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A Simple Route to Sulfur Bridged Annulenes

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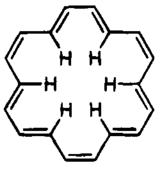
The McMurry coupling reaction of thiophene-derived dialdehydes has been employed as the key step in the synthesis of the sulfur-bridged annulenes **3**, **4**, **6−9**, and **14**. Dication **9** is the second example of a peripherally aromatic (26 π) dication of this class, while the 22 π annulene **14** is the first neutral aromatic annulene derived solely from thiophene.

The [18]annulene **1** has been regarded as a fundamental structure in annulene chemistry. It complies with Hückel's rule and clearly demonstrates the existence of an aromatic ring current by its ^{1}H NMR data.[1] Viewed as an annulene, the porphyrin system **2** can be regarded as a bridged heterocyclic structural varient of [18]-annulene. Compared to the numerous studies of nitrogen bridged porphyrin analogs, sulfur bridged annulenes have been much less studied. In 1964, the first thiophene derived annulene **3**, a heterocyclic derivative of [18]-annulene with three sulfur bridges, was reported.[2] Since then, a great deal of effort has been made toward the synthesis of annulenes containing mixed heteroatom bridges. Thus, sulfur-containing porphyrins, sulfur-containing sapphyrins, a sulfur-containing porphycene, and other mixed sulfur-containing conjugated macrocycles have been reported.[3−13] Several additional annulenes bridged only by sulfur atoms have subsequently been described. The first of these, the [24]annulene tetrasulfide **4**, a higher homolog of **3**, was synthesized in 1977 by use of a low temperature Wittig reaction.[14]



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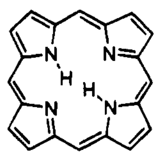

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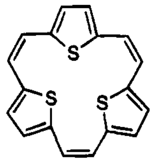
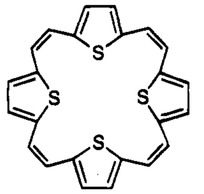


3

Even though sulfur bridged annulene **3** is a $[4n + 2]\,\pi$ system, there is no significant ring current in this 18 π annulene as evidenced by its spectroscopic data. The molecule apparently possesses no more aromaticity than that provided by the three thienyl groups. A theoretical analysis also suggested that annulene **3** is not a planar molecule, and that it may be viewed as a combination of independent thiophene and vinyl units rather than as a conjugated annulene.[15] The [24]annulene tetrasulfide **4** is also a very stable macrocycle, even though it is formally a $4n\ \pi$ antiaromatic system. Furthermore, no antiaromatic ring current was observed in this annulene.



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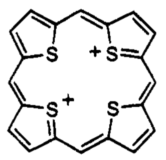

5

The only peripherally aromatic sulfur bridged annulene, the 18 π dicationic thiophene analog **5** of a porphyrin, was reported in 1989 by Vogel and co-workers.[16] They observed two singlets of the thiophene and the bridge protons appear at 10.52 and 12.46 ppm, respectively, demonstrating a very strong aromatic ring current.

It has been shown that partial replacement of the nitrogen atoms of the porphyrin system by sulfur atoms results in a longer wavelength absorption in the UV-visible spectrum.[3,4] On the other hand, the two neutral annulenes **3** and **4** behave only as arrays of isolated thiophene units, as described above. We have been interested in synthesizing new thiophene derived annulenes and in making the earlier members more accessible. We now report the synthesis of a number of additional thiophene derived annulenes and a simple route to the known **3** and **4**, using the McMurry coupling reaction as the key synthetic step.

Results and Discussion

McMurry Coupling of 2,5-Thiophenedicarboxaldehyde. The two annulenes **3** and **4** have been synthe-

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[7] DuVernet, R. B.; Wennerström, O.; Lawson, J.; Otzubo, T.; Boekelheide, V. *J. Am. Chem. Soc.* **1978**, *100*, 2457.

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[9] De Munno, G.; Lucchesini, F.; Neidlein, R. *Tetrahedron* **1993**, *49*, 6863. This paper describes the synthesis of a dithiaporphycene closely related to tetrathiaporphycene **6**.

