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Functionalized [3 + 3]Cycloalkynes: Substituent Effect on Self-Aggregation by Nonplanar $\pi-\pi$ Interactions

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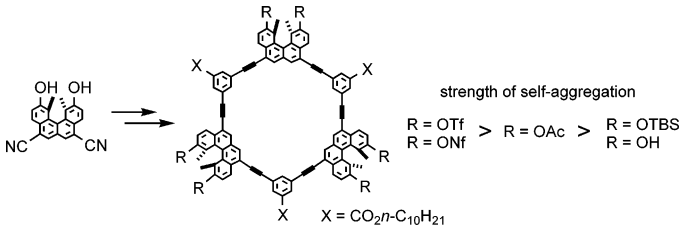
Received April 13, 2005



Optically active (*M*)-2,11-dihydroxy-1,12-dimethylbenzo[*c*]phenanthrene-5,8-dicarbonitrile was synthesized from (*M*)-1,12-dimethyl-2,11-dinitrobenzo[*c*]phenanthrene-5,8-dicarbonitrile by the reduction and hydroxylation of nitro groups. The compound was converted to several oxygen-functionalized [3 + 3]cycloalkynes with −OH, −OSiMe$_2$-*t*-Bu, −OAc, −OTf, or −ONf groups, which are chiral arylene ethynylene macrocycles containing three helicenes. The aggregation behaviors of these [3 + 3]cycloalkynes were examined in $CHCl_3$, THF, and acetone using ^{1}H NMR, CD, and vapor pressure osmometry (VPO) studies and were compared with that of the parent [3 + 3]cycloalkyne. An increasing strength of aggregation in $CHCl_3$ was observed in the following order of the substituted derivatives: −H > −ONf > −OTf > −OAc > −OSiMe$_2$-*t*-Bu. In THF the following strength of aggregation was observed: −OTf > −ONf > −OAc > −H > −OSiMe$_2$-*t*-Bu > −OH. The aggregation of the functionalized [3 + 3]cycloalkynes is stronger for the compounds with electron-withdrawing substituents than for those with electron-donating substituents. (*M*)-1,12-dimethylbenzo[*c*]phenanthrene-2,5,8,11-tetraol was also synthesized from the same intermediate. This electron-rich helicene was readily oxidized to 5,6-quinone in air, and the quinone was suggested to form a self-charge-transfer complex in solid state.

Introduction

$\pi-\pi$ Interactions are unique noncovalent interactions between aromatic systems with a face-to-face orientation and are considered to be involved in a wide range of self-assembly and molecular recognition phenomena as exemplified by the double-helical structure of DNA,[1] the three-dimensional structures of proteins,[2] and the host−guest complexation of aromatic compounds.[3] Synthetic arylene ethynylene macrocyclic compounds have recently attracted much attention, and some of them were found to self-aggregate in organic solvents via $\pi-\pi$ interactions.[4−7] Moore synthesized a series of phenylene ethynylene macrocycles (PEMs) with different ring sizes and various side chains and showed their hexamers to self-aggregate in organic solvents.[4] The self- or hetero-aggregation of phenylene diethynylene macrocycles (PDMs) in solution was investigated by Tobe.[5] Höger reported the self-aggregation of macrocycles with a phenylethynyl

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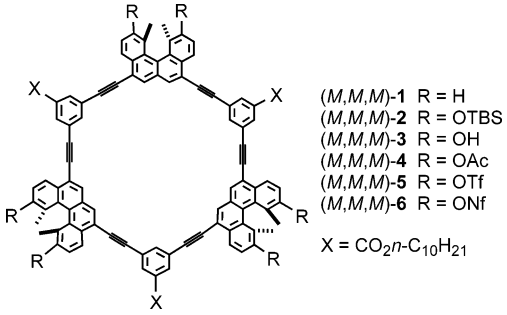
10.1021/jo050732f CCC: $30.25
Published on Web 06/11/2005

backbone.[6] Arylene ethynylene macrocycles are attractive compounds for studying the nature of π−π interactions and constructing a controlled self-assembly system, since various functionalized groups can be introduced to aromatic nuclei.

The effect of aromatic substituents on the above-mentioned aggregation is an interesting subject that can be studied using these compounds. Steric hindrances, such as the introduction of *tert*-butyl groups at a side chain, inhibit the self-aggregation of PEMs and PDMs,[4b,5a] which is understandable taking into account the face-to-face orientation in such aggregation. The electronic effect may be more intriguing, since it can control the aggregation by adjusting the electronic properties of the π electron system. Moore reported that PEMs with alkoxycarbonyl groups self-aggregate, whereas PEMs with alkoxy or acyloxy groups do not.[4b] Tobe also noted that PDMs with alkoxycarbonyl groups self-aggregate.[5a,d] These results suggest that electron-withdrawing substituents promote the self-aggregation. The origin of π−π interactions was previously explained by Hunter using π−σ interactions, in which the attractive electrostatic interactions between negatively charged π electrons and the positively charged σ framework were considered to play important roles.[8] The introduction of electron-withdrawing substituents therefore reduces the repulsion between π electrons and promotes self-aggregation. However, the above studies on the substituent effect are not quite systematic, and their results are to some extent contradictory: Höger reported that PEMs with electron-donating alkoxy groups self-aggregate;[6] Tobe reported that the substitution of *m*-phenylenes of PDMs with 2,6-pyridinediyl results in the inhibition of such self-aggregation.[5c] A systematic study of the electronic effect using a series of compounds with closely related substituents is required to understand the nature of π−π interactions.

Another issue that makes the study of π−π interactions complicated is their weak nature. Very often, the aggregation of arylene ethynylene macrocycles is largely assisted by other factors, particularly solvophobic interactions. PEMs and PDMs aggregate strongly when the solvent is changed from $CHCl_3$ to a polar solvent, such as acetone or methanol, in which the association constants increase by 2 or 3 orders of magnitude.[4c,5d] It is therefore not very easy to evaluate the substituent effect of pure π−π interactions.

During our studies of the synthesis and properties of optically active helicene derivatives, the chiral [3 + 3]-cycloalkyne (*P*,*P*,*P*)-**1**, which is an arylene ethynylene macrocycle with three (*P*)-helicenes and three *m*-phenylene moieties, was found to form a strong and selective bimolecular aggregate in $CHCl_3$ and benzene.[9] Its aggregation was ascribed to the π−π interactions between the nonplanar π electron system of a helicene, and solvophobic interactions were considered unimportant in this case. A sharp transition was observed between a monomer and a bimolecular aggregate by changing the concentration of (*P*,*P*,*P*)-**1**: (*P*,*P*,*P*)-**1** is monomeric in $CHCl_3$ below 1 mM and is dimeric above 1 mM. Another unique aspect of the aggregation is that (*P*,*P*,*P*)-**1** forms a selective bimolecular aggregate without forming higher aggregates. The phenomenon is highly contrasted to the higher-aggregate formation of known arylene ethynylene macrocycles noted above.[4c,5d] Studies of the oligomeric derivatives with connected (*P*,*P*,*P*)-**1** moieties revealed that the diversity of the aggregation behaviors of these derivatives depends on the structure of the linker moiety: Oligomers with flexible linkers form intramolecular aggregates, those with rigid and linear linkers form bimolecular aggregates,[10] and a dimer with a rigid and nonplanar *cis*-azo linker polymerizes.[11] These studies provide a novel method of inducing controlled self-aggregation employing π−π interactions. Recently, linear oligomers have also been found to exhibit unique aggregation behavior by π−π interactions: Those oligomers with more than six helicenes were under equilibrium between the helical dimer and the random coil monomer in solution.[12] The unfolding rate of a helical heptamer to the random coil structure in aromatic solvent is markedly influenced by the type of the aromatic substituent. The rate constant *k* differs by 7 orders of magnitude between iodobenzene and trifluoromethylbenzene, and log *k* exhibits good negative correlation to the hardness η of aromatic molecules (HSAB principle). This study indicates another interesting aspect of the π−π interactions of helicene.



Examined in this study is the substituent effect on the self-aggregation of [3 + 3]cycloalkyne derivatives. Five [3 + 3]cycloalkynes, (*M*,*M*,*M*)-**2**, (*M*,*M*,*M*)-**3**, (*M*,*M*,*M*)-**4**, (*M*,*M*,*M*)-**5**, and (*M*,*M*,*M*)-**6**, with different oxygen functional groups, −$OSiMe_2$-*t*-Bu, −OH, −OAc, −OTf, and −ONf, were employed. Since Hammett σ[13] increases in the order of −OH ($\sigma_p = -0.37$) < −$OSiMe_3$ ($\sigma_p = -0.27$) < −H ($\sigma_p = 0$) < −OAc ($\sigma_p = 0.31$) < −OTf ($\sigma_p = 0.53$), it was expected that the electronic effect of the substituent on π−π interactions can be clarified by comparing the aggregation of closely structurally related compounds. It should also be noted that solvophobic interactions are less important for the self-aggregation of functionalized [3 + 3]cycloalkynes, which would facilitate the analysis of the π−π interaction.

Results and Discussion

The 2,11-difunctionalized helicenes required in the present synthesis were prepared from the dinitrohelicene

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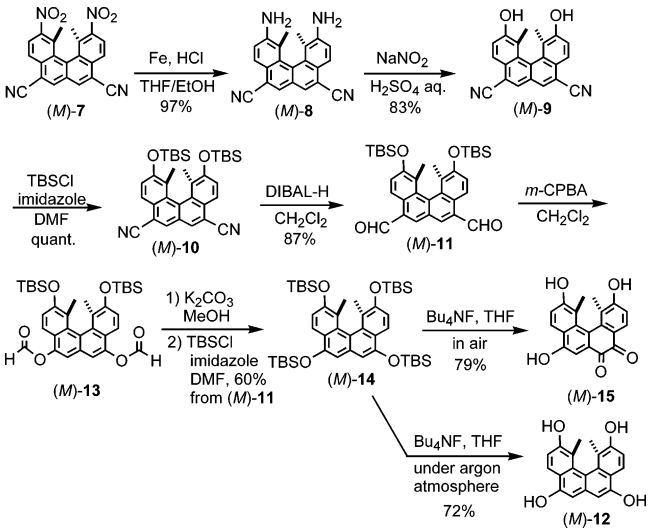
SCHEME 1



(*M*)-**7** previously obtained (Scheme 1).[14] (*M*)-**7** was reduced with iron to form the amine (*M*)-**8** in 97% yield. The diazoniation of (*M*)-**8** followed by heating in 20% aqueous sulfuric acid gave the dihydroxyhelicene (*M*)-**9** in 83% yield, which was converted to silylated (*M*)-**10** in a quantitative yield. The DIBAL-H reduction of (*M*)-**10** produced the aldehyde (*M*)-**11** in 87% yield. At this stage, it was considered interesting to prepare the 2,5,8,11-tetrahydroxyhelicene (*M*)-**12** by the oxidation of 5,8-diformyl groups, since such electron-rich helicenes are relatively rare.[15] The Baeyer−Villiger oxidation of (*M*)-**11** produced the diformylhelicene (*M*)-**13**, and hydrolysis followed by silyl protection gave the tetrakis(*tert*-butyldimethylsilanyloxy)helicene (*M*)-**14**. The desilylation of (*M*)-**14** with Bu_4NF in THF in air gave the trihydroxyquinone (*M*)-**15** in 79% yield, which indicated that (*M*)-**12** is sensitive to oxygen. Then, the solvents were degassed, and all the manipulations were conducted under argon atmospheres, which gave the desired (*M*)-**12** in 72% yield. (*M*)-**12** was unstable even under neutral conditions and was gradually oxidized to (*M*)-**15** in methanol in air. The color of (*M*)-**15** considerably differed

