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Synthesis of calixarene–cyclodextrin coupling products

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Abstract—The coupling of two or four mono-6-amino β-cyclodextrin (amino-CD) units, (unprotected or permethylated hydroxyls), to diisopropoxycalix[4]arene crown-6 (CAL) was realised using the *N*,*N*′-succinyldiamide linker. The resulting molecules in two series were characterised with the help of mass and NMR spectroscopies. The yields of all coupling products were improved for permethylated sugar series compared to the hydroxylated CD series or to our previous studies. The two β-cyclodextrin (β-CD) residues coupled to disubstituted CAL were orientated from the same side of the crown ether.

1. Introduction

In our recent papers of this series,[1,2] we identified several crown calix[4]arene compounds, which could be usefully coupled to β-cyclodextrin (β-CD) (**1**), and then proposed the synthesis of mono-crown and bis-crown calixarene derivatives by coupling them to β-CD through a succinic diamide linker. Such amphiphilic ensembles have a capacity to include a wide variety of molecules according to the availability of three sites: calixarene, crown and cyclodextrin. They represent a new family of compounds to be used as potential drug carriers and have ion affinities.[3] Among several attempts to build β-CD–calixarene systems, in particular seminal work of Reinhoudt's[4–7] and Liu's[8] groups should be mentioned. However, none of these studies used our combination of host molecules or spacer arms.

The synthesis of CD–CAL mixed-derivatives allowed us to construct molecules of new but defined architecture, and also to study their physicochemical properties. This work has some importance in the supramolecular field; the presence of crown, CD and CAL cavities available to different guests is significant in the development of encapsulation devices and molecular containers as a step in nanotechnology, leading to self-assembled, charged molecular capsules.

One difficulty in working with calixarenes is their general poor solubility in organic solvents; this problem is often resolved by the introduction of the crown ether moiety. Likewise, a CD attached to a CAL frame should provide an amphiphilic character to CAL–CD aggregates;[9,10] this would also significantly improve solubility in water, while preserving the supramolecular capacity of each of the three components (CAL, crown and CD).

The use of *n*-octyl mono-crown calix[4]arene (**2**) (a molecule of specific interest as a radioactive Cs^+ extractant in the processing of spent nuclear fuel) as a frame for such a coupling leads to the connection of either two or four CD units to this calixarene.[11] However, the bis-crown calix[4]-arene binds to only two CDs. In both series, the coupling products were obtained with relatively low yield. Purification was laborious, the solubility remained low and NMR spectra were very complex because of many overlapping proton signals. These difficulties led us to modify both the CAL and CD systems in search of friendlier ones (Fig. 1).

The permethylation of CD usually leads to derivatives with increased solubility in organic solvents. The mono-6-amino permethylated β-CD (β-CDmet-NH_2) (**4**) was thus considered as a possible substrate for this CAL–CD coupling,[12,13] according to Scheme 1, together with mono-6-amino β-CD (β-CD-NH_2) (**5**).

We thus propose the coupling of both amino-CDs (**4**, **5**) via the attachment to a free carboxyl of (*N*-succinate monoamide)$_n$CAL (where *n* indicates the number of amino groups attached to the calixarene frame). As we have previously observed, the coupling of the amino-CD to the succ-NH-CAL gives a better yield than does the opposite coupling (that is,

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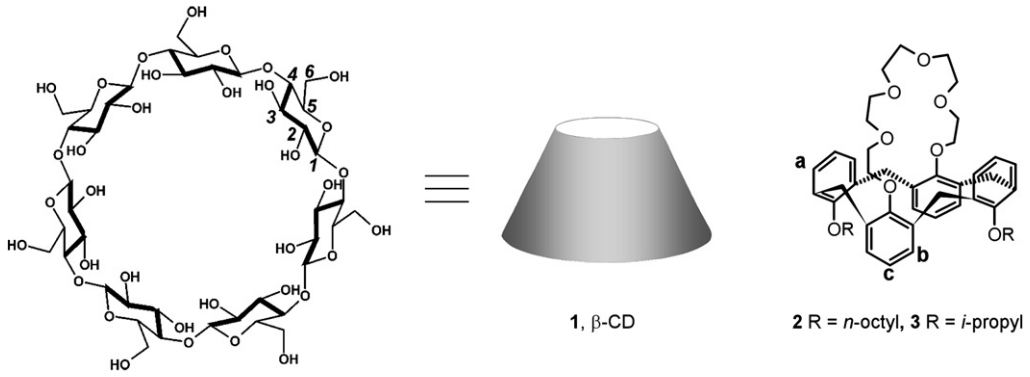


Figure 1. Structures of β-cyclodextrin (**1**) and 25,27-diisopropoxycalix[4]arene-26,28-crown-6 (**3**).

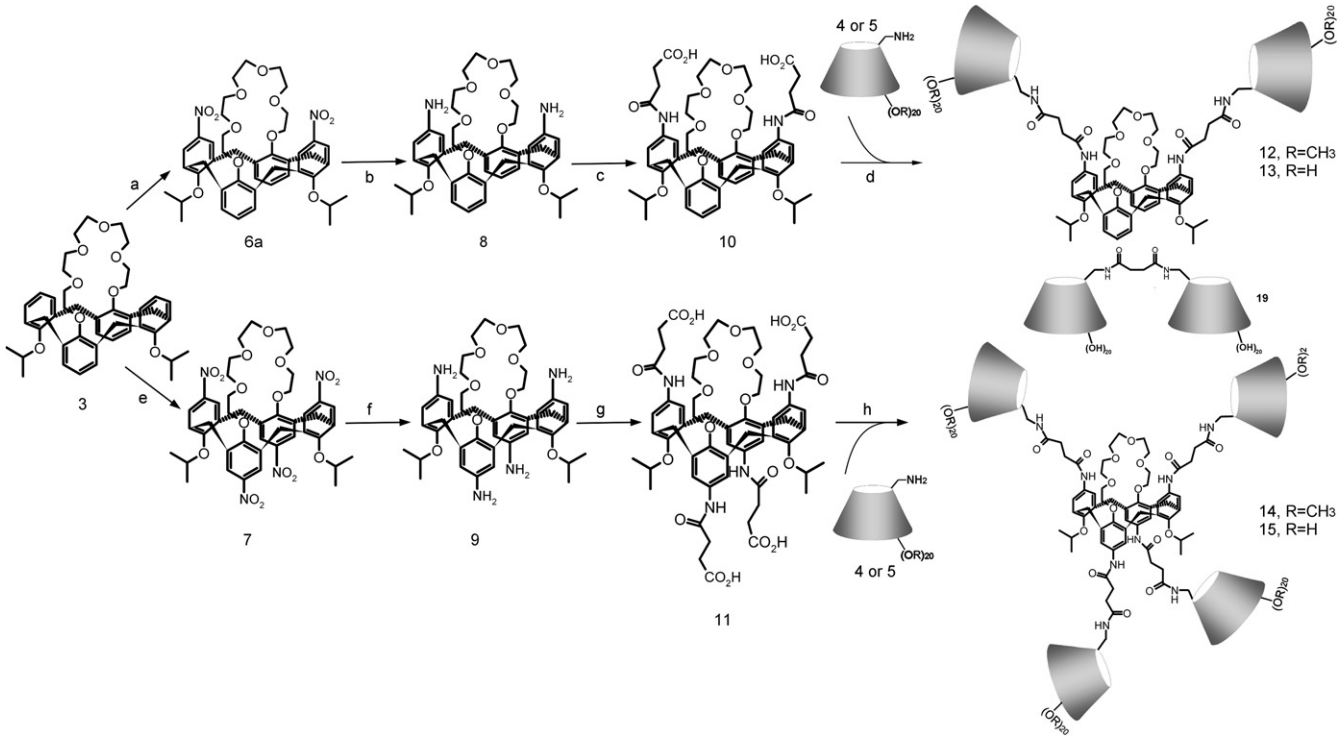
of β-CD-succ to the amino-CAL). This can be explained by the fact that an aromatic amine is less reactive to nucleophilic substitutions than is a primary amine. Furthermore, steric hindrance disfavours the peptidic coupling by this pathway.[14] Consequently, we chose not to follow this second route.

