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Dimerization Control in the Self-Assembly Behavior of Copillar[5]arenes Bearing ω-Hydroxyalkoxy Groups

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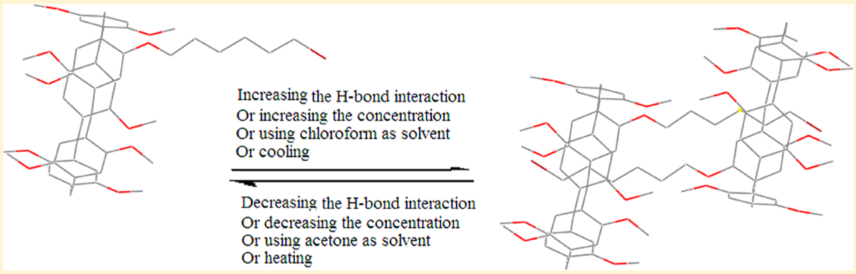
S Supporting Information



ABSTRACT: Two novel copillar[5]arenes bearing ω-hydroxyalkoxy groups are synthesized and their self-assembly properties are studied by ^{1}H NMR spectroscopy, specific viscosity, and X-ray measurements. The copillar[5]arene **2b** bearing a 6-hydroxyhexyloxy group exhibits a reversible self-assembly behavior, leading to the formation of the self-inclusion monomer and hugging dimers. The reversible self-assembly behavior can be controlled by tuning solvent, temperature, guest, and H-bond interaction. However, the copillar[5]arene **2a** bearing a short 4-hydroxybutyloxy group does not show such a self-assembly behavior to the formation of the self-inclusion monomer and hugging dimers.

The generation of well-defined self-assembled structures is based on the spontaneous organization of molecules by the assembly of several subunits by weak noncovalent interactions (van der Waals, CH−π, cation−π, H-bonding, etc.).[1] Over the past two decades, particular attention has been directed toward the design of self-assembled receptors (dimers, oligomers, or polymers) with potential applications in chemical biosynthesis,[2] nanostructures,[3] polymer science[4] or gas-storage.[5]

In contrast to the covalent receptors, the molecular self-assembled receptors have some advantages.[6] First, they avoid tedious multistep synthesis and purification, particularly for large or complicated objects which would be difficult (or impossible) to obtain directly by conventional covalent synthesis. Second, the assembly and disassembly of the molecular receptors can be reversibly controlled.[7] Third, transformation processes of different types of functional supramolecular polymers (cyclic dimers, oligomers, or linear polymers) can be regulated by simple methods. Among the molecular self-assembly, pillar[*n*]arenes,[8] a new class of macrocyclic hosts with *para*-bridges, have shown excellent host−guest binding and self-assembly properties in supramolecular chemistry due to their highly symmetrical and rigid structure and the high electron density of their cavity. Li[8e] reported that a [2]pseudorotaxane was formed via self-assembly between bis(imidazolium) dications and pillar[5]arene driven by cation−π interactions. Huang et al.[9] studied the formation of linear supramolecular polymers of copillar[5]arene bearing an octyl group via self-assembly by weak hydrogen bonds (CH−π interactions), while similar compounds with bromoalkyl groups instead of the alkyl chains produced hugging dimers.[10] Chen and Hou[8f] described the construction of two types of organic nanotubes on different preorganized columnar modules under the direction of hydrogen bonding between column end groups or template effects of water wires.

