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Hydrogen Bonding-Directed Quantitative Self-Assembly of Cyclotriveratrylene Capsules and Their Encapsulation of C_{60} and C_{70}

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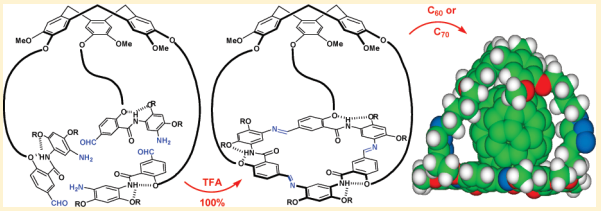
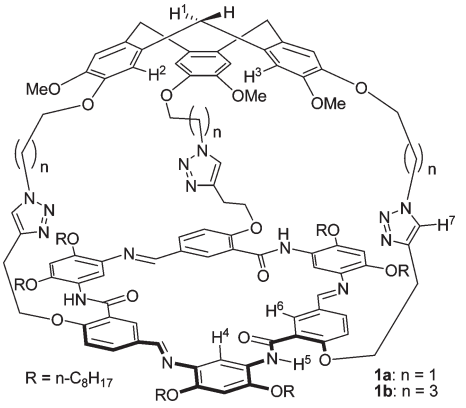
Supporting Information

ABSTRACT: Under the direction of intramolecular three-center hydrogen bonding, two cyclotriveratrylene (CTV)-based capsules are assembled quantitatively from C_3-symmetric CTV precursors by forming three imine bonds from arylamide-derived foldamer segments. ^{1}H and ^{13}C NMR and UV/vis experiments reveal that the capsules strongly encapsulate C_{60} and C_{70} in discrete solvents.



Hydrogen bonding-induced aromatic amide oligomers may adopt folded or extended conformations,[1] depending on the position of the substituents on the aromatic rings.[2] In recent years, this family of preorganized frameworks has found increasing applications in the construction of shape-persistent macrocyclic systems.[3] In this context, a variety of macrocycles of discrete sizes have been prepared through the formation of amide bonds.[4−9] Examples of the transition metal ion−ligand coordination and 1,2,3-triazole-derived macrocycles have also been reported.[10,11] We recently found that, by using the dynamic combinatorial chemistry (DCC) to build reversible imine or hydrazone bonds,[12] complicated macrocyclic structures can be constructed in very high or quantitative yields from readily accessible precursors,[13] which opens the possibility of quick assembly of new functional macrocyclic systems.

Cyclotriveratrylenes (CTVs) are a family of rigid concave cyclophanes that have been widely utilized in supramolecular chemistry.[14,15] Particularly, their concave skeletons form complexes with convex surfaces of fullerenes via complementary stacking in the solid state.[16−18] Since fullerenes are significantly larger than the CTV backbone, considerable efforts have been devoted to designing CTV-based receptors to achieve increased binding affinity for fullerenes. In the past decade, a number of aromatic units bearing CTVs have been developed,[19−23] which display enhanced binding capacity due to additional stacking between the appended aromatic units and fullerenes. It is also revealed that CTV dimers connected with rigid phenylacetylenic spacers exhibit stronger binding capacity because two CTV units can generate a tweezer or are incorporated into a macrocyclic structure to cooperatively interact with fullerenes.[24] Given the spherical feature of fullerenes, three-dimensional capsular receptors should be ideal for encapsulating them. Nevertheless, to the best of our knowledge, CTV-based receptors of this kind are not available, although hydrogen bonding-driven dimeric CTV capsules were reported.[25] We previously found that hydrogen bonded arylamide foldamers or macrocycles stacked with fullerenes in both the solution and solid state.[26,27] We thus became interested in developing novel CTV-based capsules through DCC-based macrocyclization of hydrogen bonded arylamide segments. We herein report the quantitative construction of two such CTV-derived capsules, i.e., **1a** and **1b**, by making use of this approach and their encapsulation of C_{60} and C_{70} in discrete solvents.



