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Helical polycyclic aromatics containing thiophenes: synthesis and properties

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Abstract—A series of planar and non-planar (helical) thiophene-based polycyclic aromatics has been synthesized through the Diels–Alder reaction followed by decarbonylation reactions and $FeCl_3$ oxidative cyclizations.

During the past several decades, oligothiophenes and polythiophenes have attracted significant interest due to their applications in photonic and electronic displays.[1] New synthetic methodologies and novel structures have been developed and significant effort has been devoted to the investigation of the special intrinsic properties by structural and chemical disorder,[2] and the easy modification of the thiophene structure of thiophene-based conjugated materials.[3] The incorporation of thiophene rings onto polycyclic aromatic frameworks also exhibits considerable success in the design and synthesis of unique organic semiconductors[4] for organic field effect transistors and high conductivity.[5] [*n*]Helicenes constructed through such modification have precisely ordered structures as a result of both the helical conjugation and the stiff structure.[6] Thus, they are especially suitable building blocks for organic materials with extraordinary strong chiroptical properties.[7]

Herein, we report a series of thiophene-based polycyclic aromatics including planar ladder molecules (**1** and **2**) as shown in Chart 1 and non-planar hetereohelicenes (**9** and **10**) with fused structures with the alternant benzene and thiophene rings. These thiophene-based planar polycyclic aromatics and helicenes allow for further modification at α-positions of thiophene segments and can ultimately be tuned into more extended molecules and polymeric systems. Through such elaboration, the effect of aromatization on the photophysical behaviors of these thiophene-based polycyclic structure is further investigated.

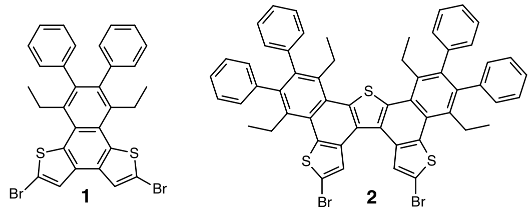

Chart 1.

Scheme 1 outlines the synthetic approach to **1**. The Diels–Alder reactions between 2,2′-bithienylethynylene and 2,5-diethyl-3,4-dipheneylcyclopentadienone followed by the decarbonylation afforded **3** in excellent yield. Before the $FeCl_3$ oxidation[6d–f] to form the carbon–carbon bond at β-positions of thiophene rings, we had to protect α-positions of thiophene rings in order to prevent the polymerization of thiophene owing to the high reactivity of α-positions. As shown in Scheme 1, the bromination only occurred at α-positions of **3**. The oxidation of **4** using $FeCl_3$ (6 equiv per C–C bond) produced **1**[8] in high yield. Neither dimerization nor polymerization happened when excess $FeCl_3$ was used, which confirmed the specificity of such oxidative cyclizations. This result also encouraged us to further prepare other thiophene-based polycyclic aromatics.

We also obtained **2** through similar procedures as shown in Scheme 2. The Diels–Alder reactions between

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Keywords: Polycyclic; Cyclization; Conjugation; Helicenes.

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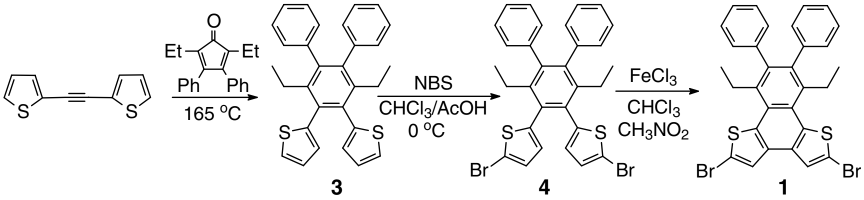
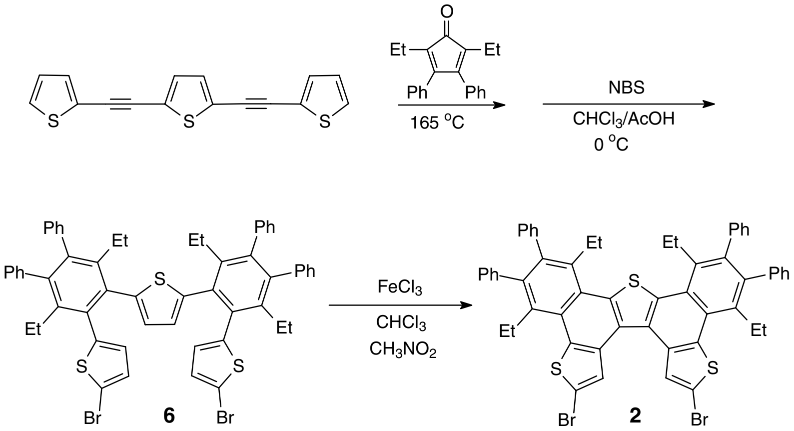