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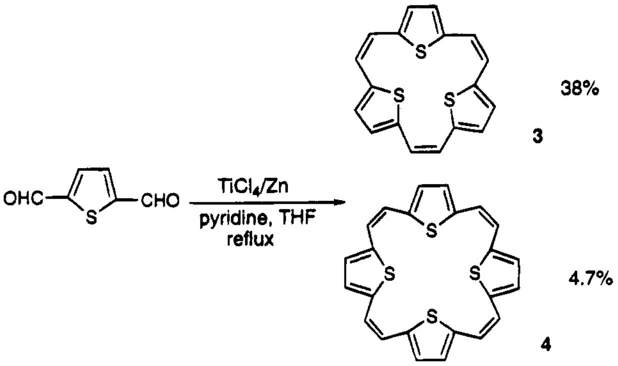
Scheme 1. Monothiophene-Derived Annulenes



sized earlier in multistep procedures in low yield, as mentioned previously. We decided to examine the possibility of obtaining them directly by the McMurry coupling of 2,5-thiophenedicarboxaldehyde, a reaction which could give numerous products, including mainly polymers and linear oligomers containing vinylene thiophene units.

2,5-Thiophenedicarboxaldehyde was prepared according to a literature procedure.[17] The McMurry coupling was then carried out using a $TiCl_4/Zn$ reagent. We were pleased to discover that in the coupling reaction, the formation of cyclic products is favored to an appreciable extent, the [18]annulene trisulfide and [24]annulene tetrasulfide being obtained together in a surprisingly high yield. The two annulenes are readily separated by column chromatography on silica with hexane as eluent. Compared to the previously reported synthesis (ca. 1% overall yield), this is a simple and efficient method to synthesize [18]annulene trisulfide (38% yield). While the yield of the tetrasulfide was only 4–5%, its direct synthesis is still the most convenient one (Scheme 1).

From spectroscopic observations and theoretical calculations, it has been suggested that annulene **3** is not planar, with three sulfur atoms pointing to the same side or one of them pointing to the other side.[2,15] An X-ray analysis of a single crystal of **3** grown from a hexane solution confirmed that the three thiophene units are totally out of plane (Figure 1). Crystal data and a summary of data collection parameters for this annulene are listed in Table 1.[18]

McMurry Coupling of 2,2′-Bithiophene-5,5′-dicarboxaldehyde. Porphycene[19a] is an isomer of porphyrin constructed from two bipyrrole and two ethene units. It behaves as a very interesting new aromatic porphyrinoid having properties similar to porphyrin. Its furan analog, tetraoxoporphycene, and the corresponding aromatic dication have been reported,[19b] as well as a thiophene-pyrrole mixed porphycene analog.[10] However, the all-thiophene analog of porphycene, namely tetrathiaporphycene, has not been described and even its possible stability has been questioned.[20] It was therefore of interest to attempt its synthesis from 2,2′-bithiophene-5,5′-dicarboxaldehyde.

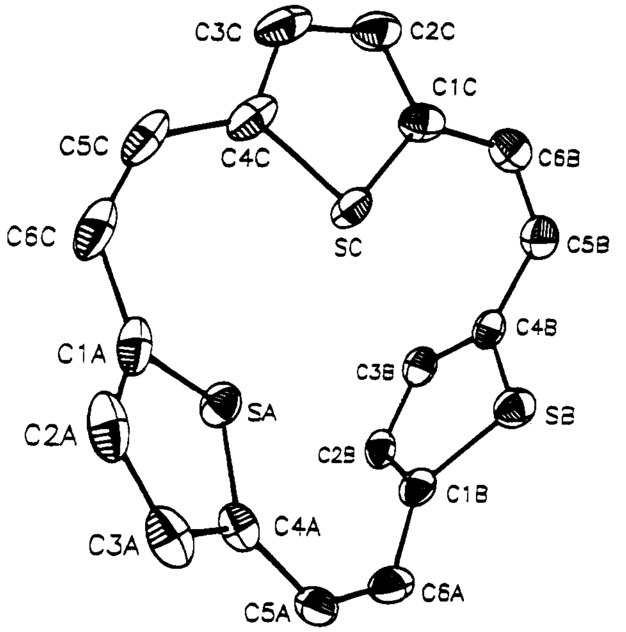
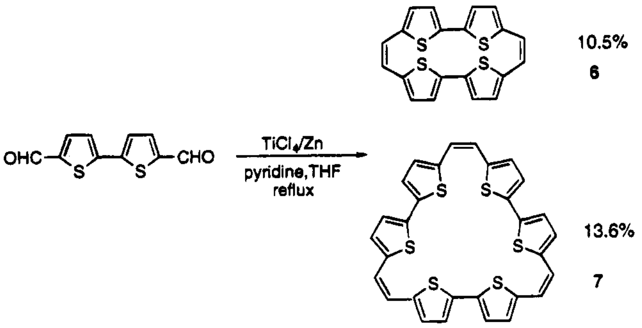


Figure 1. X-ray structure of [18]annulene trisulfide.

