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Chemistry of Anthracene–Acetylene Oligomers. XIII. Synthesis, Structures, and Spectroscopic Properties of All Possible 1,8-Anthrylene Cyclic Tetramers with Acetylene and Diacetylene Linkers[1]

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All the possible 1,8-anthrylene cyclic tetramers with acetylene and diacetylene linkers were synthesized as new types of π-conjugated compounds. Building units were connected by coupling reactions, and macrocyclization of the tetrameric precursors by Eglinton coupling gave the desired cyclic oligomers. Molecular structures examined by X-ray analysis and DFT calculations with the M05 functional revealed diamond prism structures with intramolecular contacts between facing anthracenes at ca. 3.5 Å. Restricted dynamic processes between the diamond forms were observed by VT ^{1}H NMR measurements of the cyclic tetramer with one diacetylene linker and the C_s symmetric isomer with two diacetylene linkers. The enantiomers of three chiral cyclic tetramers were resolved by spontaneous resolution or chiral HPLC, and their chiroptical properties were investigated by CD spectroscopy. Absorption and emission spectra and NMR chemical shifts of these oligomers are discussed in terms of the molecular structures.

Arylene–ethynylene oligomers are useful building units in π-conjugated compounds because their structures and properties depend on the types of arene and acetylene units.[2] Several oligomers have been applied to the chemistry of functional molecules, supramolecules, and molecular machines.[3,4] To create new types of such oligomers, we adopted anthracene groups as arene units owing to their unique shapes and properties. The first key compound in our study is cyclic tetramer **1**, which features the diamond prism structure and conformational behavior (Figure 1).[5] This fundamental structure can be modified in various ways by changing the number of repeating units, incorporating different linkers, and so on. For example, the use of three anthrylene units builds strained cyclic trimers **2** and **3**, in which diacetylene linkers are partially and fully incorporated, respectively. The smallest cyclic analogs, dimers **4** and **5**, were successfully prepared regardless of the steric hindrance of the inner hydrogen or alkyl substituents.[6,7] As for cyclic tetramers, we preliminarily reported the synthesis of cyclic tetramers with two and four diacetylene linkers, **7** and **10**, respectively, which were readily prepared from common building units by coupling reactions.[8,9] It is notable that the enantiomers of chiral cyclic tetramer **7** are separable by spontaneous resolution.[9] These studies suggested that the incorporation of diacetylene linkers substantially influences both molecular symmetry and dynamic behavior involving rotation about the acetylenic axes. Therefore, we synthesized all the possible 1,8-anthrylene cyclic tetramers with acetylene and diacetylene linkers, namely compounds **6**–**10**, carrying one to four diacetylene linkers. Then, we systematically compared their properties with those of original compound **1** to demonstrate the structure–properties relationships as well as the versatility of this molecular design based on simple building units. We herein report the synthesis, structures, and spectroscopic features of this series of 1,8-anthrylene–alkynylene cyclic tetramers as well as the enantiomeric resolution and chiroptical properties of chiral oligomers.

Results and Discussion

Synthesis. We synthesized cyclic tetramers **6**–**10** according to the routes shown in Schemes 1 and 2. A derivative with long alkyl groups was also synthesized for the all-diacetylene system **10** because of the very low solubility of parent compound **10a**.

Key building blocks for the series of syntheses were prepared by the reactions shown in Scheme 1. Compound **14b** was prepared from 4,5-dichloro-9-anthrone (**11**)[10] by the standard method in four steps. Compounds **14a**[5b] and **14b** were dimerized by oxidative Pd-catalyzed coupling in the presence of CuI and I_2[11] to give coupling products **15** in good yields. Dimers **15** were carefully desilylated with tetrabutylammonium fluoride (TBAF) in CH_2Cl_2 and singly desilylated products **16** were separated by chromatography. Another key precursor **20** was prepared from 1,8-diiodoanthracene (**17**).[12] The Sonogashira coupling[13] of **17** with (trimethylsilyl)ethyne and

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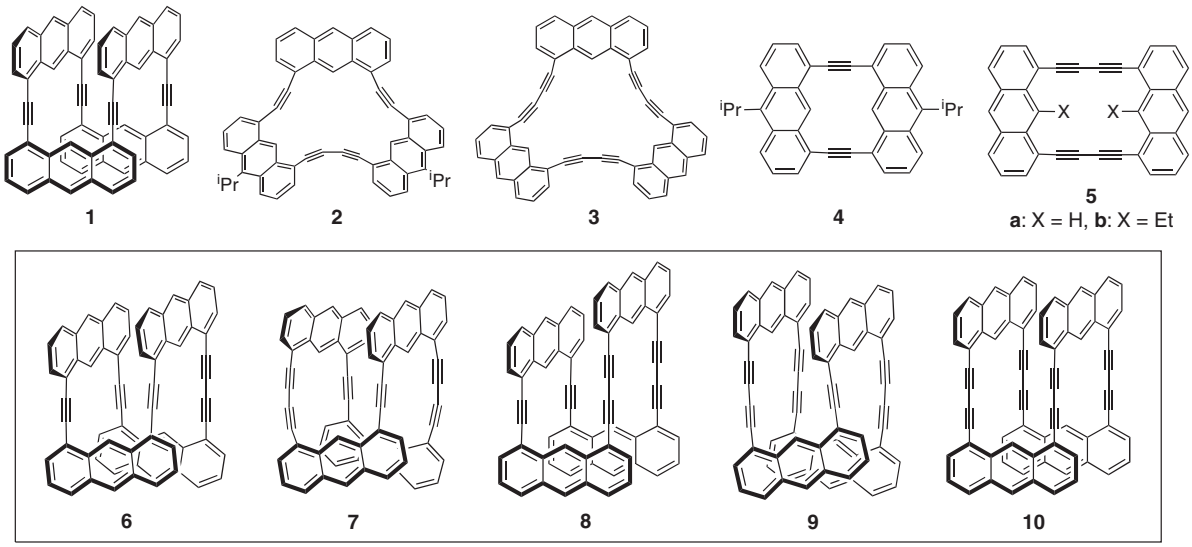
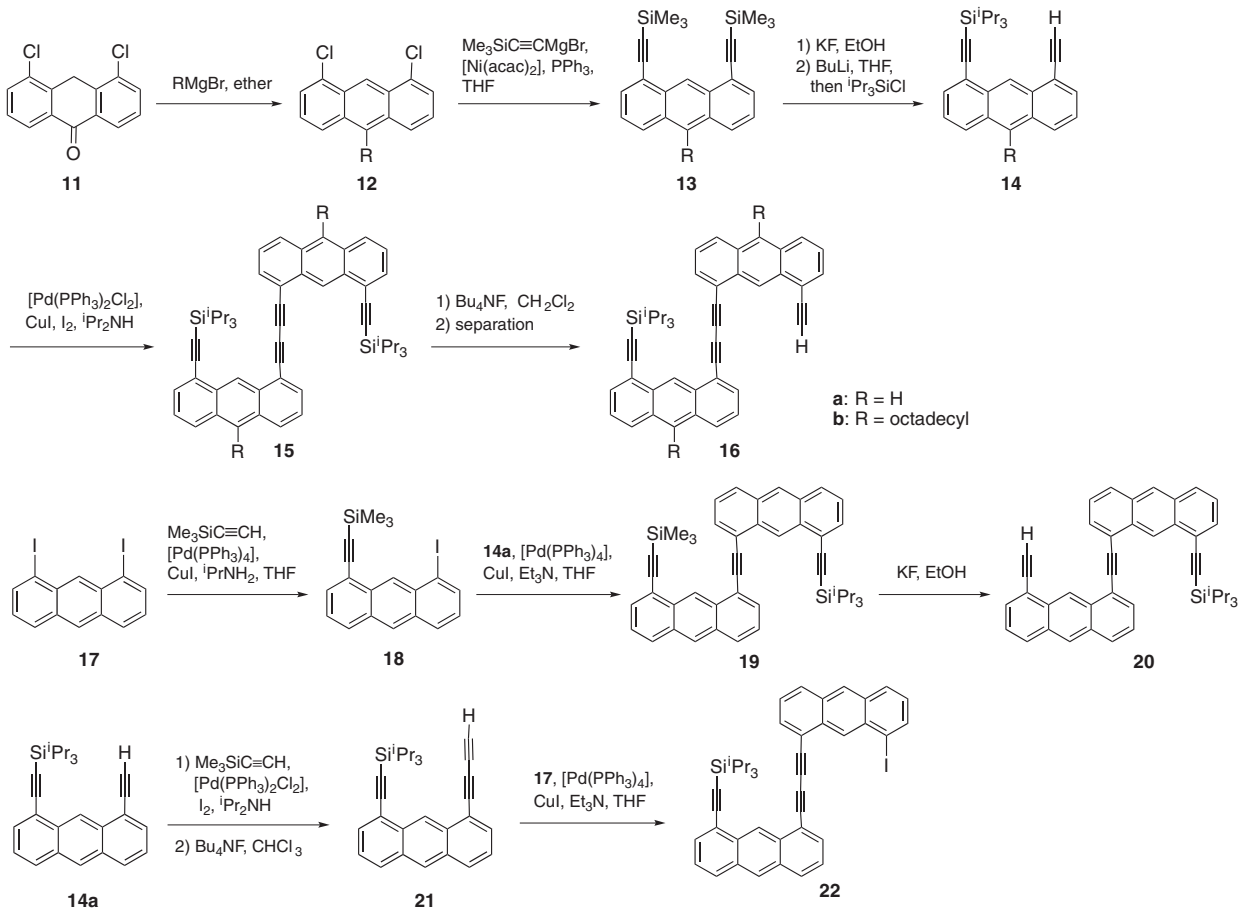
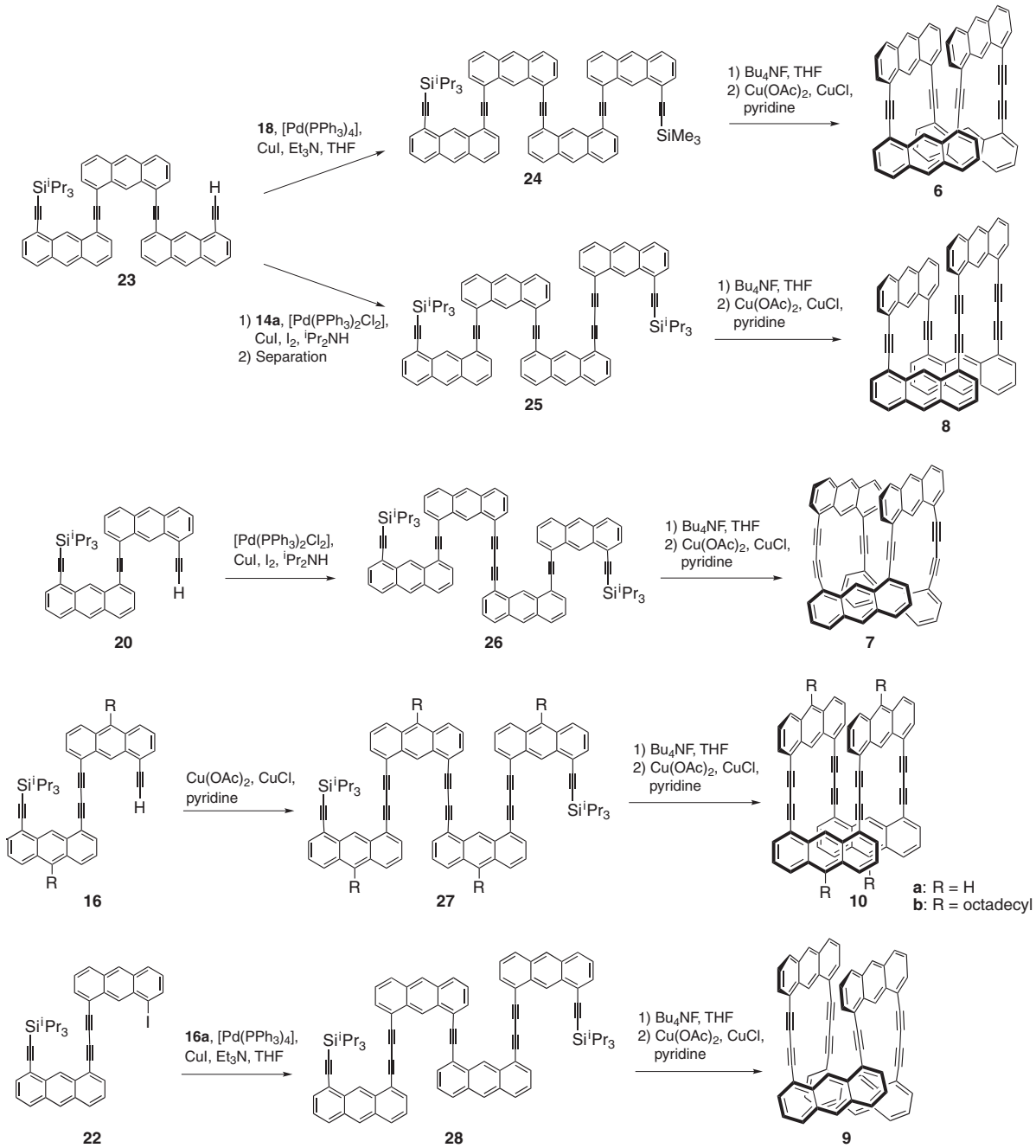


Figure 1. Various 1,8-anthrylene cyclic oligomers with acetylene and diacetylene linkers.