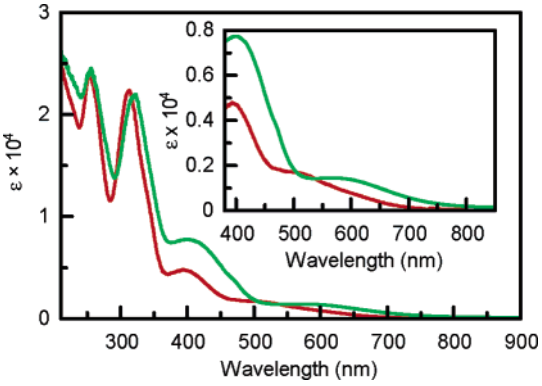
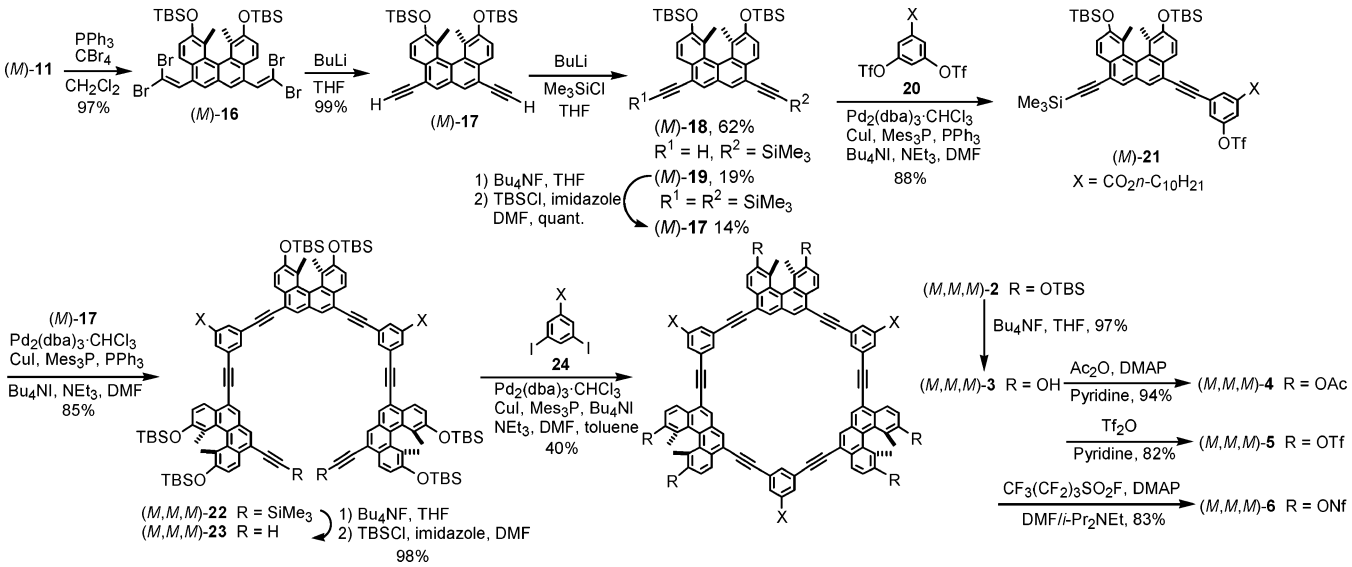


FIGURE 1. UV−vis spectra of (*M*)-**15** in methanol (10 μM, 25 °C, red line) and on quartz surface (green line). The inset is a magnification of the visible region.

in solution and in solid state: A methanol solution of (*M*)-**15** was red, whereas solid (*M*)-**15** dark green. The UV−vis spectra of (*M*)-**15** measured on a quartz surface exhibited absorption up to 800 nm with a maximum at approximately 600 nm (Figure 1), which may be assigned to a charge-transfer (CT) band.[16]

Several [3 + 3]cycloalkynes with different oxygen substituents were synthesized from (*M*)-**11** according to the method employed for the parent compound (*M*,*M*,*M*)-**1** (Scheme 2).[9] (*M*)-**11** was converted to the bis(dibromoolefin) (*M*)-**16** in 97% yield and was treated with excess butyllithium giving the diacetylene (*M*)-**17** in 99% yield. To discriminate between the two acetylene parts, (*M*)-**17** was treated with 1.1 equiv of butyllithium and chlorotrimethylsilane in THF at −100 °C, and a monoprotected acetylene (*M*)-**18** was obtained in 62% yield, which was accompanied by diprotected (*M*)-**19**. (*M*)-**19** could be converted to (*M*)-**17** in a quantitative yield. The Sonogashira coupling[17] of (*M*)-**18** and 5 equiv of ditriflate **20** gave (*M*)-**21**. Then, (*M*)-**21** was coupled with (*M*)-**17** yielding the trimer (*M*,*M*,*M*)-**22**, and exhaustive desilylation by Bu_4NF followed by the *tert*-butyldimethylsilyl protection of the hydroxyl groups produced the precursor (*M*,*M*,*M*)-**23** for cyclization. The cyclization of (*M*,*M*,*M*)-**23** and the diiodobenzene **24** under highly diluted condi-

SCHEME 2



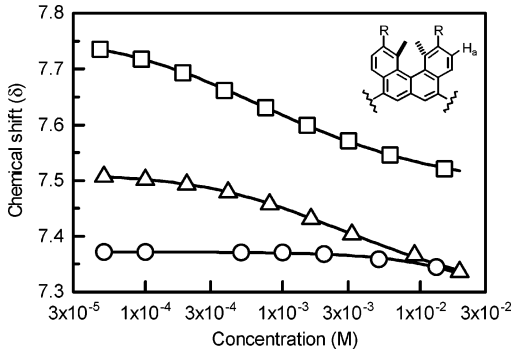


FIGURE 2. Concentration dependence of ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) chemical shifts for the aromatic proton H_a of (*M*,*M*,*M*)-**2** (○, $K = 1.3\ M^{-1}$), (*M*,*M*,*M*)-**4** (△, $K = 2.3 \times 10^2\ M^{-1}$), and (*M*,*M*,*M*)-**5** (□, $K = 9.7 \times 10^2\ M^{-1}$).

tions produced the hexakis(*tert*-butyldimethylsilanyloxy)-[3 + 3]cycloalkyne (*M*,*M*,*M*)-**2** in 40% yield. The desilylation of (*M*,*M*,*M*)-**2** gave the hexahydroxy[3 + 3]cycloalkyne (*M*,*M*,*M*)-**3**, which was treated with acetic anhydride, trifluoromethanesulfonic anhydride, and nonafluorobutanesulfonyl fluoride to produce (*M*,*M*,*M*)-**4** (94%), (*M*,*M*,*M*)-**5** (82%), and (*M*,*M*,*M*)-**6** (83%), respectively. The cyclic compounds were characterized by ^{1}H and ^{13}C NMR studies, MALDI-TOF MS, and elemental analyses.[18]

The aggregations of (*M*,*M*,*M*)-**2**, (*M*,*M*,*M*)-**4**, (*M*,*M*,*M*)-**5**, and (*M*,*M*,*M*)-**6** in $CHCl_3$ were studied using ^{1}H NMR, CD, and VPO techniques. (*M*,*M*,*M*)-**3** was not examined here because of its very low solubility in $CHCl_3$. The ^{1}H NMR ($CDCl_3$, 25 °C) spectra of (*M*,*M*,*M*)-**2** with electron-donating groups showed a very weak concentration dependence, while those of (*M*,*M*,*M*)-**4** and (*M*,*M*,*M*)-**5** with electron-withdrawing groups exhibited relatively strong concentration dependences. The ^{1}H NMR chemical shifts of the helicene proton H_a were plotted as functions of concentration (Figure 2), and assuming monomer−dimer equilibrium, the association constant K was obtained employing nonlinear least-squares approximation:[19] (*M*,*M*,*M*)-**2**, $K = 1.3\ M^{-1}$; (*M*,*M*,*M*)-**4**, $2.3 \times 10^2\ M^{-1}$; and

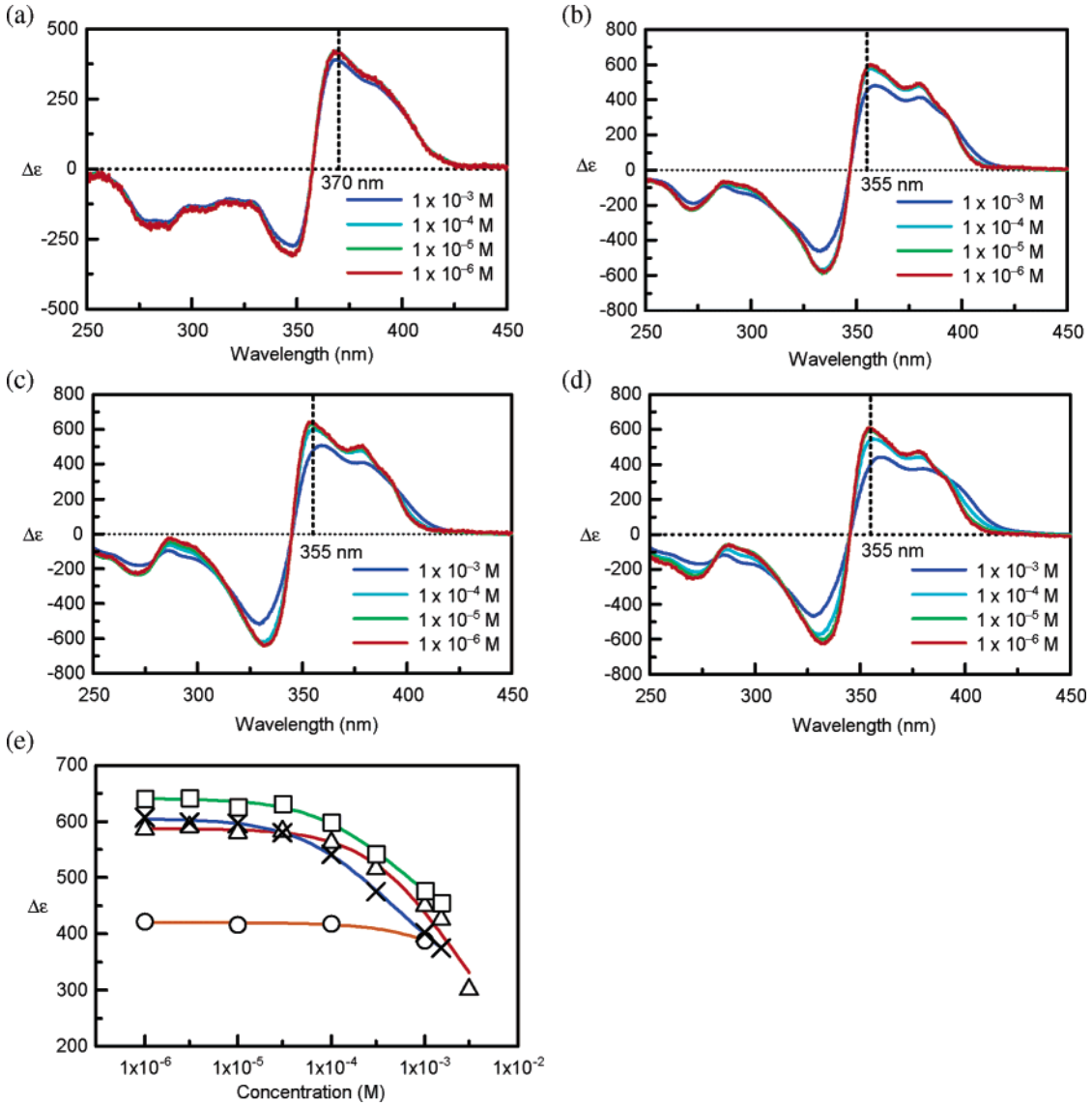


FIGURE 3. CD ($CHCl_3$, 25 °C) spectra of (a) (*M*,*M*,*M*)-**2**, (b) (*M*,*M*,*M*)-**4**, (c) (*M*,*M*,*M*)-**5**, and (d) (*M*,*M*,*M*)-**6**. (e) Concentration dependence of Δε ($CHCl_3$, 25 °C) at 355 nm of (*M*,*M*,*M*)-**4** (△, red line, $K = 2.3 \times 10^2\ M^{-1}$), (*M*,*M*,*M*)-**5** (□, green line, $K = 9.0 \times 10^2\ M^{-1}$), (*M*,*M*,*M*)-**6** (×, blue line, $K = 1.3 \times 10^3\ M^{-1}$), or Δε at 370 nm of (*M*,*M*,*M*)-**2** (○, orange line).