Table 1. Crystal Data and Summary of Data Collection Parameters for Annulene 3 ($C_{18}H_{12}S_3$)

molecular weight	324.29	D_c, g cm^{-3}	1.44
space group	$P2_1/n$	molecules/unit cell	4
cell constants		radiation	Mo Kα
a, Å	9.223	2θ range, deg	2–50
b, Å	19.246	no. of reflns collcd	1790
c, Å	9.459	no. of obsd reflns	2136
β, deg	116.88	R	0.0358
V, Å^3	1497.61	R_w	0.0358

Scheme 2. Bithiophene-Derived Annulenes



The reductive coupling of 2,2′-bithiophene-5,5′-dicarboxaldehyde[21] was carried out under high dilution conditions, and the product was chromatographed on silica. Two clean fractions were obtained by further radial chromatography. The yellow crystalline tetrathiaporphycene **6** was obtained as the first fraction in 10.5% yield (Scheme 2). In contrast to expectations, this 20 π-electron thiophene analog of porphycene is surprisingly stable even through it is a $4n$ π system and quite strained. Its molecular ion peak is observed as 100% in its mass spectrum and the doubly charged molecular ion peak as 15%. Three groups of protons are observed in its ^1H NMR spectrum, namely one singlet at 6.70 ppm, and two doublets of an AB system at 6.99 and 6.78 ppm, indicative of a symmetrical structure without an obvious ring current. From its yellow color and its UV-visible absorption maxima at 336, 274, 229, and 210 nm, it can

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[17] Feringa, B.; Hulst, R.; Rikers, R.; Brandsma, L. *Synthesis* **1988**, 316.

[18] The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

[19] (a) Vogel, E.; Kocher, M.; Schmickler, H.; Hex, J. *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 257. (b) Vogel, E.; Sicken, M.; Rohrig, P.; Schmickler, H.; Lex, J.; Ermer, O. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 411.

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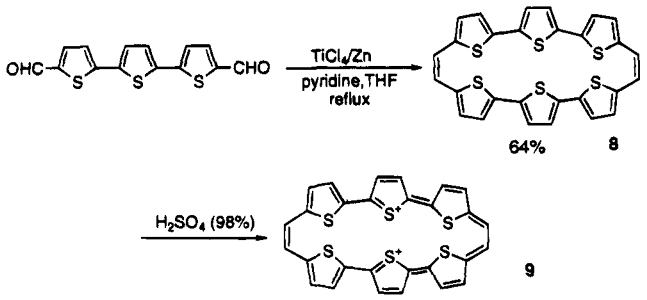
Scheme 3. Terthiophene-Derived Annulenes



be seen that there is only modest conjugation between the thiophene units in the molecule, as expected for a nonplanar structure. The attempted oxidation of tetrathiaporphycene to an 18π aromatic dication was not successful.

The red crystalline 30 π annulene hexathia[30]annulene[2,0,2,0,2,0] was obtained as the second fraction in 13.6% yield. Again, in its mass spectrum, a molecular ion peak is observed as 100%, and a doubly charged molecular ion peak as 21%. Its ^{1}H NMR is very similar to that of tetrathiaporphycene, even through it is formally a $(4n + 2)\pi$ system while tetrathiaporphycene is a $4n$ π system. The observed signals are at 7.05 ppm (doublet), 6.98 ppm (doublet), and 6.60 ppm (singlet), respectively, indicating no obvious aromatic ring current in the molecule besides that of thiophene itself. The maxima at 384, 370, 263, and 227 nm in its UV-visible absorption spectrum are also in accord with the assumed nonplanarity of the molecule.

After the completion of this work, we were made aware of an independent synthesis of **6** and **7** by a similar McMurry coupling, albeit in somewhat lower yields (8.4 and 2.9%, respectively). In this study by Ellinger et al.,[22] the nonplanarity of both **6** and **7** was confirmed by X-ray crystallographic analyses, and **6** was electrochemically reduced to a diatropic 22 π dianion.