In order to further improve the solubility, we compromised between bis-crown series and compound **2**, and chose the diisopropylcalix[4]arene crown-6 (**3**), since it has a slightly shorter aliphatic chain on two of the phenols of CAL; two others were linked via a mono-crown moiety.

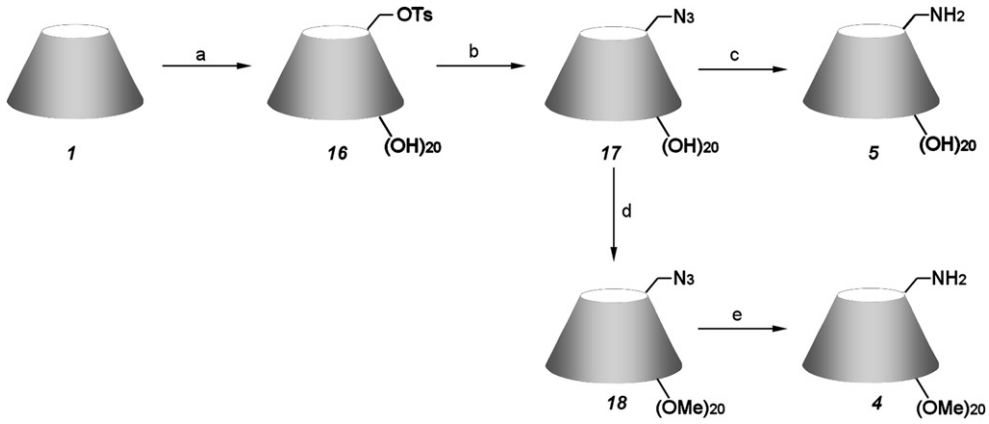
The number of amino groups on the CAL system was controlled by the selective nitration of CAL (**3**).[15] The first compound used was the dinitro cis-to-crown isomer for $CAL(NO_2)_2$ (**6a**), followed by the tetranitro derivative $CAL(NO_2)_4$ (**7**).

The identity of the $CAL(NO_2)_2$ compound was carefully proven from its NMR and X-ray spectra. Both nitro derivatives were then reduced, and coupled to the succinic linkers as per previous procedures[16] (Scheme 1), followed by a final coupling to the amino-CDs **4** and **5**, which we synthesised in parallel (Scheme 2).

The approach proposed in Scheme 1 leads to permethylated CD–CAL coupling products, with a variable number of cyclodextrins attached. Such a methylated CD greatly simplifies the step-by-step synthesis, and the solubility of the final coupling products in organic solvents should be significantly improved for the whole methylated cyclodextrin



Scheme 1. General scheme of coupling of calixarene to cyclodextrins. (a) HNO_3 concd, 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) DIC, HOBt, DMF, 24 h, 50%; (e) HNO_3 fuming, acetic anhydride, CH_2Cl_2, 1 h, 88%; (f) Ni (Raney), toluene, 70 °C, 4 h, 76%; (g) succinic anhydride, DMF, 18 h, 79%; (h) DIC, HOBt, DMF, 24 h, 63%.



Scheme 2. Synthesis of 6-monoamino-β-cyclodextrins **4** and **5**. (a) β-CD, tosylimidazol, NaOH solution, rt, 45 min, 30%; (b) NaN_3, H_2O, 80 °C, 5 h; (c) Pd/C 10%, H_2, H_2O, 60 °C, overnight, 85%; (d) NaH, MeI, DMF, rt, 6 h, 90%; (e) Pd/C 10%, H_2, H_2O/MeOH, overnight, 85%.

series. As a reference, the hydroxylated CD analogous series was synthesised in parallel. In this last case, dialysis was used to separate the final products from the reagents and other water-soluble compounds.

2. Results and discussion

The tetra *para*-nitration of various calixarenes does not present any particular difficulty. It has already been reported and can be done according to many variations to our exhaustive nitration procedures[15] with a close to quantitative yield (75–90%) in a variety of solvents and within a wide temperature range. The tetranitration, for example, can be easily achieved even in CH_2Cl_2 solution at 0 °C with HNO_3/acetic anhydride. We were able to avoid undesired excess nitration (for instance, the fifth nitro group on the benzylic carbon), as well as the oxidation of the molecule as a whole and its undernitration in a mixture of products. The dinitration was best achieved under trifluoroacetic anhydride, HNO_3 concd at −78 °C (yield: 90%),[15] under low-temperature nitration (−18 °C, 2.2 equiv of fuming HNO_3, yield: 75%[2]), and under random nitration with acetic anhydride–concd HNO_3 (yield: up to 40%). All these methods were followed by column chromatography purifications. Here, the dinitration was performed according to the method described for compound **6a** in Section 4. LC–MS of the crude mixture obtained was recorded showing the presence of isomeric mono, di- and trinitro calixarenes (Fig. 2). For example, for dinitro isomer, the presence of three isomers was detected (**6a**, **6b**,

