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Shape-persistent, double-helically twisted macrocycles with two quaterphenyl moieties: Synthesis, structure and physicochemical properties for a chiral sensor

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Abstract

Shape-persistent macrocyclic diene and diyne, which consist of two quaterphenyl units, were synthesized by McMurry coupling of 5,5′-bis(3-formylphenyl)-2,2′-dimethoxybiphenyl as a key step. The macrocycles have achiral (*meso*) and chiral (racemic) conformational isomers owing to two asymmetric axes of the biaryl units. According to the theoretical calculations, the chiral conformers are about 1 kcal mol^{-1} lower than the corresponding achiral conformers in energy. The NMR spectra indicate that the interconversion between the diastereomers occurs with relatively low energy barrier ($<$10 kcal mol^{-1}). An X-ray crystallographic analysis of the diyne reveals that it has a double-helically twisted chiral structure and low strain nature of the molecule as expected. Moreover, the molecules construct a layered structure with channels that are filled with two chloroform molecules. Potential utilities such as a chiral sensor were also investigated. ***To cite this article: T. Kawase et al., C. R. Chimie 12 (2009).***
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*Keywords:* Macrocycle; Double-helically twisted structure; Channel structure; Chiral sensor

1. Introduction

Chiral shape-persistent macrocycles are of great interest because their unique structures provide potential utilities for chirality sensing, chiral guest recognition, chiral separation, as well as ligands for asymmetric catalysts [1−4]. When the chirality of the molecules is controllable by external stimuli, they would be utilized as molecular devices for a chirality sensing and

a chiroptical memory [5,6]. Recently, we have studied phenylacetylene macrocycles (PAMs) with novel structures such as cyclic [n]paraphenyleneacetylene [7], cyclic [n]metaphenyleneacetylene [8,15a] and their related compounds [9]. The syntheses were carried out using the McMurry coupling of appropriate dialdehydes as a key step [10]. In the course of the studies, we have designed and synthesized macrocyclic cyclophanes **1** and **2** composed of two binaphthol and biphenol units (Scheme 1) [11,12]. The biarylonophanes have two possible diastereomers, achiral (*meso*) and chiral (racemic) forms owing to two asymmetric axes of the biaryl units (Fig. 1). The considerably high energy of racemization barrier of a binaphthol skeleton

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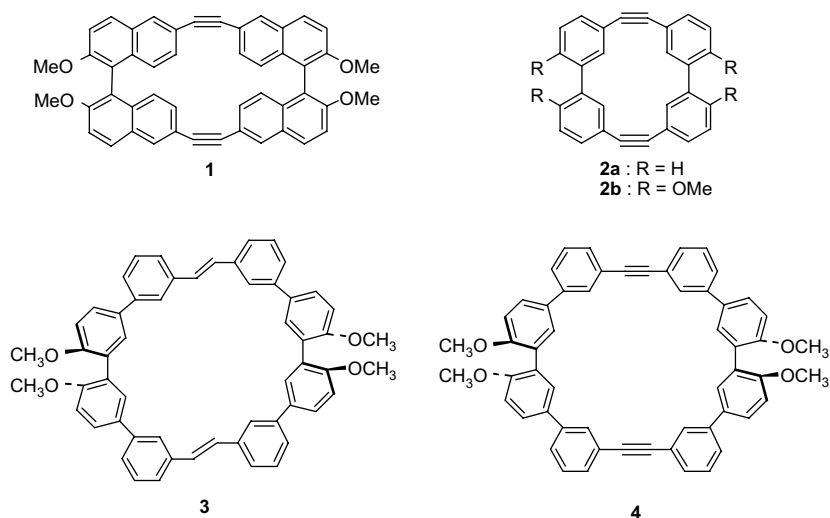
Scheme 1. Biarylonophanes **1** and **2**, and macrocyclic diene **3** and diyne **4** bearing two quaterphenyl units.

(37.8 kcal mol^{-1}) [13] enables the obtaining of the compound **1** in enantiomerically pure forms. On the other hand, the energy barrier of interconversion between two diastereomers of **2** would depend upon the bulkiness of substituents at 2,2′-positions of diphenyl units. Actually, a tetramethoxy derivative **2b** exists in an equilibrium mixture between *meso* and racemic forms in a chloroform solution; ^{1}H NMR spectrum at −50 °C indicated the ratio between major and minor isomers to be ca. 5:1. Variable-temperature (VT) NMR experiments allowed the evaluation of the activation energy for the interconversion as ca. 12 kcal mol^{-1}. The crystal analysis reveals that **2b** adopts the *meso*-form in the crystals. Combined with the theoretical predictions, the

meso-form should be predominant in solution. The biphenylonophane framework of **2** seems unsatisfactory to our purpose for the construction of molecular devices such as a chirality sensing and a chiroptical memory.