McMurry Coupling of 5,5″-Terthiophenedicarboxaldehyde. α-Terthiophene and 5,5″-terthiophenedicarboxaldehyde were prepared according to literature procedures.[21] The homolog of tetrathiaporphycene, hexathiahomoporphycene **8**, was the only compound isolated from the McMurry coupling of 5,5″-terthiophenedicarboxaldehyde and was obtained in yields as high as 64% (Scheme 3). Annulene **8** is a moderately stable, dark red microcrystalline compound, having a melting point over 250 °C. It gives a very strong molecular ion peak (100%), as well as a doubly charged molecular ion peak in its mass spectrum. The ^{1}H NMR indicated that it is not coplanar but has a centrosymmetric structure, showing all sp^2 protons in the range of 6.94 to 6.26 ppm as two singlets and an AB system. In its UV-vis spectrum, strong maxima are found at 431, 394, 381, 272, and 227 nm, indicating partial conjugation. It can be seen that this 28 π annulene is not antiaromatic, even though it is a partially conjugated $4n$ π system.

Being a 28 π macrocycle, annulene **8** may be expected to be capable of losing two electrons to form a 26 π dication. The cyclic voltammogram of **8** shows two reversible oxidation peaks at 0.51 and 0.78 V (vs SCE), respectively, indicating that a 26 π dication is being formed (Figure 2).

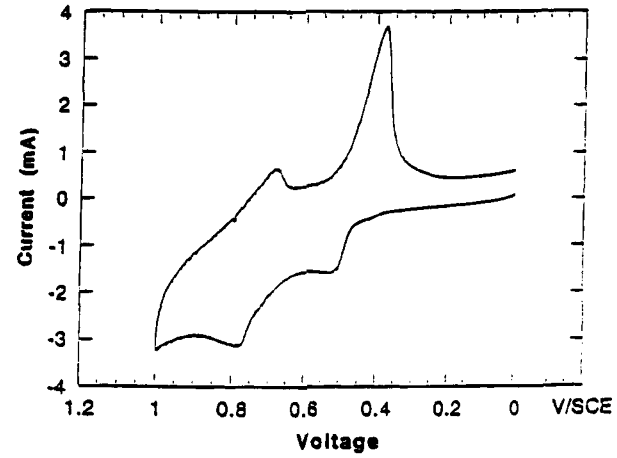


Figure 2. Cyclic voltammogram of annulene 8 (1.1×10^{-4} M + 0.1 M [NBu$_4$][PF$_6$] in CH$_2$Cl$_2$, scan rate 80 mV/s).

A purple solution was obtained when homoporphycene (**8**) was added to concentrated sulfuric acid (98%). The color change suggested the formation of the corresponding aromatic 26 π dication **9**, the sulfuric acid functioning as both oxidant and a source of counteranion. This was confirmed by its ^{1}H NMR obtained in D$_2$SO$_4$. The four kinds of protons are all greatly deshielded, ranging between 11.28 and 12.10 ppm, indicating a strong aromatic ring current effect in the aromatic 26 π dication. The purple solution also showed a typical porphyrin-like UV-visible spectrum, with maxima (in 98% H$_2$SO$_4$) at 885, 858, and 521 nm. In accord with its behavior as an electron donor, **8** forms a semiconducting charge-transfer complex with TCNQF$_4$.[23]

The McMurry reduction of terthiophenedicarboxaldehyde has been also reported by Ellinger et al., who obtained annulene **8** in only 1% yield.[22] The far higher yields which we obtained may be attributable to the long refluxing times used in our reductions.

Tetrathia[22]Annulene[2,1,2,1]. Among the thiophene-derived conjugated macrocycles so far discussed, only the dications **5** and **9** show a peripheral aromatic ring current. We now describe the synthesis of the first neutral aromatic species of this type, namely tetrathia[22]annulene[2,1,2,1] (**14**).

The acid-catalyzed condensation of 2-bromothiophene with dimethoxymethane afforded, in excellent yield, 2,2′-methylenebis[5-bromothiophene] (**11**). The unsubstituted dithienylmethane has previously been prepared in a similar manner from thiophene, but much oligomeric or polymeric material is also produced.[24] Low temperature halogen–lithium exchange of **11**, followed by reaction with DMF and subsequent hydrolysis, yielded the corresponding dialdehyde **12** (Scheme 4). The reductive McMurry coupling of the dialdehyde **12** gave the dihydro macrocycle precursor **13** in remarkably high yield (75%). The dehydrogenation by DDQ occurred immediately in methylene chloride solution to give an insoluble black complex, which was readily reduced by hydrazine to give the black crystalline tetrathia[22]annulene[2,1,2,1] (**14**) in 82% yield.