(*M*,*M*,*M*)-**5**, 9.7×10^2 M^{-1}. Since the ^1H NMR spectra of (*M*,*M*,*M*)-**6** in $CDCl_3$ were broad, *K* was not obtained.

The CD spectra of (*M*,*M*,*M*)-**2**, (*M*,*M*,*M*)-**4**, (*M*,*M*,*M*)-**5**, and (*M*,*M*,*M*)-**6** were measured in $CHCl_3$ at various concentrations. Although the CD spectra of (*M*,*M*,*M*)-**2** were concentration-independent between 0.001 mM and 0.1 mM, the Cotton effect at 350 and 370 nm slightly decreased at 1 mM (Figure 3a). (*M*,*M*,*M*)-**4**, (*M*,*M*,*M*)-**5**, and (*M*,*M*,*M*)-**6** exhibited relatively strong concentration dependences in CD above 0.01 mM, and provided isosbestic points at approximately 280, 310, 345, and 390 nm (Figure 3b–d). $\Delta\epsilon$ at 355 nm was plotted against concentration, and the association constants $K = 2.3 \times 10^2$ M^{-1}, 9.0×10^2 M^{-1}, and 1.3×10^3 M^{-1} were obtained (Figure 3e). The association constants of (*M*,*M*,*M*)-**4** and (*M*,*M*,*M*)-**5** obtained from the CD study are in very good agreement with the values obtained from the ^1H NMR study (Table 1).

TABLE 1. Association Constants of Functionalized [3 + 3]Cycloalkynes

	substituent	solvent	method	K (M^{-1})
(*M*,*M*,*M*)-**2**	$-OSiMe_2$-*t*-Bu	$CDCl_3$	^1H NMR	1.3
		THF-d_8	^1H NMR	3.4×10
(*M*,*M*,*M*)-**4**	−OAc	$CDCl_3$	^1H NMR	2.3×10^2
		$CHCl_3$	CD	2.3×10^2
		THF	CD	1.8×10^3
(*M*,*M*,*M*)-**5**	−OTf	$CDCl_3$	^1H NMR	9.7×10^2
		$CHCl_3$	CD	9.0×10^2
(*M*,*M*,*M*)-**6**	−ONf	$CHCl_3$	CD	1.3×10^3
		THF	CD	2.5×10^3
(*M*,*M*,*M*)-**3**	−OH	THF-d_8	^1H NMR	4.2×10^{-1}
		acetone-d_6	^1H NMR	1.7×10^3
		acetone	CD	2.1×10^3

The association constants *K* of the functionalized [3 + 3]cycloalkynes in $CDCl_3$ or $CHCl_3$ increase in the following order of the substituted derivatives: −ONf > −OTf > −OAc > $-OSiMe_2$-*t*-Bu. This indicates that the introduction of electron-withdrawing groups promotes aggregation. To obtain information on the aggregation structure, vapor pressure osmometry (VPO) was conducted (Figure 4). The apparent molecular weight of (*M*,*M*,*M*)-**2** in $CHCl_3$ at 35 °C was constant at the concentrations between 0.5 mM and 20 mM, indicating the monomeric nature of (*M*,*M*,*M*)-**2**. (*M*,*M*,*M*)-**4**, (*M*,*M*,*M*)-**5**, and (*M*,*M*,*M*)-**6** with electron-withdrawing substituents turned out to be under monomer−dimer equilibrium by VPO, and the aggregation became stronger in the order of (*M*,*M*,*M*)-**6** > (*M*,*M*,*M*)-**5** > (*M*,*M*,*M*)-**4**, as determined from the degree of aggregation at each concentration. The order is in accordance with the association constants *K* obtained from the ^1H NMR and CD studies. The parent (*P*,*P*,*P*)-**1**, however, exhibited the stronger aggregation in $CHCl_3$ than the oxygen-substituted derivatives.[9] These results suggest that substituents at the helicene moieties exhibit steric hindrances.

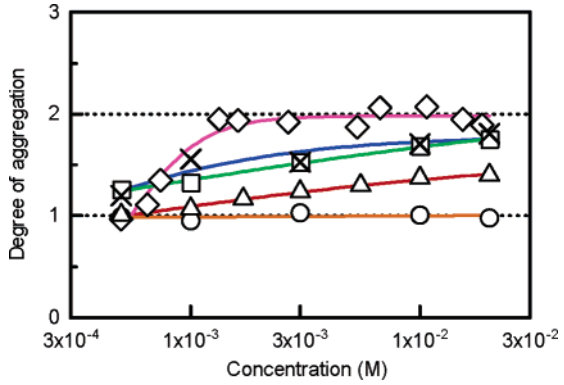


FIGURE 4. Degree of aggregation by VPO ($CHCl_3$, 35 °C) for (*P*,*P*,*P*)-**1** (◇, purple line),[9] (*M*,*M*,*M*)-**2** (○, orange line) (*M*,*M*,*M*)-**4** (△, red line), (*M*,*M*,*M*)-**5** (□, green line), and (*M*,*M*,*M*)-**6** (×, blue line). Degree of aggregation = (apparent molecular weight obtained by VPO)/(theoretical molecular weight of monomer).

Next, aggregation was examined in THF, since all the [3 + 3]cycloalkynes including (*M*,*M*,*M*)-**3** are soluble in this solvent. The aromatic H_a proton absorption of (*M*,*M*,*M*)-**2** in THF-d_8 was concentration-dependent above 1 mM giving $K = 3.4 \times 10$ M^{-1} (Figure 5), which is slightly stronger than that in $CDCl_3$. (*M*,*M*,*M*)-**3** in THF-d_8 showed a very weak concentration dependence in the chemical shifts of H_a proton above 10 mM, yielding $K = 4.2 \times 10^{-1}$ M^{-1}. Since the aromatic ^1H NMR spectra of (*M*,*M*,*M*)-**4**, (*M*,*M*,*M*)-**5**, and (*M*,*M*,*M*)-**6** were considerably broad in THF-d_8, *K* could not be determined.

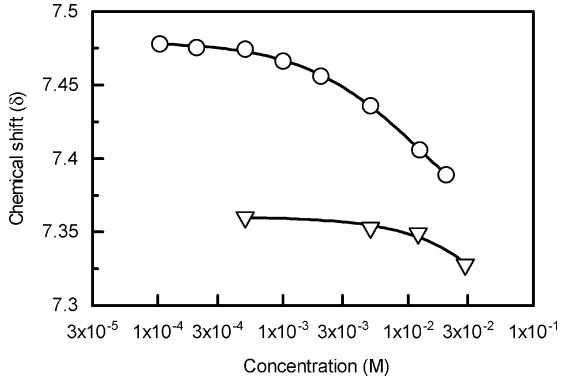


FIGURE 5. Concentration dependence of ^1H NMR (400 MHz, THF-d_8, 25 °C) chemical shifts for aromatic proton H_a of (*M*,*M*,*M*)-**2** (○, $K = 3.4 \times 10$ M^{-1}) and (*M*,*M*,*M*)-**3** (▽, $K = 4.2 \times 10^{-1}$ M^{-1}).

The CD spectra of (*M*,*M*,*M*)-**2** in THF exhibited a very weak concentration dependence above 0.1 mM (Figure 6a), which is consistent with the results of ^1H NMR. The intensity of the Cotton effect of (*M*,*M*,*M*)-**3** did not change at the concentrations between 0.001 mM and 1 mM (Figure 6b). The CD spectra of (*M*,*M*,*M*)-**4** and (*M*,*M*,*M*)-**6** were concentration-dependent above 0.01 mM (Figures 6c and e), and $K = 1.8 \times 10^3$ M^{-1} and 2.5×10^3 M^{-1}, respectively, were obtained using $\Delta\epsilon$ at 355 nm (Figure 6f). The CD spectra of (*M*,*M*,*M*)-**5** exhibited complex be-

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(19) Nogales, D. F.; Ma, J.-S.; Lightner, D. A. *Tetrahedron* **1993**, *49*, 2361−2372.

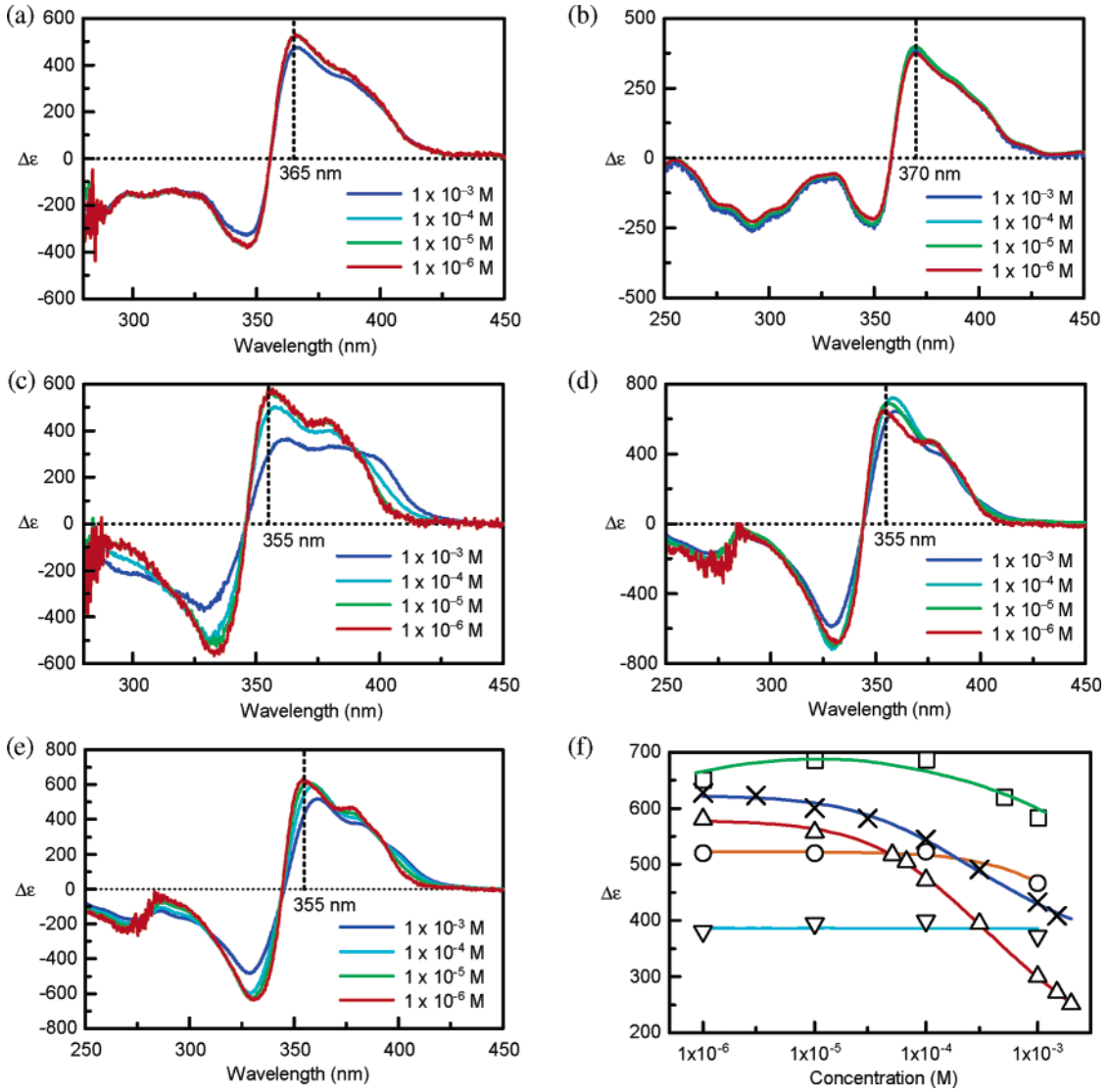

FIGURE 6. CD (THF, 25 °C) spectra of (a) (*M*,*M*,*M*)-**2**, (b) (*M*,*M*,*M*)-**3**, (c) (*M*,*M*,*M*)-**4**, (d) (*M*,*M*,*M*)-**5**, and (e) (*M*,*M*,*M*)-**6**. (f) Concentration dependence of Δε (THF, 25 °C) at 365 nm of (*M*,*M*,*M*)-**2** (○, orange line), Δε at 370 nm of (*M*,*M*,*M*)-**3** (▽, light blue line), or Δε at 355 nm of (*M*,*M*,*M*)-**4** (△, red line, $K = 1.8 \times 10^3$ M^{-1}), (*M*,*M*,*M*)-**5** (□, green line), and (*M*,*M*,*M*)-**6** (×, blue line, $K = 2.5 \times 10^3$ M^{-1}).

havior (Figure 6d), and the association constant was not determined, the reason of which is not clear at present.

