Suplementary Information

Photosensitive Ionic Nematic Liquid Crystalline Complexes based on Dendrimers and Hyperbranched Polymers and a Cyanoazobenzene Carboxylic Acid

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1. Synthesis

4-(4-Hydroxyphenylazo)benzonitrile (1) 4-Aminobenzonitrile (15 g, 0.13 mol) was disolved in a warm mixture of 240 mL of water and 80 mL of hydrochloric acid. This solution was then cooled in an ice–salt bath (0–5 °C) with vigorous stirring. A cold solution of 10.5 g (0.15 mol) of $NaNO_2$ in 100 mL of water was added slowly to the mixture until the solution became neutral. Then phenol (14.3 g, 0.15 mol) was added and the reaction mixture was stirred for 1 h. Sodium hydrogen carbonate was added to the reaction mixture till the supernatant solution was neutralized. The resulting precipitate was collected by filtration and the crude product was purified by recrystallization from methanol to give an orange solid (yield: 50%).

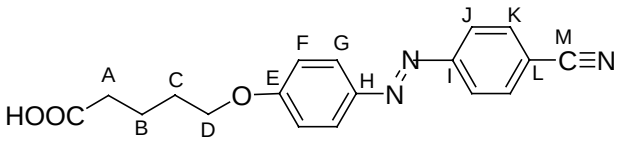
^{1}H NMR (CDCl3, 300 MHz, ppm): δ= 7.92 (d, J = 8.5 Hz, 2H), 7.90 (d, J = 8.5 Hz, 2H), 7.76 (d, J = 8.5 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 5.30 (s, OH). IR (KBr, cm^{-1}): 3312 (OH), 2233 (CN), 1458 (N=N).

*Metyl 5-(4-cyanophenylazphenyloxy)pentanoate (**2**).* A mixture of (**1**) (5.7 g, 25.6 mmol), anhydrous K_2CO_3 (7 g, 51.2 mmol) and 18-crown-6 (catalytic amount) in acetone (100 mL) was stirred at 60ºC for 1 h. To the resulting white suspension was added a solution of methyl 5-bromopentanoate (7 g, 35.9 mmol) in dry acetone (10 mL) and stirring was continued at 60ºC for 36 h. The mixture was allowed to cool to room temperature, and the solvent was evaporated. The residue was dissolved in CH_2Cl_2 and extracted three times with brine. The organic phase was dried over $MgSO_4$ and filtered, and the solvent was evaporated. The resulting product was purified by recrystallization from methanol to give an orange solid (yield: 81%).

^{1}H NMR (CDCl3, 300 MHz, ppm): 7.92 (d, J = 9.3 Hz, 4H), 7.77 (d, J = 8.5 Hz, 2H), 6.99 (d, J = 9.1 Hz, 2H), 4.03 (t, 2H), 3.64 (s, 3H), 2.48 (t, 2H), 1.83-1.73 (m, 4H), IR (KBr, cm^{-1}): 2223 (CN), 1742 (C=O), 1461 (N=N).

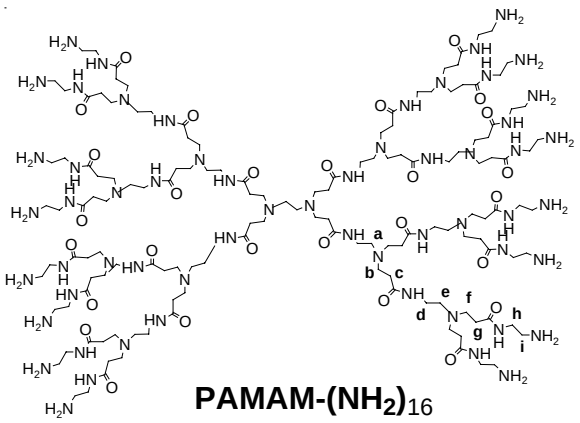
5-(4-cyanophenylazophenyloxy)pentanoic acid (CAzPA),

Metyl 5-(4-cyanophenylazphenoxy)pentanoate (**2**) (3.92 g, 12.7 mmol) was added to 70 mL of a KOH 3M solution. Then THF (ca. 15 ml) was added until a homogeneous suspension was formed. The reaction mixture was stirred at room temperature for 4 days, during which the reaction was monitored with TCL. In the case of complete hydrolysis the suspension was neutralized with a solution of HCl (5 M) at 0ºC. This furnished the crude product as an orange solid which was filtered off and washed with diethyl ether and water. The crude material was recrystallised twice from EtOH to yield pure acid *(CAzPA)* (81%) as an orange solid.

