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Synthesis for the Mesomer and Racemate of Thiophene-Based Double Helicene under Irradiation

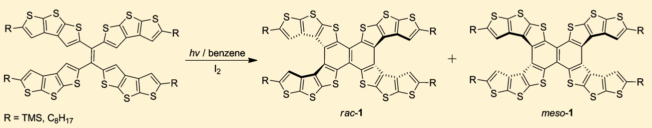
Xinming Liu,[†] Panpan Yu,[†] Li Xu,*[,‡] Juanjuan Yang,[†] Jianwu Shi,[†] Zhihua Wang,[‡] Yanxiang Cheng,*[,§] and Hua Wang*[,†]

[†]Key Lab for Special Functional Materials of Ministry of Education, Henan University, Kaifeng, 475004, China

[‡]College of Chemistry and Chemical Engineering, Henan University, Kaifeng, 475004, China

[§]Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130021, China

S Supporting Information



ABSTRACT: In this work, the racemate and mesomer of the thiophene-based naphthalene-cored double helicenes (**1**) were obtained efficiently by one-pot photocyclization of 1,1,2,2-tetrakis(dithieno[2,3-*b*:3′,2′-*d*]thiophen-2-yl)ethene in the presence of iodine in dry benzene. The structure of *meso*-**1a** was confirmed by single crystal X-ray analysis. The chiral resolution of the racemate was carried out by chiral HPLC, and the chiral properties, such as CD spectra, optical rotations, and half-life of enantiomers were characterized.

Helicenes constitute a fascinating class of ortho-annulated polycyclic aromatic or heteroaromatic compounds endowed with inherent chirality due to the helical shape of their π-conjugated system.[1] Their unique physicochemical properties have stimulated countless studies oriented toward chiral catalysts,[2] self-assembly,[3] chiroptical devices,[4] molecular recognition[5] and molecular machines.[6] The synthetic strategies for the construction of helicenes including Diels−Alder cycloaddition, photocyclization, transition-metal-mediated cyclotrimerization, olefin metathesis, intramolecular Pd-catalyzed cyclization and Friedel−Crafts cyclization have been reviewed in recent years.[1,7]

Since the first carbon−sulfur helicene, heptathio[7]-helicene, was reported by Rajca in 2000,[8b] helicenes of such type have demonstrated attractive characteristics in both synthetic challenge and potential electronic and optical properties. These helicenes feature all sulfur atoms along the outer edge of the molecular skeletons and offer opportunities to modify the electronic and optical properties due to S···S and S···π interactions in the solid state.[9] Rajca has published a series of synthetic work in making carbon−sulfur helicenes, including the [5], [7], [9] and [11]helicenes,[8] but failed in getting the [15]helicene because of strong intramolecular π−π interaction between two fused thiophene units[10] and possible poor solubility of precursor. In order to avoid the solubility issue in previous synthesis of carbon−sulfur helicenes, two types of double helicenes bearing four solubility-supporting goups (TMS) have been designed and synthesized in our previous work.[11] One naphthalene-cored double helicene, *rac*-**1a**, was efficiently prepared from macrocyclic diketone (**5**) via a McMurry method (Scheme 1).[11a]

On the other hand, photocyclization of diaryl ethenes affords an alternative efficient protocol to the synthesis of helicenes,[2c,12,13] wherein the stilbene-like diaryl ethene precursors can easily be prepared by Wittig olefination or McMurry reaction. In this work, we report a new synthetic approach to double helicene **1** via photocyclization with two precursors, 1,1,2,2-tetrakis(5-trimethylsilyl-dithieno[2,3-*b*:3′,2′-*d*]thiophen-2-yl)ethene (**4a**) and 1,1,2,2-tetrakis(5-octyldithieno[2,3-*b*:3′,2′-*d*]thiophen-2-yl)ethene (**4b**) (Scheme 2). Both the racemate (*rac*-**1**) and the mesomer (*meso*-**1**) were efficiently obtained in one pot. In addition, the resolution of *rac*-**1a** was carried out by chiral HPLC, and its enantiomers were also characterized.

The synthetic route to *rac*-**1** and *meso*-**1** is shown in Scheme 2. The Br/Li exchange on 5-bromo-2-trimethylsilanyl-dithieno-[2,3-*b*:3′,2′-*d*]thiophene (**2a**)[11] occurred smoothly with *n*-BuLi. After quenching with *N*,*N*-dimethylcarbamyl chloride (DMC), di(5-trimethylsilanyl-dithieno[2,3-*b*:3′,2′-*d*]thiophen-2-yl)-methanone (**3a**) was generated in 66−69% yield. Di(5-octyl-dithieno[2,3-*b*:3′,2′-*d*]thiophen-2-yl)methanone (**3b**) was efficiently obtained with 2-octyl-dithieno[2,3-*b*:3′,2′- *d*]thiophene (**2b**)[14] as starting material. Instead of *n*-BuLi, LDA was employed for deprotonation of **2b** to avoid a possible ring-opening reaction.[15] The intermolecular McMurry reaction of **3** was performed to afford tetrakis(5-substituted-dithieno[2,3-*b*:3′,2′-*d*]thiophen-2-yl)ethene (**4**) in a low yield (~30%).

