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Efficient Synthesis of a Chiral [4]Pseudocatenane and Its Derivatives: A Novel Ship's Wheel-like Interlocked Structure

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Abstract: A novel chiral[4]pseudocatenane $\mathbf{5}H_3[PF_6]_3$ was synthesized efficiently by treatment of a solution of chiral triptycene-based tri(crown ether) **1** and three equivalents of a bis[*p*-(but-3-enyloxy)benzyl]ammonium salt in CH_2Cl_2 with a Grubbs II catalyst, followed by hydrogenation. It was found that the ammonium groups in $\mathbf{5}H_3[PF_6]_3$ could be deprotonated by 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in acetonitrile or dimethyl sulfoxide (DMSO). Consequently, N-acylation of the ammonium groups was easily performed in the presence of DBU, which resulted in a new class of neutral highly ordered interlocked molecules in good yields. In particular, the incorporation of stopper units, for example, diethyl phosphoramidate, lead to the isolation of the interlocked molecule **10** with an interesting ship's wheel-like structure, which was structurally studied with the help of detailed NMR experiments. Compared with **1**, it was further found that the Cotton effect of (*R*)-1,1′-binaphthyl chromophore at 241 nm was greatly reduced in $\mathbf{5}H_3[PF_6]_3$ and its derivatives. Moreover, a new positive Cotton effect at 248 nm appeared in the interlocked molecules; this observation could be attributed to the chirality transfer from the binaphthyl units to the macrocycles lying in the cavities of **1**.

Keywords: catenanes · chemical topology · chirality · reactivity · template synthesis

Introduction

Mechanically interlocked molecules[1] like rotaxanes and catenanes have attracted much attention, and they have been efficiently synthesized by various template methods during the last two decades. This class of interesting molecules has a nonplanar structure, which might be provided with topological chirality.[2] Planar chirality has also been introduced to the construction of chiral catenanes.[3] However, the most convenient and useful way to produce chiral interlocked molecules with unambiguous conformation is probably to incorporate chiral groups directly into the structures of their subunits.[4] In this situation, the chirality induction between the chiral part and the achiral one has been found in several interlocked systems[5] and used for the design of molecular shuttles[6] and asymmetric benzoin condensation.[7] So far, few examples on highly ordered chiral interlocked structures have been reported. On the other hand, the studies on the reactivity of interlocked molecules are also limited,[8] although it is important not only for the construction of complexed interlocked molecules[9] but also for their further functionalization.[7,10]

Recently, we reported a highly efficient approach to [4]pseudocatenanes by threefold metathesis reactions of a triptycene-based tris[2]pseudorotaxane.[11] Follow the same strategy, more elegant topological interesting molecules with well-defined structures and functions could be constructed. For this purpose, a new triptycene-based receptor[12] containing three (*R*)-(+)-benzo-2,2′-binaphtho[26]crown-8 moieties[13,14] has been synthesized; use of this receptor has lead to various highly ordered chiral interlocked molecules. Herein, we report 1) the efficient synthesis of a novel chiral[4]pseudocatenane by dynamic covalent chemistry,[15] 2) deprotonation and N-acylation of the ammonium groups in the[4]pseudocatenane to result in a new class of neutral chiral interlocked molecules, and 3) construction of a ship's wheel-like interlocked structure.

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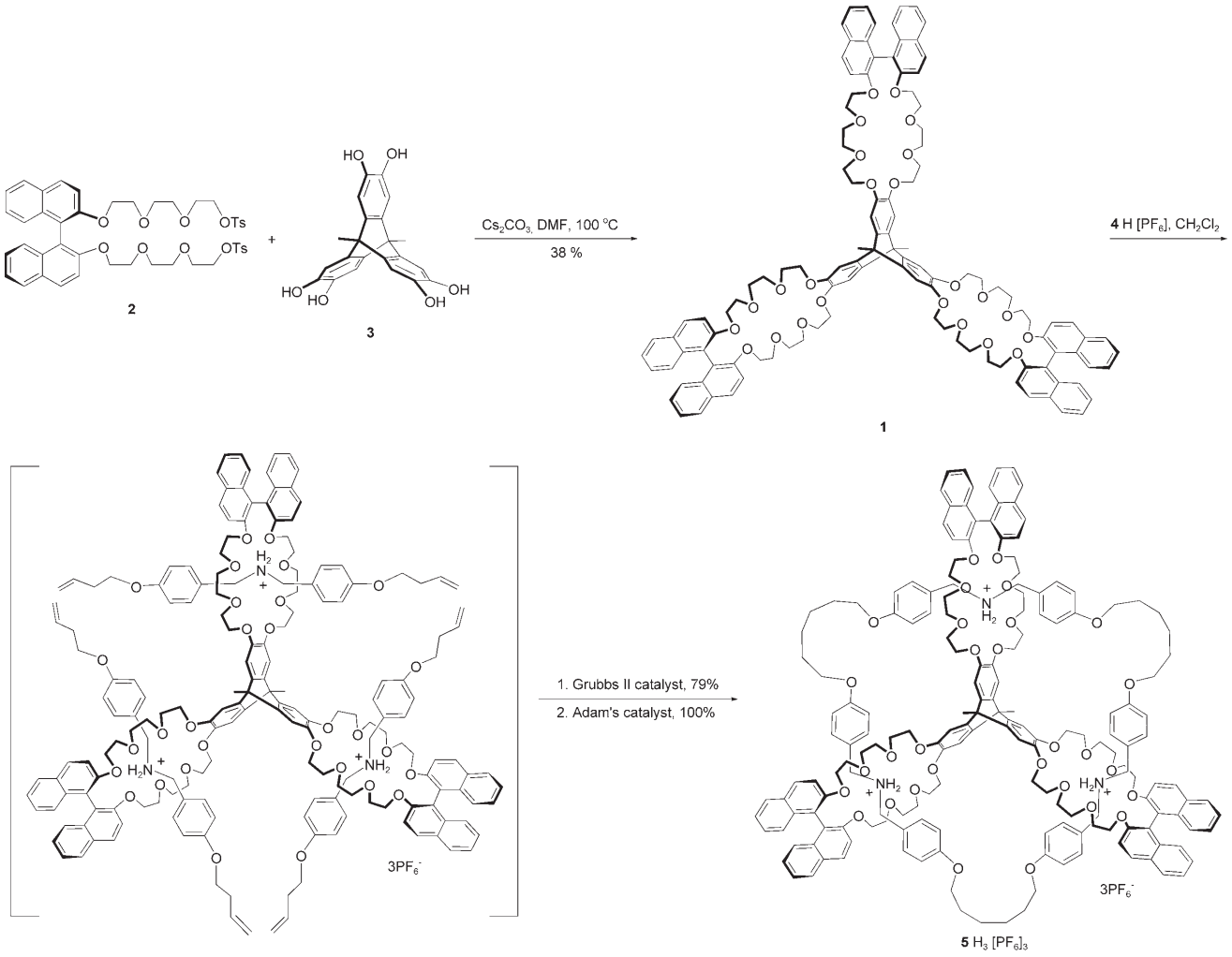
Results and Discussion

