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Supplementary Information

1. General.

All solvents and reagents were used as purchased. Ethynylaryls were purchased from ALDRICH and used without further purification, *p*-nitrophenylaceylene was prepared according to the literature.[1] Thin layer chromatography was performed on Alugram Sil G/UV254-coated aluminum sheets (Macherey-Nagel) with UV-detection at 254/365 nm. Melting points were determined on a Gallenkamp melting point apparatus and are uncorrected. NMR spectra were recorded on a Bruker AC-200 (^{1}H) and Bruker AC-300 (^{13}C) spectrometers in deuterated chloroform (deuteration grade> 99.80%) with the solvent signal serving as internal standard. Mass spectra were recorded on a HP1100MSD spectrometer. Elemental analyses were performed on a LECO CHNS 932 micro-analyzer. Spectroscopic measurements were performed using HPLC-quality solvents, and are solvent corrected. UV-Vis spectra were measured on a HP 8453 (Hewlett Packard) spectrophotometer. A Perkin Elmer LS50B luminescence spectrometer was employed for the fluorescence studies, in a four-sided quartz cell at room temperature in a right angle geometry and are corrected for the spectral response for the detection system. Quantum yields were determined using quinine sulfate in 0.1 N H_2SO_4 as standard.[2]

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2. Materials.

General procedure for the synthesis of **2**, **3**, and **4**. 5,11,17,23-Tertraiodo-25,26,27,28-tetra-(*n*-propoxy)calix[4]arene **1**[3] (275 mg, 0.25 mmol) was stirred together with $Pd(PPh_3)_2Cl_2$ (70 mg, 0.10 mmol) and CuI (19 mg, 0.10 mmol) in degased diisopropylamine (15 mL) for 30 min at room temperature before the acetylene compound (1.5 mmol) was added. The mixture was heated at 80 ºC for 48 h. The solvent was removed, the remaining residue was suspended in water (50 mL) and extracted with EtOAc (3 x 20 mL). The combined organic layers were dried ($MgSO_4$) and concentrated in vacuum. The resulting crude product was purified as described below.

5,11,17,23-Tetrakis-[(4-nitrophenyl)ethynyl]-25,26,27,28-tetra-(*n*-propoxy)-calix[4]arene (**2**). Column chromatography (CH_2Cl_2-MeOH 20:1) and final recrystallization from acetonitrile gave pure **2** as bright yellow powder. Yield: 182 mg; 62%; m.p.: 245 - 48 ºC. ^{1}H NMR: δ = 8.01 (pseudo d, *J* = 8.8 Hz, 8 H), 7.49 (pseudo d, *J* = 8.8 Hz, 8 H), 6.98 (s, 8 H), 4.76 (d, *J* = 13.9 Hz, 4 H), 3.92 (t, *J* = 7.3 Hz, 8 H), 3.22 (d, *J* = 13.9 Hz, 4 H), 1.96 (m, *J* = 8.0 Hz, 8 H), 1.02 (t, *J* = 8.0 Hz, 12 H); ^{13}C NMR: δ =157.9, 146.5, 135.1, 132.2, 131.8, 130.3, 123.3, 115.8, 95.4, 86.7, 77.2, 30.8 (Ar-*C*H_2-Ar: cone-conformation), 23.2, 10.2; MALDI-MS m/z: 1173 $[M+H]^+$. Calculated for $[C_{72}H_{60}N_4O_{12} + H_2O]$: C, 72.59; H, 5.25; N, 4.70%. Found: C, 72.94, H, 5.15; N, 4.85%.