The aromaticity of tetrathia[22]annulene[2,1,2,1] was evidenced by its ^{1}H NMR and UV-visible absorption spectra. In the ^{1}H NMR, two singlets are observed at

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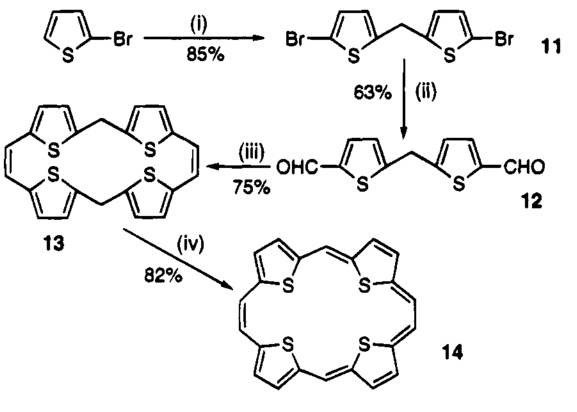
[24] Peter, A. *Chem. Ber.* **1884**, *17*, 1345.

Scheme 4. Synthesis of 22 π Aromatic Thiophene-Derived Annulene



(i) $CH_2(OMe)_2$, $HOAc/H_2SO_4$ (ii) BuLi, THF/-70 °C; DMF (iii) $TiCl_4/Zn$, pyridine, THF, reflux (iv) DDQ, then hydrazine

12.34 and 11.36 ppm, corresponding to the protons on the methine carbon and the ethene carbons and an AB system corresponding to the thiophene protons at 10.86 and 10.84 ppm. In contrast, no protons of the dihydro compound **13** appear below 6.8 ppm. The mass spectrum of **14** showed a strong molecular ion peak (100%) and little fragmentation. In the UV-visible spectrum, there are sharp and strong maxima at 417 nm and several weaker absorptions at longer wavelength (503, 540, 579, and 771 nm). The first absorption (at 417 nm) is analogous to the typical Soret band of the porphyrins and porphycenes, while the absorptions at longer wavelengths are similar to the Q-bands, but with a bathochromic shift with respect to porphycene. These spectra are clearly typical of a aromatic macrocycle. Compared to the other thiophene derived annulenes **3** and **7**, this macrocycle is less crowded, enabling it to have a planar or near-planar structure with its π-electrons fully conjugated around the periphery.

In conclusion, the first neutral aromatic annulene derived solely from thiophene, namely tetrathia[22]-annulene[2,1,2,1] (**14**), has been synthesized. In addition, the thiophene-derived annulenes **3**, **4**, and **6**–**9** were also synthesized and studied.[25]

Experimental Section

General. All melting points are uncorrected. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, GA.

[18]Annulene Trisulfide (3) and [24]Annulene Tetrasulfide (4). A solution of $TiCl_4$ (32.86 mL, 1.0 M in CH_2Cl_2) in THF (100 mL) was added under nitrogen to zinc dust (4.3 g) with stirring over a period of 30 min, and the suspension was refluxed for 1 h. To the above gently refluxing suspension was added by syringe a solution of 2,5-thiophenedicarboxaldehyde (500 mg, 3.57 mmol) and pyridine (4.29 mL) in 150 mL of THF. After refluxing for 18 h, the reaction mixture was cooled to room temperature. Then a quenching solution of K_2CO_3 (10%) was carefully introduced with stirring. The reaction mixture was filtered and the filtrate was concentrated under reduced pressure. The residue was extracted with CH_2Cl_2 (300 mL), and the extract was washed with water (twice, 100 mL each) and dried over anhydrous Na_2SO_4, and the solvent was removed *in vacuo*. The residue was subjected to column chromatography (silica, CH_2Cl_2) and the front running band was collected to give a mixture of annulenes **3** and **4**. The separation on further column chromatography (alumina, hexane) gave 148 mg of annulene **3** (38%): mp 208–210 °C (lit.[2] 210–215 °C); ^1H NMR (CDC13) 6.84 (6H, s), 6.81 (6H, s); ^{13}C NMR ($CDCl_3$) 138.6, 127.6, 124.7; MS (EI) *m/z* (%), 324 (M+, 100); and 18 mg of annulene **4**: yield 4.7%, mp 74–75 °C (lit.[14] 74.5–75.6 C); ^1H NMR ($CDCl_3$) 7.34 (8H, s), 6.19 (8H, s); ^{13}C NMR ($CDCl_3$) 140.2, 128.3, 122.2; MS (EI) *m/z* (%), 432 (M^+, 100). [18]Annulene trisulfide (50 mg) was dissolved in hexane (100 mL) in a narrow neck bottle which was then covered with filter paper. A single crystal for crystallographic analysis was obtained by placing the bottle in a dark quiet place for two weeks.