Synthesis of a chiral[4]pseudocatenane: Synthesis of the chiral triptycene-based receptor **1** and the chiral[4]pseudocatenane $\mathbf{5}H_3[PF_6]_3$ is depicted in Scheme 1. Reaction of (*R*)-(+)-1,1′-bi-2-naphthol with 8-tosyloxy-3,6-dioxaoctanol in the presence of K_2CO_3, followed by the tosylation with *p*-toluenesulfonyl chloride in the presence of Ag_2O and KI, gave compound **2** in 90% total yield.[16] Triptycene tri(catechol) **3**[11] was then treated with **2** in the presence of Cs_2CO_3 under a high dilution condition to afford **1** in 38% yield. ^{1}H and ^{13}C NMR spectra of **1** are consistent with its D_{3v} symmetry.

The ^{1}H NMR spectrum of a 1:3 mixture of **1**[17] and the PF_6 salt of bis[*p*-(but-3-enyloxy)benzyl]ammonium (**4**H[PF_6]) in $CDCl_3$ showed a great difference with those of the two components, which suggested that new complexes between **1** and **4**H[PF_6] were formed. Consequently, when a solution of **1** and three equivalents **4**H[PF_6] in CH_2Cl_2 was treated with the second-generation Grubbs catalyst[18] (5 mol%) in high dilution concentration (1 mM), the chiral[4]pseudocatenane $\mathbf{5}'H_3[PF_6]_3$ could be efficiently obtained in 79% yield by threefold metathesis reactions of a triptycene-based tris[2]pseudorotaxane. The ^{1}H NMR spectrum showed that signals of terminal vinyl protons of **4**H[PF_6] disappeared while a new broad signal appeared at $\delta = 5.59$ ppm for −CH=CH− protons in $\mathbf{5}'H_3[PF_6]_3$ as a *cis*/*trans* isomeric mixture. The MALDI-TOF mass spectrum of $\mathbf{5}'H_3[PF_6]_3$ displayed a strong peak at $m/z = 2851.3$ for the $[\mathbf{5}'-2H]^+$ ion. Furthermore, hydrogenation of $\mathbf{5}'H_3[PF_6]_3$ with Adam's catalyst ($PtO_2 \cdot H_2O$) quantitatively afforded the chiral[4]pseudocatenane $\mathbf{5}H_3[PF_6]_3$, which could be fully characterized. The interlocked molecule $\mathbf{5}H_3[PF_6]_3$ showed only 16 signals in the ^{13}C NMR spectrum for the 114 aromatic carbon atoms and 12 signals for 64 aliphatic carbon atoms; these results are in accord with D_{3v} symmetry.