5,11,17,23-Tetrakis-[(phenyl)ethynyl]-25,26,27,28-tetra-(*n*-propoxy)-calix[4]arene (**3**). Column chromatography (hex-EtOAc 10:1) and final recrystallization from *i*-PrOH-acetone (4 : 1) gave pure **3** as pale orange powder. Yield: 190 mg; 76%; m.p.: 264 - 67 ºC. ^{1}H NMR: δ = 7.43 – 7.15 (m, 20 H), 6.98 (s, 8 H), 4.45 (d, *J* = 13.2 Hz, 4 H), 3.90 (t, *J* = 7.3 Hz, 8 H), 3.19 (d, *J* = 13.2 Hz, 4 H), 1.95 (m, *J* = 6.6 Hz, 8 H), 1.01 (t, *J* = 6.6 Hz, 12 H); ^{13}C NMR: δ =156.8, 134.7, 131.9, 131.5, 128.0, 127.5, 123.7, 117.1, 89.8, 88.1, 77.0, 30.8 (Ar-*C*H_2-Ar: cone-conformation), 23.2, 10.3; MALDI-MS m/z: 1015 $[M+Na]^+$. Calculated for $[C_{72}H_{64}O_4 + H_2O]$: C, 85.51; H, 6.58%; Found: C, 85.31, H, 6.43%.

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5,11,17,23-Tetrakis-[(trimethylsilyl)ethynyl]-25,26,27,28-tetra-(*n*-propoxy)-calix[4]arene (**4**). Column chromatography (hex-EtOAc 10:1) and final recrystallization from EtOH gave pure **3** as colorless powder. Yield: 165 mg; 67%; m.p.: 148 - 51 ºC. ^{1}H NMR: δ = 6.94 (s, 8 H), 4.35 (d, *J* = 12.9 Hz, 4 H), 3.83 (t, *J* = 7.6 Hz, 8 H), 3.10 (d, *J* = 12.9 Hz, 4 H), 1.91 (m, *J* = 7.6 Hz, 8 H), 0.96 (t, *J* = 7.6 Hz, 12 H), 0.24 (s, 36 H); ^{13}C NMR: δ =156.8, 134.2, 132.4, 116.9, 105.5, 92.7, 77.0, 30.7 (Ar-*C*H_2-Ar: cone-conformation), 23.0, 10.2, 0.1; MALDI-MS m/z: 977 $[M+H]^+$. Calculated for [$C_{60}H_{80}Si_4O_4$ + 3 x H_2O]: C, 69.85; H, 8.40%. Found: C, 69.31, H, 8.01%.

5,11,17,23-Tetraethynyl-25,26,27,28-tetra-(*n*-propoxy)calix[4]arene (**5**). Compound **4** (200 mg, 0.2 mmol) was stirred in methanol (10 mL) with aqueous potassium carbonate (166 mg, 1.2 mmol) at room temperature for 18 h. After the removal of the organic solvent, CH_2Cl_2-extraction (3 x 10 mL), drying of the combined organic phases ($MgSO_4$), and final removal of the solvent in vacuo, pure **5** was obtained upon trituration of the remaining solid with boiling EtOH as pale yellow solid. Yield: 106 mg; 77%; m.p.: >300 ºC. ^{1}H NMR: δ = 6.83 (s, 8 H), 4.37 (d, *J* = 12.9 Hz, 4 H), 3.84 (t, *J* = 7.6 Hz, 8 H), 3.11 (d, *J* = 12.9 Hz, 4 H), 2.89 (s, 4 H), 1.89 (m, *J* = 7.0 Hz, 8 H), 0.98 (t, *J* = 7.0 Hz, 12 H); ^{13}C NMR: δ = 157.1, 134.7, 132.2, 115.9, 83.9, 76.9, 75.8, 30.6 (Ar-*C*H_2-Ar: cone-conformation), 23.1, 10.2; MALDI-MS m/z: 689 $[M+H]^+$. Calculated for [$C_{48}H_{48}O_4$ + H_2O]: C, 81.55; H, 7.13; %. Found: C, 81.83, H, 7.18%.

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3. Absorption data

of **2**, **3**, and **7**[4] in CH_2Cl_2, c = 1.0 μmolL^{-1}; **2**: λ_{max} = 351 nm, ε = 77810; **3**: λ_{max} = 289 nm, ε = 46900; **7**: λ_{max} = 360 nm, ε = 27200.

4. References

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