Electronic Supplementary Material (ESI) for Chemical Communications

Supporting information:

Solvent-dependent amplification of chirality in assemblies of porphyrin trimers based on benzene tricarboxamide

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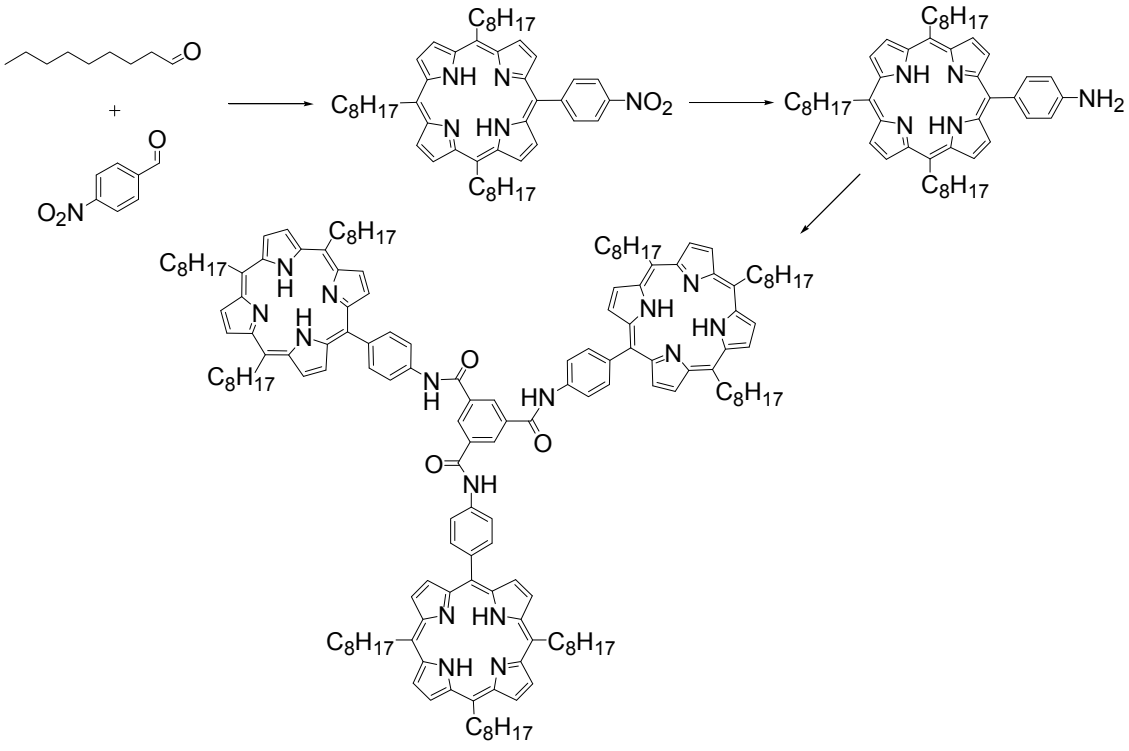
Contents:

1. Experimental procedures

All solvents and other chemicals were commercial products and used as received unless stated otherwise. Column chromatography was performed using ACROS silica gel (40–60 µm), BioRad BioBeads SX-1 were used for size-exclusion chromatography. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on Bruker DPX 200 (200 MHz) or Varian Unity Inova 400 (400 MHz) instruments. Chemical shifts are given in ppm with respect to tetramethylsilane (TMS) as internal standard. Infrared spectra were recorded on a ThermoMattson IR300 spectrometer equipped with a Harrick ATR unit and the compounds were measured as a solid or an oil. MALDI-TOF measurements were conducted on a Bruker Biflex III, with dithranol as the matrix. UV-Visible spectra were recorded on a Varian Cary 50 spectrometer and CD spectra on a Jasco 810 instrument equipped with a Peltier temperature control unit. Elemental analyses were carried out on a Carlo Erba 1180 instrument. (*S*)-Dihydrocitronellal was synthesized according to a literature procedure.[1]

