Supplementary Material (ESI) for Dalton Transactions

Crystallization of (012) Oriented Calcite Single Crystals Underneath Monolayers of Tetra(carboxymethoxy)calix[4]arenes

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Synthesis

Melting points were determined with a Electrothermal melting point apparatus and were uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX 500 spectrometer in $CDCl_3$ at room temperature (unless stated otherwise) with residual solvent.
Mass spectra were recorded with a Micromass VG Autospec X, Voyager DE spectrometer. Elemental analysis were carried out with a Perkin-Elmer 240 elemental analyzer. All reagents were reagent grade and used without further purification.

5,11,17,23-Tetrakis-(1,1,3,3-tetramethylbutyl)-25,26,27,28-tetrahydroxycalix[4]arene:
was prepared in 34 % yield by analogy to the standard procedure of the *t*-butylcalix[4]arene:[1] m.p. 249-251ºC (Toluol); ^{1}H NMR (500 MHz, 25ºC, TMS: δ = 9.97 (s, 4 H, OH), 7.18-7.16 (m, 5 H, Tol), 6.99 (s, 8 H, ArH), 4.23 (s, 4 H, Ar-CH_2), 3.46 (s, 4 H, ArCH_2), 2.36 (s, 3 H, TolCH_3), 1.57 (s, 8 H, CCH_2C), 1.23 (s, 24 H, CH_3), 0.54 (s, 36 H, CH_3). ^{13}C NMR (125 MHz) δ = 146.28 (ArCO), 143.05 (ArC*t*Oc), 129.04, 128.23, 127.61 (Ar*C*CH_2) , 126.39 (ArCH), 125.30, 57.26 (*C*$H_2C(CH_3)_3$), 37.79 (*C*$(CH_3)_2$), 32.35 (*C*$(CH_3)_3$), 32.29 ((*C*$H_3)_2C$), 31.66 ((*C*$H_3)_3C$), 31.32 (CH_2Ar), 21.47.
MS (DCI, isobutane): *m*/*z* (%) 872.4 (95) $[M]^+$, 801.5 (100); elemental analysis calcd for $C_{60}H_{88}O_4 \cdot C_7H_8$: C 83.35; H 10.02; found: C 83.51, H 9.92.

5,11,17,23-Tetrakis-(1,1,3,3-tetramethylbutyl)-25,26,27,28-tetra(ethoxycarbonyl-methoxy)calix[4]arene:
The product was prepared according to a slightly modified procedure. [2] To a well-stirred suspension of 5,11,17,23-Tetrakis-(1,1,3,3-tetramethylbutyl)-25,26,27,28-tetrahydroxycalix[4]arene (14.29 g, 14.8 mmol) in anhydrous acetone (400 mL) was added ethyl bromoacetate (30 mL, 270 mmol) and potassium carbonate (34.5 g, 250 mmol). The mixture was refluxed for 4 d under an argon stream. After filtration, the filtrate was extracted with dichloromethane (3 × 50 mL). The combined organic layers were concentrated in vacuo and the residue was diluted in dichloromethane (300 mL). The solution was washed with hydrochloric acid (50 mL, 1 N) and water (3 × 100 mL). After drying over sodium sulfate, the organic layer was concentrated in vacuo. Subsequently the crude product was recrystallized from ethanol to give the desired product in 73 % yield: m.p. 143 – 145ºC; ^{1}H NMR (500 MHz, 25ºC, TMS: δ = 6.74 (s, 8 H, ArH), 4.82 (s, 4 H, Ar-CH_2), 4.79 (s, 8 H, OCH_2COO), 4.19 (quart, J = 7.1 Hz, 8 H, OCH_2CH_3), 3.17 (d, ^{3}J = 13.0 Hz, 4 H, Ar-CH_2), 1.53 (s, 8 H, CCH_2C), 1.27 (t, ^{3}J = 7.1 Hz, 12 H,OCH_2CH_3), 1.09 (s, 24 H, CH_3), 0.69 (s, 36 H, CH_3).
^{13}C-NMR (125 MHz) δ = 170.51 (COO), 153.05 (ArCO), 144.34 (ArC*t*Oc), 133.05 (Ar*C*CH_2), 126.14 (ArCH), 71.42 (OCH_2), 60.27(OCH_2CH_3), 57.19 (*C*$H_2C(CH_3)_3$), 37.79 (*C*$(CH_3)_2$), 32.30 (*C*$(CH_3)_3$), 32.17 (C(*C*$H_3)_2$), 31.78 (C(*C*$H_3)_3$), 31.18 (CH_2Ar), 14.18 (CH_3).

[1] C. D. Gutsche, B. Dhawan, K. H. No, R. Muthukrishnan, *J. Am. Chem. Soc.* **1981**, *103*, 3782–3792.
[2] F. Arnaud-Neu, E. M. Collins, M. Deasy, G. Ferguson, S. J. Harris, B. Kaitner, A. J. Lough, M. A. McKervey, E. Marques, B. L. Ruhl, M. J. Schwing Weill, E. M. Seward, *J. Am. Chem. Soc.* **1989**, *111*, 8681–8691.