In this context, we have newly designed macrocyclic diene **3** and diyne **4** having two quaterphenyl units. Theoretical calculations (PM3) [14] predict that *chiral*-forms **3a** and **4a** (Fig. 2) are about 1 kcal mol^{-1} lower than achiral (*meso*)-forms **3b** and **4b** in the heat of formation. The relatively large differences suggest that these macrocycles should predominantly exist as the *chiral*-forms. On the other hand, racemization barrier through their diastereomers would be relatively low, because two oxygen functionalities at 2,2′-positions
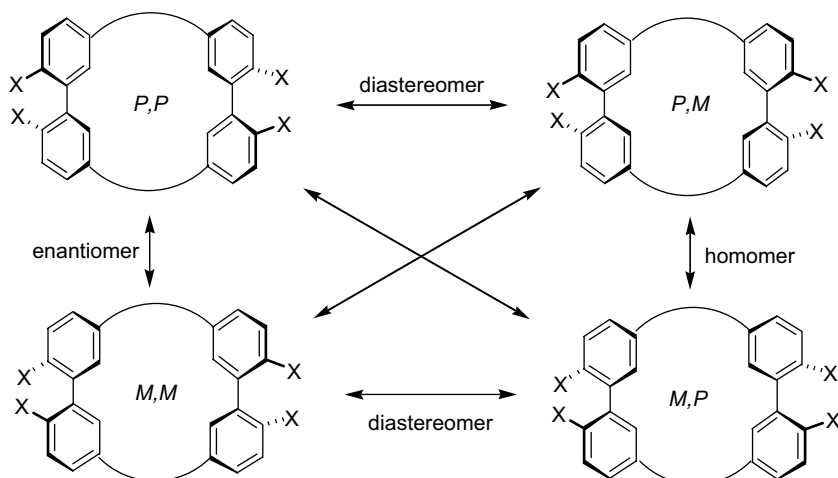

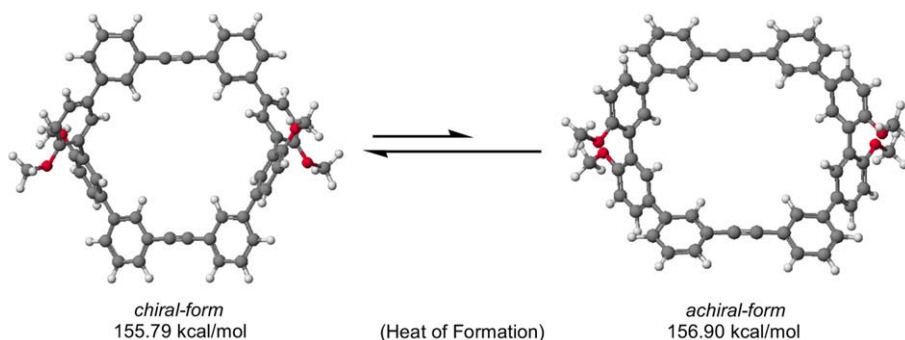Fig. 1. Relationship among stereoisomers of a molecule with two biaryl units.

Fig. 2. Predicted molecular structures of chiral and achiral conformers, **4a** and **4b**.

are not so bulk. Here we report the synthesis, properties and the molecular structure of **4**. Moreover, methyl groups of the diene **3** can be replaced with chiral camphorsulfonyl groups, though similar reaction of **4** resulted in failure. The chiroptical properties of **3** as a potential segment for chiral sensor are also discussed.

2. Results and discussion

2.1. Synthesis

The synthesis of **3** and **4** is outlined in Scheme 2. The Suzuki−Miyaura coupling of 2,2′-dimethoxy-5, 5′-bromobiphenyl **5** with commercially available 3-formylbenzene boronic acid afforded diformylquaterphenyl **6** (66%). Treatment of **6** with TiCl₄−Zn in DME−toluene (3:1) afforded the cyclophane diene **3** (37%) together with a corresponding trimer with a ratio of ca. 10:1 (from ¹H NMR). If the reaction was performed in DME only, the yield was reduced to 19%. The relatively high field shift of etheno-protons of **3**

(7.19 ppm) is indicative of the *Z*-configuration in comparison with the corresponding protons of (*E*)- and (*Z*)-stilbenes. We have previously reported that the presence of toluene as a co-solvent gives rise to highly *E*-selective double bond formation in the McMurry reaction [15]. The high *E*-selectivity seems to play a key role for the relatively high yield. The dimer **3** can be purified with gel permeation chromatography (GPC). The dimeric structure was established on the basis of NMR spectroscopic and mass spectrometric analyses. Bromination−dehydrobromination of **3** led to the diyne **4** (80%). The macrocycles were obtained as fairly stable colorless prisms.

