# Electrografting of calix[4]arenediazonium salt to form versatile robust platforms for spatially-controlled surface functionalization

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## Supplementary Figures



## Supplementary Methods



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**Supplementary Figures**

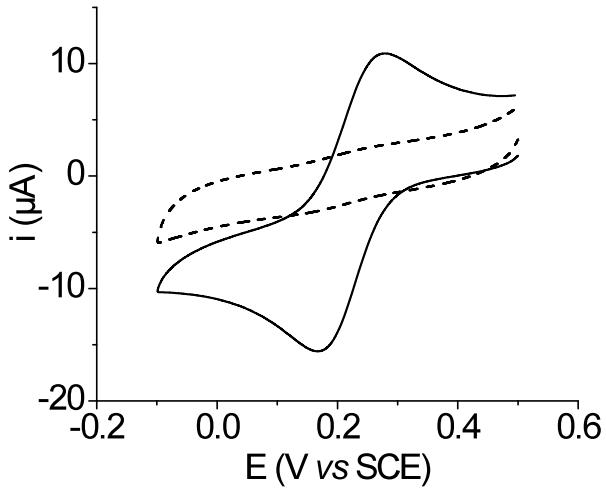



**Figure S1**. **Cyclic voltammetry of 1 mM $Fe(CN)_6^{3-/4-}$ in 1 M KCl** at a bare glassy carbon electrode (full line) and at a modified electrode after electrografting of **2** (dashed line).

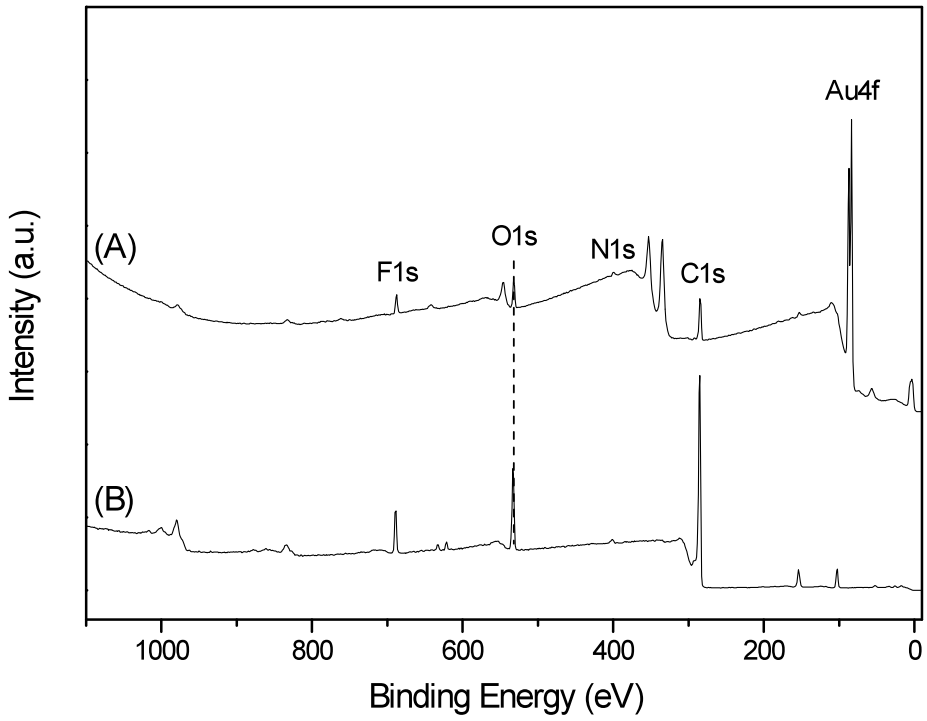



**Figure S2.** XPS survey spectra of gold (A) and PPF samples (B) modified with compound **2**.

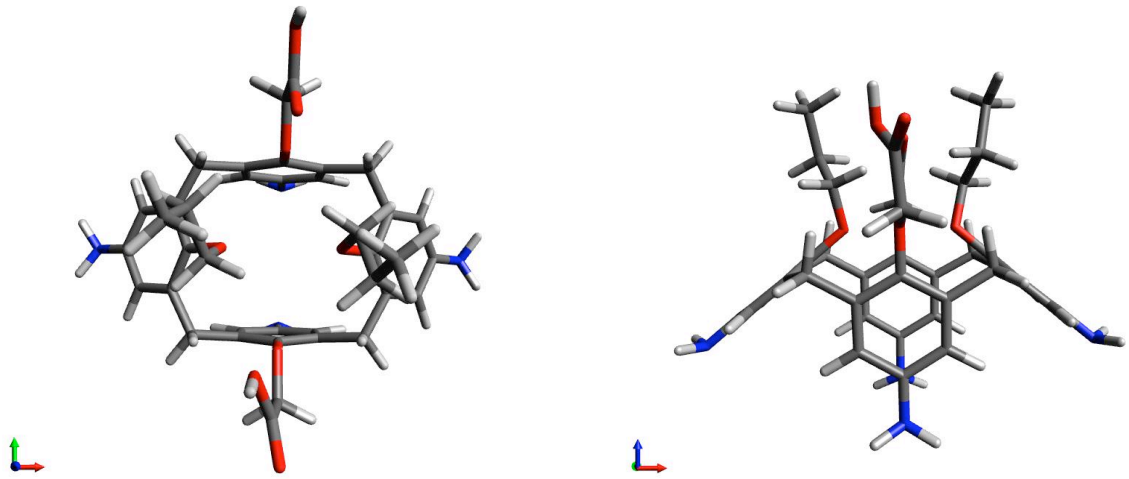


**Figure S3. B3LYP/6-31G* Optimized conformation of calixarene 3 showing the C2v conformation.** $N_2^+$ groups have been replaced by $NH_2$ to avoid electrostatic interactions in gaz phase calculations.

Gas phase geometries were calculated by full optimization without imposed symmetry of the conformations using the B3LYP DFT and the 6-31G* basis set using Gaussian G09W software package.[58] Visualization were done with the Avogadro software.[59]

