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# New tubular products from calixarene–cyclodextrin coupling

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**Abstract**—The direct coupling via succinyl-diamide links of a difunctionalised cyclodextrin (CD) to di- and tetra-functionalised calix[4]-arene-crown-6 (CAL) leads to tubular calixarene–cyclodextrin species. The product structures were characterised by high resolution $^{1}H$ and $^{13}C$ NMR and MALDI-TOF spectroscopies.


## 1. Introduction

Inclusion, complexation and molecular recognition are crucial issues in supramolecular chemistry. In addition to the widely known crown ethers, two families of cavity-forming macrocyclic compounds, which play major roles in this area are calixarenes and cyclodextrins[1–5]. We report here further syntheses of unique molecules in which all three of these structural units are incorporated into a linear array of tubular form. The products bear some analogy to 'calixtubes',[6] in which polyether chains link calix[4]arene units only, whereas here the versatility of both calixarene and cyclodextrin units as receptors can be exploited.

Previously, we reported the successful coupling of calix[4]-arene-crown-6 to β-cyclodextrin derivatives (native or permethylated)[7,8]. A succinyl-diamide unit was generated as a link between amino-β-cyclodextrin and aminocalix[4]-arene derivatives. The aminocalixarenes were obtained by reduction of the corresponding nitrocalix[4]arenes[8–12] and the coupling, which was more efficient when the initial acylation was of the aminocalixarene rather than that of the aminocyclodextrin, led to a family of new calixarene–cyclodextrin compounds. The use of permethylated β-cyclodextrin provided a much more soluble reactant, overcoming a common problem in reactions of this type.

In continuation of this work, we have investigated similar coupling of a diaminocyclodextrin with di- and tetra-aminocalixarenes in the hope of obtaining tubular cyclodextrin–calixarenes of enhanced rigidity due to multiple bridging. Three calixarenes, diisopropoxycalix[4]arene-crown-6 (**1a**), di-*n*-octyloxycalix[4]arene-crown-6 (**1b**) and biscrown-calix[4]arene (**1c**), all in the 1,3-alternate conformation, were used as precursors to amino species then used in coupling reactions with $6^{A},6^{D}$-diaminocyclodextrin (**10**). The different calixarene species were used to determine if the nature of the phenoxy substituents significantly affected the efficiency of the coupling reactions. To our knowledge, this type of structure was not previously reported in the literature.

## 2. Results and discussion

We have previously described the syntheses of the calixarene reactants.[8] An outline of the procedures and compound structures[13,14] for the reactant **1a** is given in Scheme 1. Reduction of the nitro groups to give amino substituents enabled the succinyl linker unit to be grafted onto the calixarene. In the case of the disubstituted derivative **4** (prepared for the di-isopropylcalixarene only), the succinyl groups lie to the same side of the calix[4]arene as the crown loop. The tetra-aminocalixarenes and their succinylamido derivatives were prepared for all three reactants, **1a**, **1b** and **1c**.

For the difunctionalized cyclodextrin, we used Sinay's method[15] to obtain permethylated $6^{A},6^{D}$-dihydroxy-β-cyclodextrin **8**, which was then subjected to a two-step azidation, followed by reduction of the azido to amino groups[16] to give **10** (Scheme 2).

Using conventional peptide coupling procedures,[17] reaction between **4** and **10** in a 1:1 ratio in DMF provided the 'half-tube' molecule **11**, while use of a 1:2 ratio provided the doubly-substituted calixarene **12** (Scheme 3). The relatively small succinyl linker appears to be compatible with the desired coupling reactions.

