Construction of Three-dimensional Framework with 1,8-Anthrylene and Butadiynylene Building Units: Synthesis and Properties of Cyclic Tetramers[1]

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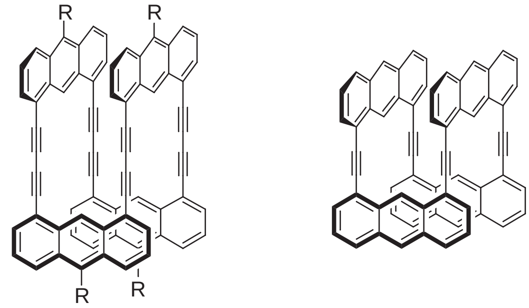
As a new type of π-conjugated macrocycles, 1,8-anthrylene–butadiynylene cyclic tetramers were synthesized by metal-catalyzed oxidative coupling reactions. The fluorescence spectrum of the nonsubstituted derivative indicated partial formation of an excimer in the excited state. The macrocyclic structure undergoes rapid interconversion between two enantiomeric diamond prism structures. These spectroscopic and structural features are compared with those of ethynylene analogues.

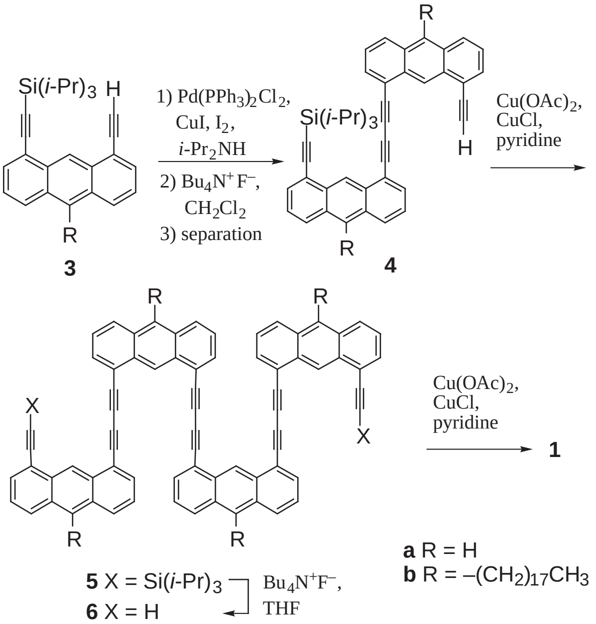
The combination of simple linear and planar building blocks enables us to construct various molecular frameworks including arylene–ethynylene oligomers, which have attracted attention as π-conjugated systems for their fascinating structures and properties.[2,3] Several types of phenylene–ethynylene structures were adopted in the molecular design of helicates and macrocyclic compounds.[4] We recently reported 1,8-anthrylene–ethynylene cyclic tetramer **2** (Figure 1) as another type of compound containing polycyclic aromatic units and featuring the diamond prism structure and conformational changes.[5] The use of butadiynylene linkers (–C≡C–C≡C–) instead of ethynylene linkers (–C≡C–) not only increases the distance between arene moieties from 4.1 to 6.7 Å but also tunes the electronic properties. This structural variation was occasionally applied in the above phenylene compounds to create longer or larger analogues, e.g., graphydiynes, shape-persistent macrocycles, and linear *p*-phenylene polymers.[2a,6] Therefore, we synthesized anthracene–diacetylene scaffold **1** with a 36-membered ring, a taller analogue of **2**, and revealed its structural and spectroscopic features.

Compounds **1** were prepared via the route shown in Scheme 1, where the chain was extended by metal-catalyzed oxidative coupling reactions. Soluble derivative **1b** bearing octadecyl groups at the 10-position was synthesized from **3b**,[5] which was dimerized with a Pd catalyst[7] and desilylated with tetrabutylammonium fluoride (TBAF) to form **4b**. Compound **4b** was further dimerized by the Eglington coupling[8] to give tetramer **5b** in 91% yield. After the complete desilylation of **5b** with TBAF, terminal alkyne **6b** was cyclized by the Eglington coupling. Cyclic tetramer **1b** was obtained as a yellow solid in 79% yield after chromatographic purification.[9] We managed to synthesize nonsubstituted derivative **1a**[9] although the yield of macrocyclization was low (11%) owing to poor solubility. Molecular ion peaks were observed at m/z 896.4 and 1905.6 for **1a** and **1b**, respectively, by MALDI-TOF mass spectrometry. Macrocycles **1** were stable in the solid form and slowly decomposed in dichloromethane solution. The symmetric structure was supported by the signal pattern of the NMR spectra: for example, **1b** gave only one set of ABC system and a singlet for the aromatic protons, and two signals for the alkynic carbons, consistent with D_{2d} symmetry.



1 **a** R = H **2**
b R = $-(CH_2)_{17}CH_3$

Figure 1. 1,8-Anthrylene–butadiynylene cyclic tetramers **1** and their ethynylene analogue **2**.



Scheme 1. Synthesis of cyclic tetramers **1**.