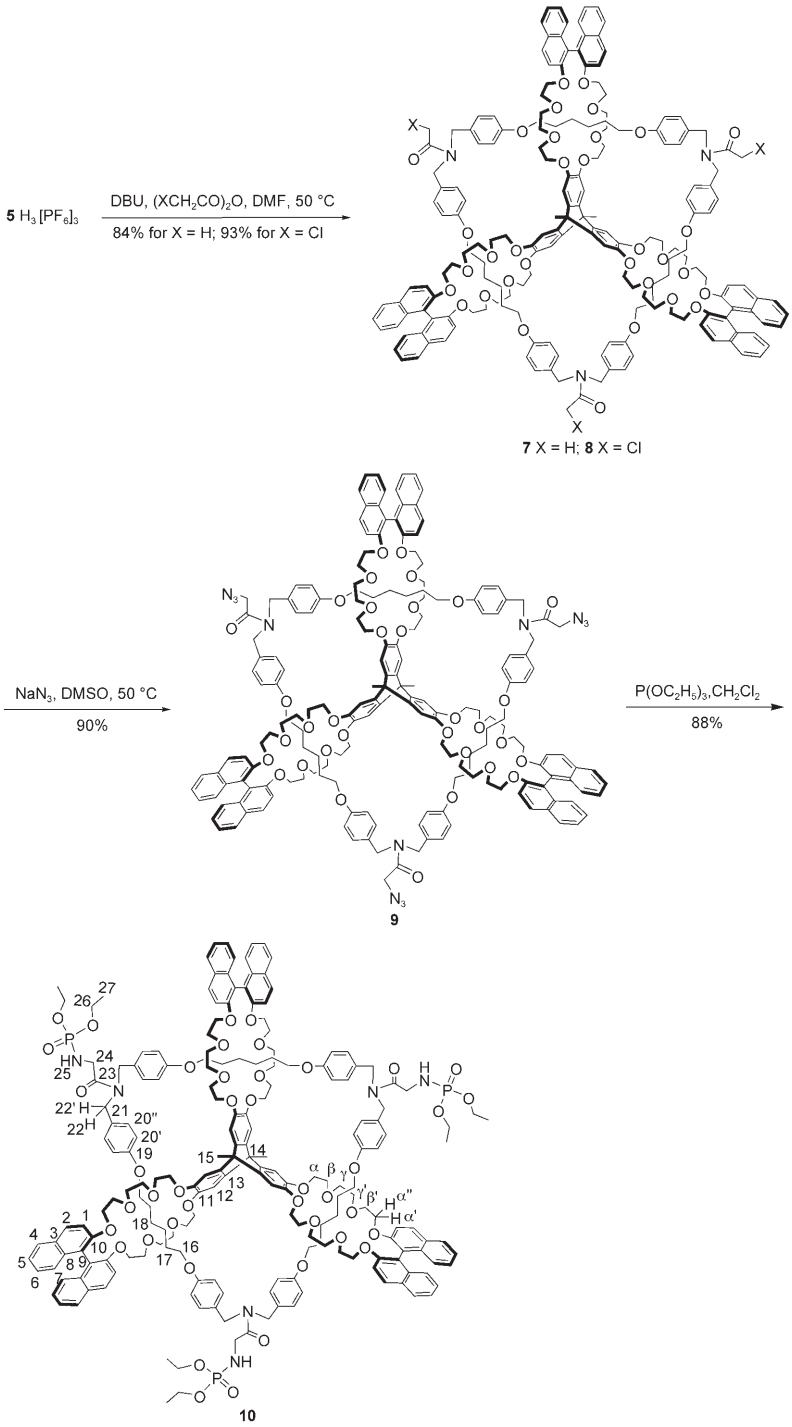
Deprotonation and N-acylation of the ammonium groups in the [4]pseudocatenane: The lower acidity of ammonium groups in $\mathbf{5}H_3[PF_6]_3$ resulted made it difficult to neutralize with triethylamine, tributylamine, or diisopropylethylamine.[8c,19] But we found that $\mathbf{5}H_3[PF_6]_3$ could be deproto-



Scheme 1. Synthesis of the chiral triptycene-based receptor **1** and the chiral[4]pseudocatenane $\mathbf{5}H_3[PF_6]_3$.

nated to neutral interlocked molecule **6** by 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU); this was proved by the ^{1}H NMR experiments in [D_3]acetonitrile or [D_6]dimethyl sulfoxide ([D_6]DMSO).[20] Compound **6** is an important precursor for further functionalization of **5**H_3-[PF_6]$_3$ to a new class of neutral chiral[4]pseudocatenanes.

As shown in Scheme 2, we first performed the N-acetylation of **5**H_3[PF_6]$_3$ by using acetic anhydride in DMF in the presence of DBU. It was found that the reaction went smoothly at room temperature to give compound **7** in 84% yield. The MALDI-TOF mass spectrum of **7** revealed a strong peak at $m/z = 3003.1$ for [**7**+Na]$^+$. Under the same conditions, the perchloroacetylated product **8** was synthesized in 93% yield by further treatment of **5**H_3[PF_6]$_3$ with chloroacetic anhydride. Active chlorine atoms in compound **8** provided us with many opportunities for further functionalization. As a result, nucleophilic substitution of the chloride with sodium azide gave compound **9** in 90% yield. Compound **10** was then synthesized in 88% yield by the reaction[21] of triethyl phosphite with azide groups in **9**.



Scheme 2. N-Acylation of **5**H_3[PF_6]$_3$ and synthesis of the interlocked molecule **10**. Proton designations of **10** are shown.

Identification of the structure of compound 10: The MALDI-TOF mass spectrum of **10** revealed a strong peak at $m/z =$ 3433.8 for [**10**]$^+$. To confirm its topological structure, detailed NMR experiments were carried out. It was found that the ^{1}H NMR spectrum of **10** changed greatly with the deuterated solvents used. Consequently, the ^{1}H NMR spectra were very intricate and assignments of signals could not be made for that taken in $CDCl_3$ (Figure 1a); however, the spectrum became very clear in [D_6]DMSO (Figure 1b). This solvent dependence might be due to the different conformations[22] of crown ethers in **10** existing in the two solvents. In chloroform, the crown ether subunits are more likely to take a conformation which the oxygen atoms of crown ethers point into the cavity; this would result in hydrophilic cavities. In this situation, the aliphatic chain with six carbon atoms would be excluded by the cavities, and the conformation of **10** would be distorted, which is reflected in the ^{1}H NMR spectrum. On the other hand, DMSO is a aprotic polar solvent, in which compound **10** can favor a regular conformation. This phenomenon has also been found in compounds **7** and **8**.[20]

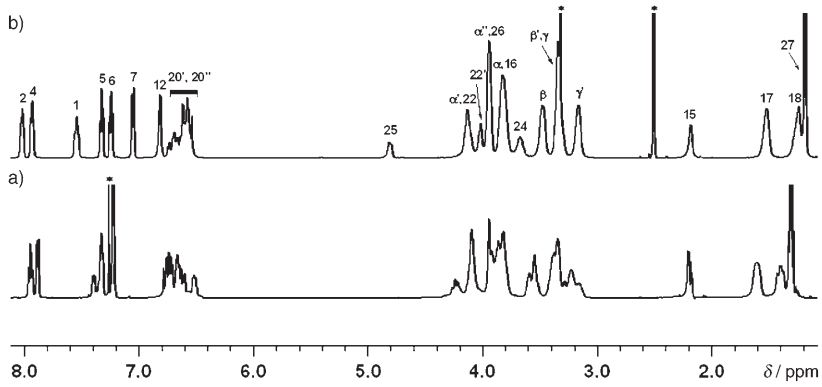


Figure 1. ^{1}H NMR spectra (600 MHz, 298.0 K) of **10** in a) $CDCl_3$ and b) [D_6]DMSO.