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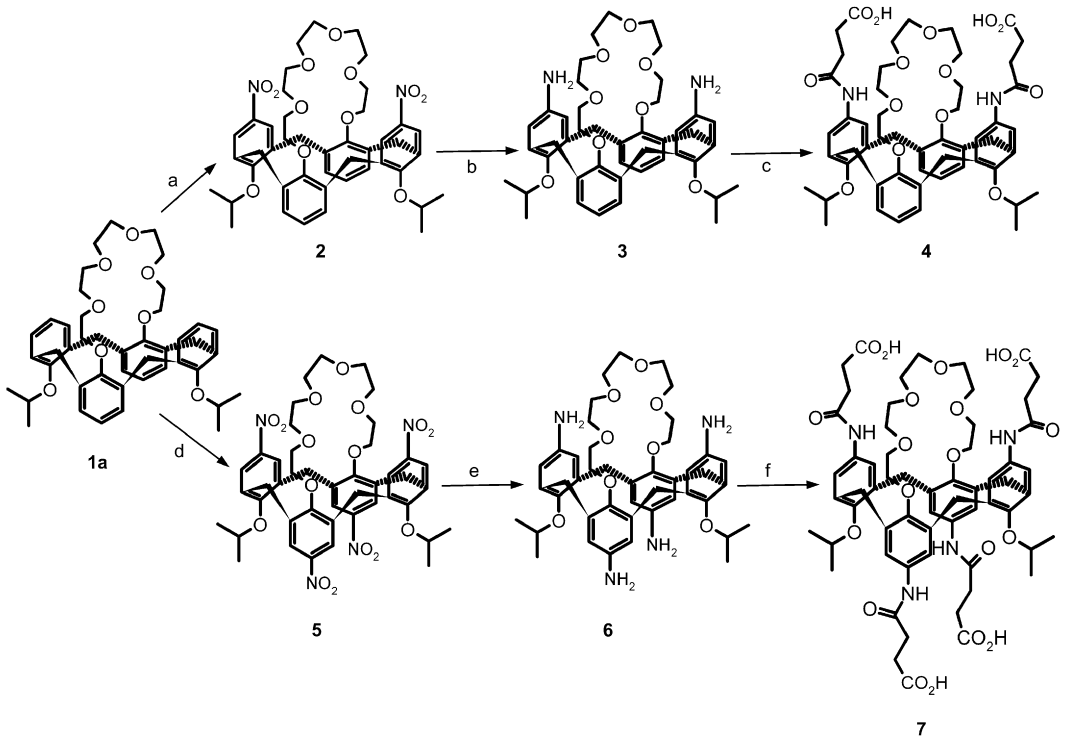
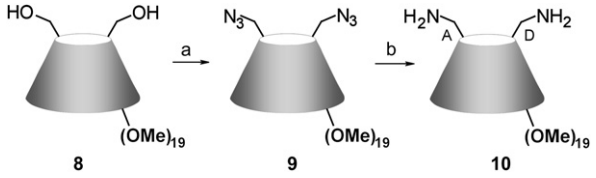


**Scheme 1**. (a) Concd $HNO_3$, acetic acid, acetic anhydride, −18 °C, 18 h, 75%; (b) $SnCl_2$, EtOH, 70 °C, 18 h, 75%; (c) succinic anhydride, DMF, 18 h, 86%; (d) fuming $HNO_3$, acetic anhydride, $CH_2Cl_2$, 1 h, 88%; (e) Ni(Raney), toluene, 70 °C, 4 h, 76%; (f) succinic anhydride, DMF, 18 h, 79%.



**Scheme 2**. (a) (i) MsCl (8 equiv), DMAP, pyridine, 0 °C, 3 h; (ii) $NaN_3$, DMF, 60 °C, overnight, 85% (2 steps); (b) $PPh_3$ (6 equiv), dioxane, $NH_4OH$, rt, overnight, 95%.

This one-pot coupling synthesis has the advantage of being short. It is an alternative to the time-consuming pathway involving monoprotection of the diaminocyclodextrin as a preliminary to intermolecular coupling followed by deprotection and macrocyclisation, though of course it necessitates the reaction condition modifications, for example the higher dilution to avoid polymer formation through multiple intermolecular steps.

At high dilution, although cyclisation (intramolecular) pathways were favoured, the reactions were slow, with typical reaction periods of 5 days at room temperature. Monitoring of the reactions (at both 1:1 and 1:2 stoichiometry) between **4** and **10** by MALDI-TOF mass spectrometry (Fig. 1) showed peaks for **11** at *m/e* 2327.57 ($[MNa]^+$) and 2343.50 ($[MK]^+$) and for **12** at *m/e* 3920.74 ($[MNa]^+$) and 3936.62 ($[MK]^+$).

