



Account / Revue

Giant macrocycles composed of thiophene, acetylene, and ethylene units

Masahiko Iyoda

Department of Chemistry, Graduate School of Science and Engineering, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan

Received 8 August 2008; accepted after revision 13 October 2008

Available online 26 November 2008

Abstract

Fully conjugated π -expanded macrocyclic oligothiophenes with 60π – 180π electron systems have been synthesized using modified McMurry coupling reaction as a key step. X-ray analyses of 60π and 72π systems revealed unique molecular and packing structures, reflecting planar cyclic structures with large inner cavities. All giant macrocycles exhibit multi-step reversible redox behavior with fairly low first oxidation potentials, reflecting their cyclic conjugation. Doping of macrocycles with iodine forms semiconductors owing to their π -donor properties and π – π stacking ability. Interestingly, 90π and 120π systems self-aggregate in the solid state to form red nanofibers. The structures of fibrous aggregates have been established by SEM and AFM analyses. Furthermore, two-photon properties of 72π , 108π , 144π , and 180π systems show that the increasing π -conjugation leads to an increase in the two-photon absorption cross-section with magnitudes as high as 100,000 GM in the visible spectral region. **To cite this article:** M. Iyoda, C. R. Chimie 12 (2009).

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Keywords: Giant macrocycles; Expanded oligothiophenes; McMurry coupling reaction; Nanofibers; Two-photon absorption cross-section

1. Introduction

Linear π -conjugated oligomers and polymers have been extensively investigated for targeting molecular electronics [1,2]. Among these, oligo- and polythiophenes seem to be one of the best candidates for using in components of electronic and optoelectronic devices [3,4], because oxidation of oligo- and polythiophenes produces highly electroconductive composites caused by polaron, bipolaron, and π -dimer formations [5]. Furthermore, oligothiophenes can be employed for an electroactive conjugated molecular

wire with high rigidity and thermal stability [6–8]. The rigidity of oligothiophenes is also of great advantage for their use as a conjugated spacer in donor–acceptor diads and triads [9].

In contrast to linear oligomers, fully conjugated macrocyclic oligoarylenes, heteroarylenes, and their π -expanded counterparts are regarded as an infinite π -conjugated system with an inner cavity [10]. Therefore, these macrocycles have attracted considerable attention due to their effective conjugation length and unusual electronic properties [11]. Recently, Bäuerle and coworkers have synthesized a series of cyclic oligothiophenes and characterized their fantastic molecular structures using X-ray and STM analyses

E-mail address: iyoda@tmu.ac.jp

[12]. We are particularly interested in shape-persistent or semishape-persistent macrocycles with extremely large molecular diameters. Although fully conjugated macrocycles within 30 Å molecular size have been reported by several groups [13–16], few π -expanded cyclic oligophenylenes and oligoheteroarylenes with full conjugation have been studied to date [17]. Recently, Mayor and Didschies have reported the largest conjugated molecular ring with a diameter of 11.8 nm [17]. This molecule has a fully conjugated periphery composed of ethynylene, butadienylidene, 1,4-thienylene, and 1,4-phenylene units, only exhibiting weak cyclic conjugation.

Here, the synthesis, novel molecular structures, electronic and optoelectronic properties, and supramolecular chemistry of π -expanded cyclic oligothiophenes are summarized to provide an introduction to the new field of giant macrocyclic oligothiophenes [18].

2. Giant macrocyclic oligothiophenes

2.1. Molecular design and synthesis

π -Expanded oligothiophenes **1–3** are shape-persistent or semishape-persistent because of their planar thiophene, acetylene, and ethylene units (Fig. 1). We planned the synthesis of **2** and **3** using successive Sonogashira and McMurry coupling reactions. Thus, **2a–2e** and **3a–3d** are suitable target molecules for constructing giant macrocycles with full π -conjugation, because **2a–2e** and **3a–3d** are expected to have a nearly circular shape with 30–80 Å molecular diameters and 18–60 Å inner cavities.¹ In addition, the calculated structures of **2a–2e** and **3a–3d** have no severe ring strain.