Compound **4** has four arms of dithieno[2,3-*b*:3′,2′-*d*]-thiophene (DTT) linked to the carbon−carbon double bond. The oxidative photocyclization of **4** was carried out in presence of iodine in dry benzene via irradiation with a 450 W unfiltered Hg medium pressure lamp. If the reaction was carried out in a quartz NMR tube, complete conversion of the starting material occurred within 5 min. A mixture of two new species was observed by ^{1}H NMR. For example, two new peaks at 7.246 and 7.167 ppm were found, and their integral areas were almost

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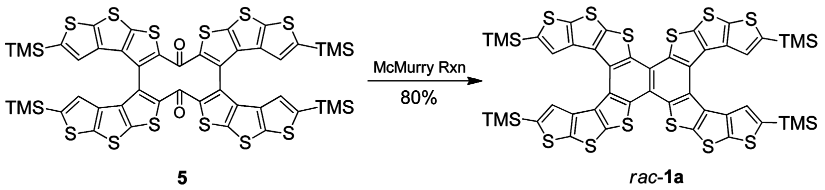
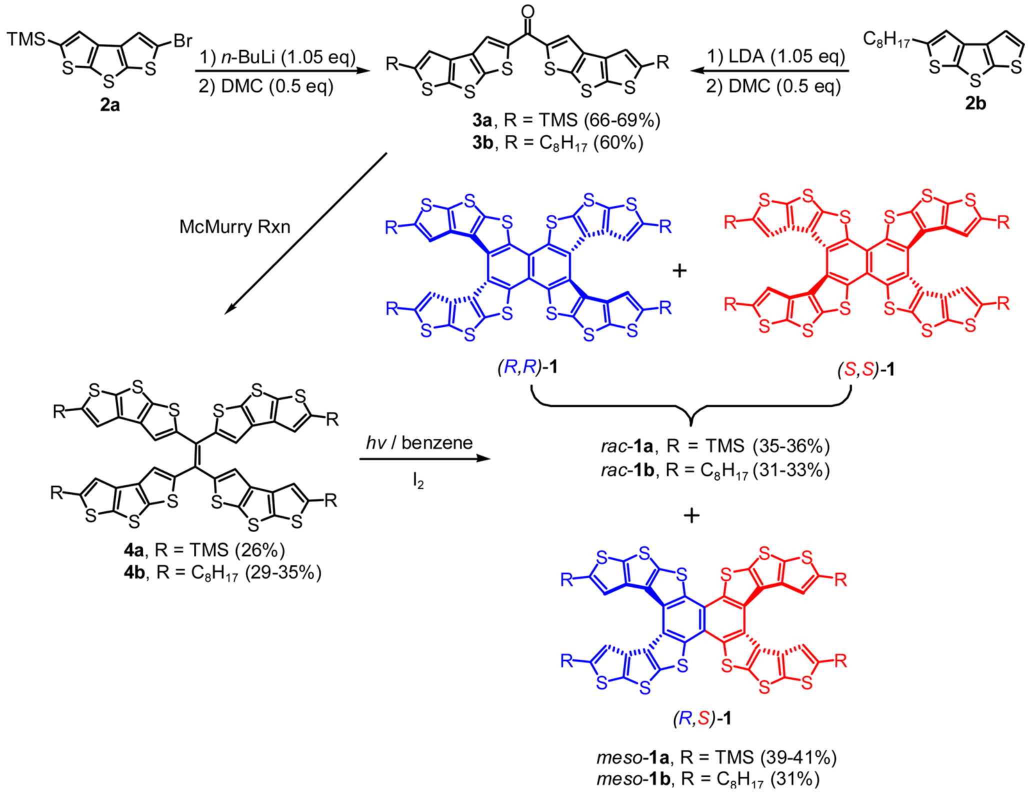
Scheme 1. Synthetic Route to *rac*-**1a** via McMurry Reaction



Scheme 2. Synthetic Route to *rac*-**1** and *meso*-**1**



equal (Figure 1) when **4a** was employed on a scale of 1.6 mg in 1.5 mL of dry benzene. The two new species had the same polarity and were separated by recrystallization due to their different solubilities. The soluble compound was confirmed as *rac*-**1a**, which is the naphthalene-cored double helicene reported in our previous work.[11a] The insoluble one was then confirmed as *meso*-**1a** via single crystal X-ray analysis (Figure 2).

