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SYNTHESIS OF 1,4-DIARYLFLUORENONE AND 1,4-DIARYLFLUORENE

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Abstract – A novel synthetic route to 1,4-diarylfluorenone and 1,4-diarylfluorene is presented by starting with ninhydrin. The retro-Diels-Alder cycloaddition was employed as a key step to construct the target fluorenones, while a highly efficient reduction from 1,4-diarylfluorenones to 1,4-diarylfluorenes is developed by using of sodium sulfide nonahydrate as reductant. The final products are confirmed by ^{1}H NMR, ^{13}C NMR and mass spectrometry.

Semiconducting π-conjugated systems have attracted much attention as futuristic materials for the development and production of the next generation of opt-electrics. A great number of π-conjugated semiconducting materials that have either been discovered or synthesized generate an exciting library of π-conjugated systems for use in the fields of organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs) and organic solar cells. Fluorene and its derivatives are useful components for construct small organic molecules and polymers suitable for organic optoelectronics. Heterocycles such as thiophene and its derivatives are often contained or incorporated in these π-conjugated systems, and they could play important roles in the properties of the materials for OLEDs, OFET or solar cells.[1] 2,7-disubstituted-fluorenes are often used as subunit both in polymers and small organic molecules applicable for material chemistry, for example, 2,7-bis(4-bromophenyl)-9,9-dialkyfluorenes and 2,7-bis(5-bromothien-2-yl)-9,9-dialkyfluorenes have been used to afford polymers suitable for organic electroluminescent devices and organic light-emitting diodes (OLEDs), while charge-transporting polymers with high hole-transporting ability, excellent solubility and excellent film-forming properties from the same monomer have also been reported.[2] Conventional multistep procedures are often required for synthesis of fluorene-based compounds.[3] Some thiophene-fused indeno-spirofluorenes have been

reported for the construction of optoelectronic materials in few cases.[4] Compared to their 2,7-diarylated congeners, 1,4-diarylfluorenes are barely reported.[5] The above reasons led us to initiate our efforts on the study of 1,4-diarylated fluorenes, which might be used as alternative building blocks for further functional transformations.