Although no host–guest complex derived from giant macrocycles of oligothiophenes has been reported to date, sulfur atoms having a dipole may incorporate an ion or small molecule in the macrocyclic rings like thiacyclic ethers [19]. Furthermore, π -expanded oligothiophenes can be envisaged as self-assembling into nanostructures such as nanowires, nanotubes, and nanoparticles using S...S and π – π interactions [20]. Giant macrocycles with long alkyl chains usually form an amorphous solid or liquid crystals different from well-known macrocyclic oligophenylenes which lead to the formation of crystal structures with π – π stacking interaction. Thus, reducing the dimensionality of

macrocycles having non-H-bonding interactions from the three-dimensional crystal structure into the one-dimensional columnar structure leads to the formation of interesting self-assembling nanostructures. Our π -expanded oligothiophene macrocycles differ from macrocyclic oligoheteroarenes, such as macrocyclic oligothiophenes and oligopyrroles [12,21], in that our oligothiophene macrocycles can flexibly form self-assembling nanostructures.

Syntheses of **2a–2e** and **3a–3d** are summarized in Schemes 1 and 2. Intermolecular cyclization of **4** under modified McMurry conditions produces a mixture of cyclic oligomers, which can be separated easily by gel permeation chromatography on polystyrene with toluene or chloroform as an eluent to afford the 30 π -dimer **2a**, 90 π -trimer **2b**, 120 π -tetramer **2c**, 150 π -pentamer **2d**, and 180 π -hexamer **2e** in 32, 9.4, 6.2, 3.9, and 2.3% yields, respectively, together with a 1:3 mixture of the *E,Z*- and *Z,Z*-isomers of **2a** (7%) (Scheme 1). Since **2a** crystallizes from chloroform–heptane, pure **2a** can be isolated from the mixture of stereoisomers. For the synthesis of cyclo[10](2,5-thienylene–ethynylene) **1a**, bromination–dehydrobromination of **2a** produces **1a** in 36% yield. All macrocycles **1a** and **2a–2e** are stable in the crystalline state and can be stored in air at room temperature for a year. VT NMR spectroscopic studies revealed that **1a** and **2a–2e** show symmetrical structures even at –60 °C, reflecting a rapid conformational change in solutions.

Intermolecular McMurry cyclization of **5** produces the 72 π -dimer **3a**, 108 π -trimer **3b**, 144 π -tetramer **3c**, and 180 π -pentamer **3d** in 39, 8.3, 2.5, and 1.2% yields, respectively (Scheme 2). In addition, 216 π -hexamer **3e** was isolated in 0.2% yield. Unfortunately, however, conversion of **3a** to **1b** with bromination–dehydrobromination procedure afforded the desired **1b** in a trace yield. Therefore, **3e** and **1b** were not fully characterized. All macrocycles are stable in air at room temperature.

2.2. X-ray structural analyses

Fantastic molecular structures of **2a** and **3a** have been determined by X-ray analysis (Figs. 2 and 3). A single crystal of **2a** from chloroform–heptane contains 1.5 molar ratio of heptane to **2a**. As shown in Fig. 2a, the 10 thiophene rings connected by unsaturated carbon–carbon linkages are arranged circularly with all the sulfur atoms in *s-cisoid* thiophene rings directed towards the inside. This *s-cisoid* conformation makes the backbone curl and forms a full circle. The intramolecular distances between two sulfur atoms of thiophene rings are 19.9 and 17.1 Å. The large cavity

¹ The molecular diameters and inner cavities of **2a–2e** and **3a–3d** were estimated based on PM3 calculations. AM1 calculations led to similar results.

