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Multifunctional $\pi$-expanded oligothiophene macrocycles

Masahiko Iyoda* and Hideyuki Shimizu

This tutorial review summarizes recent progress in the design, synthesis, and multifunctional properties of fully conjugated macrocyclic $\pi$-systems. We focus on the $\pi$-expanded oligothiophene macrocycles after a short survey of macrocyclic conjugated loops and belts such as [$n$]cycloparaphenylenes, cyclic [$n$]para-phenylacetylenes, [4]cyclo-2,8-crysénylenes, and cyclo[$n$]thiophenes. Fully conjugated $\pi$-expanded oligothiophene macrocycles possess shape-persistent but sometimes pliable $\pi$-frames, and electronic and optoelectronic properties of the macrocycles largely depend on the $\pi$-systems inserted into the oligothiophene macrocycles. Among them, the $\pi$-expanded oligothiophene macrocycle composed of 2,5-thienylenes, ethynylenes, and vinylenes is one of the most widely applicable macrocycles for constructing multifunctional $\pi$-systems. These $\pi$-expanded oligothiophene macrocycles from small to very large ring sizes can be prepared via a short step procedure, and their various solid state structures can be determined by X-ray analysis. Since these macrocycles have inner and outer domain, specific information concerning structural, electronic, and optical properties is expected. Furthermore, $\pi$-expanded oligothiophene macrocycles with alkyl substituents exhibit various morphologies depending on nanophase separation of molecules, and morphological change is available for molecular switch.

Key learning points

1. Nanosized conjugated macrocycles are fundamentally important due to the novel structures, properties, and functions.
2. Fully unsaturated macrocycles are regarded as models for infinitely conjugated $\pi$-systems with inner cavities, and exhibit unique optical, electronic, and magnetic behavior.
3. Macrocycles have interior and exterior sites, and site-specific substitution at both or either site can afford attractive structures, such as 1D, 2D, and 3D supramolecular nanostructures.
4. $\pi$-Expanded oligothiophene macrocycles have shape-persistent frameworks with medium to large inner cavities and incorporate from small to large molecules as a guest.
5. Large $\pi$-expanded oligothiophene macrocycles exhibit marked nonlinear optical properties and behave like the natural light-harvesting system.

1. Introduction

Cyclic benzenoid and nonbenzenoid conjugated molecules have important roles in chemical sciences. As synthetic and analytical techniques have advanced recently, several fully conjugated cyclic molecules have been developed to investigate cyclic conjugation in relation to the Hückel and Möbius aromaticity to examine three-dimensional conjugation in hoop- and belt-shaped molecules, and recently to create molecular machines, sensors, and switches utilizing their electric and optical properties. Among all of the different conjugated cyclic molecules, fully conjugated macrocycles with precisely defined diameters are regarded as being formally infinite $\pi$-conjugated systems free from the effect of terminal groups, and thus these $\pi$-systems have attracted considerable attention owing to their unusual optical, electronic, and magnetic properties arising from this effective cyclic conjugation. Large fully conjugated macrocycles sometimes show no diatropic (aromatic) or paratropic (antiaromatic) ring current. These macrocycles, however, also exhibit remarkable photophysical properties based on their conjugation and ring size.

Conjugated macrocycles have shape-persistent inner cavities, and small molecules or ions are incorporated in the cavity as guests to produce interesting supramolecular structures. Moreover, large macrocycles having round-shaped inner cavities of 10–11 Å can incorporate large molecules, such as fullerene C$_{60}$ or C$_{70}$ to produce inclusion complexes. These supramolecular complexes are stabilized by concave–convex $\pi-\pi$ interaction, charge-transfer (CT) interaction, CH/π interaction, and van der Waals interaction. In the case of giant macrocycles with cavities >12 Å, the flexibility of the macrocycles increases, and the cavity size becomes too large to incorporate molecules. Even though the molecular structure of these nanoscale macrocycles is sometimes not unambiguously determined, they show remarkable photophysical properties and nonlinear optical behavior.

On account of nanophase separation induced by interior and exterior sites, macrocycles with shape-persistent, noncollapsible, and fully $\pi$-conjugated backbones can assemble into columnar one-dimensional (1D) nanotubes, two-dimensional (2D) porous networks and lamellar alignments on surfaces, and three-dimensional (3D) inclusion complexes in the solid state (Fig. 1).
the case of redox-active macrocycles, therefore, these macrocycles change their charge and shape upon reduction or oxidation, and the site-specific character of macrocycles can be adjusted at both their inner and outer sites. Although polymorphism of functional macrocycles has not yet been fully elucidated owing to the lack of suitable examples, nanostructured polymorphs can be employed in a wide range of applications. 5

This tutorial review will discuss the extension of cyclic conjugation, redox properties and conducting behavior, guest molecule incorporation in the inner cavity, polymorphism of functional macrocycles, and nonlinear optical properties of π-expanded oligothiophene macrocycles.