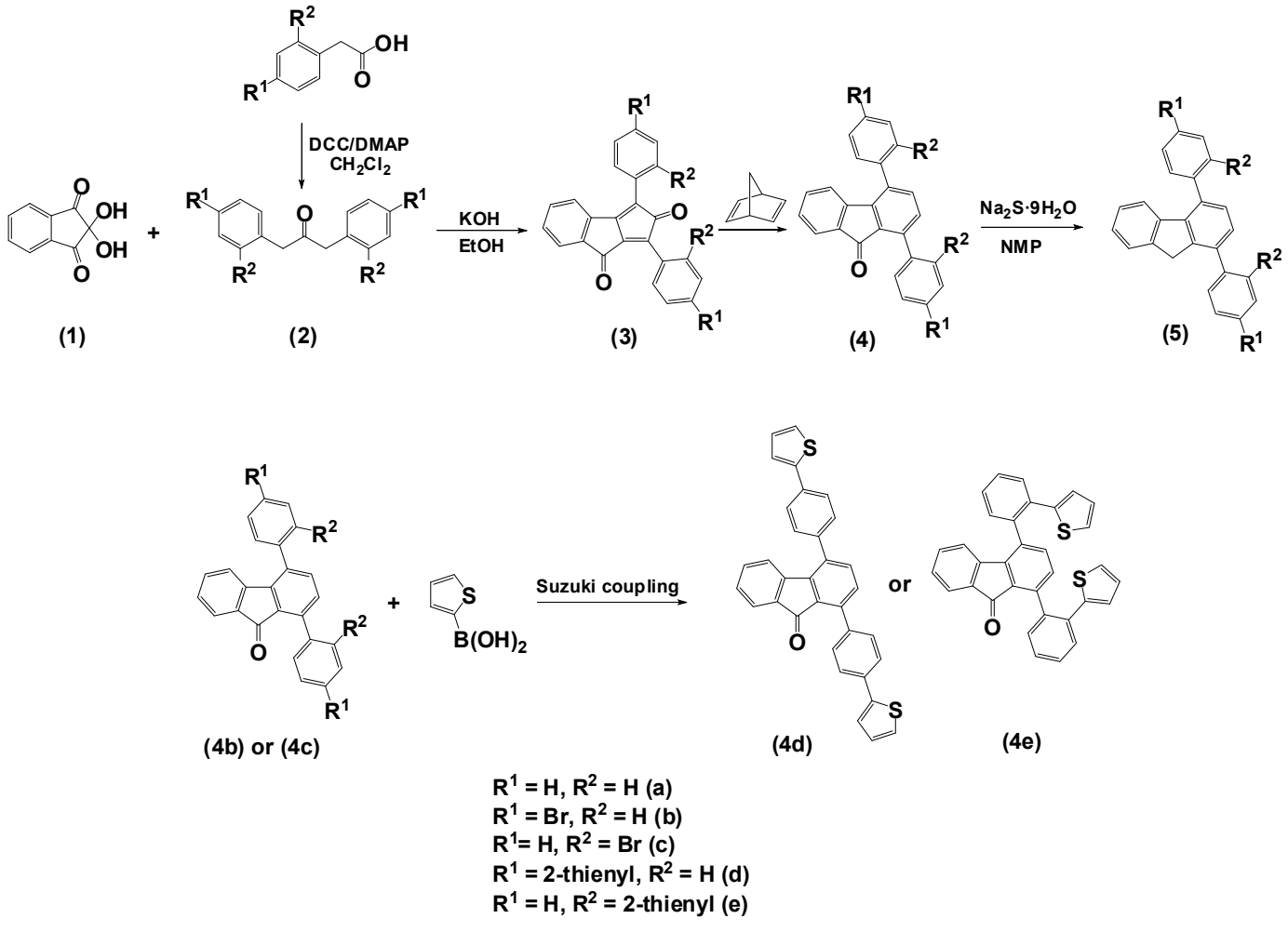
As a part of our ongoing project on heterocycle-cooperated or substituted fluorenes,[6] we describe here the latest progress on 1,4-diarylfluorenones and 1,4-diarylfluorenes through well-defined synthetic routes and utilization of sodium sulfide nonahydrate as reductant for fluorenones. The scope and synthetic applicability are quite versatile for (poly)arylated fluorenones and the results presented here afford an alternative route to fluorene-based materials, which should allow the formation of fluorene-based semiconducting materials.

It is difficult to construct 1,4-diarylfluorenones by regular synthetic route due to the limited availabilty of suitable precursors (e.g. 1,4-dihalogenated florenone or 1,4-dihydroxyfluorenone as substrates for transition metal-catalyzed cross coupling reactions). In order to prepare 1,4-diarylfluorenones and 1,4-diarylfluorenes which might be useful as subunits for material chemistry, 2,8-dioxo-1,3-diaryl-2,8-dihydrocyclopenta[*a*]indenes (indanocyclones **3a-c**) were evaluated as building block because **3a** has been used as a promising block to construct substituted fluorenones as reported by us or others.[7] For example, we have reported indenospirobifluorenes and dispirobifluorenes through indenofluorenone constructed from the reaction of **3a** with suitable dienophiles by using of Diels-Alder cycloaddition as a major tool.[7b] Bhattacharya *et al.* have reported that indanocyclone could be used to construct highly arylated fluorenones, which were reduced to the corresponding fluorenes by PhOH/aq. HI/*cat*. red phosphorous system.[5] We have also reported that this type of carbonyl reduction could be finished by Wolff-Kishner-Huang reduction in the case of indenospirbifluorenes.[7b]