Scheme 1. Synthesis of building units **16**, **20**, and **22**.

then with **14a** gave dimer **19**, which was selectively desilylated with KF to give compound **20**. Compound **21** was prepared by coupling **14a** with (trimethylsilyl)ethyne followed by desilylation of the trimethylsilyl group with TBAF, and the terminal diacetylene was coupled with an excess of **17** to give dimer **22**. Dimers **16**, **20**, and **22** and known trimer **23**[5b] were further connected by coupling reactions to yield acyclic tetrameric precursors (Scheme 2). Sonogashira coupling of **23** with **18** gave tetramer **24** in 47% yield. Pd-catalyzed oxidative coupling between **23** and **14a** gave a mixture of coupling products from which desired tetramer **25** was separated by chromatography. Monosilylated dimers **20** and **16** were dimerized by the

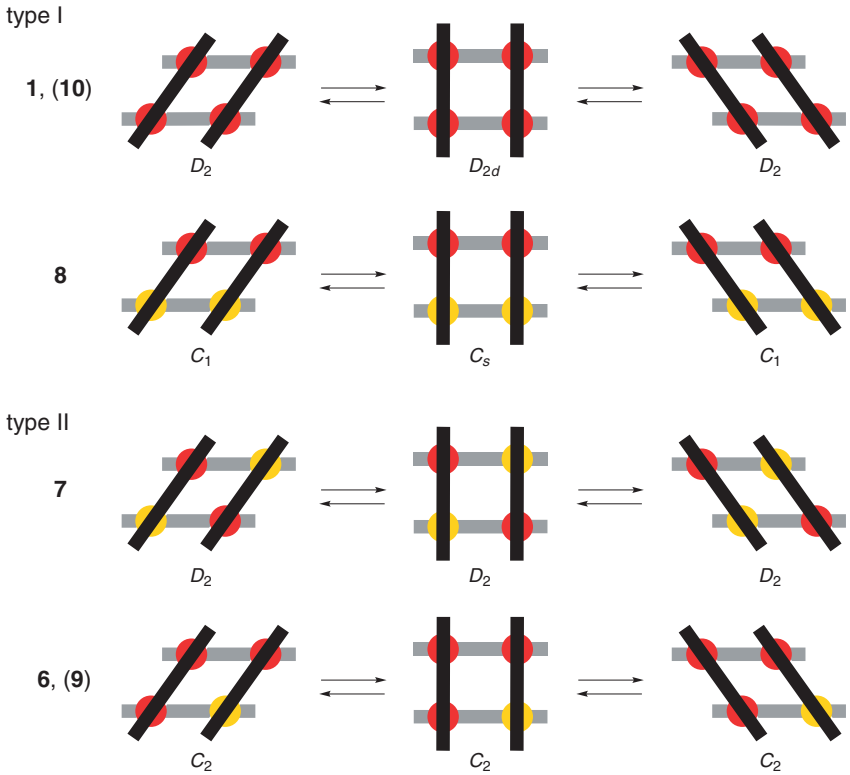


Scheme 2. Synthesis of cyclic tetramers **6**–**10**.

metal-catalyzed coupling to give tetramers **26** and **27**, respectively, in good yields. Compound **28** was prepared by Sonogashira coupling of **22** with **16a**. Thus prepared acyclic tetramers were desilylated with TBAF in THF, and the formed terminal alkynes were subjected to Eglinton coupling in pyridine at room temperature. After chromatographic purification, the desired macrocyclic compounds were obtained in good yields for **6** (67%), **8** (89%), **9** (74%), and **10b** (68%) and in low yields for **7** (27%) and **10a** (11%). The low yield of **10a** is mainly attributed to poor solubility, which greatly impeded workup and purification procedures. No macrocyclic products were obtained with the Pd-catalyst system that worked well for the linear coupling, as mentioned above. The difference between Cu and Pd systems can be deduced from the geometry of metal acetylide intermediates, as pointed out by Haley and co-workers.[14]

The cyclic tetramers were obtained as yellow or orange crystals. They are stable in solution and crystal form under ambient conditions, and melt or decompose at high temperatures $\geq$300 °C except **10b**. Molecular ion peaks of the cyclic tetramers were observed at the expected molecular weights by FAB or MALDI-TOF mass spectroscopy.

Symmetry Analysis. It is instructive to classify the geometrical features of the cyclic tetramers before discussing NMR and structural data. Each cyclic molecule has essentially one freedom of motion, namely the concurrent rotation about



Scheme 3. Stereochemical and symmetric analyses of cyclic tetramers **1** and **6–10** in the interconversion between two diamond forms via square form. Molecular models are viewed along the linker axes. Bar: 1,8-anthrylene unit, red: monoacetylene linker, yellow: diacetylene linker. Interchange red and yellow circles for **9** and **10**.

four linker axes, which allows molecules to take either the square (or pseudo-square) or diamond form. Such processes are illustrated in a simplified manner together with the point group symmetry of each structure in Scheme 3. The compounds are classified into two types in terms of molecular symmetry and strain. In type I compounds (**1**, **8**, and **10**), the molecules are chiral in the diamond forms and achiral in the square forms. The interconversion between the two diamond forms via the square form (skeletal swing) leads to enantiomerization. A rigid molecular model indicates that the bending deformations in these molecules are negligible. On the other hand, the molecules are inherently chiral in any forms in the compounds belonging to type II. For example, the molecules of **7** are always D_2 symmetric and the two diamond forms are diastereomers of each other, where the two diacetylene linkers locate either at acute or obtuse angle corners. The skeletal swing leads to diastereomerization, during which the chirality of the framework is retained. When the equilibrium between the two forms occurs rapidly, the spectral pattern should be consistent with the averaged symmetry, namely, the dynamic symmetry, which is equal to the symmetry of the square forms in these systems.

The signal patterns of the ^{1}H NMR spectra of the cyclic tetramers are characterized by the number of ABC systems due to the protons at 2–4 (or 5–7) positions and the number of singlets due to the protons at 9 and 10 positions, as listed in Table 1. For example, compounds **6** and **9** gave four sets of ABC systems and four singlets, reflecting their C_2 symmetry. Compound **7** having D_2 symmetry gave two sets of ABC systems and two singlets. The signal patterns of **8** and **10** are consistent with the dynamic symmetry, C_s and D_{2d}, respectively, indicating the facile skeletal swing at room temperature. Other features in the NMR chemical shifts are discussed in the following sections in relation to the molecular structures.

Table 1. Selected ^{1}H and ^{13}C NMR Data of **1** and **6–10** at Room Temperature[a)]

	^{1}H NMR			^{13}C NMR
	ABC[b)]	Singlet[b)]	δ 9-H[c)]	δ C_{sp}
1[d)]	1	2	9.87 (4H) AA	93.1
6	4	4	8.99 (2H) AD, 10.05 (2H) AA	—[e)]
7	2	2	9.16 (4H) AD	80.5, 83.2, 93.3
8	4	6	8.73 (1H) DD, 9.58 (2H) AD, 10.18 (1H) AA	—[e)]
9	4	4	8.67 (2H) DD, 9.85 (2H) AD	—[e)]
10a	1	2	9.29 (4H) DD	—[e)]
10b	1	1	9.38 (4H) DD	80.1, 81.1

a) Measured in $CDCl_3$ except **8** (CD_2Cl_2). b) Numbers of ABC systems and singlets in the aromatic region. c) Chemical shift and signal intensity of 9-H signals. A (acetylene) and D (diacetylene) represent the combination of linkers at 1,8-positions. d) Ref. 5. e) Not measurable due to low solubility.

X-ray Analysis. Among the newly synthesized tetramers, only **7** gave a single crystal suitable for X-ray analysis. The

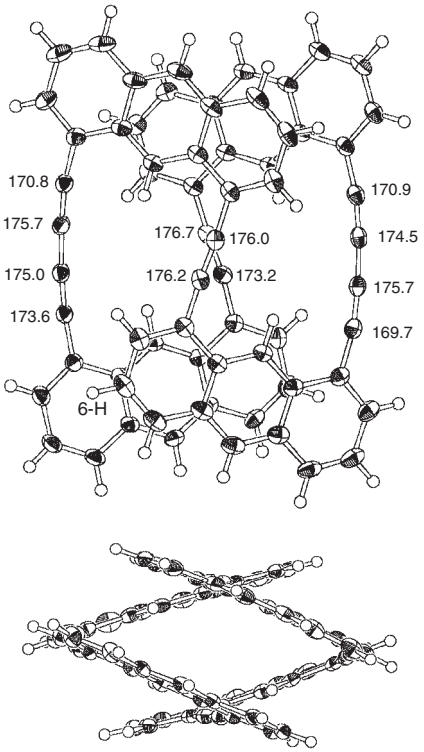


Figure 2. ORTEP drawings of X-ray structure of **7** with thermal ellipsoids at 50% probability. Bond angles are indicated at sp carbons.

X-ray structure of **7** is shown in Figure 2. The molecule takes a distorted diamond prism structure of approximately D_2 symmetry, where the diacetylene linkers occupy acute angle corners forming angles of ca. 40°. Anthracene moieties are almost planar and there are no significant out-of-plane and in-plane deformations. The bending deformation of each sp carbon is not so severe as revealed by the bond angles (170–177°) indicated in Figure 2. As for the diacetylene moieties, the bond angles are small for the outer sp carbons attaching to the anthracene groups compared with those for the inner ones. This structural feature is recognizable from the ^{13}C NMR chemical shifts of the sp carbons; namely, one of the diacetylene carbon signals of **7** is slightly shifted downfield (ca. 2 ppm) compared with the corresponding signal in strain-free compound **10b** (Table 1). Such a deshielding effect due to bending deformations, generally observed in strained alkynes,[3a,15] is significant in cyclic trimers **2** and **3**.[16] There are two pairs of parallel-oriented anthracene groups separated by 3.33 and 3.39 Å, which are nearly equal to the sum of the van der Waals radius of two aromatic carbons (1.7 Å × 2).[17] The facing anthracene planes are tilted by ca. 30° from each other because of the incorporation of linkers having different lengths. This orientation results in the upfield shift of the signal assigned to 6-H atoms (δ 6.33) in the 1-butadiynyl-8-ethynylanthracene substructure that lies in the shielding region of the facing anthracene moiety, as indicated in Figure 2.

