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Synthesis and self-assembly of novel calix[4]arenocrowns: formation of calix[4]areno[2]catenanes

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Abstract—A series of novel calix[4]arenocrowns **1a–c** were efficiently synthesized by a one-pot reaction of calix[4]monohydroquinone diacetate **5** with ditosylate **6** and its analogues in the presence of sodium hydroxide. It was found that the calix[4]arenocrowns could form stable pseudorotaxane-type complexes **2a–c** with paraquat, and further self-assemble into calix[4]areno[2]catenanes **3a–c** with dicationic salt **8** and *p*-bis(bromomethyl)benzene.

Interlocked molecules such as catenanes, pseudorotaxanes and rotaxanes have attracted great interest in the field of supramolecular chemistry not only for their unusual structures but also for their potential applications in nanotechnology and molecular machines.[1] Since Stoddart and co-workers[2] first reported the template-directed synthesis of catenanes based on the intermolecular interaction of donor and acceptor, this approach has been widely utilized to generate various interlocked molecules with unique structures and specific properties by modifying π-accepting and/or π-donating building blocks.[3]

Calixarenes[4] are a class of well-defined macrocyclic oligomers of phenol bridged by methylene groups. Owing to their (1) convenient preparation in large quantities, (2) easy chemical modification on both lower and upper rims, and (3) unique structural properties, they have been ideal platforms for the development of complex supramolecular systems with unique structures and/or properties. Consequently, calixarene-based interlocked assemblies[5] have attracted more and more attention in recent years. Li et al.[6] reported a new class of [2]catenanes based on calix[4]arene-incorporating crown ethers or tetracationic acceptor rings by using the donor–acceptor interaction principle. Arduini et al.[7] first utilized calix[6]arene as a wheel for rotaxanes, and further found that isomeric oriented calix[6]arene-based rotaxanes could be selectively synthesized. Based on the preorganization of tetraurea calix[4]arenes in hydrogen-bonded dimers, Böhmer et al.[8] recently synthesized a series of novel multicyclic bis[2]catenanes and mutiple catenanes by metathesis reactions. Inspired by the charged catenanes reported by Stoddart and co-workers[2] we deduced that calixarenocrowns **1**, in which crown chains are linked to the calixarene skeleton from the upper rim to the lower rim, could self-assemble into calixarenocatenanes **3** with unique structures (Fig. 1). Herein, we report the first synthesis of calix[4]arenocrowns **1**, and the formation of stable pseudorotaxane-type complexes **2** and novel calix[4]areno[2]catenanes **3**.

Synthesis of the calix[4]arenocrown **1a** is depicted in Scheme 1. Starting from *p-tert*-butylcalix[4]arene, calix[4]monoquinone **4** was prepared in 68% yield by the oxidation of tripropoxy-calix[4]arene[9] with $Tl(O\text{-}COCF_3)_3$ in trifluoroacetate acid. Reaction[10] of **4** with an excess of Ac_2O in refluxed HOAc in the presence of Zn powder and concentrated HCl afforded compound **5** in 73% yield. Treatment of **5** with 1,4-bis[2-(2(2(2-hydroxyethoxy)-ethoxy)ethoxy)ethoxy]benzene bis(4-toluenesulfonate) **6** in dry MeCN in the presence of NaOH resulted in the formation of desired calix[4]arenocrown **1a**[11] in 20% yield, which was confirmed by MALDI-TOF MS and NMR spectra. Compound **1a** contained a bis(*p*-phenylene)-34-crown-10 subunit, and the cone conformation of its calix[4]arene skeleton was substantiated by four characteristic doublets at 4.42, 4.39, 3.10, 3.01 ppm for the bridging methylene protons in the ^1H NMR spectrum.[12] Following the same method