In order to expand the application of these type of precursors to construct different flurenones, the diarylacetones **2b** and **2c** have been synthesized by the condensation of 4-bromophenylacetic acid or 2-bromophenylacetic acid in the presence of dicyclohexylcarbodiiimide (DCC) and 4-dimethyl-aminopyridine (DMAP) in anhydrous dichloromethane (DCM) by literature report.[8] Compounds **3b** and **3c** could be easily accessible by the reaction of ninhydrin with 1,3-diarylacetone under basic conditions similar to **3a**.[8] Then the retro-Diels-Alder reaction between indanocyclones (**3a**, **3b** and **3c**) and norbonadiene in either refluxing toluene (for **3a** and **3b**) or xylene (for **3c**) afforded compounds **4a**-**4c** (isolated yields 60-75%). Compounds **4d** and **4e** could be obtained by palladium-catalyzed Suzuki cross-coupling reactions of **4b** or **4c** with 2-thienylboronic acid. Generally Wolff-Kishner-Huang reduction is considered as one of the most efficient tools to convert carbonyl groups of aromatic ketones (e.g. fluorenone) to methylene, except those with halogenated aromatic rings. We found that sodium sulfide nonahydrate ($Na_2S·9H_2O$) could act as a sulfur surrogate to construct thiophene ring and a

reductant for reduction of fluorenone to fluorene albeit in low yield (46%).[9] The reason for this reduction might be due to the formation of H_2S from sodium sulfide nonahydate in refluxing NMP. The role of H_2S as a reductant for aromatic ketone reduction under high pressure with catalyst has been reported before albeit with low yields in general.[10] We consider that the reduction with $Na_2S{\cdot}9H_2O$ might also be applicable for the reduction of 1,4-diarylfluorenones. It is proved that $Na_2S{\cdot}9H_2O$ is highly sufficient for the reduction of 1,4-diarylfluorenone (**4a**-**4e**) to 1,4-diarylfluorenes (**5a**-**5e**) in refluxing *N*-methl-2-pyrrolidone (NMP). The isolated yields of **5a**, **5d** and **5e** are higher than 70%. While for **5b** and **5c**, the isolated yields are 29.5% and 26%, respectively.

All of **4a**-**4e** and **5a**-**5e** are confirmed by ^{1}H NMR and ^{13}C NMR and part of them are also proved by mass spectrometry.



Scheme 1. Synthetic approach to the 1,4-diarylfluorenes

In conclusion, we have developed a novel route to 1,4-diraylfluorenones and 1,4-diarylfluorenes, which are barely reported in literatures. The key step for synthesis of 1,4-diraylfluorenones is Diels-Alder

reaction between indanocyclones and norbornadiene, and the retro-Diels-Alder reaction of the adduct with the elimination of CO. While an efficient reduction reaction has been developed by employing $Na_2S·9H_2O$ in refluxing NMP for reduction of 1,4-diarylfluorenones to 1,4-diarylfluorenes, which might be potentially applicable to reduction of other highly arylated fluorenones with or without halide substituents.

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 × 300 MHz spectrometer or 400 MHz spectrometer (^{1}H NMR 300 MHz, ^{13}C NMR 75 MHz or 100 MHz). Mass spectra were measured on micOTOF II (ESI) spectrometer and Agilent 5973N mass spectrometer (EI).

