



# Synthesis and characterization of symmetrical sulfur-fused polycyclic aromatic hydrocarbons with controlled shapes



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## ABSTRACT

Here we report and establish a facile synthetic method for these unprecedented sulfur-fused polycyclic aromatic hydrocarbons (S-PAHs) with symmetrical structures ( $C_2$ -rectangle and  $D_{6h}$ -hexagonal shape). Characterization by laser desorption/ionization time-of-flight mass spectrometry unambiguously validate the successful formation of these novel S-PAHs. The  $C_2$ -rectangle and  $D_{6h}$ -hexagonal-shaped S-PAHs (**1** and **2**) are obtained by Scholl-type cyclodehydrogenation of the corresponding precursor using  $FeCl_3$  as an oxidant, and their spectral characteristics, thermal and electrical properties are investigated.

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## 1. Introduction

Enormous interest exists in the development of  $\pi$ -electron materials because they exhibit electronic, optoelectronic, and magnetic properties that are suitable for their potential application in molecular electronics.<sup>1,2</sup> Compared to  $\pi$ -conjugated polymers, polycyclic aromatic hydrocarbons (PAHs) possessing unique physicochemical characteristics that have served as active components of organic electronic devices such as field-effect transistors, light-emitting diodes, solar cells and supramolecular materials field.<sup>3</sup> Compared with full carbon analogues, partially introduced the heteroatom, such as nitrogen,<sup>4</sup> sulfur,<sup>5</sup> as well as oxygen,<sup>6</sup> into the aromatic skeleton of PAHs, will unexpectedly lead to dramatic changes in their physicochemical and/or electronic properties by changing such as polarity, electron density, dipole and band-gap of the molecule.<sup>7</sup> Sulfur has a similar electronegativity (2.58) to that of carbon (2.55) in the graphitic layers,<sup>8</sup> which is effective in modifying the electronic arrangement. Consequently, special emphasis is given to sulfur heteroatom PAHs (Scheme 1), and their unique electronic, optical, and redox properties and self-assembling properties are interesting.<sup>9</sup> Herein, we are particularly interested in S-PAHs and reported the synthesis, characterization of

symmetrical S-PAHs (**1** and **2**) with controlled shapes (Scheme 2). The  $C_2$ -rectangle and  $D_{6h}$ -hexagonal-shaped S-PAHs (**1** and **2**) in which four or six double bonds in the periphery are thieno-fused, respectively. The structures of the S-PAHs (**1** and **2**) were characterized by MALDI-TOF MS, and their spectral characteristics, thermal and electrical properties were investigated.