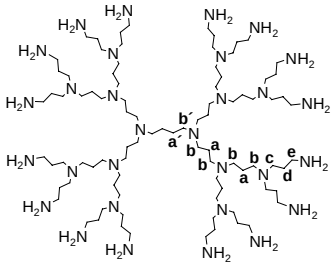


CAzPA

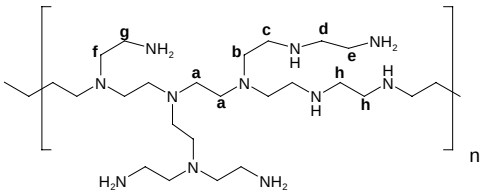
^{1}H NMR (400 MHz, DMSO-d6, 333K): δ= 12.08 (br s, 1H, OH), 8.00 (d, *J* = 8.3 Hz, 2H, K), 7.94 (d, *J* = 8.3 Hz, 2H, J), 7.92 (d, *J* = 9.0 Hz, 2H, G), 7.14 (d, *J* = 9.0 Hz, 2H, F), 4.12 (t, *J* = 6.3 Hz, 2H, D), 2.30 (t, *J* = 7.3 Hz, 2H, A), 1.79 (m, 2H, C), 1.69 (m, 2H, B). ^{13}C NMR (400 MHz, DMSO-d6, 333K): δ= 173.8 (COO), 162.2 (E), 154.1 (I), 146.0 (H), 133.4 (K), 125.0 (G), 122.6 (J), 118.2 (M), 115.1 (F), 109.0 (L), 67.7 (D), 33.1 (A), 27.8 (C), 20.9 (B). IR (KBr, cm^{-1}): 3224 (COOH), 2238 (CN), 1739 (C=O), 1496 (N=N).



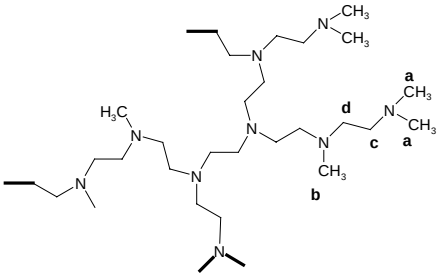
PAMAM-$(NH_2)_{16}$



PPI-$(NH_2)_{16}$



PEI-$(NH_2)_n$



PEI-$(NMe_2)_n$

PAMAM)$_{16}$-CAzPA: ^{1}H NMR (400 MHz, DMSO-d6, 333K): δ 8.00 (d, *J* = 8.3 Hz, 2H, K), 7.94 (d, *J* = 8.3 Hz, 2H, J), 7.92 (d, *J* = 9.0 Hz, 2H, G), 7.76-7.67 (br s, NH), 7.14 (d, *J* = 9.0 Hz, 2H, F), 4.12 (t, *J* = 6.3 Hz, 2H, D), 3.11 (m, 2H, NH*CH*$_2$CH$_2$NR, d), 3.09 (m, 2H, NH*CH*$_2$CH$_2$NH$_3^+$, h), 2.68 (m, 2H, N*CH*$_2$CH$_2$CONH, f,b), 2.61 (m, NCH$_2$*CH*$_2$NH$_3^+$, i), 2.46 (m, RN*CH*$_2$, a,e), 2.27 (t, *J* = 7.3 Hz, 2H, A), 2.21 (m, 4H, NCH$_2$*CH*$_2$CONH, c,g), 1.80 (m, 2H, C), 1.71 (m, 2H, B).

^{13}C NMR (400 MHz, DMSO-d6, 333K): δ 175.1(COO), 171.3-171.0 (NHCO), 162.2 (E), 154.1 (I), 146.0 (H), 133.4 (K), 125.0 (G), 122.6 (J), 118.2 (M), 115.1 (F), 109.0 (L), 67.7 (D), 52.1 (a,e), 49.6 (b,f), 41.4(h), 40.7(i), 36.8 (d), 33.3(c,g), 34.1 (A), 27.8 (C), 21.4 (B).

