Supplementary Materials

Experimental Section

General Procedure

Trisazomelamines (TAM) 4 was prepared according to known literature procedures starting from 4-(4-nitrophenylazo)-1-naphthol 1.[1] The preparation of the alkoxy-substituted intermediates 2 was carried out by the etherification of 1 with alkyl bromides incorporating a different number of methylene groups in the presence of potassium carbonate. Subsequently, the 4-(4-aminophenylazo)-1-alkoxy-naphthalene 3 was obtained by the reduction of the nitro group of the intermediates 2 with an aqueous solution of sodium hydrogen sulphide. To obtain the novel trisazomelamines 4, the anilines 3 were reacted with cyanuric chloride in the presence of potassium carbonate.

The chemical structures of the intermediates and the final products were determined by a combination of IR spectroscopy (Perkin-Elmer 782 spectrometer), ^{1}HNMR spectroscopy (Varian Unity 300-MHZ spectrometer using tetramethylsilane as external standard) and MALDI-TOF and EI mass spectral analysis (BIFLEX III, Bruker Inc.). All details are given in the following section.

4-(4-nitrophenylazo)-1-alkoxy-naphthalenes 2. The synthesis of this compound was prepared by the alkoxylation of 4-(4-nitrophenylazo)-1-naphthol following the literature method.[1]

4-(4-aminophenylazo)-1-alkoxy-naphthalenes 3. These compounds were synthesized from the prepared 4-(4-nitrophenylazo)-1-alkoxy-naphthalenes 2. Compound 2 (24.3mmol) was dissolved in hot ethanol (140ml). Aqueous sodium hydrogen sulphide (10.1ml, 9M) was added slowly to the stirred and heated solution under reflux. The reaction worked up until the mixture became clear. After cooling to room temperature, the water was added to the mixture. Then, the mixture was filtered and washed carefully with water. The residue was dried under vacuum and recrystallized from ethanol. The product was purified further by flash column chromatography (silica gel, 200-300 mesh) using dichloromethane as the eluent.

3a: This was synthesized as described above from 4-(4-nitrophenylazo)-1-octadecyloxy-naphthalene and sodium hydrogen sulphide. (59.3%) AEI MS: m/z = 515 (calcd. for $C_{34}H_{49}ON_3$ 515). IR (KBr): ν = 3462, 3379, 2919, 2849, 1620, 1599, 1577, 1505, 1242, 1089, 839, 815, 766, 722 cm^{-1}.

3b: This was synthesized as described above from 4-(4-nitrophenylazo)-1-hexadecyloxy-naphthalene and sodium hydrogen sulphide. (64.2%) AEI MS: m/z = 487 (calcd. for $C_{32}H_{45}ON_3$ 487). IR (KBr): ν = 3473, 3379, 2921, 2851, 1622, 1600, 1578, 1505, 1242, 1089, 838, 813, 766, 722 cm^{-1}.

3c: This was synthesized as described above from

4-(4-nitrophenylazo)-1-tetradecyloxy-naphthalene and sodium hydrogen sulphide. (58.0%) AEI MS: m/z = 459 (calcd. for $C_{30}H_{41}ON_3$ 459). IR (KBr): *v* = 3460, 3367, 2919, 2851, 1618, 1599, 1577, 1506, 1243, 1090, 838, 816, 763, 722 cm^{-1}.

Trisazomelamines 4

The appropriate 4-(4-aminophenylazo)-1-alkoxy-naphthalene 3 (7.8mmol) was dissolved in dry ethyl methyl ketone. Cyanuric chloride (0.48g, 2.6mmol) and potassium carbonate (1.07g, 7.8mmol) were added to the stirred mixture. This mixture was heated and stirred for 10h at reflux under an argon atmosphere. The reaction mixture was cooled to room temperature and poured into ice/water (300ml). Subsequently, the mixture was filtered and washed with water. The slowly precipitating orange solid was obtained and dried in vacuum. The rude product was purified by flash column chromatography (silica gel, 200-300mesh) using dichloromethane/ethyl acetate (10:0.2) as eluent.

4a: It was prepared as described above from 3a. (54.0%) IR (KBr): *v*=3403, 2921, 2851, 1574, 1507, 1486, 1413, 1241, 1090, 841, 804, 765, 721 cm^{-1}; ^1H NMR ($CDCl_3$, 300MHz): δ = 8.2-7.5 (m, 30H, phenyl and nathphyl), 7.3 (s, 3H, NH), 3.9 (t, 6H, O-CH_2), 1.9-1.8 (m, 6H, CH_2), 1.3 (m, 90H, CH_2), 0.9 (t, 9H, CH_3) ppm; MALDI-TOF: m/z = 1622.51 (calcd. for $[C_{93}H_{118}O_3N_{12}+H]^+$ 1621.3).

4b: It was prepared as described above from 3b. (52.1%) IR (KBr):

v=3303, 2916, 2848, 1575, 1494, 1462, 1407, 1240, 1071, 881, 809, 766, 720 cm^{-1}; ^1H NMR ($CDCl_3$, 300MHz): δ = 8.3-7.6 (m, 30H, phenyl and nathphyl), 7.3 (s, 3H, NH), 3.8 (t, 6H, O-CH_2), 1.8-1.7 (m, 6H, CH_2), 1.3 (m, 78H, CH_2), 0.9 (t, 9H, CH_3) ppm; MALDI-TOF: m/z = 1538.3 (calcd. for $[C_{93}H_{118}O_3N_{12}+H]^+$ 1537.2).

4c: It was prepared as described above from 3c. (50.3%) IR (KBr): *v* = 3384, 2924, 2853, 1578, 1492, 1459, 1416, 1241, 1091, 839, 810, 765, 722 cm^{-1}; ^1H NMR ($CDCl_3$, 300MHz): δ = 8.0-7.4 (m, 30H, phenyl and nathphyl), 7.3 (s, 3H, NH), 3.6 (t, 6H, O-CH_2), 1.9-1.8 (m, 6H, CH_2), 1.3 (m, 66H,CH_2), 0.9 (t, 9H, CH_3) ppm; MALDI-TOF: m/z = 1453.9 (calcd. for $[C_{93}H_{118}O_3N_{12}+H]^+$ 1453.0).

The preliminary simulations were performed using the Hyperchem software package to model the structure of the compound 4a.

Reference:

1 D. Goldmann, D. Janietz, C. Schmidt, J. H. Wendorff, *Liquid Crystals*, 1998, **25**, 711-719.