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Influence of Conformation of 9,10-Anthrylene Rotors on Structures and Self-association Properties of Macrocyclic Arylene–Alkynylene Oligomers[1]

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Macrocyclization of 9,10-bis[(3-ethynyl-5-octylphenyl)-ethynyl]anthracene afforded three cyclic oligomers: a dimer, a trimer, and a tetramer. Only the trimer showed significant self-association in solution because of its fully planar structure. Their structures and properties were significantly influenced by the conformation of the 9,10-anthrylene rotors depending on the ring size.

Arylene–ethynylene oligomers and polymers are a novel class of π-conjugated compounds that show fascinating properties and functions.[2] As for cyclic oligomers, the flexibility of the ring skeleton and the constituting arylene units depends on the mode of connection of the aromatic moieties and acetylene linkers. Some oligomers with a rigid and planar framework, e.g., 1,3-phenylene–ethynylene oligomers, occasionally show self-association due to $\pi\cdots\pi$ stacking.[3] When rotatable arylene units are incorporated into the rigid framework, their conformational changes result in the generation of stereoisomers[4] as well as functional motions, such as gyroscopes and turnstiles.[5] Höger et al. proposed a novel molecular design that utilizes 1,4-phenylene groups with polar and nonpolar side chains to develop switchable amphiphilic macrocycles.[3d,6] Recently, we reported an enantiopure anthrylene–ethynylene cyclic tetramer that racemized at high temperature via the rotation of anthrylene units about acetylene linkers.[7] These results inspired us to create a new type of arylene–ethynylene macrocycles bearing 9,10-anthrylene (9,10-A) units as rotors. We adopted 9,10-bis(phenylethynyl)anthracene (BPEA) as the building unit because of its strong fluorescence.[8] Macrocyclization of diethynyl precursors by the Eglinton coupling gave a mixture of cyclic products **1**–**3** (Figure 1). We here report the synthesis and properties of these cyclic oligomers. The data are discussed in terms of the conformation of 9,10-A rotors.

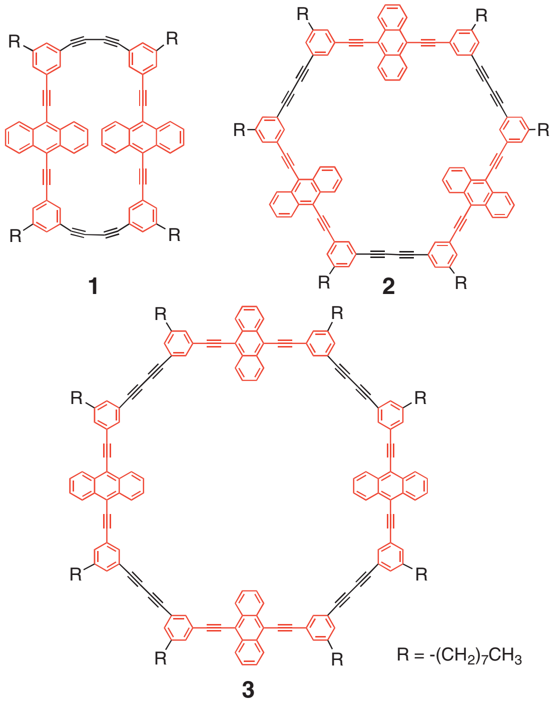
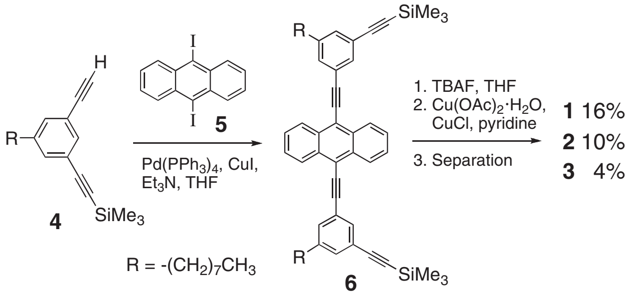


Figure 1. Cyclic oligomers **1**–**3** with 9,10-bis(phenylethynyl)-anthracene units. Core units are indicated in orange color.

Diethynylbenzene **4** was prepared from its dibromo derivative in two steps and an octyl chain was introduced to increase solubility (Scheme 1).[3e] The Sonogashira coupling of **4** with 9,10-diiodoanthracene (**5**) in a 2:1 ratio gave compound **6** in 78% yield. This precursor was desilylated with tetrabutylammonium fluoride (TBAF) and the formed terminal alkyne was treated with copper reagents to yield a mixture of Eglinton coupling products. This mixture was separated by chromatography on silica gel and then GPC to give dimer **1**, trimer **2**, and tetramer **3** in 16, 10, and 4%, yields respectively, as a yellow or orange solid. Their molecular weights were confirmed by FAB or MALDI-TOF mass spectrometry.[9] The simple signal pattern in the ^{1}H NMR spectra of the cyclic oligomers, one AA′XX′ system due to anthracene protons and three double doublets due to phenyl protons in the aromatic region, reflects the high degree of symmetry of the cyclic structures. In the UV–vis spectra of the cyclic oligomers, the maximum absorption peaks at the longest wavelength were observed at ca. 470 nm for all the compounds (Figure 2a). The absorption bands were broad and significantly weak per number of chromophores for tetramer **3**. This large ring effect[10] is attributable to the lost of vibrational structure, although a reason for this phenomenon is unclear from available data. The fluorescence spectra gave intense emission bands at 480 nm (Figure 2b) and their absolute fluorescence quantum yields (Φ_f 0.78–0.83) were comparable to that of BPEA.[8] These electronic spectral data suggest that the effects of ring size are rather small in the molecular system.



