Materials and Methods:

Compounds $\textbf{1}$, $\textbf{9}$, $\textbf{10}$, and $\textbf{11}$ were synthesized according to literature procedures, compound $\textbf{8}$ was obtained from commercial source. All compounds were characterized by $^1$H NMR and MS, compounds $\textbf{4}$ – $\textbf{7}$ additionally by HR-MS. Solvents were purified and dried according to standard procedures. Column chromatography was performed with silica gel 60 (0.035 - 0.070 mm); HPLC on SiO$_2$ columns, normal phase (NP); PTLC on 20 x 20 cm plates, height 1 mm, silica gel 60 (0.035 - 0.070 mm). NMR spectra were recorded on 400 MHz and 600 MHz spectrometer. Mass Spectra were performed on a Finnigan MAT MS 8200 or on a Bruker microTOF$_{\text{LC}}$. For UV/Vis absorption and fluorescence experiments spectroscopy grade solvents were used. UV/Vis absorption spectra were taken on a conventional UV/Vis spectrophotometer. Fluorescence emission and excitation spectra were recorded on a PTI QM4-2003 fluorescence spectrometer and are corrected against photomultiplier and lamp intensity. A long wavelength range emission corrected photomultiplier R928 was used. Fluorescence quantum yields were determined in CH$_2$Cl$_2$ vs. $N,N'-(2,6$-diisopropylphenyl)-1,6,7,12-tetraphenoxyperylene-3,4:9,10-tetracarboxylic acid bisimide ($\Phi_\text{fl} = 0.96$ in CHCl$_3$) or Nile blue perchlorate ($\Phi_\text{fl} = 0.27$ in Ethanol) as reference. The given quantum yields are averaged from values measured at three different excitation wavelengths with OD 0.02 – 0.05 in the absorption maximum (standard deviation $\sigma = 1$-3%). Fluorescence lifetimes were measured with a PTI LaserStrobe fluorescence lifetime spectrometer system containing a PTI GL-3300 nitrogen laser (337.1 nm, pulse width 600 ps, pulse energy 1.45 mJ) coupled with a dye laser PTI GL302 (pulse width 500 ps, pulse energy 220 µJ at 550 nm) as an excitation source and stroboscopic detection. Laser output was tuned within the emission curves of the laser dyes supplied by the manufacturer (PLD 421, 500, 579, 665, 735). Details of the Laser Strobe systems are described on the manufacturer’s web site, http://www.pti-nj.com and in the literature. The instrument response function was collected by scattering the exciting light of a dilute, aqueous suspension of Silica (LUDOX). Decay curves were evaluated using the software supplied with the instrument applying least square regression analysis. The quality of the fit was evaluated by analysis of $\chi^2$, DW-factor and Z-value and by inspection of residuals and autocorrelation function. The experiments were performed at room temperature. No attempt was made to remove O$_2$ from the samples.
Synthesis of Compounds 2, 3, 12.

Scheme S1. a) Et$_3$N, toluene, reflux, yield 10 %; b) CF$_3$COOH, CH$_2$Cl$_2$, rt; c) Zn(OAc)$_2$, quinoline, 150 °C, yield 17 % over two steps; d) Zn(OAc)$_2$, quinoline, 165 °C, yield 18 %.

Characterisation of compounds 2-7, 12.

Compound 12:

