

Syntheses, Structures, and Supramolecular Properties of Giant π -Expanded Macrocyclic Oligothiophenes

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ABSTRACT: Fully conjugated π -expanded macrocyclic oligothiophenes with 60π -, 90π -, 120π -, 150π -, and 180π -electron systems (**1–5**) were synthesized using modified McMurry coupling reaction as a key step. Compound **1** was converted into macrocyclic oligo(2,5-thienylene-ethynylene) **6** using bromination-dehydrobromination procedure. X-ray analysis of **1** revealed a unique molecular and packing structure, reflecting a round, planar shape with nanoscale inner cavity. Interestingly, **2** and **3** self-aggregate in the solid state to form nanowires. The structure of fibrous aggregates was established by scanning electron microscopic and atomic force microscopic analyses. Compounds **1–6** exhibit multi-step reversible redox behavior with fairly low first oxidation potentials, reflecting their cyclic conjugation. Doping of **1–3** with iodine gives semiconductors owing to their π -donor properties and π - π stacking ability. © 2007 Wiley Periodicals, Inc. *Heteroatom Chem* 18:460–466, 2007; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20337

INTRODUCTION

Linear π -conjugated oligomers and polymers represent an important class of compounds in the field

of materials science, and have been extensively investigated as potential molecular devices, machines, switches, field effect transistors (FET), light emitting diodes (LED), and solar cells [1–4]. Among these, oligo- and polythiophenes seem to be one of the best candidates as components of molecular electronics [5–10], because doped oligo- and polythiophenes possess high electrical conductivities owing to the formation of bipolaron, π -dimer, chain dimer, and σ -dimer [11] and because oligothiophenes can be employed as an electroactive conjugated molecular wire with high rigidity and thermal stability [12–14]. In addition, rigidity of oligothiophenes provides great advantage for their use as a conjugated spacer in donor–acceptor diads and triads [15–18].

In contrast to linear oligomeric systems, shape-persistent macrocyclic oligoarylenes, heteroarylenes, and their π -expanded derivatives are regarded as an infinite π -conjugated system with an inner cavity [19–24], and hence giant macrocycles attract considerable attention due to their effective conjugation length and unusual electronic properties [25–31]. Recently, Bäuerle and coworkers have synthesized and characterized a series of cyclic oligothiophenes using X-ray and scanning tunneling microscopic analyses to elucidate their molecular structures [32–35]. Here, synthesis, novel molecular structures, and supramolecular chemistry of π -expanded cyclic oligothiophenes are summarized to account for a new field of giant macrocyclic oligothiophenes.

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SYNTHESIS OF GIANT π -EXPANDED MACROCYCLIC OLIGOTHIOPHENES

Although fully conjugated macrocyclic molecules less than 30 Å molecular size have been reported by several groups [36–38], few π -expanded cyclic oligophenylenes and oligoheteroarylenes with full conjugation were studied till to date [39]. Recently, Mayor and Didschies reported the biggest conjugated molecular ring with a diameter of 11.8 nm [39]. This molecule has a fully conjugated periphery composed of ethynylene, butadienyldiene, 1,4-thienylene, and 1,4-phenylene units, exhibiting only a weak cyclic conjugation.

Although no host–guest complex derived from giant macrocycles of oligothiophenes has been reported to date, sulfur atoms of thiophene units due to the presence of dipole moment may incorporate an ion or a small molecule in the macrocyclic rings. Furthermore, π -expanded oligothiophenes can be envisaged to self-assemble into nanostructures such as nanowires, nanotubes, and nanodot rings using S··S and π – π interactions. Giant macrocycles with alkyl chains usually form amorphous solid or liquid crystals that are different from well-known macrocyclic oligophenylenes that give crystal structures with π – π stacking interaction. However, reducing the dimensions of macrocycles having non-H-bonding interactions from the three-dimensional crystal structure to the one-dimensional columnar structure leads to interesting self-assembling nanostructures. Our π -expanded oligothiophene macrocycles offer an original insight, as they differ from macrocyclic oligoheteroarenes, such as macrocyclic oligothiophenes and oligopyrroles, in their flexibility to give self-assembling nanostructures.