Compound **10** was then studied by NMR spectroscopy in [D_6]DMSO. As shown in Figure 2, the NOESY spectrum of **10** revealed that the three aliphatic links lying in the three cavities of crown ethers. With the help of the ^{1}H-^{1}H COSY and TOCSY spectra, the peaks in the aromatic and polyether regions could be assigned. As a result, two sets of signals at $\delta = 4.12$ and 3.93 ppm were assigned to the $H_{\alpha',\alpha''}$ protons and those at $\delta = 4.14$ and 4.01 ppm were assigned to benzylic protons, which might be due to the affection of binaphthyl groups. Furthermore, the carbon signals of **10** in its ^{13}C NMR spectrum could also be designated by means of the HMQC and HMBC spectra.[20] Compound **10** showed a simple ^{13}C NMR spectrum, in which only 19 signals for 114 aromatic carbon atoms and 14 signals for 79 aliphatic carbon atoms were observed.[20] Moreover, its ^{31}P NMR showed only one signal at $\delta = 9.68$ ppm.[20] All these observations proved its D_{3v} symmetry. At the same time, we found that the structure of **10** was also desymmetrized slightly so that the carbon atoms C20′, C20″, and C22 were split into two separate signals, because of the chiral binaphthyl units.

Compound **10** is an interesting neutral mechanically interlocked molecule, in which no complexation effects between the two subunits exist. The incorporation of three stopper units, that is diethyl phosphoramidate, gave it an unambiguous interlocked structure similar in shape to a ship's wheel (Figure 3). In fact, the incorporation of stopper units into interlocked structures is a very useful strategy for the synthesis of special rotaxanes[23] and molecular motors.[24]

CD spectra: The circular dichroism (CD) spectra of the host **1**, [4]pseudocatenane **5**$H_3[PF_6]_3$ and its neutral derivatives (**6, 7, 8, 10**) are depicted in Figure 4. As expected, compound **1** showed the classical negative Cotton effect of the (*R*)-1,1′-binaphthyl chromophore at 241 nm. Relative to **1**, greatly reduced intensities of the 1,1′-binaphthyl chromophore in **5**$H_3[PF_6]_3$ and its derivatives were observed; this reduction could be attributed to the interlocked structure. Interestingly, a new positive Cotton effect at 248 nm appeared in the interlocked molecules, which might be ascribed to the chirality transfer[5] from the 1,1′-binaphthyl unit to the macrocycles lying in the cavities of **1**. This observation is in accord with the aforementioned NMR spectra of the interlocked molecules. Moreover, **5**$H_3[PF_6]_3$ showed a stronger positive Cotton effect and weaker negative one than its neutral derivatives did; this result might be due to the more stabilized conformation by the complexation effects between the two subunits in **5**$H_3[PF_6]_3$. Furthermore, we found that the substituent groups on the nitrogen atoms in the neutral interlocked compounds had no evident effects on their CD spectra.

Conclusion

In conclusion, we have synthesized a novel chiral[4]pseudocatenane and demonstrated that deprotonation and N-acylation of the ammonium groups in the [4]pseudocatenane could result in a new class of neutral highly ordered interlocked molecules. In particular, the incorporation of stopper units led to the isolation of an interlocked molecule with an interesting ship's wheel-like structure; this structure of this compound was studied by the detailed NMR experiments. Moreover, the interlocked molecules showed not only a greatly reduced Cotton effect of (*R*)-1,1′-binaphthyl chromophore at 241 nm, but also a new positive Cotton effect at 248 nm, which might be ascribed to the chirality transfer from the binaphthyl units to the macrocycles lying in the cavities of **1**. Further work on the design of molecular devices and chiral catalysts based on this class of interlocked molecules are in progress in our laboratory.

Experimental Section

General: Melting points, taken on an electrothermal melting point apparatus, are uncorrected. IR spectra were recorded on a FT-IR spectrometer by using KBr discs. The ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker DMX600 NMR or a Bruker DMX300 NMR spectrometer. MALDI-TOF MS were obtained on a Bruker BIFLEXIII mass spectrometer. CD-spectra were measured on JASCO, *J*-810 spectropolarimeter. Elemental analyses were performed by the Analytical Laboratory of Institute of Chemistry, CAS. 8-Tosyloxy-3,6-dioxaoctanol, compound **3**, and ammonium salt **4**H[PF_6] were prepared as reported previously.[11] The Grubbs II catalyst was purchased from Aldrich.

