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Syntheses and Structures of Thiophene-Containing Cycloparaphenylenes and Related Carbon Nanohoops

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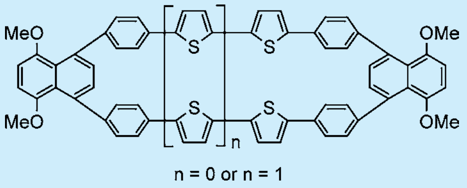
S Supporting Information

ABSTRACT: Thiophene-containing cycloparaphenylenes (CPPs) bearing 8, 10, and 16 aromatic and heteroaromatic units in the macrocyclic ring structures were synthesized. Specifically, two and four thiophene-2,5-diyl units were incorporated into functionalized [6]- and [12]CPP macrocyclic carbon frameworks, respectively. In addition, two 2,2′-bithiophene-5,5′-diyl units were inserted into a functionalized [6]CPP carbon framework. The cyclic and differential pulse voltammetry and the UV−vis and fluorescence spectra of the fully aromatized macrocycles and their precursors exhibited interesting electrochemical and optical properties.



Development of new synthetic pathways for the construction of cycloparaphenylenes (CPPs) and related carbon nanohoops is an area of intense current interest[1] because these macrocycles could serve as templates for bottom-up synthesis of armchair carbon nanotubes of a uniform chirality and diameter.[2] The ability to produce single-chirality carbon nanotubes of a uniform diameter is of crucial importance in using them for applications in a variety of nanotechnology fields.[2j] Incorporation of heteroaromatic units into the CPP structures could provide new materials possessing novel photophysical and electrochemical properties. A bipyridine-containing CPP was found to show an interesting acid/base-induced reversible fluorescence change.[3] Thiophene-containing CPPs were synthesized recently and were reported to possess unique structural and photophysical properties.[4]

We have developed synthetic pathways to allow incorporation of thiophene units into CPP structures. Specifically, macrocycles **1** and **2** (Figure 1) containing two and four thiophene-2,5-diyl units, respectively, were synthesized. In addition, macrocycle **3**, bearing two 2,2′-bithiophene-5,5′-diyl units, was also synthesized. The oxidation potentials of the fully aromatized macrocycles and the corresponding hydrogenated precursors were measured by cyclic and differential pulse voltammetry. The UV−vis and fluorescence spectra of the fully aromatized macrocycles showed a red shift from those of the corresponding precursors.

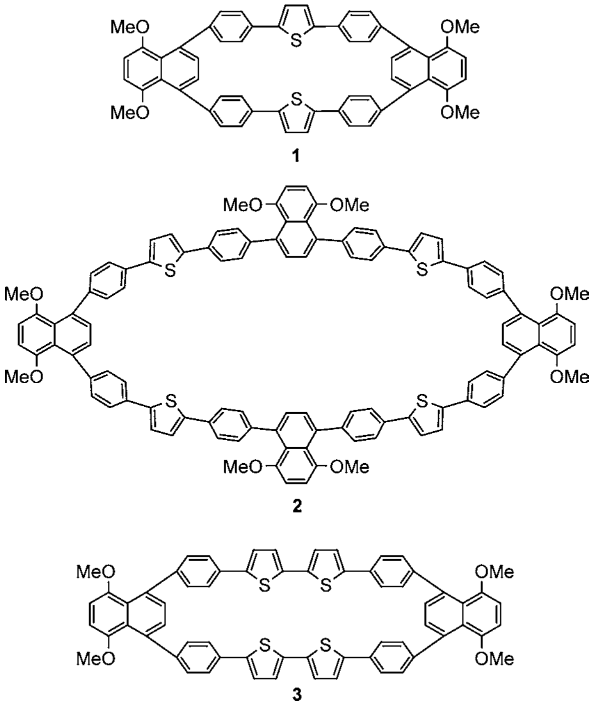


Figure 1. Structures of the thiophene-containing CPPs.