Under an argon atmosphere 90 mg (0.124 mmol, 3 equiv.) of compound 1, 41 mg (0.042 mmol, 1 equiv.) of compound 9 and 2-3 drops of triethylamine in toluene (0.5 mL) were heated to 65 °C for 20 h. The solvent was evaporated, the remaining crude product precipitated from CH$_2$Cl$_2$/methanol and the resulting solid purified by column chromatography with CH$_2$Cl$_2$/hexane 70:30 and precipitated from CH$_2$Cl$_2$/methanol. Compound 12 was obtained as a red powder (10 mg, 4.17 x 10$^{-3}$ mmol, yield 10 %). C$_{154}$H$_{168}$N$_4$O$_{20}$ (2395.00). Mp > 400 °C (dec.). TLC CH$_2$Cl$_2$/hexane 80:20; R$_f$ = 0.2. $^1$H NMR (400 MHz, CDCl$_3$, 25 °C): δ (ppm) = 8.31 (bs, 4H; Per-H); 7.24 (d, $^3$J = 8.7 Hz, 8H; Phen-H); 7.03 (s, 4H; Ar-H); 6.96 (s, 4H; Ar-H); 6.88 (d, $^3$J = 8.7 Hz, 8H; Phen-H); 6.43 (bs, 2H; Boc-N-H); 6.27 (t, 4H, $^3$J = 7.5 Hz; Ar-H); 6.20 (br dd, $^3$J = 7.6 Hz, 4H; Ar-H); 6.18 (br dd, $^3$J = 7.8 Hz, 4H; Ar-H); 4.44 and 3.11 (AX, each 4H, $^2$J = 13.4 Hz; Ar-C$_2$H$_2$-Ar); 4.39 and 3.09 (AX, each 4H, $^2$J = 13.6 Hz; Ar-C$_2$H$_2$-Ar); 4.03 and 3.93 (each t, 8H, each $^3$J = 8.2 Hz; O-C$_2$H$_4$); 3.66 (m, 8H; O-C$_2$H$_4$); 1.96-1.79 (m, 16H; Propyl-H); 1.51 (s, 18H; Boc-tert-Butyl); 1.28 (s, 36H, tert-Butyl-Phen); 1.06 (t, 12H, $^3$J = 7.4 Hz; Propyl-H); 0.86 and 0.85 (each t, 12H, each $^3$J = 7.4 Hz; Propyl-H). $^{13}$C NMR (150 MHz,
CDCl₃, 25 °C): δ (ppm) = 163.9, 158.1, 156.3, 155.4, 147.5, 137.7, 137.4, 133.3, 133.1, 133.0, 132.1, 128.7 (br), 128.6, 128.5, 128.4 (br), 128.3 (br), 127.7 (br), 127.6 (br), 126.8, 122.7 (br), 122.6 (br), 119.9, 119.6, 119.5 (br), 80.2, 77.4, 77.0, 34.5, 31.6, 31.2 (br), 23.6, 23.0, 10.0, 9.9. MS (FAB in Nitrobenzyl alcohol): calcd for C₁₅₄H₁₆₉N₄O₂₀ (m/z) 2394.23 [M+H]⁺ and C₁₅₄H₁₆₈N₄O₂₀Na (m/z) 2417.22 [M+Na]⁺; found 2394.2; 2417.4. Analysis: calcd (%) for C₁₅₄H₁₆₈N₄O₂₀ (2395.00): C 77.23; H 7.07; N 2.34; found: C 77.22; H 7.07; N 2.34.

UV/Vis (CH₂Cl₂): λ (nm) [ε (M⁻¹cm⁻¹)] = 581 [48500].

Fluorescence (CH₂Cl₂): λ (nm) = 612; Φₚ = 0.69.

Compound 2:

To a solution of 146 mg (6.09 x 10⁻² mmol) of compound 12 in 2 mL dry CH₂Cl₂ were added 3 mL of CF₃COOH under an argon atmosphere. The mixture was stirred for 1 h at room temperature, poured into ice water and adjusted to pH > 9 with NH₃ solution (25 %). CH₂Cl₂ (50 mL) was added to the mixture, and the resulting organic phase washed with water and brine and dried over Na₂SO₄. The solvent was evaporated and the resulting crude product dried and used without further purification.

