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# Linear $C_2$-symmetric polycyclic benzodithiophene: efficient, highly diversified approaches and the optical properties

Cui-Hua Wang,[a] Rong-Rong Hu,[a] Shuang Liang,[a] Jia-Hua Chen,[a] Zhen Yang[a,b,*] and Jian Pei[a,*]

[a]*Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China*
[b]*VivoQuest, Inc. 711 Executive Blvd, Valley Cottage, NY 10989, USA*

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**Abstract**—Two facile approaches to two new series of the seven-rings fused benzodithiophene-based polycyclic aromatics are developed in good yields.


Organic molecules as semiconducting materials are of great interest nowadays in electronic devices, particularly in organic film effect transistors (OFETs),[1] organic light emitting diodes (OLEDs).[2] Among π-conjugated systems, polycyclic aromatics including acenes and derivatives,[3] heteroacenes,[4] ladder-type oligo- and poly(*p*-phenylene),[5] polycyclic aromatic hydrocarbons (PAHs),[6] are most promising because of their rigid, planar, conjugated structures and ordered stacking properties. However, the application of acenes and heteroacenes derivatives is limited due to their liability and poor solubility.

Although benzodithiophene derivatives have been studied in OFETs,[1a,7] few linear sulfur-incorporated fused polycyclic aromatics were reported, probably owing to the deficiency of the feasible synthetic methods. Therefore, development of such new structures and efficient synthetic methodologies for fused polycyclic aromatics is imperative to content the requirement of new organic materials in stability, solubility and processibility.

Scheme 1 illustrates the synthetic route to the key intermediate **3**. 1,4-Dibromo-2,5-diiodobenzene **4** was obtained by selective iodination from the commercially available 1,4-dibromobenzene, and compound **4** then underwent the Sonogashira reaction with four types of terminal alkynes followed by methylthiolation to give the corresponding products **5a**–**d** in good yields. α-Positions of thiophene rings of **4c** were also methylthiolated to produce **5c**. Such mercapto end groups of **5c** were useful for the assembly of the metal surface and the conjugated oligomers to construct the semiconducting molecular wire. It was noteworthy that alkynes with various aromatic substituents could be introduced during the Sonogashira reaction to realize the diversity. Thus, the framework of compounds **3a**–**d**[8] was successfully established by the iodine-induced cyclization developed by Larock.[9]

To improve the solubility of the desired compounds in common organic solvents, **3b** and **3d** were then selected to do the further synthetic transformation with regard to their lipophilic R groups (hexyl and TIPS). Thus, **3b** and **3d** were first coupled with TMS acetylene by the Pd-catalyzed Sonogashira reaction, and then underwent desilylation to give the terminal alkynes **6b** and **6d** in a combined yield of 76% and 78%, respectively. As a result, the poly-fused aromatic molecules **1a** and **1b**[10] were eventually accomplished from **6b** and **6d** by the Pt-catalyzed double cyclization (Scheme 2).[11]

For solubility reason, another type of polyaromatic molecules was also designed based on the *n*-hexyl and TIPS substituted substrates **3b** and **3d**. As described in Scheme 3, **3b** and **3d** were first subjected to the

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* Corresponding authors. Tel.: +86 10 62758145; fax: +86 10 62759105; e-mail addresses: jianpei@pku.edu.cn; yangzhen@pku.edu.cn