## Supplementary Methods

### Synthesis of compounds 1-4

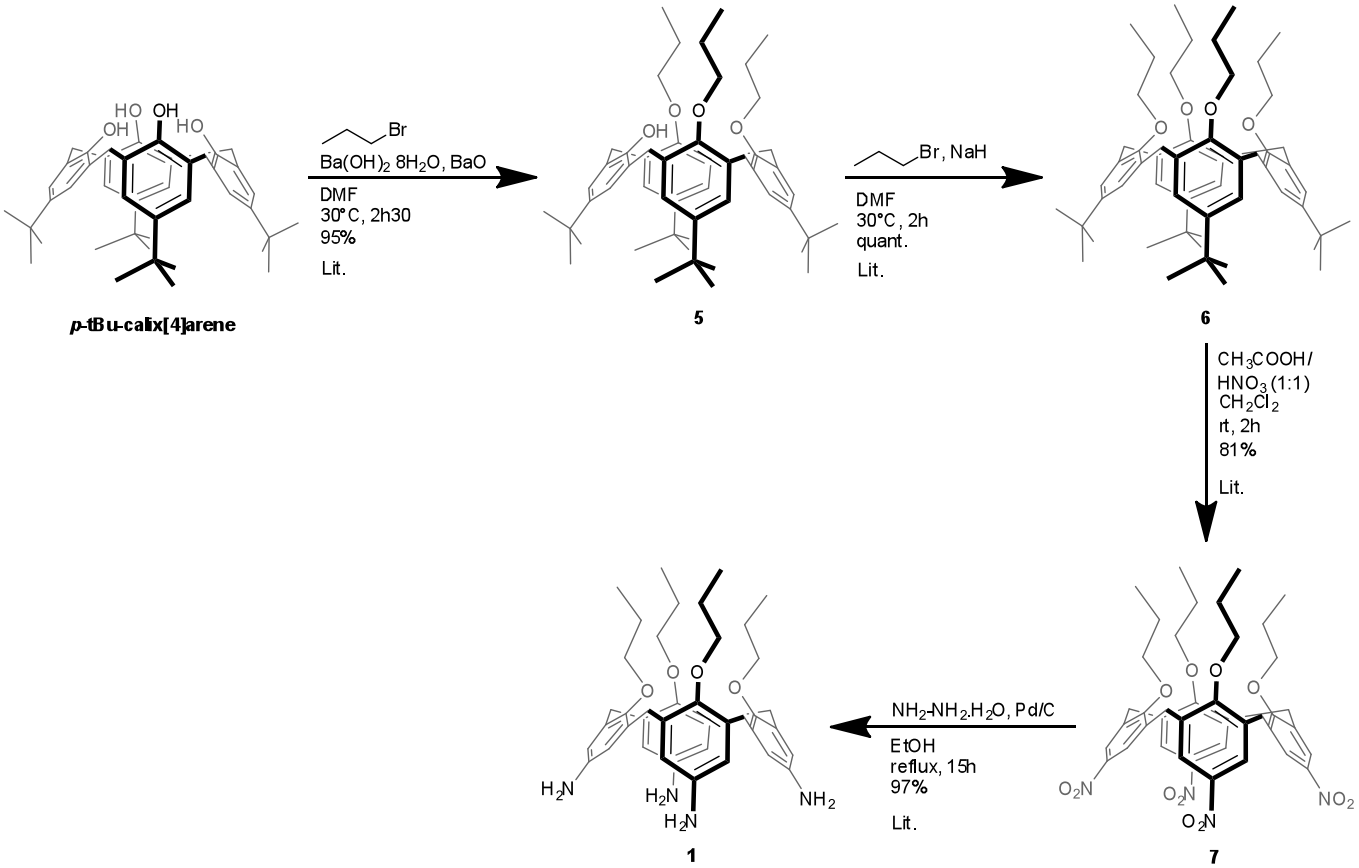
**General Information:** The $^{1}H$ NMR, $^{13}C$ NMR and 2D NMR were performed with a Bruker Avance-300 instrument, Varian-400 VNMRJ System and a Bruker Varian Unity-600. The chemical shifts are expressed in ppm and determined in comparison of the deutered solvent used as internal reference. $CDCl_3$ was filtered over a short basic alumina column to remove traces of DCl. Most of $^{1}H$ NMR signals were attributed through 2D NMR analyses (COSY, HSQC, HMBC). Abbreviation: s: singulet, d: doublet, t: triplet, m: massif, mult: multiplet.

The high resolution mass spectra were recorded with a Q-TOF 6520 Agilent Technology spectrometer (at the Organic Pharmaceutic Chemistry Laboratory, ULB). The electrospray mass spectra were recorded with a Finnigan LCQ Deca ThermoQuest spectrometer. ATR-FTIR spectra were recorded, at room temperature, on a Bruker IFS55 FTIR spectrophotometer equipped with a liquid nitrogen-cooled mercurycadmium-telluride (MCT) detector at a nominal resolution of 2 $cm^{-1}$ and encoded every 1 $cm^{-1}$. The spectrophotometer was continuously purged with air dried on a FTIR purge gas generator 75-62 Balston (Maidstone, England) at a flow rate of 5.8 L/min. For the internal reflection element (IRE), the usual configuration used is a 5 cm long, 2 mm thick and 45° angle germanium trapezoidal plate yielding 25 internal reflections.

All the reactions were performed under an inert atmosphere. Anhydrous DMF was obtained from Alfa Aesar. Anhydrous THF was obtained from distillation on Na/benzophenone. All the solvents and reagents for the syntheses were at least reagent grade quality and were used without further purification.

Silica gel (230-400 mesh) was used for flash chromatography.

**Synthesis of Compound 1**




Compound **5** was prepared according to a procedure described in the literature.[60] *p*-tBu-Calix[4]arene (5.012 g, 7.72 mmol, 1 equiv.), $Ba(OH)_2.8H_2O$ (7.42 g, 0.0235 mol, 3 equiv.) and BaO (5.54 g, 36.12 mmol, 4.7 equiv.) were suspended in DMF (190 mL). 1-bromopropane (35 mL, 385 mmol, 50 equiv.) was added and the reaction mixture was stirred for 2h30 at 30°C under inert atmosphere. The reaction mixture was concentrated under reduced pressure and dissolved in $CH_2Cl_2$ (300 mL). The organic layer was washed with $H_2O$ (4×200 mL) and the combined aqueous layers were extracted with $CH_2Cl_2$ (2×250 mL). The combined organic layers were concentrated under reduced pressure to yield compound **5** as a white solid (5.665 g, 7.31 mmol, 95%). The $^1H$ NMR characterization of compound **5** conforms to the

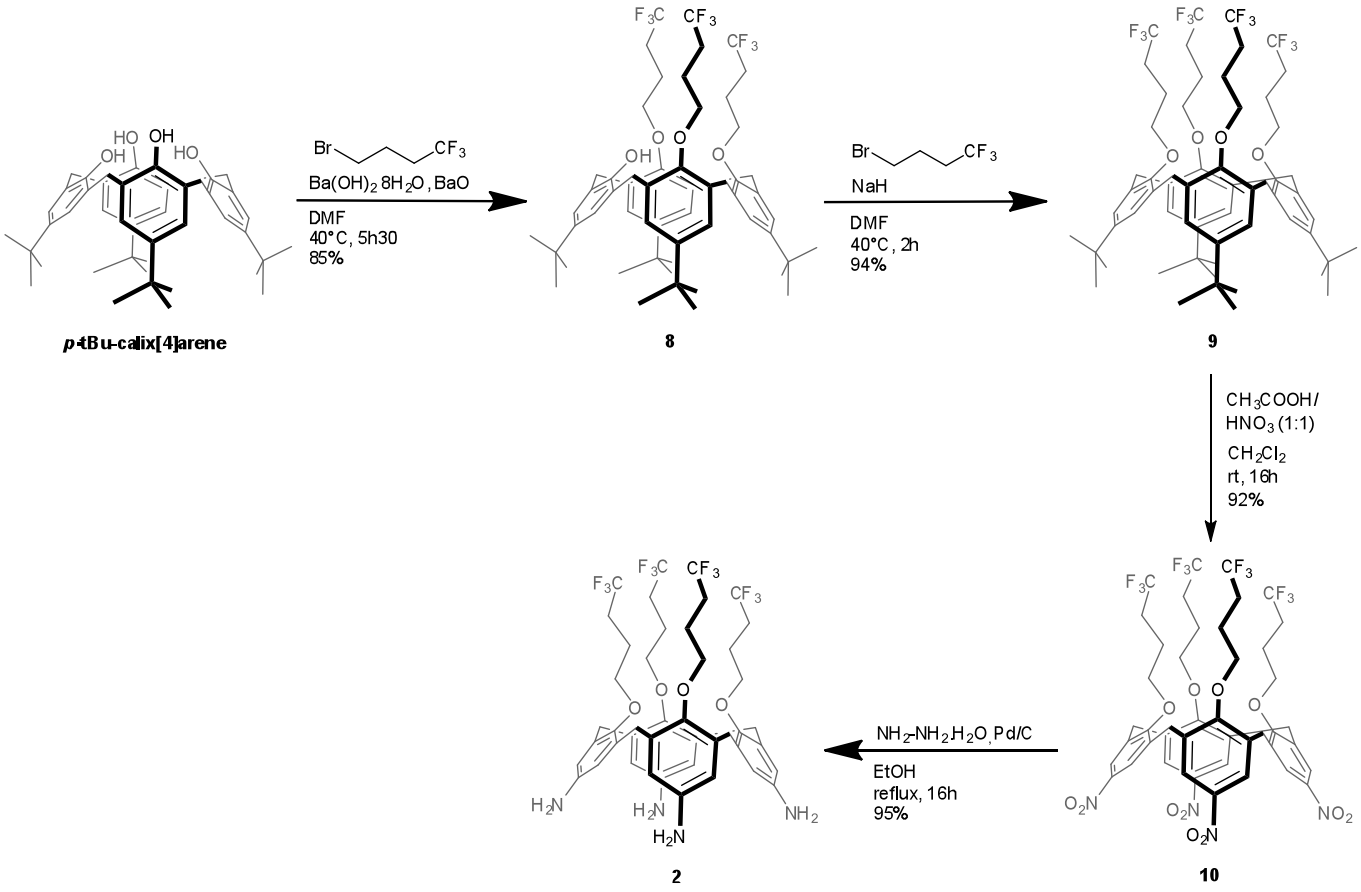
literature. $^{1}$H NMR (300 MHz, $CDCl_3$, 298K): δ 0.82 (s, 18H, *t*Bu), 0.95 (t, $^{3}J$ = 7.5 Hz, 3H, $CH_2CH_3$), 1.09 (t, $^{3}J$ = 7.4 Hz, 6H, $CH_2CH_3$), 1.32 (s, 9H, *t*Bu), 1.34 (s, 9H, *t*Bu), 1.81-2.01 (mult, 4H, $CH_2CH_3$), 2.33 (mult, 2H, $CH_2CH_3$), 3.16 (d, $^{2}J$ = 12.6 Hz, 2H, $ArCH_{2eq}$), 3.22 (d, $^{2}J$ = 13.2 Hz, 2H, $ArCH_{2eq}$), 3.75 (t, $^{3}J$ = 7.3 Hz, 4H, $OCH_2$), 3.84 (t, $^{3}J$ = 8.4 Hz, 2H, $OCH_2$), 4.31-4.39 (m, 4H, $ArCH_{2ax}$), 5.58 (s, 1H, OH), 6.49-6.53 (m, 4H, ArH), 7.05 (s, 2H, ArH), 7.13 (s, 2H, ArH). $^{13}$C NMR (75 MHz, $CDCl_3$, 298K): δ 9.8, 10.9, 22.6, 23.5, 31.2 (2C), 31.5, 31.8, 31.9, 33.8, 34.0, 34.3, 76.4, 78.0, 124.8, 124.9, 125.1, 125.7, 129.6, 132.0, 132.4, 136.2, 141.6, 145.1, 145.6, 150.8, 151.8, 154.1.