A portion of 100 mg (4.56 x 10⁻² mmol, 1 equiv.) of the obtained crude product, 24 mg (3.95 x 10⁻² mmol, 0.9 equiv.) of compound 10 and 16 mg (8.77 x 10⁻² mmol, 2 equiv.) of Zn(OAc)₂ (H₂O-free) were heated in 0.7 mL distilled quinoline at 160 °C for 5 h under an argon atmosphere. The cooled reaction mixture was poured into 10 mL of 2N HCl and stirred for 30 minutes. To the solution 50 mL of CH₂Cl₂ were added and the organic phase was washed with water and brine and dried over MgSO₄. The crude product was purified by column chromatography with CH₂Cl₂/ethylacetate 99:1 and by PTLC with CH₂Cl₂/ethylacetate 99:1. Compound 2 was obtained as a dark-blue powder that shows low stability at air (28 mg, 1.01 x 10⁻² mmol, yield 17% over two steps). C₁₈₂H₁₈₃N₇O₂₀ (2788.44). Mp > 400 °C. TLC: CH₂Cl₂/ethylacetate 98:2; Rf = 0.91. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ (ppm) = 8.60 (bs, 1H; Per-H); 8.53 – 8.50 (m, 2H, Per-H); 8.44 (d, 1H, 3J = 8.2 Hz; Per-H); 8.30 (bs, 4H, Per-H), 7.78 and 7.76 (two d, 2H, 3J = 7.5 Hz; Per-H); 7.24 – 7.23 (m, 8H; Phen-H); 7.10 and 7.05 and 6.98 (each s, 6H; Ar-H); 6.89 – 6.87 (m, 8H; Phen-H); 6.45 (s, 2H; Ar-H); 6.35 (t, 2H, 3J = 7.6 Hz; Ar-H); 6.30 – 6.15 (m, 10H; Ar-H); 5.11 – 5.05 (tt, 3J₁ = 11.9 Hz, 3J₁ = 3.5 Hz, 1H; Cy-H); 4.50 and 3.17 (AX, 4H, 2J = 13.6 Hz; Ar-CH₂-Ar); 4.48 and 3.14 (AX, 4H, 2J = 12.6 Hz; Ar-CH₂-Ar); 4.45 and 3.11 (AX, 4H, 2J = 12.8 Hz; Ar-CH₂-Ar); 4.36 and 3.00 (AX, 4H, 2J = 13.0 Hz; Ar-CH₂-Ar); 4.13 – 4.02 (m, 6H; O-C₂H₂); 3.89 (t, 2H, 3J = 8.3 Hz; O-C₂H₂); 3.79 (bs, 4H; Pyrr-H); 3.66 – 3.63 (m, 8H; O-C₂H₂); 3.44 (bs, 2H; NH₂); 2.88 (bs, 4H; Pyrr-H); 2.65 – 2.57 (m, 2H; Cy-H); 2.11 – 1.76 (m, 29H; Pyrr-H, Propyl-H, Cy-H); 1.47 – 1.37 (m, 3H; Cy-H); 1.29 and 1.28 (each s, 36H; tert-Butyl-Phen); 1.09 and 1.06 (each t, 12H, each 3J = 7.4 Hz; Propyl-H); 0.90 – 0.84 (m, 12H; Propyl-H). MS (MALDI in Dithranol): calcd for C₁₈₂H₁₈₄N₇O₂₀ (m/z) 2787.36 [M+H]⁺ and C₁₈₂H₁₈₃N₇O₂₀Na (m/z) 2809.34 [M+Na]⁺ and C₁₈₂H₁₈₃N₇O₂₀K (m/z) 2825.31 [M+K]⁺; found 2787; 2809; 2825. UV/Vis (CH₂Cl₂): λ (nm) [ε (M⁻¹cm⁻¹)] = 700 [41900], 580 [52000], 435 [29500].
**Compound 3:**