The yields of these two coupling products were approximately 45% and 20%, respectively. Yields of the bis(cyclodextrin)calix[4]arenes **15** and **16** were poorer, though that of the former, derived from the di-octyloxycalix[4]arene **13**, was approximately three times that of the product from the bis(crown)calix[4]arene **14**. MALDI-TOF mass spectrometry confirmed the presence of tubular structures **15** and **16** with a pair of $[MNa]^+$ and $[MK]^+$ ions in both cases as well as the intermediacy of the monofunctionalised calixarenes in all cases involving the 1:2 stoichiometric ratio of reactants. Steric factors are presumably responsible for the yields of cyclisation reactions.

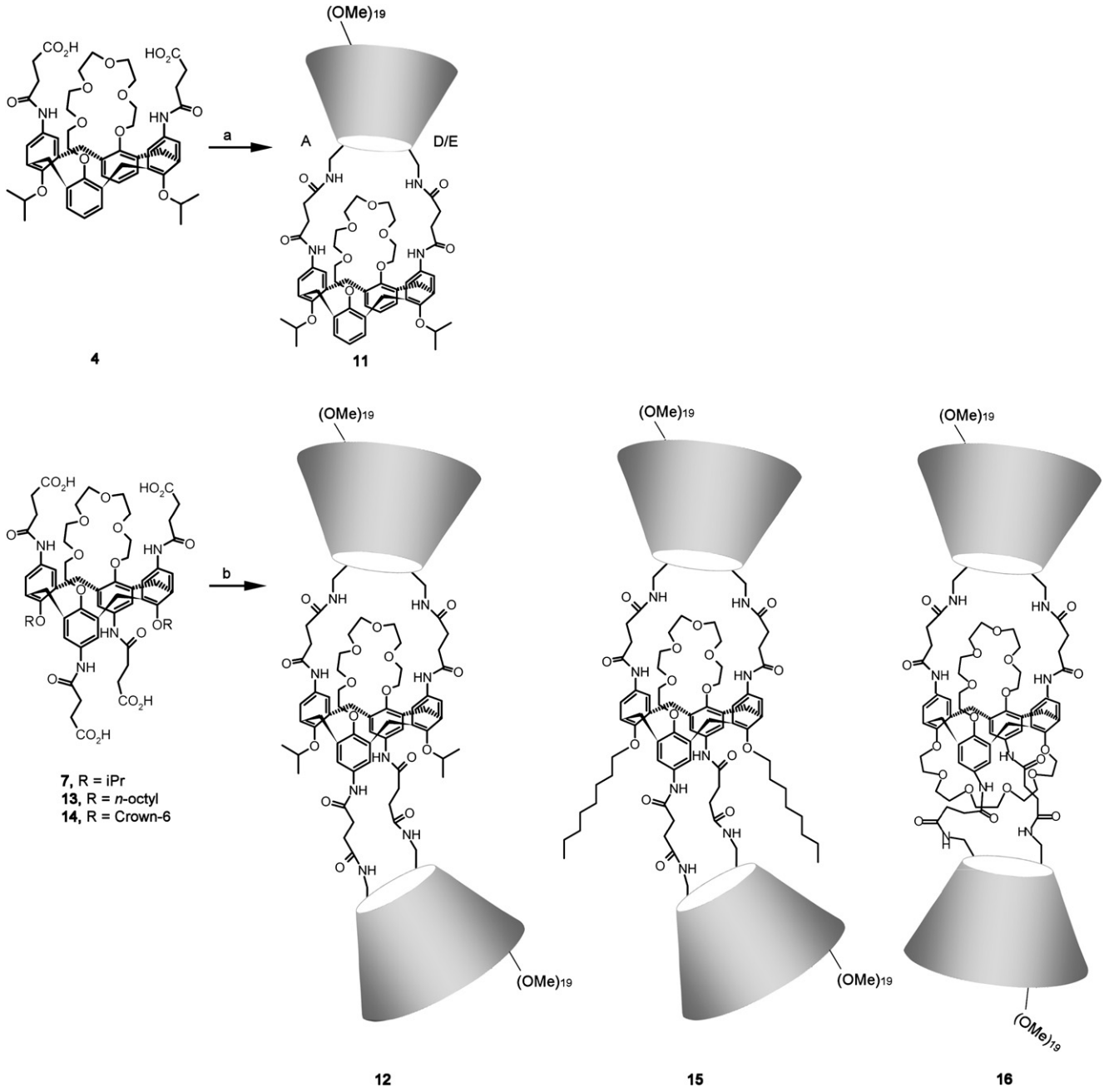
Although the tubular structures obtained led to extremely complex $^1H$ (and $^{13}C$) spectra, even at 800 MHz for proton (and 200 MHz for carbon-13), we were, for example, to totally assigned the half-tube compound **11** spectra. We also noticed several interesting features such as total non-equivalence of the eight succinate methylene protons as shown in Figure 2 and aromatic proton chemical shifts deshielded suffering from the CD capping.