We recently reported the use of the Diels−Alder reaction between diene **4** and 1,4-benzoquinone (**5**) to form, after methylation, dibromide **6** (Scheme 1) as a precursor leading to a functionalized [9]CPP and related carbon nanohoops.[1h] Dibromide **6** was again used as a key intermediate for the construction of thiophene-containing CPPs and related carbon nanohoops. The transformation of dibromide **6** to bis-boronic ester **7**[5] followed by Suzuki−Miyaura coupling reactions[6] with 2-iodothiophene (**8**)[7] produced **9**, which upon iodination with *N*-iodosuccinimide (NIS)[8] gave **10**. The Suzuki−Miyaura coupling reactions between diiodide **10** and bis-boronic ester **7** were successful in producing **11** and **12** bearing two and four thiophene-2,5-diyl units, respectively. Macrocycle **11** was a mixture of two isomers, which were comprised of the *syn* isomer with the two 1,4-dimethoxybenzene groups on the same side of the macrocyclic ring (*syn*-**11**) and the *anti* isomer with

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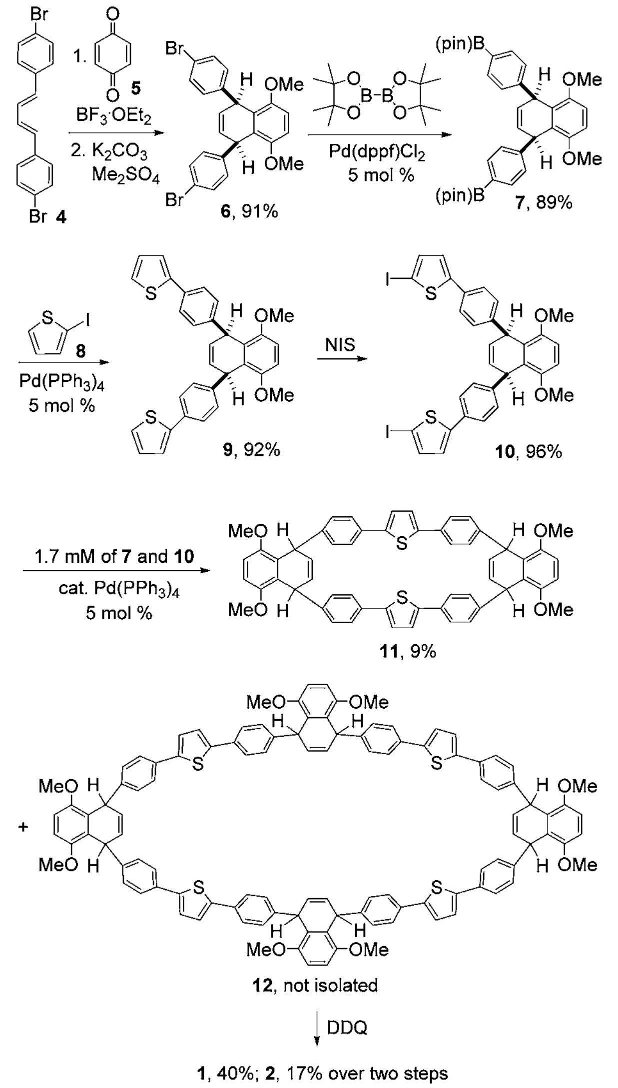
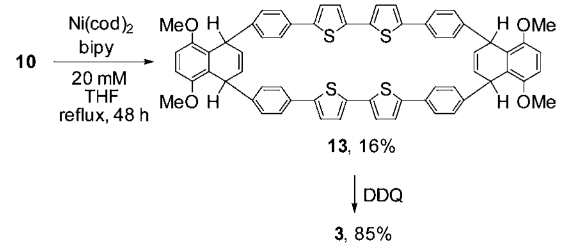
Scheme 1. Synthesis of the Thiophene-Containing CPPs 1 and 2



