



# Novel functional sulfur-bridged neutral annulene: Structure, physical properties and progress on field-effect performance



Hang Liu <sup>a,b</sup>, Yunke Qin <sup>a,b</sup>, Dazhen Huang <sup>a,b</sup>, Wei Xu <sup>a,\*</sup>, Daoben Zhu <sup>a,\*</sup>

<sup>a</sup> Beijing National Laboratory for Molecular Sciences, Organic Solids Laboratory, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, PR China

<sup>b</sup> Graduate School of Chinese Academy of Sciences, Beijing 100049, PR China

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## ABSTRACT

The novel aromatic heteromacrocycle, *p*-bromophenyl substituted tetrathia[22]annulene[2,1,2,1] was synthesized as a convenient derivable building block to obtain a variety of tetrathia[22]annulene[2,1,2,1] derivatives, which were recently found to be promising *p*-type semiconducting materials for OFETs with some unique properties. Furthermore the annulene itself was found to perform well as an active material in OFETs. A thin film transistor based on the annulene had the best hole mobility of 0.73 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> and the on/off ratio of 1.4 × 10<sup>7</sup>, which are class leading amongst the macrocyclic field-effect materials.

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## 1. Introduction

Organic field-effect transistors (OFETs), which were first reported in the 1980s [1], are not only the important building blocks for the next generation low-cost, easier fabricating, large area, flexible electronics, but also essential tools for the theoretical study of the electrical transport properties of  $\pi$ -conjugated systems [2].

With the advance in the past decades, the mobilities of organic thin film transistors and single crystal transistors have reached several tens of cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. However, the task to achieve even higher mobility to compete with traditional organic materials is much more difficult because we still lack the knowledge regarding structure-property relationships for understanding the fundamental chemical aspects behind the structural design, and realization of desired properties. Therefore, it is of great importance to develop new types of materials besides the  $\pi$ -conjugated systems widely studied in Refs. [3], for example, fused ring compounds [4–6], linear oligomers [7,8] and polymers [9,10].

Cyclic conjugated compounds have attracted increasing attention due to their potential in the fields of supramolecular chemistry and materials science. On one hand, cyclic conjugated molecules

usually have highly rigid backbones and internal cavities close to the nanometer scale, therefore they can form various supramolecular assemblies, such as extended tubular channels [11], liquid crystals [12], and host–guest complexes [13]. On the other hand, because of the well-defined structures and extended conjugation of these macrocycles, they may have interesting optical, electronic, and magnetic properties and can be ideal materials in organic conductors, organic field-effect transistors (OFETs), nonlinear optics (NLOs), and organic solar cells [14–21].

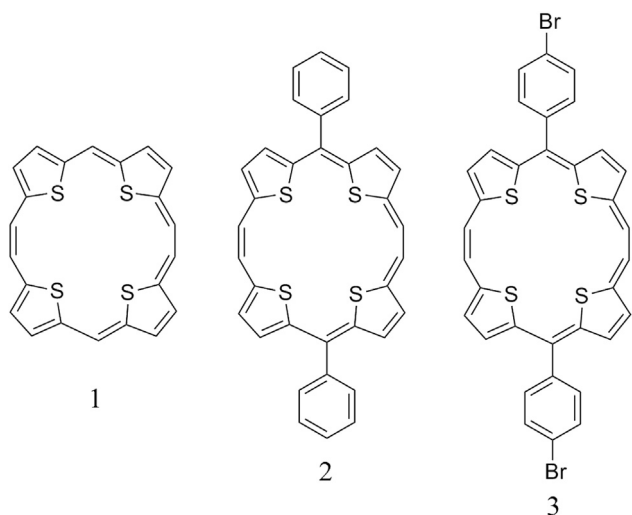
However, to the best of our knowledge, applications of cyclic conjugated compounds in modern molecular electronics were scarcely studied except a few examples including porphyrins [22,23], cyclopyrroles [24,25], and ethylene linked triphenylamine cyclic dimers [26]. Cyclic conjugated molecules have shape-persistent frameworks, well-defined structures and a propensity for crystallization, but excluding perturbing end-effects of their corresponding linear oligomers and polymers. They usually have interesting optical and electronic properties and can also provide charge transfer channels in certain stacks, therefore, the research on cyclic conjugated compounds can not only add high performance new entities to the family of electronic materials, but also provide brand-new examples regarding structure-property relationships for understanding the fundamental chemical aspects behind the structural design, and realization of desired properties.

\* Corresponding authors.

E-mail address: [wXu@iccas.ac.cn](mailto:wXu@iccas.ac.cn) (W. Xu).

Bearing this feature in mind, in recent years, we have studied a series of cyclic conjugated compounds and found tetrathia[22]annulene[2,1,2,1] (**1**) derivatives were promising organic field-effect materials [27]. The thin film transistors based on meso-phenyl substituted tetrathia[22]annulene[2,1,2,1] (**2**) depicted an average highest hole mobility of  $0.44 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , although there were some uncontrolled deficiencies such as low on/off ratios ( $3 \times 10^2$ ) [28]. Recently, we demonstrated the feasibility of growing crystals of a self-assembled mixed-stack donor–acceptor complex from a solution of equivalent donor (**2**) and acceptor (7,7,8,8-tetracyanoquinodimethane or fullerenes). The crystals exhibited ambipolar behavior as demonstrated by single-crystal field-effect transistors based on these ‘molecular level heterojunctions’ which displayed ambient stable balance electron and hole mobilities ( $>10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for electron and  $0.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for hole based on co-crystal of C70-compound **2**) [29,30]. These results provided a brand-new strategy for the construction of ambipolar devices.