The apparent molecular weights of (*M*,*M*,*M*)-**2** and (*M*,*M*,*M*)-**3** measured by VPO in THF (45 °C) corresponded to that of a monomer, being concentration-independent between 0.5 mM and 20 mM (Figure 7). The aggregation of the [3 + 3]cycloalkynes in THF became stronger in the order of (*M*,*M*,*M*)-**5** > (*M*,*M*,*M*)-**6** > (*M*,*M*,*M*)-**4** > (*M*,*M*,*M*)-**1** > (*M*,*M*,*M*)-**2** > (*M*,*M*,*M*)-**3**, which is in accordance with the electron-withdrawing ability of the substituents. It turned out that the electronic factor is important in THF as well as in $CHCl_3$, and that the introduction of stronger electron-withdrawing substituents enhances π−π interactions. The relatively small solvent effect between THF and $CHCl_3$ suggested that solvophobic interactions are not important in this system. It should be noted that (*M*,*M*,*M*)-**5** also formed a selective bimolecular aggregate above 3 mM in THF as did (*P*,*P*,*P*)-**1** in $CHCl_3$. It is likely that all [3 + 3]cycloalkynes form bimolecular aggregates without forming a higher degree of aggregation, which is an interesting aspect of nonplanar π−π interactions.

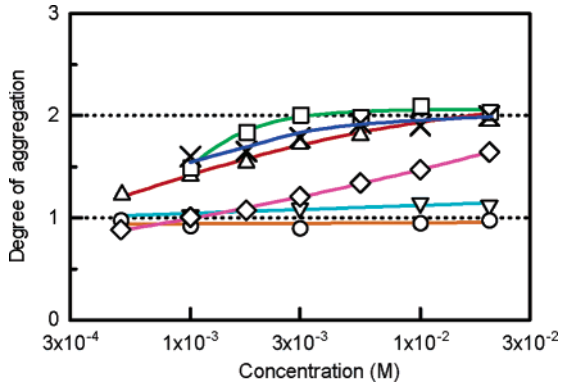

FIGURE 7. Degree of aggregation by VPO (THF, 45 °C) for (*M*,*M*,*M*)-**1** (◇, purple line), (*M*,*M*,*M*)-**2** (○, orange line), (*M*,*M*,*M*)-**3** (▽, light blue line), (*M*,*M*,*M*)-**4** (△, red line), (*M*,*M*,*M*)-**5** (□, green line), and (*M*,*M*,*M*)-**6** (×, blue line).

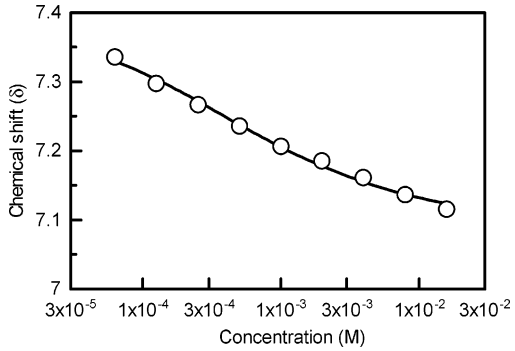

FIGURE 8. Concentration dependence of ^{1}H NMR (400 MHz, acetone-d_6, 25 °C) chemical shift for the aromatic proton H_a of (*M*,*M*,*M*)-**3** ($K = 1.7 \times 10^3$ M^{-1}).

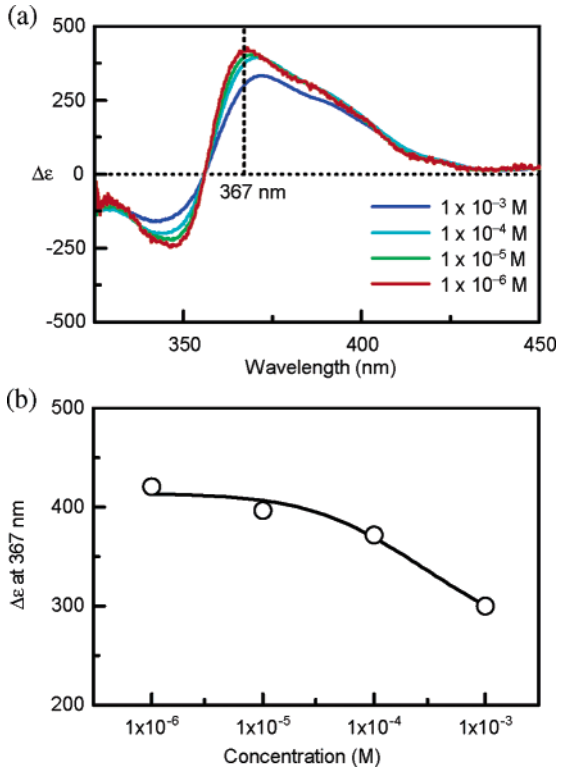

FIGURE 9. (a) CD (acetone, 25 °C) spectra of (*M*,*M*,*M*)-**3**. (b) Concentration dependence of Δε (acetone, 25 °C) at 367 nm of (*M*,*M*,*M*)-**3** ($K = 2.1 \times 10^3$ M^{-1}).

In acetone, only (*M*,*M*,*M*)-**3** was soluble, and its ^{1}H NMR and CD spectra exhibited concentration dependences giving $K = 1.7 \times 10^3$ and 2.1×10^3 M^{-1}, respectively (Figures 8 and 9). The results are in contrast to the poor aggregation ability of this compound in the less polar solvent THF. It is likely that solvophobic interactions play an important role in such aggregation.[4c,d,5d,6] A VPO study of (*M*,*M*,*M*)-**3** in acetone revealed that (*M*,*M*,*M*)-**3** forms higher aggregates than dimer above 5.5 mM, unlike (*P*,*P*,*P*)-**1** in $CHCl_3$ and (*M*,*M*,*M*)-**5** in THF (Figure 10). This may also be explained by strong solvophobic interactions.

Conclusions

Five functionalized [3 + 3]cycloalkynes with different oxygen substituents, −OSiMe$_2$-*t*-Bu, −OH, −OAc, −OTf, and −ONf, were synthesized from (*M*)-1,12-dimethyl-2,-11-dinitrobenzo[*c*]phenanthrene-5,8-dicarbonitrile, and their aggregation was examined in $CHCl_3$, THF, and acetone using ^{1}H NMR, CD, and VPO techniques. It is now clear that [3 + 3]cycloalkynes with stronger electron-withdrawing substituents exhibit stronger aggregation. The results experimentally confirmed that $\pi-\pi$ interactions are promoted in electron-deficient aromatics probably due to the reduction in the degree of electrostatic repulsion between π electrons.

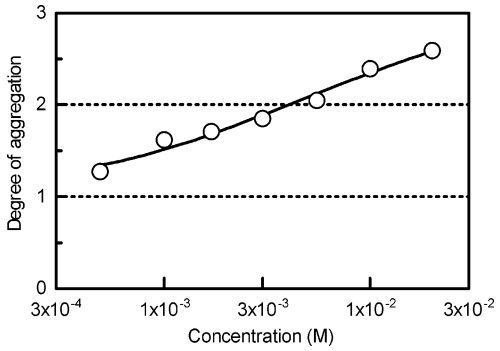

FIGURE 10. Degree of aggregation by VPO (acetone, 40 °C) for (*M*,*M*,*M*)-**3**.

Experimental Section

(*M*)-2,11-Diamino-1,12-dimethylbenzo[*c*]phenanthrene-5,8-dicarbonitrile, (*M*)-8. A solution of (*M*)-**7** (1 g, 2.53 mmol) in ethanol (40 mL) and tetrahydrofuran (40 mL) was heated to 90 °C, to which was added concentrated hydrochloric acid (1.2 mL) and reduced iron (24 g, 43 mmol). After being stirred at 90 °C for 1 h, the reaction mixture was filtered through Celite pad, and the pad was washed three times with ethyl acetate. The organic layers were washed with saturated aqueous sodium hydrogen carbonate, brine, and dried over sodium sulfate. The solvents were evaporated under reduced pressure, and recrystallization from hexane−acetone gave (*M*)-**8** (823 mg, 2.45 mmol, 97%): mp > 300 °C (hexane−acetone); $[\alpha]^{24}_D$ −1990 (*c* 0.10, acetone); LRMS (EI, 70 eV) *m/z* 336 (M^+, 100), 304 ($M^+ - 2NH_2$, 38); HRMS *m/z* calcd for $C_{22}H_{16}N_4$ 336.1375, found 336.1383; UV−vis ($CHCl_3$, 0.01 mM) λ (ϵ) 258 nm (3.3×10^4), 280 nm (2.4×10^4), 318 nm (3.3×10^4), 357 nm (2.3×10^4), 435 nm (4.4×10^3), 461 nm (6.2×10^3); IR (KBr) 3500−3200, 2224 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.53 (6H, s), 4.15 (4H, s), 7.26 (2H, d, J = 8.6 Hz), 7.97 (2H, s), 8.13 (2H, d, J = 8.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.2, 109.8, 116.9, 117.8, 118.5, 124.0, 124.6, 128.3, 128.4, 130.2, 132.5, 145.0. Anal. ($C_{22}H_{16}N_4$) Calcd: C, 78.55; H, 4.79; N, 16.66. Found: C, 78.13; H, 5.09; N, 16.19.