Tetrathiaporphycene (6) and 30 π Annulene 7. To a suspension of zinc dust (3.07 g) and THF (150 mL) was added under nitrogen a solution of $TiCl_4$ (23.57 mL, 1.0 M in CH_2Cl_2) by syringe. The suspension was refluxed for 1 h. Then a solution of 2,2′-bithiophene-5′,5″-dicarboxaldehyde (500 mg, 2.25 mmol) and pyridine (3.07 mL) was added dropwise to the above gently refluxing suspension. The reaction mixture was refluxed for 18 h and then cooled to room temperature. A quench solution of Na_2CO_3 (10%) was introduced carefully with stirring. The reaction mixture was filtered, the filtrate was evaporated almost to dryness, and the residue was extracted with methylene chloride. The extract was washed with water (twice, 100 mL each) and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was chromatographed on silica with methylene chloride as eluent. The fast running fraction was collected to give a dark red solid which was subjected again to column chromatography (silica, CH_2Cl_2). The solid obtained was dissolved in a minimum amount of methylene chloride and subjected to radial chromatography to give 45 mg of yellow crystalline tetrathiaporphycene (**6**) as the first fraction; mp 148–150 °C (10.5%); ^1H NMR ($CDCl_3$) 6.99 (4H, d, $J = 3.7$ Hz), 6.78 (4H, d, $J = 3.7$ Hz), 6.70 (4H, s); ^{13}C NMR ($CDCl_3$) 141.5, 141.2, 129.1, 125.9, 123.5; UV-vis λ_{max} (nm) (log ε) (in CH_2Cl_2) 336.2 (4.22), 274.0 (4.26), 228.8 (4.13), 210.2 (3.91); MS (EI) *m/z* (%) 380 (M^+, 100), 190 (M^{2+}, 16); HRMS calcd for $C_{20}H_{12}S_4$ 379.9822, found 379.9844. Anal. Calcd for $C_{20}H_{12}S_4$: C, 63.12; H, 3.18; S, 33.70. Found: C, 63.10; H, 3.14; S, 33.64. The second fraction afforded 58 mg of light red crystalline annulene **7** (13.6%: mp 175–177 °C; ^1H NMR ($CDCl_3$) 7.05 (6H, d, $J = 3.7$ Hz), 6.98 (6H, d, $J = 3.7$ Hz), 6.60 (6H, s); ^{13}C NMR ($CDCl_3$) 138.1, 138.0, 130.2, 123.6, 123.1; UV-vis λ_{max} (nm) (log ε) (in CH_2Cl_2) 384.2 (4.64), 369.8 (4.61), 263.0 (4.27), 227.4 4.26); MS (EI) *m/z* (%) 570 (M^+, 100), 406 (M − 164 (2T), 14), 285 (M^{2+}, 21); HRMS calcd for $C_{30}H_{18}S_6$ 569.9732, found 569.9747. Anal. Calcd for $C_{30}H_{18}S_6$: C, 63.12; H, 3.18; S, 33.70. Found: C, 63.13; H, 3.14; S, 33.63.