The synthetic routes for **1a** and **1b** are provided in Scheme 1. Tribromides **2a** and **2b**[28] were first prepared according to reported methods and then treated with an excess of sodium azide in DMF to afford **3a** and **3b** in 91% and 90% yields. Then, **6** was prepared in 82% yield from **4** and **5** in DMF and further hydrolyzed to give **7** quantitatively. The acid was then coupled with **8**[13c] in chloroform to afford **9** in 89% yield. Treatment of **9** with **3a** or **3b** in the presence of cuprous iodide in chloroform and acetonitrile afforded **10a** and **10b** in 74% and 76% yields. Finally, the two compounds were converted into **1a** and **1b** in chloroform in the presence of an excess of trifluoroacetic

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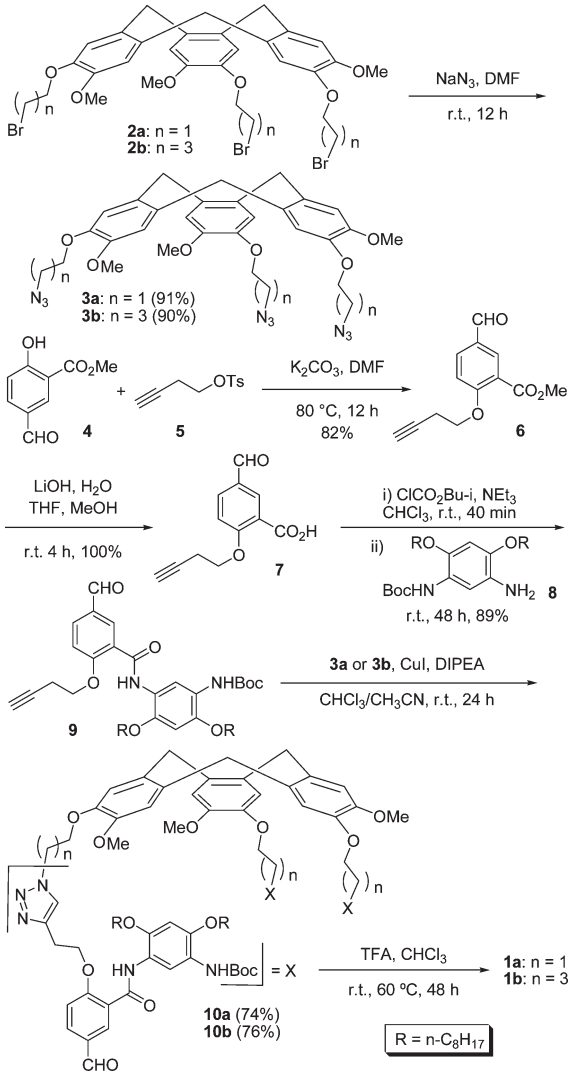
Scheme 1. Synthesis of Capsular Molecules 1a and 1b



acid (TFA). The reactions were also performed in chloroform-*d* and tracked by using ^{1}H NMR. It was revealed that at the early stage, the solution gave rise to complicated signals, implying the formation of multiple products. The spectra gradually became simplified and evolved into one set of signals after ca. 48 h, as revealed for reactions for the formation of other related macrocycles.[13c]

In principle, the target molecules may have two isomers, depending on the relative orientation of the CTV and triimine macrocyclic units. Their ^{1}H NMR spectra in $CDCl_3$ or DMSO-d_6 exhibited one set of signals of high resolution, suggesting that only one of the isomers was formed. Molecular dynamics simulations for the two isomers of **1a** and **1b** showed that the isomers with the methoxyl and imine groups being located to the opposite sides of the related linkers (see the structure, vide ante) were energetically favorable as compared to that with the two groups being located to the same side of the linker. The simulations also showed that, when the linkers adopted the extended conformation, both **1a** and **1b** could produce a cavity to host C_{60} or C_{70}. Therefore, their encapsulation for the two fullerenes was investigated.

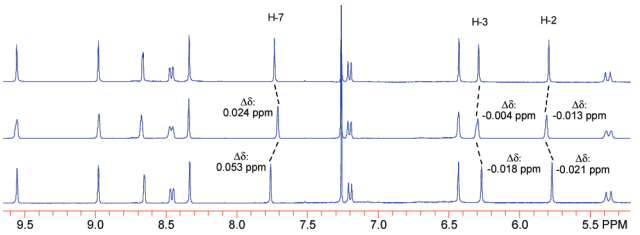


Figure 1. Partial ^{1}H NMR spectra (400 MHz) of (a) **1b** + C_{60} (1:1), (b) **1b**, and (c) **1b** + C_{70} (1:1) in $CDCl_3$ and CS_2 (1:1, v/v) ([**1b**] = 5.0 mM).

