

## Supporting Information for **Energy Transfer in Chiral Co-Assemblies of Triple Hydrogen-Bonded Oligo(*p*-phenylene vinylene)s and Porphyrin**

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**General methods.**  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra were recorded on a Varian Gemini (300 MHz for  $^1\text{H}$ -NMR and 75 MHz for  $^{13}\text{C}$ -NMR) or a Varian Mercury (400 MHz for  $^1\text{H}$ -NMR and 100 MHz for  $^{13}\text{C}$ -NMR). Unless otherwise indicated, chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) at room temperature using deuterated chloroform as a solvent and internal standard. Abbreviations used for splitting patterns are s = singlet, d = doublet, dd = double doublet, t = triplet, dt = double triplet, q = quartet, quint = quintet, m = multiplet and br = broad. IR spectra were recorded on a Perkin Elmer 1600 FT-IR (UATR). Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) was performed on a PerSeptive Biosystems Voyager-DE PRO spectrometer using an  $\alpha$ -cyano-4-hydroxycinnamic acid matrix. Gas chromatography mass spectrometry (GC-MS) was performed on a Shimadzu GCMS QP5000. Elemental analyses were carried out on a Perkin Elmer 2400. Melting points were determined using a Jenaval polarization microscope with crossed polarizers equipped with a Linkham THMS 600 heating device. Analytical thin layer chromatography (TLC) was performed on Kieselgel F-254 precoated silica plates. Column chromatography was carried out on Merck silica gel 60 (70-230 mesh or 230-400 mesh ASTM). Preparative size exclusion chromatography was performed using Bio-Rad Bio-Beads S-X1 or S-X3 (200-400 mesh). UV/vis spectra were recorded on either a Perkin Elmer Lambda 40P or a Perkin Elmer Lambda 900 UV/vis/NIR spectrometer, CD spectra on a JASCO J-600 spectropolarimeter (sensitivity, time constant, and scan-rate were chosen appropriately), fluorescence spectra on either a Perkin Elmer LS-50B luminescence spectrometer or an Edinburgh Instrument FS920 double-monochromator spectrometer with a Peltier-cooled red-sensitive photomultiplier. A PTC-348WI Peltier type temperature control system was used to measure temperature variable CD spectra. A Peltier Temperature Programmer model 1 (PTP-1) was used to measure temperature variable UV/vis and fluorescence spectra.

**Materials.** All solvents were of AR quality. Other reagents used were purchased from Acros and Aldrich and have been used without further purification. DMF was dried over 4Å molsieves. Bio-Beads S-X1 and S-X3 were obtained from Bio-Rad Laboratories.

The synthesis of **OPV3T** and **OPV4T** has been reported in: P. Jonkheijm, F. J. M. Hoeben, R. Kleppinger, J. van Herrikhuizen, A. P. H. J. Schenning and E. W. Meijer, *J. Am. Chem. Soc.*, 2003, **125**, 15941-15949 and: A. P. H. J. Schenning, P. Jonkheijm, E. Peeters and E. W. Meijer, *J. Am. Chem. Soc.* 2001, **123**, 409-416, respectively.

### **Dodecylcyanuric acid (CN-1) and bisdodecylcyanuric acid (CN-2)**

Cyanuric acid (3.1 g, 24 mmol) and ground  $\text{K}_2\text{CO}_3$  (0.83 g, 6.0 mmol) were dissolved in DMSO (100 mL) and the mixture was stirred for 30 min. After the addition of dodecylbromide (1.5 g, 6.0 mmol, 0.25 eq) the solution was heated to 60 °C and stirred for 16 h. After cooling down to room temperature the mixture was partitioned between diethylether and saturated  $\text{KHSO}_4$  and the organic fraction was washed with brine (3×50 mL). The collected organic fractions were dried over  $\text{Na}_2\text{SO}_4$ , filtrated and the solvent was evaporated *in vacuo*. Recrystallisation from hexane yielded a mixture of **CN-1** and **CN-2**. By extensive rinsing with hexane this mixture could be separated into pure **CN-2** (200 mg, 14%) and pure **CN-1** (750 mg, 42%), of which the latter is almost insoluble in hexane.

