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Giant Macrocycles Composed of Thiophene, Acetylene, and Ethylene Building Blocks

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Abstract: Fully conjugated giant macrocyclic oligothiophenes with 60π, 90π, 120π, 150π, and 180π frames (**1**, **2**, **3**, **4** and **5**) have been designed, and their butyl-substituted derivatives (**1a**, **2a**, **3a**, **4a**, and **5a**) have been synthesized using modified Sonogashira and McMurry coupling reactions as key steps. The 60−180π systems **1**−**5** are circular with 1.8−6 nm inner cavities and 3.3−7.5 nm outside molecular diameters. Compound **1a** containing ten 3,4-dibutyl-2,5-thienylene, eight ethynylene, and two vinylene units has been converted into macrocyclic oligo(3,4-dibutyl-2,5-thienylene-ethynylene) **6a** using bromination/dehydrobromination procedure. Giant macrocycles **1a**−**6a** exhibit a red shift of their absorption spectra and a fairly strong fluorescence with a large Stokes shift as compared to a linear conjugated counterpart having five thiophene rings. Compounds **1a**−**6a** exhibit multistep reversible redox behaviors with fairly low first oxidation potentials, reflecting their cyclic conjugation. Furthermore, chemical oxidation of **1a**−**6a** with $FeCl_3$ shows drastic changes of spectroscopic properties due to intramolecular and intermolecular $\pi-\pi$ interactions. Doping of **1a**−**3a** with iodine forms semiconductor due to its π-donor properties and $\pi-\pi$ stacking ability. X-ray analysis of **1a** confirmed a round, planar structure with nanoscale inner cavity, and revealed host ability for alkanes and unique packing structure. Interestingly, **2a** and **3a** self-aggregate in the solid state to form "molecular wires," which are about 200 nm thick and more than 1 mm long. The internal structures of fibrous aggregates have been investigated by optical microscope, scanning electron microscopy, atomic force microscopy, and X-ray diffraction analyses.

Introduction

Linear π-conjugated oligomers and polymers represent an important class of compounds in the field of materials science[1] and have been extensively investigated as potential molecular devices, machines, switches, field effect transistors (FET), light-emitting diodes (LED), and solar cells.[2] Among these, oligo- and polythiophenes seem to be one of the best candidates to be used as components of organic and molecular electronics,[3,4] because doped oligo- and polythiophenes possess high electrical conductivities[5] and because oligothiophenes can be employed for an electroactive conjugated molecular wire with high rigidity and thermal stability.[3f−i] The rigidity of oligothiophenes is also of great advantage for the use of a conjugated spacer in donor−acceptor diads and triads.[6]

In contrast to linear oligomeric systems with defined structures, size- and shape-persistent macrocyclic oligoarylenes, heteroarylenes, and their π-expanded derivatives are regarded as an infinite π-conjugated system with an inner cavity,[7,8] and

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hence giant cycles attract considerable attention from single-molecule electronics and unusual electronic properties.[9] Furthermore, these cyclic oligomers with an inner cavity may behave like a macrocyclic host toward a fullerene molecule.[10] Although fully conjugated macrocyclic molecules within 30 Å molecular size have reported by several groups,[11,12] a limited number of π-expanded macrocyclic oligoheteroarylenes and oligothiophenes with full conjugation[13,14] have been studied except for thiophene-fused dehydro[12]- and [18]annulenes.[15] Thus, Mayor and Didschies recently reported the biggest molecular ring with a diameter of 11.8 nm.[13] This molecule has a fully conjugated periphery composed of ethynylene, butadiynylene, 2,5-thienylene, and 1,4-phenylene units. Of particular relevance to the present work are the cyclic oligothiophenes (cyclo[n]thiophenes) reported by Bäuerle and coworkers[14] that have been synthesized and characterized by X-ray and scanning tunneling microscopy analyses to elucidate fantastic molecular structures of thiophene oligomers and intriguing arrangements of their ordered two-dimensional (2D) monolayers at the solution–HOPG interface. However, neither electroactive properties nor three-dimensional (3D) supramolecular self-assembly has been reported for cyclic oligothiophenes.

Although no host–guest complex derived from the giant cycles of oligothiophenes has been fully characterized, sulfur atoms having moderate dipole and solvophobicity may incorporate an ion or small molecule in the macrocyclic ring.[16] Futhermore, π-expanded cyclic oligothiophenes can be envisaged to self-assemble into 3D nanostructures such as nanowires, nanotubes, and nanodot rings using S–S, S–π, and π–π interactions[17] similar to a self-assembly of tetrathiafulvalene derivatives containing no hydrogen-bonding site.[18] It is known that Moore's phenylacetylene macrocycle (PAM) having ester substituents dimerizes in chloroform by π–π and polar π-stacking interactions, while it forms higher aggregates in polar solvents owing to solvophobic interaction.[11,19] In contrast, Moore's PAM-bearing alkoxy substituents exhibits no self-aggregation in solution but forms liquid crystals in the condensed phase due to weak solvophobic or polar-π interaction in solution (no aggregation) and fairly strong π–π interaction in condensed phase (formation of liquid crystals).[20] By consideration of possible intra- and intermolecular interactions of cyclic oligoheteroarenes, π-expanded oligothiophene macrocycles having 2,5-thienylene, ethynylene, and vinylene units offer an original insight as they differ from oligoheteroarene macrocycles such as π-expanded cyclic oligopyridines,[21] cyclic oligothiophenes,[14] and cyclic oligopyrroles,[8c,d,22] by their flexibility for the formation of self-assembling nanostructures such as fluorescent electroactive nanowires and nanodots using S–S, S–π, and

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$\pi-\pi$ interactions.[23] Thus, reducing the dimensionality of macrocycles from the strongly restricted crystal structure into the unidirectionally aligned columnar structure should lead to interesting self-assembling nanostructures.