The downfield signals of **1b** in the ^{1}H NMR spectrum were fully assigned based on the COSY and NOESY experiments, which also revealed NOEs between H-1,2 and H-4, H-3 and H-6, and H-5 and H-7 (see the structure for numbering). These observations suggested a close contact between the two cyclic units. Adding 1 equiv of C_{60} or C_{70} caused these NOEs to disappear, indicating that they were encapsulated in the cavity of **1b** to increase the distance of the two cyclic units of **1b**. Addition of the fullerenes also induced the signals of H-2, H-3, and H-7 of **1b** to shift slightly (Figure 1). The largest shifting was observed for the H-7 signal induced by C_{70} ($\Delta\delta$ = 0.053 ppm). These shifts were small, but distinct and repeatable.[27b,29] The mixing also caused the signal of C_{60} in ^{13}C NMR to shift upfield by 0.1 ppm, again supporting its encapsulation by **1b**.

Diffusion-ordered spectroscopic (DOSY) experiments for **1b** provided additional evidence for encapsulation.[27b,30] The diffusion coefficients (D) obtained based on H-5−7 in the absence and presence of C_{60} or C_{70} are presented in Table 1. It can be found that addition of C_{60} or C_{70} led to significant decrease of the D values of **1b** probed with all three signals. The values of the same mixtures obtained with different probes exhibited a similar changing tendency, which was in accordance with the above ^{1}H NMR observations, indicating that C_{60} and C_{70} were encapsulated in **1b** and thus led to an increase of the apparent size of **1b**. The values of the C_{70} mixture were generally lower than those of the C_{60} mixture, reflecting the increased apparent size. Vapor pressure osmometry (VPO) experiments in toluene also supported the formation of the complexes. The number-average molecular weights of **1b**, **1b**@C_{60}, and **1b**@C_{70} were determined to be 2500, 3200, and 3500 u, respectively, which are comparable to the corresponding calculated values (2340, 3060, and 3180 u).

Adding C_{60} or C_{70} to the solution of **1b** also caused a significant decrease of its absorption bands. Quantitative titration experiments were then performed (Figure 2). By applying the results to the Benesi−Hildebrand (BH) plot,[31] we determined the association constants (K_{assoc}) of complexes **1b**@C_{60} and **1b**@C_{70} to be 1.9×10^5 and 2.4×10^4 M^{-1} in chloroform and 1.5×10^5 and 1.2×10^5 M^{-1} in chlorobenzene. Under the same conditions, adding C_{60} or C_{70} to the solution of **10b** in the two solvents did not induce perceptible changes of the absorption of **10b**. The absorption of a simple triimine-based macrocycle[13c] was weakened by C_{60} or C_{70}, but no fixed stoichiometry could be derived from the Benesi−Hildebrand equations. These results clearly showed that the strong 1:1 encapsulation of **1b** for C_{60} and C_{70} was driven by cooperative stacking of its two aromatic segments with the fullerenes.

The encapsulation of **1a** for C_{60} and C_{70} was also investigated. On the basis of the UV/vis titrations, the K_{assoc} values for their 1:1 complexes were estimated to be 7.7×10^4 and 6.4×10^3 M^{-1} in chloroform and 1.1×10^4 and 1.2×10^3 M^{-1} in chlorobenzene,

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Table 1. Diffusion coefficients of 1b in the Absence and Presence of C_{60} and C_{70} at 25 °C (1:1, 5 mM) in $CDCl_3$ and CS_2 (1:1, v/v) by DOSY

	1b		**1b** + C_{60}		**1b** + C_{70}	
proton	δ (ppm)	D (10^{-9} m^2/s)	δ (ppm)	D (10^{-9} m^2/s)	δ (ppm)	D (10^{-9} m^2/s)
H-5	9.623	3.169	9.628	0.508	9.620	0.488
H-6	9.046	3.182	9.046	0.506	9.044	0.481
H-7	7.794	3.119	7.779	0.503	7.821	0.481