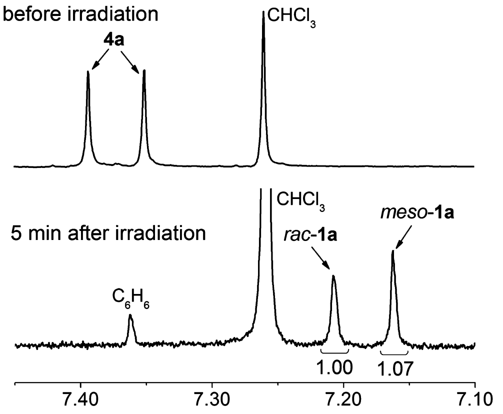


Figure 1. Partial ^{1}H NMR spectra ($CDCl_3$) of **4a** before irradiation (top) and the crude product after irradiation for 5 min (bottom).

In our one-pot photocyclization reaction of **4**, *rac*-**1a** and *rac*-**1b** were generated in 35−36 and 31−33% yields, respectively. Meanwhile, *meso*-**1a** and *meso*-**1b** were also obtained in 39−41 and 31% yields, respectively. *rac*-**1** and *meso*-**1** are diastereomers, and their observed ratio was near 1:1 (Scheme 2), which was confirmed by ^{1}H NMR (Figure 1). It is known that photochemical process induces double radical on a double bond, which may lead to the central C═C bond rotating along the resulting single C(radical)−C(radical) bond. As a result, a rac/meso mixture may be obtained in a 1:1 ratio. Therefore, the diastereoselectivity in this photochemical reaction was low. However, in the thermal process only *rac*-**1a** was formed by intramolecular McMurry reaction of macrocyclic diketone (**5**) in our previous work (Scheme 1).[11a] The reason may be that the free rotation of the four DTT moieties in **5** is not allowed, and formation of five-membered ring intermediate containing O−Ti−O bonds may disfavor the formation of mesomers.

The photocyclization of **4** to *rac*-**1** and *meso*-**1** requires the formation of two new C−C bonds. The single helicene product corresponding to the formation of only one of these two new C−C bonds was not observed; therefore, there is no evidence

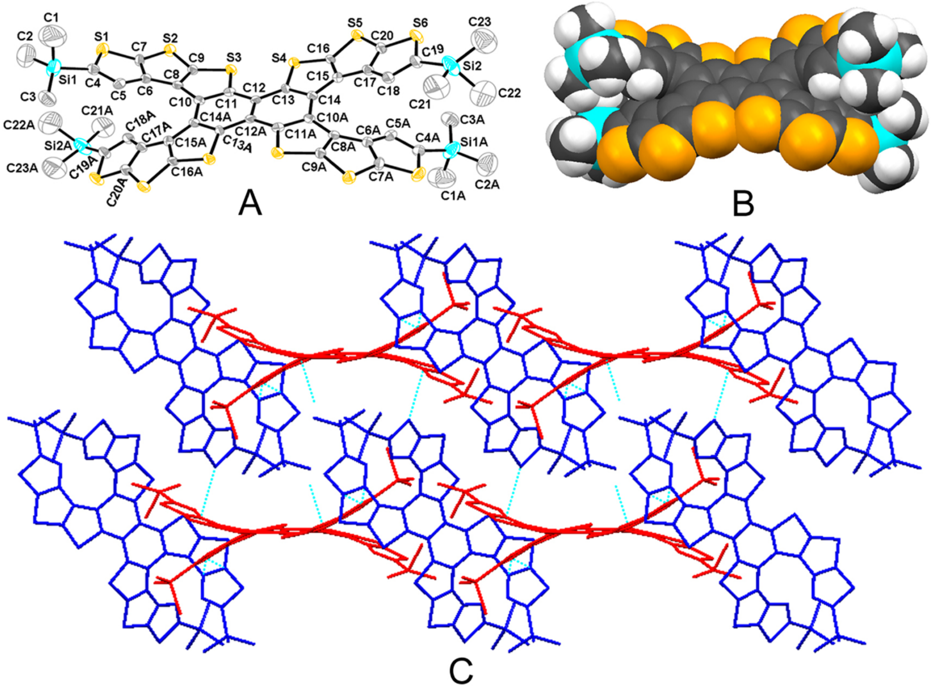


Figure 2. Molcular structure and conformation for *meso*-**1a**. Top view (A), side view of the space-filling model representation (B) and the crystal packing of *meso*-**1a** along *b* axis (C). Carbon, oxygen, silicon, and sulfur atoms are depicted with thermal ellipsoids set at the 30% probability level. All hydrogen atoms are omitted for clarity.

supporting a stepwise mechanism involving such a single helicene as an intermediate.