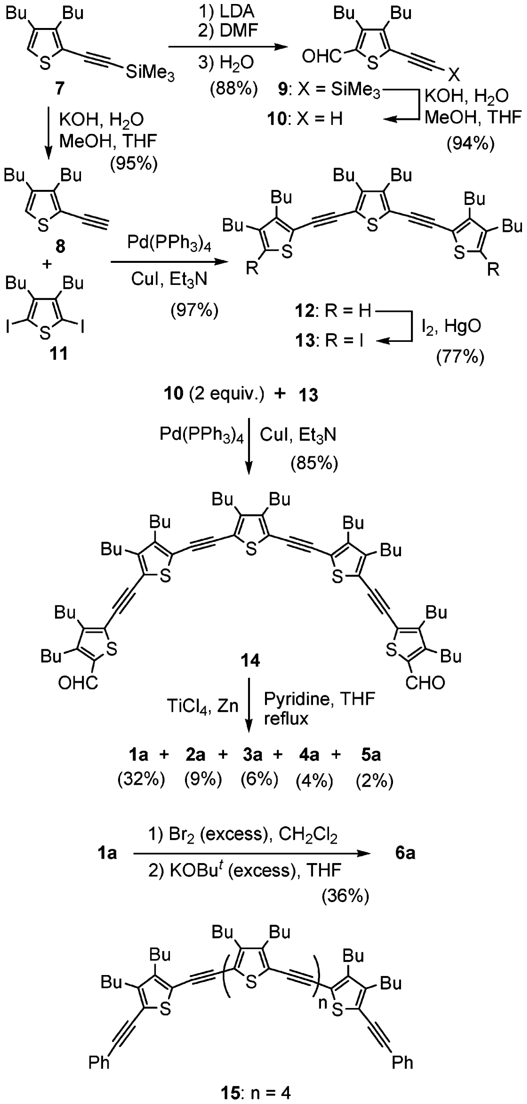
To construct giant macrocycles with full π-conjugation, we designed the titled π-expanded oligothiophenes (**1**−**5**) containing 2,5-thienylene, ethynylene, and vinylene units, together with oligo(thienylene-ethynylene) **6**. Since **1b**−**6b** are expected to have a nearly circular shape with 17.5−20, 28.5−30, 38.5−40, 48.5−50, 58.5−60, and 18.1 Å inner diameters, respectively,[24] these compounds will show interesting optical and electric properties as conjugated giant molecular rings with unique host/guest interactions. Furthermore, giant macrocycles and their cationic counterparts may be good candidates to produce mesoscopic metallic rings which show persistent currents at low temperatures.[25]

In this paper, we show that π-expanded oligothiophenes **1a**−**6a** are fluorescent electroactive macrocycles with conjugated 60π, 90π, 120π, 150π, and 180π electron systems and that chemical and electrochemical oxidations of **1a**−**6a** selectively produce cation radical, dication, trication, tetracation, etc., together with drastic changes of spectroscopic properties. On the basis of X-ray analysis, we are able to probe a planar structure and host ability of **1** with unique crystal packing due to $\pi-\pi$ stacking and molecular porosity. On the other hand, **2a**−**5a** were found to be assemble into unique nanostructures.

Results and Discussion

Syntheses of π-Expanded Macrocyclic Oligothiophenes 1a−6a and Related Compounds. Synthesis of shape-persistent macrocycles has been recently developed using convergent and divergent approaches.[7] The most important points in the synthesis of macrocycles are high yields both in the elongation of molecular chains and in the formation of macrocycles. With this in mind, we employed modified Sonogashira and McMurry coupling reactions for the synthesis of π-expanded macrocyclic oligothiophenes. We used 3,4-dibutylthiophene[26] as the starting material to diminish the solubility problem and chose linear pentamer-dialdehyde **14** as the precursor to construct macrocycles by McMurry coupling in one step as shown in Scheme 1. Thus, 3,4-dibutyl-2-trimethylsilylethynylthiophene **7**,[27] derived from 3,4-dibutylthiophene, was reacted with LDA, followed by treatment with DMF to produce aldehyde **9**. The trimethylsilyl group in **9** was deprotected with KOH in water−MeOH−THF to give **10**. For the preparation of **12** and **13**, the Sonogashira reaction of **8** with **11** in triethylamine proceeded smoothly to give **12**, and iodination of **12** with molecular iodine in the presence of mercury(II) oxide in benzene produced **13**, together with a small amount of monoiodide (5%). The Sonogashira reaction of **13** with **10** (2 equiv) in triethylamine led to key intermediate **14**.