the two groups on the opposite sides (*anti*-**11**). For **12**, there are four possible isomers. Because we were unable to separate **11** from **12**, the crude mixture of products was treated with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) at 60 °C, which converted **12** to the fully aromatized **2** while leaving **11** unaffected. It was possible to separate **2** from **11** at this stage. A sample containing mainly one of the two isomers of **11**, either *syn*-**11** or *anti*-**11**, was also separated and isolated by silica gel column chromatography for structural elucidation. Because of the smaller ring size and thus higher ring strain[9] in **1**, bearing a total of 8 benzene and thiophene units in the macrocyclic ring structure with a DFT-calculated strain energy of 41.0 kcal/mol, the oxidative aromatization reaction of the mixture of *syn*-**11** and *anti*-**11** to form **1** required a higher reaction temperature (150 °C) than for **2** (60 °C), which contains a total of 16 benzene and thiophene units with a DFT-calculated strain energy of 7.6 kcal/mol.

The Ni(cod)$_2$-mediated (cod: 1,5-cyclooctadiene) homocoupling reactions[1f−k,m] of **10** in the presence of 2,2′-bipyridyl (bipy) furnished dimer **13** containing two 2,2′-bithiophene-5,5′-diyl units as a mixture of *syn* and *anti* isomers (Scheme 2). Treatment of **13** with DDQ produced **3** bearing a total of 10 benzene and thiophene units. The ability to form dimer **13** from **10** is reminiscent of a previous observation in the Ni(cod)$_2$-mediated homocoupling reactions of **6** to form the corresponding dimers.[1h] Small amounts of the corresponding trimers from **10** were also detected by HRMS. Compared to the structure of **1**, the larger ring size and the presence of four 2,5-disubstituted thiophene units with angled orientations of the substituents further decrease the ring strain in **3** with a DFT-calculated strain energy of 25.8 kcal/mol. As a result, the oxidative aromatization reactions with DDQ proceeded smoothly under milder reaction conditions (75 °C).

Scheme 2. Synthesis of the Bithiophene-Containing CPP 3



The presence of two thiophene-2,5-diyl units and two 5,8-dimethoxynaphth-1,4-diyl units in **1** allows it to have several distinct conformers. At 25 °C, the ^{1}H NMR spectrum showed only six signals, and the ^{13}C NMR spectrum revealed only 12 signals. Rapid equilibration among its various conformers could account for the observation of only one set of NMR signals. However, at −60 °C, the ^{1}H NMR signals from the four protons on the benzene rings became four doublets, emerging at δ 7.73, 7.32, 7.15, and 6.69, whereas the three singlets from the protons on the thienyl and naphthyl rings remained as singlets. This observation is consistent with a slow rate of rotation on the NMR time scale around the carbon−carbon bond connecting the benzene rings to the 5,8-dimethoxynaphth-1,4-diyl units. The *ortho* protons on the benzene rings with respect to the 5,8-dimethoxynaphth-1,4-diyl units become nonequivalent, as are the *meta* protons. The activation energy ($\Delta G^{\ddagger}$) of the rotation is estimated to be 11 kcal/mol at the coalescence temperature of −41 °C (see the Supporting Information). On the other hand, the rate of rotation of the thienyl groups likely remains faster than the NMR time scale.

The DFT-optimized conformation of the all-*syn* conformer, *syn*-**1** (Figure 2), has the two thienyl groups and the two 5,8-dimethoxynaphth-1,4-diyl units all pointed toward the same direction. The thienyl groups tilt toward the inner plane of the