1. Conjugated macrocycles

2.1 Oligophenylene macrocycles

During the past two decades, three π-conjugated macrocyclic loops and belts have been reported (Fig. 2). In 1996, Kawase and Oda first reported the synthesis of cyclic [6]- and [8]paraphenyleneacetylenes ([6]CPPA and [8]CPPA). 9 They also reported the synthesis of [7]CPPA, [9]CPPA, and the related naphthalene derivatives. 3 In 2008, Jasti, Bertozzi, and co-workers reported the synthesis of [9]-, [12]-, and [18]cycloparaphenylenes ([9]CPP, [12]CPP, and [18]CPP). 10 These CPPs exhibited unique emission behavior, and the smaller CPPs have longer wavelength emission maxima. Recently, Isobe reported tubular macrocycles, [4]cyclo-2,8-crysenylene ([4]CC₂₈₈) and its derivatives, possessing sp²-networks of single wall carbon nanotubes. 11

![Fig. 2](image)

Fig. 2 Structures of [n]CPPAs, [n]CPPs, and [4]CC₂₈₈.

Quite recently, the synthesis of CPPs were developed very rapidly and extensively by the groups of Itami, 12 Yamago, 13 Jasti, 14 and Müllen, 15 independently, and [5]–[16]CPPs and their derivatives were newly synthesized to explore characteristic properties. CPPs are structural units of fullerenes and armchair carbon nanotubes (CNTs), affording the corresponding cationic and anionic species by oxidation and reduction, respectively. Interestingly, [8]CPP 16 showed in-plane aromaticity with 30π-electrons. 16,17 Furthermore, the cavity of the CPPs acts as a host for π-conjugated molecules, and C₆₀ was selectively encapsulated by [10]CPP, forming a 1:1 complex, [10]CPP[C₆₀] (Fig. 3). 18,19 In the case of [6]CPPA, this molecule takes C₆₀ in the cavity to form [6]CPPA[C₆₀]. Furthermore, since [9]CPPA incorporates [6]CPPA to afford [9]CPPA[C₆₀], [6]CPPA[C₆₀] is encapsulated by [9]CPPA to produce an onion-type complex [9]CPPA[C₆₀] (Fig. 3). 20 [4]CC₂₈₈ having two hexyl groups at 6 and 12 positions strongly encapsulates C₆₀ with an extremely high binding constant (log Kᵥ = 11.5 in toluene), and C₆₀ rolls anisotropically in a bearing on the molecular scale. 11

![Fig. 3](image)

Fig. 3 Inclusion complexes of [10]CPP and [6]CPPA with C₆₀ and onion-type complex [9]CPPA[C₆₀].

2.2 Macro cyclic cyclo[n]thiophenes

The pioneering study on the synthesis of cyclo[n]thiophenes C12T, C14T, and C16T by Bäuerle et al. employed copper-mediated coupling for the construction of macrorings, and oxidative coupling of 1 or 2 yielded 3 and 5 or 4 and 6, respectively. 21 The reactions of 3, 4, and 5 with sodium sulfide afforded C12T, C16T, and C18T, respectively (Scheme 1). Computational studies predicted that syn-C8T–C12T possess nearly planar structures. In syn-conformation, however, large CnT s lose their nearly planar ring shape and bent significantly for n > 4. From scanning tunnelling microscope (STM) measurements, C12T self-assembled in a hexagonal close-packed monolayer at the solid–liquid interface. Moreover, a 2D porous network of C12T formed a two-component system with C60. 22 The STM images showed 1:1 donor/acceptor complexes and a 3D supramolecular assembly.

![Scheme 1](image)

Scheme 1 Synthesis of fully a-conjugated cyclo[n]thiophenes C12T, C16T, and C18T.

Bäuerle et al. developed a new method of synthesizing cyclo[8]thiophene (C8T) via platinum intermediate 7 (Scheme 2). 22
The C–C bond formation through reductive elimination led to the strained cyclodimeric terthiophene-diyne 8, which was converted into C8T. Although C8T can be expected to possess a strained planar structure with a high donor ability, no structural information and redox behavior were reported.

Scheme 2 Synthesis of C8T via platinum complex 7.

Recently, the same research group reported a new approach to synthesize highly symmetric macrocyclic oligothiophenes C10T–C35T, which have interesting optoelectronic and supramolecular properties (Scheme 3).12 These macrocycles were prepared via multinuclear macrocyclic PtII complexes 10 and 11. The high symmetry of the cyclic structures of C10T–C35T influences their photophysical properties: the absorption maxima corresponding to an S0 → S1 electronic transition were red-shifted and showed a hyperchromic effect with an increase in the ring size. The X-ray analysis of C10T showed a nearly circular structure with inner diameters of ca. 1.0 nm, and adjacent thiophene units are twisted up and down by 26–34° to release the ring strain. The very low oxidation potential (0.03 V vs Fc/Fc+ ) of the smallest cycle C8T was attributed to a high HOMO level due to the syn conformation of the thiophene units. Interestingly, two-electron oxidation of C10T formed a two-polaron structure (polaron-pair) C10T2(·+)26

Scheme 3 Synthesis of C10T–C35T.

Quite recently, Sannicolo and co-workers reported chiral macrocyclic oligothiophenes 13 (15%) and 14 (8%) by chemical oxidation of 12 with FeCl3 (Fig. 4).27 These macrocycles showed chiroptical properties, circularly polarized luminescence effects, and enantiorecognition ability. Cyclic octathiophene 16 containing two β,β′-linkages was synthesized from cyclic platinum complex 15 (>68%).28 The fluorescence spectra of the nonplanar 16 showed a redshift as compared to the corresponding quartethiophene owing to the large structural change in the excited state.