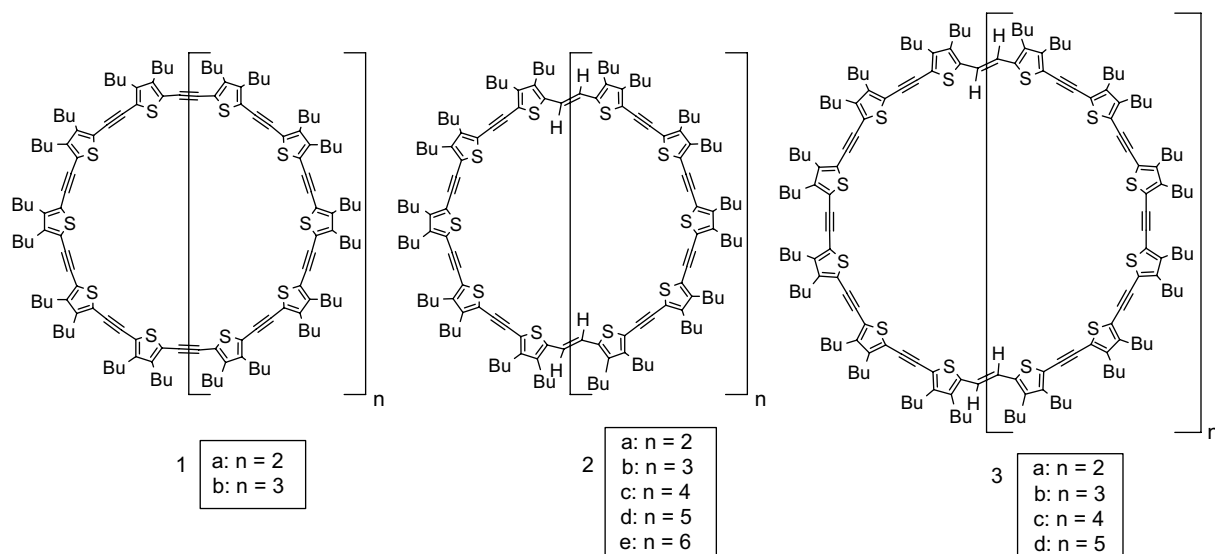


Fig. 1. Giant macrocycles 1–3.

of **2a** is filled by central heptane and edging butyl groups of neighboring molecules, and the mutual sharing of the butyl groups of the neighboring molecules causes its frame to have a slightly bent chair-like conformation (Fig. 2b). Heptane molecules incorporated in the ring are considerably mobile, despite low-temperature X-ray analysis at -180°C . The X-ray analysis reveals that **2a** serves as a host molecule to alkane guests. Linear alkanes like hexane and octane also incorporate in **2a** to form single crystals.

A single crystal suitable for X-ray analysis was obtained from chloroform–decane (Fig. 3). Although **2a** composed of 10 thiophene units has a nearly round shape structure with all thiophene units in *cisoid* form, **3a** composed of 12 thiophene units is narrow in the middle and has two thiophene units in a *transoid* form so as to fill the center of the cycle. The resultant small cavities are filled with neighboring butyl groups, and **3a** has a slightly bent chair-like structure. As a result, the single crystal involves no solvent molecule.