2.2. Spectral properties

¹H and ¹³C NMR spectra of the cyclophanes **3** and **4** exhibit expected simple pattern in agreement with the high symmetry of the molecule at 30 °C. In contrast to cyclophane **1b**, VT-NMR spectra of the macrocycles show little change down to −50 °C. The results clearly
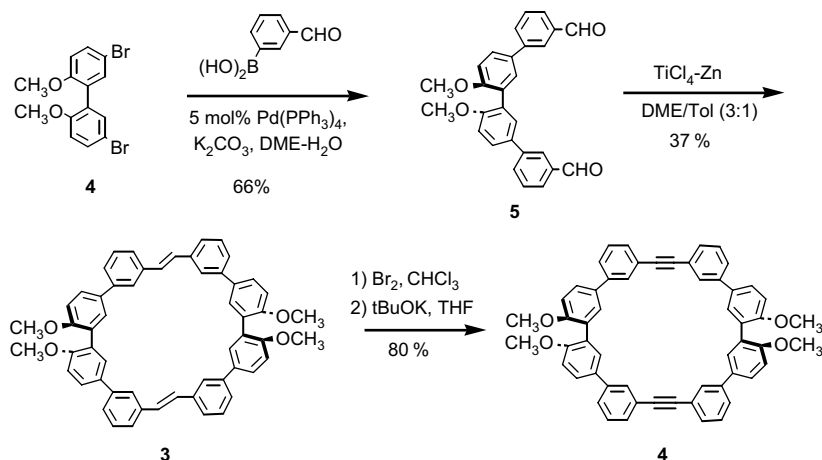
Scheme 2. Synthesis of **3** and **4**.

indicate that the interconversion between the diastereomers occurs with relatively low energy barrier (<10 kcal mol^{-1}). The protons at 8 positions of quaterphenyl units of **3** and **4** (**3** for 7.77 ppm and **4** for 7.67) appear in low fields in the ^{1}H NMR spectra, which would be due to the anisotropy effect of olefin and acetylene bonds. The sp carbons of **4** were resonated at 89.3 ppm, which is almost identical to corresponding carbons of diphenylacetylene (89.4 ppm). The results indicate the less strain nature of the compound.

UV–vis and fluorescence spectra in dichloromethane of **3** and **4** are shown in Fig. 3. Both compounds exhibit intense absorption bands at 278 nm and 272 nm, respectively. The molar absorptivity of **4** at λ_{max} is about 1.5 times as high as that of **3**, probably due to highly planar conformation of the diyne. The diene **3** has a shoulder band at 334 nm. The UV–vis spectra of **3** were measured under several concentrations ($1.28 \times 10^{-6} – 6.38 \times 10^{-4}$ mol l^{-1}). The shapes and intensities of the absorption bands including the shoulder band only show little changes. The results indicate that the shoulder band seems not an aggregation band. The cyclophanes **3** and **4** exhibit emission bands at 380 nm and 361 nm, respectively. The shoulder band of **3** would be due to the HOMO–LUMO transition. But, the transition of **4** would be submerged by the intense absorption band at 270 nm. The exact values of the Stokes' shift cannot be evaluated.