MS (DCI; ammonia): *m/z* (%) 1234.9 (100) $[M + NH_4]^+$; elemental analysis calcd. for $C_{76}H_{112}O_{12}$: C 74.96, H 9.27; found: C 74.96, H 9.08.

5,11,17,23-Tetrakis-(1,1,3,3-tetramethylbutyl)-25,26,27,28-tetra(carboxymethoxy)-calix[4]arene (1):

The product was prepared according to a slightly modified procedure.[3] To a solution of 5,11,17,23-tetrakis-(1,1,3,3-tetramethylbutyl)-25,26,27,28-tetra(ethoxy-carbonylmethoxy)calix[4]arene (1.72 g, 1.41 mmol) in tetrahydrofuran (70 mL) was added an aqueous solution of tetramethylammonium hydroxide (25 %, 36 mL, 100 mmol). After 24 h under reflux the suspension was concentrated under reduced pressure, the residue was dissolved in a 1:1 mixture of chloroform/water, washed with hydrochloric acid (2 × 30 mL) and water (3 × 30 mL). The organic layer was concentrated in vacuo and the crude product was recrystallized from acetonitrile (80 mL) to yield the final product in 86 % yield: m.p. 251-252ºC (CH_3CN); ^{1}H NMR (500 MHz, 50ºC, TMS: δ = 6.90 (s, 8H, ArH), 4.59 (br s, 12 H ($ArCH_2$, CH_2COO), 3.25 (d, ^2J = 7.1 Hz, 4 H, $ArCH_2$), 1.96 (s, 3 H, CH_3CN), 1.55 (s, 8 H, CCH_2C), 1.14 (s, 24 H, CH_3), 0.66 (s, 36 H, CH_3).

^{13}C-NMR (125 MHz) δ = 145.91 (ArCO), 132.99 (ArC*t*Oc), 126.53 (ArCH, Ar*C*CH_2), 72.62 (O*C*H_2), 57.23(*C*$H_2C(CH_3)_3$), 37.98 (*C*$(CH_3)_2$), 32.34 (*C*$(CH_3)_3$), 31.64 (C(*C*$H_3)_2$), 31.05(C(*C*$H_3)_3$), 30.66 (CH_2Ar), 1,91 (*C*H_3CN).

MALDI-MS (matrix 2,5-dihydroxybenzoic acid): *m/z* 1127 $[M + Na]^+$, 1141 $[M + K]^+$; elemental analysis calcd for $C_{76}H_{112}O_{12} \cdot CH_3CN$: C 73.33, H 8.70, N 1.22; found: C 73.67, H 9.05, N 1.11.

Calcium complex of 5,11,17,23-Tetrakis-(1,1,3,3-tetramethylbutyl)-25,26,27,28-tetra(carboxymethoxy)calix[4]arene (2):

5,11,17,23-Tetrakis-(1,1,3,3-tetramethylbutyl)-25,26,27,28-tetra(carboxymethoxy)calix[4]arene (55 mg, 0.05 mmol) was suspended with calcium hydroxide (7.4 mg, 0.1 mmol) in H_2O (5 mL). The suspension was treated ultrasonically and centrifuged. The pellet was suspended in H_2O (5 mL), treated ultrasonically and was centrifuged. The wet residue was dissolved in DMSO (5 mL) and crystallized at 98ºC. Colourless crystals were obtained after 3 days.

^{1}H NMR (500 MHz, 50ºC, TMS): δ = 7.07 (d, *J* = 19.1 Hz, 8 H, ArH), 4.27, 3.35 (dd, ^2J = 12.3 Hz, 8 H, $ArCH_2$), 5.10, 3.96 (dd, ^2J = 14.3 Hz, 8 H, CH_2COO), 1.52 (s, 8 H, CCH_2C), 1.21 (s, 24 H, CH_3), 0.48 (s, 36 H, CH_3).

^{13}C-NMR (125 MHz) δ = 175.50 (COO), 150.12 (ArCO), 147.41(ArC*t*Oc), 134.45 (Ar*C*CH_2), 126.72 (ArCH), 77.87 (O*C*H_2), 57.23 (*C*$H_2C(CH_3)_3$), 40.97 (*C*SO), 38.05 (*C*$(CH_3)_2$), 32.31 (*C*$(CH_3)_3$), 31.47 (C(*C*$H_3)_2$), 31.07 (C(*C*$H_3)_3$), 30.72 (CH_2Ar).

Elemental analysis calcd. for [Ca ($C_{68}H_{92}O_{12}Ca$) $(DMSO)_2$ (H_2O)] · $(DMSO)_{2.5}$: C 60.33, H 7.90; found: C 58.72, H 7.94.

[3] K. Ohto, M. Yano, K. Inoue, T. Yamamoto, M. Goto, F. Nakashio, S. Shinkai, T. Nagasaki, *Anal. Sci*. **1995**, *11*, 893–902.