Hexathiahomoporphycene (8). A solution of $TiCl_4$ (7.22 mL, 1.0 M in CH_2Cl_2) was added under nitrogen to a suspension of zinc dust (940 mg) in THF (50 mL) with stirring in a period of 30 min, and the suspension was refluxed for 1 h. To the above gently refluxing suspension was added by syringe a solution of α-terthiophene-5,5″-dicarboxaldehyde (210 mg, 0.69 mmol) and pyridine (0.94 mL) in 50 mL of THF. After refluxing for 18 h, the reaction mixture was cooled to room temperature. A quenching solution of K_2CO_3 (10%) was carefully introduced with stirring, the reaction mixture was filtered, and the filtrate was concentrated *in vacuo*. The residue was extracted with $CHCl_3$ (100 mL), and the extract was washed with water (twice, 100 mL each) and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was subjected to flash chromatography (silica, $CHCl_3$), the front running band being collected to give crude annulene **8**. Further rapid chromatography on silica afforded 120 mg of purple-red mirocrystalline **8** (64%), mp > 250 °C, which is stable after being purified; however, partial decomposition of **8** was observed during chromatography on silica. Prolonged contact of **8** with silica is to be avoided, since this leads to extensive loss of the compound: ^1H NMR ($CDCl_3$) 6.90 (4H, s), 6.89 (4H, d, $J = 3.74$), 6.77 (4H, d, $J = 3.74$), 6.34 (4H, s); ^{13}C NMR ($CDCl_3$) 138.1, 137.6, 137.5, 131.3, 123.8, 122.8, 121.8; UV-vis λ_{max} (nm) (log ε) (in CH_2Cl_2) 430.6 (4.53), 394.0 (4.84), 381.0 (4.83), 272.8 (4.33), 227.4 (4.41); MS (EI)

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[25] The synthesis of **8** and **14** have been reported in preliminary form: (a) Hu, Z.; Kelley, C.; Cava, M. P. *Tetrahedron Lett.* **1993**, *34*, 1879. (b) Hu, Z.; Cava, M. P. *Tetrahedron Lett.* **1994**, *35*, 3493.

m/z (%) 544 (M^+, 100), 272 (M^{2+}, 12), 202 (43), 181 (73), 149 (60); HRMS calcd for $C_{28}H_{16}S_6$ 543.9576, found 543.9575.

Oxidation of Hexathiahomoporphycene (8) to Dication 9. To 10 mL of 98% sulfuric acid was added 10 mg of hexathiohomoporphycene. After stirring for 5 min a deep purple solution was obtained. The formation of dication **9** was confirmed spectroscopically: ^1H NMR (D_2SO_4) 12.10 (4H), 11.76 (4H), 11.56 (4H), 11.28 (4H); UV-vis λ_{max} (nm) (log ϵ) (H_2SO_4) 886 (4.29), 858 (4.27), 521 (4.80).

5,5′-Dibromo-2,2′-dithienylmethane (10). To a solution of 2-bromothiophene (8.5 g, 53 mmol) and dimethoxymethane (2 g, 26 mmol) in 60 mL of acetic acid was added dropwise a mixture of acetic acid and sulfuric acid (20 mL, 1:1). The reaction mixture was stirred at room temperature for 10 min. The dark brown precipitate was washed with water and dried. After column chromatography (silica, CH_2Cl_2), 5.6 g (64%) of crude brown **10** was obtained, mp 42−44 °C. This material was used directly in the next step: ^1H NMR ($CDCl_3$) 6.88 (2H, d, $J = 3.7$ Hz), 6.63 (2H, d, $J = 3.7$ Hz), 4.18 (2H, s); ^{13}C NMR ($CDCl_3$) 143.8, 129.6, 125.8, 110.7, 30.8; MS (EI) *m/z* (%) 338 (M^+, 78), 259 (M − Br, 78), 176 (M − 2Br, 100), 134 (75); HRMS calcd for $C_9H_6S_2Br_2$ 335.8278, found 335.8279.