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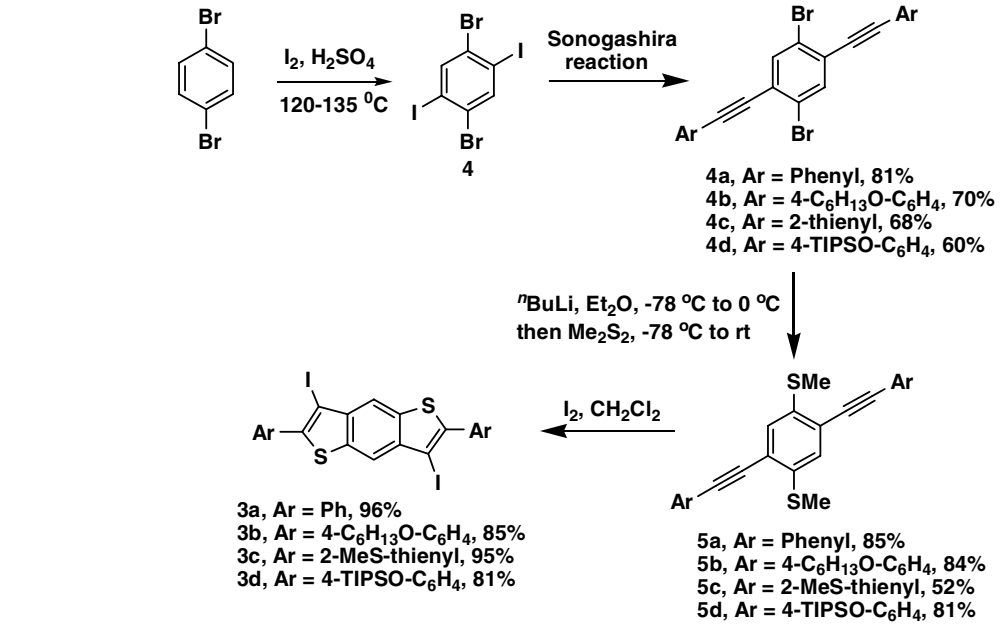
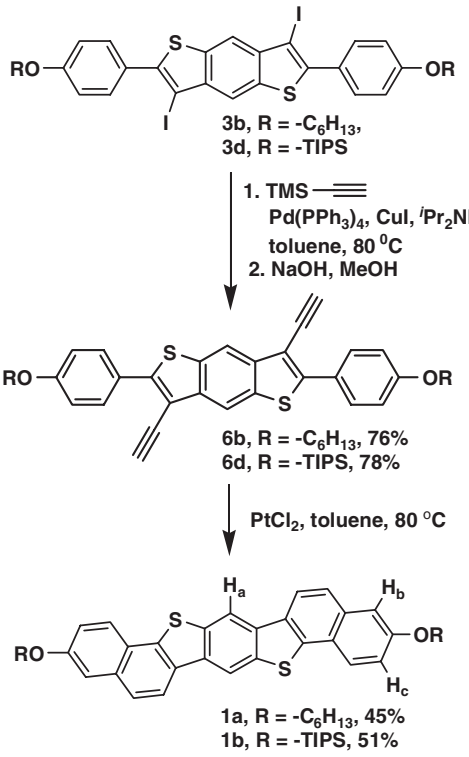