Compound **6** was prepared according to a procedure described in the literature.[60] Compound **5** (0.506 g, 0.65 mmol, 1 equiv.) and NaH (60% in oil, 0.154 g, 3.85 mmol, 6 equiv.) were suspended in DMF (20 mL). 1-bromopropane (1.2 mL, 13.21 mmol, 20 equiv.) was added and the reaction mixture was stirred for 2h at 30°C under inert atmosphere. The reaction mixture was concentrated under reduced pressure and dissolved in $CH_2Cl_2$ (50 mL). The organic layer was washed with $H_2O$ (3×20 mL) and the combined aqueous layers were extracted with $CH_2Cl_2$ (2×30 mL). The combined organic layers were concentrated under reduced pressure to yield compound **6** as a white solid (0.548 g, 0.65 mmol, quant.). The $^{1}$H NMR characterization of compound **6** conforms to the literature. $^{1}$H NMR (300 MHz, $CDCl_3$, 298K): δ 1.02 (t, $^{3}J$ = 7.5 Hz, 12H, $CH_2CH_3$), 1.10 (s, 36H, *t*Bu), 2.05 (mult, 8H, $CH_2CH_3$), 3.13 (d, $^{2}J$ = 14.0 Hz, 4H, $ArCH_{2eq}$), 3.84 (t, $^{3}J$ = 7.8 Hz, 8H, $OCH_2$), 4.44 (d, $^{2}J$ = 12.6 Hz, 4H, $ArCH_{2ax}$), 6.80 (s, 8H, ArH). $^{13}$C NMR (75 MHz, $CDCl_3$, 298K): δ 10.5, 23.5, 31.2, 31.6, 34.0, 77.4, 125.0, 140.0, 144.3, 153.9.

Compound **7** was prepared according to a procedure described in the literature.[61] Compound **6** (0.554 g, 0.68 mmol, 1 equiv.) was dissolved in $CH_2Cl_2$ (25 mL). A mixture of glacial $CH_3COOH$/fuming $HNO_3$ (1:1) (5.6 mL) was added at 0°C and the reaction mixture was stirred for 2h at room temperature to yield a purple solution which turned to yellow. The reaction mixture was concentrated under reduced pressure and dissolved in $CH_2Cl_2$ (50 mL). The organic layer was washed with $H_2O$ (3×20 mL) and the combined aqueous layers were extracted with $CH_2Cl_2$ (2×30 mL). The combined organic layers were concentrated under reduced pressure and the crude residue was washed with MeOH (2×2 mL) to yield compound 7 as a yellow solid (0.425 g, 0.55 mmol, 81%). The $^1$H NMR characterization of compound **7** conforms to the literature.[62] $^1$H NMR (300 MHz, $CDCl_3$, 298K): δ 1.02 (t, $^3J$ = 7.5 Hz, 12H, $CH_2CH_3$), 1.91 (mult, 8H, $CH_2CH_3$), 3.40 (d, $^2J$ = 14.1 Hz, 4H, $ArCH_{2eq}$), 3.96 (t, $^3J$ = 7.5 Hz, 8H, $OCH_2$), 4.53 (d, $^2J$ = 13.8 Hz, 4H, $ArCH_{2ax}$), 7.57 (s, 8H, ArH). $^{13}$C NMR (75 MHz, $CDCl_3$, 298K): δ 10.0, 23.2, 31.1, 77.7, 123.9, 135.4, 142.8, 161.7.

Compound **1** was prepared according to a procedure described in the literature.[35] Compound **7** (0.405 g, 0.52 mmol, 1 equiv.) and Pd/C (0.041 g, 0.39 mmol, 0.75 equiv.) were suspended in EtOH (15 mL). Hydrazine hydrate (2.4 mL, 0.494 mol, 94 equiv.) was added and the reaction mixture was stirred for 15h at reflux. The reaction mixture was filtered on Celite and the Celite was washed with EtOH and $CH_2Cl_2$. The filtrate was concentrated under reduced pressure to yield the compound **1** as a yellow solid (0.332 g, 0.51 mmol, 97%). The $^1$H NMR characterization of compound **7** conforms to the literature.[62] $^1$H NMR (300 MHz, $CDCl_3$, 298K): δ 0.95 (t, $^3J$ = 7.5 Hz, 12H, $CH_2CH_3$), 1.84 (mult, 8H, $CH_2CH_3$), 2.92 (d, $^2J$ = 13.2 Hz, 4H, $ArCH_{2eq}$), 3.72 (t, $^3J$ = 7.5 Hz, 8H, $OCH_2$), 4.31 (d, $^2J$ = 13.2 Hz, 4H, $ArCH_{2ax}$), 6.06 (s, 8H, ArH). $^{13}$C NMR (75 MHz, $CDCl_3$, 298K): δ 10.2, 23.0, 30.9, 76.5, 115.8, 135.6, 139.7, 150.0.