For nano-sized and shape-persistent cycles with full π -conjugation, π -expanded oligothiophenes (**1–5**) containing 2,5-thienylene, ethynylene, and vinylene units, together with oligo(thienylene-ethynylene) **6**, were designed and synthesized. Since **1**, **2**, **3**, **4**, **5**, and **6** have an almost round shape with 17.5–20, 28.5–30, 38.5–40, 48.5–50, 58.5–60, and 18.1 Å diameters, respectively, these compounds show excellent optical and electric properties as giant conjugated molecular rings with host–guest interactions. (The inner diameters of **1–6** were estimated on the basis of PM3 calculations of unsubstituted cyclic compounds. AM1 calculations led to similar results.) Synthesis of π -expanded oligothiophenes **1–5** was carried out using McMurry coupling of **7** (Scheme 1) [40]. Thus, intermolecular cyclization of **7** under modified McMurry conditions resulted in the formation of the dimer **1**, trimer **2**, tetramer **3**, pentamer **4**, and hexamer **5** in 32%,

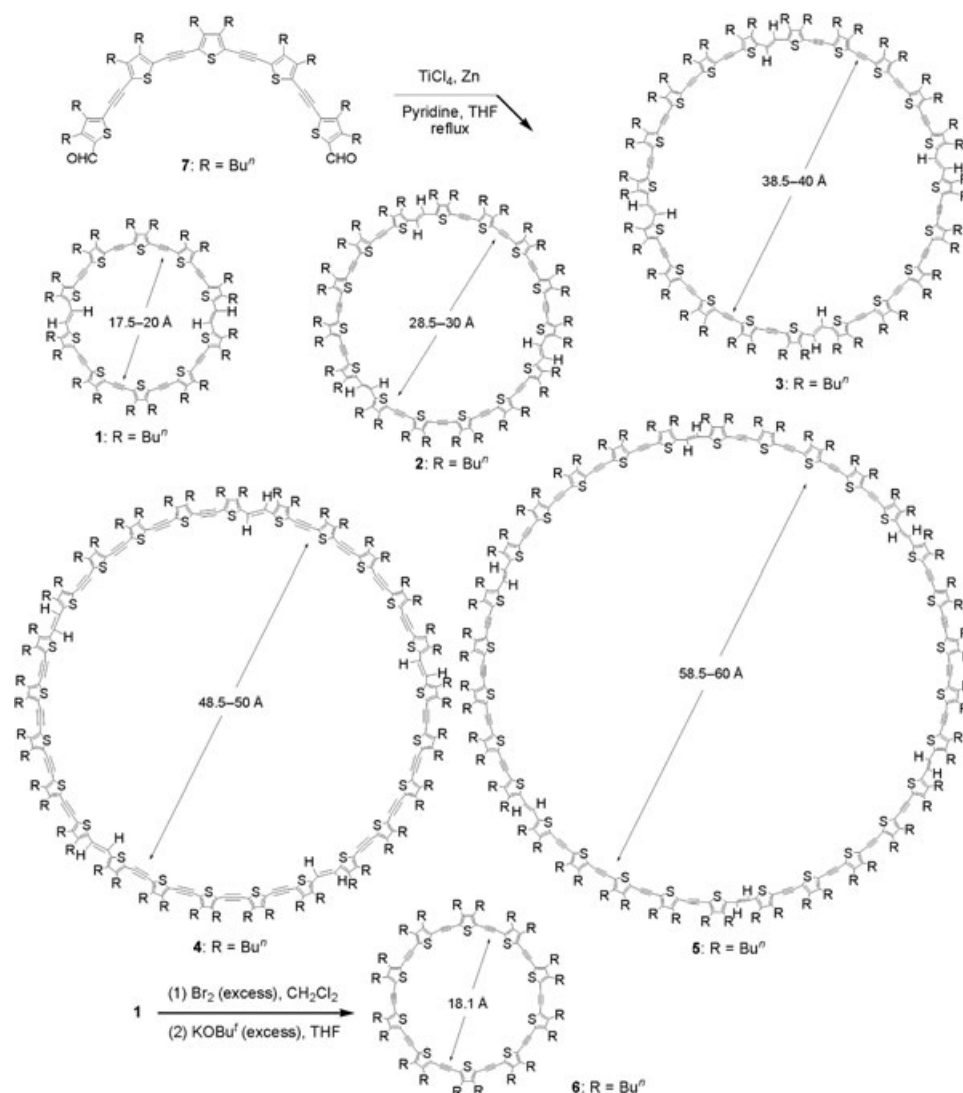
9%, 6%, 4%, and 2% yields, respectively, together with a 1:3 mixture of the *E,Z*- and *Z,Z*-isomers of **1** (7%). Structures of **1–5** were assigned on the basis of ¹H NMR and Laser Desorption/Ionization-Time-of-Flight Mass Spectrometry (LDI-TOF MS). Although LDI-TOF MS spectra of **1** showed molecular ion peaks with corresponding dimerized cation radical (**1**₂⁺), reflecting the formation of cationic aggregates (MM⁺), those of **2–5** exhibited no dimerized cation radicals (**2**₂⁺–**5**₂⁺), presumably due to a very large ring size interaction. For the synthesis of cyclo[10](3,4-dibutyl-2,5-thienylene-ethynylene) (**6**), bromination-dehydrobromination of **1** was carried out in 36% yield. Variable temperature NMR spectroscopic studies revealed that **1–6** show symmetrical structures even at –60°C, reflecting a rapid conformational change in solutions.