Keywords: Calix[4]arenocrown; Synthesis; Self-assembly; Calix[4]-areno[2]catenane.
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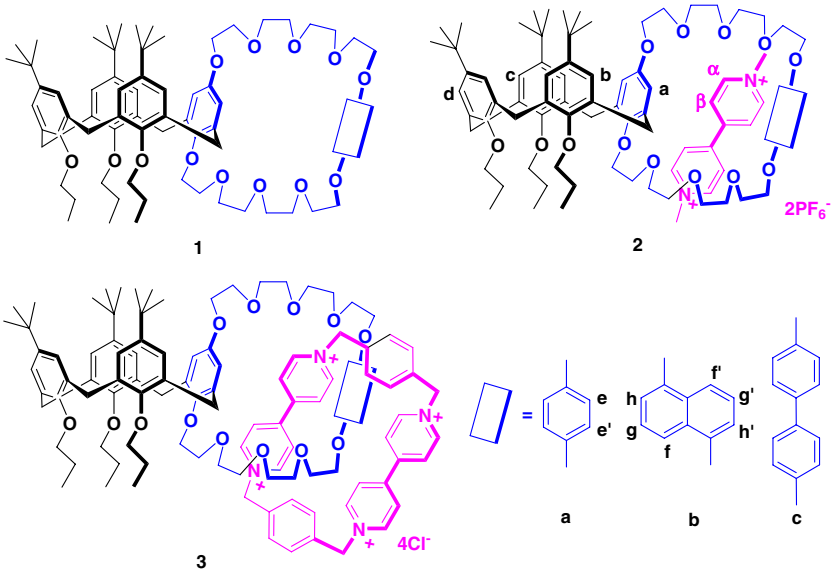
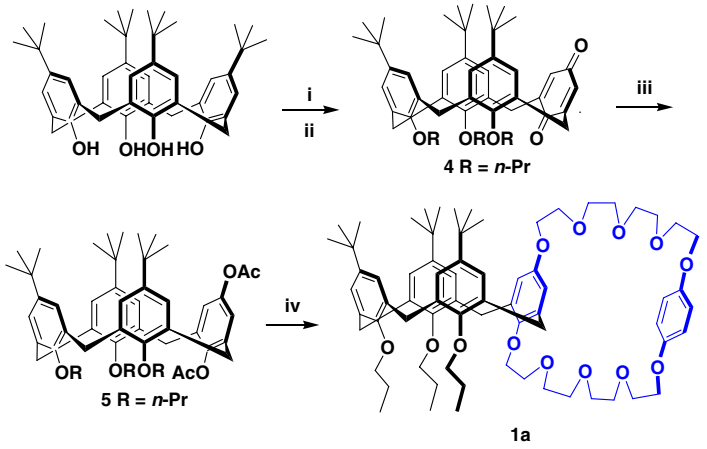


Figure 1. Structure and proton designations of calix[4]arenocrowns **1**, pseudorotaxane-type complexes **2**, and calix[4]arenocatenanes **3**.



Scheme 1. Reagents and conditions: (i) *n*-PrI, DMF, 65%; (ii) $Tl(OCOCF_3)_3$, CF_3CO_2H, 12 h, 68%; (iii) Zn, HOAc, Ac_2O, 2 h, 73% and (iv) NaOH, CH_3CN, **6**, 5d, 70%.

as above, calix[4]arenocrowns **1b,c** were also prepared by the reaction of **5** with the corresponding ditosylate.[11]

The formation of the complexes between calix[4]-arenocrowns with paraquat (4,4-bipyridinium dimethyl salt) **7** was first investigated. Consequently, it was found that when host **1a** and 1 equiv of paraquat were mixed in acetonitrile, they gave a pale brown solution due to charge transfer interaction. Similarly, a mixed solution of **1c** and **7** also gave a pale brown solution, whereas a mixed solution of **1b** and **7** gave a reddish brown one. As shown in Figure 2b, the ^1H NMR spectrum of a 1:1 mixture of **1a** and **7** in CD_3CN displayed a dispersed array of well-defined resonances and a great difference from those for host **1a** (Fig. 2a) and guest **7** (Fig. 2c). The signals of the hydroquinone protons H_a and $H_{e,e'}$ in host **1a** and the proton H_β in the guest were all shifted significantly upfield. Moreover, it was found that the bridging methylene protons adjacent to crown ether also

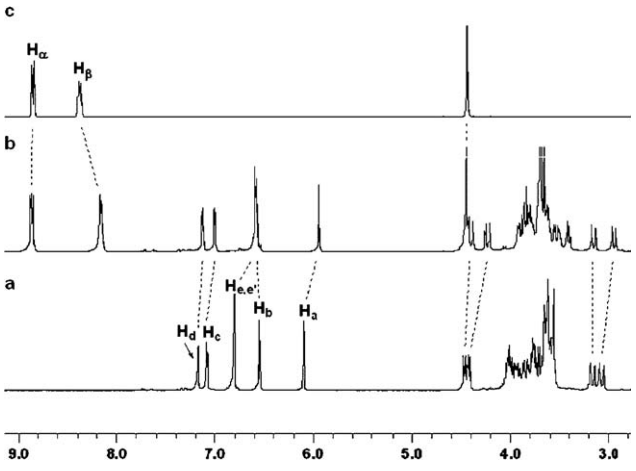


Figure 2. Partial ^1H NMR spectra (300 MHz, CD_3CN) of (a) free host **1a**, (b) **1a** and 1.0 equiv of 7 and (c) free paraquat **7**.