DFT Calculations. The structures of **7** and the other compounds were investigated by DFT calculations. It was reported that the most popular B3LYP hybrid type functional could not always reproduce the molecular structures well for macrocyclic compounds with arene units.[18] This limitation is attributed to the fact that this functional is unable to treat noncovalent medium-range interactions, such as $\pi\cdots\pi$ and C–H$\cdots\pi$ interactions.[19,20] Hence, we applied the M05 class hybrid meta exchange-correlation functionals developed by the Truhlar's group at University of Minnesota, because of the improved performance for predicting noncovalent interactions.[21] To seek an appropriate calculation method, the structures of **1** and **10a** were optimized by B3LYP and M05 series functionals with the 3-21G basis set as well as by semiempirical and HF methods. Table 2 lists the interlayer distances between facing anthracene planes as a structural parameter specifying the cyclic structure, which are sensitive to the interactions between the aromatic moieties. The AM1, PM3, HF, and B3LYP methods apparently overestimate the distances in **1**. The calculated value at the M05/3-21G level is in good agreement with the experimental one, while the M05-2X functional, which involves the double percentage of HF exchange, overestimates the attractive interactions. It is notable that the calculations with the M05 functionals well reproduce the deformations from an ideal D_2 symmetric structure leading to different interlayer distances for the two pairs of parallel planes. A similar tendency was observed in the structure of diacetylene analog **10a**, and the distance is 3.5 Å as revealed by the calculation at the M05/3-21G level. Theoretical studies of the anthracene dimer using MP2 and DFT methods suggested that the binding energy of a graphite-like orientation was 32–41 kJ mol^{-1} with separations of 3.5–3.6 Å.[22] Therefore, we adopted the calculation at the M05/3-21G level for the other compounds because of the ability to predict global minimum structures and the reasonable computational cost for large molecules.[18,23]

Table 2. Interlayer Distances between Facing Anthracene Planes in the Calculated and Experimental Structures of **1** and **10a**[a)]

Method	**1**	**10a**
AM1	4.86	5.02
PM3	4.67	5.04
HF/3-21G	4.17	4.23
B3LYP/3-21G	4.11	5.14
M05/3-21G	3.52, 3.54	3.51, 3.56
M05-2X/3-21G	3.06, 3.11	3.06, 3.07
X-ray	3.45, 3.48[b)]	—

a) Distances between the averaged plane of one anthracene and the centroid of one of the benzene rings in another anthracene. When the structure is apparently deformed from an ideal D_2 symmetry, the two pairs of facing anthracenes have independent values. b) Ref. 5.

The optimized structures of **1**, **6–9**, and **10a** are shown in Figure 3, where two diastereomeric structures are given for type II compounds. All of the structures have diamond forms rather than square forms with interlayer distances of 3.5–3.6 Å except the less stable structure of **7**. As was found in the X-ray structure, the diacetylene linkers are at acute angle corners in the global minimum structure of **7** (**7X**) although the interlayer distance is slightly overestimated. Another diamond form **7Y**, where the diacetylene linkers lie at obtuse angle corners, is

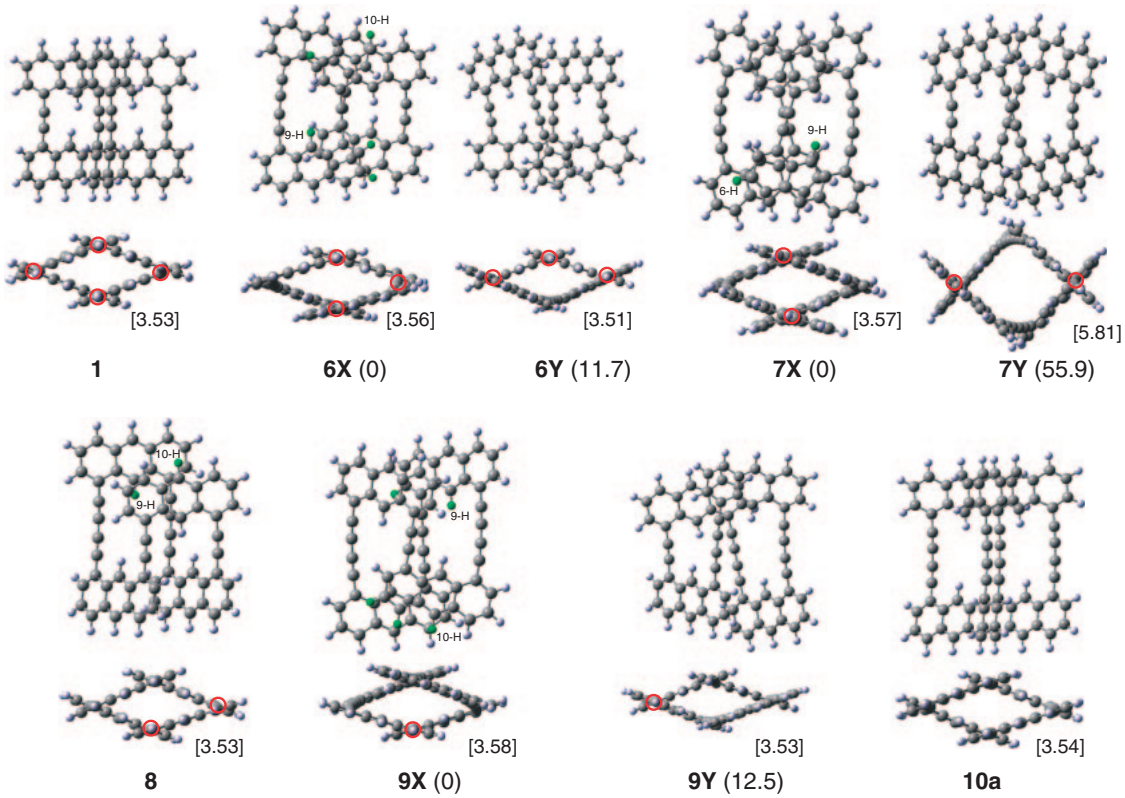


Figure 3. Two views of optimized structures of cyclic tetramers **1**, **6**–**9**, and **10a** at the M05/3-21G level. Two structures were obtained for **6**, **7**, and **9**, and the relative energies for each pair of diastereomers are given in parentheses in kJ mol^{-1}. Averaged interlayer distances between facing anthracenes are indicated in brackets in Å. Acetylene linkers are indicated by red circles in the views along the linkers. Typical protons in the shielding region are marked with green circles in **6X**, **7X**, and **9X**.

much less stable than **7X**. The diacetylene linker is at the acute angle corner in the global minimum structure of **6** (**6X**), which is more stable by 12 kJ mol^{-1} than the other structure **6Y** that has the diacetylene linker at the obtuse angle corner. For **9**, structure **9X** with the acetylene linker at the obtuse angle corner is more stable than the other structure **9Y**.

These calculated structures allow us to discuss the ^{1}H NMR chemical shifts of the cyclic tetramers in terms of the ring-current effect. The chemical shifts of 9-H signals, which appear at the low field due to the deshielding effect of triple bond moieties, are listed in Table 1. As for the 9-H atoms located between two diacetylene linkers (specified as DD in Table 1), the signals of **8** and **9** are significantly shifted upfield relative to the corresponding signals of **10a** and **10b**. The shielding effect was also found for the 9-H atoms located between an acetylene and a diacetylene linker (AD in Table 1) in **6** and **7**. These protons locate in the shielding region of nearby anthracene moieties,[24] as highlighted in Figure 3. Similar effects were also observed for the following signals: one of the 10-H signals of **6**, **8**, and **9** (δ 7.4–7.6), two dd signals and one d signal of **6** and **9** (δ 6.0–6.6) as well as the 6-H signal of **7** mentioned in the last section. In particular, the upfield shifts of one of the dd signals of **6** (δ 6.04, 3-H) and **9** (δ 6.12, 6-H) are notable. These protons are also indicated in the structures shown in Figure 3.

Electronic Spectra. UV–vis and fluorescence spectra were measured for the cyclic tetramers and their acyclic precursors in $CHCl_3$. The effects of chain length on the absorption wavelength are noted for the oligomers with diacetylene linkers

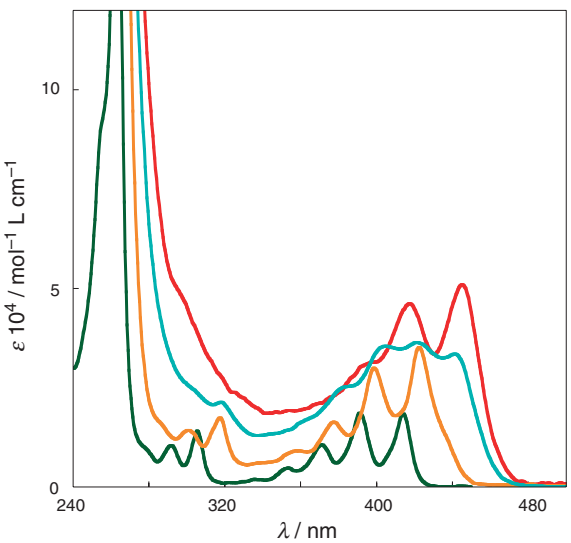


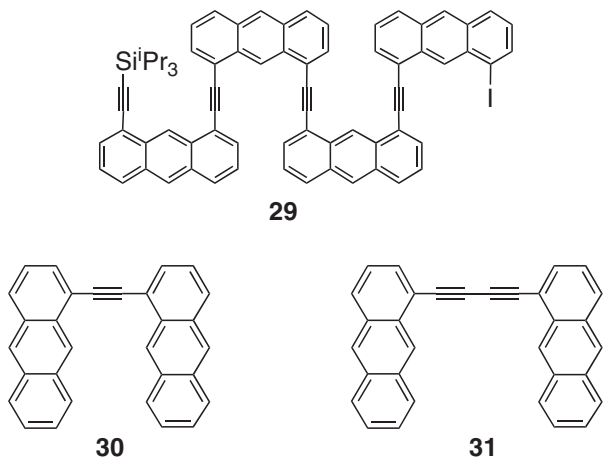
Figure 4. UV–vis spectra of **13a** (green), **15a** (orange), **27a** (light blue), and **10a** (red) in $CHCl_3$.

(Figure 4). The peaks in the *p*-band regions shift to the longer wavelength (414 → 441 nm for the peak at the longest wavelength) with increasing intensity in the order of acyclic monomer, dimer, and tetramer, as reflected by the extension of the conjugation and the increase in the number of anthracene chromophores. It should be noted that the vibrational structure of the *p*-band peaks is unclear only for acyclic tetramer **27a**.

Table 3. Photophysical Properties of Cyclic Tetramers and Their Acyclic Precursors in $CHCl_3$

	UV		FL[c]			Stokes shift /nm
	λ_{max}/nm[a]	ε[b]	λ_{em}/nm	Φ_f[d]	τ_f/ns[e]	
1[f]	411, 439	12000	478	0.40	2.4, 14.7	39
6	419, 447	49600	481	0.20	5.6	35
7	417, 447	40600	496	0.20	5.3	49
8	416, 444	39600	472	0.23	5.9	28
9	421, 448	61000	479	0.15	7.4	31
10a	417, 445	51000	469	0.10	2.0, 6.3	24
29[f]	413, 436	34000	450, 472	0.06	—	14
24	419, 446	49500	452, 475	0.10	0.8, 4.6	15
26	416, 438	43800	496	0.17	1.3, 13.1	58
25	414, 439	59700	454, 479	0.16	1.3, 4.8	15
28	421, 442	51200	442, 470	0.20	4.2, 15.9	0
27a	421, 441	33400	453, 480, 549	0.03	0.7, 6.0	10
3[g]	416, 443	48700	459, 488	0.27	2.1	16
4[h]	425, 450, 480	121000	488	0.39	—	8
5a[i]	412, 435, 462	5600	472, 501	0.41	—	10
5b[j]	438, 463, 494	28800	508, 537	0.43	—	14

a) Wavelengths of maximum absorption in the *p*-band region. b) Molar extinction coefficient of the absorption at the longest wavelength. c) Excited at 393 nm. d) Fluorescence quantum yield determined relative to 9,10-diphenylanthracene. e) Fluorescence lifetime. f) Ref. 5. g) Ref. 16. h) Ref. 6. i) Ref. 25. j) Ref. 7.



29

30 **31**

Chart 1.

Table 3 compiles the photophysical properties, including fluorescence quantum yields and lifetimes, of cyclic and acyclic tetramers as well as related compounds. The tetramers gave an intense absorption band at ca. 270 nm and structured bands in the *p*-band region (370–470 nm). Peaks at the longest wavelength were observed at 440 nm for the acyclic and cyclic tetramers as well as for cyclic trimer **3**.[16] Therefore, the effects of diacetylene linkers incorporation and cyclization are rather small. These wavelengths are slightly longer than those of di(1-anthryl)ethyne (**30**) (λ_{max} 425 nm) and its butadiyne analog **31** (λ_{max} 430 nm),[26] and are apparently shorter than those of planar cyclic dimers **4**,[6] **5a**,[25] and **5b**[7] (Chart 1). These data indicate that the planarity rather than the chain length plays a dominant role in producing the bathochromic effects.