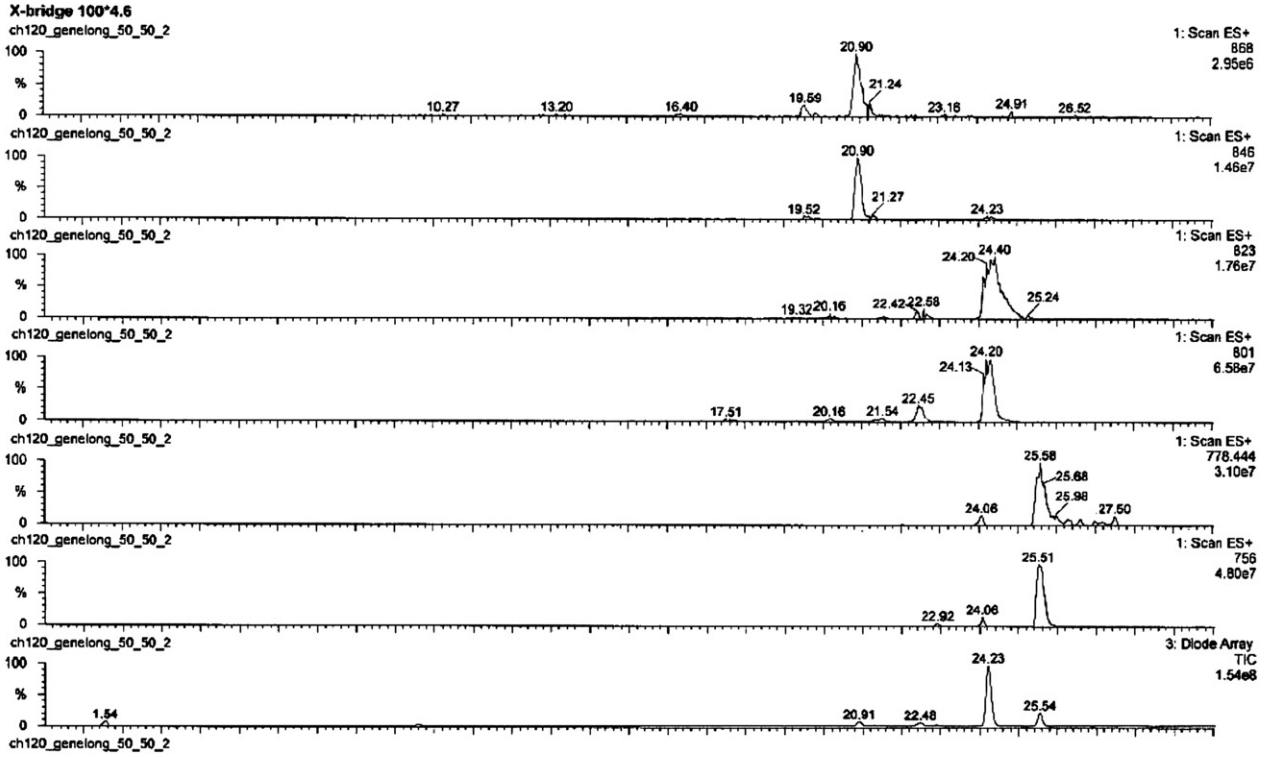


Figure 2. Ion mass chromatograms of polynitrocalixarene derivatives of **1**. Polynitro isomers (*m*/*z*, MH^+ and MNa^+, respectively): mononitro 756 and 778; dinitro 801 and 823; trinitro 847 and 869. Lower run: total ion current, TIC (diode array).

Table 1. LC retention time of nitrocalixarene mixture obtained according to dinitration procedure (see Section 4, compound **6a**)

Number of nitro group	Isomer[a]	Retention time (min)
1	**20a**	25.51
	20b	24.06
2	**6a**[b]	24.20
	6b	22.45
	6c	20.16
3	**21a**	20.90
	21b	19.52

6a: 11,23-Dinitro-25,27-diisopropoxycalix[4]arene-26,28-crown-6.
6b: 11,17-Dinitro-25,27-diisopropoxycalix[4]arene-26,28-crown-6.
6c: 11,29-Dinitro-25,27-diisopropoxycalix[4]arene-26,28-crown-6.
20a: 11-Nitro-25,27-diisopropoxycalix[4]arene-26,28-crown-6.
20b: 17-Nitro-25,27-diisopropoxycalix[4]arene-26,28-crown-6.
21a: 11,17,23-Trinitro-25,27-diisopropoxycalix[4]arene-26,28-crown-6.
21b: 11,17,29-Trinitro-25,27-diisopropoxycalix[4]arene-26,28-crown-6.
[a] Identification of isomers was done assuming similar behaviour of *n*-octyl mono-crown series and *i*-PrCAL series under LC conditions applied (see Section 4); pure compound **1**, t_R=25.71 min and dinitro compound **6a** were used as references for this determination. Traces of $CAL(NO_2)_4$, t_R=9.6 min were also observed.
[b] Major isomer.

6c). The major isomer (**6a**) ratio, as estimated from its MH^+ and MNa^+ mass chromatogram, was in the vicinity of 95% (Table 1).

The dinitro calixarene isomers were fully characterised for the *n*-octyl mono-crown series, using NMR and LC methods.[11] The polynitro diisopropoxy mono-crown series was also characterised using electrospray mass spectrometry (ESI-MS) and liquid chromatography.

The identity of the $CAL(NO_2)_2$ compound was carefully proven from its NMR and X-ray spectra. The NMR of this particular molecule showed some interesting features: the most characteristic proton signals were those associated with the aryl protons—two types of protons for the phenyl moiety without NO_2 group (7.06 ppm (d, 4H, H_b), 6.88 ppm (t, 2H, H_c)) with $^3J_{H_{b-c}} = 7.5$ Hz and a singlet at 8.02 ppm for *meta* protons on phenyls bearing NO_2. This is in conjunction with the ^{13}C signals, which follow the similar deshielding trend (C–NO_2 at 142.0 ppm), and confirmed the proposed structure. The geometry of the two nitro groups in $CAL(NO_2)_2$ was also established with 2D NMR as being in cis-to-crown orientation (compound **6a**), (that is, both NO_2 groups were orientated on the crown side of the molecule (Fig. 3)); this was confirmed via X-rays.

The exact identification of the two NO_2 groups is important because the next steps of the coupling will maintain the relative spatial orientation of both nitrogens throughout the entire scheme.

The separate reduction of both nitrated compounds, dinitro **6a** and tetranitro **7** led to the corresponding amines **8** and **9**, respectively, with high yield varying from 70% for $SnCl_2$ reduction of dinitro, to 76% for Raney nickel reduction of tetranitro derivatives.[17]

The reduction of dinitrocalix[4]arene (**6a**) to the corresponding diamino compound **8** (Scheme 1), however, was better achieved by the $SnCl_2$ reduction. When the Raney nickel

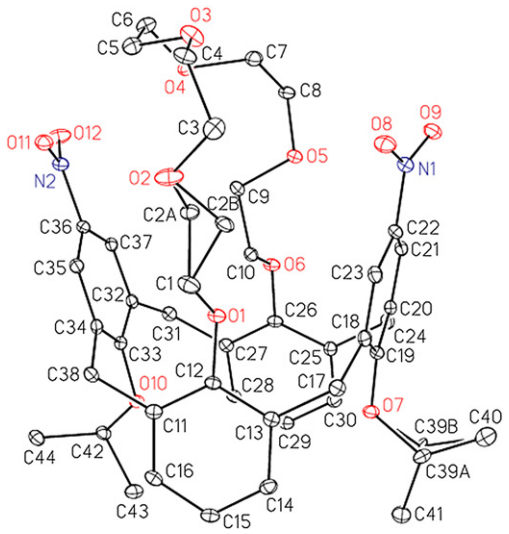


Figure 3. View of compound **6a**. Hydrogen atoms are omitted. Displacement ellipsoids are drawn at the 20% probability level.

reduction was performed on the compound **6a**, a persistent and difficult-to-purify green crystalline residue was observed: this was probably due to the complexation of the amine by Ni^{2+} cation. This difficulty was overcome by using $SnCl_2$ reduction instead;[18] however, this observation alone fully justified the relatively low yield of reduction obtained.

