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Chemistry of Anthracene–Acetylene Oligomers: Synthesis and Enantiomeric Resolution of a Chiral 1,8-Anthrylene–Ethynylene Cyclic Tetramer**

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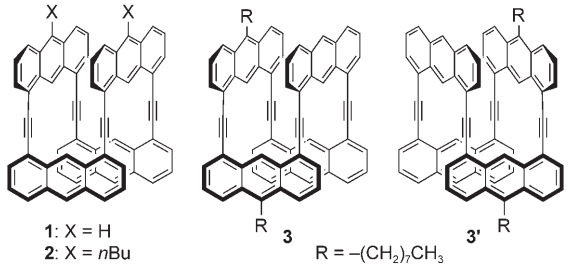
Abstract: To construct a new type of chiral π-conjugated system, the title anthracene–acetylene oligomer containing two octyl groups at position 10 of 1,2-alternating anthracene groups was synthesized. Each anthracene unit was connected by Sonogashira coupling, and the tetrameric precursor was cyclized by a cross-coupling reaction to form the desired C_2-symmetric compound. Its enantiomers were resolved by chiral HPLC with a Chiralcel OD column, and the chiroptical properties were investigated by optical rotation ($[\alpha]_D^{23} = -95$ and $+91$) and circular dichroism (CD) measurements. The structural and spectroscopic features of this oligomer were discussed in terms of the molecular symmetry and the dynamic behavior of the macrocyclic framework.

Keywords: arylene–ethynylenes · chiral resolution · cross-coupling · macrocycles · nanostructures

Introduction

Arylene-ethynylene oligomers are fascinating compounds, and have gained much interest in the areas of structural and functional organic chemistry.[1] The diversity of the molecular design, which is due to variations in the mode and connection, the degree of oligomerization, the choice of arene units, and the introduction of substituents has enabled researchers to design a huge number of molecules containing the desired molecular shape, mobility, or π-electronic properties. For example, shape-persistent macrocyclic compounds,[2] graphyne derivatives,[3] and light emitting polymers[4] have been extensively studied in the research field.

To create a new type of such oligomers, we utilized anthracene groups as arene units by taking advantage of their unique shape and electronic properties.[5] Our initial efforts were directed towards the 1,8-anthrylene oligomers, and the framework of cyclic tetramer **1** was constructed by the Sonogashira coupling as a three dimensional π-conjugated system.[6] This compound features a diamond prism structure of nearly D_2 symmetry and conformational interconversion between the two enantiomeric forms **1a** and **1a′** via the square form **1b** (Scheme 1). We also synthesized cyclic tetramer **2** containing butyl groups at position 10 of 1,3-alternating anthracene rings to improve solubility. In both compounds **1** and **2**, however, the isolation of optically active forms is impossible because of the facile racemization by the skeletal swing, as shown in Scheme 1. In contrast, the framework itself becomes chiral upon the introduction of alkyl groups at position 10 of the 1,2-alternating anthracene rings. The skeletal swing does not affect the chirality of the cyclic framework; rather, it leads to an interconversion between the two diamond forms, **3a** and **3c**, in which the two substituted anthracene planes form obtuse and acute angles, respectively. Therefore, enantiomers of such a compound are, in principle, separable regardless of the rates of the skeletal swing (these enantiomers can be designated as *M* or *P* based on the helicity of the two substituted anthracene



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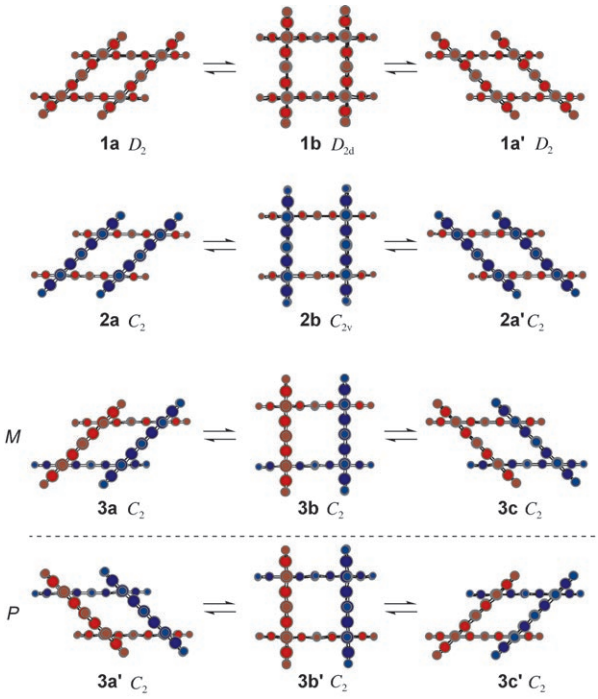


Scheme 1. Stereochemical and symmetric analyses of 1,8-anthrylene-ethynylene cyclic tetramers **1**–**3** in equilibrium between the two diamond forms via the square form. Molecular models are viewed along the acetylenic axes, where anthracene groups with and without 10-substituents are indicated in red and blue, respectively. The diastereomeric relationship is differentiated by a, b, or c, and the enantiomeric relationship is differentiated by prime.

rings, if necessary). We synthesized compound **3** with two octyl groups at position 10 as a chiral derivative of the π-conjugated macrocyclic compounds.[7] We herein report the enantiomeric resolution of this hydrocarbon by chiral HPLC and the spectroscopic features of the chiral cyclic tetramer and its related oligomers.