The UV and fluorescence spectra of **1a** are shown in Figure 2. Compound **1a** has structured absorption bands in the *p* band region with the maximum absorption appearing at 445 nm (ε 51000). This band is shifted bathochromically relative to the corresponding band in 1,8-bis(butadiynyl)anthracene (416 nm).[3a] The substitution of butadiynylene linkers for ethynylene linkers results in a small red shift and an increased intensity (cf. **2**: λ_{max} 439 nm, ε 12000).[5b] The emission bands of **1a** are relatively broad and peak at 469 nm, and their quantum yield

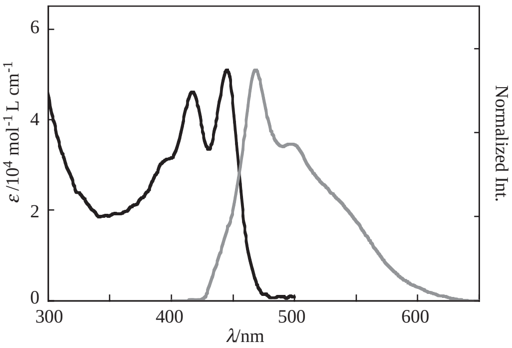


Figure 2. Electronic spectra of **1a** in $CHCl_3$ at 1.0×10^{-6} $mol\,L^{-1}$ (absorption: black. emission: gray, λ_{ex} 393 nm).

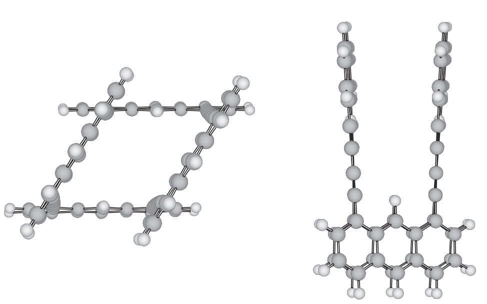


Figure 3. Molecular structures of **1a** optimized by AM1 calculation.

and lifetimes are Φ_F 0.10 and τ_F 2.0, 6.3 ns, respectively (cf. **2**: λ_{max} 478 nm, Φ_F 0.40 and τ_F 2.4, 14.7 ns).[5b] The component of the longer lifetime is attributable to an excimer type emission, and this is consistent with the broad shoulder in the emission.

Because we could not obtain single crystals suitable for X-ray analysis, the molecular structure was examined by AM1 calculation. Two views of the global minimum structure of **1a** are shown in Figure 3. The framework adopts a chiral D_2 structure similar to a diamond prism, where the dihedral angles between anthracene planes are 58° and 128°. The sp carbons are almost linear, whereas the two butadiynyl moieties at the 1,8-positions are slightly bent from the ideal parallel direction. The interfacial distance between the nearly parallel oriented anthracene planes is ca. 5.0 Å.[10] A CPK model teaches us that the conformational change into a more flattened structure requires only a small energy, allowing π–π interactions between the face-to-face anthracenes, such as the excimer formation mentioned above.[11]

The simple signal pattern in the ^{1}H NMR spectrum of **1a** was maintained even though the sample was cooled down to $-100\,°C$ in CD_2Cl_2. This indicates that the conformational interconversion between the two enantiomeric diamond forms occurs rapidly even at low temperatures (barrier $< 30\,kJ\,mol^{-1}$). This barrier is clearly lower than that of the corresponding process in **2** (ca. $38\,kJ\,mol^{-1}$). The facile conformational change in **1a** is explained by the increased mobility of the arene moieties due to the long axes.

In summary, cyclic tetramers with butadiynylene linkers were readily synthesized by repeated oxidative coupling reactions. This synthetic protocol is basically applicable to the construction of 2^n-mers. The long linkers influence the spectroscopic and structural properties of the cyclic system, particularly the electronic spectra and the dynamic structure. Studies on the reactivity and the complex formation of the tetramers, as well as the synthesis of octamer and higher oligomers, are in progress.

This work was partly supported by "High-Tech Research Center" Project for Private Universities: matching fund subsidy from MEXT (Ministry of Education, Culture, Sports, Science and Technology), 2001–2005, and by a grant from Sumitomo Foundation.

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9 Data of cyclic tetramers **1b**: Yield 79% from **6b**; mp 223–226 °C (dec); yellow solid; ^{1}H NMR ($CDCl_3$) δ 0.90–1.75 and 3.41 (148H, alkyl signals), 6.87 (8H, dd, $J = 6.8$, 8.8 Hz), 7.30 (8H, d, $J = 6.8$ Hz), 7.88 (8H, d, $J = 9.3$ Hz), 9.38 (4H, s); ^{13}C NMR ($CDCl_3$) δ 80.1, 81.1, 121.0, 123.2, 124.2, 125.0, 128.6, 130.7, 131.4, 135.6, and alkyl signals at 14–32; MS (MALDI-TOF) Found m/z 1905.61. Calcd for $C_{144}H_{176}$: M^+, 1905.38. Macrocyclization of **6b** was carried out under non high-diluted conditions (ca. 1.0×10^{-3} $mol\,L^{-1}$). **1a**: Yield 11% from **5a**; yellow solid; mp 298–301 °C (dec); ^{1}H NMR ($CDCl_3$) δ 6.90 (8H, dd, $J = 6.8$, 8.8 Hz), 7.30 (8H, d, $J = 5.9$ Hz), 7.67 (8H, d, $J = 8.3$ Hz), 8.09 (s, 4H), 9.29 (s, 4H); MS (MALDI-TOF) found m/z 896.37; calcd for $C_{72}H_{32}$, M^+, 896.25. HR MS (FAB) found m/z 896.2514; calcd for $C_{72}H_{32}$, M^+, 896.2504.

10 The AM1 (or PM3) calculation does not consider the π–π interactions well to give a large interfacial distance as pointed out in Ref. 5b.

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Published on the web (Advance View) June 5, 2006; doi:10.1246/cl.2006.684