2. Synthesis

1) Synthesis of 1,3-diarylacetones 2b and 2c: Compound **2a** is commercially available, and **2b** and **2c** are prepared as reported.[8]

a) *Preparation of 1,3-di(4-bromophenyl)-2-propanone* (**2b**)[8]

To a mixture of dicyclohexylcarbodiimide (DCC) (7.7 g, 37.3 mmol) and 4-dimethylaminopyridine (DMAP) (1.145 g, 9.35 mmol) in CH_2Cl_2 (75 mL) was added slowly a solution of 4-bromophenylacetic acid (8.05 g, 37.45 mmol) in CH_2Cl_2 (75 mL). After addition, it was stirred at room temperature for 24 h before the solid was filtered. The filtrate was evaporated under vacuum, and the residue was recrystallized from EtOH to afford white crystals (4.33 g, 68%); mp 118-120 °C (lit.,[8] mp 116-118 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.2 Hz, 4H), 7.00 (d, *J* = 8.2 Hz, 4H), 3.66 (s, 4H).

b) *Preparation of 1,3-di(4-bromophenyl)-2-propanone*

It is prepared by essentially the same procedure as described for the preparation of **2c** using DCC (15.4 g, 74.6 mmol) and DMAP (2.29 g, 18.7 mmol) in CH_2Cl_2 (150 ml), and 2-bromophenylacetic acid (16.1g, 74.9 mmol) in CH_2Cl_2 (150 ml) to afford **2c** as white crystals (68%); mp 125-127 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.8 Hz, 2H), 7.35- 6.95 (m, 6H), 3.95 (s, 4H).

2) Synthesis of indanocyclone 3a-3c

a) *1,3-Diphenylindeno[a]cyclopenta-2,8-dione (indanocyclone* **3a**) was synthesized by literature method.[8] 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), 8.08-8.0 7(m, 1H), 7.76-7.73 (m, 4H), 7.52-7.48 (m, 6H).

b) *1,3-Di(4-bromphenyl)indeno[a]cyclopenta-2,8-dione* (**3b**)

To a solution of ninhydrin (2.86 g, 14.65 mmol) and 1,3-di(4-bromophenyl)-2-propanone (4.996 g, 13.65 mmol) in hot EtOH (20 mL) was added slowly a solution of KOH in MeOH (10%, 3.5 mL). After addition, the mixture was stirred at 75 °C for 3 h with the color changed from yellow to deep brown. The solid was filtered and crystallized from EtOH to afford deep brown crystals (5.45 g, 81.5%), R_f = 0.59 (PE : DCM = 1 : 1), mp 292-294 °C; ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 8.59-8.56 (m, 2H), 8.19-8.11 (m, 2H), 7.81-7.80 (m, 2H), 7.71-7.60 (m, 6H).

c) *1,3-Di(2-bromphenyl)-indeno[a]cyclopenta-2,8-dione* (**3c**)

3c is prepared essentially the same as **3b** by employing ninhydrin (2.86 g, 14.65 mmol) and 1,3-di(2-bromophenyl)-2-propanone (4.996 g, 13.65 mmol) in EtOH (20 mL) and KOH in MeOH (10%, 3.5 mL) to afford deep red crystals (5.35 g, 80%); R_f = 0.57 (PE : DCM = 1 : 1), mp 195-197 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 8.06-8.03 (m, 1H), 7.77-7.71 (m, 5H), 7.51-7.40 (m, 4H), 7.37-7.29 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.03, 184.65, 150.44, 146.27, 143.58, 138.57, 135.68, 133.69, 133.42, 132.19, 131.94, 131.81, 131.13, 130.70, 130.40, 127.69, 127.49, 127.15, 124.93, 124.05, 123.73, 121.20.

3) The retro-Diels-Alder reaction between 3a-3c and norbornadiene to 4a-4c

a) *Synthesis of 1,4-diphenylfluorenone* (**4a**)

A 50 mL RB flask was added **3a** (1.0 g, 2.994 mmol), norbornadiene (0.275 g, 2.994 mmol) and toluene (20 mL). The mixture was refluxed for 12 h and the volatiles were removed under vacuum and the crude product was purified by column chromatography (PE : DCM = 2 : 1) to afford a pale-yellow solid (1.0 g, 70%); R_f = 0.64 (PE : DCM = 1 : 1), mp 127-129 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 7.12-7.03 (m, 10H), 6.94-6.91 (m, 1H), 6.82-6.75 (m, 4H), 6.27 (d, J = 6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 192.98, 143.60, 142.06, 141.27, 139.58, 137.58, 137.26, 136.23, 134.60, 134.17, 131.33, 130.15, 129.22, 128.93, 128.86, 128.80, 128.24, 128.22, 127.93, 123.96. MS (ESI): *m/z* = 355.1092 $[M+Na]^+$, $C_{25}H_{16}NaO$ required: 355.1093.