Results and Discussion

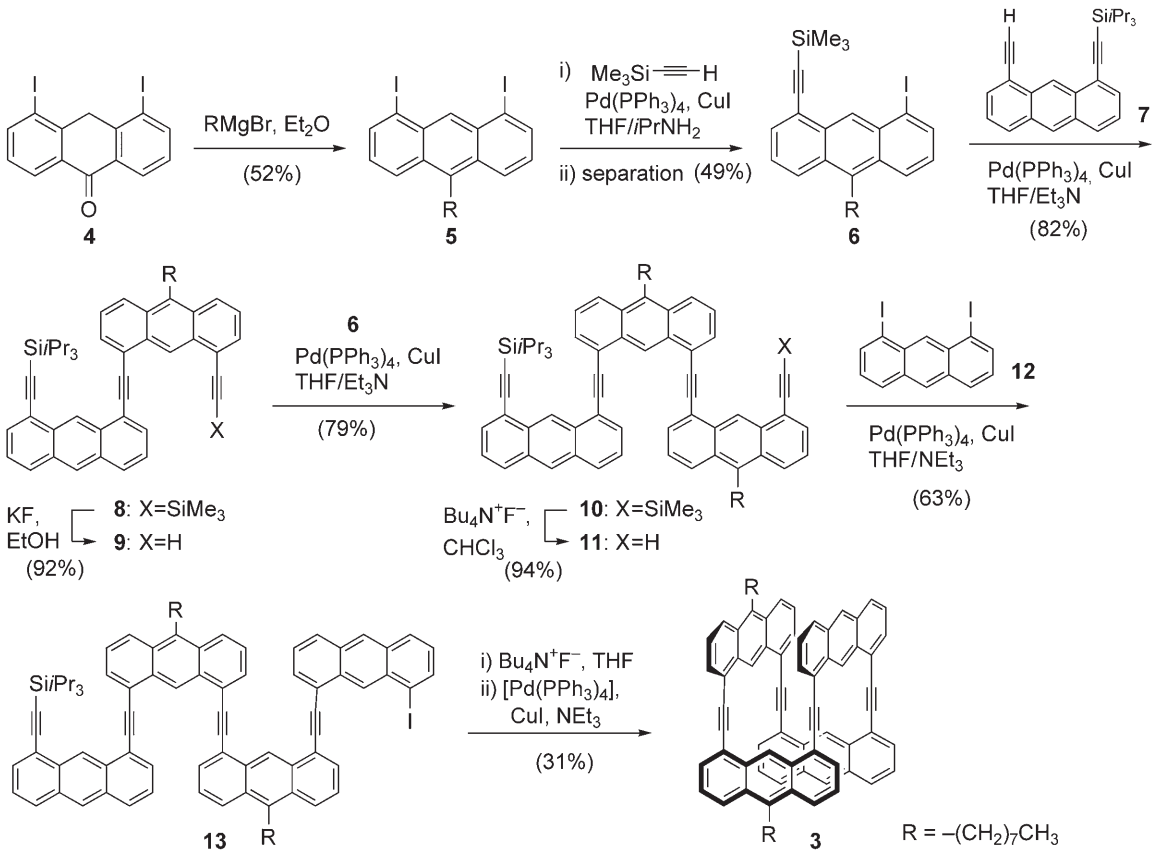
Synthesis: Compound **3** was synthesized by the Sonogashira coupling/desilylation strategy (Scheme 2).[8] Key compound **6** was prepared from 4,5-diiodo-9-anthrone **4**[9] in two steps. The cross-coupling between **6** and **7**[6b] afforded dimer **8** in 82% yield. The trimethylsilyl group in **8** was selectively removed by treatment with KF in ethanol, and terminal alkyne **9** was again coupled with **6** to give trimer **10**. This product was desilylated with tetrabutylammonium fluoride (TBAF)[10] and coupled with an excess of 1,8-diiodoanthracene **12**. Thus prepared, acyclic tetramer **13** was desilylated with TBAF and the formed terminal alkyne was treated with reagents for the Sonogashira coupling without isolation. The chromatographic purification of the crude products afforded the desired cyclic product **3** in 31% yield. Although this synthetic route, which involves the stepwise extension of each anthracene unit, requires long steps, the overall yield from **6** to the tetrameric precursor is satisfactory (35% yield in five steps). Additionally, this stepwise route is also applicable to the synthesis of cyclic tetramers with four differently substituted anthracene groups, starting from 1,8-diiodo- and 1,8-diethynylanthracene derivatives.

Compound **3** was obtained as a yellowish green solid that melted at 221 °C. A molecular ion peak was observed at 1024.5 ($C_{80}H_{64}$) by MALDI-TOF mass spectroscopy. This compound was soluble in conventional organic solvents, and the solutions were observed to glow a bright green color under room light. Whereas significant decomposition occurred in dichloromethane solution, the decomposition became slow in chloroform or aromatic solvents. As this compound was sensitive to conventional silica gel, we used an NH-type silica gel for the chromatographic separation. It was not until we overcame these technical problems that we were able to obtain the desired compound on a preparative scale.

NMR spectra: The signal modes of ^{1}H and ^{13}C NMR spectra of **3** are consistent with those for a structure of C_2 symmetry in which the rotational axis passes through the midpoints of two acetylene moieties connecting the same types of anthracene rings; namely, the two octyl groups are magnetically equivalent and the alkynic carbons give four peaks. The aromatic proton signals were observed as three singlets and complicated multiplets (exactly four sets of ABC systems), among which two singlets due to the 9-H atoms were shifted downfield to $\delta = 10.5$ ppm because of the anisotropic effect of alkynic and aromatic moieties.