2. Syntheses

Synthesis of ***3***



3

5,10,15-Tris-*meso*-*n*-octyl-20-*meso*-(4-nitrophenyl)porphyrin

0.38 g (2.5 mmol) of 4-nitrobenzaldehyde, 1.29 ml (1.6 g, 7.5 mmol) of *n*-nonylaldehyde and 0.7 ml (0.67 g, 10 mmol) of pyrrole were dissolved in 1 l of CH_2Cl_2. Under rigorous stirring 0.77 ml (1.18 g, 10 mmol) of TFA was added and the resulting solution colored yellow immediately. After 1.5 h the solution was completely black and 1.7 g (7.5 mmol) of DDQ was added and the mixture was allowed to stir for 1 h. Then 1.4 ml (1.0 g, 10 mmol) of triethylamine was added and the solvent was removed under reduced pressure. The resulting porphyrin mixture was purified and separated using column chromatography (silica, eluent: $CHCl_3$) giving 0.17 g (0.22 mmol, 9%) of a deep purple solid. ^{1}H NMR (400MHz, $CDCl_3$) δ 9.53 (d, 2H, C*H* β-pyrrole, J=4.8Hz), 9.50 (d, 2H, C*H* β-pyrrole, J=4.8Hz), 9.40 (d, 2H, C*H* β-pyrrole, J=4.8Hz), 8.66 (d, 2H, C*H* β-pyrrole, J=4.8Hz), 8.60 (d, 2H, C*H* ortho-Ph-NO_2, J=8.8 Hz), 8.32 (d, 2H, C*H* meta-Ph-NO_2, J=8.8Hz), 4.95 (m, 6H, CH_2), 2.51 (m, 6H, CH_2), 1.78 (m, 6H, CH_2), 1.52 (m, 6H, CH_2), 1.31 (m, 18H, CH_2), 0.88 (m, 9H, CH_3), -2.6 (s, 2H, N*H*);^{13}C NMR (50MHz $CDCl_3$) δ 150, 148, 135, 128 (broad), 122, 121, 120, 115, 39, 36, 32, 31, 30, 29, 23, 14; IR (cm^{-1}): 2923, 1515, 1342; UV-vis ($CHCl_3$) λ/nm (log(ε/$M^{-1}cm^{-1}$): 419.5 (5.4), 521.5 (4.1), 558 (3.9), 600.5 (3.6), 655.5 (3.7); MALDI-TOF m/z: 768 $(M)^+$.