A suspension of 35 mg (1.26 x 10^{-2} mmol, 2 equiv.) of compound 2, 2.5 mg (6.28 x 10^{-3} mmol, 1 equiv.) of compound 8 and 4.5 mg (2.51 x 10^{-2} mmol, 4 equiv.) of Zn(OAc)2 (H2O-free) was heated in 0.3 mL distilled quinoline at 160°C for 7 h under an argon atmosphere. The cooled reaction mixture was poured into 10 mL of 1N HCl and stirred for 30 minutes. The resulting precipitate was filtered and dissolved in CH2Cl2. The solution was washed with water and brine and dried over MgSO4. The crude product was purified first by column chromatography with CH2Cl2/ethylacetate 99:1 and successively by preparative TLC with CH2Cl2/ethylacetate 98:2 and HPLC with CH2Cl2 (SiO2, NP). Compound 3 was obtained as a dark-brown powder (7 mg, 1.18 x 10^{-3} mmol, 19 %). C_{388}H_{370}N_{14}O_{44} (5933.16). Mp > 450 °C. TLC: CH2Cl2/ethylacetate 98:2; R_f = 0.65. 1H NMR (400 MHz, CDCl3, 25 °C): δ (ppm) = 8.82 and 8.74 (each bd, 8H, J = 7.8 Hz and 8.0 Hz; Per-H); 8.60 (s, 2H; Per-H); 8.53 – 8.50 (m, 4H, Per-H); 8.44 and 8.34 (each d, 8H, J = 8.3 Hz; Phen-H); 8.26 and 8.24 (d, 8H, J = 8.3 Hz; Phen-H); 7.80 and 7.78 (two d, 4H, J = 8.1 Hz; Per-H); 7.26 and 7.24 (two d, J = 8.3 Hz; 16H; Phen-H); 7.14 and 7.11 (each s, 8H; Ar-H); 7.06 and 7.05 (each s, 8H; Ar-H); 6.90 (bd, 16H, J = 8.3 Hz; Phen-H); 6.36 – 6.34 (m, 8H; Ar-H); 6.25 – 6.22 and 6.17 – 6.16 (each m, 16H; Ar-H); 5.08 (tt, J1 = 11.9 Hz, J2 = 3.5 Hz, 2H; Cy-H); 4.54 – 4.47 (m, 16H; Ar-C2Ar); 4.13 – 4.10 (m, 16H; O-C2Ar); 3.79 and 3.65 (each bs, 24H; Pyrr-H and O-C2Ar); 3.19 – 3.13 (m, 32H, Ar-C2Ar); 2.88 (bs, 8H; Pyrr-H); 2.66 – 2.57 (m, 8H; Cy-H); 2.17 – 1.76 (m, 58H; Pyrr-H, Propyl-H, Cy-H); 1.50 – 1.41 (m, 8H; Cy-H); 1.30 (bs, 72H, tert-Butyl-Phen); 1.11 and 1.10 (each t, 24H, J = 7.4 Hz; Propyl-H); 0.92 – 0.83 (m, 24H; Propyl-H). MS (MALDI in DD/Dithranol 1:10): a_{calcd} for C_{388}H_{370}N_{14}O_{44} (m/z) 5933.30 [M] + and C_{388}H_{370}N_{14}O_{44}K (m/z) 5972.40 [M+K] +; found m/z = 5933.16; 5972.10. UV/Vis (CH2Cl2): λ (nm) [ε (M⁻¹ cm⁻¹)]: 701 [77100], 581 [97600], 527 [127900], 435 [57200]. Fluorescence (CH2Cl2): λ_{max} (nm) = 739 with λ_{ex}= 490 nm; Φ_Fl = 0.17.

**Compound 4:**

Under an argon atmosphere 102 mg (0.14 mmol, 2 equiv.) of compound 1 were heated to 90 °C for 23 h together with 78 mg (3.21 x 10^{-2} mmol, 1 equiv.) of compound 11 and 2-3 drops of triethylamine in toluene (1.2 mL). The solvent was evaporated, and the remaining crude product was purified by column chromatography with CH2Cl2/hexane 70:30 and precipitated from CH2Cl2/methanol.

A portion of 14 mg of the obtained product was dissolved in 1.5 mL dry CH2Cl2 and 3 mL of CF3COOH were added under an argon atmosphere. The mixture was stirred for 1 hour at room temperature, poured into ice water and adjusted to pH > 9 with NH3 solution (25%). CH2Cl2 (30 mL) was added to the reaction mixture, the two phases were separated, and the organic phase was washed with water and brine and dried over Na2SO4. The solvent was removed and the resulting crude product dried and used without further purification.

A portion of 9 mg (5.47 x 10^{-3} mmol, 1 equiv.) of the obtained crude product, 7 mg (1.14 x 10^{-2} m/z = 5988.40 [M+K+O] +, found m/z = 5988.58.