3. π-Expanded oligothiophene macrocycles

3.1 Planar and nonplanar macrocycles

Fully conjugated π-expanded oligothiophene macrocycles are a family closely related to redox-active oligothiophene macrocycles such as C[n]Ts, exhibiting potential optoelectronic application to organic light-emitting diodes (OLED), organic field-effect transistors (OFET), organic solar cells, and many others.25 These π-expanded macrocycles possess shape-persistent π-frames, and electric and optoelectronic properties of the macrocycles largely depend on the inserted π-systems to the parent oligothiophene macrocycles. Although [n]cyclopaphenylene (CPPs), [n]paraphenyleneacetylenes (CPPAs), and [4]paraphenylene-crysenylenes (CC12,s) possess a 2D ring-shape structure with π-orbitals parallel to the macroring, π-orbitals of C[n]Ts containing α,α′-linkages are aligned perpendicular to the planar macroring. On the other hand, cyclic oligothiophenes 13, 14, and 16 containing β,β′-linkage adopt a twisted structure around the β,β′-linkage (Fig. 4).

Among π-expanded oligothiophene macrocycles, Marsella and co-workers reported the synthesis of 17 containing two rings with potential use as single-molecule electrochemical actuators (Fig. 5).29 Cyclooctatetraene (COT) is oxidized to give the planar COT+, and distance d1 (3.142 Å) in the tub form increases to distance d2 (3.407 Å). Therefore, a large redox-induced conformational change between twisted and planar topologies, associated with 18% change in distance, was predicted for the four-electron oxidation of 17 on the basis of DFT calculations. Very recently, cyclo-1,4-phenylene-2′,5′-thienylenes (CPTs) were synthesized by Itami and co-workers.
pentaphyrin was reported by Vogel and co-workers. 33 Mayor and co-workers reported the synthesis of thiacalix[n]dithienothiophenes 19a-c by a simple Pd-catalyzed coupling reaction of 18 in the presence of (n-Bu3Sn)2S.31 Although X-ray analysis of 19a,b exhibited a twisted 3D structure, electrochemically generated cationic species 19a-c+ showed a 3D delocalization of π-electrons.

Hasegawa and co-workers reported the synthesis of [4]CPT using a synthetic method similar to CPPs.30 X-ray analysis revealed that [4]CPT 2cyclohexane adopts a C₆-symmetric truncated cone shape with tubular stacking along the c-axis. Hasegawa and co-workers reported the synthesis of [n]dithienothiophenes 19a-c by a simple Pd-catalyzed coupling reaction of 18 in the presence of (n-Bu3Sn)2S.31 Although X-ray analysis of 19a,b exhibited a twisted 3D structure, electrochemically generated cationic species 19a-c+ showed a 3D delocalization of π-electrons.

Hasegawa and co-workers reported the synthesis of

![Fig. 5 Nonplanar π-expanded oligothiophene macrocycles 17, [n]CPTs (m = 1-3), and 19a-c.](image)

**Scheme 4** Synthesis of π-expanded oligothiophene macrocycles 21, 22, 25, and 27.

Various synthetic methods can be employed for the synthesis of π-expanded oligothiophene macrocycles. As shown in Scheme 4, Cava and co-workers reported the intermolecular cyclization of dialdehyde 20 by using McMurry coupling to produce 21 and 22.32 The sulfur analogue 25 of 22π-pentaphyrin was reported by Vogel and co-workers.33 Mayor and Didschies synthesized one of the largest macrocycles, 27, with a diameter of 11.8 nm by using intramolecular Eglington coupling.34 27 has a fully conjugated periphery composed of ethynylene, butadiynylene, 2,5-thienylene, and 1,4-phenylene units.

Large planar macrocycles stack through π-π interaction on the surface to form a lamellar structure favourable for charge-carrier mobility. Aso and co-workers reported the synthesis and OFET performance of rectangular macrocycle 28 with benzo[18]annulene units at the corner position (Fig. 6).35 A film fabricated by spin-coating exhibited a hole mobility with a maximum value of 7.3 × 10⁻² cm²V⁻¹s⁻¹. 2D-supramolecular structures comprised of 29 and its co-deposition with C₆₀ on HOPG were investigated by Höger, Freyland, and co-workers (Fig. 6).36 High-resolution STM investigation of monolayers revealed that the presence of two individual bithiophene units as well as the size of the macrocycle led to the formation of a superstructure with a 1:2 stoichiometry. The fullerene units were located around the periphery of the bithiophene units, thus indicating the donor-acceptor interaction between C₆₀ and the electron-rich bithiophene units of 29.

![Fig. 6 Planar π-expanded oligothiophene macrocycles 28 and 29.](image)

### 3.2 Macrocycles composed of 2,5-thienylene, ethynylene, and vinylene units

A series of π-expanded oligothiophene macrocycles composed of 2,5-thienylene, ethynylene, and vinylene units has been synthesized using a modified McMurry coupling reaction of dialdehydes 30 as the key step (Scheme 5).37 Although repeated and thus monotonic synthetic procedures are inevitable for forming large cyclic structures, this method can be effectively applied to construct small 6T6A, medium 10T8A, and giant 30T25A, and other related macrorings. π-Expanded oligothiophenes with long alkyl chains can be envisaged as self-assembling into nanostructures such as nanowires, nanotubes, and nanoparticles using π-π and van der Waals interactions unlike macrocyclic oligophenylene and oligopyrroles.38 Thus, reducing the dimensionality of macrocycles having non-hydrogen-bonding interactions from a 3D crystal structure into 1D or 2D structures leads to the self-assembling nanostructures. Furthermore, these oligothiophene macrocycles show a good mobility of ring electrons and hence strong cyclic conjugation owing to fairly planar structures of 2,5-thienylene, ethynylene, and vinylene units. All oligothiophene macrocycles are stable reddish orange crystalline or amorphous powders and soluble in common organic solvents, except for methanol. Therefore, π-expanded oligothiophene macrocycles are an ideal system to investigate relationship between cyclic conjugation and photophysical behavior. Furthermore, these macrocycles can show a novel ring size effect on chemical and physical properties.
Intramolecular pinacol coupling of 34 with a low-valent vanadium complex produced the corresponding cyclic 6-mer diol 35. However, a Corey-Winter reaction of the diol afforded a complex mixture of products (Scheme 7). Since 6T5A is a strained compound, 6T5A or its precursors could not survive under the Corey-Winter conditions.