Because of the good performance of the phenyl-substituted tetrathia[22]annulene[2,1,2,1] (**2**), our further study focused on the chemical modification of **2**, including the substitution with different functional groups, introduction of linear or branched alkyl chains, construction of supermolecular donor–acceptor structures and extension of the conjugated system. Our preliminary effort had made little progress because the modification of tetrathia[22]annulene[2,1,2,1] derivatives (including **2**) from the starting materials had many restrictions and was quite condition-dependent, only a few specific examples had succeeded [28,31]. Based upon these, to reserve active positions and modify the molecule after the ring-formation would be a more feasible and effective strategy. Considering the importance and convenience of bromide in halogen exchanging reactions, nucleophilic substitutions and most importantly, metal catalyzed cross couplings, we designed the novel derivatisable *p*-bromophenyl substituted tetrathia[22]annulene[2,1,2,1] (**3**). In the first place, the bromines at the symmetrical ends of the molecule had both activation and selectivity in further derivation. Secondly, bromine had large atom diameter and weight but weak electron-drawing effect, therefore, it might greatly change the stacking pattern without much influence on the frontier orbital energy level of the molecule. That is to say, the OEFT performance of **3** itself could hopefully be improved by these controlled changes. In the last point, this work would provide a new example regarding structure–property relationships for understanding the fundamental chemical aspects behind the structural design, and realization of desired properties.



**Scheme 1.** Structure of tetrathia[22]annulenes[2,1,2,1].

In this work, we successfully synthesized **3** using a convenient four-step procedure including acid-induced condensation, Vilsmeier formylation, binary McMurry coupling and oxidative dehydrogenation. The crystal structure of **3** was determined and its optical and electronic properties were studied in detail. The thin film devices based on **3** were also fabricated using a vacuum deposition method. The derivation work using **3** as the building block and the study of these new compounds would be reported in our further publications.

## 2. Experimental

### 2.1. General

THF was distilled over sodium benzophenone ketyl before use. All other reagents and solvents were purchased from commercial suppliers and used directly without further treatment.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were performed in  $\text{CDCl}_3$ ,  $\text{CD}_2\text{Cl}_2$  or Tetrahydrofuran- $\text{D}_8$  with TMS as internal standard on Bruker Advance 400 MHz spectrometers. EI-MS measurements were performed on SHIMADZU GCMSQP2010 or UK GCT-Micromass spectrometers. MALDI-TOF mass spectrometric measurements were performed with a Bruker Biflex III 45 MALDI-TOF spectrometer. HRMS measurements were performed on a Bruker APEXII FT-ICRMS spectrometer. Elemental analyses were measured on a Carlo Erba 1106 elemental analyzer. UV–Vis spectra were recorded on a JASCO V-570 spectrometer.

Suitable crystals of **3** were obtained by slow evaporation of a tetrahydrofuran solution. X-ray crystallographic data were collected with a Bruker smart CCD diffractometer by using graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The data were collected at 173 K and the structure was resolved by the direct method and refined by full-matrix least-squares on  $F^2$ . The computation was performed with the SHELXL-97 program. H atoms bound to C were placed at calculated positions. Further details on the crystal structure investigation have been deposited with The Cambridge Crystallographic Data Centre as supplementary publication CCDC 973740. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: þ44 0 1223 336033 or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

### 2.2. Synthesis

The synthesis of **compound 3** involved 4 steps. **Scheme 2** illustrates the synthesis route of the target compound.

#### 2.2.1. 2,2'-((4-bromophenyl)methylene)dithiophene (**4**)

To the solution of 4-bromobenzaldehyde (9.25 g, 50 mmol) and thiophene (9.6 mL, 120 mmol) was added amberlyst 15 (1.0 g), the mixture was stirred for 4 h at  $80^\circ\text{C}$ . The mixture was diluted with dichloromethane (300 mL) and the solid was removed by filtration. The solvent was removed and the residue was purified by column chromatograph (100% of petroleum ether as eluent) to give compound **4** (8.40 g, 50%) as white solid. mp:  $64\text{--}65^\circ\text{C}$ ; IR (KBr,  $\text{cm}^{-1}$ ):  $\nu$ : 3093, 2873, 1585, 1482, 1431, 1403, 1275, 1231, 1123, 1069, 1006, 817, 788, 764, 708;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.85 (s, 1H), 6.83–6.84 (d, 2H,  $J = 2.8 \text{ Hz}$ ), 6.95–6.98 (t, 2H,  $J = 4.4 \text{ Hz}$ ), 7.19–7.25 (m, 4H), 7.46–7.48 (d, 2H,  $J = 8.0 \text{ Hz}$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  45.92, 120.20, 124.00, 125.29, 125.77, 129.16, 130.73, 141.78, 145.94; EI-MS  $m/z(M)^+$ : 334, 336 (1:1); Anal. Calcd for  $\text{C}_{15}\text{H}_{11}\text{BrS}_2$ : C, 53.73; H, 3.31. Found: C, 53.96; H, 3.53.

#### 2.2.2. 5,5'-((4-bromophenyl)methylene)bis(thiophene-2-carbaldehyde) (**5**)

Phosphorus oxychloride (9.5 mL, 100 mmol) was added dropwise at  $0^\circ\text{C}$  under  $\text{N}_2$  to compound **4** (6.70 g, 20 mmol) in DMF

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