Scheme 1. Synthesis of **1a**, **2a**, **3a**, **4a**, **5a**, and **6a**



For the cyclooligomerization of **14**, the reactions of **14** with low-valent titanium and vanadium were attempted. Although coupling of **14** with low-valent vanadium[28] gave no cyclization products, low-valent titanium reagent prepared by the reaction of $TiCl_3(DME)_{1.5}$ with Zn−Cu in DME[29] produced intermolecular coupling products in low yields. Finally, low-valent titanium reagent prepared from $TiCl_4$ with Zn in the presence of pyridine in THF was found to be an effective catalyst to produce intermolecular coupling products.[15a,30] Thus, intermolecular cyclization of **14** under modified McMurry conditions resulted in the formation of the dimeric **1a**, trimeric **2a**, tetrameric **3a**, pentameric **4a**, and hexameric **5a** in 32, 9, 6, 4, and 2% yields, respectively, together with a 1:3 mixture of the *E*,*Z* and *Z*,*Z* isomers of **1a** (7%).[31] By the use of the synthetic procedure shown in Scheme 1, **1a**, **2a**, **3a**, **4a**, and **5a** can be

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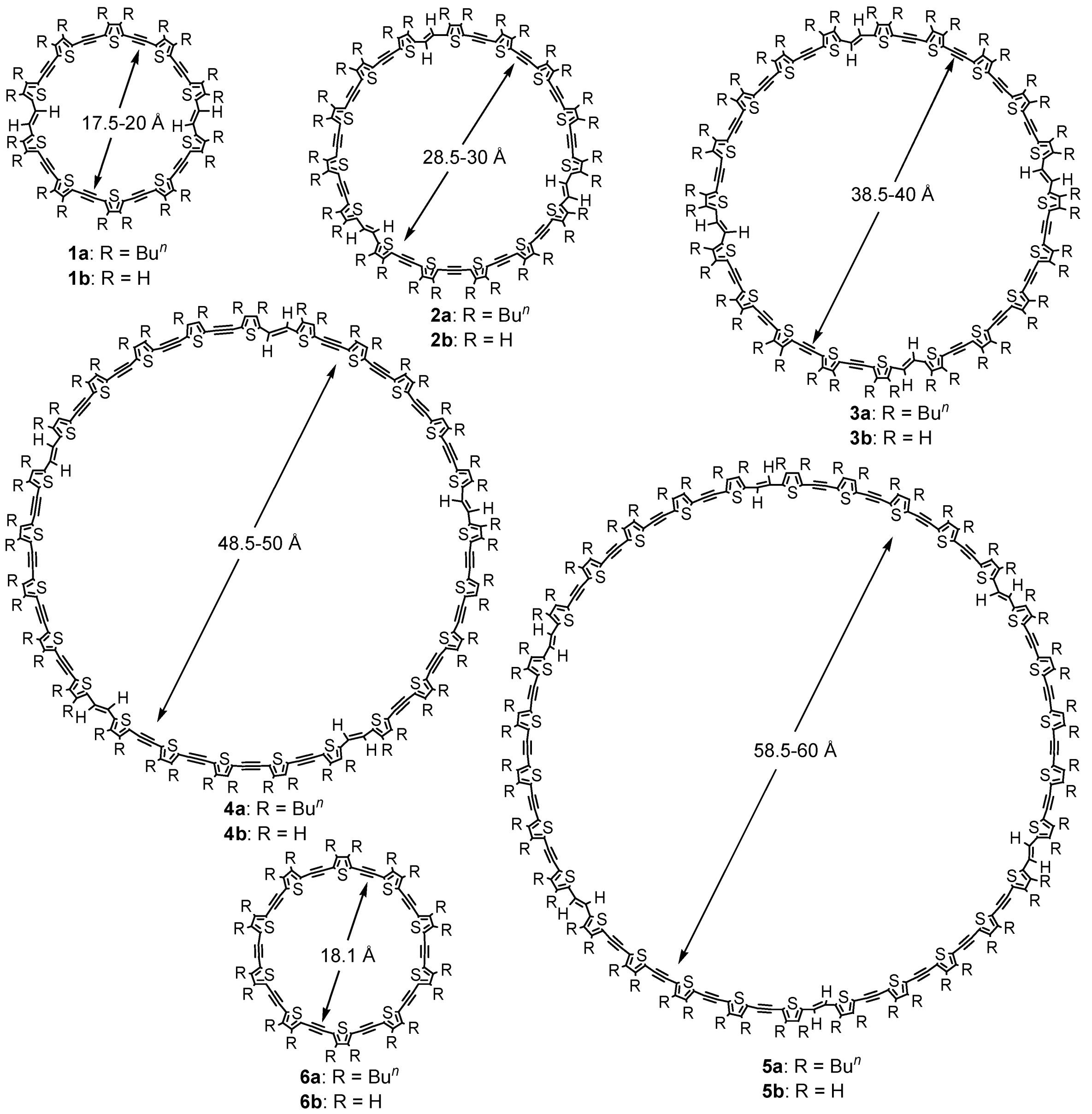

Figure 1. π-Expanded macrocyclic oligothiophenes **1a**,**b**−**6a**,**b**.

synthesized in 20, 5.7, 3.8, 2.5, and 1.3% overall yields starting from easily accessible **11**, respectively.