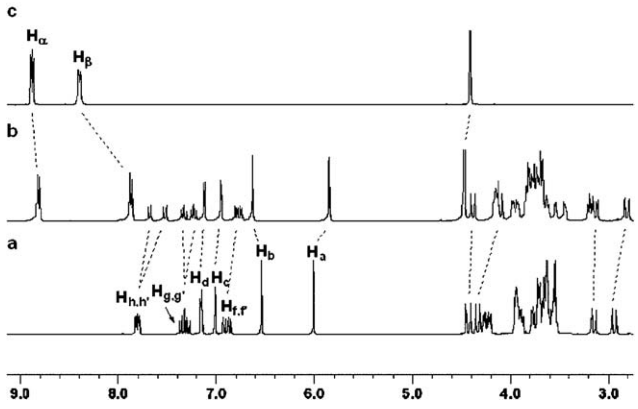


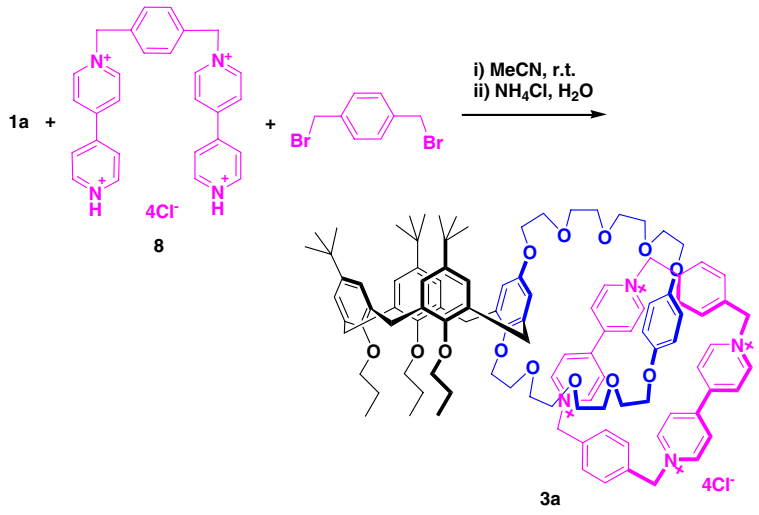
Figure 3. Partial ^{1}H NMR spectra (300 MHz, CD_3CN) of (a) free host **1b**, (b) **1b** and 1.0 equiv of **7** and (c) free paraquat **7**.

showed an upfield shift. These observations were all consistent with the formation of the pseudorotaxene-type complex **2a**. Complex **2c** showed similar spectral properties as those of **2a**. In the case of complex **2b**, its ^{1}H NMR spectrum in CD_3CN showed similar but bigger changes (Fig. 3) compared with those of **2a**. In particular, the aromatic proton H_β showed a large upfield shift (−0.54 ppm) due to the strong shielding effect of the naphthyl ring in the crown subunit.

Catenations were performed under the known reaction conditions.[2] Thus, when dicationic salt **8** reacted with 1, 4-bis(bromomethyl)benzene in the presence of **1a** in CH_3CN at room temperature for 6 d, calix[4]areno[2]-catenane **3a** was obtained in 20% yield after column chromatography (Scheme 2). Under the same conditions, calix[4]areno[2]-catenanes **3b** and **3c** were obtained in 23% and 30% yield, respectively.[13] The calix[4]arenocatenanes **3a**–**c** were all characterized by their NMR spectra. It was found that their ^{1}H NMR spectra clearly showed one set of newly emerged signals for the catenanes arising from the protons associated with tetracationic cyclophane. The chemical shifts of aromatic protons in the tetracationic cyclophane and hydroquinol units all moved upfield. In particular, large changes in the chemical shifts for the inside aromatic protons were observed because of the strong π–π stacking interaction. The calix[4]arene moieties in all [2]catenanes were in the cone conformation as confirmed by their ^{1}H NMR spectra, in which four doublets for the bridging methylene protons of the calix[4]arene moiety were present, and ^{13}C NMR spectra, characteristic signals at 30–33 ppm for the bridging methylene carbons presented.[11] Structures of calix[4]arenocatenanes **3a**–**c** were also confirmed by their MALDI-TOF MS, in which peaks corresponding to the $[M–4Cl]^+$ were observed. Moreover, treatment of catenane **3a** with a saturated aqueous NH_4PF_6 solution afforded the counterion exchange product. Its MALDI-TOF MS showed peaks at 2117, 1972, 1827 and 1682 for $[M–PF_6]^+$, $[M–2PF_6]^+$, $[M–3PF_6]^+$, and $[M–4PF_6]^+$, respectively.