The complex NMR spectra of tube **12** is probably due to non-symmetrical $6^A,6^D$-substitution of β-cyclodextrin. It can be pointed out that because of the odd number of glucose in β-CD, the positional isomers, for example, as A–D or A–E on the upper cyclodextrin (crown side) with A–D substitution on the lower cyclodextrin (dialkoxyl side) occurred. As a result, four positional isomers are formed.

Molecular modelling indicated that linkage to cyclodextrin units must significantly distort the calix[4]arene conformation, particularly in the case of the crown-6 derivative.

## 3. Conclusion

Successful synthesis of half-tube compound **11** and the three tubes **12**, **15** and **16** reported here is an example of




**Scheme 3**. (a) Compound **10**, DIC, HOBt, DMF, rt, 5 days; (b) compound **10**, DIC, HOBt, DMF, rt, 6 days. A,D/E letters on β-CD indicate the number of the substituted glucose unit. The same applies to all β-CDs involved in this scheme.

intramolecular coupling of highly hindered cyclodextrin and calixarene units using a succinyl-diamide linker. The bis(cyclodextrin)calixarene species are presumed to adopt a twisted tubular form, which should be ~30 Å in length. Although the crown loop must block passage through the tube, we have elsewhere shown that it is possible to remove such ether chains from calix[4]arenes.[18] Clearly, there are numerous possibilities for extension of these tube-forming reactions by the use of, for example, α- and γ-cyclodextrin and numerous other calixarenes. One can also consider the modification of linker's length as well as the introduction of the asymmetric centre at this level. In such a case, the tube section build should display the helicity according to the asymmetric carbon configuration introduced on the succinic linker moiety. Finally, from the cyclodextrin moiety on the periphery, supramolecular assemblies could be developed, thanks to their inclusion properties.

## 4. Experimental

### 4.1. General

All calixarene derivatives were purchased from Acros Organics. The starting cyclodextrins were gifts from Roquette Frères (France). Reagents and solvents were obtained from Sigma–Aldrich and used without further purification. TLC was performed on Silica Gel 60 $F_{254}$ plates (E. Merck),

