109.65, 65.61, 28.86, 28.65.

19) 4,10-Diphenyl-9,9'-spirobifluoreno[2,3-*c*]-2,5-dihydrothiophene (10d)

This is prepared essentially similar to **10a** by employing $Na_2S{\cdot}9H_2O$ (0.75g, 6.2 mmol), THF in EtOH (24 mL) and **9d** (1.4 g, 2.1 mmol) in THF (10 mL). It was purified (CH_2Cl_2 : PE = 1 : 4) as a white solid (0.6 g, 53%); R_f = 0.46 (CH_2Cl_2 : PE = 1 : 4); mp 269-271 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ: 7.63-7.60 (m, 2H), 7.57-7.55 (m, 3H), 7.32 (d, *J* = 7.5 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 2H), 6.97-6.87 (m, 3H), 6.83 (d, *J* = 7.5 Hz, 2H), 6.67 (t, *J* = 7.5 Hz, 2H), 6.52 (q, *J* = 7.5 Hz, 2H), 6.08 (d, *J* = 7.5 Hz, 2H), 4.09 (s, 2H), 3.77 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ: 149.90, 148.38, 145.43, 142.02, 140.75, 139.62, 139.37, 139.22, 136.36, 132.90, 129.18, 128.85, 128.00, 127.96, 127.32, 127.19, 127.15, 127.02, 126.91, 125.69, 123.71, 123.60, 122.67, 119.77, 37.87. MS (EI): m/z = 526 [M^+].

20) 4,10-Diphenyl-9,9'-spirobifluoreno[2,3-*c*]thiophene (11d)

This is prepared essentially the same as **11a** by employing **10d** (0.6 g, 1.14 mmol); wet Pd/C (10%) 0.4 g and xylenes (20 mL). It was purified (CH_2Cl_2 : PE = 1 : 6) as a white solid (0.22 g, 37%); R_f = 0.66 (PE : CH_2Cl_2 = 1 : 4); mp 279-280 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ: 7.70-7.64 (m, 4H), 7.60-7.58 (m, 1H), 7.34 (d, *J* = 7.4 Hz, 2H), 7.27-7.26 (m, 1H), 7.19 (t, *J* = 7.1 Hz, 2H), 7.07 (t, *J* = 7.2 Hz, 2H), 6.99-6.90 (m, 6H), 6.79-6.72 (m, 3H), 6.49 (d, *J* = 6.9 Hz, 1H), 6.23 (d, *J* = 6.9 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ: 150.82, 150.12, 141.70, 141.58, 140.54, 140.36, 138.93, 136.07, 135.51, 131.22, 129.81, 129.25, 128.97, 128.08, 128.04, 127.72, 127.31, 127.22, 127.10, 126.89, 125.83, 124.24, 124.01, 123.64, 119.66, 117.13, 117.06, 64.18. MS (EI): m/z = 374 [M-$C_{12}H_6$]$^+$.

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