(*R*)-2,2′-Bis(8-hydroxy-3,6-dioxa-1-octyloxy)-1,1′-binaphthyl (2′): A mixture of (*R*)-(+)-1,1′-bi-2-naphthol (2.86 g, 0.01 mol), 8-tosyloxy-3,6-dioxaoctanol (6.08 g, 0.02 mol), and K_2CO_3 (5.52 g, 0.04 mol) in dry acetonitrile (120 mL) was refluxed for 24 h. The reaction mixture was filtered and then concentrated under reduced pressure. The crude product was purified by column chromatography over silica gel (eluent: acetone) to afford the desired product **2′** (5.41 g, 98.4%) as a pale yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.93$ (d, $J = 9.0$ Hz, 2H), 7.85 (d, $J =$

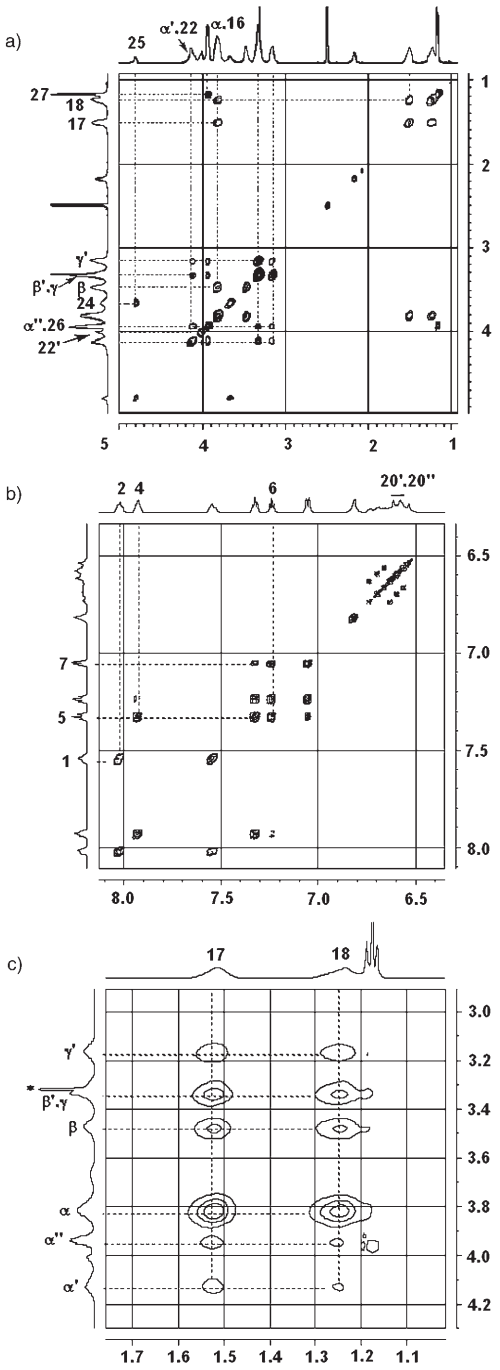


Figure 2. a) The TOCSY NMR spectrum of the aliphatic region; b) the ^{1}H-^{1}H COSY NMR spectrum of the aromatic region; and c) a selected area of the NOESY spectrum of **10** (600 MHz, [D$_6$]DMSO, 298 K). (The values on the axes represent δ in ppm.)

8.1 Hz, 2H), 7.42 (d, J=9.0 Hz, 2H), 7.34–7.29 (m, 2H), 7.18–7.24 (m, 1.2 Hz, 2H), 7.15 (d, J=8.4 Hz, 2H), 4.17–4.03 (m, 4H), 3.64–361 (m, 4H), 3.50–3.41 (m, 8H), 3.27–3.24 (m, 4H), 3.20–3.05 (m, 4H), 2.63 ppm (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=154.3, 134.1, 129.4, 129.3, 127.8, 126.3, 125.5, 123.7, 120.5, 115.6, 72.4, 70.6, 70.2, 69.9, 69.7, 61.7 ppm; MALDI-TOF MS: m/z: 550 $[M]^+$; elemental analysis calcd (%) for $C_{32}H_{38}O_8$: C 69.80, H 6.96; found: C 69.55, H 6.85.

(*R*)-2,2′-Bis(8-tosyloxy-3,6-dioxa-1-octyloxy)-1,1′-binaphthyl (2): Fresh Ag_2O (6.96 g, 30 mmol), TsCl (4.2 g, 22 mmol) and KI (0.68 g, 4.1 mmol)

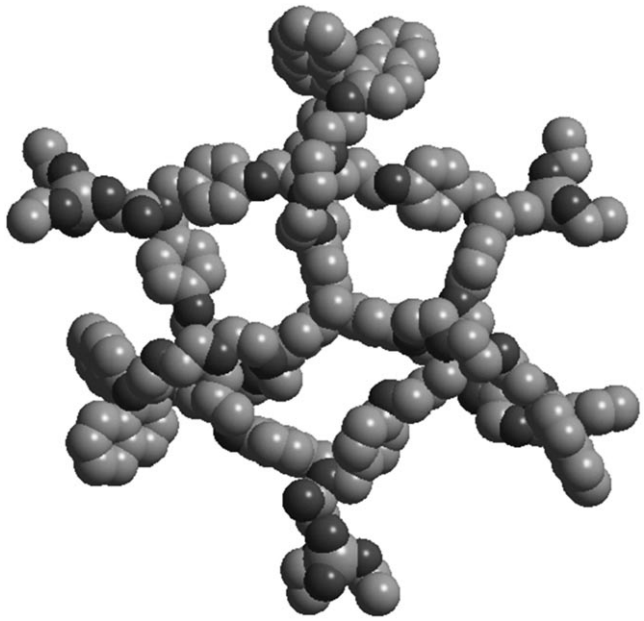


Figure 3. Structure of compound **10** as obtained from an MM2 calculation.