## Synthesis of Compound 2




*p*-tBu-Calix[4]arene (0.501 g, 0.77 mmol, 1 equiv.), $Ba(OH)_2.8H_2O$ (0.761 g, 2.41 mmol, 3 equiv.) and BaO (0.703 g, 5.09 mmol, 6.6 equiv.) were suspended in DMF (20 mL). 1-Bromo-4,4,4-trifluorobutane (0.550 mL, 4.48 mmol, 6 equiv.) was added and the reaction mixture was stirred for 5h30 at 40°C under inert atmosphere. The reaction mixture was concentrated under reduced pressure and dissolved in $CH_2Cl_2$ (50 mL). The organic layer was washed with $H_2O$ (3×25 mL) and the combined aqueous layers were extracted with $CH_2Cl_2$ (2×35 mL). The combined organic layers were concentrated under reduced pressure. The crude residue was purified by flash chromatography ($C_6H_{12}/CH_2Cl_2$ 8:2) to yield compound **8** as a white solid (0.639 g, 0.65 mmol, 85%).

mp: 82°C; TLC ($C_6H_{12}/CH_2Cl_2$ 8:2 v/v): $R_f$ = 0.27; $^1$H NMR (400 MHz, $CDCl_3$, 298K): δ 0.82 (s, 18H, *t*Bu), 1.34 (s, 9H, *t*Bu), 1.35 (s, 9H, *t*Bu), 2.12 (mult, 4H, $CH_2CH_2CF_3$), 2.25-2.44 (m, 6H, $CH_2CF_3$), 2.51 (mult, 2H, $CH_2CH_2CF_3$), 3.23 (d, ²J = 12.8 Hz, 2H, $ArCH_{2eq}$) 3.27 (d, ²J = 13.2 Hz, 2H, $ArCH_{2eq}$), 3.87 (mult, 4H, $OCH_2$), 3.96 (t, ³J = 10.8 Hz, 2H, $OCH_2$), 4.21-4.30 (m, 4H, $ArCH_{2ax}$), 5.12 (s, 1H, OH), 6.49-6.54 (m, 4H, ArH), 7.08 (s, 2H, ArH), 7.17 (s, 2H, ArH); $^{13}$C NMR (75 MHz, $CDCl_3$, 298K): δ 22.6, 22.9, 30.5, 30.9, 31.1 (2C), 31.3, 31.8, 31.9, 33.8, 34.0, 34.3, 73.0, 74.4, 125.0, 125.2 (2C), 125.3, 125.7, 126.1, 128.6 (q, $^1$J = 279 Hz), 129.5 (q, $^1$J = 272 Hz), 131.6, 131.9, 142.2, 145.8, 146.5, 150.6, 151.2, 153.4; IR: 3281, 2967, 1484, 1255, 1154, 1024, 874 $cm^{-1}$; HRMS (*m/z*): $[M+Na]^+$ calcd. for $C_{56}H_{71}O_4F_9$, 1001.5106; found, 1001.5145.

Compound **8** (0.639 g, 0.65 mmol, 1 equiv.) and NaH (60% in oil, 0.162 g, 4.05 mmol, 6 equiv.) were suspended in DMF (20 mL). 1-Bromo-4,4,4-trifluorobutane (0.162 mL, 1.31 mmol, 2 equiv.) was added and the reaction mixture was stirred for 2h at 40°C under inert atmosphere. The reaction mixture was concentrated under reduced pressure and dissolved in $CH_2Cl_2$ (75 mL). The organic layer was washed with $H_2O$ (3×40 mL) and the combined aqueous layers were extracted with $CH_2Cl_2$ (2×60 mL). The combined organic layers were concentrated under reduced pressure. The crude residue was purified by flash chromatography ($C_6H_{12}/CH_2Cl_2$ 9:1) to yield compound **9** as a white solid (0.667 g, 0.61 mmol, 94%).

mp: 197°C; TLC ($C_6H_{12}/CH_2Cl_2$, 9:1 v/v): $R_f$ = 0.32; $^1$H NMR (300 MHz, $CDCl_3$, 298K): δ 1.08 (s, 36H, *t*Bu), 2.19-2.22 (m, 16H, $CH_2CH_2CF_3$), 3.18 (d, ²J = 12.6 Hz, 4H, $ArCH_{2eq}$), 3.89 ($t_b$, ³J = 6.9 Hz, 8H, $OCH_2$), 4.28 (d, ²J = 12.6 Hz, 4H, $ArCH_{2ax}$), 6.80 (s, 8H, ArH); $^{13}$C NMR (75 MHz, $CDCl_3$, 298K): δ 23.0, 30.8, 31.1, 31.5, 34.0, 73.7,

125.4, 127.2 (q, $^{1}J$ = 276 Hz), 133.6, 142.3, 152.9; IR: 3298, 2966, 1482, 1292, 1257, 1155, 1030, 867 $cm^{-1}$; HRMS (*m/z*): $[M+Na]^{+}$ calcd. for $C_{60}H_{76}O_4F_{12}$, 1111.5450; found, 1111.5453.

Compound **9** (0.538 g, 0.49 mmol, 1 equiv.) was dissolved in $CH_2Cl_2$ (27 mL). A mixture of glacial $CH_3COOH$/fuming $HNO_3$ (1:1) (5.4 mL) was added and the reaction mixture was stirred for 16h at room temperature. The reaction mixture was concentrated under reduced pressure and dissolved in $CH_2Cl_2$ (50 mL). The organic layer was washed with $H_2O$ (3×25 mL) and combined aqueous layers were extracted with $CH_2Cl_2$ (2×30 mL). The combined organic layers were concentrated under reduced pressure. The crude residue was washed with MeOH (2×2 mL) to yield compound **10** as a yellow solid (0.475 g, 0.46 mmol, 92%).

mp: 350-352°C (dec); $^{1}H$ NMR (300 MHz, $CD_3CN$, 298K): δ 2.15-2.29 (m, 16H, $CH_2CH_2CF_3$), 3.58 (d, $^{2}J$ = 14.1 Hz, 4H, $ArCH_{2eq}$), 4.06 (t, $^{3}J$ = 7.2 Hz, 8H, $OCH_2$), 4.43 (d, $^{2}J$ = 14.1 Hz, 4H, $ArCH_{2ax}$), 7.64 (s, 8H, ArH); $^{13}C$ NMR (75 MHz, $CD_3CN$, 298K): δ 23.5, 30.9, 31.4, 75.2, 125.1, 127.5* (q, $^{1}J$ = 276 Hz), 136.9, 144.1, 162.1. IR: 3411, 2962, 1526, 1353, 1257, 1151, 1030, 841 $cm^{-1}$. ESI-MS (*m/z*): $[M+Cl]^{-}$calcd. for $C_{44}H_{40}F_{12}N_4O_{12}$, 1079.21; found, 1079.13.