X-RAY STRUCTURE OF **1**

The molecular structure of **1** was determined by X-ray analysis (Fig. 1). (The inner diameters of **1–6** were estimated on the basis of PM3 calculations of unsubstituted cyclic compounds. AM1 calculations led to similar results.) The crystal contains 1.5 molar ratio of heptane to **1**. As shown in Fig. 1a, the 10 thiophene rings connected by unsaturated carbon–carbon linkages are arranged in a circular manner, with all the sulfur atoms in *s-cisoid* thiophene rings directed toward the inside. This *s-cisoid* conformation makes the backbone to curl and form a full circle. The intramolecular distances between two sulfur atoms of thiophene rings are 19.9 and 17.1 Å, respectively (Fig. 1a). The large cavity of **1** is filled by butyl groups of neighboring molecules and heptane, and the mutual sharing of the butyl groups of the neighboring molecules causes its frame to give a chair-like conformation (Figs. 1b and 1c). Despite low-temperature X-ray analysis at –180°C, heptane molecules are highly mobile. In addition, the X-ray analysis reveals that **1** serves as a host molecule to alkane guests. Linear alkanes such as hexane and octane also incorporate in **1** to give single crystals.

NANOSTRUCTURES OF **2–5**

Interestingly, giant macrocyclic oligothiophenes **2–5** form complex supramolecular structures due to their weak amphiphilic properties. Thus, **2** forms microcrystals and nanowires from ethylacetate/octane and **3** forms nanowires from ethyl acetate/chloroform (Figs. 2a and 2b). In contrast, **4** and **5** form nanoparticles from ethyl acetate/chloroform (Figs. 2c and 2d). Microcrystals, nanowires, and nanoparticles of **2–5** contain no solvent molecules,



SCHEME 1 Synthesis of π -expanded macrocyclic oligothiophenes 1–6.

and are different from single crystals of **1**. The aggregates of **2** and **3** show well-defined fibrous structures with 100- to 200-nm thickness (Figs. 2a and 2b), whereas **4** and **5** show chained lumps of 300- to 800-nm size (Figs. 2c and 2d). Because **2–5** have both solvophilic and solvophobic moieties, their amphiphilic properties result in microscopic separation leading to the formation of nanofibers and nanoparticles.