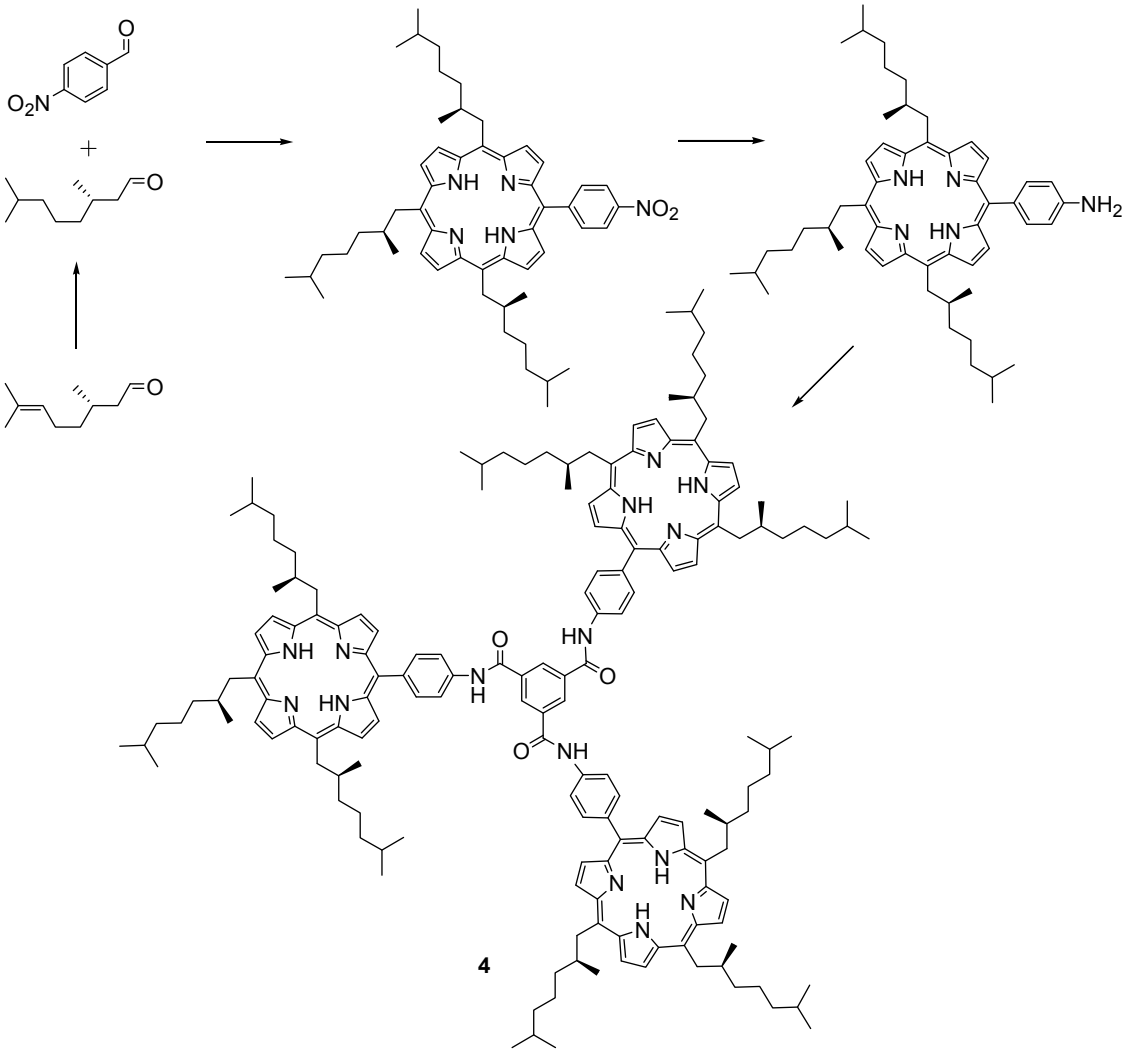
5,10,15-Tris-*meso*-*n*-octyl-20-*meso*-(4-aminophenyl) porphyrin

After bubbling HCl through 150 ml of Et_2O for 15 min, 96 mg (0.12 mmol) of 5,10,15-Tris-*meso*-*n*-octyl-20-*meso*-(4-nitrophenyl)porphyrin and 0.27 g of $SnCl_2.2H_2O$ were added and the resulting green mixture was stirred for 2 days. Then 100 ml of 3 M aqueous NaOH solution was added and the organic layer was washed with a sat. aqueous $NaHCO_3$ solution (3 × 50 ml) and brine (3 × 50 ml) and dried over $MgSO_4$. After evaporation of the solvent the product was purified by column chromatography (silica, eluent: toluene) giving 81 mg (0.11 mmol, 91%) of a purple solid. ^{1}H NMR (200MHz, $CDCl_3$) δ 9.45 (m, 4H, C*H* β-pyrrole), 9.35 (d, 2H, C*H* β-pyrrole, J=4.9Hz), 8.88 (d, 2H, C*H* β-pyrrole, J=4.9Hz), 7.92 (d, 2H, C*H* meta-Ph-NH_2, J=6.6 Hz), 7.02 (d, 2H, C*H* orto-Ph-NH_2, J=6.6Hz), 4.94 (m, 6H, CH_2), 3.97 (s, 2H, NH_2), 2.52 (m, 6H, CH_2), 1.79 (m, 6H, CH_2), 1.50 (m, 6H, CH_2), 1.30 (m, 18H, CH_2), 0.89 (m, 9H, CH_3), -2.6 (s, 2H, N*H*); ^{13}C NMR (50MHz, $CDCl_3$) δ 145.9, 135.4, 132.9, 130 (broad), 118.9, 118.7, 113.4, 38.8, 35.5, 32.0, 30.7, 29.7, 29.4, 22.7; MALDI-TOF m/z: 737 $(M)^+$.