2.3. Molecular structure

A chloroform–hexane solution provided moderately good single crystals of the cyclophane-diyne **4** by a vapor-diffusion method. The crystal contains three chloroform molecules per single macrocyclic molecule. During the sampling operation of the single crystal of **4** for X-ray crystallography, the solvent molecules desorb so rapidly from the crystal, leading to the slight loss of transparency of the crystal. The X-ray data quality of **4** was not satisfactory due to the reduction of the single crystallinity (the R_1 value is 0.140). Fig. 4 shows ORTEP drawings: (a) top view, (b) side view, and (c) a molecular packing. The molecular structure of **4** is quite similar to the one predicted by PM3 calculations; it possesses a chiral conformation and almost linear acetylenic bonds (averaged bond angle of acetylenic carbons is 179°). The aromatic rings of quaterphenyl units have an alternating up-down arrangement. The averaged dihedral angle between the planes of aromatic rings bearing a methoxy group ($\angle$AH and $\angle$DE) is 77.2°, while that of other aromatic rings ($\angle$AB, $\angle$CD, $\angle$EF, and $\angle$GH) is 35.2°. The congestion of methoxy groups increases the molecular twisting. The dihedral angles between the aromatic rings of diphenylacetylene moieties ($\angle$BC and $\angle$FG) are smaller than 30°, which indicates the good planarity of the segments. The crystal has P-1 space group; therefore, it includes both enantiomers. Each enantiomer forms a layer structure that gives rise to columns with channels (Fig. 4c). Two chloroform molecules are situated in the sizable and chiral cavity. The third chloroform molecule occupies the interspace of four columns. The preparation of co-crystals with chiral molecules is now in progress.

2.4. Potential utility as a chiral sensor

The crystallographic analysis of **4** indicates that the chiral conformer is more stable in the crystals. The configurationally flexible biphenyl chromophore for which induction of axial chirality by interaction with chiral auxiliaries is well documented and has been exploited in molecular recognition studies [16]. To explore potential utilities of the macrocycles as a chiral
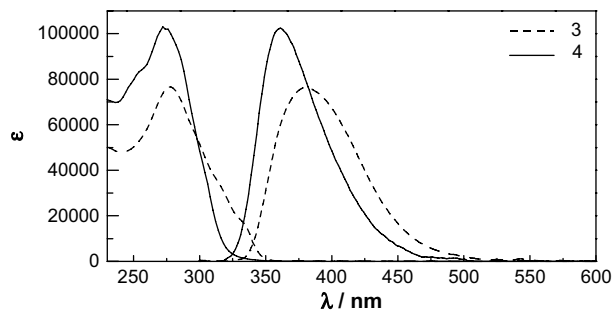

Fig. 3. Absorption and emission spectra of **3** and **4** in CH$_2$Cl$_2$. Emission spectra were obtained upon excitation at absorption maximum, and the intensities are normalized with those of absorption spectra.
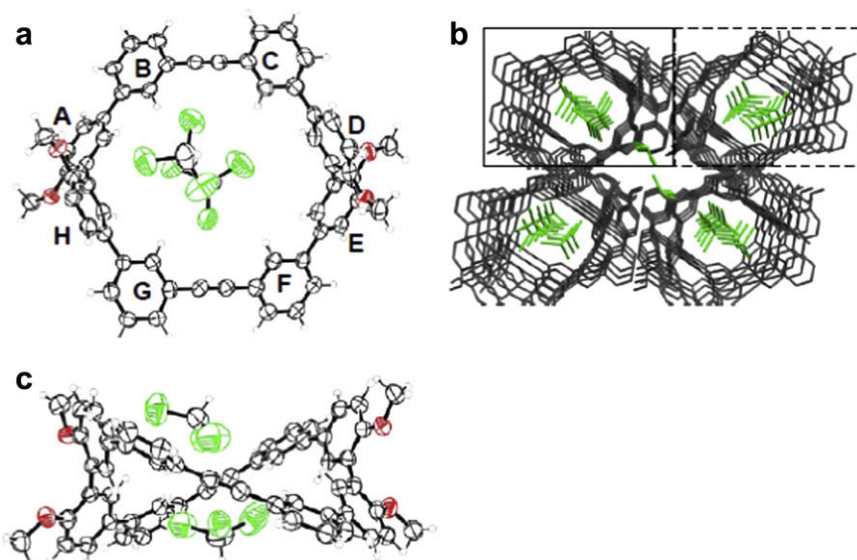
Fig. 4. ORTEP plots (50% probability): (a) top view and (b) side view. Third chloroform molecule is omitted for clarity. (c) A molecular packing of **4**.

sensor or a memory device, we introduce a chiral auxiliary, camphorsulfonyl (CS) group, in place of the methyl groups.

Demethylation of **3** with BBr$_3$ in dichloromethane at room temperature successfully afforded a tetra-phenol **7** in high yield (88%). Although **7** is poorly soluble in organic solvents, treatment with chiral camphorsulfonyl chloride ((+)- or (−)-CSCl) in the presence of triethylamine in THF led to corresponding tetra-camphorsulfonyl, [(+)- or (−)-CS]$_4$-macrocycles, (+)-**8** and (−)-**8**, in moderate yields (Scheme 3). Unfortunately, demethylation of the diyne **4** under several conditions resulted in failure. The acetylenic bonds of **4** are susceptible to the reaction conditions.