We have further investigated the charge transfer behavior of the calix[4]areno[2]catenanes by UV–vis spectroscopy. The experiments were carried out in acetonitrile at room temperature. It was found that calix[4]arenocrowns **1a**–**c** showed intense absorption bands with maxima at 283, 326, and 271 nm, respectively, arising from the aromatic rings. However, new absorption bands were observed for catenanes **3a**–**c** with maxima at 438, 517, and 463 nm, respectively, which are attributed to the donor–acceptor interactions between the aromatic rings of the crowns and the bipyridinium rings. This is in accordance with the charged [2]catenane based on π–stacking principle.[2]

In conclusion, we have synthesized a series of calix[4]-arenocrowns, and demonstrated that they could form stable pseudorotaxane-type complexes with paraquat, and further assemble into novel calix[4]areno[2]catenanes based on the donor–acceptor interactions. The novel catenanes based on calix[4]arene would find potential applications in molecular machines and devices, which are now under way.



Scheme 2. Synthesis of calix[4]areno[2]catenane **3a**.

Acknowledgements

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11. Synthesis of calix[4]arenocrowns **1**: To a solution of **5** (0.19 g, 0.23 mmol) in dry CH_3CN (10 mL) under N_2 was added NaOH (80 mg). The resulting mixture was refluxed for 2.5 h and then a solution of ditosylate (0.23 mmol) in dry CH_3CN (10 mL) was added for 10 min. The reaction mixture was refluxed for 5 d, cooled to room temperature, and then concentrated in vacuo. The residue was dissolved in CH_2Cl_2 (100 mL), washed with brine (2×30 mL) and water (2×30 mL), respectively, dried over $MgSO_4$, and then filtered. Evaporation of CH_2Cl_2 in vacuo gave a crude product, which was purified by column chromatography using ethyl acetate: petroleum ether (1:4 v/v) as eluent to provide a white solid. Compound **1a**: yield 70%; mp 102–103 °C; ^{1}H NMR ($CDCl_3$): δ 7.09 (d, $J = 2.4$ Hz, 2H), 6.99 (d, $J = 2.4$ Hz, 2H), 6.79 (s, 4H), 6.23 (s, 2H), 5.89 (s, 2H), 4.42 (d, $J = 12.8$ Hz, 2H, ArCH_2Ar), 4.39 (d, $J = 12.6$ Hz, 2H, ArCH_2Ar), 4.05 (t, $J = 4.8$ Hz, 2H), 3.98–3.92 (m, 6H), 3.82 (t, $J = 4.7$ Hz, 8H), 3.70–3.65 (m, 16H), 3.62–3.59 (m, 4H), 3.56–3.53 (m, 2H), 3.10 (d, $J = 12.8$ Hz, 2H, ArCH_2Ar), 3.01 (d, $J = 12.7$ Hz, 2H, ArCH_2Ar), 2.15–1.95 (m, 4H), 1.95–1.75 (m, 2H), 1.32 (s, 18H), 1.08 (t, $J = 7.4$ Hz, 3H), 0.89 (t, $J = 7.4$ Hz, 6H), 0.72 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 155.0, 153.1, 153.0, 152.9, 152.8, 148.9, 144.4, 143.8, 135.8, 