The emission spectra of the cyclic tetramers were observed at 470–500 nm as broad bands, corresponding to the Stokes shift of 24–49 nm. The fluorescence quantum yields are in the range of 0.10–0.40 and these values are larger than those of the corresponding precursors except **9**. Fluorescence lifetime measurements revealed that the emission consists of one component for **6**–**9** with lifetimes of 5–7 ns, and two components for **1** and **10a** as well as acyclic precursors **24**–**28**. As discussed for **1** in the previous paper,[5] the short and long components in **10a** can be attributed to monomer and excimer-type emissions, respectively.[27] The observed components of **6**–**9** could be attributed to the monomer emission although the possibility of the excimer-type emission cannot be completely ruled out from available data.

Dynamic Behavior. Variable temperature (VT) ^{1}H NMR spectra of the cyclic tetramers were measured to observe the dynamic behavior of the cyclic framework, as illustrated in Scheme 3. The signal pattern observed at room temperature was practically retained at −90 °C in CD_2Cl_2 for **7**, **9**, and **10a**. These observations indicate that the interconversion between possible diamond forms takes place rapidly on the NMR time scale at low temperature ($\Delta G^{\neq} < 32$ kJ mol^{-1}) for **9** and **10a**.[28] The structure of **7** is nearly fixed into the observed diamond form based on DFT calculations.

For **8**, the aromatic signals at δ 6.8–7.7 became broad at −70 °C and further broadened at −90 °C, while the singlets at the low magnetic field remained sharp at all the temperatures (Figure 5b). This observation means that the dynamic process between the two diamond forms is retarded at low temperature. If the structure could be frozen into either of the diamond forms on the NMR time scale, this compound should give a less symmetric NMR signal pattern: eight sets of ABC systems and eight singlets (cf. Table 1). Although the exchange was not completely frozen at −90 °C, the estimated barrier height of **8** (ca. 34 kJ mol^{-1}) seemed to be lower than that of **1** (38 kJ mol^{-1}).[5] Therefore, the barriers to skeletal swing decrease in the order of **1**, **8**, and **10a** for the type I compounds. The difference between **1** and **8** is attributed to the incorpo-

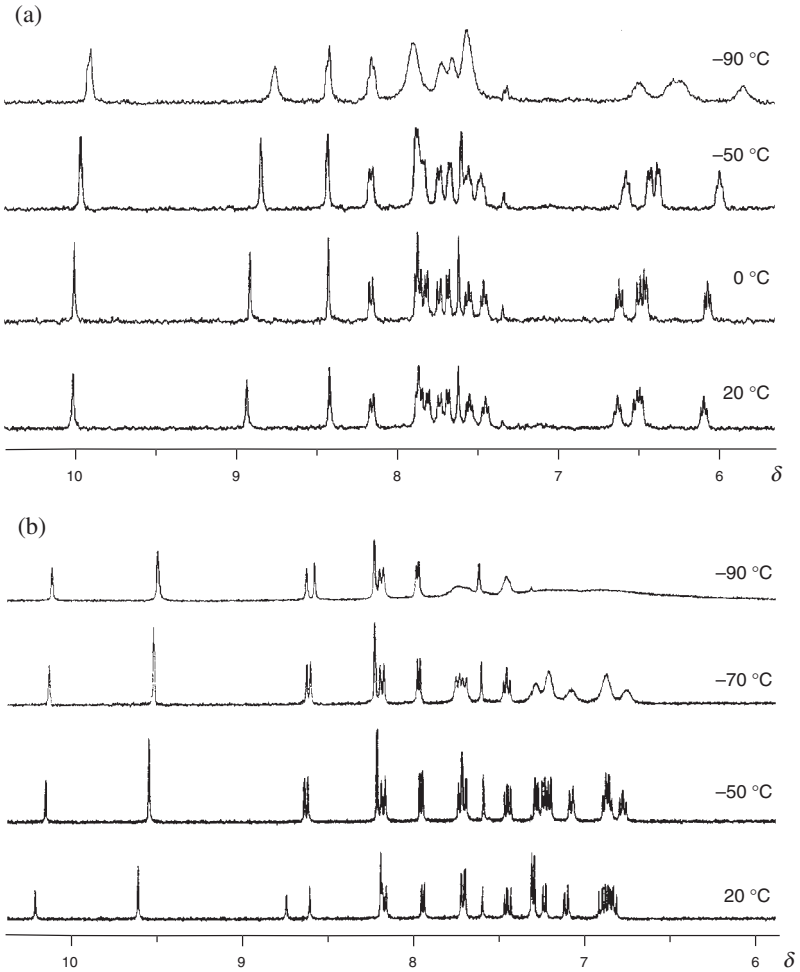


Figure 5. Variable temperature ^{1}H NMR spectra of (a) **6** and (b) **8** in CD_2Cl_2.

ration of two diacetylene linkers in the latter, which leads to the less effective overlap of the facing anthracene moieties as $\pi\cdots\pi$ interactions play an important role in the preference for the diamond form. The facile interconversion in **10a** means that long linkers tend to reduce attractive interactions probably because of the increased freedom of motion involving stretching and bending. The broad signals of **6** at −90 °C (Figure 5a) indicate that the diastereomerization takes place at a rate comparable to the NMR time scale, where all signals should be involved in the site exchange. However, it is difficult to determine the barrier height and the conformer population from the experimental data. If we base our assumption on the calculated energy difference (Figure 3), the population of the minor conformer should be small.

Enantiomeric Resolution. Compounds **6**, **7**, and **9** are inherently chiral and the racemization via highly strained structures is unlikely under ordinary conditions. To confirm this structural feature, we resolved the enantiomers by conventional methods as new enantiopure π-conjugated compounds.[29]

The crystallographic data of **7** gave the chiral space group ($P2_12_12_1$), a requirement for spontaneous resolution. Actually, each single crystal grown from chloroform solution was optically active and consisted of either of the enantiomers. Because enantiomeric crystals were indistinguishable by shape and polarizing properties, we divided a large number of single crystals into two groups by checking their CD signs at 269 nm. The enantiomers were also resolved by chiral HPLC with a Daicel Chiralpak IA column by baseline separation. The specific rotations of the first and second fractions were $[\alpha]_D^{22}$ +218 and −239, respectively. The CD spectra of the resolved enantiomers are shown in Figure 6. The (+)-isomer gave a strong trough at 241 nm and a strong peak at 269 nm in addition to positive continuous peaks up to 470 nm, and the (−)-isomer gave a mirror-image spectrum. The enantiomers of **6** and **9** were also resolved with the same column. The specific rotations of the first and second fractions were $[\alpha]_D^{24}$ +206 and −220, respectively, for **6**, and $[\alpha]_D^{22}$ +244 and −254, respectively, for **9**. The CD spectra of these enantiomers are also shown in Figure 6. Enantiopure samples of **6**, **7**, and **9** have common chiroptical features: the easily eluted enantiomers are all dextrorotatory and give an intense trough at ca. 240 nm and a series of peaks at 270–460 nm in the CD spectra. Although these signal patterns should be related to the orientation of anthracene chromophores in the chiral structure, we could not obtain any useful information on the absolute stereochemistry from available data of the theoretical calculation of CD spectra[30] and the anomalous dispersion effect of the X-ray diffractions.

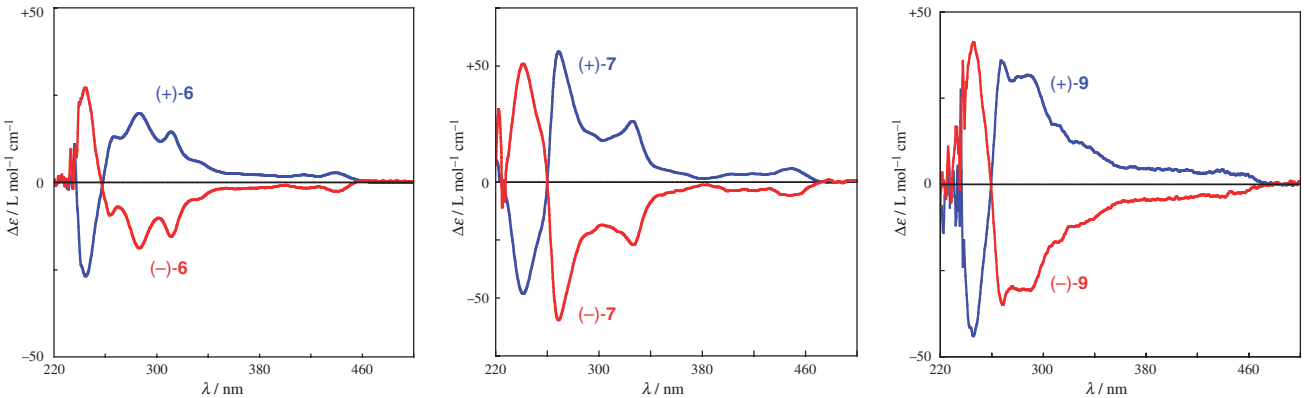


Figure 6. CD spectra of enantiomers of chiral cyclic tetramers **6**, **7**, and **9** in $CHCl_3$.

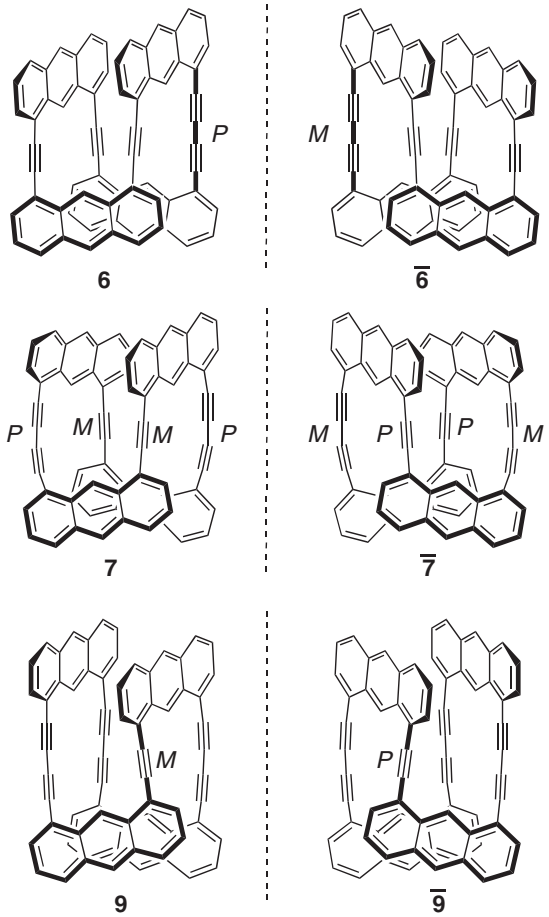


Figure 7. Enantiomers of cyclic tetramers **6**, **7**, and **9**.

These cyclic tetramers are considered to be chiral with respect to linker axes.[31] We can represent the stereochemistry by specifying the helical sense of two 1-anthryl groups about each linker with PM stereodescriptors.[32] If we chose the linker that is different from the others as the principal axis, the stereochemistry of **6** and its enantiomer $\bar{\mathbf{6}}$ will be represented by P and M, respectively, where the diacetylene linker is the specified axis (Figure 7). Similarly, the stereochemistry of **9** is characterized by the helicity about the monoacetylene linker. As for the enantiomers of **7**, the helicity is P (or M) for the two diacetylene linkers and M (or P) for the two monoacetylene linkers.

In summary, we synthesized five cyclic 1,8-anthrylene oligomers with acetylene and diacetylene linkers by successive coupling reactions. The number and position of the diacetylene linkers influence the shape, symmetry, and flexibility of the cyclic framework as revealed by NMR and X-ray spectroscopy. The enantiomers of the three chiral tetramers were successfully resolved by spontaneous resolution or chiral HPLC to show characteristic CD bands. The structural and spectroscopic data of a complete set of cyclic tetramers with two types of linkers confirm the versatility of this molecular design based on the aromatic planes and the linear linkers. The syntheses of higher cyclic oligomers and other structurally fascinating oligomers are underway.