ELECTRONIC ABSORPTION AND EMISSION SPECTRA

Absorption and emission spectra of giant macrocycles **1–6** measured in CH_2Cl_2 exhibit a unique feature (Fig. 3 and Table 1). As has been reported previously, a series of linear oligo(thienylene-ethynylene)s up

to 16-mer showed a near saturation for the absorption maximum at the octamer stage [11,41]. Therefore, doubling the conjugation length from octamer to 16-mer causes a little change in the absorption maximum. In contrast, the expanded cyclic oligothiophenes **1–5** show a red shift of the longest absorption maxima with increasing ring size ($6 \approx 1 < 2 < 3 < 4 < 5$ nm), reflecting an almost full conjugation through the rings. In the case of emission spectra, linear oligo(thienylene-ethynylene)s exhibit two major emission bands based on vibronic structure of 0–0 and 0–1 transitions [42]. As shown in Fig. 3, fluorescence spectra of **1–5** exhibit two major emissions at almost the same wavelengths (560–562 and 602–605 nm) with a large Stokes shift of 81–157 nm, whereas **6** exhibits a blue shift with a smaller Stokes shift (537 and 579 nm). Although the separation of

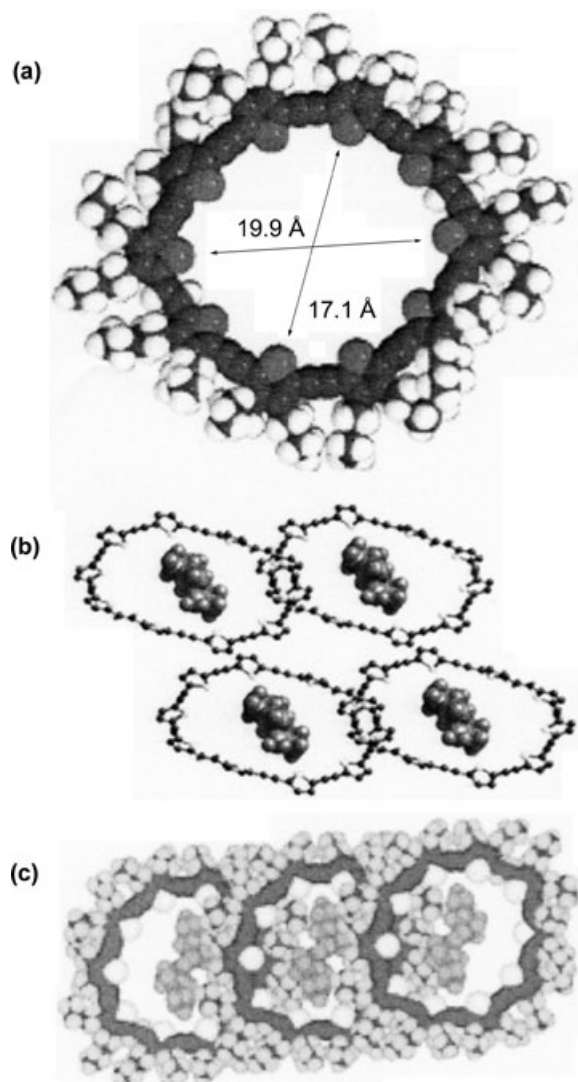


FIGURE 1 X-ray crystal structure of **1**. (a) Top view (space filling). (b) Packing diagram, with the included heptane (green). Butyl groups are omitted for clarity. (c) Packing diagram (space filling).

two emissions in the fluorescence spectra of **1–5** is estimated to be $1246\text{--}1351\text{ cm}^{-1}$, which corresponds to the vibrational energy gap, intensities of the first and second bands in **1** and **6** oppose the normal vibronic structure. Increasing quantum yield with increasing ring size ($6 \approx 1 < 2 < 3$) may reflect the decreasing ring strain in **2** and **3**, whereas decreasing quantum yield with increasing ring size ($3 > 4 \approx 5$) may reflect the mobility of the rings in **4** and **5**.