Scheme 7 Attempted synthesis of 6T5A starting from 34.

The synthesis of oligothiophene 6-mer 6T4A and related higher oligomers was carried out by using a modified McMurry reaction, as shown in Scheme 8. Reaction of the dialdehyde 36 composed of three 2,5-thienylene and two ethynylene units with a low-valent titanium reagent proceeded smoothly to mainly produce cyclic dimer 6T4A (35%) together with cyclic trimer 9T6A (5.5%) and cyclic tetramer (1.5%). Although the formation of a small amount of cyclic pentamer was observed, no linear di-, tri-, tetra-, or pentamers were isolated from the reaction mixture except for higher polymers. Cyclic dimer 6T4A was converted to cyclic[6](3,4-dibutyl-2,5-thienylene-ethynylene) 6T6A by using a bromination-dehydrobromination procedure (45%).

Scheme 8 Synthesis of 6T4A, 9T6A, and 6T6A.

To synthesize 8T6A, a McMurry coupling reaction of 37 composed of four 2,5-thienylene and three ethynylene units was carried out under very high-dilution conditions in the dark to produce ZZ-8T6A (35%) and E,E-8T6A (1%) with a trace amount of the corresponding 12-mer (Scheme 9). Although E,E-8T6A is more stable than ZZ-8T6A, the reaction mainly afforded ZZ-8T6A as a kinetic product, reflecting the

Scheme 5 Typical n-expanded macrocyclic oligothiophenes 6T6A, 10T8A, and 30T25A.

Kawase and co-workers reported that the coupling of 31a with a McMurry reagent prepared from TiCl3(DME)2-Zn(Cu) in DME gave the dimer 32 in only trace amounts together with the corresponding trimer (10–15%) (Scheme 6). On the other hand, the reaction of 31b with a McMurry reagent prepared from TiCl3-Zn in gently refluxing THF-pyridine at 60 °C produced 4T2A (15%) and 6T3A (13%), and the McMurry coupling of 31b under similar conditions at 68 °C formed 4T as a major product. Therefore, selection of the reaction condition of the McMurry coupling is the key to the synthesis of macrocyclic oligothiophenes.

Scheme 6 McMurry coupling of 31a and 31b.
stereoisomers. Variable temperature (VT) NMR spectroscopic analysis revealed that 8T8A crystallizes from chloroform-THF, whereas the Z,Z- isomer isomerizes to E,E-8T8A in ambient light, whereas Z,Z-8T8A slowly isomerizes to E,E-8T8A under UV irradiation (photocromism).

Sonogashira cyclization of 40 or bromination of 10T8A, followed by dehydrobromination with potassium tert-butoxide, produced 10T10A in 40 and 36% overall yield, respectively.

In case of cyclo[8](3,4-dibutyl-2,5-thienylene-ethynylene) 8T8A, this compound was synthesized by intramolecular Sonogashira cyclization of linear ethynylbromide 38 composed of eight 2,5-thienylene and seven ethynylene core units (14%) (Scheme 10). Furthermore, bromination of E,E-8T6A or Z,Z-8T6A, followed by dehydrobromination with potassium tert-butoxide, produced 8T8A in 21% overall yield.43

For the synthesis of 10T8A–30T24A, the coupling of 39 was carried out using TiCl4–Zn in THF–pyridine under normal dilution conditions (Scheme 11).44 This reaction produced 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 30π–10T8A (39%), 90π–15T12A (9.4%), 120π–20T16A (6.2%), 150π–25T20A (3.9%), and 180π–30T24A (2.3%), together with a 1:3 mixture of the E,Z- and Z,Z-isomers of 10T8A (7%) in total 65.5% yield (Scheme 11). Since 10T8A crystallizes from chloroform-heptane, pure 10T8A can be isolated from the mixture of stereoisomers. Variable temperature (VT) NMR spectroscopic studies revealed that 10T8A–30T24A show symmetrical D_{sh} structures even at -60 °C, reflecting a rapid conformational change in solution. Although this reaction produces a mixture of cyclic oligomers 10T8A–30T24A, the yield of 10T8A is a permissive range for synthetic chemists. Furthermore, the less easy-obtainable higher oligomers 15T12A–30T24A can also be synthesized by a one-step procedure. Intramolecular McMurry coupling of 34 with TiCl4–Zn in THF–pyridine under normal dilution conditions produced the 72π–12T10A, 108π–18T15A, 144π–24T20A, and 180π–30T25A in 39, 8.3, 2.5, and 1.2% yields, respectively, together

Scheme 9 Synthesis of Z,Z-8T6A and E,E-8T6A.