The ^{1}H NMR spectra of **3** were recorded at low temperature in [D_8]toluene (Figure 1). The multiplet signals in the aromatic region became broad at −30 °C, and the singlets also broadened at lower temperatures. The signal exchanges were not completely frozen at −100 °C, the lowest limit of the measurement, thus producing very complicated signals with the appearance of four peaks at $\delta = 5.5$–6.2 ppm and at least five peaks at $\delta = 10.2$–11.0 ppm. This dynamic behavior is explained by the skeletal swing illustrated in Scheme 1. If the skeletal swing takes place very slowly on the NMR spectroscopic timescale, this compound should exist as a mixture of two diastereomeric diamond forms (Scheme 1). The signals around $\delta = 6.0$ ppm suggest that some of the aromatic protons (2,3- or 6,7-H) are fixed in the shielding region of the facing anthracene ring in the diamond structure.

Even though the exchange is not sufficiently slow at the lowest temperature, the observed signals look more complicated than those expected for the two diastereomeric forms, each of which should give two singlets around $\delta = 10.5$ ppm. This means that another dynamic process, the rotation of the octyl groups, is involved under the given conditions. We observed that the rotation of the 10-butyl groups relative to the attaching anthracene groups was restricted at low temperature in **2** (barrier ca. 35 kJ mol^{-1}).[6b] Because the octyl group is also a primary alkyl group, compound **3** should exhibit similar dynamic behavior at comparable barriers. The restricted rotation of the two octyl groups affords three diastereomeric conformers for each diamond form; this is be-



Scheme 2. Synthesis of **3**.

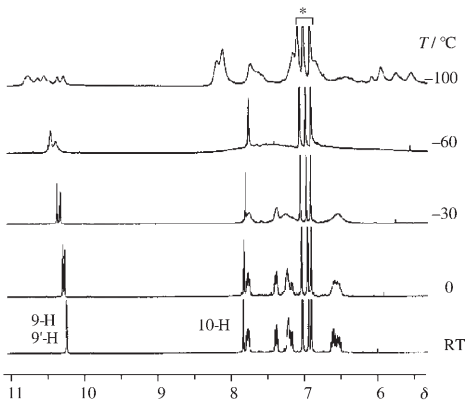


Figure 1. Variable temperature (VT) ^{1}H NMR spectra of **3** (solvent = [D_8]toluene). Signals labeled with * are due to the solvent.

Table 1. UV/Vis and fluorescence data for cyclic tetramer **3** and the related acyclic oligomers in cyclohexane.

	Absorption		Emission[d]		
	λ_{max} [nm][b]	ε[c]	λ [nm]	Φ_f[e]	Stokes shift [nm]
14[a]	351, 369, 390, 412	20900	416, 441, 469	0.53	4
8	373, 393, 405, 415	23500	445, 474	0.56	30
10	421, 443	31000	455, 477	0.35	12
13	401, 422, 449	31400	455, 480	0.02	6
3	419, 446	35000	467, 492	0.29	21

[a] **14**: 1,8-bis[(triisopropylsilyl)ethynyl]anthracene see reference [6b]. [b] Wavelengths of maximum absorption in the *p*-band region. [c] Molar extinction coefficient of the absorption at the longest wavelength. [d] Excited at 393 nm. [e] Fluorescence quantum yield determined relative to 9,10-diphenylanthracene.

cause primary alkyl groups prefer to take bisected conformations relative to the anthracene plane either inside or outside the diamond.[11]

Electronic spectra: The UV/Vis and fluorescence data of **3** and some acyclic oligomers are compiled in Table 1. The absorption at the longest wavelength was observed at approximately 415 nm for 1,8-bis[(triisopropylsilyl)ethynyl]anthracene (**14**) and dimer **8**, and that of trimer **10** was shifted by approximately 30 nm to an even longer wavelength.[12] There is no significant bathochromic effect for tetramers **13** and **3** compared with trimer **10**. This trend indicates that trimer and higher oligomers tend to take folded conformations about the acetylenic axes to avoid further extension of the π conjugation.

The emission band is shifted to a longer wavelength in the order of **8**, **10**, and **3** from 445 to 467 nm with large values of fluorescence quantum yields (Φ_f). In contrast, acyclic tetramer **13** produces a weak and broad emission band at 480 nm. This quenching is attributed to the presence of an iodine atom on the anthracene chromophore. The Stokes

shift of **3** is 21 nm, which is larger than that of the acyclic analogue **13**. There is no clear relationship between the Stokes shift and the chain length.

Enantiomeric resolution: We attempted the enantiomeric resolution of **3** by using several types of chiral HPLC columns (see Experimental Section) under various conditions. Among them, only the Daicel Chiralcel OD column permitted partial separation, even though the solubility of the sample in the eluent was very low. The chromatogram that was taken under the optimized conditions is shown in Figure 2 in which the retention times of the two enantiomers are 34.1 and 38.5 min ($\alpha = 1.16$, $R_s = 0.56$). While the easily eluted isomer was rendered practically enantiopure by a

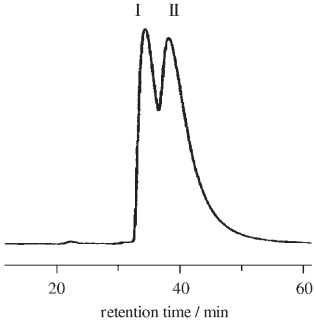


Figure 2. Chromatogram of chiral HPLC with a Chiralcel OD column (eluent = hexane/2-propanol 100:1).

single separation, the less easily eluted isomer was further chromatographed to give a sample of approximately 95% *ee* (*ee* = enantiomeric excess). This procedure was repeated several times to supply milligram order samples of both enantiomers.