3. Giant macrocycles as functional materials

3.1. Redox behavior

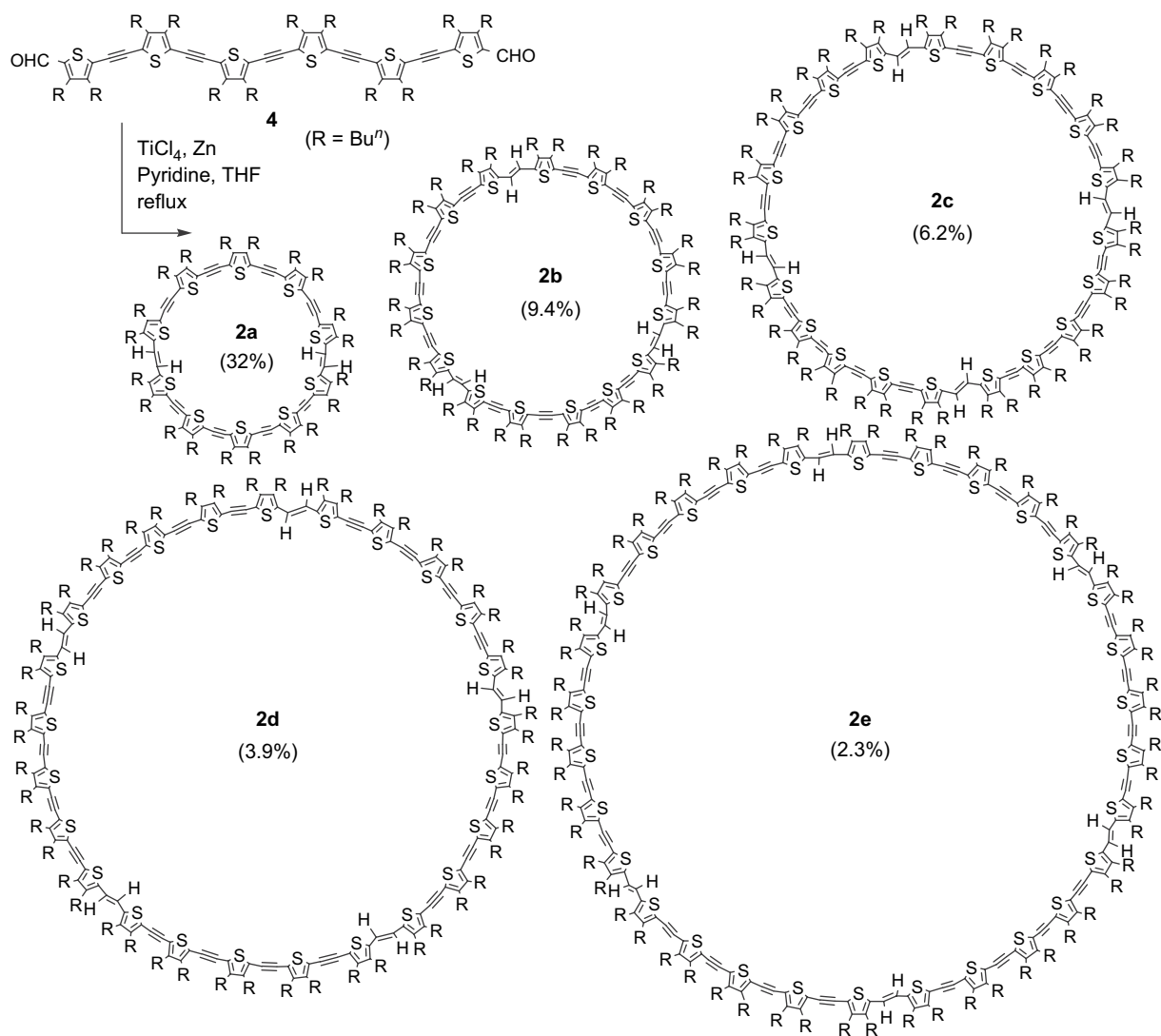
All giant macrocycles **1a**, **2a–2e**, and **3a–3d** behave as π -donors with fairly low oxidation potentials, although linear oligo(thienylene–ethynylene)s exhibit lower π -donor ability than common linear oligothiophenes [22]. Cyclic voltammetric (CV) analyses of **1a** and **2a** show them to exhibit four and three

reversible waves, respectively, whereas **2b–2e** and **3a–3d** show two reversible waves. Therefore, smaller macrocycles exhibit stronger electronic interaction corresponding to on-site Coulombic repulsion, but macrocycles larger than 72π system show only a small on-site Coulombic repulsion in the polycationic states.

Oligo- and polythiophenes are easily oxidized with 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 owing to difficulty in the formation of stable cationic species, cyclic **2a–2e** and **3a–3d** produce stable cationic species by oxidation and hence can form an electroconductive oxidation state. Actually, doping of **2a**, **2b**, and **2c** with iodine vapor resulted in the formation of black materials with moderate conductivities (**2a**: $\sigma_{\text{rt}} = 1.86 \times 10^{-3} \text{ S cm}^{-1}$; **2b**: $\sigma_{\text{rt}} = 2.63 \times 10^{-3} \text{ S cm}^{-1}$; **2c**: $\sigma_{\text{rt}} = 2.03 \times 10^{-3} \text{ S cm}^{-1}$, measured by 2 probe method). All electric conductivities of the black materials increased after exposing **2a**, **2b**, and **2c** to iodine vapor for 5–70 min, though their conductivities gradually decreased to less than one-half of their maximum values after additional exposure.