The molecular structure of *meso*-**1a** was confirmed by single-crystal X-ray analysis (Figure 2). The crystal of *meso*-**1a** belongs to triclinic space group $P\bar{1}$. *meso*-**1a** shows a novel double helical conformation, in which two helical structures are fused together with an intramolecular mirror symmetry. In *meso*-**1a**, the repulsion of the facing terminal thiophene rings (C4C5C6C7S1 and C17AC18AC19AC20AS6A) causes two interplanar angles of 54.5°. The distance between H5A···H18 is 2.861 Å. With the middle benzene rings as reference, the inner helix of (C5, C6, C8, C10, C14, C15, C17, C18) in *meso*-**1a** climbs 2.882 Å and turns in-plane by 305.4°.

In packing of *meso*-**1a**, the two helical molecules are perpendicularly together to form a "couple" (Figure 2C). There existed multiple noncovalent interactions including S···S and S···π interactions with the distances of S4···S8, 3.538 Å; C28···S1, 3.392 Å; C30···S1, 3.366 Å; S12···C17, 3.438 Å; and H24C···C8, 2.869 Å, respectively.

Compared with the crystal data of *meso*-**1a** and *rac*-**1a**, it is found that *meso*-**1a** shows a little bit lower twisting in its helical structure. For example, the naphthalene core in *meso*-**1a** is very planar with about 0° dihedral angle between two fused benzene rings, while *rac*-**1a** has about 15°.[11a] The inner helix of *meso*-**1a** climbs 2.882 Å, while *rac*-**1a** gives 2.911 Å.

The UV−vis spectra for *meso*-**1a**, *rac*-**1a** and **4a** are shown in Figure 3. Compound **4a** has four DTTs with two major absorption peaks at 339 and 423 nm and a shoulder peak at 401 nm. *meso*-**1a** has three major peaks at 353, 378, and 392 nm, and a minor peak at 425 nm. *rac*-**1a** shows two major absorption peaks at 352 and 374 nm, a minor peak at 420 nm and a shoulder peak at 388 nm. The spectrum of **4a** shows more bathochromic shift compared with that of *meso*-**1a** and *rac*-**1a**. The bathochromic shift observed with **4a** is due to two *trans*-DDT moieties being able to be achieved (near) coplanar geometry through the central (nonaromatic) double bond, thus providing extended delocalization. Similar case could be observed in tetrakis(5-(trimethylsilyl)-thiophene-2-yl)ethene,[16] in which two *trans*-thiophenes have an interplanar angle of 0.0°, and two *cis*-thiophenes have an interplanar angle of 69.8° in crystal. This type of conjugation is disturbed in the double helicene (*rac*-**1a** and *meso*-**1a**) because of the geometry deviating from planarity (as observed in the X-ray crystallographic structures for *rac*-**1a** and *meso*-**1a**) and thus decreases electron delocalization compared to **4a**. Therefore, the spectra of *meso*-**1a** and *rac*-**1a** show blue shift compared with **4a**, and they have similar spectral behaviors. The slight bathochromic shift of *meso*-**1a** may be due to the planar naphthalene core, compared to that of *rac*-**1a**. The same behaviors of *rac*-**1b**, *meso*-**1b** and **4b** are also observed (see Supporting Information).

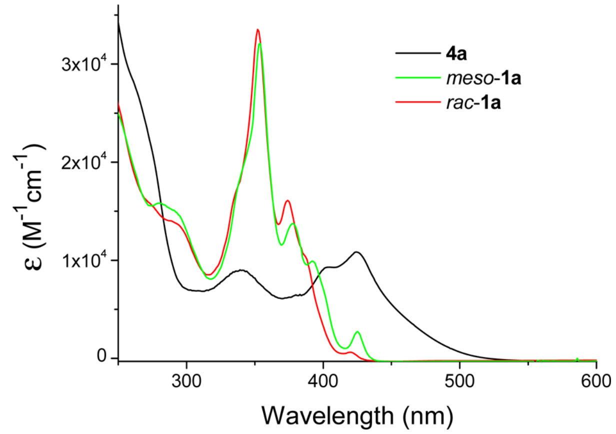


Figure 3. Absorption spectra for *rac*-**1a**, *meso*-**1a** and **4a** in chloroform at room temperature ([C] = 1×10^{-5} M).