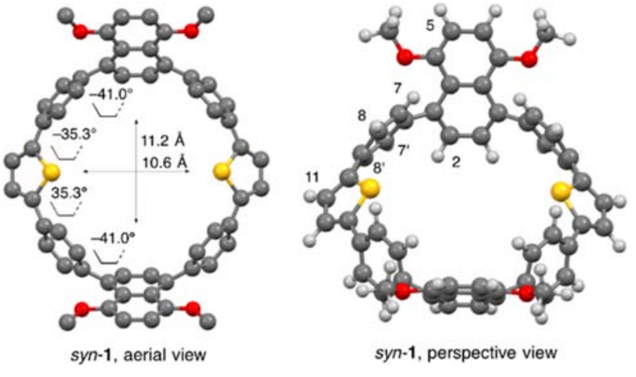
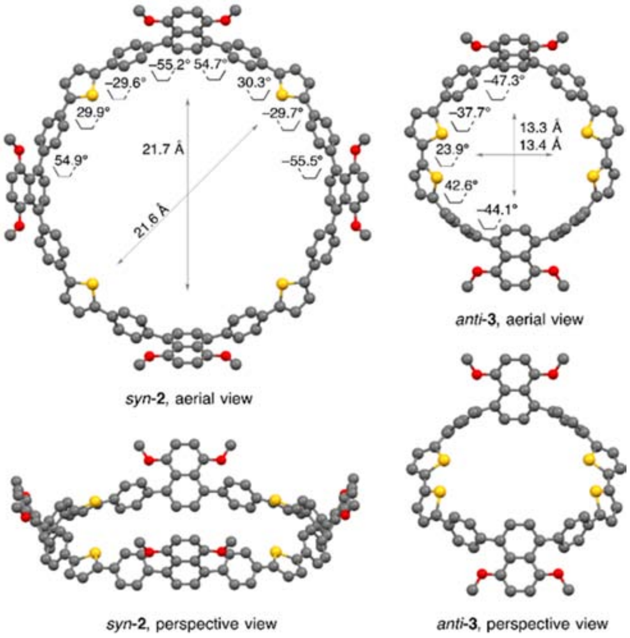


Figure 2. DFT-optimized structure of *syn*-**1** with ^{1}H NMR spectral assignments on the perspective view.

CPP circle at a 38° angle from the inner plane. This is reminiscence of an observed crystal structure of a thiophene-containing CPP.[4] However, the two 5,8-dimethoxynaphth-1,4-diyl units cant away from the inner plane at 126°. NOE studies by selective excitation of the methoxy and other signals at −80 °C allowed for the assignments of the signal at *δ* 7.15 to H8 and the signal at *δ* 6.69 to H7 with both of them on the same side of the macrocyclic ring with the methoxy groups. The signals at *δ* 7.73 and *δ* 7.32 were assigned to H7′ and H8′, respectively. The structure of *syn*-**1** showed that H7 and H8 tilt toward the inner plane with H7 being bended toward a magnetically shielded region of the 5,8-dimethoxynaphth-1,4-diyl units, which contributed to shifting the signal upfield. The conformer *anti*-**1** with one 5,8-dimethoxynaphth-1,4-diyl unit pointing toward one direction and the other unit pointing toward the opposite direction was found to be higher in energy than *syn*-**1** by 1.7 kcal/mol according to the DFT calculations (see the Supporting Information). In addition, the conformer with the two thienyl groups pointing toward the same direction but with the two 5,8-dimethoxynaphth-1,4-diyl units pointing toward the opposite direction is higher still in energy than *syn*-**1** by 2.3 kcal/mol.

The DFT-optimized structure of **2**, depicted in Figure 3, showed that the thienyl groups of the all-*syn* conformer, *syn*-**2**, tilt toward the inner plane at a 33° angle from the inner plane whereas the 5,8-dimethoxynaphth-1,4-diyl units cant away from the inner plane at a 122° angle. For **3**, the *anti* conformer with all four thiophene units pointing toward the same direction while the two 5,8-dimethoxynaphth-1,4-diyl units point toward the opposite directions appears to be the most stable conformation. The dihedral angle between the two thiophene groups of the 2,2′-bithiophene-5,5′-diyl units is 23.9°.



syn-2, aerial view

anti-3, aerial view

syn-2, perspective view

anti-3, perspective view

Figure 3. DFT-optimized structures of *syn*-**2** and *anti*-**3**.