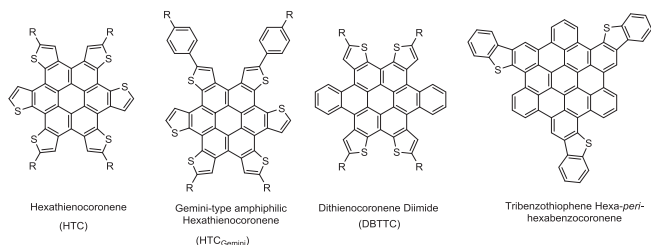
## 2. Results and discussion

### 2.1. Synthesis of S-PAHs (**1** and **2**)

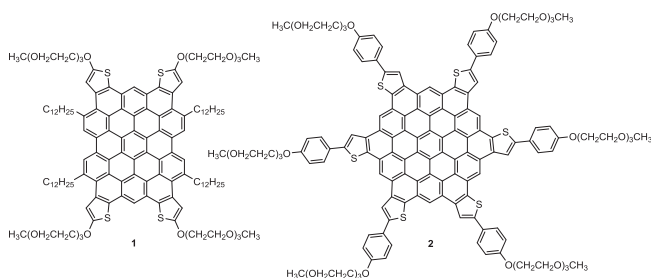
The  $C_2$ -rectangle-shaped S-PAH (**1**) possesses four hydrophilic TEG chains on the around. To achieve the  $C_2$ -symmetric functionalization of the core, a strategy with introduction of hydrophilic segments to compound **11** followed by oxidative cyclization was adopted (Scheme 3). 1,3-dibromo-5-(bromomethyl)-benzene was allowed to react with *p*-toluenesulfonylacetonitrile (**6**) in DMSO-Et<sub>2</sub>O in the presence of 37% HCl/NaOH, yielding **7** in 65% yield.<sup>10</sup> Subsequently, the reaction of 1,3-bis(3,5-dibromophenyl)-2-propanone (**7**) with 1,2-bis(4-dodecylphenyl)-1,2-ethanedione (**8**)<sup>11</sup> in dioxane using Bu<sub>4</sub>NOH afforded cyclopentadienone derivative **9** in 41% yield. Compound **9** was subjected to Diels-Alder reaction with bis(4-dodecylphenyl)acetylene (**10**),<sup>11</sup> giving **11** in high yield (71%). Then, the Suzuki-coupling reaction between **11** and thiophene- $\alpha$ -boronic esters **5** afforded the precursor **12** in 36% yield. Finally, the Oxidative cyclization of **12** by  $FeCl_3/CH_3NO_2$  in

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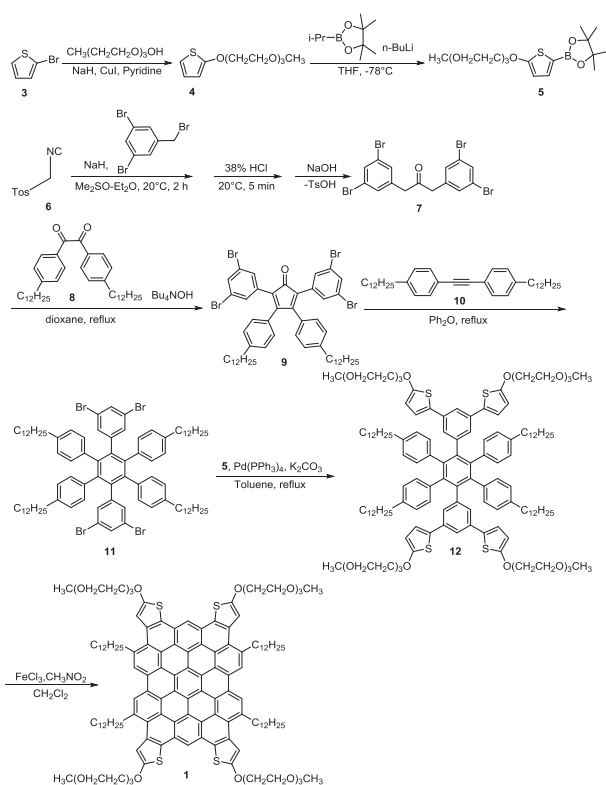
E-mail address: [wjjin@dhu.edu.cn](mailto:wjjin@dhu.edu.cn) (W. Jin).



Scheme 1. Molecular structures of S-PAHs with specific shapes.



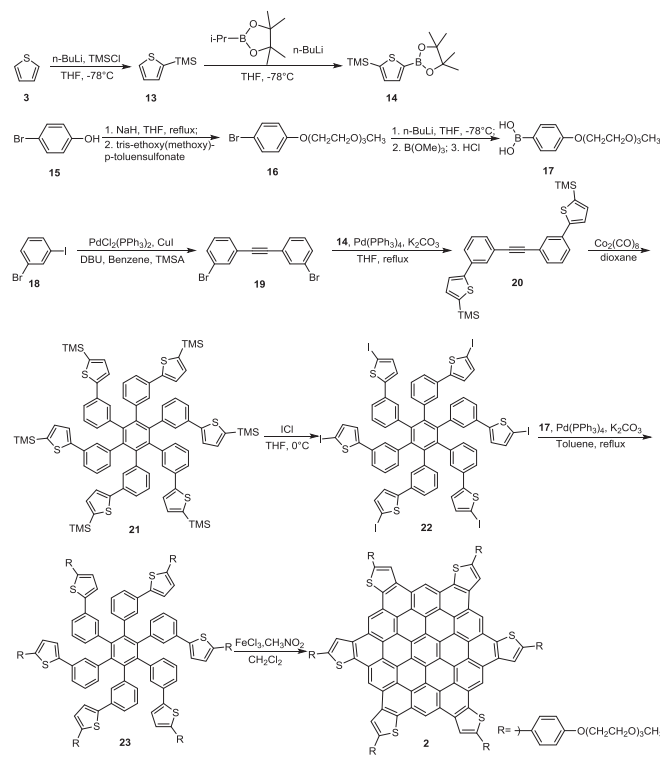
Scheme 2. Molecular structures of 1 and 2.



