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A Saddle-shaped Macrocycle Comprising 2,5-Diphenylthiophene Units

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2,5-Diphenylthiophene-based macrocycles were synthesized by Ni-mediated coupling of the corresponding building units. X-ray analysis revealed that the cyclic trimer had a saddle-shaped structure due to the steric demands of the biphenyl and thiophene-phenylene units, whereas DFT calculation showed that the cyclic dimer had a rigid and almost coplanar structure regardless of the steric hindrance between the benzene rings of the biphenyl units. Moreover, the packing diagram of the cyclic trimer showed alternating stacked layers of macrocycles and solvent molecules.

Keywords: Saddle-shaped macrocycle | Diphenylthiophene | Ni-mediated coupling

In the molecular design of π-conjugated compounds, cyclization and oligomerization of two or more arene units are one promising approach for construction of fascinating functions.[1] The structures and properties of these compounds can be modified by varying the types and numbers of arene units and the types of linkers. For example, the use of heteroaromatic rings, such as thiophene, pyrrole, and furan, in oligoarene derivatives considerably increases the number of possible structures, which exhibit a variety of properties.[2] In particular, a large number of oligoarenes comprising thiophene units have been extensively studied for the development of novel organic devices and supramolecular architectures.[3] In a previous report, we synthesized 2,5-dianthrylthiophenes with a central thiophene unit having two anthracene units, which revealed characteristic structural and spectroscopic properties.[4] Although the parent 2,5-diphenylthiophene (**DPT**) unit is already known (Figure 1),[3b,5] DPT-based cyclic dimer **2** was previously synthesized by Suzuki–Miyaura coupling and appears mainly in patents for use in organic field-effect transistors.[6] Herein, we designed and synthesized cyclic trimer **1** as a new DPT-based macrocycle as well as cyclic dimer **2** by Ni-mediated coupling, and their structures, electronic spectra, and electrochemical properties were investigated.

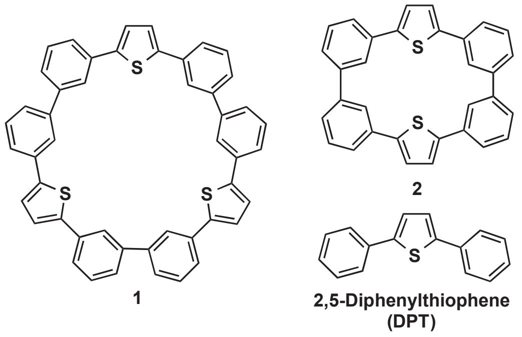
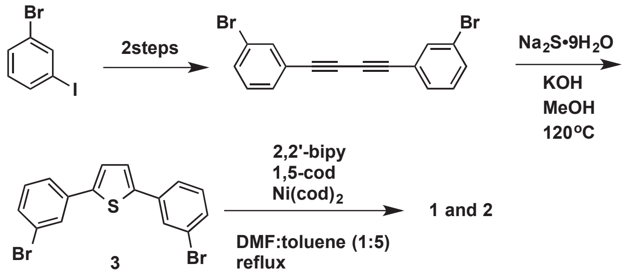


Figure 1. Structures of 2,5-diphenylthiophene (**DPT**) and DPT-based macrocycles **1** and **2**.



Scheme 1. Synthesis of 2,5-diphenylthiophene-based macrocycles **1** and **2**.

2,5-Bis(3-bromophenyl)thiophene **3** as a building unit was synthesized from 1-bromo-3-iodobenzene by Pd/Cu-catalyzed Sonogashira–Glaser coupling followed by sulfide-mediated cyclization (Scheme 1).[5,7] This precursor was subjected to Ni-mediated coupling under standard conditions.[8] Compound **1** was treated with $Ni(cod)_2$ [cod = 1,5-cyclooctadiene] in the presence of 2,2′-bipyridine and cod in a DMF/toluene solution. The crude product was purified by column chromatography to give cyclic trimer **1** and cyclic dimer **2** in 64% and 1% yields both as colorless solids (see Supporting Information). The low yield of **2** could be attributed to the large steric hindrance in the rigid and small ring structure. The molecular ion peaks of **1** and **2** were observed at m/z 702.15 and 468.04 [M^+], respectively. In the ^1H NMR spectrum of **1**, the thiophene proton signal was observed at δ 7.30 as a singlet, and the corresponding signal in **3** was observed at δ 7.29. The ^1H NMR signal of **2** assignable to the inner protons of the biphenylene units was observed at δ 8.59, and it was shifted downfield compared with the corresponding signals of **1** at δ 7.73. This value of **2** is attributed to the ring current effect based on the almost coplanar structure of biphenylene unit. Compound **1** gave eight aromatic signals in the ^{13}C NMR spectrum, which is consistent with the molecular symmetry. Unfortunately, the solubility of **2** was too low to measure its ^{13}C NMR spectrum.