The electrochemistry of each thiophene-containing CPP, along with their corresponding reduced precursors (**11** and **13**), were investigated by cyclic and differential pulse voltammetry in dichloromethane (Figure 4 and Table 1). Compounds **1**−**3** exhibit initial oxidation behavior between 0.41 and 0.53 V, which are lower than that of 2,5-diphenylthiophene at 0.96 V and 5,5′-diphenyl-2,2′-bithiophene at 0.68 V relative to Fc/Fc$^+$.[10] Precursors **11** and **13** exhibit initial oxidation behavior at 0.69 and 0.46 V, respectively. It is interesting to note that the first oxidation potential ($\Delta E_{1/2}$) decreases significantly from **11** to **1** (−0.28 V), whereas it increases slightly from **13** to **3** (+0.03 V). Increasing peak-to-peak separation with higher scan rates indicates that all redox events are quasi-reversible.

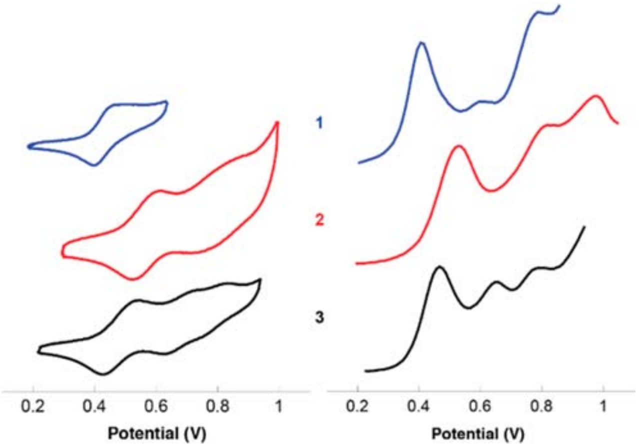


Figure 4. Cyclic (left) and differential pulse (right) voltammograms relative to Fc/Fc$^+$. See the Supporting Information for experimental details.

Table 1. Tabulated Spectroscopic and Voltammetric Data

	λ_{abs} (nm)	λ_{em} (nm)	E' vs Fc/Fc$^+$ (V)[a]
1	363	512	0.41, 0.79[b]
11	328	412	0.69, 1.01
2	350	481	0.53, 0.84, 0.98
3	376	511	0.49, 0.93
13	372	471	0.46, 0.65, 0.79

[a] Quasi-reversible waves with redox potentials (E') identified from differential pulse voltammograms. [b] Irreversible redox event.

The UV−vis spectra of **1**, **2**, and **3** exhibited the absorption maxima (λ_{abs}) at 363, 350, and 376 nm, respectively (Table 1). For the precursors **11** and **13**, the absorption maxima occurred at 328 and 372 nm, respectively. It is interesting to note that the absorption maximum exhibits a blue shift from **1** to **2** as the ring size increases. This is contrary to the effect of ring size of the thiophene-containing CPPs on the absorption maximum reported previously.[4] A significant red-shift was observed from **11** to the fully aromatized **1**, whereas a slight red-shift was observed from **13** to the fully aromatized **3**.

The fluorescence maxima (λ_{em}) of **1**, **2**, and **3** occurred at 512, 481, and 511, respectively. The blue shift of λ_{em} from **1** to **2** as the ring size increases is reminiscence of previous observations.[4,11] A red shift from **11** (λ_{em} = 412 nm) to **1** and from **13** (λ_{em} = 471 nm) to **3** were observed.

In summary, synthetic pathways for the thiophene-containing CPPs **1**, **2**, and **3** and related carbon nanohoops have been developed. The high stereoselectivity of the Diels−Alder reaction between diene **4** and 1,4-benzoquinone (**5**) allows the eventual placement of the two thienyl groups in **9** *cis* to each other, which is crucial for the macrocyclic ring formation. Iodination of **9** to form **10** provides the opportunity for using the homo- and cross-coupling reactions to form the macrocyclic thiophene-containing CPP precursors. Treatment of these precursors with DDQ for oxidative aromatization then leads to the thiophene-containing CPPs. The incorporation of thiophene-2,5-diyl or 2,2′-bithiophene-5,5′-diyl units into the CPP frameworks presents opportunities for the investigation of the photophysical and electrochemical properties of these radially π-conjugated systems.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Complete experimental details of new compounds, spectral data, DFT calculations, and crystallographic data (CIF). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01514.

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Notes

The authors declare no competing financial interest.

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