The resolution of *rac*-**1a** was carried out by chiral HPLC with *n*-hexane/isopropanol (98:2, v/v) as eluent. The two enantiomers were obtained on a semipreparative scale chiral column (RC-SCDP5). From the 30 mg scale of *rac*-**1a**, 7.7 mg (ee >99%) of (+)-**1a** and 8.6 mg (ee = 84%) of (−)-**1a** were efficiently obtained. The optical rotations of (+)-**1a**, $[\alpha]_D^{29}$ = +505° (c = 0.0046 g/mL in chloroform), and (−)-**1a**, $[\alpha]_D^{30}$ = −273° (c = 0.0070 g/mL in chloroform), were observed, respectively. The circular dichroism (CD) spectra of (+)-**1a** and (−)-**1a** were taken in *n*-hexane. The CD spectra possess both spectral envelopes and absorbances analogous to typical conjugated helicenes.[17] Enantiomers (+)- and (−)-**1a** show perfect mirror symmetric image spectra (Figure 4). The CD spectrum of (+)-**1a** has small negative dichroic signals at around 278, 331, 370, and 415 nm, intense positive signals around 252, 298, and 384 nm, and a relatively intense negative signal around 349 nm. This trend differs from the known carbon−sulfur helicenes reported by Rajca.[4b,8c,10,17,18]

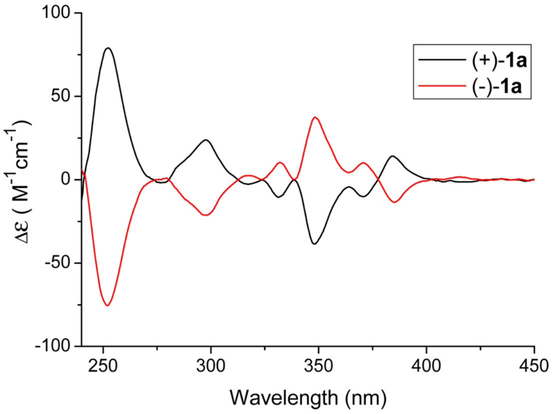


Figure 4. CD spectra of (+)-**1a** (black line, ee >99%, 9.6 × 10^{-6} M in *n*-hexane) and (−)-**1a** (red line, ee = 84%, 1.1 × 10^{-5} M in *n*-hexane) at room temperature.

Racemization of (+)-**1a** was carried out in solid state in Schlenk flask under an argon atmosphere by heating at 232 °C. The process was monitored from time to time by chiral HPLC (RC-SCDP5) to obtain the changes of ee values. No *meso*-**1a** was observed by HPLC in this case. The half-life was measured as 57.6 h from the plot of ln[(ee + 1)/2] vs time (see Supporting Information). The half-life of (+)-**1a** is higher than that of carbon−sulfur single [7]helicene reported as 11 h at 199 °C or 5 h at 203 °C in solid state[18a] and hydrocarbon single [7]helicene reported as 12.4 h at 239 °C in naphthlene solution[19a] (Figure 5). These data indicate that the double helicene of (+)-**1a** shows high chiral stability. In addition, we have also checked the possibility of molecular configuration inversion between *meso*-**1a** and *rac*-**1a**. After heating at 250 °C for 10 days, both *meso*-**1a** and *rac*-**1a** did not show any changes as monitored by ^{1}H NMR. These factors indicate that such inversion does not occur in only one part of double helicene but can change with two parts together.

The thermal racemization of helicene up to nonahelicene via a justified "conformational process" with surprisingly low potential barriers was confirmed by experimental and computational studies.[18a,19] Two helical parts in double helicene molecule can invert in one step, which may be caused by two factors. On the one hand, the necessary molecular deformations (bond torsion, bond bending, bond stretching, etc.) are spread over a large number of bonds in whole molecule for the conformational process.[19a] On the other hand, once the conformational conversion is finished in one helical part of double helicene molecule, then the fast intramolecular chirality transfer should occur immediately to result in the conformational conversion of another helical part in the same molecule. Therefore, we believe that the racemization of (+)-**1a** may proceed in one step; namely, two helical parts in (+)-**1a** are inverted together to (−)-**1a**, and no *meso*-**1a** is involved. Furthermore, no molecular configuration inversion between *meso*-**1a** and *rac*-**1a** can occur.