We obtained a good single crystal of **1** from *p*-xylene/hexane for X-ray crystallography.[9] The X-ray structure of **1** is shown in Figure 2a. The cyclic framework of **1** adopts a saddle-shaped structure of C_1 symmetry. As cyclic trimer **1** comprises three DPT units, its conformation can be characterized by the dihedral angles between the phenylene planes and the thiophene plane. The maximum and minimum of these values obtained from the X-ray structure analyses of **1** are +54.0° and +5.1°, respectively. The three biphenyl groups are considerably twisted

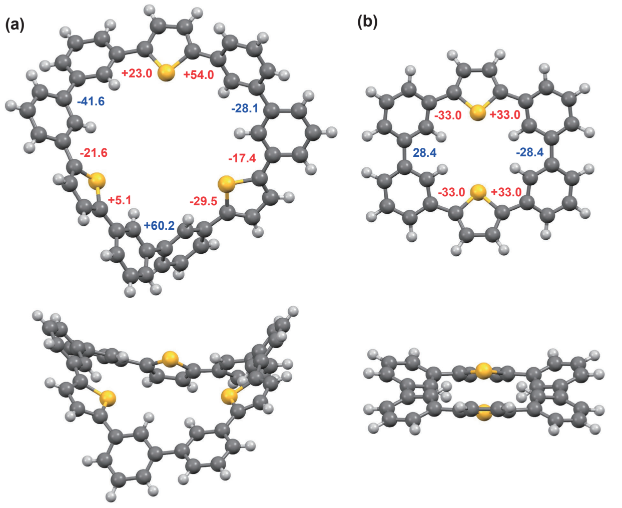


Figure 2. Molecular structures of **1** and **2**. Dihedral angles (°) of thiophene-phenylene rings (red numbers) and biphenyl moieties (blue numbers) are shown. (a) X-ray structure of **1** recrystallized from *p*-xylene/hexane. Solvent molecules are omitted for clarity. (b) Calculated structure of **2** at the B3LYP/6-311G(d,p) level.

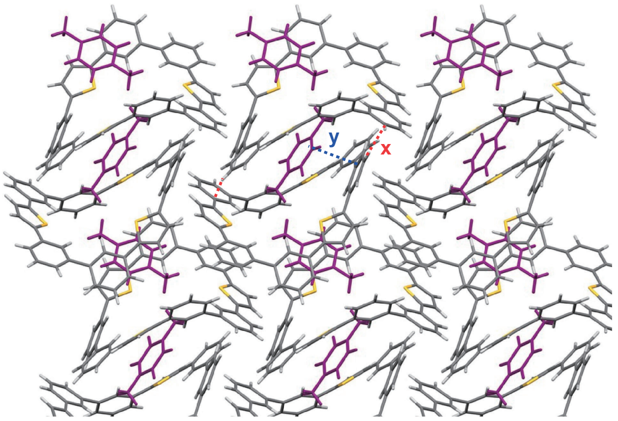


Figure 3. Packing diagram of **1** along the *a* axis. Typical C–H···π contacts and π···π interactions are shown as red broken lines and blue broken line, respectively. *x*: 3.33 Å, *y*: 2.87 Å. Solvent molecules are shown in purple for clarity.

from the planar conformation due to steric hindrance. The packing diagram of the cyclic trimer **1** showed alternating stacked layers of macrocycles and solvent molecules. Intermolecular C–H···π interactions rather than π···π interactions are dominant, and the shortest H···π distance is 3.33 Å (Figure 3). No sulfur atoms have any significant intermolecular contacts because they face toward the inside of the macrocycle.

The optimized structure of cyclic dimer **2** was calculated at the B3LYP/6-311G(d,p) level of theory (Figure 2b).[10] The calculation gave a C_{2h} symmetry with dihedral angles of ±28.4° (biphenyl) and ±33.0° (thiophene-phenyl). These structural data suggest that **2** exhibits pseudo-planarity as well as a large surface area. This structural feature should be a major reason for the low solubility due to effective intermolecular stacking in the solid state.

