Supporting Material - Experimental

General synthesis procedure for the Methyl Orange dendrimers 2-5:

1/n equivalents of the corresponding poly(propyleneamine)-dendrimer (*POPAM*) and 1.5n equivalents of triethylamine were dissolved in 50-100 mL of abs. chloroform (n: number of peripheric, primary amino groups of the dendrimer). To this mixture a solution of n equivalents of dabsyl chloride in chloroform was added slowly. The reaction mixture was stirred for 3-5 d under reflux at an argon atmosphere. The solvent was then removed in vacuo, the residue collected in chloroform and washed intensively with water, aq. sodium carbonate and again with water for three times. After drying the organic phase with sodium sulphate and evaporation of the solvent the Methyl Orange dendrimers are obtained as red solids.

Example of 3rd generation:

16-Cascade:1,4-diaminobutane[4-*N*,*N*,*N'*,*N'*]:(1-azabutylidene)^3:*N*-[4-thiodioxo-4'-(dimethylamino)azobenzene] (3):

Reaction procedure as described above. Ansatz: 16-Cascade:1,2-diaminobutane[4-*N*,*N*,*N´*,*N´*]:(1-azabutylidene)^3:(aminopropane) (101 mg, 0.06 mmol), triethylamine (200 µL, 1.44 mmol), dabsyl chloride (332 mg, 1.03 mmol, 7% excess) .
We obtained 358 mg (0.04 mmol, 94 %) of a red solid material. M.p. 126-129 °C.

^{1}H-NMR:	(400 MHz, $CDCl_3$, 25°C), δ [ppm] = 1.35-2.00 (bm, 60 H, $NCH_2C\underline{H}_2CH_2N$), 2.10-2.75 (bm, 84 H, $NC\underline{H}_2$), 2.82 (b, 32 H, $C\underline{H}_2NHSO_2$), 2.94 (b, 96 H, $N(CH_3)_2$), 6.56 (d, 32 H, je 16 H-3' und H-5', $^3J_{HH}$ = 9.1 Hz), 7.73 (d, 32 H, je 16 H-2' und H-6', $^3J_{HH}$ = 9.1 Hz), 7.76, (d, 32 H, 16 H-2 and 16 H-6, $^3J_{HH}$ = 8.6 Hz), 7.86 (bd, 32 H, 16 H-3 and 16 H-5, $^3J_{HH}$ = 6.6 Hz)
^{13}C-NMR:	(100.6 MHz, $CDCl_3$, 25°C), δ [ppm] = 25.8, 40.3, 51.2, 51.6, 111.4, 122.6, 125.7, 128.1, 139.7, 143.6, 152.9, 155.3
MALDI-TOF-MS:	Matrix: HAB, molecule was protonated with HCl; m/z (%):6284.3 (100, $M+H^+$), 3165.6 (62, $M/2+Na^+$)
$C_{150}H_{196}N_{38}O_{16}S_8$:	(6284.2)

Maldi-TOF MS of **3** *(G 3)*