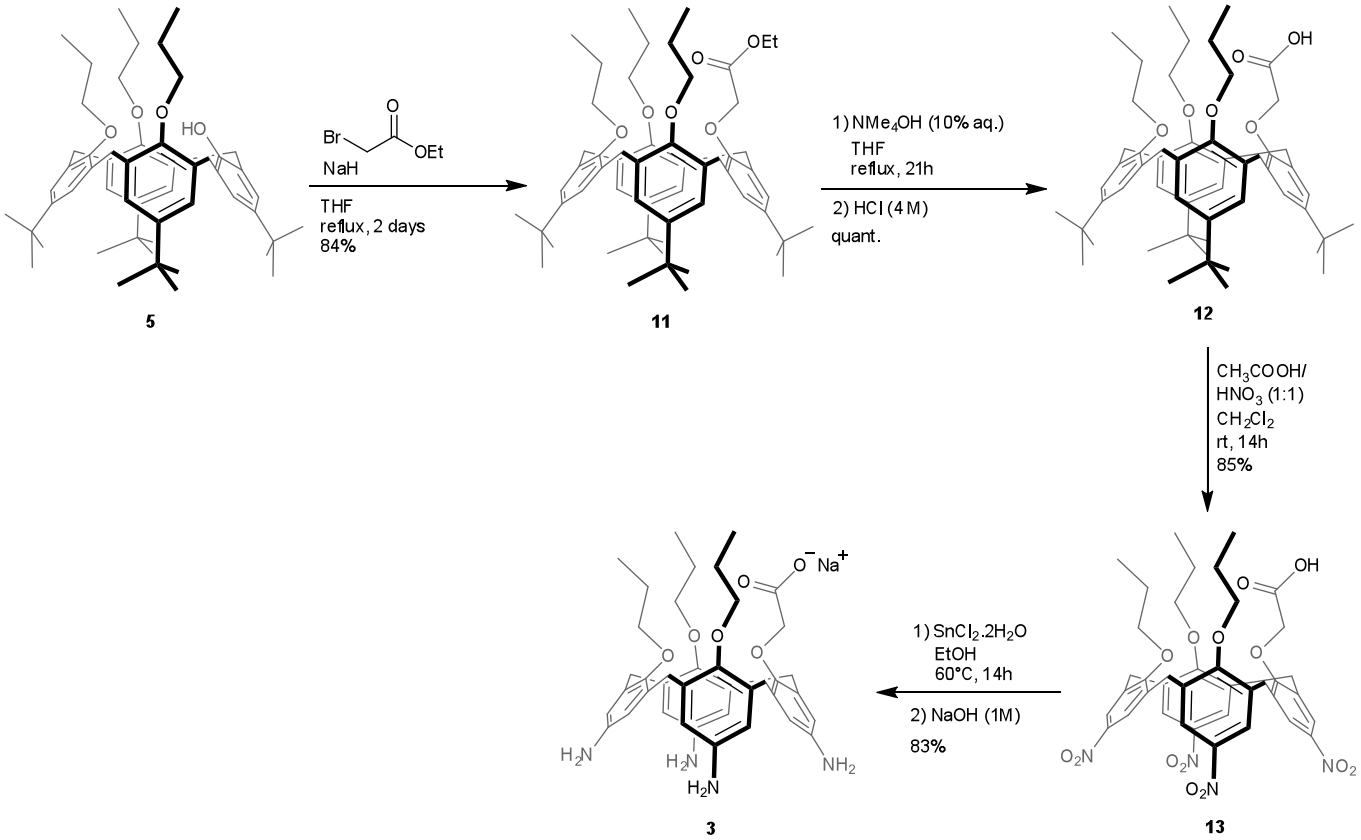
*This value was determined by HMBC analysis.

Compound **10** (0.400 g, 0.38 mmol, 1 equiv.) was suspended in EtOH (20 mL). Hydrazine hydrate (2.00 mL, 41.12 mmol, 107 equiv.) and Pd/C (0.031 g, 0.29 mmol, 0.8 equiv.) were added and the reaction mixture was stirred for 16h at reflux. The reaction mixture was filtered on Celite and the filtrate was concentrated under reduced pressure to yield compound **2** as a yellow solid (0.339 g, 0.37 mmol, 95%).

mp: 138-139°C; $^{1}$H NMR (300 MHz, $CDCl_3$, 298K): δ 2.02-2.11 (mult, 8H, $CH_2CH_2CF_3$), 2.12-2.24 (mult, 8H, $CH_2CH_2CF_3$), 2.97 (d, $^{2}J$ = 13.5 Hz, 4H, $ArCH_{2eq}$), 3.79 (t, $^{3}J$ = 6.9 Hz, 8H, $OCH_2$), 4.17 (d, $^{2}J$ = 13.2 Hz, 4H, $ArCH_{2ax}$), 6.07 (s, 8H, ArH); $^{13}$C NMR (75 MHz, $CDCl_3$, 298K): δ 22.8, 30.6, 31.2, 73.4, 116.1, 127.2* (q, $^{1}J$ = 275 Hz), 135.4, 141.1, 149.2; IR: 3375, 2931, 1614, 1474, 1254, 1155, 1029, 832 $cm^{-1}$; HRMS (*m/z*): $[M+H]^+$ calcd. for $C_{44}H_{48}O_4F_{12}N_4$, 925.3562; found, 925.3586.

*This value was determined by HMBC analysis.

**Synthesis of Compound 3**




It is noteworthy that compound **11** was already obtained according to another synthetic strategy.[63,64]

Compound **5** (0.051 g, 0.066 mmol, 1 equiv.) and NaH (60% in oil, 0.014 g, 0.35 mmol, 5.3 equiv.) were suspended in THF (1 mL) and the mixture was stirred for 15min at room temperature under inert atmosphere. Ethyl bromoacetate (0,080 mL, 0.72 mmol, 11 equiv.) was added and the reaction mixture was stirred for 2 days at reflux under inert atmosphere. EtOH (0.5 mL) was added to stop the reaction and the mixture was concentrated under reduced pressure. The residue was dissolved in $CH_2Cl_2$ and the organic layer was washed with $H_2O$ (3×10 mL). The combined aqueous layers were extracted with $CH_2Cl_2$ (2×15 mL) and the combined organic layers were concentrated under reduced pressure. The residue was washed with

EtOH (2×0.4 mL) to yield compound **11** as a white solid (0.048 g, 0.055 mmol, 84%). The $^{1}$H NMR characterization of compound **11** conforms to the literature. $^{1}$H NMR (400 MHz, $CDCl_3$, 298K): δ 0.98-1.04 (m, 27H, *t*Bu + $CH_2CH_3$), 1.17 (s, 9H, *t*Bu), 1.18 (s, 9H, *t*Bu), 1.30 (t, $^{3}$J = 7.2 Hz, 3H, $COCH_2CH_3$), 1.97 (mult, 4H, $CH_2CH_2CH_3$), 2.10 (mult, 2H, $CH_2CH_2CH_3$), 3.12 (d, ²J = 12.4 Hz, 2H, $ArCH_{2eq}$), 3.17 (d, ²J = 12.8 Hz, 2H, $ArCH_{2eq}$), 3.73-3.85 (m, 6H, $OCH_2CH_2CH_3$), 4.21 (q, $^{3}$J = 7.2 Hz, 2H, $COOCH_2CH_3$), 4.41 (d, ²J = 12.4 Hz, 2H, $ArCH_{2ax}$), 4.66 (d, ²J = 12.8 Hz, 2H, $ArCH_{2ax}$), 4.83 (s, 2H, $OCH_2CO$), 6.66-6.68 (m, 4H, ArH), 6.89 (s, 2H, ArH), 6.90 (s, 2H, ArH). $^{13}$C NMR (75 MHz, $CDCl_3$, 298K): δ 10.5, 10.9, 14.6, 23.7, 23.8, 31.4, 31.7(5), 31.9, 32.0, 34.1, 34.2, 34.3, 60.7, 71.3, 77.2, 125.1, 125.2, 125.5, 125.8, 133.4, 133.6, 134.2, 134.9, 144.5, 144.9, 145.2, 153.7, 153.8, 154.3, 171.1.