The specific rotations of the first and second eluted isomers were determined as $[\alpha]_D^{23} = -95$ and $+91$, respectively, in cyclohexane. The CD spectra of these enantiomers are shown in Figure 3. The (−)-form has an intense trough at 276 nm and complicated bands at 400–480 nm in addition to

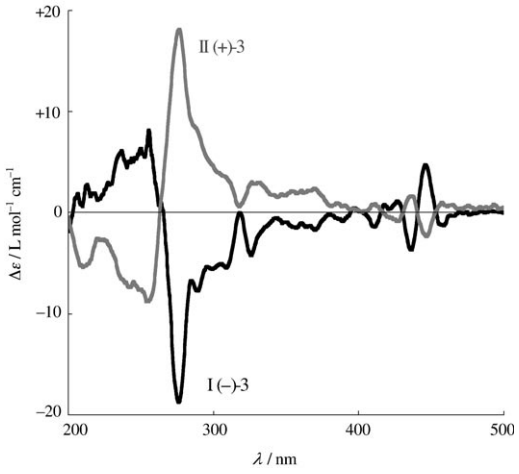


Figure 3. CD spectra of enantiomers of chiral cyclic tetramer **3** (solvent = cyclohexane).

small peaks and troughs in the other regions. The entire band shape of the (+)-form is nearly a mirror image of that of the (−)-form. The structured bands in the longer wavelength region are correlated to the *p* band absorptions in the UV spectrum. These chiroptical properties are conclusive evidence of the enantiomeric resolution. Unfortunately, the quantity of the resolved samples was too small to allow determination of the absolute stereochemistry by experiment. The theoretical approach seems to be very difficult at present as one molecule consists of many atoms (144 atoms). Further studies are needed to solve these problems.

Conclusion

The chiral 1,8-anthrylene-ethynylene cyclic tetramer containing two octyl groups was conveniently synthesized by the Sonogashira reaction. This compound is stereochemically interesting because the molecular chirality is attributed to the stereogenic axes along the acetylenic moieties rather than the center. Although the resolution of chiral hydrocarbons without significant functional groups is generally difficult, the resolution of this macrocyclic compound was achieved with an appropriate type of chiral column. The successful resolution opens a new aspect in the chemistry of anthracene–acetylene oligomers, and helps us deepen our understanding of the chiroptical properties of such a chiral macrocyclic scaffold.

Experimental Section

General: Melting points are uncorrected. Elemental analyses were performed with a Perkin–Elmer 2400 series analyzer. NMR spectra were measured on a Varian Gemini-300 (^{1}H: 300 MHz, ^{13}C: 75 MHz) or a JEOL Lambda-500 (^{1}H: 500 MHz, ^{13}C: 125 MHz) spectrometer. HRMS (FAB) were measured on a JEOL MStation-700 spectrometer. MALDI-TOF mass spectra were measured on a Voyager-Biocad spectrometer. UV/Vis spectra were measured on a Hitachi U-3000 spectrometer with a 10 mm cell. Optical rotations were measured on a JASCO DIP-370 polarimeter by using a 10 mm$\varnothing \times$100 mm cell. CD spectra were measured on a JASCO J-820 spectropolarimeter by using a 1 mm cell. Column chromatography was carried out with Merck Silica Gel 60 (70–230 mesh) or Fuji Silysia Chromatorex-NH (100–200 mesh).

1,8-Diiodo-10-octylanthracene (5): A solution of octylmagnesium bromide in diethyl ether (50 mL) was prepared from magnesium (1.39 g, 57.0 mmol) and 1-bromooctane (10.2 mL, 58.9 mmol) in an ordinary manner. After this solution had been diluted with diethyl ether (150 mL), 4,5-diiodo-9-anthrone (**4**)[9] (8.48 g, 19.0 mmol) was added and the mixture was stirred at room temperature for 20 h under Ar. The reaction mixture was then quenched with aqueous NH_4Cl (40 mL) and extracted with diethyl ether. Finally, the organic solution was dried over $MgSO_4$ and evaporated. The crude product was purified by chromatography on silica gel (hexane). Recrystallization of the first fraction ($R_f = 0.55$, hexane) gave the desired compound as a yellow solid (5.36 g, 52%). The second fraction afforded 1,8-diiodoanthracene as a byproduct (2.04 g, 25%), and the starting material (1.21 g, 14%) was recovered as the least easily eluted fraction. M.p. 85.5–86.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 0.89 (m, 3H), 1.28–1.37 (m, 8H), 1.55 (m, 2H), 1.76 (m, 2H), 3.55 (t, $J =$ 8.2 Hz, 2H), 7.21 (dd, $J = 7.2$, 8.8 Hz, 2H), 8.16 (d, $J = 7.2$ Hz, 2H), 8.23 (d, $J = 8.8$ Hz, 2H), 8.95 ppm (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 14.11, 22.65, 28.47, 29.29, 29.48, 30.25, 31.58, 31.87, 101.53, 125.36, 126.61,

130.14, 132.87, 136.34, 137.45, 137.56 ppm; HRMS (FAB): *m/z*: calcd for $C_{22}H_{24}I_2$: 541.9968; found: 541.9999 $[M]^+$; elemental analysis calcd (%) for $C_{22}H_{24}I_2$ (542.23): C 48.73, H 4.46; found: C 48.39, H 4.38.