Scheme 3. Synthetic route of 1.

$\text{CH}_2\text{Cl}_2$  resulted in the formation of the fully cyclodehydrogenated **1** in 68% yield.

The  $D_{6h}$ -hexagonal-shaped S-PAH (**2**) possesses six hydrophilic TEG chains in the periphery. To achieve the  $D_{6h}$ -symmetric functionalization of the core, a strategy with introduction of hydrophilic segments to **22** followed by oxidative cyclization was adopted (Scheme 4). 2,2'-(1,2-ethynediyl-di-3,1-phenylene)bis[5-(trimethylsilyl)-thiophene] (**20**) was synthesized using thiophene and 3-



Scheme 4. Synthetic route of 2.

bromoiodobenzene as starting materials. The reaction of thiophene with trimethylchlorosilane and further reaction with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane afforded 4,4,5,5-tetramethyl-2-[5-(trimethylsilyl)-2-thienyl]-1,3,2-dioxaborolane (**14**).<sup>12</sup> Next, the Suzuki-coupling reaction between **14** and bis(3-bromophenyl) acetylene (**19**)<sup>13</sup> in THF using  $\text{Pd}(\text{PPh}_3)_4/\text{K}_2\text{CO}_3$  afforded **20** in 80% yield. Then the cobalt-catalyzed cyclotrimerization of **20**, giving 2,2'-[2',3',5',6'-tetrakis[3-[5-(trimethylsilyl)-2-thienyl]phenyl][1,1':4',1''-terphen-yl]-3,3''-diyl]-bis[5-(trimethylsilyl)-thiophene] (**21**) in 80% yield, and further substitution with iodine monochloride afforded **22** in 62% yield. Next, the Suzuki-coupling reaction between **22** and [4-[2-[2-(2-Methoxyethoxy)-ethoxy]ethoxy]phenyl]boronic acid (**17**)<sup>14</sup> was carried out in toluene using  $\text{Pd}(\text{PPh}_3)_4/\text{K}_2\text{CO}_3$ , affording the precursor **23** in 58% yield. Finally, the Oxidative cyclization of **23** by  $\text{FeCl}_3/\text{CH}_3\text{NO}_2$  in  $\text{CH}_2\text{Cl}_2$  resulted in the formation of **2** in 60% yield. However, the Suzuki-coupling reaction between **22** and **17** generated a small amount of five sites substitution impurity, which has brought difficulty to the purification (Fig. S1). Therefore, we decided to give up this synthetic route and explore the better one.

Eventually, we established a facile and rapid synthetic method for S-PAH **2** (Scheme 5). Bis(3-bromophenyl) acetylene was allowed to react with bispinacolateboron in DMF in the presence of  $\text{PdCl}_2(\text{dppf})/\text{AcOK}$ , yielding **25** in 70%. And then the Suzuki-coupling reaction between **25** and **28** in toluene using  $\text{Pd}(\text{PPh}_3)_4/\text{K}_2\text{CO}_3$  gave **29** in 65% yield. The cobalt-catalyzed cyclotrimerization of **29**, giving the precursor **23** in 78% yield, which was transformed into the target compound **2** by cyclodehydrogenation in 60% yield.

The recording of NMR spectroscopy did not succeed for S-PAHs (**1** and **2**) due to the aggregation propensity of the molecules in solution,<sup>15</sup> so they were characterized by MALDI-TOF mass spectrometry. MALDI-TOF mass spectra showed the molecular ion-peak at 2164.3990 for **1** (Fig. 1a) and 2433.5918 for **2** (Fig. 1b) respectively, which coincided with their theoretical value of molecular

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