Experimental

General. Melting points are uncorrected. Elemental analyses were performed by a Perkin-Elmer 2400 series analyzer. NMR spectra were measured on a Varian Gemini-300 (^{1}H: 300 MHz, ^{13}C: 75 MHz), a JEOL GSX-400 (^{1}H: 400 MHz, ^{13}C: 100 MHz), or a JEOL Lambda-500 (^{1}H: 500 MHz, ^{13}C: 125 MHz) spectrometer. In the case where the number of carbon signals is fewer than the expected one due to overlapping, the numbers of missing signals are indicated in each data. VT ^{1}H NMR spectra were measured on the JEOL GSX-400 spectrometer and the sample temperature was read from a thermocouple after the calibration with the chemical shift differences of methanol signals. High-resolution FAB mass spectra 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. Column chromatography was carried out with Merck Silica Gel 60 (70–230 mesh) or Fuji Silysia Chromatorex-NH (100–200 mesh). Crystalline compounds were purified by recrystallization from hexane–chloroform unless otherwise mentioned. The elemental analyses of some higher oligomers were very difficult because of incomplete combustion, and in such cases the compounds were characterized by HRMS and their purity was confirmed by ^{1}H and ^{13}C NMR spectra.

1,8-Dichloro-10-octadecylanthracene (12b). A solution of octadecylmagnesium bromide in ether was prepared from 1-bromooctadecane (11.7 mL, 34.2 mmol), Mg (831 mg, 34.2 mmol), and ether (70 mL) in an ordinary manner. To the solution was added 4,5-dichloro-9-anthrone[10] (**11**, 3.00 g, 11.4 mmol), and the

whole was stirred for 21 h at room temperature under Ar. The reaction mixture was quenched with aq NH_4Cl (ca. 20 mL). The organic layer was separated, dried over $MgSO_4$, and evaporated. The crude product was purified by chromatography on silica gel with hexane eluent to give the desired product as a yellow solid. Yield 2.30 g (40%); mp 72–73 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (3H, t, $J = 6.8$ Hz), 1.22–1.28 (26H, m), 1.39 (2H, m), 1.57 (2H, m), 1.77 (2H, m), 3.56 (2H, t, $J = 8.3$ Hz), 7.43 (2H, dd, $J =$ 7.3, 9.3 Hz), 7.62 (2H, d, $J = 7.3$ Hz), 8.18 (2H, d, $J = 8.8$ Hz), 9.25 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.21, 22.76, 28.87, 29.43, 29.60, 29.70, 29.72, 29.75, 29.76, 30.33, 31.61, 31.98, 119.66, 123.68, 125.34, 125.52, 129.23, 130.52, 133.22, 137.14 (6 alkyl signals missing); Anal. Found: C, 77.16; H, 8.97%. Calcd for $C_{32}H_{44}Cl_2$: C, 76.93; H, 8.88%.

10-Octadecyl-1,8-bis[(trimethylsilyl)ethynyl]anthracene (13b). To a solution of (trimethylsilyl)ethyne (3.4 mL, 24.0 mmol) in THF (60 mL) was added ethylmagnesium bromide (3.0 mol L^{-1} in ether, 7.2 mL, 21.6 mmol) at 0 °C under Ar. After this solution was stirred for 1 h, **12b** (2.00 g, 4.00 mmol), [Ni(acac)$_2$] (7.2 mg, 28 μmol), and PPh_3 (26.3 mg, 0.100 mmol) were added. The reaction mixture was refluxed for 72 h under Ar, and then quenched with aq NH_4Cl (ca. 20 mL). The organic layer was separated, dried over $MgSO_4$, and evaporated. The crude product was purified by chromatography on silica gel with hexane eluent to give the desired product as a yellow solid. Yield 2.40 g (96%); mp 71–73 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.38 (18H, s), 0.88 (3H, t, $J = 7.3$ Hz), 1.22–1.28 (26H, m), 1.38 (2H, m), 1.54 (2H, m), 1.76 (2H, m), 3.56 (2H, t, $J = 8.3$ Hz), 7.43 (2H, dd, $J = 6.8$, 8.8 Hz), 7.78 (2H, d, $J = 6.8$ Hz), 8.24 (2H, d, $J = 9.3$ Hz), 9.31 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 0.52, 14.21, 22.76, 28.42, 29.43, 29.62, 29.72, 29.76, 30.33, 31.66, 31.98, 81.98, 82.57, 119.66, 123.68, 125.34, 125.52, 129.23, 130.52, 133.22, 137.14 (8 alkyl signals missing); Anal. Found: C, 81.09; H, 9.84%. Calcd for $C_{42}H_{62}Si_2$: C, 80.96; H, 10.03%.

1-Ethynyl-10-octadecyl-8-[(triisopropylsilyl)ethynyl]anthracene (14b). A solution of **13b** (2.20 g, 3.53 mmol) in ethanol (200 mL) was stirred with KF (1.03 g, 17.7 mmol) for 3 h at room temperature. The solvent was evaporated, and the residue was dissolved in dichloromethane (ca. 30 mL). The organic solution was washed with aq NaCl (ca. 20 mL), dried over $MgSO_4$, and evaporated. The crude product was purified by chromatography on silica gel with hexane eluent to give the desired product as a yellow solid. 1,8-Diethynyl-10-octadecylanthracene: yield 1.60 g (95%); mp 85–87 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (3H, t, $J = 6.8$ Hz), 1.22–1.28 (26H, m), 1.39 (2H, m), 1.56 (2H, m), 1.76 (2H, m), 3.57 (2H, t, $J = 8.3$ Hz), 3.61 (2H, s), 7.47 (2H, dd, $J =$ 6.8, 8.8 Hz), 7.79 (2H, d, $J = 7.3$ Hz), 8.29 (2H, d, $J = 9.3$ Hz), 9.25 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.21, 22.77, 28.36, 29.43, 29.62, 29.73, 29.76, 30.36, 31.73, 31.98, 81.98, 82.57, 121.03, 122.54, 124.77, 125.08, 129.13, 131.04, 131.42, 136.83 (8 alkyl signals missing); Anal. Found: C, 90.20; H, 10.02%. Calcd for $C_{36}H_{46}$: C, 90.32; H, 9.68%. To a solution of the diethynyl compound (1.47 g, 3.38 mmol) in THF (30 mL) was added butyllithium (1.56 mol L^{-1} in hexane, 2.17 mL, 3.38 mmol) at −78 °C under Ar. After this solution was stirred for 1 h at 0 °C, chlorotriisopropylsilane (0.65 mL, 3.1 mmol) was added. This reaction mixture was stirred for 1 h at room temperature, and then quenched with aq NH_4Cl (ca. 10 mL). The solvent was evaporated, and the residue was extracted with dichloromethane. The organic solution was dried over $MgSO_4$, and evaporated. The crude products were separated by chromatography on silica gel with hexane eluent. The desired compound was obtained as a yellow solid in the second fraction. The bis-silylated product was also obtained in the first elution. Yield 1.50 g (77%); mp 51–53 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (3H, t, $J = 7.3$ Hz), 1.22–1.28 (47H, m), 1.39 (2H, m), 1.54 (2H, m), 1.76 (2H, m), 3.48 (1H, s), 3.57 (2H, t, $J = 8.3$ Hz), 7.47 (2H, dd, $J = 6.8$, 8.8 Hz), 7.78 (2H, d, $J = 6.8$ Hz), 8.28 (2H, d, $J = 8.8$ Hz), 9.46 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.56, 14.21, 19.01, 22.77, 28.35, 29.43, 29.63, 29.73, 29.77, 30.33, 31.70, 31.99, 82.08, 82.50, 96.31, 105.30, 121.03, 122.41, 122.79, 124.63, 124.87, 125.28, 125.81, 129.21, 131.18, 131.20, 131.40, 131.43, 136.73 (6 alkyl and 1 aromatic signals missing); Anal. Found: C, 85.18; H, 10.19%. Calcd for $C_{45}H_{66}Si$: C, 85.10; H, 10.47%. 10-Octadecyl-1,8-bis-[(triisopropylsilyl)ethynyl]anthracene: yellow oil; yield 273 mg (11%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (3H, t, $J = 7.3$ Hz), 1.21–1.26 (68H, m), 1.39 (2H, m), 1.54 (2H, m), 1.76 (2H, m), 3.57 (2H, t, $J = 8.3$ Hz), 7.44 (2H, dd, $J = 7.3$, 8.8 Hz), 7.81 (2H, d, $J = 6.8$ Hz), 8.25 (2H, d, $J = 9.3$ Hz), 9.28 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.84, 14.21, 18.99, 22.78, 28.47, 29.44, 29.65, 29.75, 29.78, 30.35, 31.65, 32.01, 96.90, 106.36, 122.59, 122.63, 124.76, 125.28, 129.26, 130.95, 132.91, 136.67 (6 alkyl signals missing); HRMS (FAB) Found m/z 790.6237, Calcd for $C_{54}H_{86}Si_2$: [M$^+$] 790.6268.

Dimer 15b. To a solution of **14b** (43.7 mg, 68.8 μmol) in diisopropylamine (5 mL) were added [Pd(PPh$_3$)$_2$Cl$_2$] (0.62 mg, 0.89 μmol), CuI (0.65 mg, 3.44 μmol), and I_2 (8.73 mg, 34.4 μmol). After the mixture was stirred for 3 h at room temperature, the solvent was evaporated. The residual solid was submitted to chromatography on silica gel with hexane eluent to give the desired product as a yellow solid. Yield 43.2 mg (99%); mp 70–73 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (6H, t, $J = 6.8$ Hz), 1.04 (36H, d, $J = 6.8$ Hz), 1.12 (6H, septet, $J = 6.8$ Hz), 1.23–1.26 (52H, m), 1.39 (4H, m), 1.54 (4H, m), 1.76 (4H, m), 3.58 (4H, t, $J = 8.3$ Hz), 7.46 (2H, dd, $J = 6.8$, 8.8 Hz), 7.49 (2H, dd, $J = 6.8$, 8.8 Hz), 7.78 (2H, d, $J = 6.8$ Hz), 7.87 (2H, d, $J = 6.8$ Hz), 8.25 (2H, d, $J = 8.8$ Hz), 8.31 (2H, d, $J = 9.3$ Hz), 9.49 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.34, 14.21, 18.80, 22.77, 28.39, 29.43, 29.66, 29.73, 29.76, 29.77, 30.34, 31.73, 31.99, 79.76, 81.45, 97.00, 105.02, 121.16, 122.62, 122.90, 124.69, 124.98, 125.16, 126.21, 129.12, 129.35, 131.28, 131.55, 131.57, 132.51, 136.93 (5 alkyl signals missing); HRMS (FAB) Found m/z 1266.9681, Calcd for $C_{90}H_{130}Si_2$: [M$^+$] 1266.9711; Anal. Found: C, 85.30; H, 10.22%. Calcd for $C_{90}H_{130}Si_2$: C, 85.24; H, 10.33%.

Dimer 16b. To a solution of **15b** (143 mg, 0.113 mmol) in dichloromethane (29 mL) was added TBAF (1.0 mol L^{-1} in THF, 113 μL, 0.113 mmol). The solution was stirred for 70 min at room temperature with checking the course of reaction by TLC. After water (ca. 20 mL) was added, the organic layer was separated, dried over $MgSO_4$, and evaporated. The crude products were separated by chromatography on silica gel with hexane–chloroform (1:0–2:1) eluent. The desired product (the second fraction) was obtained as a yellow oil, and the starting material (the first fraction) and the bis-desilylated product (the third fraction) were obtained in 25% and 40% yields, respectively. Yield 41 mg (32%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (6H, t, $J = 6.8$ Hz), 1.10 (18H, d, $J = 6.3$ Hz), 1.14–1.26 (55H, m), 1.40 (4H, m), 1.56 (4H, m), 1.78 (4H, m), 3.57–3.61 (5H, m), 7.45–7.53 (4H, m), 7.77–7.80 (2H, m), 7.86 (1H, d, $J = 6.3$ Hz), 7.92 (1H, d, $J = 6.3$ Hz), 8.26 (1H, d, $J = 9.3$ Hz), 8.28–8.33 (3H, m), 9.49 (1H, s), 9.52 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.41, 14.21, 18.56, 22.77, 28.40, 29.43, 29.65, 29.73, 29.75, 29.78, 30.36, 31.74, 31.77, 31.99, 79.29, 80.09, 81.40, 81.61, 81.74, 83.14, 97.11, 105.06, 121.08, 121.11, 121.27, 122.52, 122.79, 124.80, 124.84, 124.89, 125.02,

125.20, 125.71, 126.23, 126.28, 129.11, 129.15, 129.25, 129.37, 130.94, 131.27, 131.45, 131.55, 131.61, 131.75, 132.92, 137.04, 137.06 (23 alkyl and 2 aromatic signals missing); HRMS (FAB) Found m/z 1110.8363, Calcd for $C_{81}H_{110}Si$: [M^+] 1110.8377. Bis-desilylated product: yellow solid; yield 43 mg (40%); mp 113–115 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (6H, t, $J = 6.8$ Hz), 1.22–1.28 (52H, m), 1.40 (4H, m), 1.57 (4H, m), 1.79 (4H, m), 3.59 (4H, t, $J = 7.8$ Hz), 3.69 (2H, s), 7.46–7.53 (4H, m), 7.79 (2H, d, $J = 6.8$ Hz), 7.89 (2H, d, $J = 6.8$ Hz), 8.28–8.34 (4H, m), 9.53 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.21, 22.77, 28.40, 29.43, 29.64, 29.75, 29.77, 30.37, 31.77, 31.99, 79.64, 81.47, 81.71, 83.48, 120.99, 121.19, 122.60, 124.91, 125.74, 126.27, 129.14, 129.26, 130.99, 131.59, 131.69, 132.01, 137.15 (8 alkyl and 1 aromatic signals missing); HRMS (FAB) Found m/z 954.7073, Calcd for $C_{72}H_{90}$: [M^+] 954.7043.