Electrospray mass spectrometry, using mostly Cs^+ but also occasionally Na^+ cationisation agents via the crown-metal complex, allowed us to easily follow the progress of these reactions and of the purification of compounds in the crown series.

For the amines **8** and **9**, the most significant proton shift is the singlet signal at ca. 8 ppm, which disappeared in the compounds **8** and **9**, giving singlet signal deshielded at 6.71 ppm for **8**, and at 6.51 ppm for **9**. The key control signal in NMR spectrum was the shift of the C–NH_2 signal to ca. 133.2 ppm in ^{13}C spectrum (*ipso-para* carbon), thus confirming the reduction to diamine; this was less pronounced for compound **9**.

The amidation of the two amines with succinic anhydride in DMF led to the production of the last synthetic intermediates before the final coupling of the β-CD-NH_2 (**8**) and β-CDmet-NH_2 (**9**) to the $CAL(succ)_n$ molecules (n=2, **10**, n=4, **11**).

From the opposite side of the synthetic scheme, the β-CD-NH_2 (**5**) and β-CDmet-NH_2 (**4**) were synthesised according to the following sequence of reactions (Scheme 2). The common starting product obtained by supramolecular tosylation of β-CD (β-CD-OTs) (**16**) was then transformed into the azide **17**. Direct reduction of compound **17** gave β-CD-NH_2 (**5**), and methylation of **17** with methyliodide in sodium hydride, followed by similar reduction with Pd/C led to β-CDmet-NH_2 (**4**) with challenging yields. The use of Pd/C for reduction of the azido group avoids an important difficulty related to Staudinger method[19,20] where the inclusion of triphenylphosphine or its oxide in the CD cavity is observed.[21]

The full NMR and ESI-MS (Na^+ cationisation) spectra give some interesting features in this series, confirming the expected structures obtained. In order to succeed in the remaining part of the synthesis, both β-CD-NH_2 and β-CDmet-NH_2 should be obtained as very high-purity compounds. This objective was realised by the combined use of column chromatography and ion exchange resin. Their purity was confirmed by NMR and ESI-MS techniques and was in the vicinity of 90–95%.[22] The most interesting signal in the NMR spectra of these amines were the dd at 2.95 ppm (CH_2–N) confirming that the mono 6-amination was overwhelmingly achieved.

2.1. Coupling of (succ)$_n$CAL to β-CD-NH_2

The coupling reactions between the two components were realised for the di- and tetrasubstituted calix[4]arene series. When the activated ester method (DIC, HOBt) was used, two expected coupling products in methylated β-CD series were respectively obtained (yields up to 50% for di-coupled product **12**, 65% for tetrasubstituted product **14**). In hydroxylated CD series the corresponding yields of compounds **13** and **15** were lower (approximately at 20% level). It should be noted that starting from this point, MALDI-TOF-MS was used for mass determination of the coupling compounds.

As in previous work in this series,[1] dimers containing the β-CDmet-succ skeleton were also detected. Their structures should be rationalised on the basis of coupling of two CD derivatives: the β-CDmet-NH_2 and the β-CDmet-succ (HOOC–CH_2–CH_2–NH)$_n$ CDmet. The coupling reaction seems to be affected by the presence of residual succinic acid, which also can react with amines **4** and **5**. Their structures will be characterised separately.

A detailed characterisation of these coupling products for the disubstituted (**12**) and tetrasubstituted calix[4]arene crown-6 (**14**), in methylated β-CD series, is presented in Section 4. However, in the hydroxylated CD series the usual impurities, in particular β–β CD dimer (**19**) and two coupling products with two or three CD residues attached to the calixarene instead of the expected four, were observed. Their separation by classical chromatography was impossible, the attempt of isolation and purification by dialysis resulted in a mixture, which when analysed by MALDI clearly indicated the presence of the above mentioned by-products.

The yield of both CDmet–CAL coupling products is however greater than in the natural CD series, the coupling in natural β-CD remains relatively low; however, the solubility of the aggregates synthesised was significantly improved and their purification was much easier (e.g., column chromatography could be used for purification).

3. Conclusion

The coupling of permethylated and hydroxylated CD series to amino-CAL was accomplished using succinic linkers for separation between two molecules.

With the help of diamino- and/or tetramino calixarene as a base, we can reasonably consider that the in-space orientation of β-CD is properly controlled, and that the calixarene–crown system represents a good example of a frame molecule for the construction of carbohydrate tubes 'dangling' from such a frame.

As it was mentioned in previous cases that were examined, the hydroxylated CD moiety is large enough to overturn the calixarene crown and form some H-bonds over the CAL–crown systems. Once again, molecular modelling calculations showed that this important stabilising interaction, absent for the CDmet series, enabled the correct orientation of both linker and CD moieties, improved the total yield of coupling product[23] and eventually involved chiral linker to target a more organised system.

In order to further develop the use of CAL frames for construction of peptide chains in a rigorously space-orientated direction, a similar synthetic scheme should be attempted for peptide–succ-NH CAL systems. This might allow the formation of interpeptide chain interactions,[24,25] and the organisation of the resulting molecules into multihelix systems; in particular, this may lead to quadruple peptide helices.[23]

In this respect, the attempts to bond various diamino-CD derivatives to a CAL frame seem particularly appealing, and could lead to dendrimeric structures. It seems, from our observations in this field, that the crown-6 system attached to CAL is small, hidden and 'crushed' by a large CD. However, we can consider its selective removal, because of its phenolic ether character, by various ablation techniques.[26]

4. Experimental

4.1. General

All calixarene derivatives were purchased from Acros Organics. The starting cyclodextrins are given from Roquette Frères (France). Most of the reagents and solvents used in this study came from the Sigma–Aldrich and used without further purification. TLC was performed on Silica Gel 60 F_{254} plates (E. Merck) followed by charring with 10% (v/v) H_2SO_4 or UV revelation. NMR experiments were performed using a Bruker DRX500 spectrometer operating at 500 and 125 MHz for ^1H and ^{13}C, respectively. In all cases, the samples were prepared in deuterium oxide, 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 on these compounds in order to unambiguously assign signals. Molecular modelling calculations were done with HyperChem 6.03 Mm+ (Hypercube, USA, 2000) in gas-phase only. The X-ray diffraction determination was done on dinitrocalix[4]arene (**6a**). The data were collected at 100(2) K on a Nonius Kappa-CCD area detector diffractometer using graphite-monochromated Mo Kα radiation (0.71073 Å). The data were processed with HKL2000.[27] The structure was solved by direct methods with SHELXS-97 and subsequent Fourier-difference synthesis and refined by full-matrix

least-squares on F^2 with SHELXL-97.[28] All non-hydrogen atoms were refined with anisotropic displacement parameters.