Scheme 10 Synthesis of 8T8A using intramolecular cyclization or bromination–dehydrobromination procedure.
with a small amount of the E,Z- and Z,Z-isomers of 12T10A (Scheme 12). Furthermore, the 216hexamer 36T30A was isolated in 0.2% yield, though 36T30A was not fully characterized. For the synthesis of 12T12A by using ‘double elimination procedure’, the sulfone dianion prepared from 41 was reacted with the dialdehyde 34 (1 equiv). The adduct formed from 41 and 34 was reacted with diethyl chlorophosphate (2 equiv), followed by treatment with lithium hexamethyldisilazide (4 equiv) producing 12T12A in 4.3% overall yield.

For the synthesis of π-expanded oligothiophene macrocycles composed of 2,5-thienylene, ethynylene, and vinylene units, McMurry coupling reaction is a versatile tool, forming from isolated in 0.2% yield, though 36T30A was not fully characterized. For the synthesis of 12T12A by using ‘double elimination procedure’, the sulfone dianion prepared from 41 was reacted with the dialdehyde 34 (1 equiv). The adduct formed from 41 and 34 was reacted with diethyl chlorophosphate (2 equiv), followed by treatment with lithium hexamethyldisilazide (4 equiv) producing 12T12A in 4.3% overall yield.

For the synthesis of π-expanded oligothiophene macrocycles composed of 2,5-thienylene, ethynylene, and vinylene units, McMurry coupling reaction is a versatile tool, and the residues were first recrystallized from crude mixtures, and the residues were separated by gel permeation chromatography (GPC).

3.3 Crystal structures of π-expanded oligothiophene macrocycles

The molecular structures of 32, 4T2A, 6T4A, 6T6A, 10T8A, and 12T10A have been determined by X-ray analysis (Fig. 7 to 11). As shown in Fig. 7a, 4T2A has an extremely twisted structure, although the corresponding unsubstituted molecule 32 is planar (Fig. 8). The 1H NMR spectrum of 4T2A at room temperature was consistent with a symmetrical D3h structure, and hence 4T2A may undergo a rapid conformational change in solution. The crystal packing of 4T2A having eight butyl groups may demand to take a twisted structure (Fig. 7b). The interatomic S···S distance (3.262 Å) in 4T2A is 12% shorter than the sum of van der Waals radii (3.70 Å), whereas the similar distances (3.014 and 3.025 Å) in 32 are 18% shorter than the sum of van der Waals radii. Therefore, π-π stacking interaction in the crystal lattice overcomes destabilization of the planar structure in 32. It is noteworthy that a flexible macroring easily forms various crystal structures depending on weak interactions in the crystal lattice.

Single crystals of E,E-8T6A and 8T8A were obtained by recrystallization from hot benzene. As shown in Fig. 10, the cell parameters of E,E-8T6A and 8T8A have a round structure and lie on a crystallographic center of symmetry (Fig. 10a and c). Although DFT calculations on unsubstituted E,E-8T6A and 8T8A predicted planar C3v and D6h structure, respectively, E,E-8T6A adopts a nonplanar zigzag conformation (Fig. 10b), and 8T8A adopts a slightly twisted oval structure (Fig. 10d and e). In the molecular packing, E,E-8T6A and 8T8A form a honeycomb, columnar structure (Fig. 10c and f), and the butyl groups lie above and below the ring, filling the inner cavity of the neighboring rings.
and hydrogen atoms omitted for clarity. (d) Crystal packing of 12T10A.

A single crystal of 12T10A suitable for X-ray analysis was obtained from chloroform–decane (Fig. 11). Although 10T8A has a nearly circular shape with all its thiophene units in the cisoid form, 12T10A composed of 12 thiophene units has a narrow “waist” with two thiophene units in the transoid conformation so as to fill the center of the cycle. The resultant small cavities are filled with neighboring butyl groups, and 12T10A has a slightly bent chair-like structure. As a result, the single crystal involves no solvent molecule.

3.4 Redox behavior of π-expanded oligothiophene macrocycles mTnA

All π-expanded oligothiophene macrocycles behave as π-donors with fairly low oxidation potentials, although linear oligothiophenes exhibit lower π-donor ability than common linear oligothiophenes. Cyclic voltammetric (CV) analyses of 4T2A and 6T4A exhibit two-electron one-step reversible waves owing to the formation of aromatic 22π and 34π dications 4T2A+ and 6T4A+ respectively, whereas E,E-8T6A, 10T8A, and 12T10 show one-electron four-step, three-step, and two-step reversible waves, respectively, indicating intramolecular cation–cation interaction. Other giant macrocycles such as 15T12A–30T24A and 18T15A–30T25A show two reversible waves like linear long oligothiophenes. Therefore, smaller macrocycles exhibit stronger electronic interaction corresponding to on-site Coulombic repulsion, but macrocycles larger than a 90π system show only a small on-site Coulombic repulsion in their polycationic states. Interestingly, 9T6A+2, a 52π cation, indicated biradical cation character. Since the ESR spectrum of 9T6A+2 (g = 2.0024 at 7 °C) is nearly similar to that of 9T6A+ (g = 2.0026 at 7 °C) (Fig. 12), the biradical state of 9T6A+2 is nearly equivalent to that of two independent monoradicals having a small exchange interaction.