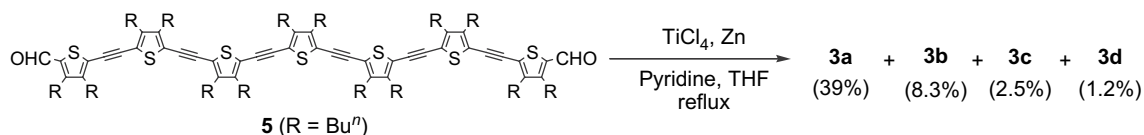
3.2. Optical properties

Absorption and emission spectra of giant macrocycles **2a–2e** and **3a–3d** measured in CH_2Cl_2 exhibit

Scheme 1. Synthesis of **2a–2e**.

a unique feature (Table 1). As has been reported previously, a series of linear oligo(thiophene–ethynylene)s up to 16-mer exhibited near saturation for the absorption maximum at the octamer stage [6,23]. Therefore, it has been concluded that doubling the conjugation length from octamer to 16-mer causes

little change in the absorption maximum. In contrast, the expanded cyclic oligothiophenes **1a**, **2a–2e**, and **3a–3b** except for **3c** and **3d** exhibit a redshift of the longest absorption maxima with increasing ring size, reflecting an almost full conjugation through the rings (Fig. 4). In the case of emission spectra, linear

Scheme 2. Synthesis of **3a–3d**.

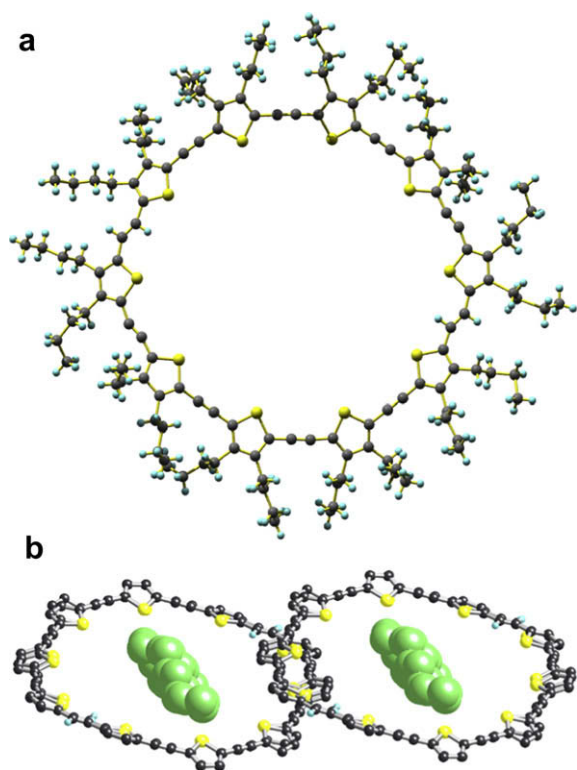


Fig. 2. X-ray crystal structure of **2a**. (a) Top view. (b) Packing diagram with the included heptane. Butyl groups are omitted for clarity.

oligo(thienylene–ethynylene)s were reported to exhibit two major emission bands based on the vibronic structure of 0-0 and 0-1 transitions [24]. As shown in Table 1, fluorescence spectra of **1–5** show two major emissions at almost the same wavelengths