**Scheme 1.**

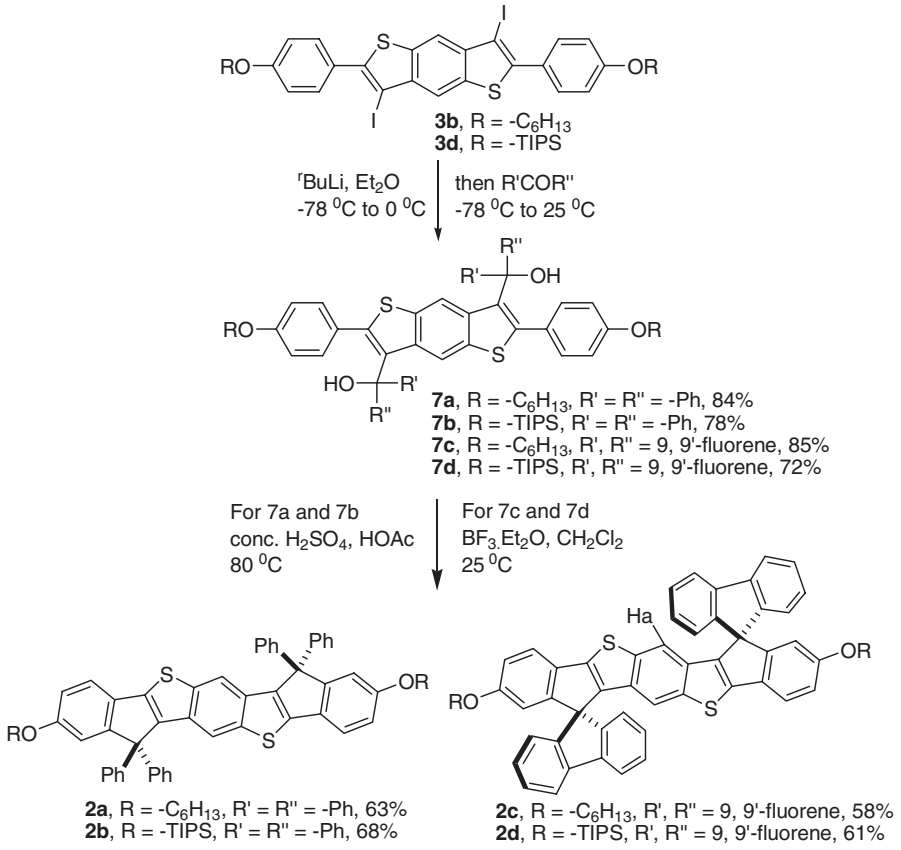



**Scheme 2.**

lithium–halogen exchange by treatment with *t*-BuLi, and then trapped with benzophenone and fluorenone to afford the corresponding tertiary alcohols **7a**–**d**. Eventually, the desired polycyclic molecules **2a**–**d**[12] were achieved by the Friedel–Craft cyclization.[13]

As expected, compounds **2a**–**d** were readily soluble in common organic solvents, which provided us the convenience to get the characterization data. The structure and the purity of all the final products were verified by $^{1}H$, $^{13}C$ NMR and MALDI-TOF MS spectra. It is noteworthy that **1a** showed little solubility in most of the organic solvents, which might be due to the strong intermolecular π–π interactions as well as the ordering aggregation of the lipophilic groups.[14] Compound **1b** had considerate solubility in common solvents, such as $CH_2Cl_2$ and THF, because the bulky –OTIPS group in **1b** effectively reduced the π–π interaction. For spiro-type compounds **2c** and **2d**, we observed the characteristic changes in $^{1}H$ NMR spectra after the cyclization in comparison with those of **7c**–**d** and **1**. For **1b**, the meta-coupling between $H_b$ and $H_c$ split $H_c$ into doublet ($J = 2.4$ Hz) in 7.40–7.41 ppm, and $H_c$ into quaterlet, respectively. The singlet assigned to $H_a$ was shifted downfield from 8.30 to 8.72 ppm because of the formation of the larger π-conjugated system. However, the singlet signal of $H_a$ in **2d** moved to upfield (6.88 ppm) due to the effect of the circle current of the spiro-cyclic structure (Scheme 3 and Fig. 1).

We also investigated the electric optical properties for **1a**–**b**, **2a**–**d** in dilute solutions. Normally, π-conjugated oligomers and polymers exhibit the strong π–π* electron absorption behaviors in the ultraviolet and visible region. All the new compounds showed strong fluorescence under UV irritation. Table 1 summarizes the results of the absorption and emission of compounds **1a**–**b** and **2a**–**d** at room temperature. Figures 2 and 3 illustrate UV–vis and fluorescent spectra of these six compounds in dilute THF solutions, respectively. Both absorption and emission spectra of all compounds revealed a characteristic behavior because of the well-defined structure of these compounds in solutions. Owing to the same backbone, **1a** showed the same absorption features as **1b**, in which the absorption peaked at 348 nm with several vibronic behaviors at 361 and 374 nm, respectively. **2a**–**d** also showed the similar