Porphyrin trimer 3

A solution of 268 mg (0.36 mmol) of 5,10,15-tris-*meso*-*n*-octyl-20-*meso*-(4-aminophenyl) porphyrin and a few drops of pyridine in 25 ml of CH_2Cl_2 was cooled to 0 °C and 24 mg (0.090 mmol) of benzene-1,3,5-tricarbonyl trichloride was added. The reaction mixture was stirred and left to warm up to rt. After 2 h the volume of the slightly green/purple solution was reduced under vacuum and the product was purified by column chromatography (silica, eluent: 1% MeOH and 1% Et_3N in $CHCl_3$). After two size exclusion columns (eluent: toluene) the compound was dissolved in $CHCl_3$ and precipitated in MeOH to yield 143 mg (0.060 mmol, 67%) of **3** as a purple solid. ^{1}H NMR (400MHz, Toluene-*d8* DMSO-*d6*) δ 11.50 (s, 3H, N*H*-amide), 9.70 (s, 3H, C*H*-benzene core), 9.45 (d, 6H, C*H* β-pyrrole, J=4.6 Hz), 9.33 (d, 6H, C*H* β-pyrrole, J=4.6 Hz), 9.0 (m, 18H, C*H*β-pyrrole + C*H*-ortho-NH), 8.33 (d, 6H, C*H*-*meta*-NH), 4.93 (m, 6H, CH_2), 4.52 (br, 12H, CH_2), 2.58 (m, 6H, CH_2), 2.25 (m, 12H, CH_2), 1.8 (m, 6H, CH_2), 1.48 (m, 30H, CH_2), 1.3 (m, 54H, CH_2), 0.85 (t, 27H, CH_3, J=7.1Hz), -2.22 (s, 6H, N*H*); MALDI-TOF m/z: 2369 $(M)^+$.

Synthesis of ***4***



5,10,15-Tris-*meso*-((*S*)-2,6-dimethylheptyl)-20-*meso*-(4-nitrophenyl) porphyrin

This compound was synthesized from (*S*)-dihydrocitronellal as described for 5,10,15-Tris-*meso*-*n*-octyl-20-*meso*-(4-nitrophenyl)porphyrin. The resulting porphyrin mixture was purified and separated by column chromatography (eluent: n-heptane:$CHCl_3$ 1:1) giving 0.8 g (0.99 mmol, 16%) of a deep purple solid. ^{1}H NMR (400MHz, $CDCl_3$) δ 9.53 (d, 2H, C*H* β-pyrrole, 4.8Hz), 9.50 (d, 2H, C*H* β-pyrrole, 4.8Hz), 9.40 (d, 2H, C*H* β-pyrrole, J=4.8Hz), 8.67 (d, 2H, C*H* β-pyrrole, J=4.8Hz), 8.60 (d, 2H, C*H* ortho-Ph-NO_2, J=8.4 Hz), 8.33 (d, 2H, C*H* meta-Ph-NO_2, J=8.4Hz), 5.0 (m, 3H, CH_2), 4.7 (m, 3H, CH_2), 2.60 (m, 3H, C*H*), 1.61 (m, 12H, CH_2), 1.42 (m, 3H, C*H*), 1.14 (m, 6H, CH_2), 1.02 (t, 9H, CH_3, J=6.8Hz) , 0.84 (m, 18H, CH_3), -2.6 (s, 2H, N*H*); FT-IR: 2952, 2923, 2866, 1519, 1344 cm^{-1}; ^{13}C NMR (50MHz $CDCl_3$) δ 150, 148, 135, 129 (broad), 121, 119, 118, 115, 42.8, 42.4, 41.9, 39.4, 38.4, 29.9, 28.1, 25.4, 22.9, 22.7, 20.4; MALDI-TOF m/z: 810 $(M)^+$.