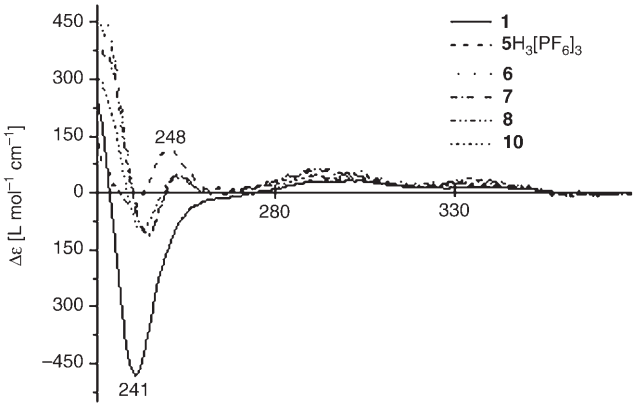


Figure 4. CD spectra (CH_2Cl_2, 20°C) of **1**, **5**H$_3$[PF$_6$]$_3$, **6**, **7**, **8**, and **10**.

were added to a solution of **2′** (5.41 g, 98 mmol) in dried CH_2Cl_2 (100 mL). The reaction mixture was stirred for 24 h, then filtered through a small pad of silica gel, and washed with acetone. Evaporation of the solvent, followed by column chromatography (SiO_2: dichloromethane to acetone) to yield **2** (7.72 g, 91.5%) as a pale yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=7.92 (d, J=9.0 Hz, 2H), 7.83 (d, J=8.1 Hz, 2H), 7.76 (d, J=8.1 Hz, 4H), 7.41 (d, J=9.0 Hz, 2H), 7.32–7.25 (m, 6H), 7.20–7.11 (m, 4H), 4.07–4.02 (m, 8H), 3.47–3.41 (m, 8H), 3.17–3.11 (m, 4H), 3.08–3.00 (m, 4H), 2.42 ppm (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=154.3, 144.8, 134.1, 133.0, 129.8, 129.4, 129.3, 127.95, 127.86, 126.3, 125.5, 123.7, 120.5, 115.6, 70.5, 70.4, 69.9, 69.6, 69.3, 68.4, 21.6 ppm; MALDI-TOF MS: m/z: 858.4 $[M]^+$; elemental analysis calcd (%) for $C_{46}H_{50}O_{12}S_2\cdot 0.5\,H_2O$: C 63.65, H 5.92; found: C 63.80, H 5.68.

Compound 1: A suspension of cesium carbonate (4.6 g, 14.1 mmol) in anhydrous DMF (60 mL) under argon atmosphere was stirred vigorously for 10 min and then heated to 100°C. A solution of triptycene tri(catechol) **3** (0.44 g, 1.2 mmol) and bistosylate **2** (3 g, 3.5 mmol) in anhydrous DMF (80 mL) was added dropwise to the mixture over a period of 12 h. The reaction mixture was stirred at 100°C for another 4 d. After cooling down to ambient temperature, the mixture was filtered and

washed with CH_2Cl_2. The filtrate was concentrated under reduced pressure to give a gray solid, which was redissolved in CH_2Cl_2 (250 mL) and washed with H_2O. The organic layer was dried over anhydrous magnesium sulfate. After removal of the solvent, the resulting oil was subjected to successive column chromatography over silica gel (eluent: 100:1 CH_2Cl_2/CH_3OH and then 60/1 CH_2Cl_2/CH_3OH).Compound **1** was obtained as an off-white solid (0.85 g, 38%). M.p. 116–118°C; $[\alpha]_D^{20}=104$ ($c=0.5$ in CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 600 MHz): $\delta=7.82$ (d, $J=9.0$ Hz, 6H), 7.75 (d, $J=8.4$ Hz, 6H), 7.40 (d, $J=9.0$ Hz, 6H), 7.27 (m, 6H), 7.19–7.16 (m, 6H), 7.09 (d, $J=7.8$ Hz, 6H), 6.93 (s, 6H), 4.20–4.00 (m, 18H), 4.00–3.90 (m, 6H), 3.79–3.66 (m, 12H), 3.59–3.51 (m, 6H), 3.51–3.42 (m, 12H), 3.42–3.34 (m, 6H), 3.34–3.21 (m, 12H), 2.28 ppm (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta=154.5$, 145.9, 142.8, 134.1, 129.5, 129.3, 127.9, 126.3, 125.5, 123.7, 120.7, 116.3, 109.6, 70.80, 70.76, 70.1, 69.9, 47.7, 14.1 ppm; MALDI-TOF MS: m/z: 1943.5 $[M+Na]^+$; HRMS calcd for $[M+2H]^{2+}$: 961.4151; found: 961.4157.