In summary, we have achieved the intriguing synthesis of mesomer and racemate of thiophene-based double helecene under irradiation of tetrakis-(aryl)ethene in the presence of iodine in one-pot, wherein formation of two C−C bonds[13a,e] occurred via photocyclization. This synthetic method gives a good example for two C−C bonds formation in making helicene via photocyclization, which can be applied to a large range of complicated fused aromatic systems. The interesting chiral conversion of double helicene (**1a**) in a concerted way is clearly observed and confirmed in our work, which might be applied in a molecular machine actuated by laser light. In addition, the multiple short interactions including S···S and S···π interactions observed in the crystal packings of both *meso*-**1a** and *rac*-**1a**[11a] may provide potential applications in organic electronics.[9] The enantiopure **1a** gives the possibility for its applications in asymmetric synthesis as chiral catalyst[2,20] and in chiral self-assembly as building blocks.[21]

■ EXPERIMENTAL SECTION

Synthesis of Bis(5-(trimethylsilyl)dithieno[2,3-*b*:3′,2′-*d*]thiophen-2-yl)methanone (3a). *n*-BuLi (2.39 M in hexane, 0.9 mL, 2.15 mmol, 1.05 equiv) was added dropwise to a solution of **2a** (0.7202 g, 2.07 mmol) in THF (80 mL) at −78 °C. After 2 h at −78 °C, DMC (0.09 mL, 1.03 mmol, 0.5 equiv; namely, 1.7 mL of DMC solution consisting of 0.3 mL of DMC in 5.0 mL of THF) was added dropwise at −78 °C, and then the reaction mixture was warmed up

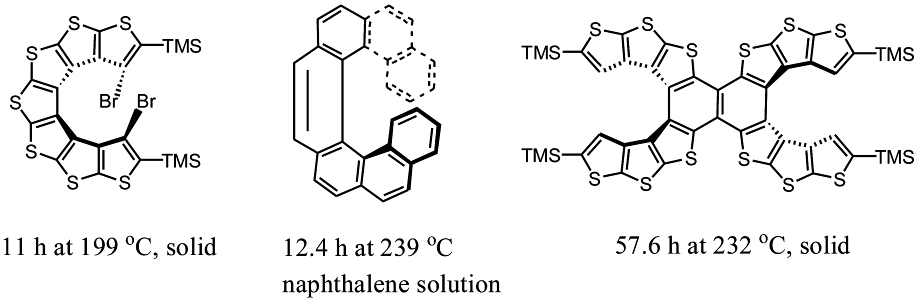


Figure 5. Racemization comparison betweene carbon−sulfur single [7]helicene (left), hydrocarbon single [7]helicene (middle) and carbon−sulfur double helicene (+)-**1a** (right).

slowly to ambient temperature overnight. The reaction mixture was quenched with water, extracted with $CHCl_3$ (3 × 20 mL). The organic layer was washed with water (3 × 15 mL) and then dried over $MgSO_4$. After the removal of the solvent in vacuo, the residue was purified by column chromatography on silica gel with petrol ether (60−90 °C)/$CHCl_3$ (2:1, v/v) as eluent to yield **3a** (0.4016 g, 68.8%) as a yellow solid. From other reaction on the 0.9820 g of **2a**, 0.5287 g (66.4%) of **3a** was obtained. mp 254−256 °C. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.20 (s, 2H), 7.56 (s, 2H), 0.40 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 178.5, 147.8, 145.7, 144.8, 144.7, 140.5, 137.8, 124.9, 124.3, −0.1. HRMS (TOF MS EI$^+$): *m/z* calcd for [$C_{23}H_{22}OS_6Si_2$] 561.9534, found 561.9539. IR (KBr): 2954 (C−H), 1590 (C=O) cm^{-1}.

Synthesis of Bis(5-octyldithieno[2,3-*b*:3′,2′-*d*]thiophen-2-yl)-methanone (3b). Compound **3b** was prepared according to the method of making **3a** except the *n*-BuLi was replaced by LDA and the reaction was taken on the 0.7991 g scale of **2b**. The crude product was purified by column chromatography on silica gel with petrol ether (60−90 °C)/$CHCl_3$ (2:1, v/v) as eluent to yield **3b** (0.4796 g, yield: 60.5%) as a yellow solid. From other two reactions on the 0.8306 and 0.2072 g scales of **2b**, 0.5119 g (61.5%) and 0.1102 g (51.0%) of **3b** were obtained, respectively. mp 132−133 °C. ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 8.07 (s, 2H); 7.11 (s, 2H); 2.89 (t, *J* = 7.6 Hz, 4H); 1.69−1.76 (m, 4H); 1.28−1.40 (m, 20 H); 0.89 (t, *J* = 6.8 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 178.4, 149.9, 146.4, 144.6, 138.6, 137.7, 136.7, 124.1, 115.8, 31.8, 31.6, 31.1, 29.3, 29.2, 29.0, 22.6, 14.1; HRMS (TOF MS ES$^+$): calcd for [$C_{33}H_{39}OS_6$] [(M + H)$^+$] 643.1325, found 643.1330.