5,10,15-Tris-*meso*-((*S*)-2,6-dimethylheptyl)-20-meso-(4-aminophenyl) porphyrin

This compound was synthesized from 0.75 g (0.93 mmol) 5,10,15-Tris-*meso*-((*S*)-2,6-dimethylheptyl)-20-*meso*-(4-nitrophenyl) porphyrin as described for 5,10,15-Tris-*meso*-*n*-octyl-20-*meso*-(4-aminophenyl) porphyrin, but by reducing the reaction time to 1 day, resulting in 470 mg (0.60 mmol, 65%) of a purple solid. ^{1}H NMR (200MHz, $CDCl_3$) δ 9.47 (m, 4H, C*H* β-pyrrole), 9.35 (d, 2H, C*H* β-pyrrole, J=4.9Hz), 8.88 (d, 2H, C*H* β-pyrrole, J=4.9Hz), 7.93 (d, 2H, C*H* meta-Ph-NH_2, J=8 Hz), 7.03 (d, 2H, C*H* orto-Ph-NH_2, J=8Hz), 5.04 (m, 3H, CH_2), 4.72 (m, 3H, CH_2), 3.99 (s, 2H, NH_2), 2.60 (m, 3H, C*H*), 1.5 (m, 15H, CH_2 and C*H*), 1.14 (m, 6H, CH_2), 1.01 (m, 18H, CH_3), 0.89 (m, 9H, CH_3), -2.6 (s, 2H, N*H*); ^{13}C NMR (50MHz $CDCl_3$) δ 145.9, 135.5, 133.0, 128 (broad), 118.7, 117.7, 113.4, 42.6, 42.3, 41.8, 41.7, 39.4, 38.3, 31.0, 28.1, 25.3, 22.8, 22.6, 20.4; MALDI-TOF m/z: 780.

Chiral porphyrin trimer 6

This compound was synthesized from 0.46 g (0.590 mmol) of 5,10,15-Tris-*meso*-((*S*)-2,6-dimethylheptyl)-20-meso-(4-aminophenyl) porphyrin as described for **4**. After the SEC the product was dissolved in $CHCl_3$ acidified with concentrated HCl (1 ml of concentrated aqueous HCl mixed with 200 ml of $CHCl_3$) and the protonated product was precipitated in n-heptane. The green solid was filtered off and redissolved in $CHCl_3$. The solution was added to MeOH with Et_3N and the product precipitated out as a purple solid. This cycle was repeated 5 times to yield 24 mg (49%) of **6**. ^{1}H NMR (400MHz, $CDCl_3$ + DMSO-*d6*) δ 10.2 (s, 3H, N*H*-amide), 9.53 (m, 12H, C*H* β-pyrrole), 9.40 (d, 6H, C*H* β-pyrrole, J=4.6Hz), 9.23 (s, 3H, C*H*-central benzene), 8.94 (d, 6H, C*H* β-pyrrole, J=4.6Hz), 8.36 (d, 6H, C*H*-*ortho*-NH, J=7.3Hz), 8.27 (d, 6H, C*H*-*meta*-NH, J=7.3Hz), 5.0 (m, 9H, CH_2), 4.7 (m, 9H, CH_2), 2.58 (m, 9H, C*H*), 1.6(m, 45H, alkyl), 1.2 (m, 18H, alkyl), 1.0 (m, 27H, CH_3), 0.8 (m, 54H, CH_3), -2.63 (s, 6H, N*H*); ^{13}C NMR (50MHz $CDCl_3$) δ 165.3, 138.9, 138.3, 135.0 (broad), 118.8, 118.3, 118.0, 117.6, 42.2, 41.8, 41.7, 41.3, 40.9, 40.5, 40.1, 39.7, 39.3, 38.8, 38.2, 29.7, 28.0, 25.3, 22.7, 22.6, 20.3; Elemental analysis: calc for $C_{168}H_{219}N_{15}O_3.6H_2O$: C 77.47, H 8.94, N 8.07 found: C 77.15, H 8.81, N 7.85; MALDI-TOF m/z: 2495 $(M)^+$.

Reference

1. L. J. Dolby and M. Debono, *J. Org. Chem*. 1964, **29**, 2306.