**Scheme 3.**

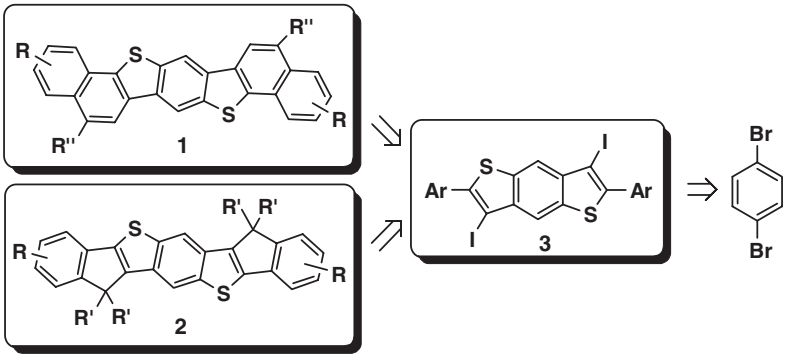



**Figure 1.** Retrosynthetic analysis.

**Table 1.** Photophysical properties of compounds **1a**–**1b** and **2a**–**d** in dilute THF solutions at room temperature (bold means the maximum peak)

| Compounds | $\lambda_{abs}$ (nm) | $\lambda_{PL}$ (nm) |
|---|---|---|
| **1a** | **348**, 360, 372 | 362, **382.5**, 407 |
| **1b** | **348**, 361, 374 | 363, **383.5**, 407.5 |
| **2a** | 349, 364, 384, **408** | 403.5, **424**, 452 |
| **2b** | 348, 363, 384, **407** | 402, **423.5**, 451.5 |
| **2c** | 348, 363, 383, **407** | 401.5, **423**, 451 |
| **2d** | 348, 362, 382, **406** | 403.5, **421.5**, 450 |

absorption spectra and exhibited the maximum absorptions at 407 and 383 nm, respectively. The aromatic substituents at methylene bridge did not play any role on

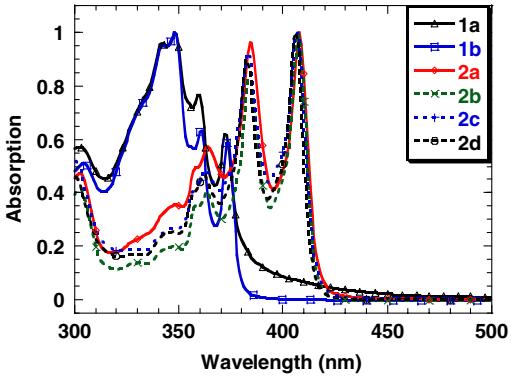



**Figure 2.** Normalized absorbance spectra of **1a**–**b**, **2a**–**d** recorded in dilute THF solutions at room temperature.

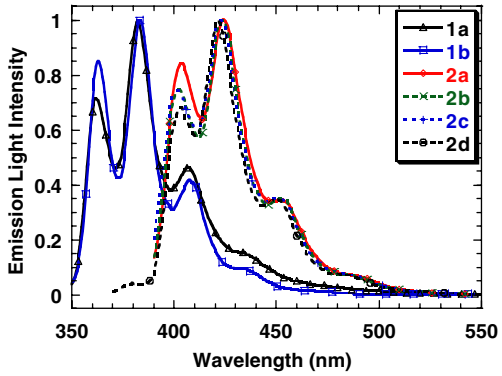



**Figure 3.** Normalized fluorescence spectra of **1a**–**b**, **2a**–**d** recorded in dilute THF solutions at room temperature.

the effective conjugation length of the backbone due to $sp^3$-hybrid carbon atoms.[10] Moreover, the absorption maximum peaks of **2a**–**d** red-shifted about 59 nm in comparison with those of **1a**–**b**, which meant that the effective conjugation length of **2a**–**d** were longer than those of **1a**–**b**. The absorption spectra of **2a**–**d** obviously red-shifted in comparison with that of the ladder oligo(*p*-aniline) (378 nm) were close to those of ladder oligo(*p*-phenylene).[5f] In comparison with the silicon-incorporated ladder oligo(*p*-phenylene), the absorption of **2a**–**d** slightly blue-shifted about 25 nm.[5d]

The emission behaviors of all compounds showed the well-defined vibronic structures. The emission spectra of compounds **1a** and **1b** exhibited the maximum at about 383 nm with two peaks at 362 and 407 nm, respectively. Compounds **2a**–**d** peaked at about 424 nm with two shoulders at about 402 and 451 nm, respectively. We also observed the smaller Stock's shift for **2a**–**d**, which indicated that no obvious aggregation or interchain interactions for **2a**–**d** were formed in the excited states due to the steric structures.

