

Supplementary Information:

Synthesis and Characterization of azobenzene 4,4'-di(carboxylic acid 1''H-1''H-perfluoro-1''-octanolate)

Reagents and solvents: All chemicals were directly used for the synthesis without further purification. The solvents for crystallisation were distilled once before use, the solvents for extraction were used in technical grade. Dry tetrahydrofuran (THF) was distilled over sodium and potassium.

Synthesis: All reactions comprising oxidation or hydrolysis sensitive reagents were done under an argon atmosphere using the Schlenk-technique. Furthermore, dry solvents were used and the glassware was heated out prior to use.

Analytics and instruments: ¹H-Nuclear Magnetic Resonance (NMR): *Bruker DPX-NMR* (400 MHz) and *Bruker BZH-NMR* (250 MHz) instruments were used to record the spectra. Chemical shifts (δ) are reported in parts per million (ppm) relative to residual solvent peaks or trimethylsilyle (TMS), and coupling constants (J) are reported in Hertz (Hz). NMR solvents were obtained from *Cambridge Isotope Laboratories, Inc.* (Andover, MA, USA). The measurements were done at room temperature. The multiplicities are indicated as: s=singlet, d=doublet, q=quartet, quin=quintet, m=multiplet and b=broad.

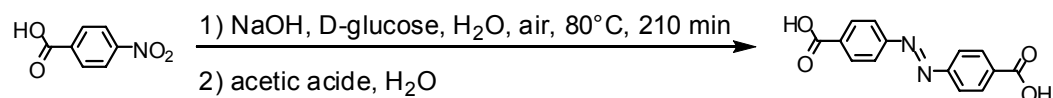
¹³C-Nuclear Magnetic Resonance (NMR): *Bruker DPX-NMR* (400 MHz) instruments were used to record the spectra. Chemical shifts (δ) are reported in parts per million (ppm) relative to residual solvent peaks. NMR solvents were obtained from *Cambridge Isotope Laboratories, Inc.* (Andover, MA, USA). The measurements were done at room

temperature. The carbons are classified as: Cp=primary, Cs=secondary, Ct=tertiary, Cq=quaternary.

Mass spectroscopy (MS): Mass spectra were recorded on a *Finnigan MAT 95Q* for Electron Impact (EI) or a *Voyager-De™ Pro* for MALDI-TOF. The peaks were measured in m/z (%).

Melting point (MP): The melting points were measured on a Stuart melting point apparatus SMP3.

Azobenzene-4,4'-dicarboxylic acid was synthesized following a reported protocol [1]:



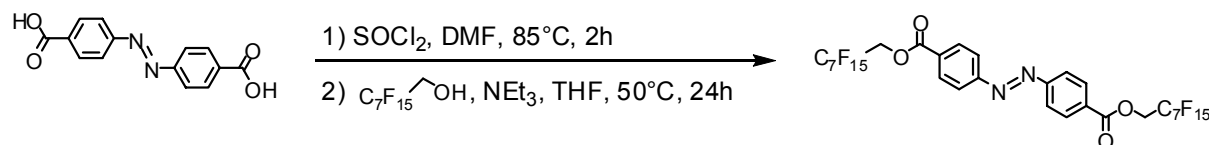
4-Nitrobenzoic acid (1.0 eq., 0.060 mol, 10.0 g) was dissolved in 200 ml water. After adding sodium hydroxide (14.0 eq., 0.838 mol, 33.5 g) portion wise, the solution was heated to 80°C and stirred for 15min. An aqueous solution of D-glucose (5.7 eq., 0.342 mol, 61.5 g) in 120 ml hot water was added drop wise, while the solution turned yellow to brown. Then a strong air stream was passed into the mixture for 210min, after cooling to 0°C a light brown precipitate was obtained. The crude was filtered, dissolved in 400 ml hot water, acidified with 20 ml acetic acid and cooled to 0°C. The light pink precipitate was filtered and dried on high vacuum to give the desired product (16.1g, C₁₄H₁₀N₂O₄, 270.24 g/mol, 83% isolated yield).

¹H-NMR (250 MHz, DMSO-*d*₆, δ/ppm): 13.29 (2H, s, -COOH); 8.18 (4H, d, ³J_{HH} = 8.6 Hz, Ar); 8.02 (4H, d, ³J_{HH} = 8.6 Hz, Ar).

¹³C-NMR (101 MHz, DMSO-*d*₆, δ/ppm): 167.5 (2C, Cq, s); 155.0 (2C, Cq, s); 134.3 (2C, Cq, s); 131.6 (4C, Ct, s); 123.7 (4C, Ct, s).

MS (EI, m/z): 271.0 (8%); 272.0 (15%); 270.0 (48%, M⁺); 149 (43%); 121 (100%); 65 (33%).

Azobenzene 4,4'-di(carboxylic acid 1''H-1''H-perfluoro-1''-octanolate)



Azobenzene-4,4'-dicarboxylic acid (1.0eq., 5.840mmol, 1.58g) was refluxed in 50ml thionyl chloride containing a few drops of DMF under an argon atmosphere for 2h. The reaction mixture was concentrated to dryness under reduced pressure and dried on high vacuum. The red crude was then dissolved in 80 ml dry THF. This solution was added drop wise to a stirred dry THF solution (80 ml) of 1H-1H-perfluoro-1-octanol (2.1 eq., 12.500 mmol, 5.0 g) and triethylamine (5.0 eq., 29.200 mmol, 2.95 g) at 0°C under an argon atmosphere. After stirring for 24h at 50°C the reaction mixture was evaporated to dryness and the red residue dissolved in 30ml DMF and poured into 300ml ice water. After 30min at -20°C the precipitate was filtered and dried on high vacuum.

The light red crystals was sublimated at 200°C at 2.7·10⁻² mbar to give the product as orange crystals (1.4 g, C₃₀H₁₂F₃₀N₂O₄, 1034 g/mol, 23%). In a second attempt the light red crystals was recrystallized from 400ml chloroform to give the product as orange crystals (4.3g, C₃₀H₁₂F₃₀N₂O₄, 1034g/mol, 72%).

¹H-NMR (400 MHz, CDCl₃, δ/ppm): 8.24 (4H, d, ³J_{HH} = 8.5 Hz, Ar); 8.03 (4H, d, ³J_{HH} = 8.5 Hz, Ar); 4.88 (4H, t, ³J_{HH} = 13.3 Hz, -CH₂-CF₂-).

¹⁹F-NMR (400 MHz, CDCl₃, δ/ppm): -81.8 (3F, t); -120.3 (2F, m); -123.1 (4F, m); -123.8 (2F, m); -124.3 (2F,m); -127.2 (2F, m).

MS (MALDI-TOF, m/z): 1034 (100%); 1036 (100%).

MP 154-156°C

[1] Ameerunisha, S., Zacharias, P. S. Characterization of simple photoresponsive systems and their applications to metal ion transport. *J. Chem. Soc. Perkin Trans. 2*, 1679-1682 (1995).