1-Iodo-10-octyl-8-[(trimethylsilyl)ethynyl]anthracene (6): A solution of **5** (3.60 g, 6.64 mmol) in a mixture of isopropylamine (14 mL) and THF (84 mL) was degassed by bubbling Ar for 20 min. TMSA (0.91 mL, 6.5 mmol), $[Pd(PPh_3)_4]$ (149 mg, 0.129 mmol), and CuI (24.6 mg, 0.129 mmol) were added to the solution, and the resulting mixture was refluxed for 17 h under Ar. After the solvent had been evaporated, the residue was chromatographed on silica gel (hexane). The desired compound was obtained as yellow oil (1.68 g, 49%) with recovery of the starting material (1.15 g, 32%). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.43$ (s, 9H), 0.86 (m, 3H), 1.28 (m, 8H), 1.46 (m, 2H), 1.65 (m, 2H), 3.39 (t, $J = 8.0$ Hz, 2H), 7.07 (dd, $J = 1.3$, 8.6 Hz, 1H), 7.36 (dd, $J = 1.6$, 8.9 Hz, 1H), 7.69 (d, $J = 7.0$ Hz, 1H), 8.05 (d, $J = 7.1$ Hz, 1H), 8.09–8.12 (m, 2H), 9.12 ppm (s, 1H); ^{13}C NMR (125 Hz, $CDCl_3$): $\delta = 0.34$, 14.13, 22.65, 28.25, 29.29, 29.46, 30.21, 31.53, 31.86, 100.60, 101.74, 103.19, 121.90, 125.07, 125.31, 125.40, 126.11, 129.26, 129.57, 129.73, 130.26, 132.05, 132.07, 136.93, 137.13 ppm; HRMS (FAB): *m/z*: calcd for $C_{22}H_{33}ISi$: 512.1396; found: 512.1376 $[M]^+$.

Dimer 8: $[Pd(PPh_3)_4]$ (67.6 mg, 58.5 μmol) and CuI (11.1 mg, 58.5 μmol) were added to a degassed solution of **6** (1.00 g, 1.95 mmol) and **7**[6b] (1.12 g, 2.93 mmol) in a mixture of triethylamine (50 mL) and THF (50 mL). After the solution had been refluxed for 26 h under Ar, the solvent was removed by evaporation. The crude product was purified by chromatography on silica gel (hexane/dichloromethane 15:1). The desired compound was obtained as yellowish green oil (1.23 g, 82%). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = -0.34$ (s, 9H), 0.70 (m, 21H), 0.92 (m, 3H), 1.25–1.41 (m, 8H), 1.59 (m, 2H), 1.82 (m, 2H), 3.62 (t, $J = 8.0$ Hz, 2H), 7.40–7.45 (m, 2H), 7.49–7.56 (m, 2H), 7.70 (d, $J = 6.7$ Hz, 1H), 7.74 (d, $J = 6.7$ Hz, 1H), 7.91 (d, $J = 6.7$ Hz, 1H), 7.95 (d, $J = 7.0$ Hz, 1H), 8.00 (d, $J = 8.6$ Hz, 1H), 8.05 (d, $J = 8.6$ Hz, 1H), 8.27 (d, $J = 8.9$ Hz, 1H), 8.33 (d, $J = 9.1$ Hz, 1H), 8.47 (s, 1H), 9.57 (s, 1H), 9.59 ppm (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = -0.76$, 11.01, 14.14, 18.33, 22.69, 28.30, 29.36, 29.59, 30.30, 31.69, 31.92, 92.21, 92.59, 96.74, 100.11, 103.03, 104.75, 121.83, 122.25, 122.53, 123.31, 124.35, 124.80, 124.91, 124.96, 125.07, 125.40, 125.46, 127.44, 128.82, 129.02, 129.27, 129.39, 130.57, 130.81, 131.42, 131.47, 131.53, 131.56, 131.68, 131.71, 136.58 ppm (three aromatic signals missing); UV/Vis (cyclohexane): λ_{max} (ε) = 266 (217000), 373 (12400), 393 (20100), 405 (22700), 415 nm (23500 $mol^{-1}Lcm^{-1}$); fluorescence (cyclohexane): $\lambda_{em} = 445$, 474 nm ($\lambda_{ex} = 393$ nm, $\Phi_f = 0.56$); HRMS (FAB): *m/z*: calcd for $C_{54}H_{62}Si_2$: 766.4390; found: 766.4409 $[M]^+$.

Desilylated dimer 9: A solution of **8** (1.22 g, 1.59 mmol) and KF (462 mg, 7.95 mmol) in ethanol (160 mL) was refluxed for 3 h. After this time, the solvent was mostly removed by evaporation, and the resulting residue was extracted with dichloromethane. The crude product was purified by chromatography on silica gel (hexane/dichloromethane 7:1). The desired compound was obtained as yellowish green oil (1.02 g, 92%). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.78$ (m, 21H), 0.89 (t, $J = 6.8$ Hz, 3H), 1.29–1.31 (m, 6H), 1.40 (m, 2H), 1.57 (m, 2H), 1.81 (m, 2H), 2.92 (s, 1H), 3.59 (t, $J = 8.2$ Hz, 2H), 7.39–7.44 (m, 2H), 7.49 (dd, $J = 1.5$, 8.3 Hz, 1H), 7.53 (dd, $J = 2.2$, 8.9 Hz, 1H), 7.69 (d, $J = 6.4$ Hz, 1H), 7.76 (d, $J = 6.7$ Hz, 1H), 7.91 (d, $J = 6.7$ Hz, 1H), 7.96 (d, $J = 8.9$ Hz, 1H), 7.98–8.02 (m, 2H), 8.26 (d, $J = 9.2$ Hz, 1H), 8.30 (d, $J = 9.2$ Hz, 1H), 8.34 (s, 1H), 9.66 (s, 1H), 9.70 ppm (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 11.21$, 14.13, 18.40, 22.68, 28.29, 29.35, 29.56, 30.33, 31.71, 31.91, 81.73, 82.64, 93.04, 93.23, 96.70, 104.89, 121.40, 121.81, 121.93, 122.57, 123.24, 124.41, 124.74, 124.96, 125.03, 125.09, 125.39, 125.66, 127.51, 128.84, 129.04, 129.20, 129.38, 129.94, 130.68, 131.29, 131.41, 131.47, 131.48, 131.50, 131.60, 131.73, 131.89, 136.68 ppm; UV/Vis (cyclohexane): λ_{max} (ε) = 263 (205000), 390 (17600), 410 (23600), 420 nm (22900 $mol^{-1}Lcm^{-1}$); HRMS (FAB): *m/z*: calcd for $C_{51}H_{54}Si$: 694.3995; found: 694.4020 $[M]^+$.