1-Iodo-8-[(trimethylsilyl)ethynyl]anthracene (18). To a degassed solution of 1,8-diiodoanthracene[12] (**17**, 200 mg, 0.465 mmol) in a mixture of THF (36 mL) and isopropylamine (6 mL) were added (trimethylsilyl)ethyne (0.197 mL, 1.40 mmol), [$Pd(PPh_3)_4$] (26.9 mg, 23.0 μmol), and CuI (4.4 mg, 23 μmol). The reaction mixture was stirred for 18 h at room temperature under Ar. The volatile materials were removed by evaporation. The crude product was purified by chromatography on silica gel with hexane–dichloromethane (1:1) eluent to give the desired product as a yellow oil. Yield 121 mg (65%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.44 (9H, s), 7.16 (1H, dd, $J = 7.0$, 8.6 Hz), 7.44 (1H, dd, $J = 6.7$, 8.6 Hz), 7.75 (1H, dd, $J = 0.9$, 7.0 Hz), 7.97–7.99 (2H, m), 8.13 (1H, dd, $J = 0.9$, 7.0 Hz), 8.30 (1H, s), 9.20 (1H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ 0.32, 100.23, 100.87, 102.78, 121.32, 125.37, 126.44, 127.67, 128.78, 129.18, 130.57, 130.74, 131.52, 131.97, 132.35, 132.58, 137.50; HRMS (FAB) Found m/z 400.0118, Calcd for $C_{19}H_{17}ISi$: [M^+] 400.0144.

Dimer 19. To a degassed solution of **18** (137 mg, 0.432 mmol) and **14a**[5] (248 mg, 0.648 mmol) in a mixture of THF (23 mL) and triethylamine (23 mL) were added [$Pd(PPh_3)_4$] (25.4 mg, 22.0 μmol) and CuI (4.2 mg, 22 μmol). After the reaction mixture was refluxed for 24 h, the solvent was evaporated. The crude product was purified by chromatography on silica gel hexane–dichloromethane (3:1) eluent to give the desired compound as a brown viscous solid. Yield 237 mg (84%); ^{1}H NMR (500 MHz, $CDCl_3$): δ −0.27 (9H, s), 0.65–0.76 (21H, m), 7.41–7.44 (2H, m), 7.51–7.54 (2H, m), 7.72 (1H, d, $J = 6.7$ Hz), 7.76 (1H, d, $J = 7.1$ Hz), 7.94–8.08 (6H, m), 8.48 (2H, s), 9.60 (1H, s), 9.62 (1H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ −0.72, 11.06, 18.34, 92.21, 92.32, 96.76, 100.26, 102.68, 104.77, 121.51, 121.72, 121.81, 121.86, 124.32, 124.45, 124.96, 125.00, 125.06, 127.38, 127.48, 128.83, 129.02, 129.06, 129.11, 130.90, 130.98, 131.13, 131.42, 131.45, 131.51, 131.55, 131.57, 131.63, 131.67, 131.69, 131.70 (1 aromatic signal missing); HRMS (FAB) Found m/z 654.3158, Calcd for $C_{46}H_{46}Si_2$: [M^+] 654.3138.

Dimer 20. A solution of **19** (228 mg, 0.348 mmol) in ethanol (50 mL) was refluxed for 1 h in the presence of KF (105 mg, 1.81 mmol). After the solvent was mostly evaporated, the residue was extracted with dichloromethane. The organic solution was washed with aq NaCl, dried over $MgSO_4$, and evaporated. The crude product was purified by chromatography on silica gel with hexane–dichloromethane (4:1) eluent to give the desired compound as a yellow solid. Yield 172 mg (85%); mp 178–179 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.70–0.87 (21H, m), 3.06 (1H, s), 7.42–7.46 (2H, m), 7.52–7.56 (2H, m), 7.75 (1H, d, $J = 6.7$ Hz), 7.81 (1H, d, $J = 6.7$ Hz), 7.96–8.07 (6H, m), 8.46 (1H, s), 8.47 (1H, s), 9.70 (1H, s), 9.73 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.31, 18.46, 81.39, 82.65, 92.63, 93.24, 96.77, 104.81, 120.62, 121.71, 121.80, 121.92, 124.34, 124.86, 125.05, 125.09, 127.29, 127.50, 128.78, 128.90, 129.07, 129.20, 130.35, 131.32, 131.41, 131.44, 131.49, 131.66, 131.80, 131.85 (6 aromatic signals missing); HRMS (FAB) Found m/z 582.2772, Calcd for $C_{43}H_{38}Si$: [M^+] 582.2743; Anal. Found: C, 88.42; H, 6.59%. Calcd for $C_{43}H_{38}Si$: C, 88.61; H, 6.57%.

Dimer 22. Compound **21** was prepared from **14a** by the known method.[16] To a degassed solution of **21** (137 mg, 0.337 mmol) and **17** (581 mg, 1.35 mmol) in a mixture of THF (27 mL) and triethylamine (27 mL) were added [$Pd(PPh_3)_4$] (20 mg, 17 μmol) and CuI (3.2 mg, 17 μmol). After the reaction mixture was stirred for 16 h at room temperature under Ar, the solvent was evaporated. The crude product was purified by chromatography on silica gel with hexane–chloroform (5:1) eluent to give the desired compound as a yellow oil. Yield 237 mg (84%); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.10–1.16 (21H, m), 7.19 (1H, dd, $J = 7.1$, 8.6 Hz), 7.41–7.54 (3H, m), 7.79 (1H, d, $J = 7.9$ Hz), 7.89 (1H, d, $J = 7.1$ Hz), 7.94 (1H, d, $J = 7.1$ Hz), 7.97–8.10 (4H, m), 8.15 (1H, d, $J = 7.1$ Hz), 8.40 (1H, s), 8.46 (1H, s), 9.26 (1H, s), 9.48 (1H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.32, 18.82, 79.14, 80.27, 80.79, 81.52, 97.05, 100.21, 104.78, 120.22, 120.36, 121.78, 123.98, 125.00, 125.21, 125.35, 126.66, 127.81, 128.03, 128.90, 129.13, 129.56, 130.04, 130.35, 131.27, 131.46, 131.51, 131.56, 131.66, 131.80, 132.08, 132.40, 132.44, 132.84, 133.48, 137.74; HRMS (FAB) Found m/z 708.1709, Calcd for $C_{43}H_{37}ISi$: [M^+] 708.1666.

Tetramer 24. To a degassed solution of trimer **23**[5] (22.0 mg, 28.0 μmol) and **18** (22.4 mg, 56 μmol) in a mixture of THF (10 mL) and triethylamine (10 mL) were added [$Pd(PPh_3)_4$] (8.1 mg, 7.0 μmol) and CuI (1.3 mg, 6.8 μmol). After the solution was refluxed for 13 h under Ar, the solvent was evaporated. The crude product was purified by chromatography on silica gel with hexane–chloroform (3:1) eluent to give the desired compound as a yellow solid. Yield 14 mg (47%); mp 217–218 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ −0.27 (9H, s), 0.59–0.74 (21H, m), 6.60 (1H, dd, $J = 6.8$, 8.3 Hz), 6.63 (1H, dd, $J = 6.8$, 8.3 Hz), 6.78 (1H, dd, $J = 6.8$, 8.8 Hz), 6.86 (1H, dd, $J = 6.8$, 8.3 Hz), 7.18 (1H, d, $J = 6.3$ Hz), 7.23–7.39 (5H, m), 7.45–7.49 (4H, m), 7.57–7.66 (4H, m), 7.72–7.81 (6H, m), 8.00 (1H, s), 8.03 (1H, s), 8.05 (1H, s), 8.09 (1H, s), 9.17 (1H, s), 9.23 (1H, s), 9.61 (1H, s), 9.68 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.73, 18.78, 18.83, 92.87, 93.04, 93.10, 93.29, 93.40, 93.59, 96.68, 99.98, 103.49, 105.30, 121.33, 121.35, 121.56, 121.77, 121.98, 122.33, 122.48, 123.94, 124.06, 124.68, 124.70, 124.74, 124.90, 124.94, 124.96, 125.09, 126.94, 127.01, 127.34, 127.36, 127.55, 128.21, 128.37, 128.44, 128.70, 129.01, 129.10, 129.37, 129.97, 130.00, 130.05, 130.94, 131.02, 131.08, 131.09, 131.13, 131.21, 131.31, 131.32, 131.35, 131.43, 131.45, 131.51, 131.61, 131.75, 131.80 (10 aromatic signals missing); UV ($CHCl_3$) λ_{max} (ε) 250 (202000), 419 (41600), 446 nm (49500); FL ($CHCl_3$) λ_{em} 452, 475 nm, Φ_f 0.10, τ_f 0.8, 4.6 ns; HRMS (MALDI-TOF) Found m/z 1054.40, Calcd for $C_{78}H_{62}Si_2$: [M^+] 1054.44.

Cyclic Tetramer 6. To a solution of tetramer **24** (14 mg, 13 μmol) in THF (5 mL) was added TBAF (1.0 mol L^{-1} in THF, 26 μL, 26 μmol). After the solution was stirred for 20 min at room temperature, the solvent was evaporated. The residue was dissolved in pyridine (13 mL), and $Cu(OAc)_2 \cdot H_2O$ (65 mg, 0.33 mmol) and CuCl (26 mg, 0.26 mmol) were added. The reaction mixture was stirred for 5 h at room temperature. After the solvent was mostly evaporated, the residual solid was submitted to chromatography on silica gel (NH) with hexane–chloroform (3:1) eluent. Recrystallization from toluene gave the desired compound

as orange crystals. Yield 9.0 mg (67%); mp 301–341 °C (dec); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.04 (2H, dd, $J = 7.3$, 8.3 Hz), 6.44 (4H, d, $J = 6.8$ Hz), 6.57 (2H, dd, $J = 6.8$, 8.3 Hz), 7.43 (2H, dd, $J = 6.8$, 8.3 Hz), 7.49–7.51 (2H, m), 7.56 (2H, s), 7.67–7.70 (4H, m), 7.78–7.83 (4H, m), 7.87 (2H, d, $J = 6.8$ Hz), 8.11 (2H, d, $J = 8.3$ Hz), 8.37 (2H, s), 8.99 (2H, s), 10.05 (2H, s); UV ($CHCl_3$) λ_{max} (ε) 250 (202000), 419 (41600), 447 nm (49600); FL ($CHCl_3$) λ_{em} 481 nm, Φ_f 0.20, τ_f 5.6 ns; HRMS (FAB) Found m/z 824.2462, Calcd for $C_{66}H_{32}$: [M^+] 824.2504; Anal. Found: C, 95.88; H, 3.82%. Calcd for $C_{66}H_{32}$: C, 96.09; H, 3.91%.