Crystal data and refinement details: $C_{44}H_{52}N_2O_{12}$, M=800.88, triclinic, space group $P\bar{1}$, a=9.4077(9), b=12.6984(8), c=17.5132(15) Å, α=75.357(5), β=86.167(4), γ=83.820(5)°, V=2010.8(3) Å^3, Z=2, μ=0.096 mm^{-1}, F(000)=852. Refinement of 545 parameters on 6982 independent reflections out of 15247 measured reflections (R_{int}=0.081) led to R_1=0.069, wR_2=0.161 and S=1.054, CCDC 612684.

The mass spectra were recorded on triplequad Quattro II Micromass ESI-MS system as solutions of ca. 0.1 mg mL^{-1} in methanol/water (1:1) introduced with Harward Apparatus syringe-pump. The working range of the instrument was from m/z 100 to 2000. For the details of ESI analytical conditions see Ref. 11. The MALDI-TOF spectra were recorded for superior than 1500 mass compounds only on MALDI-TOF Voyager DE, Applied Biosystem of Université de Lille using DHB matrix and usual protein calibration standards within 1200 to 5700 mass range. The acceleration voltage was fixed at 20 kV and the number of laser shots at 100.

For LC–MS experiment, the mass spectrometer is the Waters Micromass® ZQ™ (quadrupole with ESI source) and the UV detector is the Waters 2996 photodiode array. The instrumental parameters were: capillary voltage at 3.5 kV, source temperature at 120 °C and cone voltage was fixed at 20 V. The column is a Waters XBridge™ C18, 4.6×100 mm, 3.5-μm particle size. Elution solvents are: A, acetonitrile (containing 0.1% formic acid) and B, water (containing 0.1% formic acid). A linear gradient elution was used: from A/B, 50:50 (v:v) to A, 100 (v) in 25 min at a flow rate of 1 mL/min. Spectra were recorded in continuum mode by scanning the quadripole between m/z 130 and 2000.

4.2. Synthesis

4.2.1. 6^{I}-(*O*-*p*-Tolylsulfonyl)-cyclomaltoheptaose (16). This compound was synthesised from β-CD (**1**) according to the Bittman method.[29] Yield: 26%. Mp=179 °C; R_f=0.6 (BuOH/MeOH/H_2O/NH_3 3:3:3:1); ^{1}H NMR (500 MHz, DMSO-d_6, 298 K): δ=7.75 (d, 2H; $H_{b/b'}$), 7.42 (d, 2H; $H_{c/c'}$), 5.6–5.9 (14O*H*, O*H*-2, O*H*-3), 4.81–4.86 (m, 6H; H-1$^{II-VII}_{CD}$), 4.76 (d, 1H; H-1$^{I}_{CD}$), 4.33 (d, 1H; H-6$^{I}_{CD}$), 4.18 (dd, 1H; H-6′$^{I}_{CD}$), 3.4–3.7 (m, 18H; H-5$^{I-VII}_{CD}$/H-6$^{II-VII}_{CD}$/H-6′$^{II-VII}_{CD}$/H-3$^{I-VII}_{CD}$), 3.2–3.4 (m, 14H; H-2$^{I-VII}_{CD}$/H-4$^{I-VII}_{CD}$), 2.42 (s, 3H; C$_e$*H*); ESI-MS+: m/z 1290.2 [M+H]$^+$ (calcd for $C_{49}H_{77}O_{37}S$: 1290.2).

4.2.2. 6^{I}-Azido-6^{I}-deoxy-cyclomaltoheptaose (17). This azide was obtained with sodium azide according to Ueno method.[30] R_f=0.5 (BuOH/MeOH/H_2O/NH_3 3:3:3:1); ^{1}H NMR (500 MHz, D_2O): δ=5.10 (d; H-1$_{CD}$), 3.99 (t; H-3$_{CD}$), 3.86–3.97 (m; H-5$_{CD}$/H-6$_{CD}$/H-6′$_{CD}$), 3.68 (dd; H-2$_{CD}$), 3.61 (d; H-4$_{CD}$); ESI-MS+: m/z 1166.5 [M+H]$^+$ (calcd for $C_{42}H_{70}O_{34}N_3$).

4.2.3. 6^{I}-Azido-6^{I}-deoxy-2^{I},3^{I}-di-*O*-methyl-hexakis (2$^{II–VII}$,3$^{II–VII}$,6$^{II–VII}$-tri-*O*-methyl) cyclomaltoheptaose (18). The compound **17** is dissolved in dry DMF (100 mL) and cooled down at 0 °C. NaH is added in portions (1.55 g, 65 mmol, dispersed in oil 60%). After 20 min, iodomethane (18.35 g, 129 mmol) is slowly added. The reaction is stirred overnight at room temperature under argon. Salts formed are filtered off, washed with dichloromethane and the filtrate is concentrated. Oily residue is dissolved in a minimum amount of water and extracted with chloroform (3×50 mL). The organic phase is washed with water (2×50 mL), dried with sodium sulfate, filtered and evaporated. Removal of the oily residue was achieved by filtration through a silica bed yielding 1.65 g (90%) of compound **18**. R_f=0.8 ($CHCl_3$/MeOH 9:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ=5.31–5.36 (H-1$_{CD}$), 3.88–3.96 (H-5$_{CD}$/H-6$_{CD}$), 3.69–3.84 (H-4$_{CD}$/H-6′$_{CD}$/H-3$_{CD}$), 3.65 (OCH_3-6$_{CD}$), 3.56 (OCH_3-3$_{CD}$), 3.43 (OCH_3-2$_{CD}$), 3.38–3.42 (H-2$_{CD}$); ESI-MS+: m/z 1462.8 [M+Na]$^+$ (calcd for $C_{62}H_{109}N_3NaO_{34}$).