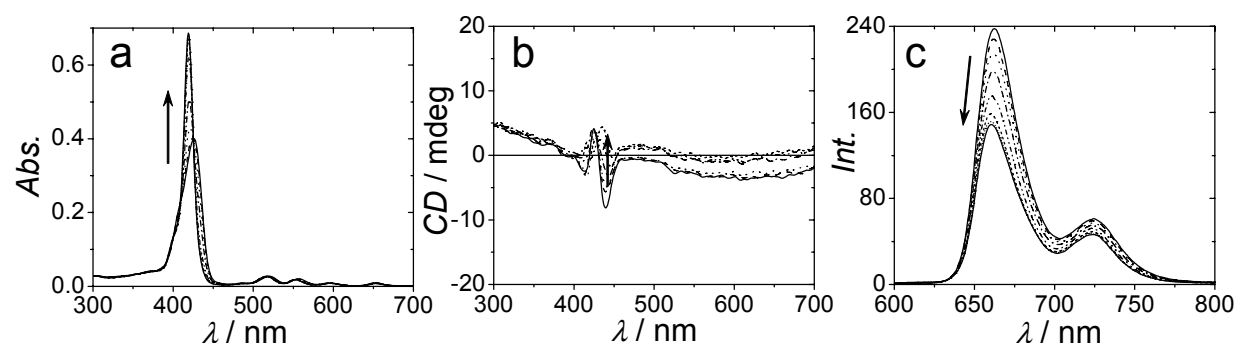
**CN-1:**  $^1\text{H}$ -NMR (ppm,  $d_6$ -DMSO):  $\delta$  0.83 (t, 3H,  $\text{CH}_3$ ), 1.22 (m, 18H,  $(\text{CH}_2)_9$ ), 1.46 (m, 2H,  $\text{NCH}_2\text{CH}_2$ ), 3.58 (t, 2H,  $\text{NCH}_2$ ), 11.34 (br, 2H, NH).  $^{13}\text{C}$ -NMR (ppm,  $d_6$ -DMSO):  $\delta$  14.6, 22.8, 26.8, 28.0, 29.37, 29.39, 29.6, 29.69, 29.72, 41.0, 149.3, 150.5. IR (UATR):  $\nu$  ( $\text{cm}^{-1}$ ) = 3207, 3088, 2956, 2915, 2849, 1773, 1752, 1674, 1456, 1409, 1378, 1073, 1038, 813, 790, 756, 738, 721, 684. GC/MS (MW=297.40):  $m/z$  = 130.1 [ $\text{M}-\text{C}_{12}\text{H}_{25}+2\text{H}$ ] $^+$ . Anal. Calcd. for  $\text{C}_{15}\text{H}_{27}\text{N}_3\text{O}_3$  (%): C, 60.58; H, 9.15; N, 14.13. Found: C, 58.31; H, 8.65; N, 13.18. mp = 39.0 °C.

**CN-2:**  $^1\text{H}$ -NMR:  $\delta$  0.88 (t, 6H,  $\text{CH}_3$ ), 1.25 (m, 36H,  $(\text{CH}_2)_9$ ), 1.62 (m, 4H,  $\text{NCH}_2\text{CH}_2$ ), 3.84 (t, 4H,  $\text{NCH}_2$ ), 7.93 (br, 1H, NH).  $^{13}\text{C}$ -NMR:  $\delta$  14.2, 22.8, 26.7, 27.9, 29.3, 29.4, 29.58, 29.63, 29.7, 32.0, 42.6, 148.8, 149.7. IR (UATR):  $\nu$  ( $\text{cm}^{-1}$ ) = 3221, 3118, 2957, 2919, 2850, 1742, 1659, 1479, 1468, 1443, 1411, 1373, 1334, 793, 759, 738, 722, 676. GC/MS (MW=465.72):  $m/z$  = 298.4 [ $\text{M}-\text{C}_{12}\text{H}_{25}+2\text{H}$ ] $^+$ . Anal. Calcd. for  $\text{C}_{27}\text{H}_{51}\text{N}_3\text{O}_3$  (%): C, 69.63; H, 11.04; N, 9.02. Found: C, 69.32; H, 10.83; N, 8.93. mp = 85.5 °C.