REDOX BEHAVIOR

Giant macrocycles **1a–6a** behave as π -donors with fairly low oxidation potentials, although linear

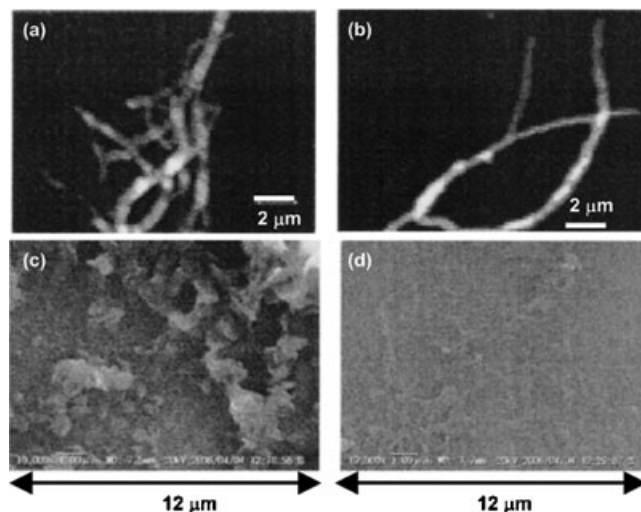


FIGURE 2 Atomic force microscopic images of **2** (a) and **3** (b) and scanning electron microscopic images of **4** (c) and **5** (d).

oligo(thienylene-ethynylene)s exhibit lower π -donor ability than common linear oligothiophenes [43]. Cyclic voltammetric (CV) analysis of redox potentials exhibits three reversible waves in **1a** and two reversible waves in **2a–5a** (Table 2). In contrast, **6a** shows four reversible redox waves. The penta(thienylene-ethynylene) units in **1a–5a** can be oxidized to give the corresponding cationic species, that is, **1a** generates **1a**²⁺, **1a**³⁺, and **1a**⁴⁺, whereas **2a–5a** form **2a**³⁺ and **2a**⁶⁺, **3a**⁴⁺ and **3a**⁸⁺, **4a**⁵⁺ and **4a**¹⁰⁺, and **5a**⁶⁺ and **5a**¹²⁺, respectively.³⁶ In the case of **6a**, fully conjugated thienylene-ethynylene units generate **6a**⁺, **6a**²⁺, **6a**³⁺, and **6a**⁴⁺. Linear sweep voltammetric measurements of **1a** by rotating disk

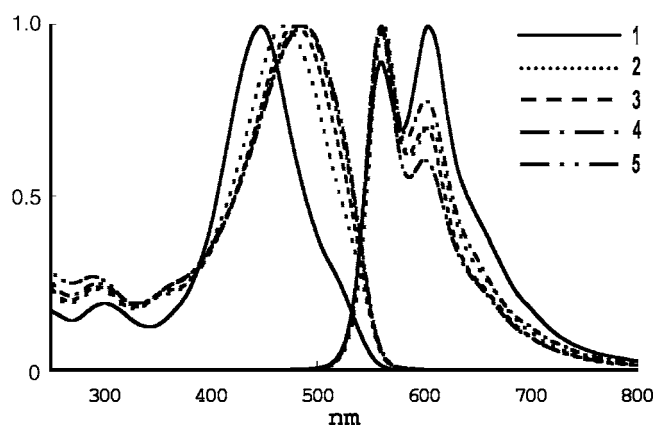


FIGURE 3 Electronic absorption and emission spectra of **1–5**.