Synthesis of cyclo[10](3,4-dibutyl-2,5-thienylene-ethynylene) **6a** was carried out using bromination/dehydrobromination procedure. A large excess (15 equiv) of bromine in CH_2Cl_2−CCl_4 was necessary to complete the bromination of the double bonds. Dehydrobromination with a large excess of potassium *tert*-butoxide in THF at −90 °C to room temperature produced the desired **6a** in 36% yield based on **1a**. Giant macrocycles **1a**−**6a** are stable red compounds and can be stored at room temperature under air for a year. To compare conjugation effect, absorption and emission spectra, and redox properties, linear oligothiophene **15** was synthesized (see Supporting Information) in good yields using similar reactions employed for the preparation of **12**−**14**. Linear hexamer **15** was obtained as stable red crystals.

All the new compounds **1a**−**6a** and **15** were definitely characterized by NMR and laser desorption−ionization time-of-flight mass spectrometry (LDI-TOF MS) spectroscopic measurements and by elemental analyses. The ^{1}H NMR spectrum of **1a** in $CDCl_3$ exhibits a vinyl singlet at δ 6.92, together with butyl signals. Similarly, all of the ^{1}H NMR spectra of **2a**−**5a** in $CDCl_3$ show analogous signals of a vinyl singlet (δ 6.98) and butyl groups, although retention times of **1a**−**5a** under the conditions of GPC separation show clear differences. The LDI-TOF MS spectrum of **1a** shows molecular ion peaks with corresponding dimerized cation radical (**1a**$_2^+$), reflecting the formation of cationic aggregates (MM$^+$). In contrast, LDI-TOF MS spectra of **2a**−**5a** exhibit no dimerized cation radicals, presumably due to too large a ring size to interact with each other. The ^{1}H and ^{13}C NMR spectra of **6a** show very simple signals, reflecting a highly symmetrical structure. LDI-TOF MS

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(31) Separation of **1a**−**5a** can be carried out using gel permeation chromatography (GPC) [HPLC, polystyrene column, toluene or $CHCl_3$ as eluent]. Because **1a** easily crystallizes from hexane and chloroform, the separation of **1a** from its *E*,*Z* and *Z*,*Z* isomers and **2a**−**5a** is also easy to do. In concern for *E*,*Z* and *Z*,*Z* isomers of **2a**−**5a**, their formation was not observed, and only pure *E*,*E*-isomers of **2a**−**5a** were isolated and characterized.

Table 1. Absorption Coefficients and Fluorescence Quantum Yields of **1a**−**6a** and **15** in Dichloromethane

	absorption		fluorescence	
compd	λ_{max} (nm)	ϵ (M^{-1} cm^{-1})	λ_{max} (nm)	Φ_F[a]
1a	447	249 000	560, 604	0.069
2a	469	311 000	562, 605	0.084
3a	479	405 000	560, 602	0.11
4a	485	551 000	560, 603	0.089
5a	488	639 000	560, 600	0.086
6a	442	235 000	537, 579	0.062
15	433	119 000	513, 548	0.30

[a] Fluorescence quantum yields (Φ_F) were determined by comparison with quinine sulfate in 0.5 M H_2SO_4 ($\Phi_F = 0.51$).

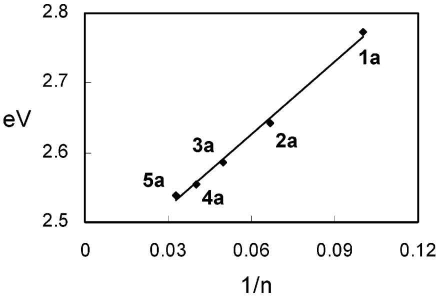

Figure 2. Relationship between the longest absorption maxima (eV) and the number of thiphenes (*n*) of **1a**−**5a**.

spectra of **6a** exhibit molecular ion peaks with corresponding dimerized cation radical (**6a**$_2{}^{+}$) due to cationic aggregates (MM$^+$).

Electronic Absorption and Emission Spectra of 1a−6a and 15. Absorption and emission spectra of giant cycles **1a**−**6a** measured in CH_2Cl_2 exhibit a unique feature (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 maxima (435−445 nm) at the octamer stage.[3c,32] Therefore, the longest absorption maximum of shorter hexamer **15** ($\lambda_{max} = 433$ nm) showed a slight blue shift compared to the saturated absorption maximum. In contrast, the expanded cyclic oligothiophenes **1a**−**5a** show a red shift of the longest absorption maxima with increasing ring size [**6a** = 442 ≈ **1a** = 447 < **2a** = 469 < **3a** = 479 < **4a** = 485 < **5a** = 488 (nm)], reflecting an almost full conjugation through the rings (Figure S23, Supporting Information). As shown in Figure 2, a linear relationship between the longest absorption maxima (eV) and the reciprocal of the number of thiophenes (1/*n*) suggests that the considerable $\pi-\pi$ overlapping in **1a**−**5a** is maintained, although **4a** and **5a** may adopt bent or twisted conformation in solution.