Compound $5H_3[PF_6]_3$: A solution of **1** (200 mg, 0.10 mmol) and **4**H$[PF_6]$ (0.15 g, 0.31 mmol) in anhydrous CH_2Cl_2 (80 mL) was purged with Ar for 10 min. Then, a solution of Grubbs II catalyst (15 mg, 5 mol%) in CH_2Cl_2 (20 mL) was added by syringe and the reaction mixture was heated at 40°C for 6 h under Ar. The solvent was evaporated off under reduced pressure and the crude product was subjected to column chromatography over silica gel with CH_2Cl_2/CH_3OH (200:1 to 160:1) as the eluent to yield **5′**$H_3[PF_6]_3$ (0.27 g, 79%) as a white solid. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=8.01$ (d, $J=9.0$ Hz, 6H), 7.91 (d, $J=8.1$ Hz, 6H), 7.48 (d, $J=9.0$ Hz, 6H), 7.44–7.34 (m, 6H), 7.34–7.18 (m , 12H), 7.07–6.88 (m, 18H), 6.75–6.63 (m, 12H), 5.59 (brs, 6H), 4.27–3.72 (m, 48H), 3.31–2.98 (m, 48H), 2.65–2.29 ppm (m, 18H); MALDI-TOF MS: m/z: 2549.1 $[M-2H-3PF_6]^+$. A mixture of **5′**$H_3[PF_6]_3$ (0.36 g) and PtO_2 (36 mg) in chloroform (15 mL) was stirred under H_2 atmosphere for 6 h. After the mixture was filtrated and the filtrate was concentrated, **5**$H_3[PF_6]_3$ was quantitatively obtained as a white solid. M.p. 214–216°C; $[\alpha]_D^{20}=184$ ($c=0.5$ in CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=8.00$ (d, $J=9.0$ Hz, 6H), 7.91 (d, $J=8.1$ Hz, 6H), 7.47 (d, $J=9.0$ Hz, 6H), 7.43–7.32 (m, 6H), 7.32–7.16 (m, 12H), 7.04–6.88 (m, 18H), 6.69 (d, $J=8.4$ Hz, 12H), 4.32–4.17 (m, 6H), 4.17–3.81 (m, 36H), 3.80–3.64 (m, 6H), 3.55–2.90 (m, 48H), 2.39 (s, 6H), 1.78 (brs, 12H), 1.49 ppm (brs, 12H); ^{13}C NMR ($CDCl_3$, 75 Hz): $\delta=159.7$, 154.8, 143.4, 142.5, 133.8, 130.9, 130.1, 128.2, 126.7, 125.2, 124.5, 123.1, 121.5, 117.6, 114.7, 106.3, 71.3, 70.9, 70.7, 70.2, 69.2, 68.5, 68.0, 52.1, 48.0, 28.8, 25.7, 13.6 ppm; IR: $\tilde{\nu}=$ 2930 (C–H), 844 (P–F_{as}), 557 cm^{-1} (P–F_s); HRMS calcd for $[M]^{3+}$: 952.4681; found: 952.4648.

Compound 6: To a solution of **5**$H_3[PF_6]_3$ (40 mg, 0.009 mmol) in DMSO was added DBU (12 μL, 0.08 mmol) and then the mixture was poured into water. The resulted precipitate was filtrated, washed with water and then dried in air. 34 mg (85%) of **6** as a white solid was obtained. ^{1}H NMR ([D$_6$]DMSO, 600 MHz): $\delta=8.04$ (d, $J=9.0$ Hz, 6H), 7.94 (d, $J=$ 7.8 Hz, 6H), 7.58 (d, $J=8.4$ Hz, 6H), 7.38–7.30 (m, 6H), 7.30–7.19 (m, 6H), 7.07 (d, $J=7.8$ Hz, 6H), 6.92 (d, $J=7.2$ Hz, 12H), 6.82 (s, 6H), 6.56 (d, $J=7.8$ Hz, 12H), 4.14 (brs, 6H), 3.94 (brs, 6H), 3.87 (brs, 6H), 3.76 (brs, 12H), 3.53–3.38 (m, 24H), 3.29 (brs, 24H), 3.17 (brs, 6H), 3.11 (brs, 6H), 2.16 (s, 6H), 1.52 (brs, 12H), 1.23 ppm (brs, 12H); ^{13}C NMR ([D$_6$]DMSO, 150 MHz): $\delta=157.7$, 154.8, 144.9, 142.2, 133.7, 132.7, 129.7, 129.3, 129.1, 128.4, 126.5, 125.1, 123.8, 119.3, 116.1, 114.3, 107.6, 69.9, 69.8, 69.6, 69.5, 68.8, 68.6, 67.6, 52.1, 47.6, 29.2, 25.5, 13.8 ppm; MALDI-TOF MS: m/z: 2855.4 $[M+1]^+$.

Compound 7: A solution of **5**$H_3[PF_6]_3$ (80 mg, 0.018 mmol), acetic anhydride (100 μL, 0.11 mmol) and DBU (36 μL, 0.24 mmol) in anhydrous DMF (0.5 mL) was stirred overnight. The reaction mixture was extracted with dichloromethane. The organic layer was dried over anhydrous Na_2SO_4 and then concentrated under reduced pressure. The crude product was purified by column chromatography over silica gel with CH_2Cl_2/CH_3OH (40:1 to 20:1) as the eluent to yield **7** (60 mg, 84%) as a white solid. M.p. 151–152°C; $[\alpha]_D^{20}=196$ ($c=0.5$ in CH_2Cl_2); ^{1}H NMR ([D$_6$]DMSO, 600 MHz): $\delta=8.05$–7.98 (m, 6H), 7.95–7.89 (m, 6H), 7.59–7.48 (m, 6H), 7.36–7.29 (m, 6H), 7.28–7.21 (m, 6H), 7.10–7.02 (m, 6H), 6.81 (s, 6H), 6.73–6.51 (m, 24H), 4.19–4.04 (m, 12H), 4.01 (brs, 6H), 3.94 (brs, 6H), 3.80 (brs, 24H), 3.47 (brs, 12H), 3.22–3.04 (brs, 24H), 3.16 (brs, 12H), 2.17 (s, 6H), 2.04–1.96 (m, 9H), 1.58–1.45 (m, 12H), 1.35–1.19 ppm (m, 12H); ^{13}C NMR ([D$_6$]DMSO, 150 MHz): $\delta=169.7$, 157.8, 157.6, 154.2, 144.3, 141.8, 133.1, 129.2, 128.8, 128.3, 127.9, 127.1, 126.0, 124.7, 123.3, 118.7, 115.5, 114.9, 114.5, 107.0, 69.4, 69.1, 68.2, 68.1, 67.9, 67.1, 49.1, 47.2, 46.1, 28.4, 24.9, 21.4, 13.4 ppm; IR: 2927 (C–H), 1645 cm^{-1} (C=O, amide); MALDI-TOF MS: m/z: 2980.2 $[M-3PF_6]^+$; HRMS calcd for $[M+1]^{2+}$: 1491.2143; found: 1491.2138.