Consequently, supramolecular polymers of pillararenes can be formed by self-assembly or host−guest assembly by van der Waals interactions and/or hydrogen bonds. It is well-known that competition between linear and cyclic assemblies (self-inclusion monomers, dimers), which plays an essential role in pillararene assembly, is influenced strongly by steric interactions, monomer spatial size, solvents, etc.[6b,8e,11] Thus, understanding the mechanism of the formation of pillararene self-assemblies—what would prevent the cyclization or what would be efficient to yield a specific cyclic structure—is a key physical chemistry problem in the controllable fabrication of supramolecular polymers. Recently, we reported a series of copillar[5]arenes with different alkyl groups that exhibit excellent binding properties to alkyl bromide by the interaction

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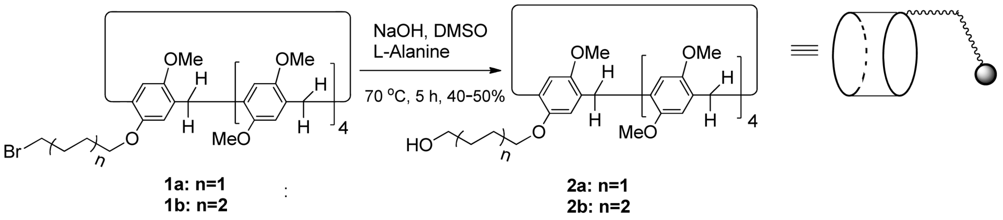
Scheme 1. Synthesis of Copillar[5]arenes 2a and 2b Bearing 4- and 6-Hydroxyalkoxy Groups



1a: n=1
1b: n=2

2a: n=1
2b: n=2

of O⋯H_2CBr or CH_2⋯π electron cloud (benzene).[12] Thus, it is expected that if an alkyl group is introduced into pillar[5]arenes as the side chain, it might lead to the formation of the self-inclusion monomers, hugging dimers, or oligomers. In addition, if the interaction of H-bonds increases, the self-assembly transformation process from the monomer to dimer might be possibly controlled. In this paper, we synthesized two novel copillar[5]arenes (**2a**, **2b**) bearing 4- and 6-hydroxyalkoxy groups, respectively, and studied their self-assembly properties. The synthetic route is shown in Scheme 1.

The effect of deuterated solvents and monomer concentrations on self-assembly properties of **2b** were investigated by ^{1}HNMR spectra, as shown in Figure 1. When deuterated solvent was changed from CD_3COCD_3 (Figure 1a) to $CDCl_3$ (Figure 1f), the protons H^{4-9} of the ω-hydroxyalkoxy group shifted significantly to high field, which was similar to pillar[5]arene **1b**.[12] This phenomenon indicated that ω-hydroxyalkoxy groups could complex with copillar[5]arenes in $CDCl_3$, but not in CD_3COCD_3. In $CDCl_3$, **2b** could form intramolecular or intermolecular self-assembled structures. As the concentration of **2b** increased, the signals of H^{4-9} moved upfield sharply at first (spectra b–d of Figure 1, $\Delta\delta_{\mathrm{H}^4} = 0.548$ ppm, Δ[**2b**] = 11.96 mM) and then slowly (spectra g–h of Figure 1, $\Delta\delta_{\mathrm{H}^4} = 0.004$ ppm, Δ[**2b**] = 24.08 mM). When the concentration of **2b** further increased to 71.77 mM, the signals of H^{4-9} showed nearly no change. These results suggested that the self-assembly of **2b** should be concentration dependent and its equilibrium system should reach the saturation point at 71.77 mM. Compound **2b** formed the self-inclusion monomer at low concentration, but the intermolecular complexes, cyclic dimers rather than linear polymers, occurred as the concentration increased, in agreement with the hugging dimer crystal structure (see Figure 3). It should be mentioned that the critical polymerization concentrations (CPC) of self-assembly systems always exceeded 100 mM (some of them even reached 275 mM).[9,11a]

