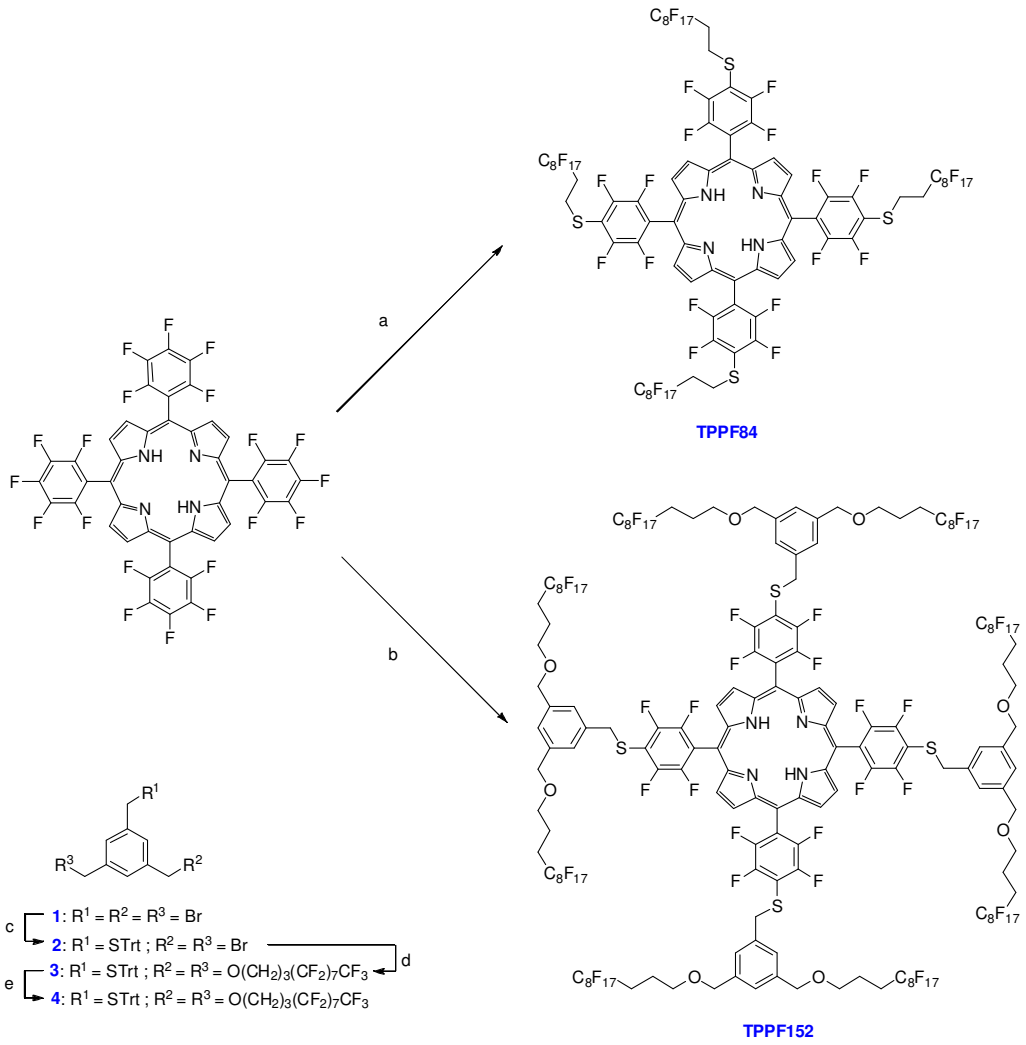
Supplementary Methods:

Synthesis of TPPF84 and TPPF152

The syntheses of the porphyrin derivatives comprising peripheral fluorous ponytails **TPPF84** and **TPPF152** are displayed in Fig. S1. Synthetic protocols and analytical data of both porphyrins and their precursors **2**-**4** are provided.



Reagents and conditions: (a) $HS(CH_2)_2C_8F_{17}$, diethylamine, EtOAc, DMF, rt, 1.5 h, 81%; (b) **4**, diethylamine, EtOAc, DMF, rt, 3.5 h, 64%; (c) trityl thiol, K_2CO_3, THF, reflux, 20 h, 33%; (d) $HO(CH_2)_3C_8F_{17}$, NaH, THF, reflux, 4 h, 52%; (e) $HSiEt_3$, TFA, CH_2Cl_2, 1 h, 77%.