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4 Due to the resolution of the mass spectrometer only a peak with the average molecular weight of the compound can be observed. An additional peak due to oxidation of the sample during the measurement is observed in the spectrum: calcd for C_{388}H_{370}N_{14}O_{44}K m/z = 5988.40 [M+K+O] +, found m/z = 5988.58.
mmol, 2 equiv.) of compound 10 and 2 mg (5.47 x 10^{-3} mmol, 2 equiv.) Zn(OAc)_2 (H_2O-free) were heated in quinoline (0.75 mL) at 160 °C for 4 h under an argon atmosphere. The cooled reaction mixture was poured into 10 mL of 1N HCl and stirred for 30 minutes. The resulting precipitate was filtered and dissolved in CH_2Cl_2. The solution was washed with saturated NaHCO_3 solution and water and dried over MgSO_4. The crude product was purified first by column chromatography with CH_2Cl_2/hexane 70:30 and successively by preparative TLC with CH_2Cl_2/hexane 55:45 and HPLC with CH_2Cl_2 (SiO_2, NP). Compound 4 was obtained as a dark-blue powder (5 mg, 2.23 x 10^{-3} mmol, yield 8% over three steps). C_{146}H_{144}N_6O_{16} (2238.74). Mp > 400 °C. TLC: CH_2Cl_2; R_f = 0.18. ^1H NMR (400 MHz, CDCl_3, 25 °C): δ (ppm) = 8.60 (bs, 1H; Per-H); 8.53 - 8.50 (m, 2H; Per-H); 8.44 (d, 1H, ^3J = 8.1 Hz; Per-H); 8.30 and 8.25 (bs and s, 4H; Per-H); 7.81 and 7.79 (two d, 2H, ^3J = 7.9 Hz; Per-H); 7.24 and 7.23 (two d, 8H, ^3J = 8.7 Hz; Phen-H); 7.10 (s, 2H; Ar-H); 7.03 (s, 2H; Ar-H); 6.86 and 6.85 (two d, 8H, ^3J = 8.7 Hz; Phen-H); 6.34 (t, 2H, ^3J = 7.6 Hz; Ar-H); 6.23 (d, 2H, ^3J = 7.5 Hz; Ar-H); 6.14 (d, 2H, ^3J = 6.5 Hz; Ar-H); 5.08 (tt, ^3J_1 = 12.4 Hz, ^3J_1 = 3.5 Hz, 1H; Cy-H); 4.50 and 3.17 (AX, 4H, 2J = 13.5Hz; Ar-C_H_2-Ar); 4.47 and 3.13 (AX, 4H, 2J = 13.6 Hz; Ar-C_H_2-Ar); 4.14 – 4.07 (m, 6H; O-C_H_2 and N-C_H_2); 3.78 (bs, 4H; Pyrr-H); 3.64 (t, 4H, 3J = 6.6 Hz); 2.88 (bs, 4H; Pyrr-H); 2.66 – 2.57 (m, 2H; Cy-H); 2.09 – 1.63 (m, 23H; Butyl-H, Propyl-H, Cy-H); 1.43 – 1.37 (m, 5H; Butyl-H, Cy-H); 1.30 and 1.29 (two s, 36H, tert-Butyl-Phen-H); 1.09 (t, 6H, ^3J = 7.4 Hz; Propyl-H); 0.94 and 0.89 and 0.86 (three t, 9H; each ^3J = 7.4 Hz, Butyl-H, Propyl-H). MS (MALDI in Dithranol): calcd for C_{146}H_{145}N_6O_{16} [M+H]^+ (m/z) 2238.07; found 2238.0. HR-MS (ESI in acetonitrile/CHCl_3): calcd for C_{146}H_{144}N_6O_{16} [M]^+ (m/z) 2237.0639; found 2237.0633. UV/Vis (CH_2Cl_2): λ (nm) [ε (M^{-1}cm^{-1})] = 701 [44600], 580 [50800]. Fluorescence (CH_2Cl_2): λ_{max} (nm) = 738 with λ_{ex} = 560 nm; Φ_F = 0.18.