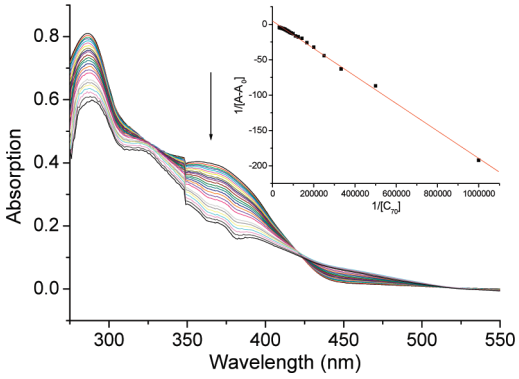

Figure 2. Absorption spectral changes of **1b** (1.0×10^{-5} M) with the addition of C_{70} ($0-30 \times 10^{-5}$ M) in chloroform (inset: the Benesi–Hildebrand plot with a 1:1 stoichiometry).

respectively. These relatively large values indicate that this molecule is also a good receptor for the two fullerenes, although its cavity is smaller than that of **1b**.

In summary, we have developed a strategy to quickly build CTV-based capsular structures by combining hydrogen bonding-induced preorganization of aromatic amide segments with the DCC principle. The new capsules are good receptors for fullerenes. Future works will point to the development of new porous or multiply layered architectures. Particularly, the possibility of building systems with closed space for molecular recognition or tunable function will be exploited.

EXPERIMENTAL SECTION

Compound 3b. A solution of **2b** (1.39 g, 1.70 mmol) and NaN_3 (1.10 g, 17.0 mmol) in DMF (30 mL) was stirred at rt for 12 h and then concentrated. The resulting residue was extracted with CH_2Cl_2 (30 mL). The organic phase was washed with water (3×10 mL) and brine (10 mL), then dried over $MgSO_4$. Upon removal of the solvent, the crude product was recrystallized from AcOEt to yield **3b** as a yellow solid (1.07 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.83 (s, 3H), 6.82 (s, 3H), 4.75 (d, J = 13.7 Hz, 3H), 4.08–3.92 (m, 6H), 3.81 (s, 9H), 3.53 (d, J = 13.8 Hz, 3H), 3.34 (t, J = 6.7 Hz, 6H), 1.92–1.72 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.3, 147.0, 132.3, 131.8, 115.5, 113.8, 68.6, 56.2, 51.1, 36.4, 26.4, 25.7. MS (ESI): m/z 722.4 $[M + Na]^+$. HRMS (ESI): calcd for $C_{36}H_{45}N_9Na_1O_6$ $[M + H]^+$ 722.3385, found 722.3392.

Compound 6. A suspension of **4** (5.00 g, 27.8 mmol), **5** (7.50 g, 33.3 mmol), K_2CO_3 (11.5 g, 83.2 mmol), and KI (0.20 g, 1.20 mmol) in DMF (120 mL) was stirred at 80 °C for 12 h and then cooled to rt. The solid was filtered off and the filtrate concentrated with a rotavapor. The resulting slurry was extracted with AcOEt (500 mL). The organic phase was washed with water (4×200 mL) and brine (200 mL) and dried over $MgSO_4$. After removal of the solvent, the resulting residue was purified by column chromatography (petroleum ether/AcOEt 15:1) to give **6** as a white solid (5.29 g, 82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.92 (s, 1H), 8.32 (d, J = 2.2 Hz, 1H), 8.01 (dd, J_1 = 8.7 Hz, J_2 = 2.2 Hz, 1H), 7.09 (d, J = 8.7 Hz, 1H), 4.26 (t, J = 7.1 Hz, 2H), 3.92 (s, 3H), 2.78 (td, J_1 = 7.1 Hz, J_2 = 2.7 Hz, 2H), 2.09–2.04 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.7, 165.2, 162.1, 134.1, 134.0, 129.2, 120.9, 113.2, 79.3, 70.3, 67.0, 52.0, 19.1. MS (EI): m/z 232 $[M]^+$. Anal. Calcd for $C_{13}H_{12}O_4$: C, 67.23; H, 5.21. Found: C, 67.20; H, 5.19.