In summary, we have developed an efficient and highly diversified route to construct novel, unique linear fused π-conjugated polycyclic systems. These sulfur-incorporated fused polycyclic aromatics show interesting optical properties. The maximum absorption peaks of **2a**–**d** obviously red-shifted compared to those of **1a**–**b**. The properties in thin solid films including the carrier mobility are still under investigation in our laboratory. These linear polycyclic aromatic derivatives should also be of potential application as semiconducting materials.

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8. Compounds **3a**–**d** were obtained as solids. **3b** (yield: 87%): $^1$H NMR (300 MHz, $CDCl_3$, ppm): $\delta$ 0.91–0.95 (t, 6H), 1.36–1.50 (m, 12H), 1.80–1.85 (m, 4H), 4.01–4.06 (t, 4H), 7.0–7.03 (d, $J = 9.0$ Hz, 4H), 7.66–7.69 (d, $J = 9.0$ Hz, 4H); 8.21 (s, 2H); $^{13}$C NMR (100.6 MHz, $CDCl_3$, ppm): $\delta$ 14.1, 22.6, 25.7, 29.2, 31.6, 68.1, 103.5, 114.4, 119.1, 126.5, 131.2, 136.8, 140.6, 143.3, 159.8; MS *m*/*z* (EI): 794 ($M^+$, 100%). **3c**: $^1$H NMR (300 MHz, $CDCl_3$, ppm): $\delta$ 2.60 (s, 6H), 7.10–7.12 (d, 2H), 7.49–7.51 (d, 2H), 8.14–8.16 (d, 2H); MS *m*/*z* (EI): 698 ($M^+$, 100%). **3d** (yield: 80%): $^1$H NMR (300 MHz, $CDCl_3$, ppm): $\delta$ 1.13–1.16 (d, 36H), 1.27–1.34 (m, 6H), 6.98–7.01 (d, $J = 8.4$ Hz, 4H), 7.60–7.63 (d, $J = 8.4$ Hz, 4H), 8.21 (s, 2H); $^{13}$C NMR (100.6 MHz, $CDCl_3$, ppm): $\delta$ 12.7, 17.9, 119.2, 119.9, 127.1, 131.2, 136.8, 140.7, 143.4, 157.0; MS *m*/*z* (EI): 938 ($M^+$, 100%).