PPI)$_{16}$-CAzPA: ^{1}H NMR (400 MHz, DMSO-d6, 333K): δ 8.00 (d, *J* = 8.3 Hz, 2H, K), 7.94 (d, *J* = 8.3 Hz, 2H, J), 7.92 (d, *J* = 9.0 Hz, 2H, G), 7.14 (d, *J* = 9.0 Hz, 2H, F), 4.12 (t, *J* = 6.3 Hz, 2H, D), 2.60 (t, 2H, *CH*$_2$NH$_3^+$,e), 2.37 (t, 2H, N*CH*$_2$CH$_2$CH$_2$NH$_3^+$, c), 2.34 (m,

2H, N*CH*$_2$, b,b´), 2.25 (t, *J* = 7.3 Hz, 2H, A), 1.80 (m, 2H, C), 1.69 (m, 2H, B), 1.49 (m, 2H, NCH$_2$*CH*$_2$CH$_2$NH$_3^+$, d), 1.46 (m, 2H, NCH$_2$*CH*$_2$CH$_2$N, a,a´).

^{13}C NMR (400 MHz, DMSO-d6, 333K): δ 174.1 (COO), 162.2 (E), 154.1 (I), 146.0 (H), 133.4 (K), 125.0 (G), 122.6 (J), 118.2 (M), 115.1 (F), 109.0 (L), 67.7 (D), 53.5-51.3 (b´,b,c), 39.1 (e), 33.8 (A), 29.6 (d), 27.8 (C), 24.5 (a,a´), 21.1 (B).

PEI-CAzPA: ^{1}H NMR (400 MHz, DMSO-d6, 333K): δ 8.00 (d, *J* = 8.3 Hz, 2H, K), 7.94 (d, *J* = 8.3 Hz, 2H, J), 7.92 (d, *J* = 9.0 Hz, 2H, G), 7.14 (d, *J* = 9.0 Hz, 2H, F), 4.12 (t, *J* = 6.3 Hz, 2H, D), 2.67 (m, *CH*$_2$NH$_3^+$, g,e), 2.60-2.58 (m, HN*CH*$_2$, c,h,d), 2.5 (m, R$_2$N*CH*$_2$, a,b,f), 2.25 (t, *J* = 7.3 Hz, 2H, A), 1.80 (m, 2H, C), 1.69 (m, 2H, B).

^{13}C NMR (400 MHz, DMSO-d6, 333K): δ 175.0 (COO), 162.2 (E), 154.1 (I), 146.0 (H), 133.4 (K), 125.0 (G), 122.6 (J), 118.2 (M), 115.1 (F), 109.0 (L), 67.7 (D), 55.3 (f), 53.7 (b), 52.3 (a), 50.2 (d), 48.2 (h), 46.7 (c), 40.2 (e), 35.4 (g), 34.7 (A), 27.8 (C), 21.1 (B).

PEIMe-CAzPA: ^{1}H NMR (400 MHz, DMSO-d6, 333K): δ 8.00 (d, *J* = 8.3 Hz, 2H, K), 7.94 (d, *J* = 8.3 Hz, 2H, J), 7.92 (d, J = 9.0 Hz, 2H, G), 7.14 (d, J = 9.0 Hz, 2H, F), 4.12 (t, J = 6.3 Hz, 2H, D), 2.4-2.3 (m, CH$_2$NCH$_3$, c), 2.5 (m, CH$_2$CH$_2$NCH$_3$, d), 2.29 (t, J = 7.3 Hz, 2H, A), 2.18 (m, R$_2$NCH$_3$, b), 2.15 (m, N(CH$_3$)$_2$, a), 1.80 (m, 2H, C), 1.69(m, 2H, B).

^{13}C NMR (400 MHz, DMSO-d6, 333K): δ 175.0 (COO), 162.2 (E), 154.1 (I), 146.0 (H), 133.4 (K), 125.0 (G), 122.6 (J), 118.2 (M), 115.1 (F), 109.0 (L), 67.7 (D), 54.5-57.5 (CH$_2$NCH$_3$, c), 53.6-51.5 (CH$_2$CH$_2$NCH$_3$,d), 45.2 (N(CH$_3$)$_2$, a), 42.5 (R$_2$NCH$_3$,b), 33.1 (A), 27.8 (C), 21.1 (B).

2. Supporting information tables

Table S1. Main IR data (cm^{-1}, KBr) and 5-(4-cyanophenylazophenyloxy)pentanoic acid and ionic complexes

Compound	OC-OH	NH amide	NH_3^+	CN	CO acid	CO amide	$\nu_{as}(COO^-)$	$\nu_s(COO^-)$	-N=N-
CAzPA	3224 libre			2238	1739				1496
PAMAM)$_{16}$-CAzPA		3280	2935	2224		1645	1554	1408	1462
PPI)$_{16}$-CAzPA			2946	2224			1598	1403	1499
PEI-CAzPA			2942	2221			1559	1403	1416
PEIMe-CAzPA			2946	2224			1559	1413	1499