(*M*)-2,11-Dihydroxy-1,12-dimethylbenzo[*c*]phenanthrene-5,8-dicarbonitrile, (*M*)-9. To a solution of (*M*)-**8** (823 mg, 2.45 mmol) in 50% aqueous sulfuric acid (85 mL) was added sodium nitrite (355 mg, 5.14 mmol) in water (5 mL) at 0 °C. The mixture was stirred for 30 min at that temperature and was added dropwise to refluxing 20% aqueous sulfuric acid (255 mL). The mixture was stirred for 30 min at that temperature. The resulting solid was collected by filtration, and silica gel chromatography (hexane/ethyl acetate = 2:1) gave (*M*)-**9** (687 mg, 2.03 mmol, 83%): mp > 211 °C dec (hexane−ethyl acetate); $[\alpha]^{23}_D$ −614 (*c* 0.98, methanol); LRMS (EI, 70 eV) *m/z* 338 (M^+, 100), 321 ($M^+ - OH$, 40), 304 ($M^+ - 2OH$, 23); HRMS *m/z* calcd for $C_{22}H_{14}N_2O_2$ 338.1055, found 338.1045; UV−vis (methanol, 0.01 mM) λ (ϵ) 204 nm (6.3×10^4), 237 nm (3.6×10^4), 269 nm (2.5×10^4), 306 nm (4.0×10^4), 338 nm (2.5×10^4), 414 nm (5.2×10^3), 439 nm (6.4×10^3); IR (KBr) 3600−3100, 2228 cm^{-1}; ^{1}H NMR (400 MHz,

DMSO-d_6) δ 1.52 (6H, s), 7.56 (2H, d, J = 9.2 Hz), 8.07 (2H, d, J = 9.2 Hz), 8.45 (2H, s), 10.36 (2H, s); ^{13}C NMR (100 MHz, DMSO-d_6) δ 16.1, 108.7, 117.6, 119.1, 120.6, 123.2, 124.1, 128.6, 129.4, 129.7, 131.9, 155.9. Anal. ($C_{22}H_{14}N_2O_2 \cdot {}^1/_2H_2O$) Calcd: C, 76.07; H, 4.35; N, 8.06. Found: C, 76.07; H, 4.25; N, 8.09.

(*M*)-2,11-Bis(*tert*-butyldimethylsilanyloxy)-1,12-dimethylbenzo[*c*]phenanthrene-5,8-dicarbonitrile, (*M*)-10. Under an argon atmosphere, a mixture of (*M*)-**9** (687 mg, 2.03 mmol), imidazole (692 mg, 10.2 mmol), *tert*-butyldimethylsilyl chloride (766 mg, 5.08 mmol), and *N*,*N*-dimethylformamide (5 mL) was stirred for 12 h at room temperature. The reaction was quenched by adding saturated aqueous sodium hydrogen carbonate, and the organic materials were extracted with toluene. The organic layer was washed with water and brine and dried over magnesium sulfate. The solvent was evaporated under reduced pressure, and silica gel chromatography (hexane/ethyl acetate = 10:1) gave (*M*)-**10** (1.15 g, 2.03 mmol, 100%): mp 264−266 °C (hexane−diethyl ether); $[\alpha]^{24}_D$ −287 (*c* 1.00, $CHCl_3$); LRMS (EI, 70 eV) *m/z* 566 (M^+, 100), 509 (M^+ − *tert*-butyl, 36); HRMS *m/z* calcd for $C_{34}H_{42}N_2O_2Si_2$ 566.2785, found 566.2774; UV−vis ($CHCl_3$, 0.01 mM) λ (ϵ) 269 nm (2.1×10^4), 308 nm (4.7×10^4), 339 nm (3.3×10^4), 409 nm (4.3×10^3), 435 nm (4.9×10^3); IR (KBr) 2225 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.30 (6H, s), 0.39 (6H, s), 1.06 (18H, s), 1.66 (6H, s), 7.40 (2H, d, J = 8.7 Hz), 8.10 (2H, s), 8.20 (2H, d, J = 8.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ −3.7, −3.5, 17.1, 18.5, 25.8, 110.0, 117.5, 121.5, 123.7, 125.8, 126.1, 129.59, 129.65, 129.8, 132.5, 154.2. Anal. ($C_{34}H_{42}N_2O_2Si_2$) Calcd: C, 72.04; H, 7.47; N, 4.94. Found: C, 71.77; H, 7.45; N, 4.86.

(*M*)-2,11-Bis(*tert*-butyldimethylsilanyloxy)-1,12-dimethylbenzo[*c*]phenanthrene-5,8-dicarbaldehyde, (*M*)-11. Under an argon atmosphere, to a solution of (*M*)-**10** (578 mg, 1.02 mmol) in dichloromethane (10 mL) was added 1.0 M diisobutylaluminum hydride in hexane (10.2 mL, 10.2 mmol) at −98 °C, and the mixture was stirred for 30 min at that temperature. The reaction was quenched by adding 1 M aqueous hydrochloric acid, and the organic materials were extracted with chloroform. The organic layer was washed with saturated aqueous sodium hydrogen carbonate and brine and dried over magnesium sulfate. The solvents were evaporated under reduced pressure, and silica gel chromatography (toluene) gave (*M*)-**11** (510 mg, 0.892 mmol, 87%): mp 236−238 °C (toluene−methanol); $[\alpha]^{26}_D$ −45 (*c* 0.99, $CHCl_3$); LRMS (EI, 70 eV) *m/z* 572 (M^+, 100); HRMS *m/z* calcd for $C_{34}H_{44}O_4Si_2$ 572.2778, found 572.2784; UV−vis ($CHCl_3$, 0.01 mM) λ (ϵ) 266 nm (3.1×10^4), 325 nm (3.9×10^4), 450 nm (6.5×10^3); IR (KBr) 1685 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.29 (6H, s), 0.38 (6H, s), 1.05 (18H, s), 1.67 (6H, s), 7.36 (2H, d, J = 9.0 Hz), 8.23 (2H, s), 9.16 (2H, d, J = 9.0 Hz), 10.44 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ −3.7, −3.5, 17.2, 18.5, 25.8, 121.6, 123.6, 124.7, 125.6, 130.0, 131.1, 132.7, 133.8, 135.6, 153.6, 192.6. Anal. ($C_{34}H_{44}O_4Si_2$) Calcd: C, 71.28; H, 7.74. Found: C, 71.18; H, 7.78.

(*M*)-2,5,8,11-Tetrakis(*tert*-butyldimethylsilanyloxy)-1,12-dimethylbenzo[*c*]phenanthrene, (*M*)-14. Under an argon atmosphere, to a solution of (*M*)-**11** (510 mg, 0.892 mmol) in dichloromethane (10 mL) was added *m*-chloroperbenzoic acid (616 mg, 3.57 mmol) at 0 °C, and the mixture was stirred for 12 h at room temperature. The reaction was quenched by adding saturated aqueous sodium hydrogen carbonate, and the organic materials were extracted with chloroform. The organic layer was washed with water and brine and dried over magnesium sulfate. The solvents were evaporated under reduced pressure giving (*M*)-**13**, which was used for the next step without further purification.

Under an argon atmosphere, to a mixture of (*M*)-**13** and anhydrous potassium carbonate (369 mg, 2.68 mmol) was added degassed methanol (5 mL), and the mixture was stirred for 3 min at room temperature. The reaction was quenched by adding saturated aqueous ammonium chloride, and the organic materials were extracted with ethyl acetate. The organic layer was washed with brine and dried over sodium sulfate. The solvents were evaporated under reduced pressure. Under an argon atmosphere, to the residue were added imidazole (3.64 g, 53.5 mmol), *tert*-butyldimethylsilyl chloride (4.03 g, 26.8 mmol), and *N*,*N*-dimethylformamide (10 mL), and the mixture was stirred for 4 h at room temperature. The reaction was quenched by adding saturated aqueous sodium hydrogen carbonate, and the organic materials were extracted with toluene. The organic layer was washed with water and brine and dried over magnesium sulfate. The solvent was evaporated under reduced pressure, and silica gel chromatography (hexane/toluene = 10:1) gave (*M*)-**14** (417 mg, 0.536 mmol, 60% from (*M*)-**11**): mp 228−230 °C (toluene−methanol); $[\alpha]^{24}_D$ +28 (*c* 0.52, $CHCl_3$); LRMS (EI, 70 eV) *m/z* 776 (M^+, 100); HRMS *m/z* calcd for $C_{44}H_{72}O_4Si_4$ 776.4508, found 776.4536; UV−vis ($CHCl_3$, 0.01 mM) λ (ϵ) 303 nm (4.9×10^4), 314 nm (6.5×10^4); CD ($CHCl_3$, 1 mM) λ ($\Delta\epsilon$) 272 nm (−45), 293 nm (43), 313 nm (−46), 365 nm (17); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.27 (6H, s), 0.33 (6H, s), 0.36 (6H, s), 0.37 (6H, s), 1.05 (18H, s), 1.12 (18H, s), 1.73 (6H, s), 6.79 (2H, s), 7.10 (2H, d, J = 8.8 Hz), 8.08 (2H, d, J = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ −4.0, −3.9, −3.6, −3.5, 17.3, 18.5, 18.6, 26.0, 26.1, 108.0, 115.7, 117.2, 120.7, 122.3, 124.1, 134.9, 135.1, 150.5, 152.6. Anal. ($C_{44}H_{72}O_4Si_4$) Calcd: C, 67.98; H, 9.34. Found: C, 68.14; H, 9.25.

(*M*)-2,8,11-Trihydroxy-1,12-dimethylbenzo[*c*]phenanthrene-5,6-dione, (*M*)-15. To a solution of (*M*)-**14** (100 mg, 0.129 mmol) in tetrahydrofuran (5 mL) was added 1.0 M tetrabutylammonium fluoride in tetrahydrofuran (1.6 mL, 1.6 mmol), and the mixture was stirred for 1 h at room temperature. The reaction was quenched by adding saturated aqueous ammonium chloride, and the organic materials were extracted with ethyl acetate. The organic layer was washed with water and brine and dried over sodium sulfate. The solvents were evaporated under reduced pressure, and silica gel chromatography (hexane/ethyl acetate = 2:1) gave (*M*)-**15** (34 mg, 0.10 mmol, 79%): mp > 213 °C dec (hexane−acetone); $[\alpha]^{23}_D$ −1420 (*c* 0.01, methanol); LRMS (EI, 70 eV) *m/z* 334 (M^+, 69), 306 (M^+ − CO, 100), 291 (M^+ − CO − CH_3, 79); HRMS *m/z* calcd for $C_{20}H_{14}O_5$ 334.0841, found 334.0843; UV−vis (methanol, 0.01 mM) λ (ϵ) 254 nm (2.4×10^4), 314 nm (2.2×10^4), 394 nm (4.8×10^3); CD (methanol, 0.1 mM) λ ($\Delta\epsilon$) 258 nm (30), 297 nm (−17), 335 nm (20), 410 nm (−9), 462 nm (−2), 563 nm (−7); IR (KBr) 3500−3000, 1651 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.41 (3H, s), 1.74(3H, s), 6.80 (1H, d, J = 8.1 Hz), 7.06 (1H, s), 7.25 (1H, d, J = 9.0 Hz), 7.63 (1H, d, J = 8.1 Hz), 7.98 (1H, d, J = 9.0 Hz), 9.93 (1H, s), 10.79 (2H, s); ^{13}C NMR (100 MHz, DMSO-d_6) δ 14.9, 16.4, 100.4, 112.9, 117.3, 119.3, 120.1, 122.2, 123.3, 123.6, 128.8, 128.9, 131.0, 135.5, 142.7, 154.8, 155.6, 162.9, 181.2, 182.7. Anal. ($C_{20}H_{14}O_5 \cdot H_2O$) Calcd: C, 68.18; H, 4.58. Found: C, 68.45; H, 4.77.