Compound **11** (4.872 g, 5.66 mmol, 1 equiv.) was dissolved in THF (250 mL) and an aqueous $NMe_4OH$ solution (10%, 250 mL, 276 mmol, 50 equiv.) was added. The reaction mixture was stirred for 21h at reflux under inert atmosphere. The reaction was stopped by addition of an aqueous HCl solution (4 M, 50 mL) until pH = 1 and the THF was removed under reduced pressure. The precipitate was filtered and washed with $H_2O$ to yield compound **12** as a white solid (4.709 g, 5.65 mmol, quant.).

mp: 249°C; $^{1}$H NMR (400 MHz, $CDCl_3$, 298K): δ 0.83 (s, 18H, *t*Bu), 0.89 (t, $^{3}$J = 7.2 Hz, 3H, $CH_2CH_3$), 0.99 (t, $^{3}$J = 7.2 Hz, 6H, $CH_2CH_3$), 1.32-1.37 (m, 18H, *t*Bu), 1.83-1.97 (m, 6H, $CH_2CH_2CH_3$), 3.16 (d, ²J = 12.8 Hz, 2H, $ArCH_{2eq}$), 3.23 (d, ²J = 13.2 Hz, 2H, $ArCH_{2eq}$), 3.66-3.81 (mult, 4H, $OCH_2CH_2CH_3$), 4.01 (mult, 2H, $OCH_2CH_2CH_3$), 4.23 (d, ²J = 12.8 Hz, 2H, $ArCH_{2ax}$), 4.46 (d, ²J = 12.4 Hz, 2H, $ArCH_{2ax}$), 4.65 (s, 2H, $OCH_2COOH$), 6.49 (d, $^{4}$J = 2.0 Hz, 2H, ArH), 6.60 (d, $^{4}$J = 2.4 Hz, 2H, ArH), 7.14 (s,

2H, ArH), 7.16 (s, 2H, ArH); $^{13}$C NMR (75 MHz, $CDCl_3$, 298K): δ 10.0, 10.5, 22.6, 23.3, 31.1, 31.2, 31.3, 31.7, 31.9, 33.8, 34.2, 34.4, 70.9, 77.8, 78.4, 124.7, 125.3, 125.5, 126.1, 131.7, 132.7, 135.2, 135.6, 145.0, 145.2, 147.2, 151.2, 152.0, 154.3, 170.9; IR: 3428, 2964, 1766, 1478, 1363, 1203, 1008, 871 $cm^{-1}$; HRMS (*m/z*): $[M+H]^+$ calcd. for $C_{55}H_{76}O_6$, 833.5720; found, 833.5731.

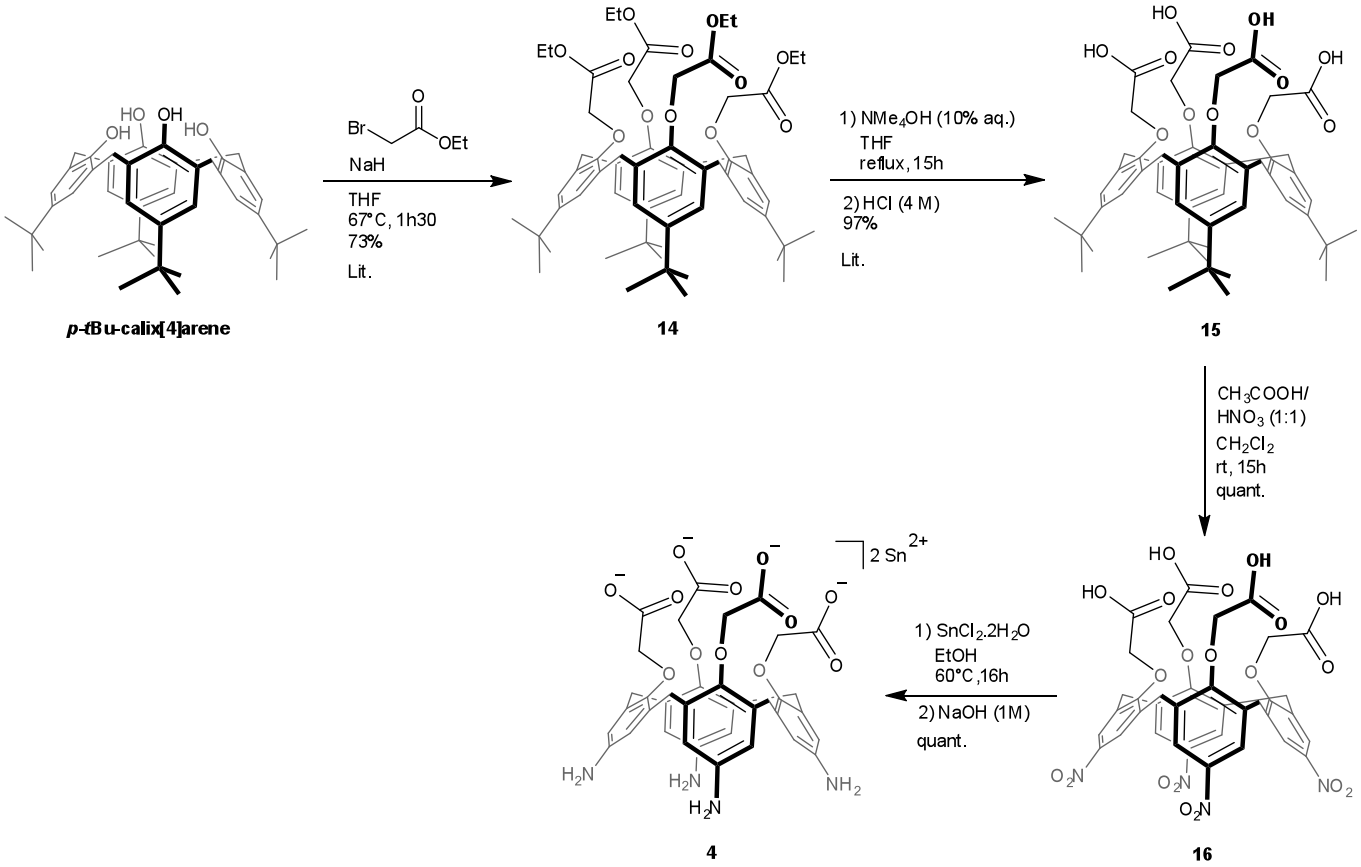
It is noteworthy that compound **13** was already obtained according to another synthetic strategy.[63]

Compound **12** (1.753 g, 2.10 mmol, 1 equiv.) was dissolved in $CH_2Cl_2$ (100 mL). A mixture of glacial $CH_3COOH$/fuming $HNO_3$ (1:1) (18 mL) was added and the reaction mixture was stirred for 14h at room temperature. The reaction mixture was concentrated under reduced pressure and dissolved in $CH_2Cl_2$ (100 mL). The organic layer was washed with $H_2O$ (4×50 mL) and the combined aqueous layers were extracted with $CH_2Cl_2$ (1×100 mL). The combined organic layers were concentrated under reduced pressure. The crude residue was washed with EtOH (2×5 mL) to yield the compound **13** as a yellow solid (1.402 g, 1.78 mmol, 85%). The $^1$H NMR characterization of compound **13** conforms to the literature. $^1$H NMR (400 MHz, $CDCl_3$, 298K): δ 0.94 (t, $^3$J = 7.6 Hz, 3H, $CH_2CH_3$), 1.05 (t, $^3$J = 7.6 Hz, 6H, $CH_2CH_3$), 1.81-1.98 (m, 6H, $CH_2CH_2CH_3$), 3.45 (d, ²J = 13.6 Hz, 2H, $ArCH_{2eq}$), 3.54 (d, ²J = 14.0 Hz, 2H, $ArCH_{2eq}$), 3.90 (t, ³J = 7.2 H, 4H, $OCH_2CH_2CH_3$), 4.05 (t, ³J = 8.0 Hz, 2H, $OCH_2CH_2CH_3$), 4.53-4.60 (m, 4H, $ArCH_{2ax}$), 4.88 (s, 2H, $OCH_2CO$), 7.23-7.26 (m, 4H, ArH), 8.02-8.06 (m, 4H, ArH). $^{13}$C NMR (75 MHz, $CDCl_3$, 298K): δ 10.0, 10.5, 23.3(8), 23.4(2), 31.4, 31.8, 71.3, 79.1, 123.9, 124.2, 125.0, 125.4, 134.2, 135.0, 135.8, 136.6, 143.9, 144.3, 160.2, 162.4, 169.1.