In the case of emission spectra, **15** shows two major emission bands based on vibronic structure of 0−0 and 0−1 transitions, as has been reported for linear oligo(thienylene-ethynylene)s.[33] In contrast, fluorescence spectra of **1a**−**6a** show two major emissions at almost the same wavelengths (560−562 and 602−605 nm) with a large Stokes shift of 72−157 nm (Table 1). Fluorescence quantum yields of **1a**−**6a** are much smaller than those of cyclic oligo(phenylene-ethynylene)s[34] and linear hexamer **15**, reflecting their strained and/or mobile structures. At any rate, **1a**−**6a** show characteristic emissions of orange color (Figure S24, Supporting Information). Increasing quantum yield with increasing ring size (**6a** ≈ **1a** < **2a** < **3a**) may reflect the counterbalance between π-extension and increasing structural mobility.

Table 2. Redox Potentials [V] of **1a**−**6a** in Dichloromethane[a]

compd	$E^{ox1}_{1/2}$	$E^{ox2}_{1/2}$	$E^{ox3}_{1/2}$	$E^{ox4}_{1/2}$
1a	0.32 (2e$^-$)	0.48 (1e$^-$)	0.61 (1e$^-$)	
2a	0.29 (3e$^-$)	0.59 (3e$^-$)		
3a	0.31 (4e$^-$)	0.58 (4e$^-$)		
4a	0.31 (5e$^-$)	0.57 (5e$^-$)		
5a	0.30 (6e$^-$)	0.57 (6e$^-$)		
6a	0.43 (1e$^-$)	0.61 (1e$^-$)	0.77 (1e$^-$)	0.94 (1e$^-$)

[a] Conditions: 0.1 M *n*-Bu_4NClO_4, room temperature, Pt working and counter electrode. Potentials were measured against Ag/Ag$^+$ electrode and converted to the value vs Fc/ Fc$^+$.

Chemical and Electrochemical Oxidations. All giant macrocycles **1a**−**6a** behave as π donors with fairly low oxidation potentials, although linear oligo(thienylene-ethynylene)s exhibit lower π-donor ability than common linear oligothiophenes.[35] 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, i.e., **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**$^{10+}$, **5a**$^{6+}$ and **5a**$^{12+}$, respectively.[36] In the case of **6a**, fully conjugated thienylene-ethynylene units generate **6a**$^{\bullet+}$, **6a**$^{2+}$, **6a**$^{3+}$, and **6a**$^{4+}$ (Figure S32−34, Supporting Information). Linear sweep voltammetric measurements of **1a** by rotating disk electrode confirmed that the first oxidation wave contains one two-electron step, whereas the second and third oxidations are two one-electron steps. Similarly, the electrochemical oxidation of **6a** was assigned to four one-electron redox process.

In a similar manner to the electrochemical oxidation, chemical oxidation of **1a**−**3a** with $FeCl_3$ in CH_2Cl_2 resulted in the formation of the corresponding cationic species,[37] and typical electronic spectra of the cationic species were observed (Figure S35−37, Supporting Information). Thus, chemical oxidation of **1a**−**3a** with 2 equiv. of $FeCl_3$ formed **1a**$^{\bullet+}$, **2a**$^{\bullet+}$, and **3a**$^{\bullet+}$. Electron spin resonance (ESR) measurements of **1a**$^{\bullet+}$, **2a**$^{\bullet+}$, and **3a**$^{\bullet+}$ showed broad signals at $g = 2.0024$, 2.0025, and 2.0025, respectively.[37,38]

Oligo- and polythiophenes are easily oxidized with electron acceptors to form corresponding radical salts. One important concept to realize high electric conductivity is $\pi-\pi$ stacking and π-dimer formation of cationic species derived from oligo- and polythiophenes. Although linear poly(thienylene-ethy-

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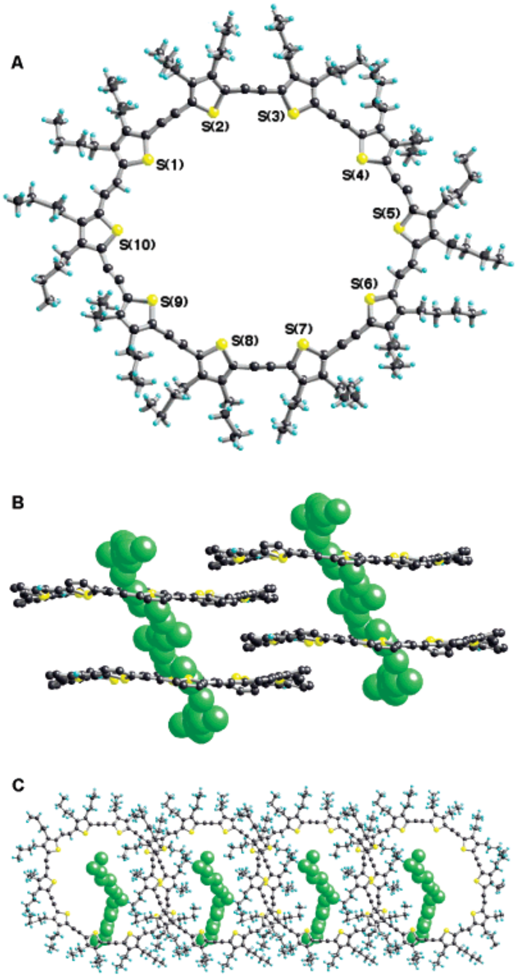

Figure 3. X-ray crystal structure of **1a**. (A) Top view. (B) Packing diagram (side view) with the included heptane (green). Butyl groups are omitted for clarity. (C) Packing diagram (top view).