(*M*)-1,12-Dimethylbenzo[*c*]phenanthrene-2,5,8,11-tetraol, (*M*)-12. Since (*M*)-**12** was sensitive to oxygen, all the procedures were conducted for this experiment under argon atmospheres. The solvents were freeze-evacuated three times before use. To a solution of (*M*)-**14** (30 mg, 0.039 mmol) in tetrahydrofuran (1 mL) was added 0.1 M tetrabutylammonium fluoride in tetrahydrofuran (1.7 mL, 0.17 mmol) at 0 °C, and the mixture was stirred for 30 s at that temperature. The reaction was quenched by adding saturated aqueous ammonium chloride, and the organic materials were extracted with ethyl acetate. The organic layer was washed with water and brine and dried over sodium sulfate. The solvents were evaporated under reduced pressure. The residue was triturated with chloroform, and was collected by filtration. Washing with chloroform and hexane gave pure (*M*)-**12** (8.9 mg, 0.028 mmol, 72%): $[\alpha]^{24}_D$ −220 (*c* 0.01, methanol); LRMS (EI, 70 eV) *m/z* 320 (M^+, 100); HRMS *m/z* calcd for $C_{20}H_{16}O_4$ 320.1049, found 320.1036; IR (KBr) 3500−3000 cm^{-1}; UV−vis (methanol, 0.01 mM) λ (ϵ) 254 nm (3.6×10^4), 311 nm (5.9×10^4); CD (methanol, 0.13 mM) λ ($\Delta\epsilon$) 252 nm (11), 273 nm (−14), 295 nm (6), 303 nm (4), 311 nm (9); 319 nm (1), 327 nm (4), 360

nm (4); ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.53 (6H, s), 6.66 (2H, s), 7.06 (2H, d, J = 8.7 Hz), 7.93 (2H, d, J = 8.7 Hz), 9.42 (2H, s), 10.00 (2H, s); ^{13}C NMR (150 MHz, DMSO-d_6) δ 16.3, 102.1, 112.4, 113.6, 118.1, 118.5, 120.5, 135.2, 136.3, 152.5, 154.3.

(*M*)-5,8-Bis(2,2-dibromoethenyl)-2,11-bis(*tert*-butyldimethylsilanyloxy)-1,12-dimethylbenzo[*c*]phenanthrene, (*M*)-16. Under an argon atmosphere, to a solution of triphenylphosphine (3.06 g, 11.7 mmol) in dichloromethane (5 mL) was added carbon tetrabromide (1.93 g, 5.82 mmol) at 0 °C. After being stirred for 30 min at that temperature, (*M*)-**11** (835 mg, 1.46 mmol) in dichloromethane (5 mL) was added dropwise. The mixture was stirred for 1 h at that temperature. Then, the solvent was evaporated under reduced pressure, and silica gel chromatography (toluene) gave (*M*)-**16** (1.25 g, 1.42 mmol, 97%): mp 170−172 °C (chloroform−methanol); $[\alpha]^{24}_D$ +124 (*c* 0.96, $CHCl_3$);. LRMS (FAB, NBA) *m/z* 880 (M^+), 882 ($M^+ + 2$), 884 ($M^+ + 4$), 886 ($M^+ + 6$), 888 ($M^+ + 8$); HRMS (FAB, NBA) *m/z* calcd for $C_{36}H_{44}Br_4O_2Si_2$ 879.9613, found 879.9601; UV−vis ($CHCl_3$, 0.01 mM) λ (ϵ) 265 nm (2.7×10^4), 327 nm (4.2×10^4); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.27 (6H, s), 0.37 (6H, s), 1.05 (18H, s), 1.71 (6H, s), 7.22 (2H, d, J = 9.0 Hz), 7.74 (2H, s), 7.80 (2H, d, J = 9.0 Hz), 7.94 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ −3.6, −3.5, 17.4, 18.5, 25.9, 92.8, 119.0, 122.3, 124.0, 124.9, 125.1, 125.2, 131.6, 132.3, 133.5, 135.7, 152.8. Anal. ($C_{36}H_{44}Br_4O_2Si_2$) Calcd: C, 48.88; H, 5.01; Br, 36.13. Found: C, 48.70; H, 5.04; Br, 36.23.

(*M*)-2,11-Bis(*tert*-butyldimethylsilanyloxy)-5,8-diethynyl-1,12-dimethylbenzo[*c*]phenanthrene, (*M*)-17. Under an argon atmosphere, to a solution of (*M*)-**16** (1.13 g, 1.28 mmol) in tetrahydrofuran (10 mL) was added 1.56 M butyllithium in hexane (3.6 mL, 5.6 mmol) at −100 °C. The mixture was stirred for 30 min at that temperature. The reaction was quenched by adding saturated aqueous ammonium chloride, and the organic materials were extracted with ethyl acetate. The organic layer was washed with water and brine and dried over magnesium sulfate. The solvents were evaporated under reduced pressure, and silica gel chromatography (hexane/toluene = 10:1) gave (*M*)-**17** (716 mg, 1.27 mmol, 99%): mp 167−168 °C (chloroform−methanol); $[\alpha]^{26}_D$ −46 (*c* 1.03, $CHCl_3$); LRMS (EI, 70 eV) *m/z* 564 (M^+, 100%); HRMS *m/z* calcd for $C_{36}H_{44}O_2Si_2$ 564.2880, found 564.2875; UV−vis ($CHCl_3$, 0.01 mM) λ (ϵ) 331 nm (5.1×10^4); IR (KBr) 3292, 2102 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.27 (6H, s), 0.37 (6H, s), 1.05 (18H, s), 1.69 (6H, s), 3.51 (2H, s), 7.26 (2H, d, J = 8.8 Hz), 7.86 (2H, s), 8.30 (2H, d, J = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ −3.7, −3.5, 17.1, 18.5, 25.9, 81.9, 82.0, 118.8, 119.6, 124.2, 125.1, 125.6, 127.2, 128.4, 131.5, 133.0, 153.0. Anal. ($C_{36}H_{44}O_2Si_2$) Calcd: C, 76.54; H, 7.85. Found: C, 76.40; H, 8.00.

(*M*)-2,11-Bis(*tert*-butyldimethylsilanyloxy)-5-ethynyl-1,12-dimethyl-8-(trimethylsilylethynyl)benzo[*c*]-phenanthrene, (*M*)-18, and (*M*)-2,11-Bis(*tert*-butyldimethylsilanyloxy)-1,12-dimethyl-5,8-bis(trimethylsilylethynyl)benzo[*c*]phenanthrene, (*M*)-19. Under an argon atmosphere, to a solution of (*M*)-**17** (371 mg, 0.658 mmol) in tetrahydrofuran (5 mL) was added 1.56 M butyllithium (0.46 mL, 0.72 mmol) at −100 °C. After being stirred for 30 min at that temperature, chlorotrimethylsilane (0.13 mL, 0.99 mmol) was added. The mixture was stirred for 15 min at that temperature. The reaction was quenched by adding saturated aqueous ammonium chloride, and the organic materials were extracted with ethyl acetate. The organic layer was washed with water and brine and dried over magnesium sulfate. The solvents were evaporated under reduced pressure and separation by recycling GPC gave (*M*)-**18** (259 mg, 0.407 mmol, 62%) and (*M*)-**19** (89 mg, 0.13 mmol, 19%). (*M*)-**17** (52 mg, 0.092 mmol, 14%) was recovered. (*M*)-**18**: mp 99−100 °C (chloroform−methanol); $[\alpha]^{26}_D$ +74 (*c* 1.09, $CHCl_3$); LRMS (EI, 70 eV) *m/z* 636 (M^+, 100); HRMS *m/z* calcd for $C_{39}H_{52}O_2Si_3$ 636.3275, found 636.3275. UV−vis ($CHCl_3$, 0.01 mM) λ (ϵ) 333 nm (5.7×10^4); IR (KBr) 3310, 2148, 2104 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.28 (6H, s), 0.37 (6H, s), 0.37 (9H, s), 1.05 (9H, s), 1.05 (9H, s), 1.68 (3H, s), 1.69 (3H, s), 3.49 (1H, s), 7.25 (1H, d, J = 8.8 Hz), 7.27 (1H, d, J = 8.2 Hz), 7.83 (1H, s), 7.84 (1H, s), 8.28 (1H, d, J = 8.8 Hz), 8.29 (1H, d, J = 8.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ −3.8, −3.7, 0.14, 16.9, 17.0, 18.3, 25.8, 81.9, 82.1, 99.6, 103.3, 118.8, 119.6, 119.7, 119.8, 124.3, 124.4, 125.1, 125.2, 125.6, 127.2, 127.3, 128.1, 128.6, 131.7, 133.08, 133.13, 153.11, 153.13. Anal. ($C_{39}H_{52}O_2Si_3$) Calcd: C, 73.53; H, 8.23. Found: C, 73.34; H, 8.16. (*M*)-**19**: mp 115−117 °C (chloroform−methanol); $[\alpha]^{24}_D$ +155 (*c* 1.22, $CHCl_3$); LRMS (EI, 70 eV) *m/z* 708 (M^+, 100); HRMS *m/z* calcd for $C_{42}H_{60}O_2Si_4$ 708.3670, found 708.3674; UV−vis ($CHCl_3$, 0.01 mM) λ (ϵ) 336 nm (6.4×10^4); IR (KBr) 2149 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.28 (6H, s), 0.37 (6H, s), 0.37 (18H, s), 1.05 (18H, s), 1.67 (6H, s), 7.25 (2H, d, J = 8.7 Hz), 7.81 (2H, s), 8.27 (2H, d, J = 8.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ −3.7, −3.5, 0.34, 17.1, 18.5, 25.9, 99.5, 103.3, 119.5, 119.6, 124.3, 125.0, 125.4, 127.1, 128.0, 131.7, 133.0, 152.9. Anal. ($C_{42}H_{60}O_2Si_4$) Calcd: C, 71.12; H, 8.53. Found: C, 70.92; H, 8.34.

(*M*)-3-[2,11-Bis(*tert*-butyldimethylsilanyloxy)-1,12-dimethyl-8-(trimethylsilylethynyl)benzo[*c*]phenanthren-5-ylethynyl]-5-trifluoromethanesulfonyloxybenzoic Acid Decyl Ester, (*M*)-21. Under an argon atmosphere, a mixture of decyl 3,5-bis(trifluoromethanesulfonyloxy)benzoate (1.56 g, 2.79 mmol), tris(dibenzylideneacetone)dipalladium(0) chloroform adduct (15 mg, 0.014 mmol), cuprous iodide (32 mg, 0.17 mmol), trimesitylphosphine (33 mg, 0.085 mmol), triphenylphosphine (22 mg, 0.084 mmol), tetrabutylammonium iodide (414 mg, 1.12 mmol), triethylamine (0.33 mL), and *N*,*N*-dimethylformamide (6.5 mL) was freeze-evacuated three times in flask A. In flask B, a solution of (*M*)-**18** (357 mg, 0.561 mmol) in *N*,*N*-dimethylformamide (2 mL) was freeze-evacuated three times and then added to flask A dropwise. The mixture was stirred for 1 h at room temperature. The reaction was quenched by adding saturated aqueous ammonium chloride, and the organic materials were extracted with toluene. The organic layer was washed with brine and dried over magnesium sulfate. The solvents were evaporated under reduced pressure, and separation by recycling GPC gave (*M*)-**21** (512 mg, 0.490 mmol, 88%): mp 55−58 °C (chloroform−methanol); $[\alpha]^{23}_D$ +203 (*c* 1.05, $CHCl_3$); HRMS (FAB, NBA) *m/z* calcd for $C_{57}H_{75}F_3O_7SSi_3$ 1044.4493, found 1044.4481; UV−vis ($CHCl_3$, 0.01 mM) λ (ϵ) 347 nm (5.2×10^4). IR (KBr) 2208, 2149, 1731 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.29 (3H, s), 0.30 (3H, s), 0.38 (3H, s), 0.38 (9H, s), 0.39 (3H, s), 0.87 (3H, t, J = 6.6 Hz), 1.06 (9H, s), 1.06 (9H, s), 1.24−1.50 (14H, m), 1.70 (3H, s) 1.71 (3H, s), 1.82 (2H, quin, J = 6.9 Hz), 4.39 (2H, t, J = 6.9 Hz), 7.28 (1H, d, J = 8.8 Hz), 7.32 (1H, d, J = 8.8 Hz), 7.73 (1H, dd, J = 2.4, 1.2 Hz), 7.86 (1H, s), 7.90 (1H, s), 7.91 (1H, dd, J = 2.4, 1.2 Hz), 8.30 (1H, d, J = 8.8 Hz), 8.31 (1H, d, J = 8.8 Hz), 8.33 (1H, t, J = 1.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ −3.8, −3.7, 0.13, 14.1, 16.9, 17.0, 18.3, 22.7, 25.8, 25.9, 28.6, 29.25, 29.29, 29.50, 29.52, 31.9, 66.2, 91.1, 91.3, 99.8, 103.2, 117.7, 118.5, 119.7, 119.79, 119.83, 120.0, 122.0, 124.1, 124.5, 125.2, 125.4, 125.9, 126.4, 126.8, 127.4, 128.0, 128.5, 131.8, 132.5, 133.1, 133.2, 133.3, 149.2, 153.2, 153.3, 164.2. Anal. ($C_{57}H_{75}F_3O_7SSi_3$) Calcd: C, 65.48; H, 7.23; F, 5.45; S, 3.07. Found: C, 65.41; H, 7.18; F, 5.75; S, 3.06.