Scheme 1.



Scheme 2.

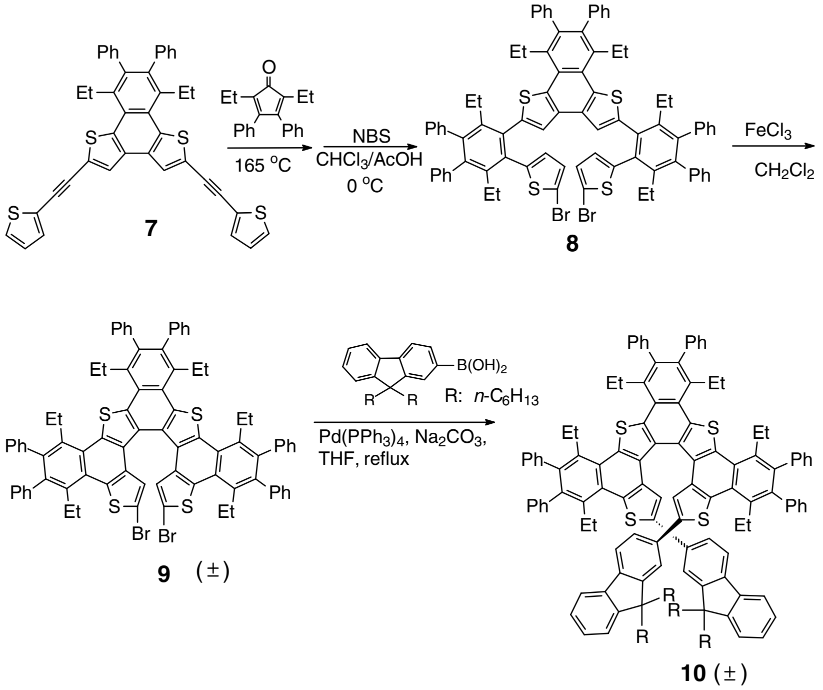
2,5-bis(2-thienylethynyl)thiophene and 2,5-diethyl-3,4-dipheneylcyclopentadienone followed by decarbonylation as well as the bromination produced **6** with alternant benzene and thiophene rings. In the presence of more than two thiophene rings within one molecule, $FeCl_3$ oxidation of thiophenes usually polymerized rather than underwent discrete monomer cyclization due to the highly reactive nature of thiophene rings. Fortunately, we obtained **2** without apparent polymerization by the formation of two C–C bonds in one step in excellent yield.[9] Therefore, such oxidative cyclizations were efficient to develop well-defined, thiophene-centered polycyclic aromatics.

Most recently, thiahetereohelicenes consisting of fused thiahetereocycles have attracted extensive interest due to their unique optical and physical properties and their stable doped and neutral states owing to the π-conjugation on the thiophene rings.[10] Both **1** and **2** were very good building blocks for constructing the novel helicenes. The synthetic route to helicenes **9** and **10** is illustrated in Scheme 3.[11] Compound **7** was produced by the Sonogashira reactions. After the Diels–Alder reactions and decarbonylation as well as the oxidation, we obtained helicene **9**. Only two carbon–carbon bonds were formed during the oxidation due to the helical framework. To further confirm this structure, we obtained **10** through Suzuki cross-coupling in excellent yield of over 90%.