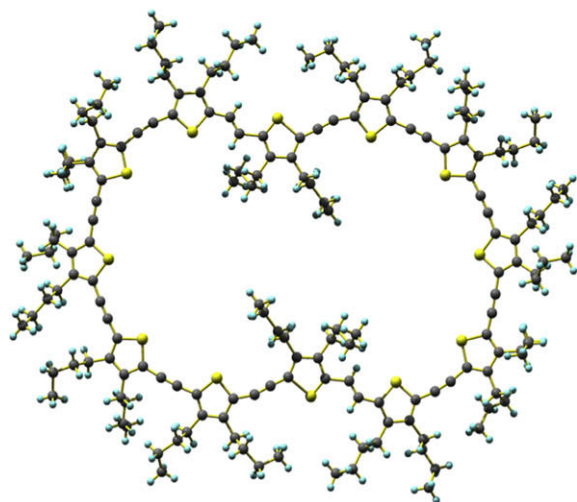


Fig. 3. X-ray crystal structure of **3a** (top view).

Table 1

Absorption coefficients and fluorescence quantum yields of **1a**, **2a–2e**, and **3a–3d** in CH_2Cl_2 .

Compd.	Absorption		Fluorescence	
	λ_{max} [nm]	ϵ [$\text{M}^{-1} \text{cm}^{-1}$]	λ_{max} [nm]	$\Phi_{\text{F}}^{\text{a}}$
1a (60π)	442	235,000	537, 579	0.062
2a (60π)	447	249,000	560, 604	0.069
3a (72π)	452	295,000	562, 606	0.11
2b (90π)	469	311,000	562, 605	0.084
3b (108π)	473	418,000	560, 603	0.085
2c (120π)	479	405,000	560, 602	0.11
3c (144π)	478	528,000	559, 600	0.10
2d (150π)	485	551,000	560, 603	0.089
3d (180π)	480	618,000	559, 600	0.095
2e (180π)	488	639,000	560, 600	0.086

^a Fluorescence quantum yields (Φ_{F}) were determined by comparison with quinine sulfate in 0.5 M H_2SO_4 ($\Phi_{\text{F}} = 0.51$).

(559–562 and 600–606 nm) with a large Stokes shift of 72–157 nm. The separation of two emissions in the fluorescence spectra corresponds to the vibrational energy gap.

Among giant macrocycles, the two-photon properties of **3b–3d** were investigated [18c]. The two-photon absorption cross-sections (δ_{max}) are **3a**: 15,100 GM, **3b**: 66,700 GM, **3c**: 82,600 GM, and **3d**: 107,800 GM. Therefore, increasing ring size and π -character from **3a** (72π) to **3b** (108π), **3a** to **3c** (144π), and **3a** to **3d** (180π) result in 4.4-, 5.5-, and 7.1-fold amplifications of the maximum two-photon absorption cross-section, respectively. These large enhancements of two-photon absorption cross-section are due to intramolecular interactions among these giant macrocycles. Note that the increasing π -conjugation leads to an increase in the two-photon absorption cross-section with magnitudes as high as 100,000 GM in the visible spectral region.

3.3. Nanostructures and fiber formation

Interestingly, giant macrocycles **2b–2e** and **3b–3d** form complex supramolecular structures owing to their weak amphiphilic properties. Although **2a** and **3a** form single crystals by recrystallization, **2b** forms microcrystals and nanowires from ethyl acetate/octane, and **2c** forms nanowires from ethyl acetate/chloroform (Fig. 4a and b). In contrast, **2d** and **2e** form nanoparticles from ethyl acetate/chloroform (Fig. 4c and d). All microcrystals, nanowires, and nanoparticles of **2b–2e** contain no solvents, different from single crystals of **2a**. The aggregates of **2b** and **2c** have well-defined fibrous structures with 100–200 nm thickness, whereas **2d** and **2e** form chained lumps of