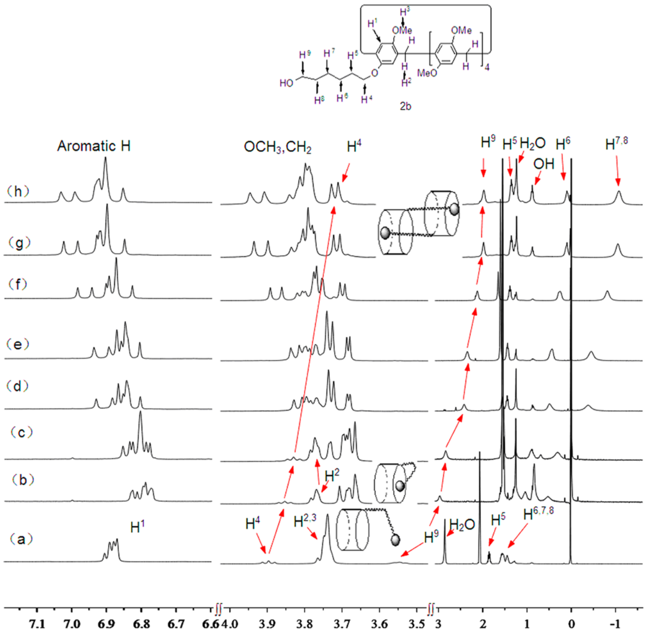


Figure 1. Partial ^{1}H NMR spectra (400 MHz, 293 K) of **2b** at different monomer concentrations: (a) 47.85 mM in CD_3COCD_3, (b) 1.20, (c) 2.39, (d) 13.16, (e) 18.66, (f) 47.85, (g) 71.77, (h) 95.69 mM in $CDCl_3$.

Furthermore, specific viscosities of **2b** at high concentration in chloroform confirmed the formation of cyclic dimers rather than linear polymers. The logarithmic representation of the data was given in Figure 2. For the concentrations between 1.20–95.69 mM, the values of specific viscosities were very small and the slope constant showed a linear relation between specific viscosity and concentration, which is characteristic for cyclic dimers and is in agreement with the literature[11a] which reported characteristics of specific viscosities for cyclic dimers of 2-ureido-4[1*H*]-pyrimidinone (UPy) derivatives in low concentration.

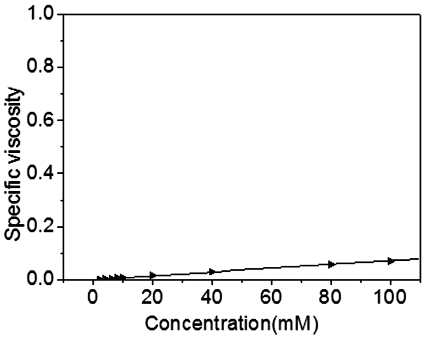


Figure 2. Specific viscosity of chloroform solutions of **2b** versus the concentration (295 K).

The single crystal of hugging dimer **2b•2b** was obtained by slow evaporation of chloroform of the solution of **2b** in the range of 71.77–95.69 mM. This crystal further confirmed that the major formation of self-assembly of **2b** at high concentration was cyclic dimers rather than linear polymers or other oligomers, which is consistent with the ^{1}HNMR and viscosities experiment. In the crystal structure (Figure 3), the threading of the 6-hydroxyalkoxy groups deeply inserted the electron-rich cavity of copillar[5]arene each other in a tail-to-tail manner to create a near C_i symmetric hugging dimer. Ten O⋯O distances and the five O⋯π distances for **2b•2b** (Table 1) indicated that intercomponent bonding was a combination of O–H⋯O_{up} and C–H⋯O hydrogen bonds as well as C–H⋯π interaction. Since the O–H⋯O hydrogen bond was stronger than the O⋯H_2C interaction in each cavity, both O–H⋯O

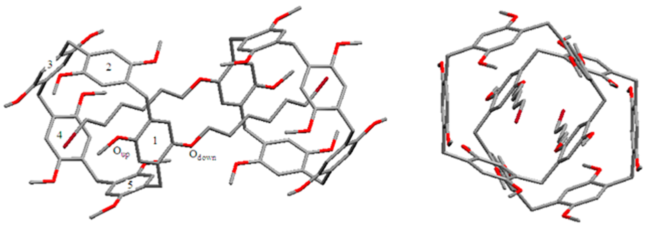


Figure 3. Cyclic dimers in crystals of **2b·2b** from the side (left) and upper view (right).