In addition to ^1H and ^{13}C NMR spectra and analytical data, MALDI-TOF MS we also employed to characterize the structure and molecular weight of all new compounds (see the Supporting Information). We obtained the proper analytical data to substantiate the accurate structure of **9**. We observed the exact loss of four hydrogen atoms from the MALDI-TOF MS spectrum of **9** in comparison with that of **8**. From the ^1H NMR spectra of **10**, we observed the two doublet signals contributed from the protons at the fluorene moieties moving to the upfield at about 7.69 and 6.58 ppm ($J = 7.8$ Hz), respectively, which were different with those of 2-thienylfluorene.[3d,6a] This indicated the helical conformations caused by the overlap of two fluorene rings.

The absorption spectra for **1**, **2**, **9**, and **10** in dilute CH_2Cl_2 solutions are shown in Figure 1. We observed that the absorption of **2** peaked at 321 nm with a shoulder at 367 nm, which was red-shifted about 28 nm in comparison with that of **1** (293 nm) due to the increase of the effective conjugation length. Similarly, the absorption maximum peak (343 nm) of **10** was red-shifted about 34 nm related to that of **9** (309 nm). However, the absorption λ_{max} of **9** was blue-shifted about 12 nm in comparison with that of **2**, which also suggested the formation of helical structure. Therefore, compared to those of all thiophene [7]helicene (256 nm)[10d] and all benzene helicene,[12] the absorption λ_{max} of **9** obviously red-shifted. The optical properties of all new compounds in dilute CH_2Cl_2 solutions are summarized in Table 1.

In conclusion, we have developed a reaction sequence to synthesize a new series of planar and non-planar (helical) thiophene-based polycyclic aromatics. The Diels–Alder reactions followed by decarbonylation produce the precursors of the cyclizations. The regioselective bromination of the unsubstituted α-positions of thiophene rings ensures the success of the oxidative cycliza-



Scheme 3.

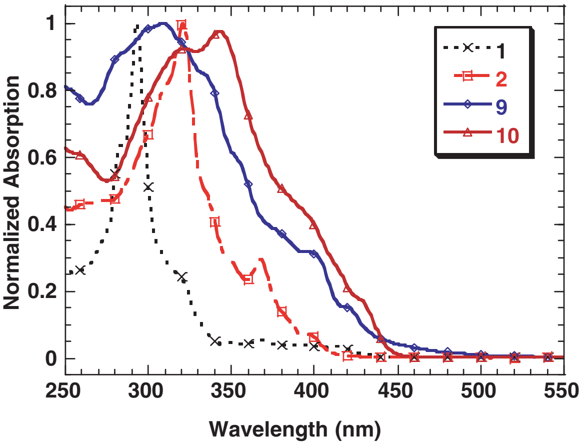


Figure 1. The absorption spectra of **1**, **2**, **9**, and **10** in dilute CH_2Cl_2 solutions.

Table 1. The optical properties of compounds **1**, **2**, **7**, **8**, **9**, and **10** in dilute CH_2Cl_2 solutions

Compounds	λ_{abs} (nm)	λ PL (nm)
1	293	305
2	321	338
7	337	395
8	298	312
9	309	342
10	343	424

tions. The $FeCl_3$ oxidative cyclizations of β-thiophene moieties afford the thiophene-containing polycyclic aromatics with excellent yields without dimerization or polymerization. All characterization data demonstrate that **9** exhibits the helical framework. The photophysical properties of all compounds are investigated by UV–vis measurement. The absorption spectra of the desired materials are liable to be tuned by the introduction of more conjugated moieties. These helicenes are good candidates for studying the one- or two-dimension molecular wire in the field of organic semiconductors.

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Supplementary data

Synthetic details for all new compounds **1**–**10** are available. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.01.006.