b) *1,4-Di(4-bromophenyl)fluorenone* (**4b**)

4b is prepared essentially the same as **4a** by employing **3b** (1.0 g, 2.0408 mmol), norbornadiene (0.1878 g, 2.0408 mmol) and toluene (20 mL) and purified by column chromatography (PE : DCM = 2 : 1) to afford a pale-yellow solid (0.667 g, 67%); R_f = 0.65 (PE : DCM = 1 : 1), mp 198-200 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 7.80 (d, J = 8.0 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.57-7.47 (m, 3H), 7.44-7.37 (m, 3H), 7.35-7.26 (m, 2H), 7.22-7.18 (m, 3H), 6.41(d, J = 5.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 192.67, 143.19, 142.13, 140.21, 138.31, 136.21, 136.18, 136.13, 134.41, 134.38, 132.10, 131.11, 130.84,

130.61, 130.14, 129.12, 124.18, 123.04, 122.66, 122.58.

c) *1,4-Di(2-bromophenyl)fluorenone* (**4c**)

4c is prepared essentially the same as **4a** by employing **3c** (1.0 g, 2.0408 mmol), norbornadiene (0.1878 g, 2.0408 mmol) and xylene (20 mL) and purified by column chromatography (PE : DCM = 2 : 1) to afford a pale-yellow solid (0.60 g, 60%); R_f = 0.64 (PE : DCM = 1 : 1); mp 235-237 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 7.80 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.57-7.55 (m, 1H), 7.50-7.35 (m, 5H), 7.35-7.26 (m, 3H), 7.22-7.18 (m, 2H), 6.41 (d, *J* = 5.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.62, 143.82, 142.20, 140.31, 140.25, 139.67, 139.23, 139.14, 136.28, 135.76, 134.66, 134.53, 133.39, 133.33, 132.77, 132.71, 131.18, 131.13, 130.91, 130.78, 130.49, 130.23, 129.65, 129.15, 128.14, 128.09, 127.28, 127.23, 124.22, 123.84, 123.74, 123.20, 123.11, 122.73.

4) Syntheses of 4d-4e by Suzuki cross-coupling reaction

a) *Synthesis of 1,4-Di[4-(2-thienyl)phenyl]fluorenone* (**4d**)

A 50ml RB flask was charged with 1,4-di(4-bromophenyl)fluornone **4b** (0.151 g, 0.31 mmol), 2-thienyl-boronic acid (0.0947 g, 0.74 mmol), $Pd(PPh_3)_4$ (22 mg, 0.031 mmol), toluene (7 mL), EtOH (7 mL) and *aq*. Na_2CO_3 (0.1 g, 0.93 mmol) in water (3 mL), and the mixture was refluxed for 8 h before it was poured into water and extracted with EtOAc, and the organic phase was dried over $MgSO_4$. After workup, the residue was purified by column chromatography (PE : DCM = 2 : 1) to afford a yellow solid (0.125 g, 81%); R_f = 0.64 (PE : DCM = 1 : 1); mp 233-235 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 7.78 (d, *J* = 8.5 Hz, 2H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.61-7.56 (m, 3 H), 7.52-7.49 (m, 2H), 7.46-7.45 (m, 1H), 7.40-7.34 (m, 3H), 7.32-7.30 (m, 1H), 7.27-7.24 (m, 1H), 7.22-7.19 (m, 2H), 7.16-7.10 (m, 2H), 6.88-6.85 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 192.96, 143.72, 143.49, 140.76, 138.56, 137.30, 137.24, 136.77, 136.77, 136.55, 136.26, 134.55, 134.31, 134.27, 131.22, 129.81, 129.51, 128.90, 128.28, 128.10, 126.18, 125.44, 125.32, 125.03, 124.05, 123.53, 123.38, 123.19. MS(ESI): *m/z* = 519.0857 $[M+Na]^+$, $C_{33}H_{20}NaOS_2$ required 519.0848.