Compound **13** (0.401 g, 0.51 mmol, 1 equiv.) and $SnCl_2.2H_2O$ (2.682 g, 11.92 mmol, 23 equiv.) were suspended in EtOH (20 mL). The reaction mixture was stirred at 60°C for 14h. An aqueous NaOH solution (1 M, 15 mL) was added until pH >10 and the mixture was concentrated under reduced pressure. The crude residue was dissolved in MeOH (5 mL) and the precipitate was filtered. The filtrate was concentrated under reduced pressure to yield compound **3** (0.291 g, 0.42 mmol, 83%).

mp: 258-261°C (dec); $^1$H NMR (400 MHz, $CD_3OD$, 298K): $\delta$ 0.92 (t, $^3$J = 7.6 Hz, 6H, $CH_2\mathit{CH_3}$), 1.08 (t, $^3$J = 7.2 Hz, 3H, $CH_2\mathit{CH_3}$), 1.79-1.98 (mult, 4H, $CH_2\mathit{CH_2}CH_3$), 2.03-2.13 (mult, 2H, $CH_2\mathit{CH_2}CH_3$), 3.16-3.25 (m, $^2$J = 12.4 Hz, 4H, $ArCH_{2eq}$), 3.82-3.89 (mult, 4H, $O\mathit{CH_2}CH_2CH_3$), 3.92-3.98 (m, 2H, $O\mathit{CH_2}CH_2CH_3$), 4.14 (d, $^2$J = 12.4 Hz, 2H, $ArCH_{2ax}$), 4.23 (s, 2H, $O\mathit{CH_2}CO$), 4.27 (d, $^2$J = 12.4 Hz, 2H, $ArCH_{2ax}$), 6.56 (d, $^4$J = 2.4 Hz, 2H, ArH), 6.58 (d, $^4$J = 2.4 Hz, 2H, ArH), 6.59-6.63 (m, 4H, ArH); $^{13}$C NMR (100 MHz, $CD_3OD$, 298K): $\delta$ 10.1, 10.3, 23.8, 24.6, 31.2 (2C), 76.2, 80.4, 80.5, 117.0(9), 117.1(4), 117.2, 117.3, 137.1(5), 137.2(4), 137.5, 137.6, 144.1, 145.2 (2C), 145.7, 146.1, 146.2, 175.9; IR: 3379, 2966, 1610, 1480, 1223, 1001, 839 $cm^{-1}$; HRMS (*m/z*): $[M+Na]^+$ calcd. for $C_{39}H_{48}O_6N_4$, 691.3472; found, 691.3427.

**Synthesis of Compound 4**




Compound **14** was prepared according to a procedure described in the literature.[60,65] *p*-tBu-Calix[4]arene (1.021 g, 1.57 mmol, 1 equiv.) was dissolved in THF (40 mL). NaH (60% in oil, 0.981 g, 24.61 mmol, 16 equiv.) and ethyl bromoacetate (8.5 mL, 0.0768 mol, 49 equiv.) were added and the reaction mixture was stirred for 1h30 at 67°C under inert atmosphere. EtOH (2 mL) was added to the reaction mixture which was concentrated under reduced pressure. The residue was dissolved in $CH_2Cl_2$ (100 mL). The organic layer was washed with $H_2O$ (3×50 mL) and combined aqueous layers were extracted with $CH_2Cl_2$ (2×70 mL). The combined organic layers were concentrated under reduced pressure and the crude residue was washed with EtOH (2×4 mL) to yield compound **14** as a white solid (1.138 g, 1.15 mmol, 73%).

The $^{1}$H NMR characterization of compound **14** conforms to the literature.[66] $^{1}$H NMR (300 MHz, $CDCl_3$, 298K): δ 1.07 (s, 36H, *t*Bu), 1.29 (t, $^{3}J$ = 7.2 Hz, 12H, $CH_2CH_3$), 3.19 (d, $^{2}J$ = 14.3 Hz, 4H, $ArCH_{2eq}$), 4.21 (q, $^{3}J$ = 8.0 Hz, 8H, $OCH_2CH_3$), 4.80 (s, 8H, $OCH_2$), 4.85 (d, $^{2}J$ = 12.9 Hz, 4H, $ArCH_{2ax}$), 6.78 (s, 8H, ArH). $^{13}$C NMR ($CDCl_3$, 298K): δ 14.2, 31.4, 31.9, 33.8, 60.3, 71.3, 125.3, 133.5, 145.1, 153.0, 170.49.

Compound **15** was prepared according to a procedure described in the literature.[67] Compound **14** (0.719 g, 0.72 mmol, 1 equiv.) was dissolved in THF (40 mL). An aqueous $NMe_4OH$ solution (10%, 60 mL, 66.21 mmol, 91 equiv.) was added and the reaction mixture was stirred for 15h at reflux. An aqueous HCl solution (4 M, 7 mL) was added until pH = 1 and the reaction mixture was stirred for 24h at room temperature. THF was concentrated under reduced pressure and the precipitate was filtered. The crude residue was washed with $H_2O$ (3×5 mL) to yield compound **15** as a white solid (0.617 g, 0.70 mmol, 97%). The $^{1}$H NMR characterization of compound **15** conforms to the literature. $^{1}$H NMR (300 MHz, $CDCl_3$/DMSO- $d_6$ (1:1, v/v), 298K): δ 1.03 (s, 36H, *t*Bu), 3.15 (d, $^{2}J$ = 12.9 Hz, 4H, $ArCH_{2eq}$), 4.57 (s, 8H, $OCH_2$), 4.78 (d, $^{2}J$ = 12.9 Hz, 4H, $ArCH_{2ax}$), 6.82 (s, 8H, ArH), 12.0 ($s_b$, 1H, COOH). $^{13}$C NMR (75 MHz, $CDCl_3$/DMSO- $d_6$ (1:1, v/v), 298K): δ 31.2, 31.7, 33.9, 71.3, 124.6, 136.2, 143.0, 161.7, 170.9.

It is noteworthy that compound **16** was already obtained according to another synthetic strategy.[68] Compound **15** (0.565 g, 0.64 mmol, 1 equiv.) was dissolved in $CH_2Cl_2$ (20 mL). A mixture of glacial $CH_3COOH$/fuming $HNO_3$ (1:1) was added at 0°C and the reaction mixture was stirred for 15h at room temperature. The reaction

mixture was concentrated under reduced pressure. The crude residue was washed with $H_2O$ (3×5 mL) to yield compound **16** (0.536 g, 0.64 mmol, quant.).

mp: 255-258°C (dec); $^1$H NMR (300 MHz, DMSO-$d_6$, 298K): δ 3.69 (d, $^2$J = 14.7 Hz, 4H, $ArCH_{2eq}$), 4.77 (s, 8H, $OCH_2$), 4.91 (d, $^2$J = 13.5 Hz, 4H, $ArCH_{2ax}$), 7.67 (s, 8H, ArH), 12.96 ($s_b$, 4H, COOH). $^{13}$C NMR (150 MHz, DMSO-$d_6$, 298K): δ 30.5, 70.9, 123.8, 135.6, 142.3, 161.3, 170.3; IR: 3276, 2962, 1743, 1529, 1350, 1208, 1058 $cm^{-1}$; ESI-MS (*m/z*): $[M+Na]^+$ calcd. for $C_{36}H_{28}N_4O_{20}$, 859.12; found, 859.13.