Compound 7. A solution of **6** (2.00 g, 8.60 mmol) and lithium hydroxide monohydrate (1.45, 34.4 mmol) in a mixture of THF (20 mL), methanol (10 mL), and water (5 mL) was stirred for 4 h and then neutralized with hydrochloric acid (1 N) to pH 3. The mixture was then concentrated to ca. 10 mL and the resulting slurry was extracted with AcOEt (200 mL). The organic phase was washed with water (2×80 mL) and brine (80 mL), then dried over sodium sulfate. After removal of the solvent under reduced pressure, compound **7** was obtained as a white solid (1.85 g, 100%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.98 (s, 1H), 9.91 (s, 1H), 8.16 (d, J = 2.2 Hz, 1H), 8.03 (dd, J_1 = 8.6 Hz, J_2 = 2.2 Hz, 1H), 7.35 (d, J = 8.6 Hz, 1H), 4.26 (t, J = 6.7 Hz, 2H), 3.34 (s, 1H), 2.67 (t, J = 6.6 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 191.2, 166.4, 161.4, 134.1, 132.5, 129.0, 122.3, 1134.0, 80.8, 72.7, 67.0, 18.7. MS (ESI): m/z 218.0 $[M]^+$. Anal. Calcd for $C_{12}H_{10}O_4$: C, 66.05; H, 4.62. Found: C, 66.01; H, 4.59.

Compound 9. To a stirred solution of **7** (0.14 g, 0.66 mmol) and NEt_3 (0.1 L) in chloroform (4 mL), cooled in an ice-bath, was added isobutyl chloroformate (0.086 mL, 0.66 mmol). Stirring was continued for 40 min and then a solution of **8** (0.26 g, 0.55 mmol) in $CHCl_3$ (2 mL) was added slowly. After the mixture was stirred for 48 h, 100 mL of $CHCl_3$ was added. The solution was washed with water (2×50 mL) and brine (50 mL), then dried over Na_2SO_4. The solvent was then removed under reduced pressure and the resulting residue was purified by column chromatography (petroleum ether/EtOAc 6:1) to give **9** as a white solid (0.38 g, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.99 (s, 1H), 9.69 (s, 1H), 8.99 (s, 1H), 8.82 (s, 1H), 8.11–7.98 (m, 1H), 7.15 (d, J = 8.7 Hz, 1H), 6.78 (s, 1H), 6.51 (s, 1H), 4.43 (t, J = 7.2 Hz, 2H), 4.05–3.96 (m, 4H), 2.83 (dd, J_1 = 7.2 Hz, J_2 = 4.5 Hz, 2H), 2.07–2.05 (m, 1H), 1.88–1.72 (m, 4H), 1.53 (s, 9H), 1.48–1.15 (m, 20H), 0.87–0.83 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.4, 161.1, 160.1, 152.6, 144.5, 144.3, 136.7, 132.0, 130.4, 123.3, 121.3, 120.7, 113.7, 113.1, 98.1, 78.6, 77.3, 77.0, 76.7, 71.2, 69.6, 69.2, 67.4, 31.6 (d), 29.2 (d), 29.1, 28.2, 25.9, 25.8, 22.5 (d), 19.2, 14.0, 13.9. MS (MALDI-TOF): m/z 687.7 $[M + Na]^+$, 703.7 $[M + K]^+$. HRMS (FT): calcd for $C_{39}H_{56}N_2O_7Na$ $[M + H]^+$ 687.3980, found 687.3984.

Compound 10b. A suspension of **3b** (1.06 g, 1.50 mmol) and **9** (2.57 g, 4.50 mmol), CuI (0.17 g, 0.90 mmol), and DIPEA (1.56 mL, 9.00 mmol) in a mixture of $CHCl_3$ (15 mL) and MeCN (15 mL) was stirred for 24 h. The solid was filtrated and the filtrate concentrated under reduced pressure. The resulting residue was triturated with $CHCl_3$ (40 mL) and the solution was washed with water (2×20 mL) and brine (20 mL), then dried over Na_2SO_4. Upon removal of the solvent, the crude product was purified by column chromatography (CH_2Cl_2/MeOH 50:1) to give **10b** as a white solid (3.00 g, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.87 (s, 3H), 9.59 (s, 3H), 9.07 (s, 3H), 8.65 (d, J = 2.1 Hz, 3H), 7.92 (dd, J_1 = 8.6 Hz, J_2 = 2.1 Hz, 3H), 7.46 (s, 3H), 7.12 (d, J = 8.6 Hz, 3H),