Compound 5:

A suspension of 30 mg (4.93 x 10^{-2} mmol, 2 equiv.) of 5-Monoamino-25,26,27,28-tetrakis(propyloxy)-calix[4]arene, 10 mg (2.46 x 10^{-2} mmol, 1 equiv.) of compound 8 and 18 mg (9.87 x 10^{-2} mmol, 4 equiv.) Zn(ac)_2 (H_2O-free) was heated in quinoline (0.4 mL) at 160 °C for 5 h under an argon atmosphere. The cooled reaction mixture was poured into 35 mL of 2N HCl and stirred for 30 minutes. The resulting precipitate was filtered, washed with water, dried and heated to 100 °C together with 15 mL NaOH (0.5 M) for 30 minutes. The remaining precipitate was filtered, dissolved in CH_2Cl_2, and the solution was washed with water to pH neutral and dried over MgSO_4. The crude product was purified by column chromatography with CH_2Cl_2 and precipitated from CH_2Cl_2/Methanol to yield compound 5 as a light red powder (11 mg, 7.00 x 10^{-3} mmol, yield 28%). C_{104}H_{102}N_2O_{12} (1571.93). Mp = 314 - 315 °C. TLC: CH_2Cl_2; R_f = 0.23. ^1H NMR (400 MHz, CDCl_3, 25 °C): δ (ppm) = 8.80 and 8.71 (each d, 8H, ^3J = 7.8 Hz; Per-H); 7.09 (d, 4H, ^3J = 7.7 Hz; Ar-H); 7.08 (s, 4H; Ar-H); 6.92 (t, 2H, ^3J = 7.5 Hz; Ar-H); 6.73 – 6.30 (m, 8H; Ar-H); 6.16 (dd, 4H, ^3J = 7.3 Hz, ^4J = 1.6 Hz; Ar-H); 4.53 and 3.19 (AX, 8H, ^3J = 13.4 Hz; Ar-C_H_2-Ar); 4.47 and 3.17 (AX, 8H, ^3J = 13.5 Hz; Ar-C_H_2-Ar); 4.11 and 4.03 (each t, 8H, ^3J = 8.2 Hz and 8.1 Hz; O-C_H_2); 3.74 – 3.68 (m, 8H; O-C_H_2); 2.06 – 1.84 (m, 16H; Propyl-H); 1.10 (t, 12H, ^3J = 7.4 Hz; Propyl-H); 0.94 and 0.91 (each t, 12H, each ^3J = 7.4 Hz; Propyl-H). MS (MALDI in DCTB): calcd for C_{104}H_{102}N_2O_{12}
(m/z) 1570.74 [M]^+; found 1570.77. **HR-MS** (ESI in CHCl₃/Acetonitrile): calcd for C₁₀₄H₁₀₂N₂NaO₁₂ [M+Na]^+ m/z = 1593.7329; found 1593.7325. **UV/Vis** (CH₂Cl₂): λ (nm) [ε (M⁻¹ cm⁻¹)] = 526 [97200], 490 [60700], 458 [22300]. **Fluorescence** (CH₂Cl₂): Φ_Fl < 0.001.