Compound 8: A solution of **5**$H_3[PF_6]_3$ (320 mg, 0.036 mmol), chloroacetic anhydride (0.6 g, 3.95 mmol) and DBU (0.36 mL, 2.41 mmol) in anhydrous DMF (0.8 mL) was stirred at 50°C for 24 h. The reaction mixture was extracted with dichloromethane. The organic layer was dried over anhydrous Na_2SO_4 and then concentrated under reduced pressure. The crude product was purified by column chromatography over silica gel with CH_2Cl_2/CH_3OH (80:1 to 60:1) as the eluent to yield **8** (280 mg, 93%) as a white solid. M.p. 161–163°C; $[\alpha]_D^{20}=216$ ($c=0.5$ in CH_2Cl_2); ^{1}H NMR ([D$_6$]DMSO, 600 MHz): $\delta=8.03$–8.00 (m, 6H), 7.93 (d, $J=$ 7.8 Hz, 6H), 7.56–7.51 (m, 6H), 7.36–7.28 (m, 6H), 7.28–7.19 (m, 6H), 7.06–7.04 (m, 6H), 6.81 (s, 6H), 6.75–6.51 (m, 24H), 4.41–4.28 (m, 6H), 4.20–4.00 (m, 18H), 3.93 (brs, 6H), 3.80 (brs, 24H), 3.30 (brs, 12H), 3.20–3.06 (m, 24H), 3.16 (brs, 12H), 2.18 (s, 6H), 1.52 (brs, 12H), 1.24 ppm (brs, 12H); ^{13}C NMR ([D$_6$]DMSO, 150 MHz): $\delta=166.0$, 158.0, 157.8, 154.2, 144.3, 141.8, 133.1, 129.2, 128.7, 128.1, 127.9, 127.5, 126.0, 124.6, 123.2, 118.7, 115.5, 114.8, 114.5, 106.9, 69.4, 69.0, 68.1, 67.8, 67.0, 48.6, 47.2, 46.6, 42.1, 28.3, 24.9, 13.3 ppm; IR: $\tilde{\nu}=2931$ (C–H), 1654 cm^{-1} (C=O, amide); MALDI-TOF MS: m/z: 3082.2 $[M]^+$; HRMS calcd for $[M+1]^{2+}$: 1542.1559; found: 1542.1523.

Compound 9: A mixture of **8** (0.2 g, 0.065 mmol) and sodium azide (50 mg, 0.77 mmol) in DMSO (2 mL) at 70°C was stirred for 10 h. Then methanol (15 mL) was added to the reaction mixture. The resulting mixture was filtrated, washed with water and methanol, and then dried in air to give **9** (0.18 g, 90%) as a white solid. Compound **9** was used without further purification. M.p. 179–181°C; IR: $\tilde{\nu}=2931$ (C–H), 2104 (–N≡N), 1654 cm^{-1} (C=O, amide); MALDI-TOF MS: m/z: 3103.9 $[M]^+$.

Compound 10: After a solution of **9** (62 mg, 0.02 mmol) and triethylphosphine (24 μL, 0.18 mmol) in dichloromethane was stirred at room temperature for 24 h, another amount of triethylphosphine (24 μL, 0.18 mmol) was added. The reaction mixture was stirred for another 12 h and then concentrated. The resulting crude product was purified by column chromatography over silica gel with CH_2Cl_2/CH_3OH (50:1 to 40:1) as the eluent to yield **10** (60 mg, 88%) as a white solid. M.p. 157–159°C; $[\alpha]_D^{20}=$ 204 ($c=0.5$ in CH_2Cl_2); ^{1}H NMR ([D$_6$]DMSO, 600 MHz): $\delta=8.06$–7.98 (m, 6H), 7.96–7.88 (m, 6H), 7.59–7.50 (m, 6H), 7.36–7.29 (m, 6H), 7.28–7.20 (m, 6H), 7.06 (d, $J=8.4$ Hz, 6H), 6.82 (s, 6H), 6.76–6.48 (m, 24H), 4.81–4.79 (m, 3H), 4.13 (brs, 12H), 4.01 (brs, 6H), 3.94 (brs, 18H), 3.82 (brs, 24H), 3.66 (brs, 6H), 3.47 (brs, 12H), 3.33 (brs, 24H), 3.16 (brs, 12H), 2.18 (s, 6H), 1.51 (brs, 12H), 1.23 (brs, 12H), 1.18 ppm (t, $J=$ 3.6 Hz, 18H); ^{13}C NMR ([D$_6$]DMSO, 150 MHz): $\delta=169.4$, 157.8, 157.7, 154.2, 144.3, 141.8, 133.1, 129.2, 128.8, 128.2, 127.9, 127.0, 125.9, 124.6, 123.2, 118.7, 115.5, 114.7, 114.5, 107.0, 69.4, 69.0, 68.2, 67.9, 67.1, 61.30, 61.3 ($J_{PC}=4.4$ Hz), 47.2, 46.9, 46.8, 42.2, 28.3, 24.8, 16.0 ($J_{PC}=6.6$ Hz), 13.3 ppm; ^{31}P NMR ([D$_6$]DMSO, 243 MHz): $\delta=9.7$ ppm; IR: $\tilde{\nu}=2933$ (C–H), 1643 (C=O, amide), 1252 (P=O, phosphoramide), 1059 cm^{-1} (P–O–Me); MALDI-TOF MS: m/z: 3433.8 $[M]^+$; HRMS calcd for $[M+1]^{2+}$: 1717.7741; found: 1717.7771.

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