Compound **16** (0.103 g, 0.12 mmol, 1 equiv.) was suspended in EtOH (5 mL). $SnCl_2.2H_2O$ (0.600 g, 2.66 mmol, 22 equiv.) was added and the reaction mixture was stirred for 16h at 60°C under inert atmosphere. The reaction mixture was poured on $H_2O$ (12 mL) at 0°C and an aqueous NaOH solution (1 M, 10 mL) was added until pH>10. $CH_2Cl_2$ (30 mL) was added and the mixture was stirred for 10 min at 0°C. Then, the organic layer was washed with $H_2O$ (2×10 mL). The combined aqueous layers were concentrated under reduced pressure and MeOH (4×0.3 mL) was added onto the residue. The filtrate was concentrated under reduced pressure to yield compound **4** (0.119 g, 0.13 mmol, quant.).

mp: 277°C (dec); $^1$H NMR (300 MHz, $CD_3OD$, 298K): δ 3.13 (d, $^2$J = 12.0 Hz, 4H, $ArCH_{2eq}$), 4.23 (s, 8H, $OCH_2$), 4.51 (d, $^2$J = 12.0 Hz, 4H, $ArCH_{2ax}$), 6.58 (s, 8H, ArH); $^{13}$C NMR (75 MHz, $CD_3OD$, 298K): δ 31.2*, 77.2*, 117.6, 137.4, 144.6, 147.2, 176.8; IR: 3368, 2940, 1611, 1480, 1225 $cm^{-1}$; HRMS (*m/z*): $[M+H]^+$ calcd. for $C_{36}H_{36}O_{12}N_4$, 717.2408; found, 717.2403.

*These values were determined by HSQC analysis.

**Calculation of surface coverage on gold sample**

Let us consider the simple situation of a full coverage of gold (the main signal of which is $Au_{4f}$) by the calix[4]arenes molecules (detected through their fluorine signal $F_{1s}$). The expressions for the intensity of peaks from the substrate and the calix[4]arenes are given by

calix[4]arenes, $$I_{F1s} \propto \sigma_{F1s} \cdot Ts_{F1s} \cdot \lambda_{F1s} \cdot C_F \cdot \left[1 - exp\left(\frac{-d}{\lambda_{F1s} \cos\theta}\right)\right] \quad \text{S1}$$

Gold substrate, $$I_{Au4f} \propto \sigma_{Au4f} \cdot Ts_{Au4f} \cdot \lambda_{Au4f} \cdot C_{Au} \cdot \left[exp\left(\frac{-d}{\lambda_{Au4f/calix} \cos\theta}\right)\right] \quad \text{S2}$$

where $\sigma_{Au4f}$ and $\sigma_{F1s}$ are the photoionization cross-section for $Au_{4f}$ and $F_{1s}$, respectively; $\lambda_{F1s}$ is the mean free path of the photoelectrons $F_{1s}$ in the calix[4]arene overlayer, $\lambda_{Au4f}$ is the mean free path of the photoelectrons $Au_{4f}$ in the substrate and $\lambda_{Au4f/calix}$ is the mean free path of the photoelectrons $Au_{4f}$ in the calix[4]arenes overlayer; *d* is the calix[4]arene layer thickness estimated from ellipsometry; $\theta$ is the analysis take-off angle relative to the surface normal (here 0 so that $\cos\theta = 1$); and $T_{S(i)}$ are the analyzer transmission functions of the spectrometer for the given kinetic energy. $C_F$ is the number of fluorine atoms per unit volume of calix[4]arenes and $C_{Au}$ is the number of Au atoms per unit volume of gold.

In order to eliminate instrumental factors, one can consider the ratio $F_{1s}/Au_{4f}$:

$$\frac{I_{F1s}}{I_{Au4f}} = \left(\frac{\sigma_{F1s}}{\sigma_{Au4f}}\right) \cdot \left(\frac{Ts_{F1s}}{Ts_{Au4f}}\right) \cdot \left(\frac{\lambda_{F1s}}{\lambda_{Au4f}}\right) \cdot \left(\frac{C_F}{C_{Au}}\right) \cdot \frac{[1 - exp(-d/\lambda_{F1s} \cos\theta)]}{exp\left(-d/\lambda_{Au4f/calix} \cos\theta\right)} \quad \text{S3}$$

It is possible to consider that the layer of calix[4]arenes does not fully cover the gold surface and to introduce a coverage fraction α of the surface by the calix[4]arene overlayer: in this case, one has to consider a coated substrate with a fraction α and free sites with a fraction of 1 − α.

A similar equation has successfully been employed by Chehimi and coworkers[69] to estimate the coverage fraction of a surface by the protein BSA.

The peak intensities are now given by:

Calix[4]arene, $$I_{F1s} \propto \sigma_{F1s} \cdot Ts_{F1s} \cdot \lambda_{F1s} \cdot C_F \cdot \left[1 - exp\left(\frac{-d}{\lambda_{F1s} \cos\theta}\right)\right] \times \alpha \quad \text{S4}$$

Gold substrate,

$$I_{Au4f} \propto \sigma_{Au4f} \cdot Ts_{Au4f} \cdot \lambda_{Au4f} \cdot C_{Au} \cdot \left[exp\left(\frac{-d}{\lambda_{Au4f/calix} \cos\theta}\right)\right] \times \alpha + \sigma_{Au4f} \cdot Ts_{Au4f} \cdot \lambda_{Au4f} \cdot C_{Au} \times (1-\alpha) \quad \text{S5}$$

Finally, the peak intensity ratio $F_{1s}/Au_{4f}$ is now given by:

$$\frac{I_{F1s}}{I_{Au4f}} = \left(\frac{\sigma_{F1s}}{\sigma_{Au4f}}\right) \cdot \left(\frac{Ts_{F1s}}{Ts_{Au4f}}\right) \cdot \left(\frac{\lambda_{F1s}}{\lambda_{Au4f}}\right) \cdot \left(\frac{C_F}{C_{Au}}\right) \cdot \frac{[1 - exp(-d/\lambda_{F1s} \cos\theta)] \times \alpha}{exp(-d/\lambda_{Au4f/calix} \cos\theta) \times \alpha + (1-\alpha)} \quad \text{S6}$$

from which it is possible to extract the value of α. The calculations were made using d=1.1 nm for the calix[4]arenes overlayer thickness, as estimated from ellipsometry, 17.2 for $\sigma_{Au4f}$ and 4.43 for $\sigma_{F1s}$ corresponding to the Scofield coefficients and $C_{Au}$ = 0.098 mol.cm$^{-3}$ for the number of Au atoms per unit volume of gold substrate. $C_F$ was calculated by dividing the density of calix[4]arenes ($\rho_{calix}$) by their molar mass ($M_{calix}$) and considering 12 fluorine atoms per molecule:

$$C_F = (\rho_{calix}/M_{calix}) \times 12 = 0.011 \text{ mol.cm}^{-3} \quad \text{S7}$$

The value of the mean free path in the uncoated gold substrate was obtained from the QUASES-IMPF-TPP2M software, developed by Sven Tougard[70] based on the Tanuma Powell and Penn algorithm (TPP2M). $\lambda_{Au4f}$ was found equal to 15.78 Á. The values of the mean free paths in the organic coating, $\lambda_{F1s}$ and $\lambda_{Au4f/calix}$ can be computed using the Dench and Seah equation[71]:

$$\lambda_i \approx 0.11 (E_K)^{0.5} \text{ in mg.m}^{-2} \quad \text{S8}$$

where $E_K$ is the kinetic energy of the ejected core–hole electron.

To convert λ into nanometer units, one has to divide λ in mg.m$^{-2}$ by the density of the calix[4]arene overlayers, assumed here to be equal to 0.8446 g.cm$^{-3}$. For Au4f7/2, $\lambda_{Au4f/calix}$ is calculated to be 4.88 nm while for F1s, $\lambda_{F1s}$ is equal to 3.68 nm.

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