There are three possible diastereomers, [(+)-CS]$_4$-*PP*, [(+)-CS]$_4$-*MM* and [(+)-CS]$_4$-*PM*, in (+)-**8**.

These diastereomers are distinguishable and separable under appropriate conditions. ^{1}H NMR spectrum of **8** exhibits two sets of unequivalent signals assignable to α-protons of camphorsulfonyl groups (Fig. 5). VT-NMR spectra in toluene-d_8 did not show coalescence of the signals even at 100 °C, which suggests that the activation energy of interconversion between diastereomers is relatively high (>19 kcal mol^{-1}). The diastereo excess (d.e.) can be estimated to be ca. 10% from the integration of the signals. Despite the small d.e., the well-defined circular dichroism (CD) spectrum was observed (λ_{ext} (THF); $\Delta\varepsilon = +9.9$, 266 nm). Because the spectral curve is apparently different from that of (+)-camphorsulfonic acid ($\Delta\varepsilon = \pm 1.535$, 290 nm) [17], the CD absorption is attributed to chirality of the macrocycle moiety. The two diastereomers can be separated with a chiral HPLC
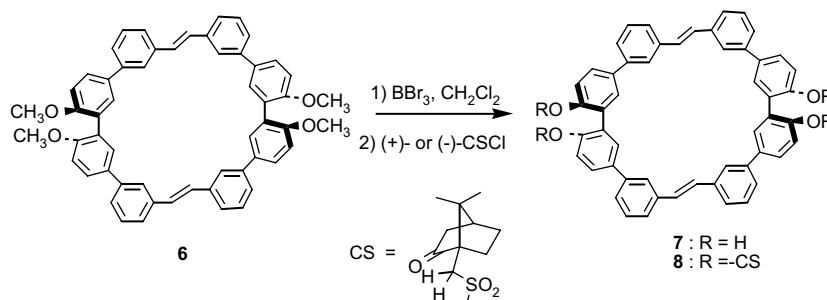
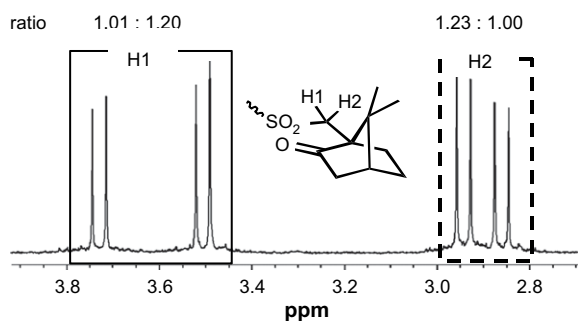Scheme 3. Preparation of tetra-camphorsulfonylated macrocycle **8**.

Fig. 5. A partial NMR spectrum of (+)-**8**.

(CHIRALCEL OD, Daicel Co. Flow rate 1.0 ml/min, Hexane:EtOH = 1:1, 35 °C). The CD absorption (270 nm) of two elusions shows almost mirror images, which indicate that two diastereomers, [(+)-CS]$_4$-*PP* and [(+)-CS]$_4$-*MM*, were separated under the conditions (Fig. 6a). The CD curve of a separated diastereomer, [(+)-CS]$_4$-**8**, decreases with time even at 25 °C (Fig. 6b). The half-life period is estimated to be about 2.5 h from the spectral change, which gives the activation energy to be ca. 23.0 kcal mol^{-1}. These results indicate the potential ability of the macrocylic system as a chiral sensor. The intensity at ca. 260 nm decreases with time, however; the intensity at 325 nm appears unchanged with time. The weak CD band at 325 nm would not come from the cyclophane framework, but the biaryl moieties with chiral camphorsulfonyl groups. Theoretical studies to determine the absolute configuration of diastereomers will be reported in due course [18,19].
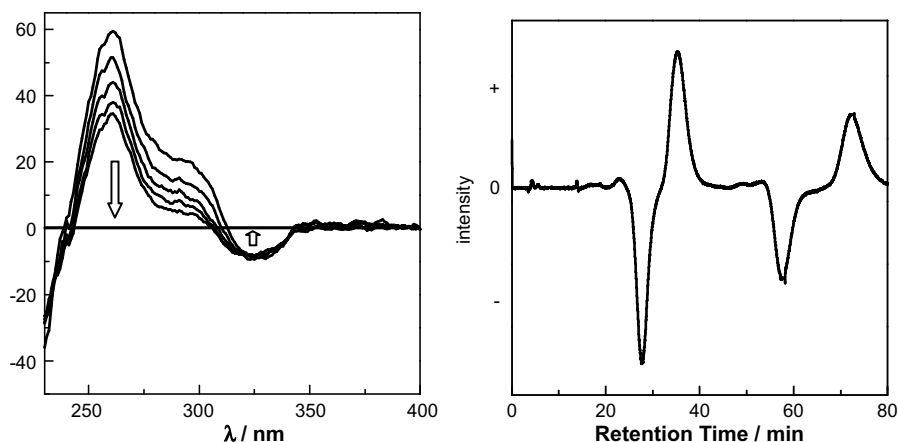
3. Experimental