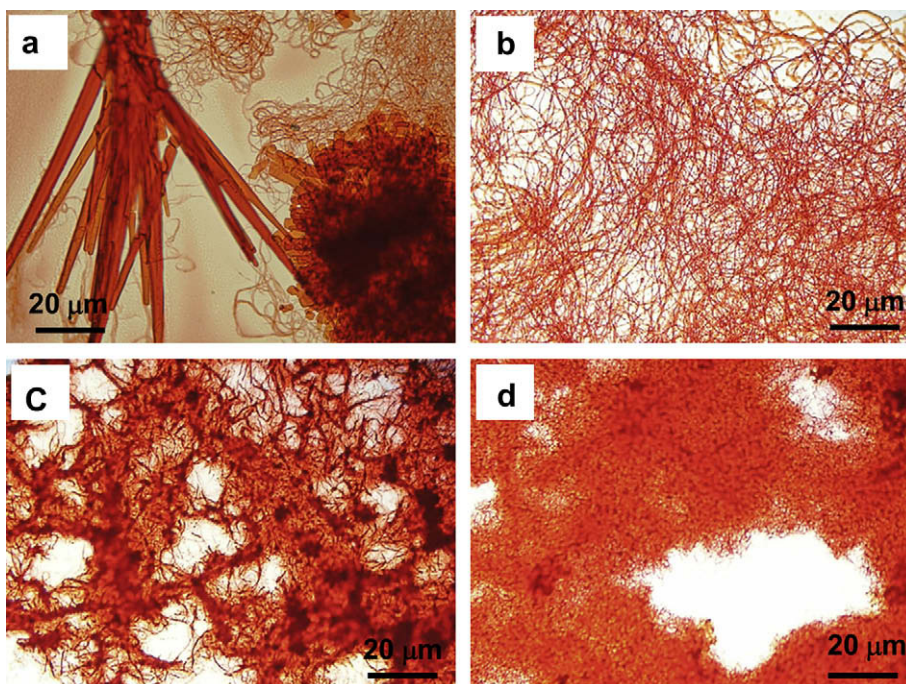


Fig. 4. Microscopic images of **2b** (a), **2c** (b), **2d** (c) and **2e** (d) with 1000 \times magnification.

300–800 nm size. Similarly, **3b** has a petal structure, whereas **3c** and **3d** form chained lumps. Because **2b–2e** and **3b–3d** have solvophilic and solvophobic moieties, the amphiphilic properties result in microscopic separation which leads to the formation of nanofibers and nanoparticles.

4. Conclusion

McMurry coupling reaction was found to be a versatile tool for the construction of giant macrocycles **2a** (60π)–**2e** (180π) and **3a** (72π)–**3d** (180π). Giant macrocycles **1a**, **2a–2e**, and **3a–3b** exhibit a redshift of the longest absorption maxima with increasing ring size owing to cyclic conjugation through the rings. In contrast, emissions in the fluorescence spectra of **1a**, **2a–2e**, and **3a–3d** are observed at almost the same position, reflecting the similar HOMO–LUMO gaps. The absorption and emission spectra of **6** exhibit a blue shift as compared with **1**. The infinite cyclic **1a**, **2a–2e**, and **3a–3d** can be easily oxidized to show reversible redox potentials by CV analysis, and doping of **2a–2c** with iodine vapor forms semiconductors. X-ray analysis has indicated that **2a** adopts an almost planar round shape with *s-cisoid* thiophene rings, and that a 1.5 molar ratio of heptane to **2a** locates inside in the cavity. In contrast,

3a is narrow in the middle and has two thiophene units in *s-transoid* form filling the center of the cycle. Therefore, the single crystal of **3a** involves no solvent molecule. One of the most interesting properties of giant macrocycles is their different morphology, when these compounds are precipitated from aprotic solvents. Thus, **2a** and **3a** form single crystals from chloroform–heptane/decane, whereas **2b** and **2c** yield nanowires, and **2d–2e** and **5** form microscale lumps. Another remarkable property of giant macrocycles is the inherent large two-photon absorption cross-section. The extremely large nonlinear optical effects of giant macrocycles will open up a new window on two-photon properties.

Acknowledgements

This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan and by CTREST of JST (Japan Science and Technology Corporation). I would like to thank all researchers, including collaborators, colleagues and coworkers, whose work has been presented in this chapter. I would also like to thank Dr. Masaharu Akiba (Fujifilm Corporation) for the preliminary measurements of the two-photon properties of giant macrocycles.

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