Trimer 10: $[Pd(PPh_3)_4]$ (50 mg, 43 μmol) and CuI (8.2 mg, 43 μmol) were added to a degassed solution of **9** (831 mg, 1.20 mmol) and **6** (738 mg, 1.44 mmol) in a mixture of triethylamine (30 mL) and THF (30 mL). After the solution had been refluxed for 43 h under Ar, the solvent was removed by evaporation. The crude product was purified by chromatography on silica gel (hexane/dichloromethane 7:1). Recrystallization (hexane/dichloromethane) gave the pure material as a yellowish green solid (1.02 g, 79%). M.p. 205–207 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = -0.14$ (s, 9H), 0.76 (m, 21H), 0.90–0.92 (m, 6H), 1.31–1.48 (m, 16H), 1.54 (t, $J = 8.3$ Hz, 2H), 1.62 (m, 2H), 1.70 (m, 2H), 1.87 (m, 2H), 3.41 (t, $J = 8.3$ Hz, 2H), 3.67 (t, $J = 8.3$ Hz, 2H), 6.42 (dd, $J = 2.2$, 8.9 Hz, 1H), 6.80 (dd, $J = 1.6$, 8.6 Hz, 1H), 7.26–7.32 (m, 3H), 7.48 (d, $J = 6.7$ Hz, 1H), 7.51–7.56 (m, 2H), 7.61–7.66 (m, 3H), 7.73 (d, $J = 8.9$ Hz, 1H), 7.78 (d, $J = 8.9$ Hz, 1H), 7.88 (d, $J = 6.7$ Hz, 1H), 7.91 (d, $J = 6.7$ Hz, 1H), 8.02 (d, $J = 8.9$ Hz, 1H), 8.13 (s, 1H), 8.32–8.35 (m, 2H), 9.28 (s, 1H), 9.32 (s, 1H), 10.00 ppm (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) $\delta = -0.38$, 11.23, 14.14, 14.16, 18.43, 22.70, 28.29, 29.37, 29.40, 29.59, 29.62, 30.35, 31.51, 31.75, 31.93, 92. 66, 92.73, 92.97, 93.69, 96.43, 99.59, 103.47, 104.91, 121.05, 121.58, 121.81, 122.11, 122.62, 122.90, 122.92, 123.79, 123.89, 124.34, 124.37, 124.64, 124.67, 124.95, 124.98, 125.17, 125.26, 126.99, 128.13, 128.54, 128.64, 128.77, 129.51, 129.53, 129.80, 129.96, 130.33, 130.66, 130.84, 130.87, 130.89, 131.04, 131.16, 131.50, 131.83, 135.74, 136.50 ppm (five aromatic signals missing); UV/Vis (cyclohexane): λ_{max} (ε) = 254 (214000), 421 (30800), 443 nm (31000 $mol^{-1}Lcm^{-1}$); fluorescence (cyclohexane): $\lambda_{em} = 455$, 477 nm ($\lambda_{ex} = 393$ nm, $\Phi_f = 0.35$); HRMS (FAB): *m/z*: calcd for $C_{78}H_{86}Si_2$: 1078.6268; found: 1078.6304 $[M]^+$; elemental analysis calcd (%) for $C_{78}H_{86}Si_2$ (1079.69): C 86.77, H 8.03; found: C 86.38, H 7.99.