4.2.4. 6^{I}-Amino-6^{I}-deoxy-2^{I},3^{I}-di-*O*-methyl-hexakis (2$^{II–VII}$,3$^{II–VII}$,6$^{II–VII}$-tri-*O*-methyl) cyclomaltoheptaose (4). This compound was synthesised according to the method described by Carofliglio[22] from compound **18** and purified using ionic exchange resin BioRad AG 50W-X_4 (50–100 mesh), the residue was acidified at a pH of 4–5. The aqueous solution was put into the resin column, eluted with 900 mL of water and then with 400 mL of aqueous ammonia (10%). The pure compound appeared in ammonia fractions. These fractions were evaporated almost to dryness and lyophilised. Yield: 86% of the desired compound **4**. R_f=0.2 (CH_2Cl_2/MeOH 8:2); ^{1}H NMR (500 MHz, D_2O): δ_H=5.36 (d, 1H; H-1$^{I}_{CD}$, $^3J_{1^I-2^I}$=3.6 Hz), 5.30–5.35 (m, 6H; H-1$^{II-VII}_{CD}$), 3.86–3.96 (m; H-5$^{II-VII}_{CD}$), 3.87–3.92 (m; H-6$^{II-VII}_{CD}$), 3.83 (H-5$^{I}_{CD}$), 3.75–3.83 (m; H-4$^{II-VII}_{CD}$), 3.76 (H-3$^{I}_{CD}$), 3.69–3.79 (m; H-3$^{II-VII}_{CD}$), 3.71 (H-4$^{I}_{CD}$), 3.65–3.73 (m; H-6′$^{II-VII}_{CD}$), 3.64–3.66 (m; OCH_3-6$_{CD}$), 3.55–3.57 (m; OCH_3-3$_{CD}$), 3.43 (H-2$^{I}_{CD}$), 3.42–3.43 (m; OCH_3-2$_{CD}$), 3.36–3.44 (m; H-2$^{II-VII}_{CD}$), 3.05 (dd, 1H; H-6$^{I}_{CD}$, $^3J_{6^I-5^I}$=5.5 Hz, $^3J_{6^I-6'^I}$=14.2 Hz), 2.96 (dd, 1H; H-6′$^{I}_{CD}$, $^3J_{6'^I-5^I}$=3.0 Hz, $^3J_{6'^I-6^I}$=14.2 Hz); ^{13}C NMR (125 MHz, D_2O): δ_C=97.1–97.8 (C-1$^{I-VII}_{CD}$), 80.9–81.6 (C-3$^{I-VII}_{CD}$), 80.2–80.6 (C-2$^{I-VII}_{CD}$), 76.7–78.6 (C-4$^{I-VII}_{CD}$), 71.0–71.4 (C-6$^{II-VII}_{CD}$), 70.7–71.7 (C-5$^{I-VII}_{CD}$), 59.8–60.4 (O*C*H$_3$-6$_{CD}$), 58.3–59.0 (O*C*H$_3$-3$_{CD}$/O*C*H$_3$-2$_{CD}$), 41.6 (C-6$^{I}_{CD}$); ESI-MS+: m/z 1414.8 [M+Na]$^+$ (calcd for $C_{62}H_{112}NNaO_{34}$).

4.2.5. 11,23-Dinitro-25,27-diisopropoxycalix[4]arene-26,28-crown-6 (6a). 1,3-Diisopropoxycalix[4]arene-crown-6 (200 mg, 0.281 mmol) **3** was dissolved in 10 mL of acetic anhydride and maintained under −15 °C. A mixture of 5 mL of acetic anhydride, 5 mL of acetic acid and fuming nitric acid (26 μL, 2.2 equiv) is added dropwise to the calixarene solution. After addition, the reaction mixture is warmed at room temperature and stirred overnight. The mixture is then poured into ice water and extracted twice with ether. Organic phases were extracted with a solution of saturated $NaHCO_3$ three times, dried over $MgSO_4$, filtered and evaporated. The residue is purified on silica gel column chromatography eluted with cyclohexane/ethyl acetate 9:1 to 8:1 to give 168 mg of the desired product. Yield: 75%. R_f=0.5 (cyclohexane/AcOEt 7:3); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H=8.02 (s, 4H; H_a); 7.06 (d, 4H; H_b, J_{b-c}=7.5 Hz), 6.88 (t, 2H; H_c, J_{b-c}=7.5 Hz), 4.40 (sept., 2H; C*H*(CH$_3$)$_2$, J=6 Hz), 3.91 (d, 4H; ar–H_αCH$_\beta$–ar, $J_{\alpha-\beta}$=16.1 Hz), 3.85 (d, 4H; ar–H$_\alpha$CH_β–ar, $J_{\alpha-\beta}$=16.1 Hz), 3.61 (t, 4H; ar–OCH_2, J=6.3 Hz), 3.58 (s, 4H; O–CH$_2$), 3.51 (m, 4H; O–CH$_2$),

3.48 (m, 4H; O–CH_2), 3.22 (t, 4H; ar–OCH_2CH_2–O, J=6.3 Hz), 0.91 (d, 12H; CH_3, J=6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C=160.7, 156.6 (C–O), 142.0 ($C_{arom.}NO_2$), 135.5, 132.4 ($C_{arom.}CH_2$), 130.8 (C_c), 125.2 (C_a), 122.7 (C_b), 71.9 ($CH(CH_3)_2$), 71.5, 71.1, 70.6, 69.6, 69.4 (CH_2–O), 38.9 (ar–CH_2–ar), 22.0 (CH_3); ESI-MS+: m/z measured at 933.5 $[M+Cs]^+$ (calcd for $C_{44}H_{52}N_2O_{12}Cs$).

4.2.6. 11,23-Diamino-25,27-diisopropoxycalix[4]arene-26,28-crown-6 (8). A suspension of 62 mg of compound **6a** (0.077 mmol) and 175 mg of $SnCl_2\cdot 2H_2O$ (0.77 mmol) in 3.7 mL of ethanol was refluxed overnight. The reaction mixture is poured into ice water. The solution is adjusted to pH=9 with 1 N NaOH and extracted three times with dichloromethane. Organic phases were washed with distilled water and dried over $MgSO_4$, filtered and evaporated. The product is used without further purification. Yield: 75%. R_f=0.5 (chloroform/methanol 9:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H=6.93 (d, 4H; H_b, J_{b-c}=7.5 Hz), 6.71 (s, 4H; H_a), 6.61 (t, 2H; H_c, J_{b-c}=7.5 Hz), 4.12 (sept., 2H; C$H(CH_3)_2$), 3.86–3.96 (m, 16H; OCH_2), 3.70 (s, 4H; OCH_2), 3.54 (d, 4H; ar–$H_\alpha CH_\beta$–ar, $J_{\alpha-\beta}$=13.1 Hz), 3.41 (d, 4H; ar–$H_\alpha CH_\beta$–ar, $J_{\alpha-\beta}$=13.1 Hz), 1.25 (d, 12H; CH_3, J=6 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C=156.1, 133.8 (C–O), 133.2 ($C_{arom.}NH_2$), 130.1 (C_c), 128.3 ($C_{arom.}CH_2$), 121.8 (C_b), 120.1 (C_a), 73.9 ($CH(CH_3)_2$), 72.4, 72.0, 71.7, 71.6, 69.4 (CH_2–O), 36.1 (ar–CH_2–ar), 22.8 (CH_3); ESI-MS+: m/z measured at 873.5 $[M+Cs]^+$ (calcd for $C_{44}H_{56}N_2O_8Cs$).