**Compound 6:**

Under an argon atmosphere 50 mg (8.22 x 10⁻² mmol, 2 equiv.) of 5-Monoamino-25,26,27,28-tetrakis(propyloxy)-calix[4]arene were heated to 90 °C for 14 h together with 41 mg (4.11 x 10⁻² mmol, 1 equiv.) compound 9 and 2-3 drops of triethylamine in toluene (0.6 mL). The solvent was evaporated, the remaining crude product purified by column chromatography with CH₂Cl₂/hexane 50:50 and precipitated from CH₂Cl₂/methanol. Compound 6 was obtained as a red powder (42 mg, 1.94 x 10⁻² mmol, yield 47 %). C₁₄₄H₁₅₀N₂O₁₆ (2164.74). Mp = 392 – 393 °C. TLC: CH₂Cl₂/hexane 80:20; R_f = 0.87. **¹H NMR** (400 MHz, CDCl₃, 25 °C): δ (ppm) = 8.31 (bs, 4H; Per-H); 7.24 (d, 8H; 3J = 8.6 Hz; Phen-H); 7.10 (bd, 4H; 3J = 7.1 Hz; Ar-H); 7.00 (s, 4H; Ar-H); 6.93 – 6.87 (m, 10H; Phen-H and Ar-H); 6.25 (bt, 4H; 3J = 7.1 Hz; Ar-H); 6.17 (bd, 4H; 3J = 6.3 Hz; Ar-H); 6.07 (bd, 4H; 3J = 7.0 Hz; Ar-H); 4.47 and 3.14 (AX, 8H, 2J = 13.2 Hz; Ar-C₄H₂-Ar); 4.44 and 3.13 (AX, 8H, 2J = 13.3 Hz; Ar-Ch₂-Ar); 4.07 and 4.01 (two bt, 8H, each 3J = 7.9 Hz; O-CH₂); 3.69 – 3.61 (m, 8H; O-C₂H₄); 2.00 – 1.81 (m, 16H, Propyl-H); 1.29 (s, 36H, tert-Butyl-Phen); 1.09 (t, 12H, 3J = 7.3 Hz; Propyl-H); 0.88 and 0.87 (two bt, 12H, each 3J = 7.2 Hz; Propyl-H). **MS** (MALDI in DCTB): calcd for C₁₄₄H₁₅₀N₂O₁₆ (m/z) 2163.10 [M]^+; found 2163.07. **HR-MS** (ESI in CHCl₃/Acetonitrile): calcd for C₁₄₄H₁₅₀N₂NaO₁₆ [M+Na]^+ (m/z) 2186.0881; found 2186.0877. **UV/Vis** (CH₂Cl₂): λ (nm) = 579; Φ_Fl = 0.71.

**Compound 7:**

A suspension of 25 mg (4.11 x 10⁻² mmol, 1 equiv.) of 5-Monoamino-25,26,27,28-tetrakis(propyloxy)-calix[4]arene, 38 mg (6.16 x 10⁻² mmol, 1.5 equiv.) of compound 10 and 15 mg (8.22 x 10⁻² mmol, 2 equiv.) Zn(OAc)₂ (H₂O-free) was heated in quinoline (0.5 mL) at 140 °C for 5.5 h under an argon atmosphere. The cooled reaction mixture was poured into 30 mL of 1N HCl and stirred for 60 minutes. The resulting precipitate was filtered, washed with water, dissolved in CH₂Cl₂, and the obtained solution was washed with water to pH neutral and dried over MgSO₄. The crude product was purified by column chromatography with CH₂Cl₂ and precipitated from CH₂Cl₂/methanol. Compound 7 was obtained as a green powder (19 mg, 1.94 x 10⁻² mmol, yield 38 %). C₇₈H₈₀N₄O₈ (1201.49). Mp > 450 °C (340 °C phase transition). TLC: CH₂Cl₂/ethylacetate 98:2; R_f = 0.70. **¹H NMR** (400 MHz, CDCl₃, 25 °C): δ (ppm) = 8.56 (bs, 1H; Per-H); 8.47 and 8.45 (d and s, 2H; Per-H); 8.38 (d, 1H, 3J = 7.8 Hz; Per-H); 7.72 and 7.69 (each bd, 2H, each 3J = 7.8 Hz; Per-H); 7.11 (d, 2H; 3J = 7.5 Hz; Ar-H); 7.08 (s, 2H; Ar-H); 6.93 (t, 1H, 3J = 7.5 Hz; Ar-H); 6.35 – 6.29 (m, 4H, Ar-H); 6.12 (dd, 2H, 3J = 7.1 Hz, 4J = 1.9 Hz; Ar-H); 5.08 (tt, 1H, 3J = 12.1 Hz, 3J = 3.4 Hz, Cy-H); 4.52 and 3.19 (AX, 4H, 2J = 13.5 Hz; Ar-Ch₂-Ar); 4.47 and 3.17 (AX, 4H, 2J = 13.5 Hz; Ar-Ch₂-Ar); 4.12 (t, 2H, 3J = 8.2 Hz; O-Ch₂); 4.04 (t, 2H, 3J = 8.1 Hz; O-Ch₂); 3.75 and 3.69 (bs and t, 8H, 3J = 6.8 Hz; Pyr-H
and O-CH₂); 2.85 (bs, 4H; Pyrr-H); 2.66 – 2.57 (m, 2H; Cy-H); 2.08 – 1.84 (m, 18H; Pyrr-H, Propyl-H, Cy-H); 1.79 – 1.73 (m, 3H; Cy-H); 1.53 – 1.34 (m, 3H; Cy-H); 1.11 (t, 6H, 3J = 7.5 Hz; Propyl-H); 0.93 and 0.90 (two t, 6H, each 3J = 7.5 Hz; Propyl-H). MS (MALDI in DCTB): calcd for C₇₈H₈₀N₄O₈ (m/z) 1200.60 [M]+; found 1200.59. HR-MS (ESI in THF/Acetonitrile): calcd for C₇₈H₈₀N₄O₈ [M]+ (m/z) 1200.5976; found 1200.5971. UV/Vis (CH₂Cl₂): λ (nm) [ε (M⁻¹cm⁻¹)] = 701 [47300]. Fluorescence (CH₂Cl₂): λₘₐₓ (nm) = 742; Φᵢ ≈ 0.19.