Scheme 1. Synthesis of cyclic oligomers **1**–**3**.

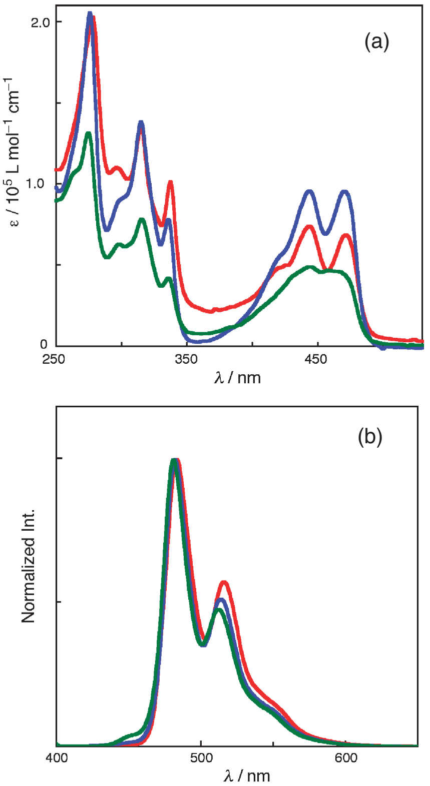


Figure 2. UV–vis (a) and fluorescence (b) spectra of cyclic oligomers in $CHCl_3$. **1** (red), **2** (blue), and **3** (green).

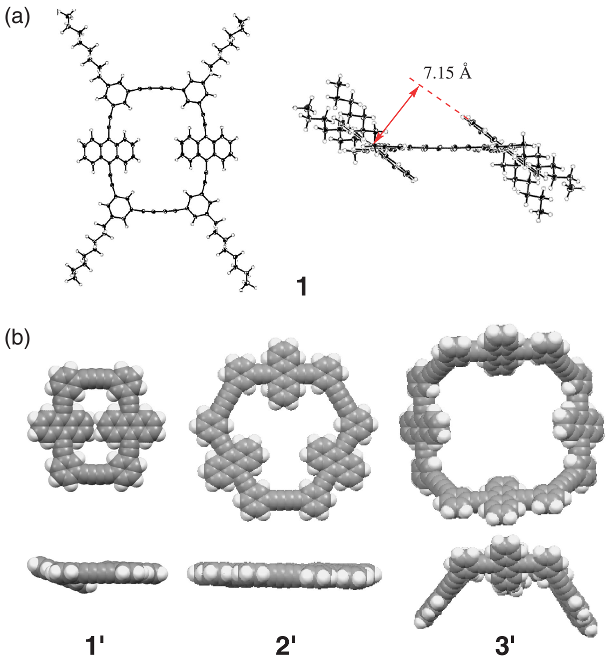


Figure 3. X-ray structures of **1** (a) and calculated structures of **1′**–**3′** at B3LYP/6-31G(d) level (b).

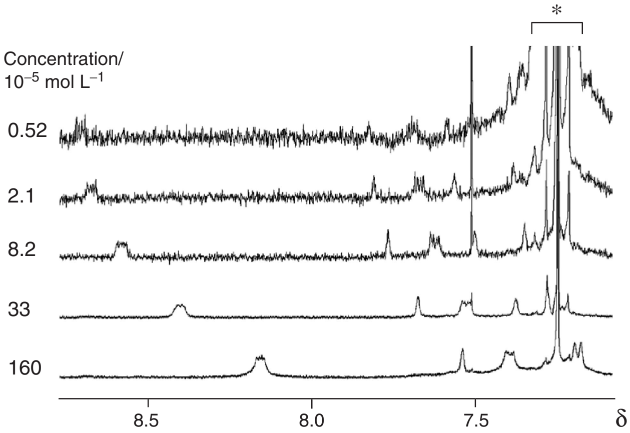
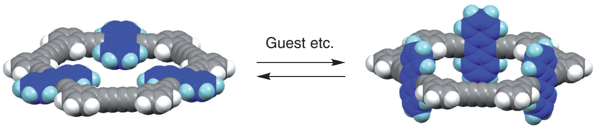


Figure 4. ^{1}H NMR spectra (aromatic signals) of **2** at variable concentrations in $CDCl_3$. * Signals due to solvent.