3.1. General remarks

Melting points were recorded on a Yanaco MP 500D apparatus and uncorrected. FAB, EI and ESI mass spectra were measured on JEOL JMS-SX102, Shimadzu GCMS QP-5050A, and Applied Biosystems QSTAR, respectively. ^{1}H NMR spectra (tetramethylsilane; 0 ppm as an internal standard) and ^{13}C NMR spectra (CDCl$_3$; 77.0 ppm as an internal standard) were recorded on JEOL lambda-500, JEOL JNM-GSX-400, and JEOL EX-270 apparatus. The chemical shifts are given in ppm. IR spectra were obtained from a JASCO FT-IR-460K2 spectrometer. Electronic (UV–vis) and circular dichroism (CD) spectra were obtained on Jasco V-570 and J-725 spectrophotometers, respectively. Column chromatography was performed with Merck Kiesel-gel 60.

3.2. Materials

All reagents of commercial quality were used as supplied unless otherwise stated; tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) were dried where necessary using standard procedures.

3.2.1. 5,5′-bis(3-formylphenyl)-2,2′-dimethoxybiphenyl **5**

A 100 ml of two-necked round-bottomed flask equipped with a reflux condenser bearing a nitrogen inlet tube and septum was charged with 5,5′-dibromo-2,2′-dimethoxybiphenyl (372 mg, 1 mmol), 3-formylphenylboronic acid (450 mg, 3 mmol), Na$_2$CO$_3$

Fig. 6. (a) CD spectral changes of a diastereomer (the first eluted fraction) of (+)-**8** in THF with each 30 min at 25 °C. (b) Chromatogram for the diastereomeric separation of (+)-**8**. CD detection (λ = 275 nm). Conditions: CHIRALCEL OD, flow rate 1.0 ml/min, Hexane:EtOH = 1:1 at 35 °C.

(636 mg, 6 mmol), Pd(PPh$_3$)$_4$ (173 mg, 0.15 mmol) and a magnetic stirring bar. DME (10 ml) and water (5 ml) were added, and the mixture was heated at reflux under a nitrogen atmosphere for 17 h. The reaction mixture was cooled to room temperature, and diluted with 20 ml of water, and extracted with CH$_2$Cl$_2$ (20 ml × 3). The separated organic layers were combined, washed with water and brine, and dried over Na$_2$SO$_4$. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (30 g), eluted by *n*-hexane-CH$_2$Cl$_2$ (v/v = 1/1) to give **5** (280 mg: 66%) as a colorless solid.

5. Colorless fine solid; mp 176.1–176.8 °C; ^{1}H NMR (270 MHz, CDCl$_3$) δ 10.1 (s, 2H), 8.09 (t, *J* = 1.5 Hz, 2H), 7.86 (dt, *J* = 7.6, 2.0 Hz, 2H), 7.79 (dt, *J* = 7.6, 1.5 Hz, 2H), 7.63 (dd, *J* = 8.6, 2.5 Hz, 2H), 7.59–7.53 (m, 4H), 7.09 (d, *J* = 8.6 Hz, 2H), 3.84 (s, 6H); ^{13}C NMR (67.8 MHz, CDCl$_3$) δ 192.4, 157.3, 141.6, 136.9, 132.7, 131.9, 130.2, 1290.4, 128.1, 128.0, 127.7, 127.5, 111.6, 55.9; MS (EI, 70 eV) *m/z* (rel intensity) 422 (100, M$^+$), 364 (9), 336 (8); IR (KBr, cm^{-1}) 2995 (w), 2950 (w), 2828 (w), 2727 (w), 1698 (s), 1603 (s), 1505 (s), 1479 (m), 1438 (m), 1277 (s), 1182 (s), 1023 (m), 800 (s), 693 (m), 651 (m), 576 (m); Anal. Found: C, 79.21; H, 5.23. Calcd. for C$_{28}$H$_{22}$O$_4$: C, 79.60; H, 5.25.