4.2.7. 11,23-Diamidosuccinyl-25,27-diisopropoxycalix[4]arene-26,28-crown-6 (10). $CAL(NH_2)_2$ **8** (95 mg, 128 μmol) is dissolved in 3 mL of DMF together with 26.9 mg of succinic anhydride (269 μmol). The reaction mixture is stirred overnight, evaporated and the 140 mg of product is used without further purification. Yield: 86%. ^{1}H NMR (500 MHz, DMSO-d_6): δ_H=9.67 (s, 2H; C(O)NH), 7.33 (s, 4H; H_a), 7.00 (d, 4H; H_b, J_{b-c}=7.4 Hz), 6.74 (t, 2H; H_c, J_{b-c}=7.4 Hz), 4.10 (sept., 2H; C$H(CH_3)_2$, J=5.8 Hz), 3.77 (d, 4H; ar–$H_\alpha CH_\beta$–ar, $J_{\alpha-\beta}$=15.9 Hz), 3.65 (d, 4H; ar–$H_\alpha CH_\beta$–ar, $J_{\alpha-\beta}$=15.9 Hz), 3.5 (s, 4H; O–CH_2), 3.43–3.48 (m, 4H; O–CH_2), 3.36–3.40 (m, 4H; O–CH_2), 3.12–3.19 (m, 4H; O–CH_2), 3.05–3.12 (m, 4H; OCH_2), 2.43–2.57 (m, 4H; CH_{2succ}), 0.76 (d, 12H; CH_3, J=5.6 Hz); ^{13}C NMR (125 MHz, DMSO-d_6): δ_C=173.8 (C(O)NH), 169.1 (C(O)OH), 156.3, 149.9 (C–O), 134.0 ($C_{arom.}NH$), 133.2, 133.0 ($C_{arom.}CH_2$), 129.8 (C_c), 121.3 (C_b), 119.5 (C_a), 69.9, 69.7 (CH_2–O), 69.6 ($CH(CH_3)_2$), 69.4, 68.7, 68.4 (CH_2–O), 39.4 (ar–CH_2–ar), 30.9, 28.9 (CH_{2succ}), 21.3 (CH_3); ESI-MS+: m/z measured at 963.4 $[M+Na]^+$ (calcd for $C_{53}H_{65}O_{14}N_2Na$).

4.2.8. 5,11,17,23-Tetranitro-25,27-diisopropoxycalix[4]arene-26,28-crown-6 (7). 1,3-Diisopropoxycalix[4]arene-crown-6 **3** (200 mg, 294 μmol) is dissolved in 5 mL of dichloromethane and cooled to 0 °C. A mixture of 400 μL of nitric acid, 500 μL acetic anhydride dissolved in 2 mL of dichloromethane is cooled to 0 °C and added dropwise to the calix[4]arene solution. After several minutes the reaction is stopped by addition of 4 mL of triethylamine and diluted with 50 mL of dichloromethane. The mixture is extracted twice with a saturated solution of $NaHCO_3$, dried over $MgSO_4$, filtered and evaporated. The residue is purified on silica gel column. The elution with cyclohexane/AcOEt, 6:4 gives 230 mg of the desired product. Yield: 88%. R_f=0.6 (cyclohexane/AcOEt 1:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H=8.07 (s, 4H; $H_{arom.}$), 8.02 (s, 4H; $H_{arom.}$), 4.47 (sept., 2H; C$H(CH_3)_2$; J=6.5 Hz), 3.96 (d, 4H; ar–$H_\alpha CH_\beta$–ar, $J_{\alpha-\beta}$=16 Hz), 3.91 (d, 4H; ar–$H_\alpha CH_\beta$–ar, $J_{\alpha-\beta}$=16 Hz), 3.60 (t, 4H; O–CH_2–, J=5.5 Hz), 3.53 (s, 4H; O–CH_2–), 3.31 (br s, 8H; O–CH_2–CH_2–O), 3.47 (t, 4H; O–CH_2–, J=5.5 Hz), 1.05 (d, 12H; CH_3, J=6.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C=161.8 (2C–NO_2), 160.2 (2C–NO_2), 142.3 (4C–CH_2), 134.5 (2C–O), 133.9 (2C–O), 126.6 (4$CH_{arom.}$), 126.1 (4$CH_{arom.}$), 73.1 (2$CH(CH_3)_2$), 71.6 (2CH_2–O), 71.3 (2CH_2–O), 71.1 (2CH_2–O), 70.8 (2CH_2–O), 69.7 (2CH_2–O), 38.2 (4ar–CH_2–ar), 22.0 (4CH_3); ESI-MS+: m/z measured at 1023 $[M+Cs]^+$ (calcd for $C_{44}H_{50}N_4O_{16}Cs$).

4.2.9. 5,11,17,23-Tetramino-25,27-diisopropoxycalix[4]arene-26,28-crown-6 (9). $CAL(NO_2)_4$ **7** (78 mg, 88 μmol) is dissolved in 3 mL of methanol and one spatula of Raney nickel. The mixture is placed under hydrogen atmosphere and stirred vigorously overnight. The mixture is filtered under Celite® pad and evaporated to dryness. The residue is purified by silica gel column chromatography eluted with CH_2Cl_2/MeOH, 9:1 to give 51 mg of the desired product. Yield: 76%. R_f=0.3 (CH_2Cl_2/MeOH 9:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H=6.52 (s, 4H; $H_{arom.}$), 6.41 (s, 4H; $H_{arom.}$), 4.11 (sept., 2H; C$H(CH_3)_2$; J=6.0 Hz), 3.81–3.80 (m, 16H; 4O–CH_2), 3.76 (s, 4H; O–CH_2–), 3.55 (se, 8H; $4NH_2$), 3.46 (d, 4H; ar–$H_\alpha CH_\beta$–ar, $J_{\alpha-\beta}$=13.5 Hz), 3.38 (d, 4H; ar–$H_\alpha CH_\beta$–ar, $J_{\alpha-\beta}$=13.5 Hz), 1.25 (d, 12H; CH_3, J=6.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C=149.6 (2C–O), 146.8 (2C–O), 140.6 (2C–NH_2), 139.9 (2C–NH_2), 134.3 (2$C_{arom.}$–CH_2), 133.8 (2$C_{arom.}$–CH_2), 118.42 (2$CH_{arom.}$), 118.0 (4$CH_{arom.}$), 73.3 (2$CH(CH_3)_2$), 72.3 (2CH_2–O), 71.9 (2CH_2–O), 71.6 (2CH_2–O), 71.4 (2CH_2–O), 69.7 (2CH_2–O), 36.7 (4ar–CH_2–ar), 22.6 (4CH_3); ESI-MS+: m/z measured at 903 $[M+Cs]^+$ (calcd for $C_{44}H_{58}N_4O_8Cs$).