![Fig. 10](image1.png)

Fig. 10 (a) ORTEP diagram of E,E-8T6A. Butyl groups and hydrogen atoms omitted for clarity. (b) Side view and (c) packing structure of E,E-8T6A. (d) ORTEP diagram of 8T8A. Butyl groups and hydrogen atoms omitted for clarity. (e) Side view and (f) packing structure of 8T8A.

A single crystal of 10T8A from chloroform–heptane contains 1.5 molar ratio of heptane to 10T8A. As shown in Fig. 11, the 10 thiophene rings 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 form a full circle. The intramolecular distances between the sulfur atoms in 10T8A are also incorporated in the ring are considerably mobile, despite low-temperature X-ray analysis at −180 °C. The X-ray analysis reveals that 10T8A serves as a host molecule to alkane molecules. Linear alkanes like hexane and octane are also incorporated in 10T8A to form single crystals.

![Fig. 11](image2.png)

Fig. 11 (a) ORTEP diagram of 10T8A heptane. Butyl groups and hydrogen atoms omitted for clarity. (b) Crystal packing of 10T8A heptane. (c) ORTEP diagram of 12T10A. Butyl groups and hydrogen atoms omitted for clarity.

Oligo- and polythiophenes are easily oxidized by electron acceptors to form the corresponding electroconductive radical salts. Important concepts for realizing high electrical conductivity are π–π stacking and π-dimer formation of cationic species derived from oligo- and polythiophenes. Although linear poly(thiophene–ethylenylene) seems to produce no electroconductive cationic species owing to difficulty in the formation of stable cationic species, macrocyclic oligothiophenes mTnA produce stable cationic species by oxidation and hence can form an electroconductive oxidation state. Actually, doping of 10T8A, 15T12A, and 20T16A with iodine vapor resulted in the formation of black materials with moderate conductivities (10T8A: σm = 1.86 × 10−3 Scm−1).
amorphous film (AF-6T) expanded oligothiophenes is the polymorphism of decomposition without showing a melting point. Since crystal related macrocycles formed amorphous solids and exhibited a twisted structure in the single crystal. However, the formation in the solid state, whereas the cast films of structures: single crystal, lamellar film (LC-6T) observed for in the third heating process, an exothermic process with a melt temperature (inset in Fig. 13) was due to the thickness of the process (blue line), determined by using differential scanning calorimetry (DSC) analysis. When cooled to room temperature, 6T4A showed an exothermic process (red line in the inset) at 80 °C to form crystals that melted at 139 °C, and in the third heating process, an exothermic process with a melt memory effect (green line in the inset) occurred at 83 °C to form crystals that melted again at 139 °C. Based on the analysis of the exothermic process by changing the heating and cooling rates, it was concluded that the difference of the exothermic temperature (inset in Fig. 13) was due to the thickness of the sample on the surface. Thus, 6T4A has three solid state structures: single crystal, lamellar film (LC-6T), and amorphous film (AF-6T). This polymorphism was only observed for 6T4A due to the number of stable conformations in the solid state, whereas the cast films of 6T6A, 9T5A, and related macrocycles formed amorphous solids and exhibited decomposition without showing a melting point. Since crystal structures should be ordered in the crystal lattice, 6T4A adopts a twisted structure in the single crystal. However, the formation of an edge-on structure is favorable on the surface through π-π stacking interaction, and consequently, it was assumed that 6T4A adopts a lamellarily aligned structure on the glass and metal surfaces.

![Fig. 13 DSC analysis of 6T4A (2 °C/min). The inset shows the region 50 < T < 100 °C. Reproduced with permission from ref. 42. Copyright 2014 American Chemical Society.](image)

Polymorphs of 6T4A have different optical and electronic properties such as absorption and emission spectra, XRD patterns, FET behavior, and electrical conductivity of AF-6T and LC-6T on the surfaces of glass and metal plates. The absorption and emission spectra of LC-6T (λ_{max} 418 and λ_{em} 674 nm) were redshifted compared to those of AF-6T (λ_{max} 384 and λ_{em} 607 nm) due to an increase in the π-π interactions (Fig. 14a). The colors of AF-6T and LC-6T are orange and reddish orange, respectively (Fig. 14b and d), consistent with the absorption spectra. The colors of AF-6T and LC-6T under UV-light (λ = 254 nm) were also different (Fig. 14c and e), and AF-6T fluoresced, whereas LC-6T only exhibited weak emission. The π-π stacked structure of LC-6T showed FET properties (μ = 2.8 × 10^{-3} cm²/V·s, I_{ON}/I_{OFF} = 10^4, and V_{th} = -4.7 V) and an increased conductivity (σ = 4.0 × 10^{-2} Scm⁻¹) compared with that of AF-6T (σ = 2.6 × 10^{-10} Scm⁻¹). Furthermore, after doping with iodine, the conductivities of AF-6T and LC-6T (2.5 × 10^{-10} and 1.1 × 10^{-5} Scm⁻¹, respectively) were higher than those of the corresponding neutral films, and the conductivity of doped LC-6T was 440-times higher than that of doped AF-6T.

![3.5 Polymorphism in 6T4A](image)

![3.6 Nanostructured polymorphs of E,E-8T6A and 15T9A–30T24A](image)

A conformationally restricted structure stabilizes various mesophases, and hence fibrous structure of E,E-8T6A precipitated from solution. As shown in Fig. 15, fibers, rods, and square tubes of E,E-8T6A precipitated from hexane/benzene (Fig. 15a), chloroform (Fig. 15b), and benzene/disisopropyl ether (IPE) (Fig. 15c and d). None of these fibers, rods, and square tubes of E,E-8T6A contained any solvent. The XRD patterns for the fibers corresponded to those for a 1D structure, whereas the XRD patterns for the rods and square tubes indicated microcrystalline structures.