All commercially available starting materials were of reagent grade and used as received. Dry tetrahydrofuran (THF), dry dimethylformamide (DMF) and dry dichloromethane were purchased from *Fluka*, stored over 4 Å molecular sieves, and handled under Argon. The solvents for chromatography and extraction were of technical grade and distilled prior to use. Column chromatography purifications were carried out on *silica gel 60* (particle size 0.040-0.063 mm) from *Fluka*. Deuterated solvents were purchased from *Cambridge Isotope Laboratories*. ^{1}H, ^{19}F and ^{13}C

NMR spectra were recorded with a *Bruker DMX 400* instrument (^{1}H resonance 400 MHz) or a *Bruker DRX 500* instrument (^{1}H resonance 500 MHz) at 298 K. UV/Vis spectra were recorded on a *UV-1800* spectrophotometer from *Shimadzu*. Matrix Assisted Laser Desorption Ionisation Time of Flight (MALDI-ToF) mass spectra were performed on an *Applied Bio Systems Voyager-De™ Pro* mass spectrometer. ESI-TOF mass spectra were recorded on a *Bruker MicrOTOFQ* instrument. Elemental analyses were performed on a *Perkin-Elmer Analysator 240.*

(3,5-Bis(bromomethyl)benzyl)(trityl)sulfane (2): 1,3,5-Tris(bromomethyl)benzene (5.00 g, 14.0 mmol, 1.0 eq.) and triphenylmethanethiol (3.87 g, 14.0 mmol, 1.0 eq.) were dissolved in dry tetrahydrofuran (40 mL) under an atmosphere of argon. Potassium carbonate (2.90 g, 21.0 mmol, 1.5 eq.) was added and the mixture was heated to reflux for 20 hours. After cooling to room temperature, water was added and the mixture was extracted with *tert*-butyl methyl ether. The combined organic fractions were washed with brine, dried over magnesium sulfate and evaporated to dryness. After purification by column chromatography (silica gel, hexane/dichloromethane 3:1), the product **2** (2.55 g) was obtained as a colorless solid in a yield of 33%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 – 7.42 (m, 6H), 7.35 – 7.20 (m, 10H), 7.01 (s, 2H), 4.39 (s, 4H), 3.33 (s, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ 144.5, 138.7, 138.4, 129.7, 129.6, 128.2, 128.0, 126.8, 67.3, 36.4, 32.6; MS (ESI-Q-ToF, m/z): 575 (31%, $[M+Na]^+$), 217 (100%); Elemental analysis (calcd., found for $C_{28}H_{24}Br_2S$): C (60.89, 60.53), H (4.38, 4.50).

(3,5-Bis((3-perfluorooctylpropoxy)methyl)benzyl)(trityl)sulfane (3): 3-(Perfluorooctyl)propanol (2.16 g, 4.53 mmol, 5.0 eq.) was dissolved in dry tetrahydrofuran (10 mL) under an atmosphere of argon. This solution was added to a suspension of sodium hydride (freshly washed, 109 mg, 4.53 mmol, 5.0 eq.) in dry tetrahydrofuran (5 mL) at 0 °C. After 15 minutes the mixture was allowed to warm to room temperature and then a solution of (3,5-bis(bromomethyl)benzyl)(trityl)sulfane (**2**, 500 mg, 0.91 mmol, 1.0 eq.) in dry tetrahydrofuran (20 mL) was added dropwise. The reaction mixture was stirred for 4 hours at reflux. After cooling to room temperature it was quenched with an saturated aqueous ammonium chloride solution. The mixture was extracted with diethylether and the organic fractions were washed with brine, dried over magnesium sulfate, filtered and evaporated to dryness. Purification by column chromatography (silica gel, cyclohexane/dichloromethane 1:1) gave the title compound (632 mg) as a white solid in a yield of 52%.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 (d, J = 7.4 Hz, 6H), 7.30 (t, J = 7.4 Hz, 6H), 7.22 (t, J = 7.4 Hz, 3H), 7.14 (s, 1H), 6.99 (s, 2H), 4.44 (s, 4H), 3.51 (t, J = 5.9 Hz, 4H), 3.31 (s, 2H), 2.24 – 2.14 (m, 4H), 1.92 – 1.87 (m, 4H); ^{19}F NMR (377 MHz, $CDCl_3$): δ -81.0 (t, J = 10 Hz, 6F), -114.7 (m, 4F), -122.0 (m, 4F), -122.2 (m, 8F), -123.0 (m, 4F), -123.7 (m, 4F), -126.4 (m, 4F); ^{13}C-NMR (126 MHz, $CDCl_3$): δ 144.7,

138.7, 137.5, 129.6, 128.0, 127.7, 126.8, 125.5, 72.7, 68.8, 67.5, 36.8, 28.0, 20.8; MS (ESI-Q-ToF, m/z): 1369 (54%, $[M+Na]^+$), 685 (100%); Elemental analysis (calcd., found for $C_{50}H_{36}F_{34}O_2S$): C (44.59, 44.83), H (2.69, 2.65).