Synthesis of 1,1,2,2-Tetrakis(5-(trimethylsilyl)dithieno[2,3-*b*:3′,2′-*d*]thiophen-2-yl)ethene (4a). $TiCl_4$ (0.3 mL, 2.73 mmol, 5.0 equiv) was carefully added into dry THF (30 mL) at 0 °C, and after keeping at 0 °C for 10 min, zinc dust (0.3689 g, 5.64 mmol, 10.0 equiv) was added, and then the mixture was refluxed for 2 h. After that, pyridine (0.23 mL, 2.76 mmol, 5.0 equiv) was added, and the reaction mixture was refluxed for another 2 h. After cooling to ambient temperature, a solution of **3a** (0.3103 g, 0.55 mmol) in dry THF (10 mL) was added, and the reaction mixture was refluxed overnight. The reaction was quenched with water at 0 °C, and then extracted with $CHCl_3$ (3 × 20 mL) and washed with saturated NH_4Cl (3 × 20 mL) and H_2O (2 × 30 mL), and then dried over $MgSO_4$. After removing the solvent in vacuo, the crude product was purified by column chromatography on silica gel with petrol ether (60−90 °C)/$CHCl_3$ (6:1, v/v) as eluent to yield yellow solid **4a** (0.0771g, yield: 25.8%). From other reaction on the 0.3936 g of **3a**, 0.1007 g (26.4%) of **4a** was obtained. mp >300 °C. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.39 (s, 4H), 7.35 (s, 4H), 0.34 (s, 36H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 145.7, 144.8, 143.7, 142.7, 140.7, 136.8, 128.1, 125.2, 122.8, −0.1. HRMS (TOF MS EI$^+$): *m/z* calcd for [$C_{46}H_{44}Si_4S_{12}$] 1091.9169, found 1091.9175. IR: 2953 (C−H), 1638 (C=C) cm^{-1}. UV−vis ($CHCl_3$): λ (ε) = 339 (9011), 401 (9189), 423 nm (10806).

Synthesis of 1,1,2,2-Tetrakis(5-octyldithieno[2,3-*b*:3′,2′-*d*]-thiophen-2-yl)ethane (4b). Compound **4b** was prepared according to the method of making **4a**, and the reaction was taken on the 0.4458 g scale of **3b**. The crude product was purified by column chromatography on silica gel with petrol ether (60−90 °C)/$CHCl_3$ (6:1, v/v) as eluent to yield **4b** (0.1538 g, yield: 34.5%) as a yellow solid. From other two reactions on the 0.3410 g and 67.9 mg scales of **3b**, 0.1043 g (31.4%) and 19.2 mg (29.2%) of **4b** were obtained, respectively. mp 184−187 °C. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.29 (s, 4H); 6.98 (s, 4H); 2.85 (t, *J* = 7.6 Hz, 8H); 1.69 (quint, *J* = 7.6 Hz, 8H); 1.37−1.26 (m, 40 H); 0.87 (t, *J* = 6.8 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 149.1, 145.6, 141.3, 137.9, 137.6, 135.6, 128.0, 122.7, 116.0, 31.8, 31.6, 31.1, 29.3, 29.2, 29.0, 22.6, 14.1. HRMS (MALDI-DHB): *m/z* calcd for [$C_{66}H_{76}S_{12}$] 1252.2590, found 1252.2573. IR: 2924 (C−H), 1646 (C=C) cm^{-1}. UV−vis ($CHCl_3$): λ (ε) = 337 (11200), 401 (11400), 425 nm (14200).