![Giant macrocycles 10T8A–30T24A exhibit a ring-size dependence of the morphology. As shown in Fig. 11, 10T8A formed single crystals; however, 15T12A formed microcrystals and fibers from ethyl acetate/octane (Fig. 16a), and 20T16A](image)
formed fibers from ethyl acetate/chloroform (Fig. 16b). In contrast, 25T20A and 30T24A formed nanoparticles from ethyl acetate/chloroform (Fig. 16c and d). Unlike single crystals of 10T8A, none of these polymorphs of 15T12A–30T24A contained any solvent.

3.7 Photoisomerization between \( \text{E,E-S8T6A} \) and \( \text{Z,Z-S8T6A} \)

In solution, \( \text{E,E-S8T6A} \) and \( \text{Z,Z-S8T6A} \) isomerized to \( \text{Z,Z-S8T6A} \) and \( \text{E,E-S8T6A} \), respectively, by irradiation.43 As shown in Fig. 17, \( \text{E,E-S8T6A} \) and \( \text{Z,Z-S8T6A} \) exhibit different UV-vis spectra. In other words, irradiation of orange solutions of \( \text{E,E-S8T6A} \) in cyclohexane, chloroform, toluene, and benzene with green light (\( \lambda = 525 \text{ nm} \)) produced \( \text{Z,Z-S8T6A} \) nearly quantitatively. On the other hand, irradiation of a yellow solution of \( \text{Z,Z-S8T6A} \) in cyclohexane with UV light (\( \lambda = 365 \text{ nm} \)) produced \( \text{E,E-S8T6A} \) in 96% yield with a trace amount of \( \text{E,Z-S8T6A} \), and only \( \text{E,E-S8T6A} \) crystallized from the mixture of products. In summary, \( \text{S8T6A} \) exhibited reversible photochromic behavior between two geometric isomers in solution.

3.8 Nonlinear optical properties and light harvesting behavior

Absorption and emission spectra of macrocycles \( \text{10T8A–30T24A} \) and \( \text{12T10A–30T25A} \) measured in dichloromethane show an important feature. As has been reported previously, a series of linear oligothienylene-ethynylenes up to 16-mer exhibited near saturation for the absorption maximum at the 8-mer stage.59 Therefore, doubling the conjugation length from 8-mer to 16-mer causes little change in the absorption maximum. In contrast, \( \text{10T8A–30T24A} \) and \( \text{12T10A–30T25A} \) exhibited a redshift of their longest absorption maxima with increasing ring size (Fig. 19). A linear relationship between the longest absorption maxima (\( \text{eV} \)) and the reciprocal of the number of thiophenes \( (1/n) \) in \( \text{10T8A–30T24A} \) suggests that the considerable \( \pi–\pi \) overlapping is maintained (Fig. 19a). Recent studies on the exciton delocalization of linear and cyclic oligothiophenes exhibited that a cyclic geometry of \( \text{10T8A} \) reduces conformational disorder of the chain, and a rigid planar structure thus formed effectively delocalizes exciton over the molecular backbone.51

![Fig. 16 Microscopic images of (a) 15T12A, (b) 20T16A, (c) 25T20A, and (d) 30T24A. Reproduced with permission from ref. 44. Copyright 2006 American Chemical Society.](image1)

![Fig. 17 (a) Photochromism between \( \text{Z,Z-S8T6A} \) and \( \text{E,E-S8T6A} \). (b) Absorption and emission spectra of \( \text{Z,Z-S8T6A} \) and \( \text{E,E-S8T6A} \) in cyclohexane at 25°C. Reproduced with permission from ref. 43. Copyright 2015 American Chemical Society.](image2)

![Fig. 18 STM height images of a hexagonal network of (a) \( \text{E,E-S8T6A} \), unit cell: \( a = (2.97 ± 0.03) \text{ nm} \), \( b = (2.95 ± 0.03) \text{ nm} \), \( \theta = (59 ± 3)° \); \( U_t = 1.12 \text{ V}, I_t = 58 \text{ pA} \) and (b) image of \( \text{E,E-S8T6A} \) from B3LYP calculation. (c) \( \text{Z,Z-S8T6A} \), unit cell: \( a = (2.83 ± 0.11) \text{ nm} \), \( b = (2.83 ± 0.09) \text{ nm} \), \( \theta = (60 ± 1)° \); \( U_t = 1.14 \text{ V}, I_t = 57 \text{ pA} \), (d) image of \( \text{Z,Z-S8T6A} \) from B3LYP calculation. Reproduced with permission from ref. 43. Copyright 2015 American Chemical Society.](image3)
Fig. 19 Relationship between the longest absorption maxima (eV) and the number of thiophenes (n). (a) 10T8A–30T24A. (b) 12T10A–30T25A.