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10. Compounds **1a**–**b** were obtained as solids. **1b** (yield: 51%): $^{1}$H NMR (400 MHz, $CD_2Cl_2$, ppm): $\delta$ 1.12–1.16 (d, 36H), 1.32–1.34 (m, 6H), 7.27–7.30 (q, $J = 2.4$ Hz, $J = 8.8$ Hz, 2H), 7.40–7.41 (d, $J = 2.4$ Hz, 2H), 7.77–7.79 (d, $J = 8.8$ Hz, 2H), 8.02–8.04 (d, $J = 8.8$ Hz, 2H), 8.19–8.21 (d, $J = 8.8$ Hz, 2H), 8.72 (s, 2H); $^{13}$C NMR (100.6 MHz, $CDCl_3$, ppm): $\delta$ 12.8, 18.0, 114.7, 115.1, 116.2, 119.9, 122.4, 124.3, 124.7, 125.9, 130.3, 131.7, 134.0, 135.7, 136.1, 137.1, 138.0; MS *m*/*z* (EI): 734 ($M^+$, 100%).
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12. Compounds **2a**–**b** were obtained as solids. **2a** (yield: 63%): $^{1}$H NMR (300 MHz, $CDCl_3$, ppm): $\delta$ 0.87–0.90 (t, 6H), 1.30–1.32 (m, 8H), 1.42–1.55 (m, 4H), 1.71–1.75 (m, 4H), 3.89–3.92 (t, 4H), 6.83–6.86 (q, 2H), 7.00 (d, 2H), 7.21–7.38 (m, 20H), 7.38–7.40 (d, 2H), 7.87 (s, 2H); $^{13}$C NMR (100.6 MHz, $CDCl_3$, ppm): $\delta$ 14.0, 22.6, 25.7, 29.2, 31.6, 64.4, 68.3, 112.9, 113.0, 116.4, 120.3, 126.9, 128.4, 128.5, 130.4, 131.0, 141.7, 142.3, 143.0, 145.2, 158.1, 158.8; MALDI-TOF MS: 870 ($M^+$, 100%). **2b** (yield: 68%): $^{1}$H NMR (300 MHz, $CDCl_3$, ppm): $\delta$ 0.99–1.05 (d, 36H), 1.14–1.21 (m, 6H), 6.83–6.86 (q, $J = 2.1$ Hz, 2H), 6.95–6.96 (d, $J = 2.1$ Hz, 2H), 7.21–7.29 (m, 22H), 7.90 (s, 2H); $^{13}$C NMR (100.6 MHz, $CDCl_3$, ppm): $\delta$ 12.5, 17.8, 64.3, 116.4, 117.8, 119.0, 120.3, 126.9, 128.3, 128.4, 130.7, 131.0, 141.7, 142.9, 145.3, 155.5, 158.0; MALDI-TOF MS: 1014 ($M^+$, 100%). **2c** (yield: 53%): $^{1}$H NMR (300 MHz, $CDCl_3$, ppm): $\delta$ 0.81–0.86 (m, 6H), 1.23–1.34 (m, 12H), 1.54–1.63 (m, 4H), 3.72–3.77 (m, 4H), 6.23–6.24 (d, $J = 2.1$ Hz, 2H), 6.71–6.74 (d, $J = 7.5$ Hz, 4H), 6.78–6.82 (q, $J = 2.4$ Hz, 4H), 6.85 (s, 2H), 7.04–7.09 (t, 4H), 7.37–7.42 (m, 6H), 7.93–7.95 (d, $J = 7.5$ Hz, 4H); $^{13}$C NMR (100.6 MHz, $CDCl_3$, ppm): $\delta$ 14.0, 22.5, 25.6, 29.2, 31.5, 63.7, 68.1, 110.8, 112.9, 114.9, 115.8, 120.1, 120.3, 123.9, 127.9, 128.0, 130.1, 131.6, 141.5, 141.7, 143.9, 146.0, 154.3, 158.7; MALDI-TOF MS: 866 ($M^+$, 100%). **2d** (yield: 61%): $^{1}$H NMR (300 MHz, $CDCl_3$, ppm): $\delta$ 0.91–0.94 (d, 36H), 1.04–1.09 (m, 6H), 6.17–6.18 (d, $J = 2.4$ Hz, 2H), 6.70–6.73 (d, $J = 7.8$ Hz, 4H), 6.77–6.80 (q, $J = 2.4$ Hz, 4H), 6.88 (s, 2H), 7.03–7.08 (t, 4H), 7.32–7.42 (m, 6H), 7.93–7.95 (d, $J = 7.8$ Hz, 4H); $^{13}$C NMR (100.6 MHz, $CDCl_3$, ppm): $\delta$ 12.5, 17.8, 63.6, 114.9, 116.2, 118.7, 119.9, 120.2, 123.8, 127.8, 128.0, 130.2, 132.1, 141.5, 141.6, 141.8, 144.0, 145.8, 154.2, 155.4; MALDI-TOF MS: 1010 ($M^+$, 100%).
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