Tetramer 25. To a solution of **23** (23.2 mg, 29 µmol) and **14a** (34.0 mg, 89 µmol) in a mixture of THF (5 mL) and diisopropylamine (5 mL) were added [$Pd(PPh_3)_2Cl_2$] (3.1 mg, 4.5 µmol), CuI (1.0 mg, 4.5 µmol), and I_2 (11.0 mg, 45 µmol). After the reaction mixture was stirred for 16 h, the solvent was evaporated. The crude products were separated by chromatography on silica gel with hexane–chloroform (3:1) eluent to give the desired cross coupling product as a yellow solid. The homo-coupling product of the trimer (12 mg, 51%) was also obtained.[5] Yield 12 mg (36%); mp 233–235 °C; ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.35 (3H, septet, $J = 7.3$ Hz), 0.56 (18H, d, $J = 7.3$ Hz), 0.92–1.02 (21H, m), 6.49 (1H, dd, $J = 6.8$, 8.3 Hz), 6.74 (1H, dd, $J = 6.8$, 8.8 Hz), 6.84 (1H, dd, $J = 6.8$, 8.3 Hz), 7.07 (2H, d, $J = 6.8$ Hz), 7.16–7.20 (2H, m), 7.24 (1H, dd, $J = 6.8$, 8.8 Hz), 7.25 (1H, dd, $J = 6.8$, 8.3 Hz), 7.31 (1H, dd, $J = 6.8$, 8.3 Hz), 7.39–7.55 (6H, m), 7.63–7.67 (3H, m), 7.74–7.81 (4H, m), 8.01 (1H, d, $J = 8.8$ Hz), 8.04–8.07 (3H, m), 8.49 (1H, s), 8.81 (1H, s), 9.21 (1H, s), 9.34 (1H, s), 9.95 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.22, 11.36, 18.32, 18.72, 79.04, 79.79, 80.39, 81.05, 92.64, 92.72, 92.82, 93.28, 96.43, 96.88, 104.47, 104.69, 120.01, 120.32, 121.11, 121.16, 121.61, 121.75, 121.86, 121.90, 123.73, 123.84, 124.31, 124.43, 124.45, 124.63, 124.67, 124.73, 124.78, 125.00, 126.61, 126.84, 126.97, 127.33, 127.77, 128.10, 128.21, 128.52, 128.55, 129.34, 129.39, 129.77, 130.02, 130.28, 130.71, 130.72, 130.79, 130.83, 130.86, 130.90, 130.92, 131.06, 131.10, 131.15, 131.20, 131.29, 131.35, 131.38, 131.42, 131.45, 131.61, 131.77, 133.06 (5 aromatic signals missing); UV ($CHCl_3$) λ_{max} (ε) 264 (389000), 414 (65600), 439 nm (59700); FL ($CHCl_3$) λ_{em} 454, 479 nm, Φ_f 0.16, τ_f 1.3, 4.8 ns; HRMS (FAB) Found m/z 1162.5321, Calcd for $C_{86}H_{74}Si_2$: [M^+] 1162.5329; Anal. Found: C, 88.69; H, 6.74%. Calcd for $C_{86}H_{74}Si_2$: C, 88.76; H, 6.41%.

Cyclic Tetramer 8. To a solution of **25** (37 mg, 32 µmol) in THF (20 mL) was added TBAF (1.0 mol L^{-1} in THF, 0.136 mL, 0.136 mmol). After this solution was stirred for 20 min at room temperature, the solvent was evaporated. The residue was dissolved in pyridine (80 mL), and $Cu(OAc)_2 \cdot H_2O$ (160 mg, 0.80 mmol) and CuCl (63 mg, 0.64 mmol) were added to the solution. After the reaction mixture was stirred for 20 h, the solvent was evaporated. The residual solid was submitted to chromatography on silica gel (NH) with hexane–chloroform (2:1) eluent to give the desired product as a yellow solid. Yield 24 mg (89%); mp 301–303 °C (dec); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 6.80–6.92 (6H, m), 7.10 (2H, d, $J = 8.8$ Hz), 7.23 (2H, d, $J = 6.3$ Hz), 7.30 (4H, d, $J = 6.3$ Hz), 7.43 (2H, dd, $J = 6.8$, 8.3 Hz), 7.60 (1H, s), 7.70 (4H, d, $J = 8.8$ Hz), 7.93 (2H, d, $J = 6.3$ Hz), 8.17 (2H, d, $J = 8.3$ Hz), 8.20 (2H, s), 8.60 (1H, s), 8.73 (1H, s), 9.58 (2H, s), 10.18 (1H, s); UV ($CHCl_3$) λ_{max} (ε) 262 (178000), 416 (35400), 444 nm (39600); FL ($CHCl_3$) λ_{em} 472 nm, Φ_f 0.23, τ_f 5.9 ns; HRMS (FAB) Found m/z 848.2479, Calcd for $C_{68}H_{32}$: [M^+] 848.2504.

Tetramer 26. To a solution of **20** (120 mg, 0.206 mmol) in a mixture of THF (1 mL) and diisopropylamine (3 mL) were added [$Pd(PPh_3)_2Cl_2$] (2.3 mg, 3.3 µmol), CuI (2.0 mg, 10 µmol), and I_2 (27 mg, 0.10 mmol). After this solution was stirred for 16 h at room temperature, the solvent was evaporated. The crude product was purified by chromatography on silica gel (NH) with hexane–chloroform (2:1) eluent to give the desired compound as a yellow solid. Yield 115 mg (96%); mp 263–264 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.69 (6H, septet, $J = 7.8$ Hz), 0.83 (36H, d, $J = 6.8$ Hz), 6.69 (2H, t, $J = 8.8$ Hz), 6.82 (2H, d, $J = 8.3$ Hz), 7.21 (2H, t, $J = 8.3$ Hz), 7.32 (2H, d, $J = 6.8$ Hz), 7.39–7.49 (8H, m), 7.61 (2H, d, $J = 6.3$ Hz), 7.74 (2H, d, $J = 6.8$ Hz), 7.77 (2H, d, $J = 6.8$ Hz), 8.04 (2H, d, $J = 8.3$ Hz), 8.10 (2H, d, $J = 8.8$ Hz), 8.53 (2H, s), 9.10 (2H, s), 9.37 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.43, 18.55, 78.98, 80.27, 91.92, 93.90, 95.89, 105.44, 120.37, 120.72, 121.55, 122.15, 123.62, 124.25, 124.44, 124.59, 124.88, 125.14, 126.85, 126.97, 128.13, 128.29, 128.74, 129.29, 129.67, 130.83, 130.91, 131.03, 131.17, 131.47, 131.54, 131.71, 131.77, 131.88 (2 aromatic signals missing); UV ($CHCl_3$) λ_{max} (ε) 257 (278000), 416 (45000), 438 nm (43800); FL ($CHCl_3$) λ_{em} 496 nm, Φ_f 0.17, τ_f 1.3, 13.1 ns; HRMS (FAB) Found m/z 1162.5374, Calcd for $C_{86}H_{74}Si_2$: [M^+] 1162.5329.

Cyclic Tetramer 7. To a solution of **26** (44 mg, 38 µmol) in THF (50 mL) was added TBAF (1.0 mol L^{-1} in THF, 76 µL, 76 µmol). After the solution was stirred for 20 min at room temperature, the solvent was evaporated. The residue was dissolved in pyridine (30 mL), and $Cu(OAc)_2 \cdot H_2O$ (188 mg, 0.95 mmol) and CuCl (76 mg, 0.77 mmol) were added. The solution was stirred for 19 h at room temperature. After the solvent was mostly evaporated, the residual solid was submitted to chromatography on silica gel (NH) with hexane–chloroform (2:1) eluent. The desired compound was obtained as orange crystals. Yield 8.6 mg (27%); mp 355–358 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.33 (4H, dd, $J = 6.8$, 8.3 Hz), 6.71 (4H, d, $J = 8.3$ Hz), 7.47 (4H, dd, $J = 7.3$, 8.8 Hz), 7.59 (4H, d, $J = 6.3$ Hz), 7.76 (4H, d, $J = 6.8$ Hz), 7.81 (4H, s), 7.97 (4H, d, $J = 8.8$ Hz), 9.16 (4H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 80.50, 83.21, 93.27, 120.36, 121.22, 123.68, 124.15, 124.27, 126.05, 126.37, 128.91, 129.79, 130.20, 130.25, 130.50, 130.67, 131.88; UV ($CHCl_3$) λ_{max} (ε) 261 (205000), 417 (45000), 447 nm (40600); FL ($CHCl_3$) λ_{em} 496 nm, Φ_f 0.20, τ_f 5.3 ns; HRMS (FAB) Found m/z 848.2525, Calcd for $C_{68}H_{32}$: [M^+] 848.2504; Anal. Found: C, 95.82; H, 3.88%. Calcd for $C_{68}H_{32}$: C, 96.20; H, 3.80%.

Tetramer 27b. To a solution of **16b** (36 mg, 33 µmol) in pyridine (3.3 mL) were added $Cu(OAc)_2 \cdot H_2O$ (163 mg, 0.815 mmol) and CuCl (65 mg, 0.65 mmol). After the mixture was stirred for 24 h at temperature, the solvent was evaporated. The residue was submitted to chromatography on silica gel (NH) with hexane–chloroform (4:1) eluent to give the desired compound as a yellow solid. Yield 33 mg (91%); mp 156–158 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (12H, t, $J = 6.3$ Hz), 1.14 (36H, d, $J = 6.3$ Hz), 1.17–1.29 (110H, m), 1.43 (8H, m), 1.55 (8H, m), 1.68 (8H, m), 3.34 (4H, d, $J = 7.8$ Hz), 3.46 (4H, d, $J = 7.8$ Hz), 6.58 (2H, dd, $J = 6.6$, 6.8 Hz), 6.75 (2H, dd, $J = 6.8$, 8.8 Hz), 7.25–7.29 (4H, m), 7.37 (2H, d, $J = 6.8$ Hz), 7.43 (2H, dd, $J = 6.8$, 8.8 Hz), 7.71 (2H, d, $J = 6.3$ Hz), 7.75–7.82 (6H, m), 7.97 (2H, d, $J = 8.8$ Hz), 8.19 (2H, d, $J = 8.8$ Hz), 9.01 (2H, s), 9.40 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.27, 14.58, 19.39, 23.39, 28.89, 29.07, 30.07, 30.33, 30.37, 30.42, 30.92, 30.98, 32.29, 32.32, 32.63, 80.02, 80.46, 81.30, 81.80, 81.86, 82.21, 97.52, 105.92, 121.00, 121.22, 121.84, 122.91, 123.14, 123.36, 124.85, 124.92, 125.12, 125.27, 125.56, 125.64, 125.89, 126.24, 129.02, 129.15, 129.36, 129.60, 131.22, 131.68, 131.77, 132.05, 132.20, 133.29, 136.77, 136.97 (23 aliphatic and 2 aromatic signals missing); UV ($CHCl_3$) λ_{max} (ε) 260 (242000), 416 (43500), 434 (42800), 452 nm

(40700); FL ($CHCl_3$) λ_{em} 460 nm, Φ_f 0.094; MS (MALDI-TOF) Found m/z 2219.93. Calcd for $C_{162}H_{218}Si_2$: [M^+] 2219.66.

Tetramer 27a. This compound was similarly synthesized from **16a** (35.0 mg, 57.0 μmol) as above. The reaction mixture was stirred for 48 h. The crude product was purified by chromatography on silica gel with hexane–chloroform (10:1) eluent. Yellow solid; yield 25 mg (71%); mp 250–253 °C (dec); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.12 (36H, d, $J = 6.8$ Hz), 1.20 (6H, septet, $J = 6.8$ Hz), 6.52 (2H, dd, $J = 6.8$, 8.3 Hz), 6.76 (2H, dd, $J = 7.3$, 8.3 Hz), 7.11 (2H, dd, $J = 6.8$, 8.3 Hz), 7.20 (2H, d, $J = 6.3$ Hz), 7.33–7.42 (8H, m), 7.51 (2H, d, $J = 8.8$ Hz), 7.65–7.69 (4H, m), 7.78 (2H, s), 7.83 (2H, d, $J = 8.3$ Hz), 8.01 (2H, s), 8.82 (2H, s), 9.34 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.71, 18.97, 79.45, 80.03, 80.80, 80.82, 80.84, 81.23, 96.91, 104.85, 119.86, 120.10, 120.75, 122.02, 123.48, 123.96, 124.25, 124.28, 124.45, 124.62, 126.77, 126.83, 128.43, 128.50, 128.75, 129.00, 130.48, 130.50, 130.53, 130.68, 131.04, 131.14, 131.32, 131.49, 131.58, 132.87 (2 aromatic signals missing); UV ($CHCl_3$) λ_{max} (ε) 258 (216000), 318 (21300), 385 (25300, sh), 405 (35400), 421 (36400), 441 (33400); FL ($CHCl_3$) λ_{em} 453, 480, 549 nm, Φ_f 0.030, τ_f 0.7, 6.0 ns; HRMS (FAB) Found m/z 1210.5308, Calcd for $C_{90}H_{74}Si_2$: [M^+] 1210.5329.