4.2.10. 5,11,17,23-Tetramido-25,27-diisopropoxycalix[4]arene-26,28-crown-6 (11). $CAL(NH_2)_4$ **9** (60 mg, 77.8 μmol) is dissolved in 4 mL of DMF together with 31.2 mg of succinic anhydride (311 μmol). The reaction mixture is stirred overnight, evaporated and the 72 mg of product is used without further purification. Yield: 79%. ^{1}H NMR (500 MHz, $CDCl_3$), δ_H=12.03 (se, 2H; C(O)OH), 9.65 (s, 2H; C(O)NH), 9.60 (s, 2H; C(O)NH), 7.31 (s, 8H; $H_{arom.}$), 4.07 (sept., 2H; C$H(CH_3)$), 3.08–3.65 (OCH_2/ar–CH_2–ar), 0.79 (s, 12H; CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C=173.3 (C(O)NH), 168.7 (C(O)OH), 151.3, 149.5 (C–O), 133.6, 132.8, 132.7, 132.4 ($C_{arom.}CH_2$/$C_{arom.}NH$), 120.0, 119.2 ($C_{arom.}H$), 69.6, 69.5, 69.2, 69.1, 68.3 (CH_2–O, $CH(CH_3)_2$), 38.3 (ar–CH_2–ar), 30.5, 28.6 (CH_{2succ}), 20.8 (CH_3); ESI-MS+: m/z measured at 1193.40 $[M+Na]^+$ (calcd for $C_{60}H_{74}N_4O_{20}Na$).

4.2.11. Calix di-β-CDmet (12). $CAL(succ)_2$ (83 mg, 88 μmol) was dissolved in 2 mL of DMF. DIC (109 μL, 705 μmol) and 95 mg of HOBt (705 μmol) were added successively. Then 249 mg of **4** (176 μmol) was added. After 30 h, the mixture was evaporated, diluted in CH_2Cl_2 and extracted with HCl 0.1 M. The product is purified on silica gel column, eluted with CH_2Cl_2, then CH_2Cl_2/MeOH 95:5,

to give 120 mg of the desired compound **12**. Yield: 35%. R_f=0.5 (CH_2Cl_2/MeOH, 9:1); ^{1}H NMR (500 MHz, DMSO-d_6): δ_H=9.61 (t, 2H; CONH), 7.61 (t, 2H; CONH), 7.33 (s, 4H; Ha), 6.99 (d, 4H; Hc), 6.74 (t, 2H; Hb), 5.21–5.03 (m, 14H; H-1_{CD}), 4.09 (m, 2H; C*H*CH_{3calix}), 3.57–3.83 (m; H-5_{CD}), 3.14–3.58 (H-6_{CD}/H-4_{CD}/H-3_{CD}/CH_2–O_{calix}/ar–CH_2–ar), 3.0–3.1 (m; H-2_{CD}), 0.75 (s, 12H; CH_{3calix}); ^{13}C NMR (125 MHz, DMSO-d_6): δ_C=171.3, 169.4 (C(O)NH), 156.3, 149.8 (C–O), 134.0 ($C_{arom.}$NH), 133.2, 133.0 ($C_{arom.}CH_2$), 129.9 (C_c), 121.5 (C_b), 119.5 (C_a), 97.9–97.1 (C-1_{CD}), 81.0–79.0 (C-3_{CD}/C-2_{CD}/C-4_{CD}), 68.4–71.1 (C-6_{CD}/C-5_{CD}/CH_2–O_{calix}/*C*H$(CH_3)_{2calix}$), 60.3–60.8 (OCH_3-6_{CD}), 57.6–58.3 (OCH_3-3_{CD}/OCH_3-2_{CD}), 30.4 (CH_{2succ}), 21.2 (CH_{3calix}); MALDI-TOF MS: *m*/*z* measured at 3756.3 $[M+Na]^+$ (calcd for $C_{176}H_{282}N_4O_{80}Na$).

4.2.12. Calix tetra-β-CDmet (14). CAL(succ)$_4$ **11** (60 mg, 51 μmol) was dissolved in 5 mL of DMF. DIC (127 μL, 820 μmol) and 111 mg of HOBt (820 μmol) were added successively. Then 297 mg of **4** (210 μmol) was added. After 30 h, the mixture was evaporated, diluted in CH_2Cl_2 and extracted with HCl 0.1 M. The product is purified via silica gel column chromatography, eluted with CH_2Cl_2/acetone 1:1, then another column chromatography is done with CH_2Cl_2/MeOH 95:5 to give 217 mg of **14**. Yield: 63%. R_f= 0.5 (CH_2Cl_2/MeOH, 9:1); ^{1}H NMR (500 MHz, DMSO-d_6), δ_H=9.61 (s, 2H; C(O)NH), 9.55 (s, 2H; C(O)NH), 7.61 (se, 4H; NH_{CD}C(O)), 7.24–7.34 (m, 8H; $H_{arom.}$), 5.00–5.22 (m; H-1_{CD}), 4.04 (m, 2H; CH$(CH_3)_2$), 3.64–3.75 (m; H-5_{CD}), 3.18–3.55 (H-6_{CD}/H-4_{CD}/H-3_{CD}/CH_2–O_{calix}/ar–CH_2–ar), 3.0–3.1 (m; H-2_{CD}), 2.30–2.50 (m; CH_{2succ}), 0.76 (s, 12H; CH_{3calix}); ^{13}C NMR (125 MHz, DMSO-d_6): δ_C=97.7–97.9 (C-1_{CD}), 81.5–81.6 (C-3_{CD}), 81.1–81.2 (C-2_{CD}), 69.7–71.0 (C-6_{CD}/C-5_{CD}/CH_2–O_{calix}/*C*H$(CH_3)_{2calix}$), 60.6–60.7 (OCH_3-6_{CD}), 57.7–58.2 (OCH_3-3_{CD}/OCH_3-2_{CD}), 31.2 (CH_{2succ}), 21.1 (CH_{3calix}); MALDI-TOF MS: *m*/*z* measured at 6780.4 $[M+Na]^+$ (calcd for $C_{308}H_{510}N_8O_{152}Na$).

4.2.13. Calix di-β-CD (13) and calix tetra-β-CD (15). CAL(succ)$_n$ (n=2, 36 mg and n=4, 24 mg) was dissolved in 4 mL of DMF. DIC (for **13**, 47 μL and for **15**, 51 μL) and HOBt (for **13**, 41 mg and for **15**, 44 mg) were added successively. Then **5** (for **13**, 91.1 mg and for **15**, 95.3 mg) dissolved in DMF was added. After three days, the mixture was evaporated, diluted in water and precipitated in acetone. The residues were dialysed with ester cellulose membrane MWCO=2000 for **13** and MWCO=3000 for **15**. MALDI-TOF spectra proved the existence of compound **19** ($[M+Na]^+$, 2372.6) in the synthesis of compound **13**, 3195.4 $[M+Na]^+$. For synthesis of compound **15**, presence of 2373 $[M+Na]^+$ of compound **19**, 5657.1 $[M+Na]^+$ of compound **15** and partially substituted calixarene structures such as 3433.9 (calix di-β-CD disucc) and 4523.0 (calix tri-β-CD monosucc) was detected.

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