b) *Synthesis of 1,4-Di[2-(2-thienyl)phenyl]fluorenone* (**4e**)

4e is prepared essentially the same as **4d** by employing **4c** (0.15 g, 0.31 mmol), 2-thienylboronic acid (0.095 g, 0.74 mmol), Pd $(PPh_3)_4$ (22 mg, 0.031 mmol), THF (15 mL) and *aq*. Na_2CO_3 (0.1 g, 0.93 mmol) in water (3 mL) and purified by column chromatography (PE : DCM = 2 : 1) to afford a yellow solid (0.116 g, 76%), R_f = 0.63 (PE : DCM = 1 : 1), mp 132-134 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 7.73 (d, *J* = 7.9 Hz, 1H), 7.63 (d, *J* = 7.1 Hz, 1H), 7.56-7.35 (m, 7H), 7.19-7.01 (m, 5H), 7.03-7.01 (m, 1H), 6.84-6.77 (m, 4H), 6.47-6.42 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.60, 143.58, 142.87, 142.68, 141.93, 140.18, 137.29, 136.58, 136.14, 134.27, 133.66, 133.42, 131.80, 131.31, 130.74, 130.44, 130.14, 130.07, 129.90, 128.84, 128.71, 128.32, 128.00, 127.22, 126.99, 126.93, 126.85, 126.81, 126.73, 125.88,

125.35, 123.78, 122.67. MS (ESI): *m/z* = 519.0836 $[M+Na]^+$, $C_{33}H_{20}NaOS_2$ required 519.0848.

5) Reduction of 4a-4e to 5a-5e by $Na_2S·9H_2O$

a) *1,4-Diphenyfluorene* (**5a**)

To a 100 mL RB flask was added $Na_2S·9H_2O$ (1.056 g, 4.4 mmol), *N*-methyl-2-pyrrolidone (NMP, 60 mL), the mixture was stirred at RT for 15 min, followed by adding 1,4-diphenylfluorenone (0.666 g, 2 mmol) and the mixture was refluxed for 12 h under N_2 atmosphere before it was poured into saturated NH_4Cl (100 mL) and the solid was filtered and purified by column chromatography with petroleum ether (PE) to afford a white solid (0.46 g, 72%), R_f = 0.59 (PE), mp 83-85 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 7.59 (d, *J* = 7.5 Hz, 2H), 7.55-7.37 (m, 9H), 7.35-7.29 (m, 2H), 7.22-7.17 (m, 1H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.97 (d, *J* = 7.4 Hz, 1H), 3.99 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.76, 141.63, 141.45, 141.18, 141.06, 139.03, 138.07, 136.96, 129.45, 129.23, 128.53, 127.53, 127.29, 126.90, 126.48, 126.21, 124.61, 122.98, 36.93.

b) *1,4-Di(4-bromophenyl)fluorene* (**5b**)

5b is prepared essentially the same as **5a** with $Na_2S·9H_2O$ (1.056 g, 4.4mmol), NMP (60 mL) and **4b** (0.976 g, 2 mmol), which was purified by column chromatography with PE to afford a white solid (0.28 g, 29.5%), R_f = 0.52 (PE), mp 80-82 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 7.65-7.62 (m, 2H), 7.56-7.45 (m, 8H), 7.40-7.34 (m, 1H), 7.29-7.22 (m, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 7.5 Hz, 1H), 4.04 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 142.71, 140.59, 140.41, 140.14, 140.02, 137.99, 137.03, 135.91, 128.41, 128.19, 127.63, 127.48, 126.48, 126.24, 125.85, 125.44, 125.17, 123.57, 121.94, 35.89.