Cyclic Tetramer 10b. To a solution of **27b** (33 mg, 15 μmol) in THF (3 mL) was added TBAF (1.0 mol L^{-1} in THF, 30 μL, 30 μmol). After the solution was stirred for 30 min at room temperature, the solvent was evaporated. The residue was dissolved in pyridine (10 mL), and $Cu(OAc)_2 \cdot H_2O$ (74 mg, 0.38 mmol) and CuCl (30 mg, 0.30 mmol) were added. The solution was stirred for 20 h at room temperature. After the solvent was mostly evaporated, the residual solid was submitted to chromatography on silica gel (NH) with hexane–chloroform (1:1) eluent. The desired compound was obtained as a yellow solid. Yield 19 mg (68%); mp 223–226 °C (dec); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (12H, t, $J = 6.3$ Hz), 1.20–1.31 (104H, m), 1.48 (8H, m), 1.61 (8H, m), 1.75 (8H, m), 3.41 (8H, t, $J = 7.8$ Hz), 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 (100 MHz, $CDCl_3$): δ 14.17, 22.78, 28.50, 29.45, 29.76, 29.83, 30.55, 31.76, 32.02, 80.12, 81.13, 120.97, 123.19, 124.20, 125.04, 128.59, 130.66, 131.35, 135.64 (9 aliphatic signals missing); UV ($CHCl_3$) λ_{max} (ε) 265 (191000), 405 (27600), 428 (48700), 457 nm (63900); FL ($CHCl_3$) λ_{em} 475 nm, Φ_f 0.16, τ_f 5.2 ns; MS (MALDI-TOF) Found m/z 1905.61. Calcd for $C_{144}H_{176}$: [M^+] 1905.38.

Cyclic Tetramer 10a. This compound was similarly synthesized from **27a** (25 mg, 15 μmol) as above. The reaction times were 10 min and 14 h for the desilylation and macrocyclization steps, respectively. The crude product was purified by chromatography on silica gel (NH) with hexane–chloroform (10:1–1:1) eluent. The desired compound was obtained as orange crystals. Yield 2.0 mg (11%); mp 298–301 °C (dec); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.90 (8H, dd, $J = 6.8$, 8.8 Hz), 7.30 (8H, d, $J = 6.8$ Hz), 7.67 (8H, d, $J = 8.3$ Hz), 8.09 (4H, s), 9.29 (4H, s); UV ($CHCl_3$) λ_{max} (ε) 262 (214000), 398 (31400, sh), 417 (46100), 445 nm (51000); FL ($CHCl_3$) λ_{em} 469 nm, Φ_f 0.10, τ_f 2.0, 6.3 ns; HRMS (FAB) Found m/z 896.2514, Calcd for $C_{72}H_{32}$: [M^+] 896.2504.

Tetramer 28. To a degassed solution of **16a** (95 mg, 0.13 mmol) and **22** (106 mg, 0.17 mmol) in a mixture of THF (20 mL) and triethylamine (20 mL) were added [$Pd(PPh_3)_4$] (7.7 mg, 6.7 μmol) and CuI (1.3 mg, 6.7 μmol). After the reaction mixture was refluxed for 24 h under Ar, the solvent was evaporated. The crude product was purified by chromatography on silica gel with hexane–chloroform (3:1) eluent to give the desired compound as yellow crystals. Yield 181 mg (76%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.04–1.14 (42H, m), 6.76 (2H, dd, $J = 7.1$, 8.6 Hz), 7.22–7.48 (8H, m), 7.67 (2H, d, $J = 8.3$ Hz), 7.73 (2H, d, $J = 7.1$ Hz), 7.79 (2H, d, $J = 7.1$ Hz), 7.90 (2H, s), 8.03 (2H, d, $J = 8.6$ Hz), 8.07 (4H, m), 8.09 (2H, d, $J = 9.2$ Hz), 8.51 (2H, s), 9.15 (2H, s), 9.84 (2H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.36, 18.73, 79.35, 79.91, 80.73, 81.46, 93.51, 97.14, 104.53, 114.44, 118.14, 119.39, 120.13, 120.39, 121.64, 121.99, 123.95, 124.29, 124.54, 124.98, 125.27, 127.12, 127.59, 128.33, 128.72, 129.65, 131.02, 131.26, 131.57, 131.84, 133.22 (6 aromatic signals missing); UV ($CHCl_3$) λ_{max} (ε) 267 (307000), 318 (30200), 421 (58700), 442 nm (51200); FL ($CHCl_3$) λ_{em} 442, 470 nm, Φ_f 0.20, τ_f 4.2, 15.9 ns; HRMS (FAB) Found m/z 1186.5329, Calcd for $C_{88}H_{74}Si_2$: [M^+] 1186.5332.

Cyclic Tetramer 9. To a solution of **28** (25 mg, 21 μmol) in THF (6 mL) was added TBAF (1.0 mol L^{-1} in THF, 42 μL, 42 μmol). After the solution was stirred for 20 min at room temperature, the solvent was evaporated. The residue was dissolved in pyridine (20 mL), and $Cu(OAc)_2 \cdot H_2O$ (105 mg, 0.530 mmol) and CuCl (42 mg, 0.420 mmol) were added. The solution was stirred for 3 h at room temperature. After the solvent was mostly evaporated, the residual solid was submitted to chromatography on silica gel (NH) with chloroform eluent. Recrystallization from *o*-dichlorobenzene gave the desired compound as yellow crystals. Yield 14 mg (74%); mp 329–331 °C (dec); ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.12 (2H, dd, $J = 6.4$, 8.6 Hz), 6.37 (4H, d, $J = 6.4$ Hz), 6.54 (2H, dd, $J = 6.4$, 7.1 Hz), 7.36 (2H, dd, $J = 8.6$, 10.0 Hz), 7.43 (2H, s), 7.53 (2H, t, $J = 8.6$ Hz), 7.63 (2H, d, $J = 8.6$ Hz), 7.75 (2H, d, $J = 8.6$ Hz), 7.81 (4H, d, $J = 6.4$ Hz), 7.83 (2H, d, $J = 7.8$ Hz), 8.07 (2H, d, $J = 8.6$ Hz), 8.32 (2H, s), 8.67 (2H, s), 9.85 (2H, s); UV ($CHCl_3$) λ_{max} (ε) 257 (211000), 343 (13500), 421 (48800), 448 nm (61000); FL ($CHCl_3$) λ_{em} 479 nm, Φ_f 0.15, τ_f 7.4 ns; MS (MALDI-TOF) Found m/z 872.2504. Calcd for $C_{70}H_{32}$: [M^+] 872.2524; Anal. Found: C, 95.95; H, 3.73%. Calcd for $C_{70}H_{32}$: C, 96.31; H, 3.69%.

Enantiomeric Resolution. Enantiomers of **6**, **7**, and **9** were resolved by Chiral HPLC with a HITACHI L-6250 pump using a Daicel Chiralpak® IA column (10 mmϕ × 250 mm) with hexane–chloroform (3:1) eluent. Optical rotations were measured on a JASCO DIP-1000 digital polarimeter with a 3.5ϕ × 100 mm cell. CD spectra were measured on a JASCO J-810 polarimeter with a 10- or 1-mm cell. Enantiomers of **6** were eluted at 56.4 and 69.0 min. (+)-**6** (first fraction): $[\alpha]_D^{24}$ +206 ($CHCl_3$, *c* 0.063); CD ($CHCl_3$, 1.0×10^{-4} mol L^{-1}) λ ($\Delta\varepsilon$) 245 (−26.8), 267 (+13.1), 286 (+19.7), 311 (+14.5), 439 nm (+2.7). (−)-**6**: (second fraction): $[\alpha]_D^{24}$ −220 ($CHCl_3$, *c* 0.044); CD ($CHCl_3$, 7.0×10^{-5} mol L^{-1}) λ ($\Delta\varepsilon$) 244 (+27.1), 264 (−9.4), 286 (−18.8), 311 (−15.5), 438 nm (−2.6). Enantiomers of **7** were eluted at 44.5 and 58.1 min. (+)-**7** (first fraction): $[\alpha]_D^{22}$ +218 ($CHCl_3$, *c* 0.085); CD ($CHCl_3$, 4.4×10^{-4} mol L^{-1}) λ ($\Delta\varepsilon$) 241 (−48.1), 269 (+56.3), 326 (+26.2), 380 (+1.5), 448 nm (+5.70). (−)-**7** (second fraction): $[\alpha]_D^{22}$ −239 ($CHCl_3$, *c* 0.14); CD ($CHCl_3$, 4.0×10^{-4} mol L^{-1}) λ ($\Delta\varepsilon$) 241 (+50.8), 269 (−59.5), 326 (−27.0), 380 (−1.2), 447 nm (−6.0). A single crystal of **7** grown from a chlorobenzene solution was enantiopure and either of the above enantiomers. Enantiomers of **9** were eluted at 51.6 and 61.0 min. (+)-**9** (first fraction): $[\alpha]_D^{22}$ +244 ($CHCl_3$, *c* 0.085); CD ($CHCl_3$, 2.5×10^{-4} mol L^{-1}) λ ($\Delta\varepsilon$) 244 (−44.1), 267 (+35.9), 275 (+30.0), 289 nm (+31.7). (−)-**9** (second fraction): $[\alpha]_D^{22}$ −254 ($CHCl_3$, *c* 0.085); CD ($CHCl_3$, 2.5×10^{-4} mol L^{-1}) λ ($\Delta\varepsilon$) 246 (+41.2), 269 (−34.9), 276 (−29.6), 290 nm (+30.9).

X-ray Analysis. A single crystal of **7** was obtained by crystallization from a chlorobenzene solution. The diffraction data were collected on a Rigaku RAXIS-IV imaging plate diffractometer with Mo Kα radiation ($\lambda = 0.71070$ Å) to a maximum 2θ value of 55.0° at −150 °C. The reflection data were corrected for the Lorentz-polarization effects and secondary extinction. The structure was solved by the direct method (SIR2002)[33] and refined by the full-matrix least-squares method. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined isotropically. All calculations were performed using the CrystalStructure crystallographic software package. Formula $C_{68}H_{32}$, FW 849.00, crystal size $0.45 \times 0.30 \times 0.20\,mm^3$, orthorhombic, space group $P2_12_12_1$ (No. 19), $a = 13.0389(2)$, $b = 16.5850(3)$, $c = 20.1096(3)$ Å, $V = 4348.70(12)$ Å^3, $Z = 4$, $D_{calcd} = 1.297$ g cm^{-3}, μ(Mo Kα) = 0.737 cm^{-1}, No. of data 9664, $R1 = 0.0378$ [$I > 2.00\sigma(I)$], $wR2 = 0.0725$, GOF = 0.867. Flack parameter calculated from 4281 Friedel pairs was 3(4), which was ambiguous for the assignment of the absolute stereochemistry.[34] Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as deposition number CCDC 630820. Copies of the data can be obtained free of charge via http://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; e-mail: deposit@ccdc.cam.ac.uk).

DFT Calculations. The calculations were carried out with Gaussian 03 program[35] on a Windows computer. The structures were optimized by the DFT method with the M05/3-21G functional and basis set. The structures of **1** and **10a** were also calculated by AM1, PM3, HF/3-21G, B3LYP/3-21G, and M05-2X/3-21G methods.

Fluorescence Measurements. Fluorescence spectra were measured on a JASCO FP-6500 spectrofluorometer with a 10 mm cell at room temperature upon excitation at 393 nm. The fluorescence quantum yields were determined with a 9,10-diphenylanthracene sample as the standard. The fluorescence lifetimes were measured on a Spectra-Physics time-resolved spectrofluorometer system (Tsunami 3960/50-M2S) with a Ti:Sapphire laser.

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