Trimer, (*M*,*M*,*M*)-22. Under an argon atmosphere, a mixture of (*M*)-**21** (499 mg, 0.478 mmol), tris(dibenzylideneacetone)dipalladium(0) chloroform adduct (12 mg, 0.012 mmol), cuprous iodide (27 mg, 0.14 mmol), trimesitylphosphine (28 mg, 0.072 mmol), triphenylphosphine (19 mg, 0.072 mmol), tetrabutylammonium iodide (353 mg, 0.956 mmol), triethylamine (0.38 mL), and *N*,*N*-dimethylformamide (7.5 mL) was freeze-evacuated three times in flask A. In flask B, a solution of (*M*)-**17** (135 mg, 0.238 mmol) in *N*,*N*-dimethylformamide (3 mL) was freeze-evacuated three times and then added to flask A dropwise. The mixture was stirred for 1 h at room temperature. The reaction was quenched by adding saturated aqueous ammonium chloride, and the organic materials were extracted with toluene. The organic layer was washed with brine, and dried over magnesium sulfate. The solvents were evaporated

under reduced pressure, and separation by recycling GPC gave (*M,M,M*)-**22** (476 mg, 0.202 mmol, 85%): mp 170−171 °C (chloroform−methanol); $[\alpha]^{23}_D$ +341 (*c* 1.04, $CHCl_3$); MALDI-TOF MS *m/z* calcd for $^{12}C_{147}{}^{13}CH_{192}O_{10}Si_8$ 2354.3, found 2354.5; UV−vis ($CHCl_3$, 1 μM) λ (ε) 346 nm (1.8×10^5); IR (KBr) 2205, 2148, 1726 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.29 (6H, s), 0.30 (6H, s), 0.31 (6H, s), 0.38 (18H, s), 0.38 (6H, s), 0.39 (6H, s), 0.41 (6H, s), 0.86 (6H, t, *J* = 6.8 Hz), 1.06 (18H, s), 1.06 (18H, s), 1.08 (18H, s), 1.20−1.54 (28H, m), 1.71 (6H, s), 1.72 (6H, s), 1.76 (6H, s), 1.86 (4H, quin, *J* = 6.8 Hz), 4.42 (4H, t, *J* = 6.8 Hz), 7.28 (2H, d, *J* = 8.8 Hz), 7.33 (2H, d, *J* = 9.2 Hz), 7.36 (2H, d, *J* = 9.4 Hz), 7.88 (2H, s), 7.93 (2H, s), 7.99 (2H, s), 8.17 (2H, dd, *J* = 1.7, 1.5 Hz), 8.30 (2H, d, *J* = 8.8 Hz), 8.33 (2H, dd, *J* = 1.7, 1.6 Hz), 8.34 (2H, dd, *J* = 1.6, 1.5 Hz), 8.42 (2H, d, *J* = 9.2 Hz), 8.44 (2H, d, *J* = 9.4 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ −3.8, −3.70, −3.67, 0.16, 14.1, 16.96, 17.03, 17.1, 18.3, 18.4, 22.7, 25.8, 25.9, 26.0, 28.7, 29.3, 29.5, 29.6, 31.9, 65.8, 89.5, 89.6, 92.6, 92.7, 99.6, 103.3, 119.3, 119.5, 119.7, 119.8, 119.9, 124.39, 124.43, 124.46, 124.49, 125.2, 125.26, 125.33, 125.7, 125.9, 127.1, 127.2, 127.4, 128.0, 128.1, 131.5, 131.9, 132.0, 132.3, 133.1, 133.26, 133.29, 138.3, 153.15, 153.23, 153.3, 165.5. Anal. ($C_{148}H_{192}O_{10}Si_8$) Calcd: C, 75.46; H, 8.21. Found: C, 75.35; H, 8.50.

Deprotected Trimer, (*M,M,M*)-23. To a solution of (*M*)-**22** (476 mg, 0.202 mmol) in tetrahydrofuran (7.5 mL) was added 1.0 M tetrabutylammonium fluoride in tetrahydrofuran (3.3 mL, 3.3 mmol) at 0 °C. After the mixture was stirred for 15 min at that temperature, saturated aqueous ammonium chloride was added. The organic materials were extracted with ethyl acetate. The organic layer was washed with brine and dried over sodium sulfate. The solvents were evaporated under reduced pressure. To the residue were added *tert*-butyldimethylsilyl chloride (366 mg, 2.43 mmol), imidazole (330 mg, 4.85 mmol), and *N,N*-dimethylformamide (10 mL), and the mixture was stirred for 12 h at room temperature. The reaction was quenched by adding saturated aqueous sodium hydrogen carbonate, and the organic materials were extracted with toluene. The organic layer was washed with water and brine and dried over magnesium sulfate. The solvent was evaporated under reduced pressure, and silica gel chromatography (hexane/toluene = 1:2) gave (*M,M,M*)-**23** (439 mg, 0.199 mmol, 98%): mp 161−163 °C (chloroform−methanol); $[\alpha]^{22}_D$ +318 (*c* 1.16, $CHCl_3$); MALDI-TOF MS *m/z* calcd for $^{12}C_{141}{}^{13}CH_{176}O_{10}Si_6$ 2210.2, found 2210.7; UV−vis ($CHCl_3$, 1 μM) λ (ε) 341 nm (1.6×10^5); IR (KBr) 3309, 2205, 2103, 1725 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.29 (6H, s), 0.30 (6H, s), 0.32 (6H, s), 0.38 (6H, s), 0.40 (6H, s), 0.42 (6H, s), 0.86 (6H, t, *J* = 6.8 Hz), 1.07 (18H, s), 1.07 (18H, s), 1.08 (18H, s), 1.20−1.57 (28H, m), 1.73 (6H, s), 1.73 (6H, s), 1.77 (6H, s), 1.86 (4H, quin, *J* = 6.8 Hz), 3.52 (2H, s), 4.42 (4H, t, *J* = 6.8 Hz), 7.28 (2H, d, *J* = 8.8 Hz), 7.35 (2H, d, *J* = 8.8 Hz), 7.37 (2H, d, *J* = 8.8 Hz), 7.91 (2H, s), 7.95 (2H, s), 7.99 (2H, s), 8.17 (2H, dd, *J* = 1.7, 1.5 Hz), 8.32 (2H, d, *J* = 8.8 Hz), 8.34 (2H, dd, *J* = 1.7, 1.6), 8.35 (2H, dd, *J* = 1.6, 1.5 Hz), 8.43 (2H, d, *J* = 8.8 Hz), 8.45 (2H, d, *J* = 8.8 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ −3.85, −3.83, −3.70, −3.67, 14.1, 17.0, 17.1, 18.3, 18.4, 22.7, 25.80, 25.82, 26.0, 28.7, 29.3, 29.5, 29.6, 31.9, 65.8, 81.96, 82.03, 89.49, 89.51, 92.6, 92.7, 119.0, 119.4, 119.5, 119.7, 119.78, 119.82, 124.36, 124.40, 124.44, 125.26, 125.31, 125.4, 125.8, 125.9, 127.1, 127.2, 127.3, 127.99, 128.03, 128.6, 131.5, 131.8, 132.0, 132.3, 133.16, 133.23, 133.3, 138.3, 153.2, 153.27, 153.33, 165.5. Anal. ($C_{142}H_{176}O_{10}Si_6$) Calcd: C, 77.12; H, 8.02. Found: C, 76.97; H, 7.99.

(*M,M,M*)-Hexakis(*tert*-butyldimethylsilanyloxy)[3 + 3]-cycloalkyne, (*M,M,M*)-2. Under an argon atmosphere, a mixture of tris(dibenzylideneacetone)dipalladium(0) chloroform adduct (3 mg, 2.9 μmol), cuprous iodide (7 mg, 0.037 mmol), trimesitylphosphine (7 mg, 0.018 mmol), tetrabutylammonium iodide (67 mg, 0.18 mmol), triethylamine (5 mL), and *N,N*-dimethylformamide (100 mL) was freeze-evacuated three times in flask A. In flask B, a solution of (*M,M,M*)-**23** (50 mg, 0.023 mmol) and decyl 3,5-diiodobenzoate (12 mg, 0.023 mmol) in toluene (4 mL) was freeze-evacuated three times and was added dropwise using a syringe pump to flask A at 45 °C for 4 h. The mixture was stirred for 3 h at that temperature. The reaction was quenched by adding saturated aqueous ammonium chloride, and the organic materials were extracted with toluene. The organic layer was washed with brine and dried over magnesium sulfate. The solvents were evaporated under reduced pressure, and separation by recycling GPC gave (*M,M,M*)-**2** (22 mg, 8.9 μmol, 40%): mp > 268 °C dec (chloroform−methanol); $[\alpha]^{23}_D$ +1198 (*c* 0.10, $CHCl_3$); MALDI-TOF MS *m/z* calcd for $^{12}C_{158}{}^{13}CH_{198}O_{12}Si_6$ 2468.3, found 2468.8; UV−vis ($CHCl_3$, 1 μM) λ (ε) 352 nm (2.1×10^5); CD ($CHCl_3$, 0.01 mM) λ (Δε) 254 nm (−16), 279 nm (−200), 288 nm (−205), 301 nm (−139), 306 nm (−146), 319 nm (−119), 348 nm (−305), 370 nm (416); IR (KBr) 2206, 1725 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 2 mM) δ 0.32 (18H, s), 0.42 (18H, s), 0.86 (9H, t, *J* = 6.8 Hz), 1.09 (54H, s), 1.20−1.54 (42H, m), 1.75 (18H, s), 1.90 (6H, quin, *J* = 7.0 Hz), 4.42−4.50 (6H, m), 7.37 (6H, d, *J* = 8.6 Hz), 8.02 (6H, s), 8.24 (3H, t, *J* = 1.5 Hz), 8.35 (6H, d, *J* = 1.5 Hz), 8.45 (6H, d, *J* = 8.6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$, 10 mM) δ −3.8, −3.7, 14.1, 17.1, 18.4, 22.7, 25.8, 26.1, 28.8, 29.3, 29.4, 29.6, 31.9, 65.8, 89.6, 92.8, 119.5, 119.8, 124.5, 125.3, 125.8, 127.1, 128.3, 131.4, 131.9, 132.0, 133.3, 138.5, 153.3, 165.6. Anal. ($C_{159}H_{198}O_{12}Si_6$) Calcd: C, 77.32; H, 8.08. Found: C, 77.04; H, 8.13.