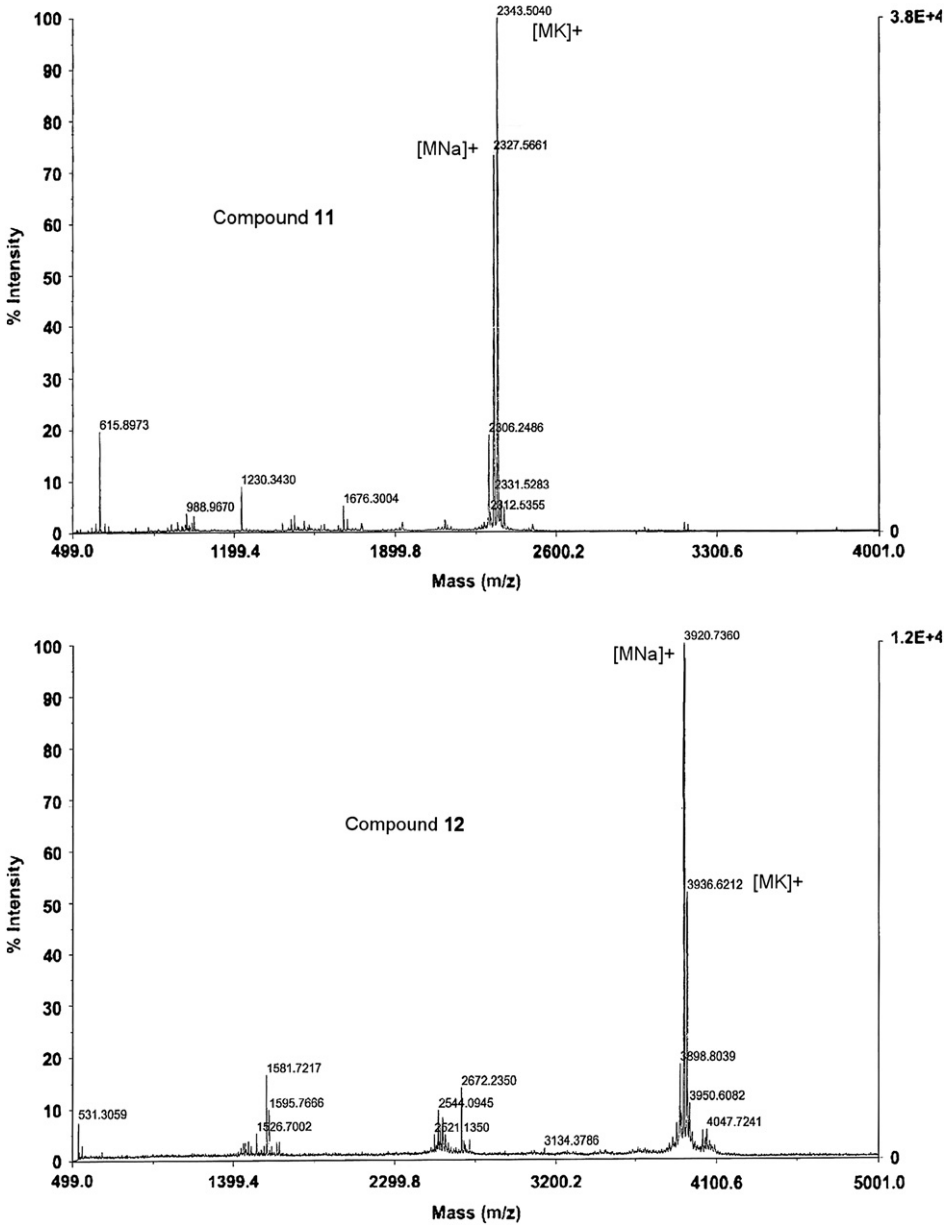



**Figure 1**. MALDI-TOF spectra of compounds **11** and **12**.

with development by charring with 10% (v/v) $H_2SO_4$ or examination under UV. NMR experiments were performed using a Bruker DRX500 spectrometer operating at 500 and 125 MHz for $^1H$ and $^{13}C$, respectively, and a Bruker DRX800 spectrometer (18.7 T) operating at 800 and 200 MHz for $^1H$ and $^{13}C$, respectively, and equipped with a 5-mm z-gradient H/C/N cryoprobe. In all cases, the samples were prepared in deuterium oxide or DMSO-$d_6$ (Euriso-Top, Saclay, France) and measurements were performed at 25 °C. Chemical shifts are given relative to external $Me_4Si$ (0 ppm) and calibration was performed using the signal of the residual protons of the solvent as a secondary reference. Selected 2D experiments were run to unambiguously assign signals. Details of the NMR spectra are available on request to the authors. The MALDI-TOF spectra were recorded on a MALDI-TOF Voyager DE, Applied Biosystems instrument at the Université de Lille using a DHB matrix and protein calibration standards within 1200–5700 mass range. The acceleration voltage was fixed at 20 kV and a number of laser shots at 100. All MALDI-TOF spectra are available on request from the corresponding author.