Synthesis of *meso*-1a and *rac*-1a under Irradiation. To a solution of **4a** (62.1 mg, 0.0568 mmol) in dry benzene (60 mL), iodine (6.4 mg, 0.0252 mmol, 0.5 equiv) was added. The reaction solution was kept in an quartz tube (Φ = 16 mm) and irradiated with a 450 W unfiltered Hg medium pressure lamp. The reaction was monitored by TLC every 10 min, and irradiation was stopped when **4a** was consumed (about 50 min). After normal workup, the crude product was purified by column chromatography on silica gel with petrol ether (60−90 °C)/$CHCl_3$ (4:1, v/v) as eluent to yield **1a**, 49.1 mg. On one hand, to obtain *meso*-**1a** and *rac*-**1a**, **1a** was centrifugally washed five times with petrol ether (60−90 °C)/$CHCl_3$ (6:1, v/v, 3 mL each time); the *meso*-**1a** (24.1 mg, yield: 38.9%) was afforded as a light yellow solid. On the other hand, the filtrate was concentrated and sedimentated at low temperature (0−5 °C) to obtain the *rac*-**1a** (21.7 mg, yield: 35.1%) as a light yellow solid. From other reaction on the 35.5 mg of **4a**, 14.4 mg (40.9%) of *meso*-**1a** and 12.8 mg (36.1%) of *rac*-**1a** were obtained. *meso*-**1a**, mp >300 °C. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.17 (4H, s), 0.15 (s, 36H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 143.9, 142.5, 142.2, 141.8, 136.8, 134.2, 130.1, 124.4, 120.0, −0.2. HRMS (MALDI-DHB): *m/z* calcd for [$C_{46}H_{40}S_{12}Si_4$] 1087.8850, found 1087.8827. IR (KBr): 2953 (C−H) cm^{-1}. UV−vis ($CHCl_3$): λ (ε) = 353 (32078), 378 (13744), 392 (9918), 425 nm (2735). *rac*-**1a**, mp >300 °C. ^1H NMR (400 MHz, CDCl3): δ (ppm) 7.25 (s, 4H), 0.22 (s, 36H). ^1H NMR of *rac*-**1a** is same to the result published in our previous work.[11a] UV−vis ($CHCl_3$): λ (ε) = 352 (33524), 374 (16109), 420 nm (638).

Synthesis of *meso*-1b and *rac*-1b under Irradiation. Compound **1b** was prepared according to the method of making **1a**, and the reaction was taken on the 37.1 mg scale of **4b**. After workup, the crude product was purified by column chromatography on silica gel with petrol ether (60−90 °C)/$CHCl_3$ (4:1, v/v) as eluent to yield **1b**, 27.8 mg. After **1b** was centrifugally washed for five times with petrol ether (60−90 °C)/$CHCl_3$ (6:1, v/v, 3 mL each time), the *meso*-**1b** (11.4 mg, yield: 30.9%) was afforded as a light yellow solid. The *rac*-**1b** (12.1 mg, yield: 32.8%) was afforded by sedimentation from the filtrate at low temperature (0−5 °C) as a light yellow solid. From other reaction on the 67.8 mg of **4b**, 20.6 mg (30.5%) of *meso*-**1b** and 21.3 mg (31.5%) of *rac*-**1b** were obtained. *meso*-**1b**, mp 169−172 °C. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.84 (s, 4H), 2.74−2.67 (m, 8H), 1.57−1.50 (m, 8H), 1.38−1.25 (m, 40H), 0.89 (t, *J* = 6.8 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 146.6, 141.1, 140.2, 137.0, 136.2, 135.3, 124.6, 121.0, 120.3, 32.0, 31.5, 31.1, 29.5, 29.3, 29.2, 22.7, 14.0. IR (KBr): 2923, 2851 (C−H) cm^{-1}. HRMS (MALDI-DHB): *m/z* calcd for [$C_{66}H_{72}S_{12}$] 1248.2277, found 1248.2281. UV−vis ($CHCl_3$): λ (ε) = 354 (33300), 376 (16500), 392 (11800), 426 nm (3770). *rac*-**1b**, mp 222−225 °C. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.85 (s, 4H), 2.84−2.70 (m, 8H), 1.62−1.55 (m, 8H), 1.41−1.26 (m, 40H), 0.90 (t, *J* = 6.4 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, 333K) δ (ppm) 146.0, 140.4, 139.9, 135.8, 135.0, 134.8, 123.6, 121.0, 118.9, 32.0, 31.7, 31.1, 29.5, 29.4, 29.3, 22.7, 14.2. IR (KBr): 2923, 2852 (C−H) cm^{-1}. HRMS (MALDI-DHB): *m/z* calcd for [$C_{66}H_{72}S_{12}$] 1248.2277, found 1248.2258. UV−vis ($CHCl_3$): λ (ε) = 353 (32800), 374 (17600), 422 nm (1100).

Small Scale of 4a Employed for the Test of Making *meso*-1a and *rac*-1a under Irradiation. A scale of 1.6 mg of **4a** was dissolved in 1.5 mL of dry benzene containing iodine (0.2 mg) in a quartz NMR tube. Then the reaction mixture was irradiated with a 450 W unfiltered Hg medium pressure lamp. The reaction was completed within 5 min monitored by TLC. After removing the solvent by N_2 flow, the crude product was examined by ^1H NMR analysis.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Characterization of all compounds and crystallographic CIF files of *meso*-**1a**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: (0086)-378-3897112. Fax: (0086)-378-3881358. E-mail: xuli@henu.edu.cn; yxcheng@ciac.jl.cn; hwang@henu.edu.cn.

Notes

The authors declare no competing financial interest.

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