Desilylated trimer 11: A solution of TBAF (0.50 mL, 0.50 mmol) in THF (1.0 $mol\,L^{-1}$) was added to a solution of **10** (865 mg, 0.801 mmol) in chloroform (120 mL). The solution was stirred for 5 h at room temperature, and was then quenched with water. The organic layer was separated, dried over $MgSO_4$, and evaporated. The crude product was purified by chromatography on silica gel (hexane/dichloromethane 5:1) to give the pure compound as a yellowish green solid (757 mg, 94%). M.p. 165–167 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.75$ (m, 21H), 0.89–0.92 (m, 6H), 1.31–1.45 (m, 16H), 1.54 (m, 2H), 1.63 (m, 2H), 1.71 (m, 2H), 1.87 (m, 2H), 3.00 (s, 1H), 3.36 (t, $J = 8.2$ Hz, 2H), 3.65 (t, $J = 8.3$ Hz, 2H), 6.58 (dd, $J = 2.2$, 8.9 Hz, 1H), 6.80 (t, $J = 7.7$ Hz, 1H), 7.14 (d, $J = 6.7$ Hz, 1H), 7.16–7.22 (m, 2H), 7.48 (d, $J = 7.3$ Hz, 2H), 7.52–7.57 (m, 3H), 7.61 (d, $J = 6.7$ Hz, 1H), 7.72 (d, $J = 8.6$ Hz, 1H), 7.76 (d, $J = 9.2$ Hz, 1H), 7.89–7.91 (m, 2H), 7.93 (d, $J = 9.2$ Hz, 1H), 7.99 (s, 1H), 8.31–8.35 (m, 2H), 9.33 (s, 1H), 9.34 (s, 1H), 10.09 ppm (s, 1H); ^{13}C NMR ($CDCl_3$) $\delta = 11.27$, 14.15, 14.16, 18.45, 22.71, 28.24, 28.41, 29.39, 29.59, 29.61, 30.39, 30.41, 31.50, 31.76, 31.94, 81.95, 82.58, 92.93, 93.13, 93.43, 93.58, 96.25, 105.02, 121.05, 121.23, 121.72, 121.83, 122.72, 122.99, 123.12, 123.78, 124.08, 124.17, 124.28, 124.30, 124.42, 124.50, 125.01, 125.11, 125.16, 125.18, 125.22, 126.90, 128.07, 128.60, 128.62, 129.34, 129.47, 129.50, 129.83, 129.91, 130.10, 130.57, 130.61, 130.82, 130.85, 130.87, 131.00, 131.08, 131.51, 131.63, 131.77, 135.50, 136.53 ppm (one aromatic signal missing); UV/Vis (cyclohexane): λ_{max} (ε) = 252 (215000), 419 (32200), 445 nm (38600 $mol^{-1}Lcm^{-1}$); HRMS (FAB): *m/z*: calcd for $C_{75}H_{78}Si$: 1006.5873; found: 1006.5897 $[M]^+$.

Tetramer 13: $[Pd(PPh_3)_4]$ (64 mg, 56 μmol) and CuI (11 mg, 56 μmol) were added to a degassed solution of **11** (600 mg, 0.56 mmol) and 1,8-diiodoanthracene **12** (717 mg, 1.67 mmol) in a mixture of triethylamine (24 mL) and THF (24 mL). After the solution had been refluxed for 41 h under Ar, the solvent was removed by evaporation. The crude product was purified by chromatography on silica gel (hexane/dichloromethane 5:1) to give the pure material as a yellowish green solid (460 mg, 63%), along with some recovered **12** (131 mg). M.p. 208–210 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.60$ (m, 21H), 0.89–0.95 (m, 6H), 1.35–1.52 (m, 16H), 1.61–1.64 (m, 4H), 1.76–1.79 (m, 4H), 3.38–3.41 (m, 4H), 6.58 (t, $J = 8.3$ Hz, 1H), 6.63 (t, $J = 8.2$ Hz, 1H), 6.72 (t, $J = 8.5$ Hz, 1H), 6.86 (t, $J = 8.6$ Hz, 1H), 6.94 (t, $J = 8.0$ Hz, 1H), 7.14 (d, $J = 6.7$ Hz, 1H), 7.18–7.24 (m, 2H), 7.27–7.37 (m, 4H), 7.42 (d, $J = 6.4$ Hz, 1H), 7.55 (d, $J = 6.4$ Hz, 1H), 7.60 (d, $J = 6.4$ Hz, 1H), 7.68–7.70 (m, 2H), 7.74–7.79 (m, 3H), 7.81 (s, 1H), 7.86 (s, 1H), 7.92–7.98 (m, 4H), 9.00 (s, 1H), 9.10 (s, 1H), 9.70 (s, 1H), 9.72 ppm (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 11.24$, 14.17, 14.18, 18.32, 22.74, 28.30, 28.40, 29.44, 29.66, 29.68, 30.50, 30.53, 31.50, 31.53, 31.97, 92.76, 92.88, 93.11, 93.37, 93.68, 93.77, 96.11, 100.87, 105.06, 120.87, 120.95, 120.97, 121.02, 121.90, 122.11, 122.35, 122.78, 122.93, 123.50, 123.55, 123.66, 123.94, 124.01, 124.21, 124.38, 124.41, 124.57, 124.94, 125.63, 126.60, 126.66, 126.70, 126.75, 127.09, 127.44, 128.46, 128.68, 128.75, 128.78, 128.85, 129.02, 129.23, 129.38,

129.69, 130.18, 130.48, 130.51, 130.58, 130.66, 130.73, 130.74, 130.75, 130.91, 131.15, 131.21, 131.23, 131.34, 131.83, 135.02, 135.07, 136.65, 136.73, 137.70 ppm; UV/Vis (cyclohexane): λ_{max} (ε) = 248 (304 000), 401 (30 400), 422 (33 700), 449 nm (31 400 $mol^{-1}Lcm^{-1}$); fluorescence (cyclohexane): λ_{em} = 455, 480 nm (λ_{ex} = 393 nm, Φ_f = 0.02); HRMS (MALDI-TOF): *m/z*: calcd for $C_{89}H_{85}ISi$: 1308.39; found: 1308.55 $[M]^+$.