Table 1. Ten O···O Distances and the Five O···π Distances for 2b·2b

no.	distances (O···O$_{up}$) (Å)	distances (O···O$_{down}$) (Å)	distances (O···π) (Å)
1	4.708	7.011	4.190
2	4.860	7.390	4.523
3	4.626	6.937	4.585
4	3.170	6.357	3.269
5	4.176	6.014	3.389

hydrogen bond interactions were strong enough to hold the alkyl chain in the electron-rich cavity of copillar[5]arene in the solid state.

From the above-mentioned data, we can conclude that **2b** existed as a hugging dimer species with intermolecular interactions at high concentrations. ^{1}H NMR spectra of **2b** at variable temperature were performed at 13.16 mM to probe its self-assembly characteristics (Figure 4). As the temperature decreased, the H$^{4-9}$ signals of ω-hydroxyalkoxy groups significantly moved to high field, suggesting that the self-assembly behavior of **2b** occurred. It means that at low temperature the equilibrium system between the hugging dimer **2b·2b** (D) and the self-inclusion **2b** (S) moved to form more hugging dimer, and the partial chemical shift of **2b** in different formations is shown in Table 2. When temperature decreased to −50 °C, chemical shifts of H$^{4-9}$ showed a barely variation at both concentration of 13.16 mM and 46.65 mM of **2b**, indicating that the saturation point concentration of the equilibrium system was bellow 13.16 mM. This concentration was much smaller than that of self-assembly at 20 °C (71.77 mM). When the temperature changed from +20 to −50 °C, the protons of H^{7,8} were shifted to −2.341 ppm from −1.080 ppm. Obviously, self-assembly of **2b·2b** is easily affected by the temperature. If the temperature decreased, the degree of dimerization increased.

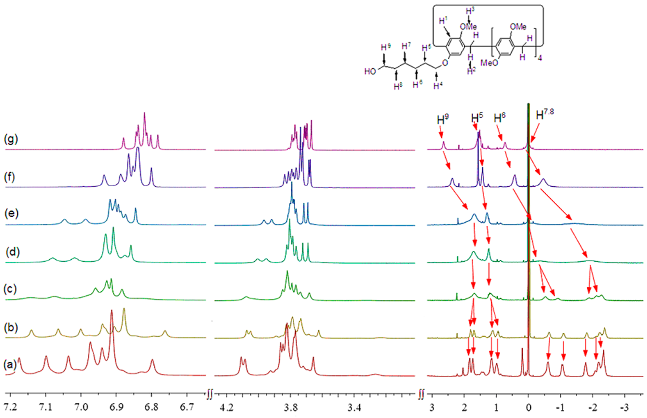


Figure 4. Variable-temperature ^{1}H NMR spectra of **2b** (400 MHz, 13.16 mM for b−g, 46.65 mM for a, CDCl$_3$): (a) −50 °C, (b) −50 °C, (c) −30 °C, (d) −10 °C, (e) 0 °C, (f) 20 °C, (g) 30 °C.

Table 2. Partial Chemical Shift of 2b in the Different Formation in the Self-Assembly System

structure	H^1 (ppm)	H^5 (ppm)	H^6 (ppm)	H^{7,8} (ppm)	H^9 (ppm)
S	6.77−6.82		0.50−1.60 (H$^{5-8}$)		2.96
U	6.87−6.90	1.86	1.44−1.60 (H$^{6-8}$)	3.55	
D^a	6.85−7.03	1.35	0.09	−1.08	1.97
D^b	6.80−7.17	1.00; 1.13^c	−0.62; −1.07^c	−1.79; −2.18; −2.34^c	1.83; 1.73^c