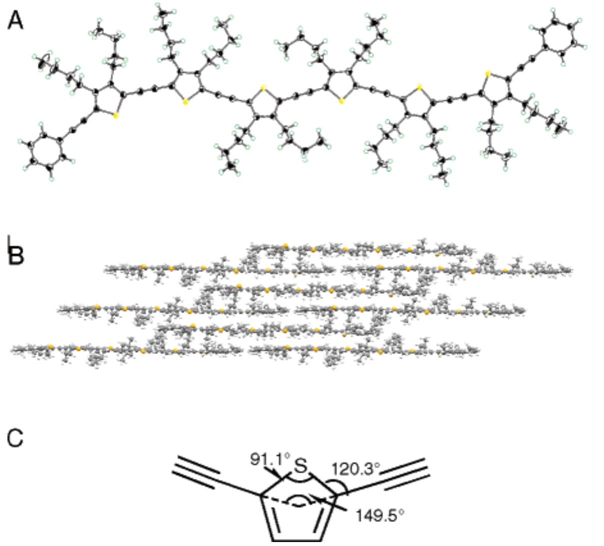

Figure 4. X-ray crystal structure of **15**. (A) ORTEP drawing (50% probability). (B) Packing structure. (C) The averaged angles of $C_{thiophene}-S-C_{thiophene}$ and $S-C_{thiophene}-C_{alkyne}$ and the calculated angle between acetylene bonds.

nylene)s seem to produce no electroconductive cationic species due to difficulty in the formation of stable cationic species,[39] cyclic **1a**−**6a** produce stable cationic species by oxidation and hence can form an electroconductive oxidation state. Actually, doping of **1a**, **2a**, and **3a** with iodine in vapor resulted in the formation of black materials with moderate conductivities (**1a**, $\sigma_{rt} = 1.86 \times 10^{-3}$ S cm^{-1}; **2a**, $\sigma_{rt} = 2.63 \times 10^{-3}$ S cm^{-1}; **3a**, $\sigma_{rt} = 2.03 \times 10^{-3}$ S cm^{-1}, measured by the two-probe method).[40] All electric conductivities of the black materials increased after exposing **1a**, **2a**, and **3a** to iodine vapor for 5−70 min, though their conductivities gradually decreased to less than one-half of their maximum values after additional exposure.

Molecular Structures. The structure of **1a** has been determined unambiguously by X-ray analysis (Figure 3). The crystal contains 1.5 molar ratio of heptane to **1a**. Although heptane molecules and two acetylene linkages next to the double bonds are disordered, the final results fill our requirement. As shown in Figure 3a, the ten thiophene rings connected by the unsaturated carbon−carbon linkages are arranged circularly with all the sulfur atoms in s-cisoid thiophene rings directed toward the inside. This s-cisoid conformation makes the backbone curl and form a full circle. The molecule shows a slight chairlike conformation, and intramolecular distances between two sulfur atoms at S(5)−S(10) and S(3)−S(8) are 19.9 and 17.1 Å, respectively. Maximum diameter of **1a** including the butyl groups is extended to 3.6 nm. The large cavity of **1a** 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 adopt a chairlike conformation. Macrocyclic rings are partially stacked with a distance of 3.6 Å to form channels (Figures 3b and 3c), and there is S(5)···S(10) short contact (3.65 Å) along the *a*-axis. The S(5)···S(10) intermolecular distance is less than the S···S van der Waals diatance (3.7 Å). Heptane molecules incorporated in the ring are considerably mobile, despite low-temperature X-ray analysis at −180 °C.

The X-ray analysis reveals that macrocycle **1a** serves as a host molecule to alkane guests. Linear alkanes like hexane and octane are also incorporated in the crystal lattice of **1a** to form single crystals, but pentane and decane are not suitable guests to **1a**. Moreover, **1a** incorporates ethyl acetate in the crystals. In a similar manner, **6a** forms a host−guest complex with heptane, although the crystals are too thin to determine its crystal structure. On the contrary, **2a**−**5a** produce no host−guest complexes with alkanes, presumably due to larger cavity size of **2a**−**5a** than **1a** and **6a**.

