Experimental Section

^{1}H NMR spectra were recorded at 400 MHz on a Bruker AMX 400 with TMS as internal reference in $CDCl_3$ solutions. The 2D DQF-COSY consisted of 2048 datapoints in t_2 and 512 increments in t_1. The data were apodized with a shifted sine-bell square function in both dimensions and processed to a 2K x 1K matrix. For the TOCSY experiment, the total TOCSY mixing time was set to 65 ms. The spectrum was acquired with 1024 data points in t_2 and 512 FIDs in t_1. The data were apodized with a shifted sine-bell square function in both dimensions and processed to a 1K x 1K matrix. The NOESY experiments were acquired with a mixing time of 150ms, 1024 datapoints in t_2 and 512 increments in t_1.

Hydrogen-bonded assemblies 2_3•$(DEB)_6$ were prepared by mixing calix[4]arene dimelamines 2 with 2.1 equivalents of DEB in $CDCl_3$ for 15 min.

Calix[4]arene dimelamine 2a. Bis(chlorotriazine) **3** (0.5 g, 0.57 mmol) and 2,2-dimethyl-1,3-propanediamine (10 mL) were heated at 90°C overnight. Addition of H_2O gave **2a** as a white precipitate in 96% yield. Assembly **2a**$_3$•$(DEB)_6$: ^{1}H NMR (400 MHz, $CDCl_3$, 298K) δ = 14.12 (s, 2 H; H_a), 13.33 (s, 2 H; H_b), 8.41 (s, 2 H; H_c) 7.60-7.58 (m, 2 H; H_d), 7.13-7.10 (m, 4 H; ArH), 6.95 (s, 2H; H_f), 6.88 (t, ^3J(H,H)=7.6 Hz, 2 H; ArH), 6.66 (s, 2 H; H_e), 6.00 (s, 2 H; H_h), 4.53, 4.43, 3.15, 3.12 (2ABq, ^2J(H,H)=13.6 Hz, 8 H; $ArCH_2Ar$), 4.11-3.93 (m, 6 H; OCH_2, H_i), 3.62 (t, ^3J(H,H)=6.4 Hz, 4 H; OCH_2), 2.63 (d, ^2J(H,H)=10.4 Hz, 2 H; H_j), 2.34 (d, ^2J(H,H)=13.6 Hz ,2 H; H_k), 2.26-1.80 (m, 18 H; H_l, CH_2(DEB), $OCH_2\underline{CH_2}$), 1.36-0.74 (m, 36 H; CH_3).

Calix[4]arene dimelamine 2b. Calix[4]arene dimelamine **2a** (0.22 g, 0.22 mmol) was dissolved in THF (10 mL) and propyl isocyanate (0.2 mL) was added. The mixture was stirred at rt for 2h. The mixture was evaporated to dryness and CH_2Cl_2 was added. The solution was washed with H_2O and brine and dried (Na_2SO_4). Evaporation of the solvent gave the crude product as a white solid, which was purified by column chromatography (CH_2Cl_2:MeOH:NH_4OH (90:9.5:0.5)) to give the pure product in 78% yield. Assembly

$2b_3$•(DEB)$_6$: ^{1}H NMR (400 MHz, $CDCl_3$, 298K) δ=14.04 (s, 2 H; H_a), 13.23 (s, 2 H; H_b) 8.62 (s, 2 H; H_c) 7.81-7.78 (m, 2 H; H_d), 7.14-7.11 (m, 6 H; ArH, H_g), 7.00 (s, 2 H; H_f), 6.89 (t, ^3J(H,H)=7.4 Hz, 2 H; ArH), 6.71 (s, 2 H; H_e), 6.13 (s, 2 H; H_h), 5.24 (d, ^3J(H,H)=10.4 Hz, 2 H; H_m), 4.51 (ABq, ^2J(H,H)=13.2 Hz, 4 H; $ArCH_2Ar$), 4.14-4.00 (m, 4 H; OCH_2), 3.93 (m, 2 H; H_i), 3.64 (t, ^3J(H,H)=6.6 Hz, 4 H; OCH_2), 3.24-3.06 (m, 8 H; H_k, H_o, $ArCH_2Ar$), 2.64 (d, ^2J(H,H)=10.8 Hz, 2 H; H_j), 2.48-2.45 (m, 2 H; H_n), 2.37 (d, ^2J(H,H)=12.8 Hz, 2 H; H_l), 2.18-1.84 (m, 18 H; H_p, CH_2), 1.15-0.82 (m, 40 H; $NHCH_2\underline{CH_2}CH_3$, CH_3), 0.66 (t, ^3J(H,H)=7.2 Hz, 6 H; $NHCH_2CH_2\underline{CH_3}$).

General Procedure for the Preparation of Calix[4]arene Dimelamines 2c-2e. Calix[4]arene dimelamine **2a** was dissolved in CH_2Cl_2 and the corresponding acid derivative (50 equivalents) was added. The mixture was stirred at rt for 1h and then evaporated to dryness. The residue was taken up in Na_2CO_3 (4% w/w) solution and heated for 10 min at 60°C in order to hydrolyze the excess of chloride. The product was extracted with CH_2Cl_2 and washed with water and brine and dried (Na_2SO_4). Evaporation of the solvent gave the crude product as a white solid, which was purified by column chromatography or preparative TLC (CH_2Cl_2:MeOH:NH_4OH (90:9.5:0.5)) to give pure product in 47-53% yield.