Figure 3a shows the X-ray structures of compound **1**.[11] The macrocyclic framework is nearly planar and each sp carbon suffers from small bending deformation (bond angle: 171.1–177.8°). The two 9,10-A planes rotate by 38° in the same direction relative to the macrocyclic plane, leading to parallel orientation separated by 7.15 Å. The structures of **1′**–**3′** (R = H) were optimized by DFT calculation at the B3LYP/6-31G(d) level (Figure 3b). Although the calculation of **1′** reasonably reproduced the macrocyclic framework of the X-ray structure of **1**, the conformation of the 9,10-A moieties was somewhat different: one 9,10-A was nearly coplanar and the other rotated by 22° relative to the macrocyclic plane in the calculated structure.[12] The optimized structure of **2′** is planar and hexagonal with three fully coplanar 9,10-A units. Tetramer **3′** has a nonplanar tub-like structure, where each 9,10-A unit is coplanar to the attaching phenylethynyl groups.[13] Thus, each cyclic oligomer has characteristic structural features depending on the ring size.

Among the cyclic oligomers, only trimer **2** showed a large effect of concentration on the chemical shifts of ^{1}H NMR signals (Figure 4). For example, the signal due to 1,4,5,8-protons shifted from δ 8.70 to 8.15 as the concentration was increased from 5.2×10^{-6} to 1.6×10^{-3} M. This observation is attributable to the self-association of large and planar molecules by $\pi \cdots \pi$ stacking interactions: namely, the population of associated species increases in the concentrated solution. Assuming the monomer–dimer equilibrium model, the association constant K_a was estimated to be $1100 \pm 70\,M^{-1}$ at 24 °C in $CDCl_3$.[14] This value is larger than those of 1,3-phenylene cyclic hexamers with acetylene or diacetylene linkers determined in the same solvent (ca. 200 or smaller),[3a–3c] but smaller than those of analogous oligomers with polar aromatic units.[3e] The strong association of **2** is attributed to the large surface area of the planar macrocyclic system involving three anthracene units.[15] In contrast, the concentration dependence is negligible for the dimer and the tetramer, which have nonplanar structures in common. Therefore, not only the area but also the planarity is a key factor in the formation of associated species.

To gain further insight into the conformation of 9,10-A units, rotational processes were pursued by the DFT calculation. In dimer **1′**, the conformational change occurs relatively easily except for the fully coplanar conformation where the inner hydrogen atoms of the rotor moieties suffer from steric



Scheme 2. Switching of molecular shape via rotation of 9,10-anthrylene units in **2′**. The nonplanar structure is less stable by 26 kJ mol^{-1} than the planar one at B3LYP/6-31G(d) level.

hindrance. In contrast, the rotation of 9,10-A moieties requires a small amount of energy (ca. 8 kJ mol^{-1} per one moiety) in **2′** and **3′** because of the large inner space in the macrocyclic framework. Facile rotation of the rotors in the trimeric structure would result in the switching of molecular shapes between planar and tube-like structures, as illustrated in Scheme 2. The latter structure possesses a large inner cavity (ca. 16 Å diameter) available for an external molecule. Therefore, trimer **2** potentially can have dual properties depending on the conformation of the 9,10-A units. We are seeking suitable host molecules and conditions to optimize this interesting property.

In summary, we synthesized novel rigid cyclic oligomers consisting of 9,10-bis(phenylethynyl)anthracene units and diacetylene linkers by coupling reactions. The structure of the framework and the conformational mobility of the rotor moieties are strongly dependent on the ring size. The fully coplanar structure of the trimer is an important requirement for the strong self-association in solution, and the facile rotation of the 9,10-A moieties influences both structure and properties. Further studies are in progress to realize the construction of host–guest systems and nanostructures and the control of emission properties.

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9 **1**: HRMS (FAB) m/z: found 1296.7478, calcd for $C_{100}H_{96}$: 1296.7512 $[M]^+$. **2**: MS (MALDI-TOF) m/z: found 1945.53, calcd for $C_{150}H_{144}$: 1945.13 $[M]^+$. **3**: MS (MALDI-TOF) m/z: found 2593.84, calcd for $C_{200}H_{192}$: 2593.50 $[M]^+$. Other spectroscopic data are available electronically on the CSJ-Journal Web site as Electronic Supporting Information; http://www.csj.jp/journals/chem-lett/index.html.

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11 Crystal data for **2**: $1/2(C_{100}H_{96})\cdot(C_4H_8O)$, $M_r = 720.99$, triclinic, space group $P\bar{1}$ (#2), $a = 11.0135(13)$, $b = 12.4572(12)$, $c = 16.3876(17)$ Å, $\alpha = 74.789(9)$, $\beta = 76.9617(14)$, $\gamma = 80.543(6)°$, $V = 2100.4(4)$ Å^3, $Z = 2$, $D_{calcd} = 1.140$ g cm^{-3}, μ(Mo Kα) $= 0.066$ mm^{-1}, $T = 123$ K, 7670 reflections, $R1 = 0.0683$ ($I > 2.0\sigma(I)$), $wR2 = 0.1697$. GOF 0.993. Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-756295. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

12 The structural optimization of **1′** gave other two structures, which differed in conformation of the 9,10-anthrylene units (Electronic Supporting Information).

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