## 4.2. Synthesis

**4.2.1. Permethylated $6^I,6^{IV}$-diazido-β-cyclodextrin (9).** Permethylated diol (713 μmol) was dissolved in 20 mL of anhydrous pyridine, 528 mg of DMAP (4.3 mmol) was added and the mixture was cooled to 0 °C. Methanesulfonylchloride (446 μL) dissolved in 10 mL of pyridine was added dropwise. After 3 h of stirring, the mixture was evaporated to dryness, dissolved in $CH_2Cl_2$ and washed twice with water. The organic phase was dried with $MgSO_4$, filtered and evaporated to dryness. The residue was then dissolved in 50 mL

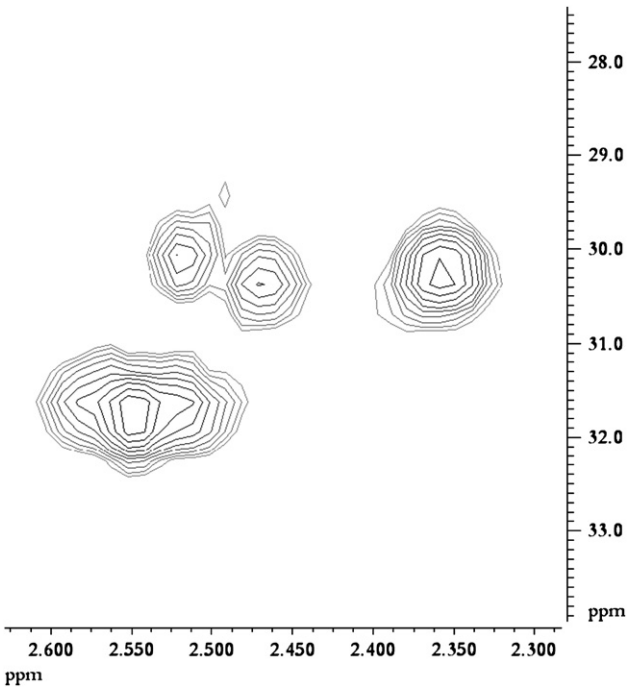



**Figure 2**. Expanded HSQC of compound **11** in the succinyl-methylene area (800 MHz in DMSO-$d_6$ at 298 K).

of DMF and 1.3 g of sodium azide (20 mmol) was added, then the mixture was stirred for 18 h at 65 °C. After evaporation of the final mixture to dryness, the residue was dissolved in $CH_2Cl_2$ washed with water, and the product was then purified on silica gel column chromatography (ethyl acetate then ethyl acetate/ethanol 20:1 and 10:1) to afford 880 mg of **9** as a white powder. Yield 85%; $R_f$=0.5 (AcOEt/EtOH/$H_2O$ 45:5:3); IR (KBr): 2100 $cm^{-1}$ ($N_3$); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta_H$=5.12 (d, 5H, $J_{H1\text{-}H2}$=3.3 Hz, H-1), 5.07 (d, 1H, $J_{H1\text{-}H2}$=3.6 Hz, H-1), 5.06 (d, 1H, $J_{H1\text{-}H2}$=3.7 Hz, H-1), 3.70–3.97 (m, H-5/H-6), 3.42–3.70 (m, H-3/H-4/H-5/H-6/$OCH_3$), 3.37–3.39 ($OCH_3$-2), 3.14–3.20 (m, 7H, H-2); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta_C$=98.33, 98.37, 98.97, 99.10, 99.21, 99.27 (C-1), 80.43–82.09 (C-2/C-3/C-4), 80.15, 80.21, 80.27 (C-4), 71.08, 71.27, 71.59 (C-6), 70.77–70.95 (C-5), 61.28, 61.40, 61.43, 61.53, 61.56, 61.58 ($OCH_3$-6), 58.45–59.00 ($OCH_3$-2/$OCH_3$-3), 51.99, 52.04 (C-$6^I$/C-$6^{IV}$); ESI-MS$^+$: *m/z* measured at 1473 (calcd for $C_{61}H_{106}N_6O_{33}Na$).