TABLE 1 Absorption Coefficients and Fluorescence Quantum Yields of **1–6** in CH₂Cl₂

Compound	Absorption		Fluorescence	
	$\lambda_{max}[nm]$	$\epsilon[M^{-1} cm^{-1}]$	$\lambda_{max}[nm]$	Φ_F^a
1	447	249,000	560,604	0.069
2	469	311,000	562,605	0.084
3	479	405,000	560,602	0.11
4	485	551,000	560,603	0.089
5	488	639,000	560,600	0.086
6	442	235,000	537,579	0.062

^aFluorescence quantum yields (Φ_F) were determined by comparison with quinine sulfate in 0.5 M H₂SO₄ ($\Phi_F = 0.51$).

electrode confirmed that the first oxidation wave contains one 2-electron step, whereas the second and third oxidation waves contain two 1-electron steps. Similarly, the electrochemical oxidation of **6a** was assigned to four 1-electron redox processes.

Oligo- and polythiophenes are easily oxidized by electron acceptors to form corresponding radical salts. One important concept to realize high electric conductivity is π - π stacking and π -dimer formation of cationic species derived from oligo- and polythiophenes. Although linear poly(thienylene-ethynylene)s seem to produce no electroconductive cationic species due to difficulty in the formation of stable cationic species, cyclic oligothiophenes **1–6** produce stable cationic species by oxidation, and hence can give an electroconductive oxidation state. Actually, doping of **1–3** with iodine vapor results in the formation of black materials with moderate conductivities (**1**: $\sigma_{rt} = 1.86 \times 10^{-3} S cm^{-1}$; **2**: $\sigma_{rt} = 2.63 \times 10^{-3} S cm^{-1}$; **3**: $\sigma_{rt} = 2.03 \times 10^{-3} S cm^{-1}$, measured by two-probe method). Electric conductivities of the black materials increased after exposing **1–3** to iodine vapor for 5 to 70 min, though their conductivities gradually decreased to less than

TABLE 2 Redox Potentials [V] of **1–6** in CH₂Cl₂^a

Compound	$E^{OX1}_{1/2}$	$E^{OX2}_{1/2}$	$E^{OX3}_{1/2}$	$E^{OX4}_{1/2}$
1	0.32 (2e ⁻)	0.48 (1e ⁻)	0.61 (1e ⁻)	
2	0.29 (3e ⁻)	0.59 (3e ⁻)		
3	0.31 (4e ⁻)	0.58 (4e ⁻)		
4	0.31 (5e ⁻)	0.57 (5e ⁻)		
5	0.30 (6e ⁻)	0.57 (6e ⁻)		
6	0.43 (1e ⁻)	0.61 (1e ⁻)	0.77 (1e ⁻)	0.94 (1e ⁻)

^aConditions: 0.1 M *n*-Bu₄NClO₄, room temperature, Pt working and counter electrodes. Potentials were measured against Ag/Ag⁺ electrode and converted to the value versus Fc/Fc⁺.

one half of their maximum values after additional exposure.

SUMMARY

The efficient synthesis and novel properties of a series of π -expanded macrocyclic oligothiophenes **1–5**, together with macrocyclic oligo(2,5-thienylene-ethynylene) **6**, were described. Giant macrocycles **1–5** show a red shift of the longest absorption maxima with increasing ring size, presumably due to cyclic conjugation through the rings. In contrast, emissions in the fluorescence spectra of **1–5** are observed at almost the same position, reflecting the similar HOMO-LUMO gaps. The absorption and emission spectra of **6** exhibit a blue shift in comparison with **1**. The infinite cyclic oligothiophenes **1–6** can be easily oxidized to show reversible redox potentials by CV analysis, as doping of **1–3** with iodine vapor results in the formation of semiconductors. X-ray analysis indicated that **1** adopts an almost planar, round structure with *s-cisoid* thiophene rings and that 1.5 molar ratio of heptane to **1** locates inside the cavity. When compounds **1–5** are precipitated from aprotic solvents, they give different morphologies. Thus, **1** forms single crystals from chloroform/heptane, whereas **2** and **3** yield nanowires and **4** and **5** form microscale lumps, respectively. Although **1–5** possess similar structures and polarities (dipole moments) in solutions, the difference in conformation and alignment in the solid state brings about fairly big change in their morphologies.

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