135.1, 134.6, 134.0, 126.1, 125.8, 125.1, 124.5, 115.6, 112.8, 73.7, 70.9, 70.8, 70.8, 70.7, 70.7, 70.6, 70.5, 70.2, 69.8, 69.7, 69.5, 68.5, 68.2, 68.1, 67.9, 66.1, 34.0, 33.3, 31.7, 31.1, 30.9, 23.5, 23.0, 10.8, 9.9; MALDI-TOF MS: m/z 1160.3 M^+, 1183.3 $(M+Na)^+$, 1199.2 $(M+K)^+$. Anal. Calcd for $C_{71}H_{100}O_{13}$: C, 73.42; H, 8.68. Found: C, 73.43; H, 8.96. Compound **1b**: yield 68%; mp 65–66 °C; ^{1}H NMR ($CDCl_3$): δ 7.40 (d, $J = 3.0$ Hz, 2H), 7.37 (d, $J = 3.0$ Hz, 2H), 7.07 (d, $J = 2.1$ Hz, 2H), 7.00–6.93 (m, 6H), 6.21 (s, 2H), 5.83 (s, 2H), 4.42 (d, J=12.8 Hz, 2H, ArCH_2Ar), 4.32 (d, $J = 12.6$ Hz, 2H, ArCH_2Ar), 4.20–4.16 (m, 4H), 3.91 (t, $J = 8.2$ Hz, 4H), 3.87 (t, $J = 4.5$ Hz, 4H), 3.74–3.61 (m, 20H), 3.56 (t, $J = 5.1$ Hz, 4H), 3.48 (t, $J = 4.7$ Hz, 2H), 3.04 (d, $J = 12.3$ Hz, 2H, ArCH_2Ar), 2.91 (d, $J = 12.7$ Hz, 2H, ArCH_2Ar), 2.12–1.98 (m, 4H), 1.95–1.79 (m, 2H), 1.30 (s, 18H), 1.07(t, $J = 7.3$ Hz, 3H), 0.88 (t, $J = 7.5$ Hz, 6H), 0.71 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 158.0, 155.0, 152.9, 152.7, 148.8, 144.3, 143.7, 135.9, 135.2, 133.9, 133.6, 132.0, 127.6, 125.7, 125.1, 124.4, 115.2, 114.8, 112.7, 73.8, 71.0, 70.83, 70.80, 70.7, 70.6, 70.5, 70.4, 69.8, 69.6, 67.8, 65.9, 34.0, 33.4, 31.7, 31.5, 31.1, 30.9, 23.5, 22.9, 10.8, 10.7; MALDI-TOF MS: m/z 1259.7 $(M+Na)^+$. Anal. Calcd for $C_{77}H_{104}O_{13}\cdot 1.5H_2O$: C, 73.13; H, 8.53. Found: C, 72.90; H, 8.61. Compound **1c**: yield 65%; mp 70–72 °C. ^{1}H NMR ($CDCl_3$): δ 7.86 (d, $J = 6.3$ Hz, 2H), 7.30–7.21 (m, 2H), 7.07 (s, 2H), 6.95 (s, 2H), 6.80–6.77 (m, 2H), 6.24 (s, 2H), 5.86 (s, 2H), 4.42 (d, $J = 12.8$ Hz, 2H, ArCH_2Ar), 4.35 (d, $J = 12.6$ Hz, 2H, ArCH_2Ar), 4.29 (t, $J = 3.7$ Hz, 2H), 4.22 (t, $J = 3.7$ Hz, 2H), 4.01–3.94 (m, 4H), 3.81–3.77 (m, 4H), 3.72–3.69 (m, 4H), 3.61–3.58 (m, 16H), 3.59–3.58 (m, 4H), 3.52–3.42 (m, 2H), 3.10 (d, $J = 12.9$ Hz, 2H, ArCH_2Ar), 2.93 (d, $J = 12.8$ Hz, 2H, ArCH_2Ar), 2.10–1.92 (m, 4H), 1.92–1.79 (m, 2H), 1.27 (s, 18H), 1.09 (t, $J = 5.9$ Hz, 3H), 0.90 (t, $J = 5.3$ Hz, 6H), 0.73 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 154.0, 153.32, 153.27, 151.9, 151.8, 147.7, 143.3, 142.8, 134.8, 134.1, 132.9, 131.1, 125.7, 124.7, 124.14, 124.07, 124.02, 123.8, 123.4, 113.5, 111.7, 104.7, 74.0, 70.12, 69.96, 69.89, 69.85, 69.7, 69.6, 69.4, 69.1, 68.76, 68.67, 68.5, 67.0, 65.6, 32.9, 32.3, 30.9, 30.7, 30.4, 29.9, 28.6, 28.3, 22.5, 21.9, 21.6, 13.1, 9.8, 8.9; MALDI-TOF MS: m/z 1210.5 M^+, 1233.5 $(M+Na)^+$, 1249.5 $(M+K)^+$. Anal. Calcd for

$C_{75}H_{102}O_{13}$·0.5 H_2O: C, 73.80; H, 8.51. Found: C, 73.84; H, 8.48.