For linear oligo(2,5-thienylene-ethynylene) **15**, single crystals suitable for X-ray analysis were also obtained from methanol/ethyl acetate. The X-ray diffraction data were collected at −150 °C to give a well-refined structure (Figure 4A), even though some butyl side chains are disordered. In the packing structure, **15** stacks in a stairlike manner with the nearest $C_{thiophene}-C_{thiophene}$ contact of 3.48 Å (Figure 4B). There is no space to be filled with small molecule, and hence the single crystal does not include any solvent molecules despite of the relatively large

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(39) Oxidation potentials ($E^{ox1}_{1/2}$ = 0.53 and $E^{ox2}_{1/2}$ = 0.68 V vs Fc/Fc^{+}) of **15** are much higher than **1a**−**6a**. HOMO level of **15** is also lower than those of **1a**−**6a** based on PM3 calculations.

(40) Doping of iodine vapor was carried out using a compressed pellet of ca. 1 × 0.5 × 0.01 mm^3 size, to which two gold wires were attached apart through ca. 0.5 mm distance. Before doping, each sample prepared from **1a**−**3a** was an insulator. After doping of iodine vapor for 5−70. min, all samples showed electric conductivities.

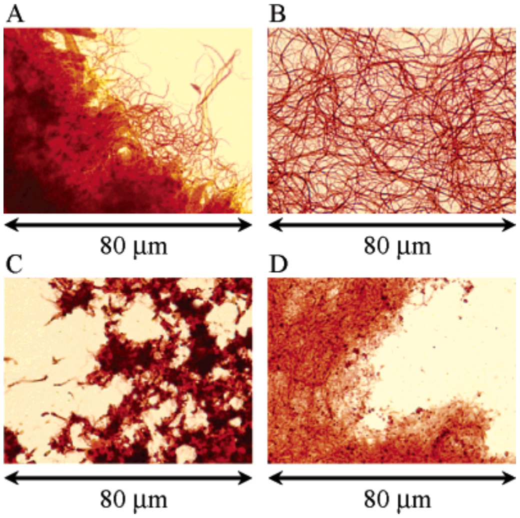

Figure 5. Microscopic images of **2a**−**5a**. Micrographs on a glass plate using a light microscope with 1000× magnification. (A) Fibrous structure of **2a** with microcrystals. (B) Fibrous structure of **3a**. (C) Microlumps of **4a**. (D) Nanoparticles of **5a**.

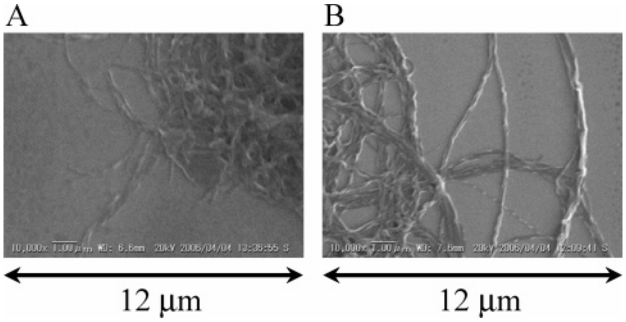

Figure 6. SEM images of **2a** (A) and **3a** (B) on a silicon wafer with 10 000× magnification.

molecular size of **15**. The result is in contrast to the formation of host−guest complex of **1a** and **6a** with several types of alkanes.

The solid-state structure of **15** adopts a nearly linear conformation with the central four thiophene rings in s-transoid form and two terminal thiophene rings in s-cisoid form. Because the energy difference and rotational barrier between the s-transoid and s-cisoid conformers are considered to be small,[41] the mixed s-transoid and s-cisoid conformation in the X-ray structure would be due to crystal packing force. In any case, the conformational flexibility affects favorably in the synthesis of macrocycles **1a**−**5a**. On the other hand, the optimum size for the thienylene-ethynylene macrocycles can be roughly estimated from the bond angles of the almost strain-free linear structure. As shown in Figure 3C, the average angles of $C_{thiophene}-S-C_{thiophene}$ and $S-C_{thiophene}-C_{alkyne}$ are 91.1 and 120.3°, respectively. Thus, the angle between the two adjacent acetylene bonds is calculated to be 149.5°, which is closest to the inner angle of regular dodecagon (150°). Since macrocycles **1a** and **6a** consist of ten thiophene rings, the macrocyclic rings would be somewhat smaller than the optimum size, i.e., twelve thiophenes, and hence lose some conformational flexibility. This rigidity may be the reason why the formation of host−guest complexes takes place only for **1a** and **6a** among the series of macrocycles. Although the molecular structures of **2a**−**5a** have not yet been determined by X-ray analysis, ^{1}H NMR spectra of **2a**−**5a** in $CDCl_3$ at −60 °C exhibited similar spectral patterns to those at room temperature. Therefore, a rapid conformational exchange can be concluded for the structures of **2a**−**5a**.[42,43]