Assembly **$2c_3$**•(DEB)$_6$: ^{1}H NMR (400 MHz, $CDCl_3$, 298K) δ = 14.09 (s, 2 H; H_a), 13.28 (s, 2 H; H_b), 8,58 (s, 2 H; H_c), 7.77 (m, 2 H; H_d), 7.13-7.02 (m, 8 H; H_f, H_g, ArH), 6.87 (t, ^3J(H,H)=7.4 Hz, 2 H; ArH), 6.71 (s, 2 H; H_e), 6.33 (d, ^3J(H,H)=8.8 Hz, 2 H; H_m), 6.06 (s, 2 H; H_h), 4.52, 4.46 and 3.10, 3.08 (2ABq, ^2J(H,H)=13.2 and 13.6 Hz, 8 H; $ArCH_2Ar$), 4.13-4.00 (m, 6 H; OCH_2, H_i), 3.60 (m, 4 H; OCH_2), 3.42 (t, ^2J(H,H)=9.0 Hz, 2 H; H_k), 2.66 (d, ^2J(H,H)=8.4 Hz, 2 H; H_j), 2.36 (d, ^2J(H,H)=12.4 Hz, 2 H; H_l), 2.17-1.83 (m, 18 H; CH_2), 1.38-1.31 (m, 2 H; $H_{n/o}$), 1.20-0.81 (m, 40 H; CH_3, N_p), 0.54 (m, 8 H; H_r, $H_{n/o}$).

Assembly **$2d_3$**•(DEB)$_6$: ^{1}H NMR (400 MHz, $CDCl_3$, 298K) δ=14.01 (s, 2 H; H_a), 13.25 (s, 2 H; H_b) 8.52 (s, 2 H; H_c) 7.80-7.79 (m, 2 H; H_d), 7.13-7.04 (m, 4 H; ArH), 6.95 (s, 2 H; H_f), 6.89-6.83 (m, 4 H, H_g, ArH), 6.67 (s, 2 H; H_e), 6.04 (s, 2 H; H_h), 5.14 (m, 2 H; NH_m), 4.54, 4.48 and 3.28, 3.10 (2ABq, ^2J(H,H)=13.6 and 14.0 Hz, 8 H; $ArCH_2Ar$), 4.15-4.02 (m, 4 H, OCH_2), 3.91-3.82 (m, 4 H; H_i, OCH_2), 3.61 (m, 2 H; OCH_2), 2.76-

2.58 (m, 6 H; H_j, H_k, H_l), 2.41-2.34 (m, 2 H; H_n), 2.05-1.83 (m, 18 H; H_o, $OCH_2\underline{CH_2}$, CH_2(DEB)), 1.25-0.80 (m, 44 H; H_p, H_q, CH_3), 0.73 (t, ^3J(H,H)=7.4 Hz, 6 H; H_r).

Assembly $\mathbf{2e_3}$•$(DEB)_6$: ^{1}H NMR (400 MHz, $CDCl_3$, 298K) δ=14.13 (s, 2 H; H_a), 13.34 (s, 2 H; H_b), 8.43 (s, 2 H; H_c), 7.67 (m, 2 H; H_d), 7.12 (m, 6 H; ArH + H_g), 6.90 (s, 2 H; H_f), 6.86 (t, 2H, *J* = 7.4 Hz, ArH), 6.67 (s, 2 H; H_e), 6.03 (s, 2 H; H_h), 4.51, 4.47 (2d, ^2J(H,H)=13.2 and 13.6 Hz, 4 H; $ArCH_2Ar$), 4.14-3.64 (m, 18 H; OCH_2, H_i), 3.22-3.08 (m, 6 H; $ArCH_2Ar$, H_k), 2.74-2.64 (m, 4 H; H_j, H_l), 2.10-1.83 (m, 16 H; $OCH_2\underline{CH_2}$, CH_2 (DEB)), 1.31-0.86 (m, 42 H; CH_3), 0.81 (t, ^2J(H,H)= 7.4 Hz, 6 H; CH_3(ethyl)).

General Procedure for the Preparation of Calix[4]arene Dimelamines 4a-4e. Calix[4]arene dimelamine **2a** was dissolved in CH_2Cl_2 or DMF and the corresponding *N*-protected amino acid or peptide (2.2 equivalents) was added, followed by addition of EDC or HATU (2.2 equivalents) and a base (4 equivalents). The reaction was stirred at rt for 1-2 days. In the case of DMF as a solvent, the solvent was first removed and the residue was taken up in CH_2Cl_2. The product was washed with HCl (1N), H_2O, sat. Na_2CO_3 solution and brine and dried ($MgSO_4$). Evaporation of the solvent gave the crude product as a white solid, which was purified by column chromatography or preparative TLC (CH_2Cl_2:MeOH:NH_4OH (90:9.5:0.5)) to give pure product in 24-66%.

MALDI-TOF mass spectrometry characterization of assemblies $2b_3•(CNCYA)_6$ - $2e_3•(CNCYA)_6$ after Ag^+-labeling.

Assembly	Calc. Mass (Da) of Ag^+-complex	Observed Mass (Da)
$\mathbf{2b_3}•(CNCYA)_6$	5029.0	5031.0
$\mathbf{2c_3}•(CNCYA)_6$	4939.3	4942.4
$\mathbf{2d_3}•(CNCYA)_6$	5239.2	5240.1
$\mathbf{2e_3}•(CNCYA)_6$	5271.2	5274.6