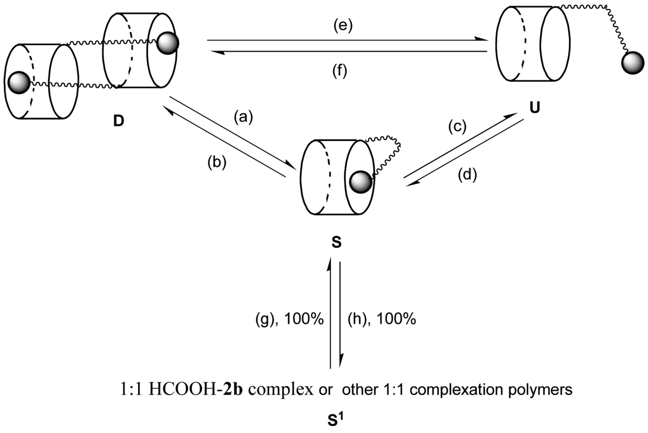
^{a}25 °C. ^{b}−50 °C. ^{c}The peaks of H^5, H^6, and H^9 in the 6-hydroxyalkoxy groups have been separated into two new peaks, while for H^{7,8} has been separated into three new peaks.

At temperatures below −30 °C, the peaks of H^5, H^9, and H^6 in the 6-hydroxyalkoxy groups began to broaden and separate, suggesting that the rate of hugging dimer ⇄ monomer (k_c) became slow on the ^{1}H NMR time scale and most molecules resided in the hugging dimer form. Thus, the rotation of the geminal proton in ω-hydroxyalkoxy groups was suppressed and their conformations were immobilized, which led to their signal separations due to the chiral-micro environment for the geminal protons. The H$^{4-9}$ of **2b** could also be confirmed by (^{1}H,^{1}H) COSY at −50 °C (see the Supporting Information). This planar chirality of pillar[5]arene agreed with the literature[13] that a viologen guest located in the cavity of pillar[5]arene or the self-complexation in the low temperature[14] could inhibit the rotation of the phenylene units through its cavity.

We have also explored the effect of guest on the assembly properties of **2b**. The ^{1}H NMR spectra (Supporting Information) of formic acid solution (HCOOH) in CDCl$_3$ in the absence and in the presence of approximately 1 equiv of host **2b** were studied. The proton H^{10} of H^{10}-COOH in complex exhibited substantial upfield shifts compared to that in the free acid (Δδ = 0.151 ppm), while there was less significant shift for the protons of the pillararene. However, there was a large difference when HCOOH increased to 50 equiv. The signals of H^4 moved downfield and could separate with the other protons (OCH$_3$, CH$_2$), which is similar to the ^{1}H NMR spectroscopy of diluted solution of **2b** (Figure 1), suggesting that the HCOOH could bind with the ω-hydroxyalkoxy groups of **2b** via H-bonds and the equilibrium system would move to the formation of the self-complex **2b** (S) from the hugging dimer **2b·2b** (D). That is to say that the self-assembly behavior of **2b** could be influenced by tuning the driven interaction of H-bonds. In order to confirm this hypothesis, we synthesized **2b**·HCOOH complex (1:1) and found that its self-assembly properties (Supporting Information) were concentration dependent like **2b**, but the shifted values of the chemical shift of the ω-hydroxyalkoxy groups were lower at the same concentration. For example, the signals of H^{7,8} of **2b** and **2b**·HCOOH (71.77 mM) were shifted to −1.080 and −0.350 ppm, respectively. Consequently, the self-assembly properties of **2b** was easier and stronger than **2b**·HCOOH due to the weaker H-bond interaction when the **2b**·HCOOH complex was formed.