Fibrous Self-Assembly of 2a and 3a from Solution States. Although cyclic oligothiophene-10-mer **1a** forms single crystals from chloroform−hexane, the corresponding 15−30-mers **2a**−**5a** bring about no single crystals under the same conditions. Interestingly, however, weak amphiphilic properties of **2a**−**5a** having solvophilic and solvophobic moieties lead to microscopic separation, resulting in the fabrication of complex supramolecular architectures (Figure 5). In the case of 15-mer **2a**, the macrocycle forms a mixture of microcrystals and nanowires from ethyl acetate−octane (Figure 5A). Macrocyclic 20-mer **3a** easily forms stable nanowires from chloroform−ethyl acetate (Figure 5B), and 25-mer **4a** leads to the formation of microscale lumps from chloroform−ethyl acetate (Figure 5C), whereas 30-mer **5a** forms nanoparticle from chloroform−ethyl acetate (Figure 5D). All microcrystals, nanofibers, and nanoparticles of **2a**−**5a** contain no solvents, different from single crystals of **1a**. The aggregates of **2a** and **3a** exhibit marked fibrous structures with ca. 100 and 200 nm thickness, respectively (Figure 6), whereas the aggregates of **4a** and **5a** rather show chained lumps of 300−800-nm size (Figure S19, Supporting Information). Interestingly, nanofibers of **3a** possess a helical form which exists in seemingly equal distribution of both right and left helical structures. Although **2a**−**5a** have a poor molecular amphiphilicity, their size-persistent nature may enhances the formation of nanofibers, and nanoparticles.

X-ray diffraction (XRD) patterns for a mixture of microcrystals and nanofibers prepared from **2a** exhibits five sharp reflections for d = 30.1 (weak), 18.0 (very strong), 15.1 (medium), 11.8 (strong), and 4.14 Å (weak). In contrast, XRD analyses of nanofibers and nanoparticles from **3a**−**5a** show a broad strong reflection (d = 11.9−12.7 Å) with a very broad weak reflection (d = 4.1−4.2 Å) corresponding to partial alignment and weak $\pi-\pi$ stacking, although their molecular morphology is different. Similarly, XRD analyses of drop-cast films of **1a**−**5a** on the aluminum surface exhibit a different feature. Although diffractogram of a film prepared from a solution of **1a** in chloroform is almost similar to that of single crystals, diffractogram of a film of **2a** shows very broad (d = 11.9 and 12.7 Å) and broad reflections (d = 3.9 Å). Furthermore, diffractograms of films prepared from solutions of **3a**−**5a** exhibit two strong reflections (d = 12 and 4.2 Å), and the latter reflection corresponds to a weak stacking structure.

Conclusion

We have here described the efficient synthesis and novel properties of a series of π-expanded macrocyclic oligothiophenes **1a**−**5a**, together with macrocyclic oligo(2,5-thienylene-ethynylene) **6a**. VT NMR spectroscopic studies revealed that these

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(42) Macrocyclic cyclo[n]thiophenes less than n = 14 are calculated to possess *s-cisoid* conformation with a planar structure, but larger cyclic oligothiophenes adopt a more energetically favorable *s-transoid* conformation: Zade, S. S.; Bendikov, M. *J. Org. Chem.* **2006**, *71*, 2972−2981.

(43) The energy differences between planar and nonplanar conformations of **3b**−**5b** are less than 1 kcal/mol based on PM3 calculations.

compounds show symmetrical structures even at −60 °C, reflecting a rapid conformational change in solutions. Giant macrocycles **1a**−**5a** 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 **1a**−**5a** are observed at almost the same position, reflecting the similar highest-occupied molecular orbital (HOMO)−lowest-unoccupied molecular orbital (LUMO) gaps. The absorption and emission spectra of **6a** exhibit a blue shift as compared to **1a**. As is distinct from linear oligomer **15**, the infinite cyclic **1a**−**6a** can be easily oxidized to show reversible redox potentials by CV analysis. Similarly, chemical oxidation of **1a**−**3a** produces corresponding cationic species which can be characterized by UV−vis−NIR and ESR spectra, and doping of **1a**−**3a** with iodine vapor forms semiconductors. X-ray analysis has indicated that **1a** adopts an almost planar round shape with s-cisoid thiophene rings and that 1.5 molar ratio of heptane to **1a** locates inside in the cavity. The most interesting properties of **1a**−**5a** are their different morphology, when these compounds are precipitated from aprotic solvents. Thus, **1a** forms single crystals from chloroform−hexane, whereas **2a** yields a mixture of microcrystals and nanowires. The 20-mer **3a** forms stable nanowires with 200 nm thickness from chloroform−ethyl acetate, and **4a** and **5a** form microscale lumps with 300−800 nm from chloroform−ethyl acetate. Although **1a**−**5a** possess similar structures and polarities (dipole moments) in solutions, the difference in conformation and alignment in the solid state brings about fairly big change of the morphology.

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Supporting Information Available: All experimental details for the synthesis of π-expanded macrocyclic oligothiophenes **1a**−**6a** and linear hexamer **15**, ^{1}H and ^{13}C NMR, LDI-TOF-MS, absorption and emission spectra of **1a**−**6a**, X-ray analyses of **1a** and **15**, scanning electron microscopy images of **4a** and **5a**, atomic force microscopy images of **2a** and **3a**, XRD patterns of nanowires, particles, and films of **2a**−**5a**, cyclic voltammograms of **1a**−**6a**, and electronic absorption spectra of oxidized **1a**−**3a** with CIF files of **1a** and **15**. This material is available free of charge via the Internet at http://pubs.acs.org.

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