5,5′-Diformyl-2,2′-dithienylmethane (11). To a cooled (−70 °C) solution of 5,5′-dibromo-2,2′-dithienylmethane (**10**) (5.7 g, 16.8 mmol) in 150 mL of THF was added dropwise under nitrogen 15.5 mL of n-butyllithium (2.5 M in hexane). The reaction mixture was stirred for 15 min, allowing the temperature to rise to −50 °C, and then was cooled again to −70 °C. After dropwise addition of DMF (3 mL), the reaction mixture was stirred for another 4 h, allowing the temperature to rise to 0 °C, and then was poured into 150 mL of ice−water. The reaction mixture was stirred for 10 min and extracted with methylene chloride, which was then washed with water (twice, 50 mL each) and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the residue was subjected to chromatography (silica, 1:1 hexane/methylene chloride). A solid residue of 5,5′-diformyl-2,2′-dithienylmethane (2.5 g, 64%) (**12**) was obtained as the major product: mp 82−84 °C (lit.[13a] 95 °C); ^1H NMR ($CDCl_3$) 9.84 (2H, s), 7.64 (2H, d, $J = 3.7$ Hz), 7.02 (2H, d, $J = 3.6$ Hz), 4.43 (2H, s); ^{13}C NMR ($CDCl_3$) 182.6, 151.8, 143.2, 136.7, 127.3, 31.6; MS 236 (M^+, 85), 207 (100), 179 (33), 135 (29); HRMS calcd for $C_{11}H_8S_2O_2$ 235.9966, found 235.9958. A yellow oil consisting of 5-formyl-2,2′-dithienylmethane (0.3 g) was obtained as a side product: ^1H NMR ($CDCl_3$) 9.81 (1H, s), 7.61 (1H, d, $J = 3.7$ Hz), 7.20 (1H, d, $J = 5.0$ Hz), 6.98 (1H, d, $J = 3.9$ Hz), 6.96 (1H, t, $J = 5.0$ Hz), 6.91 (1H, d, $J = 3.7$ Hz); ^{13}C NMR ($CDCl_3$) 182.6, 154.5, 142.5, 140.7, 136.7, 127.0, 126.6, 126.0, 124.7, 30.8.

5,16-Dihydrotetrathia[22]annulene[2,1,2,1] (13). To a suspension of zinc dust (1.76 g) in 100 mL of THF was added under nitrogen with stirring a solution of 13.6 mL of 1.0 M $TiCl_4$ (in CH_2Cl_2) over 20 min. The reaction mixture was refluxed for 1 h, and then a solution of dialdehyde **12** (310 mg, 1.31 mmol) and pyridine (1.76 mL) in 100 mL of THF was added through a syringe over 30 min to the gently refluxing suspension. After refluxing under nitrogen for 18 h, a quenching solution of K_2CO_3 (10%, 24 mL) was carefully introduced. The reaction mixture was filtered, and the filtrate was concentrated *in vacuo* and then extracted with 150 mL methylene chloride. The extract was washed with water (twice 50 mL each) and dried over anhydrous sodium sulfate. The solvent was evaporated under reduced pressure and the residue was subjected to column chromatography (silica, chloroform) to give 210 mg (78%) of yellow 5,16-dihydrotetrathia[22]annulene[2,1,2,1] **13**: mp 153.5−155.5 °C; ^1H NMR ($CDCl_3$) 6.78 (8H, s), 6.52 (4H, s), 6.77 (4H, s); ^{13}C NMR ($CDCl_3$) 145.2, 138.5, 128.3, 124.8, 123.5, 31.6; UV-vis λ_{max} (nm) (log ϵ) (in CH_2Cl_2) 348 (4.30), 259 (4.29), 223 (4.23); MS (EI) *m/z* (%) 408 (M^+, 100), 300 (16); HRMS calcd for $C_{22}H_{16}S_4$ 408.0135, found 408.0137.

Tetrathia[22]annulene[2,1,2,1] (14). To a solution of **13** (0.5 g, 1.2 mmol) in 20 mL of methylene chloride was added a solution of DDQ (1.3 g, 5.7 mmol) in 50 mL of methylene chloride. Upon mixing the two solutions, a black precipitate formed immediately. The black precipitate was filtered and added to 10 mL of hydrazine (95%). After boiling for 10 min, the solid was filtered, washed with water, and dried. The resulting product was dissolved in methylene chloride and chromatographed on basic alumina. Evaporation of the purple solution gave 0.42 g (82%) of black crystalline **14**: mp > 270 °C; ^1H NMR (DMSO-d_6) 12.34 (2H, s), 11.36 (4H, s), 10.86 (4H, d, $J = 4.7$ Hz), 10.84 (4H, d, $J = 4.7$ Hz); ^{13}C NMR (DMSO-d_6) 136.2, 135.5, 135.2, 131.1, 113.3, 111.6; UV-vis λ_{max} (nm) (log ϵ) (in CH_2Cl_2) 771 (3.62), 579 (4.71), 540 (4.01), 503 (3.70), 417 (5.18), 387 (4.50), 311 (4.23) MS (EI) *m/z* (%), 406 (M^+, 100), 203 (M^{2+}, 22); HRMS calcd for $C_{22}H_{14}S_4$ 405.9978, found 405.9977. Anal. Calcd for $C_{22}H_{14}S_4$: C, 64.99; H, 3.47; S, 31.54. Found: C, 64.80; H, 3.51; S, 31.40.

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