3.2.2. Macrocyclic diene **3**

A 100 ml of well-dried, three-necked round-bottomed flask equipped with a reflux condenser bearing a nitrogen inlet tube and a pressure-equalizing funnel was charged with zinc powder (1.309 g, 20 mmol), copper(I) iodide (136 mg, 0.7 mmol) and a magnetic stirring bar. Freshly distilled DME (15 ml) and dried toluene (5 ml) were added through a rubber septum by syringes, followed by the addition of TiCl$_4$ (1.1 ml). The mixture was heated to reflux for 3 h under a nitrogen atmosphere and cooled to room temperature. A solution of dialdehyde **5** (310 mg, 0.73 mmol) in DME (15 ml) was added dropwise through the dropping funnel over 30 min at room temperature. The mixture was stirred overnight at the temperature and then refluxed for 8 h. The reaction mixture was passed through a short alumina column chromatography (50 g) with CH$_2$Cl$_2$. The filtrate was concentrated and residue was purified by column chromatography on silica gel (50 g) eluted by CH$_2$Cl$_2$ to give a macrocycle **3** (106 mg, 37%).

3: White powder; mp 333 °C (decomp); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.68 (s, 4H), 7.54 (dd, *J* = 8.5, 2.4 Hz, 4H), 7.50 (d, *J* = 2.4 Hz, 4H), 7.48–7.39

(m, 12H), 7.18 (s, 4H), 7.03 (d, *J* = 8.5 Hz, 4H), 3.76 (s, 12H); ^{13}C NMR (67.8 MHz, CDCl$_3$) δ 156.7, 141.6, 137.8, 133.4, 130.5, 129.1, 128.9, 127.9, 127.4, 126.4, 125.4, 124.8, 111.3, 55.8; MS (EI, 70 eV) *m/z* (rel intensity) 780 (100, M$^+$), 390 (52, M^{2+}); UV–vis (CH$_2$Cl$_2$) λ$_{max}$ (log ε) 278 nm (4.88), 334 nm (4.22); Fluorescence (CH$_2$Cl$_2$) λ$_{max}$ 380 nm; IR (KBr, cm^{-1}) 3023 (w), 2952 (w), 2834 (w), 1600 (s), 1499 (s), 1252 (s), 1028 (m), 799 (m); Anal. Found: C, 85.94; H, 5.53. Calcd. for C$_{56}$H$_{44}$O$_4$: C, 86.13; H, 5.68.

3.2.3. Macrocyclic diyne **4**

The diene **3** (96 mg, 0.12 mol) was dissolved in chloroform (15 ml) in a 50 ml of round-bottomed flask equipped with a calcium chloride tube. A few drops of bromine (ca. 100 mg) were added and stirred at room temperature for 5 min. The solvent and bromine were removed under reduced pressure and dried in vacuum to give tetrabromide as pale yellow solid. Without further purification, the solid was dissolved in 15 ml of THF. To the solution was added potassium *t*-butoxide (275 mg, 2.45 mmol) and stirred at room temperature overnight. After quenching with water, the reaction mixture was extracted with CH$_2$Cl$_2$ (20 ml), and the organic layer was washed with water and brine, and dried over Na$_2$SO$_4$. After filtering the dry agent, the solvent was removed by evaporator. The residue was purified by column chromatography on silica gel (30 g) eluted by *n*-hexane-CH$_2$Cl$_2$ (v/v = 1/1) to give **4** (76 mg: 80%) as a colorless solid.

4. White powder; mp 290 °C (decomp); ^{1}H NMR (270 MHz, CDCl$_3$) δ 7.77 (s, 4H), 7.63–7.37 (m, 20H), 7.03 (d, *J* = 8.2 Hz, 4H), 3.81 (s, 12H); ^{13}C NMR (67.8 MHz, CDCl$_3$) δ 156.9, 140.8, 132.6, 130.2, 130.0, 129.5, 128.6, 128.3, 127.1, 126.6, 123.5, 111.2, 89.2, 55.9; MS (EI, 70 eV) *m/z* = 777 (100, [M + H]$^+$), 776 (97, M$^+$), 428 (55), 388 (M^{2+}); UV–vis (CH$_2$Cl$_2$) λ$_{max}$ (log ε) 272 nm (5.01); Fluorescence (CH$_2$Cl$_2$) λ$_{max}$ 361 nm; IR (KBr, cm^{-1}) 2793 (w), 2834 (w), 1601 (s), 1500 (s), 1254 (s), 1029 (m), 795 (m); Anal. Found: C, 80.85; H, 4.95. Calcd. for C$_{56}$H$_{40}$O$_4$·0.5CHCl$_3$: C, 81.11; H, 4.88.