c) *1,4-Di(2-bromophenyl)fluorene* (**5c**)

5c is prepared essentially the same as **5a** with $Na_2S·9H_2O$ (1.056 g, 4.4 mmol), NMP (60 mL) and **4c** (0.976 g, 2 mmol), which was purified by column chromatography with PE to afford a white solid (0.246 g, 26.0%), R_f = 0.51 (PE), mp 76-78 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 7.65-7.55 (m, 2H), 7.55-7.45 (m, 6H), 7.43-7.41 (m, 1H), 7.36-7.29 (m, 2H), 7.23-7.18 (m, 1H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.97 (d, *J* = 7.4 Hz, 1H), 4.00 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.78, 141.66, 141.48, 141.21, 141.09, 139.06, 138.10, 136.99, 129.48, 129.26, 128.70, 128.55, 127.55, 127.31, 126.93, 126.51, 126.24, 124.64, 123.01, 36.96.

d) *1,4-Di[4-(2-thienyl)phenyl]fluorene* (**5d**)

5d is prepared essentially the same as **5a** with $Na_2S·9H_2O$ (0.106 g, 0.44 mmol), NMP (6 mL), and **4d** (0.099 g, 0.2 mmol) and purified by column chromatography with PE to afford a white solid (0.070 g, 73%), R_f = 0.18 (PE), mp 231-233 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 7.76 (t, *J* = 7.7 Hz, 4H), 7.62 (d, *J* = 7.8 Hz, 2H), 7.55 (d, *J* = 7.8 Hz, 2H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.45-7.44 (m, 1H), 7.41-7.39 (m, 1H), 7.37-7.29 (m, 4H), 7.22-7.20 (m, 1H), 7.17-7.07 (m, 4H), 4.04 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$)

δ 144.18, 144.10, 143.72, 141.71, 141.31, 140.27, 140.07, 139.16, 137.58, 136.49, 133.67, 133.50, 129.80, 129.54, 129.17, 128.16, 126.80, 126.63, 126.34, 126.07, 125.97, 124.98, 124.96, 124.68, 123.26, 123.24, 123.07, 37.01. MS (ESI): *m/z* = 505.1106 $[M+Na]^+$, $C_{33}H_{22}NaS_2$ required 505.1055.

e) *1,4-Di[2-(2-thienyl)phenyl]fluorene* (**5e**)

5e is prepared essentially the same as **5a** with $Na_2S·9H_2O$ (0.106 g, 0.44 mmol), NMP (6 mL), and **4e** (0.099 g, 0.20 mmol) and purified by column chromatography with PE to afford a white solid (0.061 g, 63%), R_f = 0.25 (PE), mp 68-70 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.7 Hz, 1H), 7.68 (d, *J* = 7.4 Hz, 1H), 7.54-7.47 (m, 1H), 7.43-7.38 (m, 5H), 7.32 (d, *J* = 7.5 Hz, 1H), 7.17-7.05 (m, 5H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.67-6.75 (m, 4H), 6.68 (d, *J* = 7.7 Hz, 1H), 3.58 (s, 1H), 3.43 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.73, 142.77, 142.56, 141.48, 139.64, 138.99, 138.92, 137.78, 135.75, 133.68, 133.27, 130.92, 130.77, 129.79, 129.74, 129.26, 128.14, 127.95, 127.85, 127.63, 127.40, 126.89, 126.70, 126.54, 126.31, 126.27, 125.43, 125.32, 124.50, 122.50, 36.36. MS (ESI): *m/z* = 505.1066 $[M+Na]^+$, $C_{33}H_{22}NaS_2$ required 505.1055.

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