On the other hand, the **2b**·HCOOH complex was very stable in CHCl$_3$, petroleum ether, and ethyl acetate, even by heating at 60 °C for 3 h. Meanwhile, the R_f values of **2b**·HCOOH complex and **2b** in silica gel thin-layer chromatography (TLC, petroleum ether/ethyl acetate = 3/1) were 0.5 and 0.23, respectively. The melting point of the **2b**·HCOOH complex decreased to 152−153 °C, while the melting point of **2b** was 195 °C. More surprisingly, the 1:1 **2b**·HCOOH complex could be quantitatively formed from **2b** in $CHCl_3$/HCOOH (v/v = 6/1) solution when stirring at room temperature for 24 h. Compound **2b**·HCOOH complex could also be readily destroyed with $CH_3OH/CHCl_3$ (v/v = 3/1), regenerating **2b** monomer quantitatively. The formation and transformation process of the self-assembled structures of **2b** are summarized in Scheme 2.

Scheme 2. Self-Assemblies of Copillar[5]arene 2b Can Be Controlled by (a) Decreasing the Concentration of Monomer, $CHCl_3$, (b) Increasing the Concentration of Monomer, $CHCl_3$, (c) CH_3COCH_3, (d) Low Concentration of Monomer, $CHCl_3$, (e) CH_3COCH_3, (f) High Concentration of Monomer, $CHCl_3$, (g) $CH_3OH/CHCl_3$ (v/v = 3/1), (h) HCOOH/$CHCl_3$ (v/v = 6/1)



Copillar[5]arene **2a** bearing a butyl alcohol group was prepared for comparison. The results show that **2a** could not assemble to a hugging dimer or other oligomer in $CHCl_3$, indicating that the length of the butyl alcohol group was not suitable for self-assembly. However, the host−guest binding between **2a** and HCOOH could occur. The 1:1 **2a**·HCOOH complex was confirmed by TOF-MASS and ^{1}H NMR spectra (Supporting Information).

In summary, we synthesized two novel copillar[5]arenes bearing ω-hydroxyalkoxy groups of different carbon chain length and studied their self-assembly properties. The formation of a hugging dimer **2b·2b** based on a supramolecular cryptand driven by H-bond interaction was found in the solid state but was not suitable for **2a** bearing the shorter alcohol chain. On the other hand, both **2a** and **2b** are very capable of binding HCOOH guest to form stable 1:1 complexes. More importantly, supramolecular complexes of copillar[5]arene **2b** such as self-inclusion monomer, dimer, and 1:1 host−guest complex could be formed, and their transformation processes can be reversibly controlled (Scheme 2) by tuning solvent, temperature, guest, carbon chain length of ω-hydroxyalkoxy group, and appropriate H-bond interaction. Further studies on the self-assembly properties of **2b**·HCOOH complex are in progress.

■ EXPERIMENTAL SECTION

Copillar[5]arenes **1a** and **1b** were synthesized according to the literature procedure.[12] Solvents were either employed as purchased or dried according to the procedures described in the literature.

General Procedure for the Preparation of Copillar[5]arenes Bearing ω-Hydroxyalkoxy Groups. To a solution of **1** (0.22 mmol) and L-alanine (19 mg, 0.22 mmol) in DMSO (5 mL) was added NaOH (10 mg, 0.25 mmol) under nitrogen atmosphere, and the mixture was stirred at 70 °C for 5 h. After completion of the reaction, water (30 mL) was added, and the product was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phase was dried with anhydrous Na_2SO_4. The crude product was chromatographed over silica gel column using a mixture of ethyl acetate and petroleum ether (bp 40−70 °C) (1:12).

Copillar[5]arene **2a**: colorless crystals; yield 71 mg (40%); mp 169−170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.73−6.80 (m, 10H), 3.78−3.83 (m, 12H), 3.62−3.67 (m, 27H), 3.46 (m, 2H), 1.65 (m, 2 H), 1.51 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.0, 150.8, 150.8, 150.7, 128.67, 128.5, 128.4, 128.3, 115.0, 114.6, 114.2, 114.1, 114.0, 58.3, 62.3, 56.0, 55.9, 55.8, 29.8, 29.7, 29.6, 29.1, 25.9, 14.2; MS (MALDI-TOF) calcd for $C_{48}H_{56}O_{11}$ 808.382, found 808.382 $[M]^+$, 831.359 $[M + Na]^+$, 847.366 $[M + K]^+$. Anal. Calcd for $C_{48}H_{56}O_{11}$: C, 71.27; H, 6.98. Found: C, 71.31; H, 6.93.