Of these oligothiophene macrocycles, the two-photon properties of 12T10A–30T25A were chosen for investigation. The two-photon absorption cross section ($\delta$) is 12T10A: 15,100 GM, 18T115A: 66,700 GM, 24T20A: 82,600 GM, 30T25A: 107,800 GM. Therefore, the increasing ring size and $\pi$-character from 12T10A (72\pi) to 18T115A (108\pi), 12T10A to 24T20A (144\pi), and 12T10A to 30T25A (180\pi) result in respectively 4.4-, 5.5-, and 7.1-fold amplifications of the maximum two-photon absorption cross section (Fig. 20). These large enhancements in two-photon absorption cross section are due to intramolecular interactions between these giant macrocycles. It should be noted that the increasing $\pi$-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. Interestingly, for the largest giant macrocycle 30T25A, the initial localized excited state is followed by incoherent hopping to form the exciton delocalization along the whole ring (Fig. 20b). As a result, the life time of the excited state of 30T25A is extended. These experiments suggest that the initial delocalized state increases with ring size, a result comparable to the natural light-harvesting system.

Fig. 20 Characteristic properties of 12T10A–30T25A. (a) Large enhancements of two-photon absorption cross sections of 12T10A, 18T115A, and 24T20A. (b) Incoherent hopping of exciton in the excited state of 30T25A with large two-photon properties.

3.9 Formation of C60 complexes

Macrocycles with precise shapes and inner cavities form various kinds of C60-containing complexes. Among them, convex-concave $\pi$–$\pi$ interactions between the spherical C60 and $\pi$-conjugated tublar molecules play an important role in stabilizing inclusion complexes, whereas van der Waals interactions between C60 and macrocycles help to construct 1:1 inclusion complexes. Although van der Waals interactions are usually too weak to allow for the formation of stable complexes, E,E-8T6A and 8T8A incorporate C60 in their inner cavities to form unique Saturn-like complexes using mainly van der Waals interactions between C60 and the sulfur atoms of oligothiophene 8-mers.

In contrast to the weak interactions of E,E-8T6A and 8T8A with C60 in solution, these macrocycles formed stable C60 complexes in the solid state. Single crystals of E,E-8T6A ⊃ C60 and 8T8A ⊃ C60 were obtained by crystallization of E,E-8T6A and 8T8A with C60, respectively, in hot toluene, and their Saturn-like structures were determined by using X-ray analysis (Fig. 21). In E,E-8T6A ⊃ C60, the face-to-face S···S distances (13.607(2)–14.661(3) Å, average S···S distance: 13.99 Å) indicate that the oligothiophene ring is nearly circular, and the short S···S distances (13.607 and 13.661 Å) are 1.0% shorter than the sum (13.72 Å) of the van der Waals radii of the sulfur atoms (3.70 Å) and C60 (10.02 Å). The short contacts between the sulfur atoms and C60 stop the rotation of C60, which is different from complexes with convex-concave $\pi$–$\pi$ interactions in a ball bearing system.11

Fig. 21 X-ray structure of E,E-8T6A ⊃ C60. (a) Top view, (b) side view, and (c) packing structure along the a-axis. Reproduced with permission from ref. 43. Copyright 2015 American Chemical Society.

Interestingly, 19a, a nonplanar system, formed 1:2 complex with C60 in the single crystal (Fig. 22). The two C60 molecules were incorporated in the cavities on each side of 19a with 1,3-alternating geometry. Opposite pairs of DTT rings incorporate one C60 on each side of the macrocycle. The ring of 19a captured the C60 through $\pi$–$\pi$ interactions as well as sulfur–$\pi$ contacts. Since the crystal has an $\alpha$ axis in the center of the macrocycle, the cavities are crystallographically identical, which gives rise to the “Janus-head” in 19a.

Fig. 22 (a) Nonplanar $\pi$-expanded oligothiophene macrocycle 19a. X-ray structure of 19a{C60}2: (b) side view and (c) a columnar array along the c-axis. o-Xylene omitted for clarity.

4. Conclusion

Numerous shape-persistent $\pi$-conjugated macrocycles have been constructed and investigated to satisfy synthetic challenges and theoretical interests. Among them, $\pi$-expanded oligothiophene macrocycles are redox-active $\pi$-donors with
characteristic optical and electronic properties. Therefore, molecular design and synthesis of these molecules can realize their remarkable multifunctional properties in solution and the solid state. First, oligothiophene macrocycles exhibit a larger effective conjugation length than oligophenylene macrocycles, and large macrocycles can often be treated as a fully conjugated system. This extended π-conjugation makes giant macrocyclic oligothiophenes extremely attractive. Especially, π-expanded oligothiophene macrocycles composed of 2,5-thienylene, ethynylene, and vinylene units show very effective cyclic conjugation, because these macrocycles possess almost no steric repulsion between neighboring thiophene rings, and because torsional strain in the small or large ring is diminished by bending of ethynylene and/or vinylene units without significant loss of molecular stability. Second, inner cavities of oligothiophene macrocycles are easily adjustable to guest molecule through selecting numbers of 2,5-thienylene, ethynylene, and vinylene units. Thus, the cavity size of macroring is adjusted to fullerenes to produce Saturn-like complexes. Furthermore, π-expanded oligothiophene macrocycles exhibit unique redox behavior, electric conductivity, polymorphism, photochromism, nonlinear optical properties, and light harvesting behavior, and therefore, these macrocycles find functions in mass use devices, if full conductivity, polymorphism, photochromism, nonlinear optical properties, and light harvesting behavior, and therefore, these macrocycles find functions in mass use devices, if full advantages can be taken of these systems. Finally, π-expanded oligothiophene macrocycles face the new century as one of the target molecules to be exploited in depth.

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Notes and references

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