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8. Compound **1** was obtained as white solids (yield: 85%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm, δ): 7.74 (s, 2H, Th), 7.09 (m, 10H, Ph), 3.22 (q, $J = 7.2$ Hz, 4H, CH_2), 1.19 (t, $J = 7.2$ Hz, 6H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, ppm, δ): 141.3, 141.2, 135.7, 135.0, 133.3, 130.2, 127.2, 127.1, 126.1, 124.4, 115.3, 26.3, 15.5; MS *m*/*z*: 606.0 [(M+4)$^+$, 100%]. Elemental analysis calcd for $C_{30}H_{22}Br_2S_2$: C 59.42%, H 3.66%, Br 26.35%, S 10.57%. Found: C 59.47%, H 3.44%, Br 26.62%, S 10.37%.
9. Compound **2** was obtained as yellow solids (yield: 88%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm, δ): 8.15 (s, 2H, Th), 7.13 (m, 20H, Ph), 3.41 (m, 8H, CH_2), 1.27 (m, 12H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, ppm, δ): 141.6, 141.5, 141.4, 141.3, 136.4, 136.3, 135.5, 135.1, 133.6, 130.3, 130.2, 128.1, 127.4, 127.2, 126.9, 126.1, 113.6, 26.8, 26.2, 15.7, 15.3; MALDI-TOF MS *m*/*z*: 969.9 (M$^+$, 100%) (calcd for $C_{56}H_{42}Br_2S_3$ 970.1). Elemental analysis calcd for $C_{56}H_{42}Br_2S_3$: C 69.27%, H 4.36%, Br 16.46%, S 9.91%. Found: C 69.49%, H 4.66%, Br 16.08%, S 9.62%.
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11. Compound **9** was obtained as yellow solids (yield: 86%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm, δ): 7.11 (m, 32H, Ph and Th), 3.44 (m, 12H, CH_2), 1.36 (m, 18H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, ppm, δ): 141.6, 141.5, 141.4, 141.2, 141.0, 140.9, 136.4, 136.1, 135.7, 135.1, 134.9, 134.3, 133.7, 131.0, 130.9, 130.7, 130.5, 130.2, 130.0, 129.8, 128.6, 128.4, 128.3, 127.2, 126.9, 126.0, 112.1, 29.7, 27.0, 26.0, 15.8, 15.5, 15.4; MALDI-TOF MS *m*/*z*: 1134.0 [(M+4)$^+$, 100%], (calcd for $C_{82}H_{62}Br_2S_4$ 1334.2). Elemental analysis calcd for $C_{82}H_{64}Br_2S_4$: C 73.75%, H 4.68%, Br 11.97%, S 9.60%. Found: C 73.48%, H 4.33%, Br 12.05%, S 9.48%. Compound **10** was obtained as yellow solids (yield: 92%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm, δ): 7.70 (d, $J = 7.8$ Hz, 2H, Ar), 7.46 (s, 2H, Th), 7.13 (m, 40H, Ar), 6.57 (d, $J = 7.8$ Hz, 2H, Ar), 3.55 (m, 12H, CH_2), 1.86 (s, 8H, CH_2), 1.45 (m, 18H, CH_3), 0.67 (m, 44H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$, ppm, δ): 151.2, 151.0, 144.1, 141.9, 141.6, 141.3, 141.1, 140.8, 140.5, 136.5, 136.0, 135.7, 135.5, 134.9, 133.3, 132.9, 130.9, 130.5, 130.0, 129.8, 129.2, 128.5, 127.5, 127.2, 126.7, 126.0, 125.5, 122.9, 120.8, 120.6, 119.8, 119.5, 119.4, 55.0, 47.0, 40.1, 40.0, 31.3, 29.5, 27.1, 26.9, 26.3, 26.0, 23.5, 22.4, 16.1, 15.5, 15.4, 13.9; MALDI-TOF MS *m*/*z*: 1841.8 (M$^+$, 100%) (calcd for $C_{132}H_{128}S_4$ 1841.9). Elemental analysis calcd for $C_{132}H_{128}S_4$: C 86.04%, H 7.00%, S 6.96%. Found: C 85.82%, H 7.11%, S 6.76%.
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