Copillar[5]arene **2b**: colorless crystals; yield 83 mg (45%); mp 195 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.80−6.94 (m, 10H), 3.68−3.84 (m, 39H), 2.38 (s, 2H), 1.43 (m, 2 H), 0.42 (s, 2H), −0.47 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 150.9, 150.7, 150.6, 150.5, 150.4, 150.0, 129.1, 128.4, 128.3, 128.3, 128.2, 128.1, 128.0, 115.1, 115.0, 113.8, 113.7, 113.6, 113.5, 113.2, 69.8, 62.5, 56.5, 55.8, 55.70, 55.7, 55.5, 55.3, 31.0, 29.8, 29.6, 29.5, 29.2, 25.5, 23.5; MS (MALDI-TOF) calcd for $C_{50}H_{60}O_{11}$ 836.414, found 836.392 $[M]^+$. Anal. Calcd for $C_{50}H_{60}O_{11}$: C, 71.75; H, 7.23. Found: C, 71.68; H, 7.30.

General Procedure for the Preparation of 1:1 Complex (2·HCOOH). To a solution of **2** (0.1 mmol) in $CHCl_3$ (0.5 mL) was added HCOOH (3 mL) under nitrogen atmosphere and the mixture stirred at room temperature for 24 h. Water (3 mL) was added, and product was extracted with $CHCl_3$ (3 × 3 mL). The combined organic phase was dried with anhydrous Na_2SO_4. The $CHCl_3$ was then removed under reduced pressure, leading to the expected product.

1:1 Complex (2a·HCOOH): colorless crystals; yield 83 mg (100%); mp 119−121 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.94 (s, 1H), 6.71−6.79 (m, 10H), 4.03 (brs, 2H), 3.83−3.85 (m, 2H), 3.78 (brs, 10H), 3.63−3.66 (m, 27H), 1.77 (brs, 3H), 1.26 (brs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 161.2, 150.9, 150.8, 149.9, 128.4, 128.3, 128.2, 115.0, 114.2, 114.1, 67.8, 63.7, 55.9, 55.8, 29.8, 29.7, 29.6, 26.0, 25.4; MS (MALDI-TOF) calcd for $C_{49}H_{58}O_{13}$ 854.388, found 836.329 $[M - H_2O]^+$.

1:1 Complex (2b·HCOOH): colorless crystals; yield 86 mg (100%); mp 152−153 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.49 (brs, 1H), 6.83−6.94 (m, 10H), 3.82 (m, 12 H), 3.71−3.80 (m, 27H), 2.39 (brs, 2H), 1.53 (brs, 2H), 0.87−1.29 (m, 2H), 0.58 (brs, 2H), −0.10 (brs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 161.9, 151.0, 150.6, 150.5, 150.4, 149.9, 129.1, 128.3, 128.2, 128.1, 128.0, 115.0, 114.7, 114.2, 113.7, 113.5, 114.3, 69.0, 64.5, 56.1, 55.6, 55.5, 55.4, 29.8, 29.7, 29.7, 29.4, 29.4, 29.3, 27.0, 25.1, 24.3; MS (MALDI-TOF) calcd for $C_{51}H_{62}O_{13}$ 882.419, found 864.350 $[M - H_2O]^+$.

■ ASSOCIATED CONTENT

S Supporting Information

NMR and MS spectra of **2** and their host−guest complexes; the crystal data and structure refinement parameters of the hugging dimer **2b·2b** (CCDC reference no. 882877). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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