(*M,M,M*)-Hexahydroxy[3 + 3]cycloalkyne, (*M,M,M*)-3. To a solution of (*M,M,M*)-**2** (90 mg, 0.036 mmol) in tetrahydrofuran (3 mL) was added 1.0 M tetrabutylammonium fluoride in tetrahydrofuran (0.36 mL, 0.36 mmol) at 0 °C. After the mixture was stirred for 30 min at that temperature, saturated aqueous ammonium chloride was added. The organic materials were extracted with ethyl acetate. The organic layer was washed with brine and dried over sodium sulfate. The solvents were evaporated under reduced pressure, and silica gel chromatography (ethyl acetate) gave (*M,M,M*)-**3** (63 mg, 0.035 mmol, 97%): mp > 179 °C dec (hexane−ethyl acetate); $[\alpha]^{24}_D$ +1594 (*c* 0.10, acetone); MALDI-TOF MS *m/z* calcd for $^{12}C_{122}{}^{13}CH_{114}O_{12}$ 1783.8, found 1783.8; UV−vis (THF, 1 μM) λ (ε) 354 nm (1.8×10^5); CD (THF, 0.01 mM) λ (Δε) 253 nm (−12), 293 nm (−245), 330 nm (−61), 349 nm (−236), 369 nm (395); IR (KBr) 3600−3000, 2206, 1699 cm^{-1}; ^1H NMR (400 MHz, THF-d_8, 5 mM) δ 0.88 (9H, t, *J* = 6.8 Hz), 1.25−1.59 (42H, m), 1.73 (18H, s), 1.88 (6H, quin, *J* = 7.0 Hz), 4.40−4.49 (6H, m), 7.35 (6H, d, *J* = 8.5 Hz), 8.06 (6H, s), 8.25 (3H, t, *J* = 1.5 Hz), 8.34 (6H, d, *J* = 1.5 Hz), 8.43 (6H, d, *J* = 8.5 Hz), 8.73 (6H, s); ^{13}C NMR (150 MHz, DMSO-d_6, 15 mM) δ 14.0, 16.4, 22.2, 25.9, 28.4, 28.9, 29.0, 29.1, 29.3, 31.5, 65.4, 89.5, 91.9, 116.5, 118.4, 119.6, 123.3, 123.9, 124.6, 125.3, 127.5, 130.8, 131.0, 131.9, 132.5, 137.1, 154.7, 164.5. Anal. ($C_{123}H_{114}O_{12}\cdot {}^3/_2H_2O$) Calcd: C, 81.56; H, 6.51. Found: C, 81.65; H, 6.63.

Hexaacetoxy[3 + 3]cycloalkyne, (*M,M,M*)-4. Under an argon atmosphere, to a mixture of (*M,M,M*)-**3** (23 mg, 0.013 mmol), 4-(dimethylamino)pyridine (5 mg, 0.041 mmol), pyridine (0.5 mL), and dichloromethane (0.5 mL) was added acetic anhydride (0.1 mL) at room temperature. The mixture was stirred for 3 h at that temperature. The reaction mixture was diluted with ethyl acetate, and aqueous potassium hydrogen sulfate was added. The organic layer was separated, washed with saturated aqueous sodium hydrogen carbonate and brine, and dried over magnesium sulfate. The solvents were evaporated under reduced pressure, and silica gel chromatography (hexane/ethyl acetate = 1:1) gave (*M,M,M*)-**4** (25 mg, 0.012 mmol, 94%): mp > 210 °C dec (chloroform−methanol); $[\alpha]^{24}_D$ +1666 (*c* 0.10, $CHCl_3$); MALDI-TOF MS *m/z* calcd for $^{12}C_{134}{}^{13}CH_{126}O_{18}$ 2035.9, found 2036.1; UV−vis ($CHCl_3$, 1 μM) λ (ε) 338 nm (2.4×10^5); CD ($CHCl_3$, 0.01 mM) λ (Δε) 272 nm (−229), 288 nm (−73), 334 nm (−589), 358 nm (586), 374 nm (464), 380 nm (486); IR (KBr) 2207, 1764, 1722 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 1.6 mM) δ 0.87 (9H, t, *J* = 6.9 Hz), 1.25−1.59 (42H, m), 1.69 (18H, s), 1.93 (6H, quin, *J* = 7.1 Hz), 2.43 (18H, s), 4.45−4.56 (6H, m), 7.43 (6H, d, *J* = 8.6 Hz), 8.09 (6H, s), 8.19 (3H, t, *J* = 1.5 Hz), 8.22 (6H, d, *J* = 1.5 Hz), 8.35

(6H, d, J = 8.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 19 mM) δ 14.3, 16.4, 21.1, 22.8, 26.2, 29.0, 29.5, 29.6, 29.77, 29.80, 32.0, 65.9, 88.5, 93.4, 119.9, 121.6, 123.8, 124.7, 125.6, 127.7, 129.3, 129.7, 131.0, 131.6, 132.1, 132.2, 138.0, 148.4, 165.3, 169.1. Anal. ($C_{135}H_{126}O_{18}$) Calcd: C, 79.62; H, 6.24. Found: C, 79.36; H, 6.35.

(*M*,*M*,*M*)-Hexakis(trifluoromethanesulfonyloxy)[3 + 3]-cycloalkyne, (*M*,*M*,*M*)-5. Under an argon atmosphere, to a mixture of (*M*,*M*,*M*)-**3** (25 mg, 0.014 mmol), 4-(dimethylamino)-pyridine (5 mg, 0.041 mmol), pyridine (0.5 mL), and dichloromethane (0.5 mL) was added trifluoromethanesulfonic anhydride (0.1 mL, 0.59 mmol) at −40 °C. The mixture was warmed to room temperature and stirred for 3 h at that temperature. The reaction mixture was diluted with ethyl acetate, and aqueous potassium hydrogen sulfate was added. The organic layer was separated, washed with saturated aqueous sodium hydrogen carbonate and brine, and dried over magnesium sulfate. The solvents were evaporated under reduced pressure, and silica gel chromatography (hexane/toluene = 1:2) gave (*M*,*M*,*M*)-**5** (30 mg, 0.012 mmol, 82%): mp > 218 °C dec (chloroform−methanol); $[\alpha]^{26}_D$ +1340 (*c* 0.10, $CHCl_3$); MALDI-TOF MS *m*/*z* calcd for $^{12}C_{128}{}^{13}CH_{108}F_{18}O_{24}S_6$ 2575.5, found 2441.9 ($M^+ - SO_2CF_3$), 2309.4 ($M^+ - 2SO_2CF_3$), 2176.9 ($M^+ - 3SO_2CF_3$); UV−vis ($CHCl_3$, 1 μM) λ (ϵ) 338 nm (2.5×10^5); CD ($CHCl_3$, 0.01 mM) λ ($\Delta\epsilon$) 271 nm (−236), 287 nm (−48), 332 nm (−637), 354 nm (627), 372 nm (474), 378 nm (492). IR (KBr) 2210, 1726 cm^{-1}; ^{1}H NMR (400 MHz, toluene-d_8, 6.9 mM, 100 °C) δ 0.92 (9H, t, J = 6.8 Hz), 1.20−1.62 (42H, m), 1.75 (18H, s), 2.01 (6H, quin, J = 6.8 Hz), 4.55−4.69 (6H, m), 7.58 (6H, d, J = 8.6 Hz), 7.91 (6H, s), 7.96 (6H, d, J = 8.6 Hz), 8.09 (3H, s), 8.13 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$, 15 mM, 60 °C) δ 14.1, 17.0, 22.8, 26.2, 29.1, 29.45, 29.54, 29.7, 29.8, 32.1, 66.3, 87.7, 94.4, 117.2, 120.4, 120.77, 120.83, 123.4, 125.3, 125.9, 129.2, 130.3, 130.7, 131.8, 132.4, 132.6, 137.7, 147.7, 164.5. Anal. ($C_{129}H_{108}F_{18}O_{24}S_6$) Calcd: C, 60.13; H, 4.22; F, 13.27; S, 7.47. Found: C, 60.01; H, 4.32; F, 12.98; S, 7.60.

(*M*,*M*,*M*)-Hexakis(nonafluorobutanesulfonyloxy)[3 + 3]cycloalkyne, (*M*,*M*,*M*)-6. Under an argon atmosphere, to a mixture of (*M*,*M*,*M*)-**3** (10 mg, 5.6 μmol), 4-(dimethylamino)-pyridine (5 mg, 0.041 mmol), *N*,*N*-dimethylformamide (0.75 mL), and diisopropylethylamine (0.25 mL) was added nonafluorobutanesulfonyl fluoride (0.2 mL, 1.1 mmol) at 0 °C. The mixture was warmed to room temperature and stirred for 12 h at that temperature. The reaction was quenched by adding saturated aqueous sodium hydrogen carbonate. The organic materials were extracted with ethyl acetate, and the organic layer was washed with saturated aqueous sodium hydrogen carbonate and brine and dried over magnesium sulfate. The solvents were evaporated under reduced pressure, and silica gel chromatography (hexane/toluene = 1:2) gave (*M*,*M*,*M*)-**6** (16 mg, 4.5 μmol, 80%): mp > 195 °C dec (chloroform−methanol); $[\alpha]^{22}_D$ +1052 (*c* 0.10, $CHCl_3$); MALDI-TOF MS *m*/*z* calcd for $^{12}C_{146}{}^{13}CH_{108}F_{54}O_{24}S_6$ 3475.5, found 3194.2 ($M^+ - SO_2CF_2CF_2CF_2CF_3$), 2911.1 ($M^+ - 2SO_2CF_2CF_2CF_2CF_3$), 2628.2 ($M^+ - 3SO_2CF_2CF_2CF_2CF_3$), 2345.4 ($M^+ - 4SO_2CF_2CF_2CF_2CF_3$), 2062.1 ($M^+ - 5SO_2CF_2CF_2CF_2CF_3$), 1779.1 ($M^+ - 6SO_2CF_2CF_2CF_2CF_3$); UV−vis ($CHCl_3$, 1 μM) λ (ϵ) 337 nm (2.7×10^5). CD ($CHCl_3$, 0.01 mM) λ ($\Delta\epsilon$) 270 nm (−231), 287 nm (−56), 332 nm (−602), 355 nm (597), 372 nm (455), 378 nm (471); IR (KBr) 2211, 1728 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 0.5 mM, 60 °C) δ 0.86 (9H, t, J = 6.6 Hz), 1.20−1.60 (42H, m), 1.86−2.00 (6H, m), 1.92 (18H, s), 4.45−4.57 (6H, m), 7.73 (6H, d, J = 8.4 Hz), 8.14 (6H, s), 8.16 (3H, s), 8.21 (6H, s), 8.42 (6H, br); ^{13}C NMR (150 MHz, $CDCl_3$, 14 mM) δ 14.0, 17.0, 22.6, 26.0, 28.9, 29.3, 29.4, 29.6, 29.7, 31.9, 66.3, 87.6, 94.3, 106.4, 106.6, 106.9, 107.1, 108.0, 108.16, 108.22, 108.4, 108.6, 108.7, 108.91, 108.94, 109.6, 109.8, 110.0, 110.3, 110.5, 111.6, 111.9, 112.1, 112.4, 112.7, 112.9, 114.1, 114.3, 114.4, 114.7, 114.9, 116.0, 116.2, 116.4, 116.5, 116.7, 117.0, 117.9, 118.1, 118.4, 119.8, 120.1, 120.3, 120.4, 120.7, 120.9, 123.3, 125.2, 125.8, 129.1, 130.2, 130.6, 131.5, 132.3, 132.5, 132.6, 137.5, 147.9, 164.6. Anal. ($C_{147}H_{108}F_{54}O_{24}S_6$) Calcd: C, 50.78; H, 3.13; F, 29.51; S, 5.53. Found: C, 50.95; H, 2.91; F, 29.24; S, 5.76.

Acknowledgment. We thank the Japan Society for the Promotion of Science (JSPS) for financial support. A fellowship to H.S. from JSPS for young Japanese scientists is also gratefully acknowledged.

Supporting Information Available: Copies of ^{1}H and ^{13}C NMR spectra of all new compounds and the calculation method for the association constant *K*. This material is available free of charge via the Internet at http://pubs.acs.org.

JO050732F