Mass spectrum of compound 3.

![Mass spectrum of compound 3](image)

**Figure S1:** Mass spectrum of compound 3 (MALDI in DD/Dithranol 1:10).a

¹H-NMR-Spectrum of compound 3.
Figure S2: $^1$H-NMR spectrum (400 MHz, CDCl$_3$, rt) of compound 3.

Optical Spectra of Compound 4.
**Figure S3:** UV/Vis absorption (black, solid), fluorescence emission (black, dashed; $\lambda_{ex} = 560$ nm) and fluorescence excitation spectra (red, solid; $\lambda_{det} = 850$ nm) of compound 4 in CH$_2$Cl$_2$. Inset: Magnification of fluorescence emission spectrum in the range of 550 nm to 680 nm.

**Spectroscopic data of an orange/violet bichromophoric compound 12.**

**Figure S4:** UV/Vis absorption (black, solid), fluorescence emission (black, dashed; $\lambda_{ex} = 490$ nm) and fluorescence excitation spectra (red, solid; $\lambda_{det} = 700$ nm) of compound 12 in CH$_2$Cl$_2$.

**Table S1.** Photophysical Properties of Compound 12 in CH$_2$Cl$_2$.\textsuperscript{a}
<table>
<thead>
<tr>
<th>UV/Vis abs.</th>
<th>fluorescence emission</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_{\text{max}}$ (nm)</td>
<td>$\epsilon$ (M$^{-1}$cm$^{-1}$)</td>
</tr>
<tr>
<td>12</td>
<td>578</td>
</tr>
</tbody>
</table>

$^a$ All spectra were recorded at room temperature. $^b$ $\lambda_{\text{ex}} = 490$ nm, $\lambda_{\text{det}} = 610$ nm; $^c$ $\lambda_{\text{ex}} = 490$ nm, $\lambda_{\text{det}} = 525$ nm, lifetime could not be determined due to low signal intensity; $^d$ $\lambda_{\text{ex}} = 560$ nm, $\lambda_{\text{det}} = 610$ nm; $^e$ $\lambda_{\text{ex}} = 490$ nm; $^f$ $\lambda_{\text{ex}} = 490$ nm and 540 nm.

Fluorescence Decay Curves.

Figure S5: Fluorescence intensity decay curves of compound 4 in CH$_2$Cl$_2$. $^b$

$^b$ For compound 4 with $\lambda_{\text{ex}} = 560$ nm and $\lambda_{\text{det}} = 610$ nm a biexponential decay with $\tau_1 = 0.8$ ns (67.0%) and $\tau_2 = 5.4$ ns (33.0%) was observed.
Figure S6: Fluorescence intensity decay curves of compound 3 in CH$_2$Cl$_2$.

References

For compound 3 with $\lambda_{ex} = 560$ nm and $\lambda_{det} = 610$ nm a biexponential decay with $\tau_1 = 1.2$ ns (86.0%) and $\tau_2 = 5.5$ ns (14.0%) was observed.