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13. Synthesis of calix[4]arenocatenanes **3**: To a stirred solution of compound **1** (0.043 mmol) in dry MeCN (8 mL) under N_2 was added a solution of **8** (0.016 mmol) in dry MeCN (2 mL). The resulting mixture was stirred for 30 min at room temperature and we then added a solution of 1,4-bis(bromomethyl)benzene (0.016 mmol) in dry MeCN (2 mL). The reaction mixture was stirred at room temperature for 6 d and then concentrated in vacuo. The residue was subjected to column chromatography on silical gel with MeOH–2N NH_4Cl–$MeNO_2$ (7:2:1) as eluent to give product. Compound **3a**: yield 20%; mp 135 °C (dec.); ^{1}H NMR (CD_3OD): δ 9.28 (d, $J = 7.0$ Hz, 8H), 8.14 (d, $J = 5.9$ Hz, 8H), 7.95 (s, 8H), 6.94 (s, 2H), 6.84 (s, 2H), 6.41 (s, 2H), 5.87 (ABq, $J = 12.1$ Hz, 8H), 5.66 (s, 2H), 4.35 (d, $J = 12.7$ Hz, 2H, ArCH_2Ar), 4.05 (d, $J = 12.6$ Hz, 2H, ArCH_2Ar), 4.06–3.83 (m, 14H), 3.81–3.77 (m, 10H), 3.75–3.69 (m, 8H), 3.53–3.51 (m, 2H), 3.14–3.11 (m, 2H), 3.06 (d, $J = 12.8$ Hz, 2H, ArCH_2Ar), 2.83 (d, $J = 12.8$ Hz, 2H, ArCH_2Ar), 2.68 (t, $J = 7.4$ Hz, 2H), 1.99–1.84 (m, 6H), 1.18 (s, 18H), 1.05 (t, $J = 7.4$ Hz, 3H), 0.96 (t, $J = 7.4$ Hz, 6H), 0.80 (s, 9H); ^{13}C NMR: δ 153.9, 146.5, 144.9, 144.3, 135.5, 134.6, 134.5, 133.6, 132.6, 131.0, 130.7, 128.4, 125.7, 125.4, 124.6, 124.7, 115.3, 115.3, 113.3, 112.8, 76.6, 76.4, 71.5, 70.3, 70.2, 70.9, 69.9, 69.6, 69.4, 69.2, 68.8, 67.2, 66.7, 64.2, 33.4, 33.0, 31.6, 30.8, 30.7, 30.3, 29.3, 29.0, 23.0, 22.3, 18.1, 13.0, 9.7, 9.3; HRMS calcd for $C_{107}H_{132}N_4O_{13}$ $(M–4Cl^––2H)^+$ 1678.9435, found 1678.9460. Compound **3b**: yield 23%; mp 154 °C (dec.); ^{1}H NMR (CD_3OD): δ 9.24 (d, $J = 6.2$ Hz, 8H), 8.02 (s, 8H), 7.95 (br s, 8H), 6.96 (d, $J = 2.1$ Hz, 2H), 6.77 (d, $J = 2.4$ Hz, 2H), 6.35 (s, 2H), 5.91 (Abq, $J = 12.3$ Hz, 8H), 5.86 (d, $J = 2.7$ Hz, 2H), 5.60 (t, $J = 4.1$ Hz, 2H), 5.17 (Abq, $J = 5.8$ Hz, 4H), 4.57 (br s, 2H), 4.36 (d, $J = 12.7$ Hz, 2H, ArCH_2Ar), 4.18–4.16 (m, 2H), 4.13 (d, $J = 12.5$ Hz, 2H, ArCH_2Ar), 4.02–3.98 (m, 2H), 3.97–3.93 (m, 4H), 3.91–3.83 (m, 8H), 3.82–3.79 (m, 8H), 3.77–3.75 (m, 2H), 3.68 (t, $J = 6.7$ Hz, 4H), 3.70–3.60 (m, 8H), 3.52–3.48 (m, 2H), 3.39–3.37 (m, 2H), 3.41 (t, $J = 6.1$ Hz, 2H), 3.26 (br s, 4H), 3.13 (br s, 2H), 3.06 (d, $J = 12.9$ Hz, 2H, ArCH_2Ar), 2.76 (d, $J = 12.7$ Hz, 2H, ArCH_2Ar), 2.05–1.98 (m, 2H), 1.96–1.83 (m, 4H), 1.18 (s, 18H), 1.01 (t, $J = 7.7$ Hz, 3H), 0.93 (t, $J = 7.5$ Hz, 6H), 0.78 (s, 9H); ^{13}C NMR: δ 152.8, 146.7, 144.9, 137.2, 135.6, 135.0, 133.9, 133.4, 131.9, 130.7, 128.4, 127.1, 126.0, 125.5, 125.3, 124.9, 124.2, 114.8, 114.0, 112.6, 76.6, 76.3, 73.3, 71.4, 70.3, 70.2, 69.9, 69.7, 69.3, 67.5, 64.2, 33.4, 30.8, 30.7, 30.3, 27.5, 22.8, 17.9, 9.9, 9.2; HRMS calcd for $C_{113}H_{134}N_4O_{13}$ $(M–4Cl^––2H)^+$ 1754.9948, found 1754.9906. Compound **3c**: yield 30%; mp 173 °C (dec.); ^{1}H NMR (CD_3OD): δ 9.26 (d, $J = 6.4$ Hz, 2H), 9.13 (t, $J = 5.7$ Hz, 4H), 9.07 (d, $J = 6.4$ Hz, 2H), 8.26 (s, 2H), 8.21 (s, 2H), 8.09 (d, $J = 6.2$ Hz, 4H), 7.74–7.71 (m, 2H), 7.64–7.58 (m, 6H), 6.90 (d, $J = 2.4$ Hz, 2H), 6.77 (d, $J = 2.4$ Hz, 2H), 6.43 (d, $J = 7.9$ Hz, 1H), 6.39 (s, 2H), 6.37 (d, J=7.9 Hz, 1H), 6.09–6.06 (m, 2H), 6.02 (d, $J = 13.1$ Hz, 2H), 5.90 (ABq, $J = 13.0$ Hz, 8H), 5.56 (s, 2H), 4.44 (t, $J = 6.0$ Hz, 4H), 4.32 (d, $J = 12.7$ Hz, 2H, ArCH_2Ar), 4.31–4.25 (m, 4H), 4.17–4.12 (m, 4H), 3.99–3.97 (br s, 4H), 3.90 (d, $J = 12.6$ Hz, 2H, ArCH_2Ar), 3.93–3.86 (m, 4H), 3.78–3.68 (m, 10H), 3.49–3.47 (m, 2H), 3.05 (t, $J = 6.7$ Hz, 2H), 3.03 (d, $J = 13.0$ Hz, 2H, ArCH_2Ar), 2.72 (d, $J = 12.8$ Hz, 2H, ArCH_2Ar), 2.63 (t, $J = 7.0$ Hz, 2H), 2.52 (t, $J = 8.7$ Hz, 2H), 1.90–1.83 (m, 6H), 1.04 (s, 18H), 1.02 (t, $J = 7.6$ Hz, 3H), 0.93 (t, $J = 7.5$ Hz, 6H), 0.78 (s, 9H); ^{13}C NMR: δ 155.2, 154.4, 154.0, 152.6, 152.5, 150.7, 146.8, 146.3, 146.0, 145.7, 145.4, 145.0, 138.2, 136.1, 135.8, 134.8, 134.0, 132.8, 132.6, 132.5, 132.4, 129.6, 127.6, 127.3, 126.9, 126.0, 125.9, 115.0, 109.6, 105.8, 105.5, 78.1, 77.8, 73.5, 72.9, 72.7, 71.8, 70.8, 70.5, 70.3, 69.1, 66.0, 66.8, 34.8, 34.4, 32.1, 31.8, 31.7, 24.5, 24.3, 19.6, 11.0, 10.6; HRMS calcd for $C_{111}H_{132}N_4O_{13}$ $(M–4Cl^––2H)^+$ 1728.9791, found 1728.9804.