**4.2.2. Permethylated $6^A$,$6^D$-diamino-β-cyclodextrin (10).** The diazido compound (880 mg, 606 μmol) was dissolved in 10 mL of dioxane and triphenyl phosphine (954 mg, 3.63 mmol) was added. After 4 h, 2.4 mL of ammonia was added. After overnight stirring, 150 mL of water was added and pH adjusted to 4 with 1 M HCl. The aqueous phase was extracted five times with toluene, then made basic with 2 M NaOH solution before being extracted five times with $CH_2Cl_2$. The combined extracts were dried over $MgSO_4$, filtered and evaporated to give 790 mg of **10** as a white powder. Yield 93%; $R_f$=0.5 ($CH_2Cl_2$/MeOH, 9:1); $^1H$ NMR (500 MHz, DMSO-$d_6$): $\delta_H$=5.15 (d, 2H, H-1), 5.06 (t, 2H, H-1), 5.03 (t, 2H, H-1), 3.68–3.74 (m, 5H, H-5/H-6), 3.41–3.57 (m, 14H, H-4/H-5/H-6), 3.48 (s, 21H, $OCH_3$-3), 3.37–3.39 (4×s, 21H, $OCH_3$-2), 3.25–3.33 (m, 7H, 7×H-3), 3.22–3.24 (4×s, 21H, $OCH_3$-6), 3.02–3.07 (m, 7H, 7×H-2), 2.87 (m, 2H, H-$6^I$/H-$6^{IV}$); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta_C$=97.47–97.76 (7×C-1), 81.54–81.62 (7×C-3), 81.20–81.41 (7×C-2), 79.05, 79.21, 79.38, 79.45, 79.52, 79.67 (7×C-4), 70.26–70.89 (7×C-5/5×C-6), 60.51, 60.59, 60.64 ($OCH_3$-3), 59.07, 58.10, 58.21, 58.28 ($OCH_3$-6), 57.68, 57.73, 57.80, 57.85, 57.91 ($OCH_3$-2), 41.7 (C-$6^I$/C-$6^{IV}$); ESI-MS$^+$: *m/z* measured at 1399.8 $[M]^+$ (calcd for $C_{61}H_{110}N_2O_{33}$).

**4.2.3. $CD^{A,D/E}$=(NH–CO–$CH_2$–$CH_2$–CO–NH)$_2$=CAL (11).** (Detailed structures are presented in Scheme 3.) Compound **4** of 89 mg (93.6 μmol) was dissolved in 4 mL of DMF. DIC of 117 μL (749 μmol) and 102 mg of HOBt (749 μmol) were added successively. After 3 h, the mixture was diluted with 42 mL of DMF and 145 mg of compound **10** (103 μmol) dissolved in 3 mL of DMF added. After 5 days, the mixture was evaporated, the residue dissolved in $CH_2Cl_2$ and extracted with 0.1 M HCl. The product was purified by silica chromatography, eluting first with acetone, then $CH_2Cl_2$/MeOH 97:3, 96:4, 94:6, 9:1, to give 95 mg of the desired compound **11** as an amorphous white solid. Yield: 45%; $R_f$=0.4 ($CH_2Cl_2$/MeOH, 95:5); $^1H$ NMR (800 MHz, DMSO-$d_6$): $\delta_H$=9.56 (t, 2H, N*H*CO), 9.46 (t, 2H, N*H*CO), 7.09, 7.28, 7.41, 7.52 (4s, 4H, $H_a$), 6.99 (m, 4H, $H_c$), 6.72 (t, 2H, $J_{Hb\text{-}Hc}$=7.5 Hz, $H_b$), 5.20 (d, 1H, $J_{H1\text{-}H2}$=3.6 Hz, H-$1_{CD}$), 5.17 (d, 1H, $J_{H1\text{-}H2}$=3.6 Hz, H-$1_{CD}$), 5.08 (d, 1H, $J_{H1\text{-}H2}$=3.7 Hz, H-$1_{CD}$), 5.20 (d, 1H, $J_{H1\text{-}H2}$=3.6 Hz, H-$1_{CD}$), 5.06 (t, 2H, $J_{H1\text{-}H2}$=3.2 Hz, H-$1_{CD}$), 5.05 (d, 1H, $J_{H1\text{-}H2}$=3.5 Hz, H-$1_{CD}$), 5.02 (d, 1H, $J_{H1\text{-}H2}$=3.5 Hz, H-$1_{CD}$), 4.13 (sept, 2H, $J_{CH\text{-}CH3}$=6.2 Hz, C*H*($CH_3$)$_2$), 3.90 (m, 1H, H-6), 3.14–3.80 (m, H-3/H-4/H-5/H-6/$CH_{2ether}$/ar–$CH_2$–ar/$OCH_3$), 3.05–3.10 (m, H-$2_{CD}$), 2.89 (m, $H_{CD}$), 2.34–2.57 (m, 8H, $CH_{2succ}$), 0.825 (d, 3H, $J_{CH\text{-}CH3}$=6.0 Hz, CH(C*H*$_3$)), 0.82 (d, 3H, $J_{CH\text{-}CH3}$=6.0 Hz, CH(C*H*$_3$)), 0.81 (d, 3H, $J_{CH\text{-}CH3}$=6.0 Hz, CH(C*H*$_3$)), 0.80 (d, 3H, $J_{CH\text{-}CH3}$=6.0 Hz, CH(C*H*$_3$)); $^{13}C$ NMR (200 MHz, DMSO-$d_6$): $\delta_C$=171, 169.6 (*C*(O)NH), 149.9, 156.1 (C–O), 132.9–133.4 ($C_{arom.}$NH/$C_{arom.}$$CH_2$), 130.2 ($C_c$), 121.5 ($C_b$), 119.3–119.6 ($C_a$), 98.0–98.7 (C-$1_{CD}$), 81.5–83.0 (C-$2_{CD}$/C-$3_{CD}$), 78.7–79.9 (C-$4_{CD}$), 69.3–71.2 (C-$5_{CD}$/C-$6_{CD}$/$CH_2$-$O_{ether}$), 69.6 (*C*H($CH_3$)2), 58.0–61.2 ($OCH_3$), 38.6, 39.9 (C-$6_{CD}$), 38.2–38.4 (ar–*C*$H_2$–ar), 30.2–31.8 ($CH_{2succ}$), 21.8–22.0 (CH(*C*$H_3$)$_2$); MALDI-TOF MS: *m/z* measured at 2327.57 $[MNa]^+$ (calcd for $C_{113}H_{170}N_4O_{45}Na$).