(3,5-Bis((3-perfluorooctylpropoxy)methyl)phenyl)methanethiol (4): (3,5-Bis((3-perfluorooctyl-propoxy)methyl)benzyl)(trityl)sulfane (**3**, 650 mg, 0.48 mmol, 1.0 eq.) and triethylsilane (117 µL, 84 mg, 0.72 mmol, 1.5 eq.) were dissolved in dry dichloromethane (20 mL). Trifluoroacetic acid (800 µL) was added dropwise and the reaction mixture was stirred for one hour at room temperature. The reaction was quenched by the addition of a saturated aqueous solution of sodium hydrogen carbonate. After completion of the gas formation, the phases were separated and the aqueous phase was extracted with dichloromethane. The combined organic fractions were dried over magnesium sulfate, filtered and evaporated to dryness. After purification by column chromatography (silica gel, cyclohexane/dichloromethane 2:1, then 1:1, then 1:2), the thiol **4** (413 mg) was obtained as a white solid in a yield of 77%.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.21 (s, 2H), 7.18 (s, 1H), 4.50 (s, 4H), 3.75 (d, J = 7.6 Hz, 2H), 3.55 (t, J = 6.0 Hz, 4H) 2.27 – 2.16 (m, 4H), 1.95 – 1.89 (m, 4H), 1.77 (t, J = 7.6 Hz, 1H); ^{19}F NMR (377 MHz, $CDCl_3$): δ -81.0 (t, J = 10 Hz, 6F), -114.7 (m, 4F), -122.0 (m, 4F), -122.2 (m, 4F), -123.0 (m, 4F), -123.7 (m, 4F), -126.4 (m, 4F); ^{13}C-NMR (126 MHz, $CDCl_3$): δ 141.6, 139.0, 126.6, 125.4, 72.7, 68.9, 28.8, 28.0, 20.8; MS (ESI-Q-ToF, m/z): 1127 (100%, $[M+Na]^+$). Elemental analysis (calcd., found for $C_{31}H_{22}F_{34}O_2S_1$): C (33.71, 33.74), H (2.01, 2.05).

5,10,15,20-Tetrakis[4-(2-perfluorooctylethylthio)-2,3,5,6-tetrafluorophenyl]-porphyrin TPPF84: 1*H*,1*H*,2*H*,2*H*-Perfluorodecanethiol (704 µL, 1.18 g, 2.46 mmol, 8.0 eq.) was added under an atmosphere of argon to a mixture of ethyl acetate (60 mL) and dry dimethylformamide (20 mL). To this solution was added diethylamine (0.45 mL) and a solution of 5,10,15,20-tetrakis(pentafluorophenyl)-porphyrin (300 mg, 308 µmol, 1.0 eq.) in dry dimethylformamide (30 mL). The reaction mixture was stirred under argon at room temperature for 1.5 hours and was then quenched by the addition of water and subsequently diluted with diethyl ether. After phase separation the aqueous phase was extracted with diethylether. The combined organic phases were washed with brine and evaporated to dryness. The crude was purified by column chromatography using silica gel (hexane/acetone 9:1) to give **TPPF84** (700 mg) as a purple solid in a yield of 81%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.91 (s, 8H), 3.51 – 3.47 (m, 8H), 2.77 – 2.64 (m, 8H), -2.87 (s, 2H); ^{19}F NMR (377 MHz, $CDCl_3$): δ -81.0 (t, J = 10 Hz, 12F), -114.1 (m, 8F), -121.8 (m, 8F), -122.1 (m, 16F), -123.0 (m, 8F), -123.4 (m, 8F), -126.4 (m, 8F), -133.9 (m, 8F), -136.3 (m, 8F); MS (MALDI-ToF, m/z):

2814 (100%, M^+); Elemental analysis (calcd., found for $C_{84}H_{26}F_{84}N_4S_4$): C (35.84, 35.79), H (0.93, 1.10), N (1.99, 2.16); UV/Vis (CH_2Cl_2): λ_{max} = 415, 508, 536, 584 nm.

5,10,15,20-Tetrakis[4-((3,5-bis((3-perfluorooctylpropoxy)methyl)phenyl)methanethio)-2,3,5,6-tetrafluorophenyl]porphyrin TPPF152: **TPPF152** was synthesized by following the procedure for **TPPF84**. (3,5-Bis((3-perfluorooctylpropoxy)methyl)phenyl)methanethiol (136 mg, 123 µmol, 8.0 eq.) was added to ethyl acetate (2 mL) and dimethylformamide (1 mL). Diethylamine (100 µL) and a solution of 5,10,15,20-tetrakis(pentafluorophenyl)-porphyrin (15 mg, 15.4 µmol, 1.0 eq.) in dimethylformamide (2 mL) were subsequently added. After a reaction time of 3.5 hours, aqueous workup and purification by column chromatography using silica gel (hexane/acetone 8:1) **TPPF152** (52 mg) was obtained as a purple solid in a yield of 64%.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.75 (s, 8H), 7.42 (s, 8H), 7.36 (s, 4H), 4.61 (s, 16H), 4.48 (s, 8H), 3.55 (t, J = 6.0 Hz, 16H), 2.21 – 2.05 (m, 16H), 1.89 – 1.81 (m, 16H), -2.94 (s, 2H); ^{19}F NMR (377 MHz, $CDCl_3$): δ -81.2 (t, J = 10 Hz, 24F), -114.9 (m, 16F), -122.2 (m, 16F), -122.4 (m, 32F), -123.1 (m, 16F), 123.9 (m, 16F), -126.5 (m, 16F), -133.8 (m, 8F), -137.7 (m, 8F); MS (MALDI-ToF, m/z): 5310 (100%, M^+); UV/Vis (CH_2Cl_2): λ_{max}=415, 508, 537, 585 nm.

Synthesis of PFNS8 and PFNS10

The molecules **PFNS8** and **PFNS10** were synthesized and characterized as described in the literature[17].