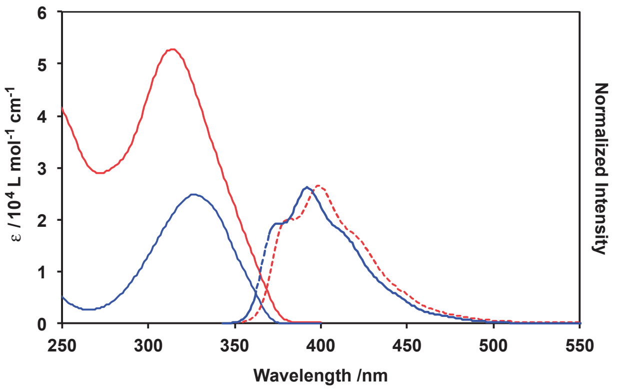


Figure 4. Absorption (solid lines) and fluorescence (dashed lines) spectra of **1** (red) and **DPT** (blue) in $CHCl_3$.

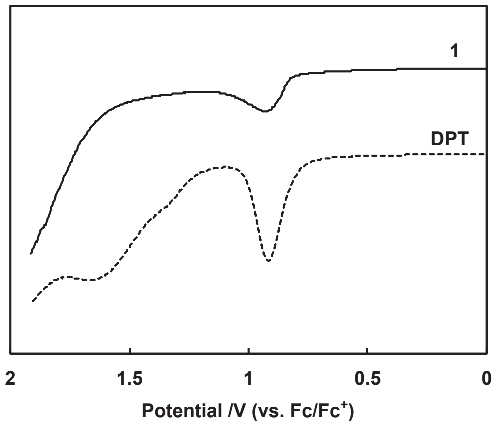


Figure 5. Differential pulse voltammograms of **1** and **DPT** in CH_2Cl_2.

The electronic spectra of **1** and **DPT** were measured in $CHCl_3$. In the UV-vis spectra (Figure 4), compound **1** gave an absorption at λ_{max} 317 nm at the *p*-band, whereas the corresponding band at the longest wavelength was observed at 327 nm for **DPT**. The absorption band of **1** is blue-shifted by 10 nm relative to that of the parent **DPT** because the π-conjugation through the whole molecule is diminished by the saddle-shaped structure. In the fluorescence spectra, compound **1** gave an emission band at 399 nm with a fluorescence quantum yield Φ_f of 0.14, whereas the emission peak of **DPT** was observed at 392 nm with a quantum yield Φ_f of 0.12. The large Stokes shift of **1** (82 nm, 6480 cm^{-1}) was attributed to a significant structural difference between the excited state and the ground state.

The oxidation potentials of **1** and **DPT** were investigated by cyclic voltammetry. Compound **1** exhibited some obscure redox waves in CH_2Cl_2 with ^{n}Bu$_4$NPF$_6$ as the supporting electrolyte at room temperature (Figure S1). In order to determine the correct potentials, we performed differential pulse voltammetry under the same conditions, and the results are shown in Figure 5. The first oxidation peak (E_1^{ox}) of **1** was found at 0.93 V (vs. Fc/Fc$^+$), which was weak and complicated. This potential occurs almost at the same potential as that of **DPT** (0.92 V), which can be attributed to the independent HOMO of the DPT unit in the macrocyclic framework (Figure S2).

In summary, 2,5-diphenylthiophene-based macrocycles **1** and **2** were successfully synthesized by Ni-mediated coupling. We could only evaluate the properties of cyclic trimer **1** by spectroscopic and electrochemical measurements. X-ray analysis and DFT calculations revealed that cyclic trimer **1** had a saddle-shaped structure depending on the steric hindrance between the biphenyl and thiophene-phenylene units. The structures of DPT-based cyclic oligomers are attractive for the design of molecular devices based on twisted π-conjugated macrocycles. Further studies focusing on the synthesis of higher cyclic oligomers introducing the soluble substitution as well as their applications in organic electronic devices are in progress.

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Supporting Information is available on http://dx.doi.org/10.1246/cl.180187.

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9 Crystal data of **1**: Formula $C_{48}H_{30}S_3 \cdot C_8H_{10}$, $M = 809.06$, triclinic, space group $P\bar{1}$, $a = 11.8691(17)$, $b = 12.775(2)$, $c = 14.277(2)$ Å, $\alpha = 79.069(4)$, $\beta = 81.974(5)$, $\gamma = 82.994(5)°$, $V = 2094.6(5)$ Å^3, $Z = 2$, $D_c = 1.283\ \mathrm{g\,cm^{-3}}$, $\mu(\mathrm{Mo}\ K\alpha) = 0.216\ \mathrm{mm^{-1}}$. Number of data 9433, number of data used 6618 $[I > 2.0\sigma(I)]$, $R1 = 0.0549$, $wR2 = 0.1266$, GOF = 1.044. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre: Deposition number CCDC 1824756.

10 M. J. Frisch, et al., *Gaussian 09 (Revision C.01)*, The full list is given the Supporting Information.