**4.2.4. General procedure for synthesis of $CD^{A,D/E}$=(NH–CO–$CH_2$–$CH_2$–CO–NH)$_2$=CAL=(NH–CO–$CH_2$–$CH_2$–CO–NH)$_2^{A,D/E}$CD tube structures 12, 15 and 16.** (Detailed structures are presented in Scheme 3.) Compound **7** of 76 mg (64.8 μmol) was dissolved in 2 mL of DMF. DIC of 161 μL (1.04 mmol) and 140 mg of HOBt (1.04 μmol) were added successively. After 3 h, the mixture was diluted with 32 mL of DMF and 191 mg of compound **10** (136.2 μmol) dissolved in 8 mL of DMF was added. After 6 days, the mixture was evaporated, the residue dissolved in $CH_2Cl_2$ and extracted with 0.1 M HCl. The product was purified by chromatography on silica, eluting first with acetone, then $CH_2Cl_2$/MeOH 97:3, 96:4, 94:6, to give 48 mg of the desired compound **12** as amorphous white solid. The same procedure was applied with compound **13** (starting with 70 mg) and **14** (starting with 34 mg) to obtain, respectively, **15** and **16**. Compound **12**: yield: 20%; $R_f$=0.3 ($CH_2Cl_2$/MeOH 95:5); $^1H$ NMR (800 MHz, DMSO-$d_6$):

$\delta_H$=9.4–9.5 (N*H*CO), 6.87–7.60 ($H_{arom.CAL}$), 5.02–5.19 (H-$1_{CD}$), 4.07 (C*H*($CH_3$)$_2$), 3.00–3.92 (m, H-2/H-3/H-4/H-5/H-6/$CH_{2ether}$/ar–$CH_2$–ar/$CH_3$), 2.33–2.58 ($CH_{2succ}$), 0.71–0.83 (CH(C$H_3$)$_2$); MALDI-TOF MS: *m/z* measured at 3920.74 $[MNa]^+$ (calcd for $C_{182}H_{286}N_8O_{82}Na$). Compound **15**: MALDI-TOF MS: *m/z* measured at 4060.99 $[MNa]^+$ (calcd for $C_{192}H_{306}N_8O_{82}Na$). Compound **16**: MALDI-TOF MS: *m/z* measured at 4039 $[MNa]^+$ (calcd for $C_{186}H_{292}N_8O_{86}Na$).

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