3.2.4. Tetrahydroxyl **7**

Diene (45 mg, 0.058 mmol) **3** was dissolved with dichloromethane (10 ml) in a 50 ml of round-bottomed flask equipped with a calcium chloride tube. To the solution was added BBr$_3$ (64 mg, 0.25 mmol) and the mixture was stirred for 24 h at room temperature. The reaction mixture was quenched with water

(10 ml), and the separated aqueous layer was extracted with dichloromethane (10 ml). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. After removing the dry agent by filtration, the filtrate was evaporated to give sparingly soluble white solid (36 mg: 88%).

3.2.5. Tetra-(+)-camphorsulfonyloxy-diene 8

In a 100 ml of two-necked round-bottomed flask equipped with a reflux condenser and a nitrogen inlet tube, a suspension of tetrahydroxy-diene **7** (37 mg, 0.052 mmol), camphorsulfonyl chloride (657 mg, 2.62 mmol), THF (25 ml) and triethylamine (1 ml) was heated at reflux with stirring for 17 h under N_2. After cooling at room temperature, the reaction mixture was quenched with water (10 ml) and extracted with ethyl acetate (10 ml × 3). The separated organic layer was washed with water and brine, and dried over anhydrous Na_2SO_4. After removing the dry agent by filtration, the filtrate was evaporated. The residue was diluted with ethanol to precipitate white solid. The filtered solid was purified by GPC to give (+)-**8** as white solid (40 mg, 48%). Similar procedure afforded (−)-**8** as white solid (9 mg, 14%). **8**; white powder; mp 211.5−212.3 °C; MS (FAB) m/z 1582 $[(M + 2H)^+]$; HRMS(ESI) Found: m/z $C_{92}H_{92}O_{16}NaS_4$ 1603.5234; Calcd for $C_{92}H_{92}O_{16}NaS_4$ $[M^+]$, 1603.5160; [1] H NMR (500 MHz, toluene-d_8) δ 7.92−7.89 (4 peaks, 4H), 7.75−7.64 (4 peaks, 4H), 7.53−7.51 (2 peaks, 4H), 7.39−7.22 (m, 16H), 6.89 (s, 4H), 3.75−3.49 (4 peaks, 4H), 2.96−2.85 (4 peaks, 4H), 2.35−2.22 (m, 4H), 1.92−1.82 (m, 4H), 1.43−1.34 (m, 12H), 0.84−0.78 (m, 8H), 0.86−0.72 (2 peaks, 12 H), 0.43−0.42 (2 peaks, 12H); UV−vis (THF) λ_{max} (log ε) 263 nm (4.96), 311 nm (4.66), 334 nm (4.32); (+)-**8**, CD (THF) λ_{ext} ($\Delta\varepsilon$) 243 nm (−3.1), 266 nm (+9.9), 299 (+2.2), 329 (−1.2); (−)-**8**, CD (THF) λ_{ext} ($\Delta\varepsilon$) 242 nm (+3.4), 263 nm (−7.8), 302 (−2.9), 321 (+1.1).

3.2.6. X-ray crystallographic analysis of 4

Intensity data were collected on a Rigaku/MSC Mercury diffractometer CCD at −123 °C. The structure was solved with direct method on F^2 with SHELXS-97. A total of 11,879 reflections were collected, 5561 unique reflections were measured and used in the refinement, 649 parameters, $R_1 = 0.140$, $R_w = 0.444$ for 1687 reflections with $I > 2\sigma(I)$, GOF = 1.31, max. peak in final diff. Map 0.78 e$Å^{-3}$. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed geometrically and refined by using a rigid model. Crystal data for **4**·3(CHCl$_3$), $M = 1135.06$; triclinic, P-1(#2), $a = 12.27(9)$ Å,

$b = 14.76(4)$ Å, $c = 15.40(5)$ Å, $\alpha = 92.0(2)°$, $\beta = 103.3(2)°$, $\gamma = 102.5(2)°$, $V = 2640(2)$ Å^3, $Z = 2$, $\rho = 1.428$ g cm^{-3}. CCDC 701618. The supplementary material has been sent to the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

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