Cyclic tetramer 3: A solution of TBAF (80 μL, 80 μmol) in THF (1.0 $mol\,L^{-1}$) was added to a solution of **13** (100 mg, 76.4 μmol; R_f = 0.54, hexane/$CHCl_3$ 2:1) in THF (10 mL) under Ar. After this solution had been stirred for 10 min at room temperature, the TLC spot due to **13** disappeared. Triethylamine (38 mL), THF (28 mL), $[Pd(PPh_3)_4]$ (27 mg, 23 μmol), and CuI (4.3 mg, 23 μmol) were added to the solution of the desilylated compound (R_f = 0.44, hexane/$CHCl_3$ 2:1). The resulting mixture was then stirred for 8 h at room temperature. After this time, the solvent was evaporated, and the residue was subjected to chromatography on NH-type silica gel (hexane/$CHCl_3$ 5:1). Recrystallization (hexane/$CHCl_3$) afforded the cyclic tetramer as a yellowish green solid (24.5 mg, 31 %, R_f = 0.48 with hexane/$CHCl_3$ 2:1). M.p. 221–223 °C; ^{1}H NMR (500 MHz, [D_6]benzene: δ = 0.97–0.98 (m, 6H), 1.29–1.45 (m, 16H), 1.55–1.59 (m, 4H), 1.77–1.83 (m, 4H), 3.37–3.41 (m, 4H), 6.59–6.71 (m, 8H), 7.30–7.37 (m, 8H), 7.46–7.49 (m, 4H), 7.83–7.86 (m, 4H), 7.93 (s, 2H), 10.44 (s, 2H), 10.46 ppm (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.19, 22.75, 28.51, 29.47, 29.68, 30.54, 31.58, 31.97, 93.07, 93.17, 93.47, 93.58, 121.26, 121.34, 121.99, 122.09, 123.47, 124.25, 124.28, 124.37, 124.56, 124.62, 126.89, 128.07, 128.18, 128.83, 128.85, 129.46, 129.52, 129.71, 129.73, 130.75, 130.80, 130.98, 135.68 ppm (five aromatic signals missing); UV/Vis (cyclohexane): λ_{max} (ε) = 261 (196 000), 419 (35 000), 446 nm (35 000 $mol^{-1}Lcm^{-1}$); fluorescence (cyclohexane): λ_{em} = 467, 492 nm (λ_{ex} = 393 nm, Φ_f = 0.29); HRMS (MALDI-TOF): *m/z*: calcd for $C_{80}H_{64}$: 1024.50; found: 1024.47 $[M]^+$; elemental analysis calcd (%) for $C_{80}H_{64}$ (1025.36): C 93.71, H 6.29; found: C 93.33, H 6.18.

Enantiomeric resolution of 3: Chiral HPLC was carried out with a HITACHI L-6250 pump by using Daicel Chiralcel OD, Chiralpak AD, and Chiralpak IA columns (semi-preparative size: 10 mm∅ × 250 mm). The resolution was successful with the OD column under the following conditions: eluent, hexane/2-propanol 100:1; flow rate, 2.0 $mL\,min^{-1}$; and approximately 0.2 mg of racemic sample in 1.0 mL of the eluent. The enantiomers were eluted at the retention times of 34.1 and 38.5 min with partial separation. For preparative purposes, a racemic sample (0.8 mg in 2.0 mL of eluent) was injected for each batch, and a total of 21 mg of sample was subjected to separation. The easily eluted part was collected (before the valley of the two peaks, ca. 6 mg), which was practically enantiopure as checked by HPLC analysis. The second fraction (after the valley, ca. 14 mg) was separated again by chromatography to give an almost enantiopure sample (ca. 4 mg) of the less easily eluted isomer. Further purification was far from practical as the sample gradually decomposed in the eluent system.

First fraction (−)-form: M.p. 114–116 °C; >98 % *ee*; $[\alpha]_D^{23} = -95$ (*c* = 0.075 in cyclohexane); CD (1.9×10^{-4} $mol\,L^{-1}$ in cyclohexane): λ ($\Delta\varepsilon$) = 255 (+7.9), 276 (−18.8), 318 (−0.1), 326 (−4.2), 344 (−0.5), 411 (−1.4), 427 (+1.1), 436 (−3.6), 446 (+4.7), 459 nm (−1.3 $mol^{-1}Lcm^{-1}$); HRMS (MALDI-TOF): *m/z*: calcd for $C_{80}H_{64}$: 1024.50; found: 1024.40 $[M]^+$.

Second fraction (+)-form: M.p. 114–117 °C; 95 % *ee*; $[\alpha]_D^{23} = +91$ (*c* = 0.03 in cyclohexane); CD (1.4×10^{-4} $mol\,L^{-1}$ in cyclohexane): λ ($\Delta\varepsilon$) = 255 (−8.8), 276 (+18.0), 318 (+0.6), 327 (+2.9), 344 (+1.5), 410 (+0.8), 427 (−0.9), 437 (+1.6), 447 (−2.4), 458 nm (+0.9 $mol^{-1}Lcm^{-1}$); HRMS (MALDI-TOF): *m/z*: calcd for $C_{80}H_{64}$: 1024.50; found: 1024.52 $[M]^+$.

Fluorescence measurements: Fluorescence spectra were measured on a JASCO FP-6500 spectrofluorometer with a 10 mm cell at room temperature. The sample was dissolved in cyclohexane (1.0×10^{-5}–1.0×10^{-6} $mol\,L^{-1}$), which was degassed with Ar immediately before the measurement. The spectra were measured upon excitation at 393 nm. The fluorescence quantum yields were determined with a 9,10-diphenylanthracene sample as standard by the standard method.[13]

Variable temperature (VT) ^{1}H NMR spectroscopic measurements: VT ^{1}H NMR spectra were measured on a JEOL GSX-400 at 400 MHz in [D_8]toluene. The sample temperatures were read from a thermocouple equipped with the instrument after calibration by using the chemical shift differences of the methanol signals.

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