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6.82−6.72 (m, 9H), 6.48 (s, 3H), 4.68 (d, J = 13.6 Hz, 3H), 4.59 (t, J = 6.0 Hz, 6H), 4.22 (t, J = 6.9 Hz, 6H), 4.04−3.78 (m, 18H), 3.72 (s, 9H), 3.48 (d, J = 13.6 Hz, 3H), 3.32 (t, J = 6.0 Hz, 6H), 1.90−1.85 (m, 6H), 1.82−1.69 (m, 12H), 1.68−1.55 (m, 6H), 1.48 (s, 27H), 1.43−1.11 (m, 60H), 0.86 (t, J = 6.8 Hz, 9H), 0.79 (t, J = 6.8 Hz, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.3, 161.3, 160.3, 152.6, 147.9, 146.7, 144.2, 143.8, 142.8, 136.1, 132.2, 132.1, 131.7, 130.1, 123.3, 122.4, 121.4, 120.9, 114.9, 113.5, 113.1, 112.9, 98.2, 79.9, 69.7, 69.2, 68.7, 68.3, 56.0, 49.5, 36.2, 31.6, 31.5, 29.5, 29.2, 29.1 (d), 29.0 (d), 28.2, 27.1, 25.9, 25.7, 25.6, 22.5, 22.4, 13.9 (d). MS (MALDI-TOF): m/z 2416.5 $[M - 3Boc + Na]^+$, 2516.6 $[M - Boc + Na]^+$.

Compound 1b. A solution of **10b** (0.13 g, 0.05 mmol) and TFA (0.20 mL, 2 0.00 mmol) in $CHCl_3$ (10 mL) was stirred at 60 °C for 48 h and then diluted with $CHCl_3$ (100 mL). The solution was washed with saturated $NaHCO_3$ solution (2 × 50 mL), water (2 × 50 mL), and brine (50 mL), then dried over Na_2SO_4. Removal of the solvent afforded **1b** as a yellow solid (0.12 g, 100%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.62 (s, 3H), 9.03 (s, 3H), 8.72 (d, J = 2.2 Hz, 3H), 8.51 (dd, J_1 = 8.6 Hz, J_2 = 2.2 Hz, 3H), 8.33 (s, 3H), 7.74 (s, 3H), 7.22 (d, J = 8.6 Hz, 3H), 6.47 (s, 3H), 6.37 (s, 3H), 5.86 (s, 3H), 5.43 (d, J = 13.3 Hz, 3H), 4.70−4.47 (m, 9H), 4.13−4.00 (m, 9H), 3.97−3.83 (m, 6H), 3.59 (d, J = 13.3 Hz, 3H), 3.56−3.47 (m, 6H), 3.45−3.35 (m, 6H), 3.09 (s, 9H), 2.02−1.86 (m, 6H), 1.73 (m, 12H), 1.64−1.50 (m, 6H), 1.48−1.18 (m, 60H), 0.95−0.81 (m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.6, 157.9, 156.6, 149.9, 148.1, 146.4, 145.9, 143.7, 137.2, 132.4, 132.3, 132.0, 130.6, 130.2, 123.5, 121.6, 121.3, 113.6, 113.1, 112.9, 112.1, 99.1, 70.6, 68.9, 68.5, 68.1, 54.8, 48.8, 38.5, 31.8, 31.7, 29.4 (d), 29.3 (d), 29.2, 28.7, 28.4, 26.1, 25.9, 25.8, 23.6, 22.7, 22.6, 14.1, 14.0. MS (MALDI-TOF): m/z 2339.5 $[M + H]^+$, 2361.8 $[M + Na]^+$. HRMS (FT): calcd for $C_{138}H_{184}N_{15}O_{18}$ $[M + H]^+$ 2339.3895, found 2339.3938.

■ ASSOCIATED CONTENT

Supporting Information. General experimental methods, ^{1}H and ^{13}C NMR and UV/vis spectra, and dynamic simulation details. This material is available free of charge via the Internet at http://pubs.acs.org.

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