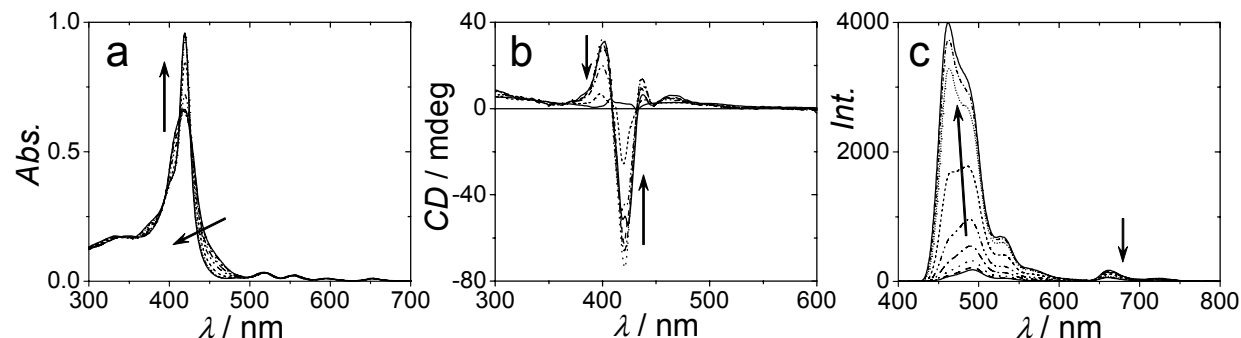
### **5-(4-(3-isocyanylpropyloxy)phenyl)-10,15,20-tris(4-((3*S*)-3,7-dimethyloctyloxy)phenyl)porphyrin (CN-Por)**

Cyanuric acid (218 mg, 1.69 mmol) and ground  $\text{K}_2\text{CO}_3$  (54 mg, 0.39 mmol) were dissolved in anhydrous DMF (15 mL) at 80 °C. After stirring for 20 min, a solution of 5-(4-(3-bromopropyloxy)phenyl)-10,15,20-tris(4-((3*S*)-3,7-dimethyloctyloxy)phenyl)porphyrin (257 mg, 0.20 mmol, 0.12 eq, R.G. Little, *J. Heterocycl. Chem.* 1978, **15**, 203-208) in anhydrous DMF (20 mL) was added dropwise and the resulting mixture was stirred at 80 °C for

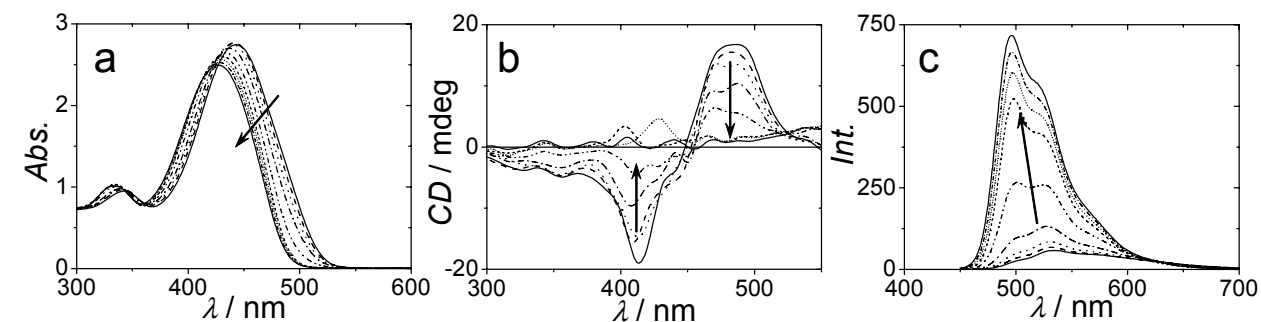
16 h. After cooling to room temperature the solvent was evaporated *in vacuo* and the solid was redissolved in dichloromethane (25 mL). The organic phase was washed with saturated NaHSO<sub>4</sub> (10 mL) and water (3×10 mL), after which the collected aqueous phases were extracted with dichloromethane (15 mL). The collected organic fractions were evaporated to dryness and column chromatography (pentane/dichloromethane 1:1, then 1% MeOH in dichloromethane) yielded pure **CN-Por** (151 mg, 0.12 mmol, 56%). <sup>1</sup>H-NMR: δ -2.50 (s, 2H, NH), 0.98 (d, 18H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.11 (d, 9H, CHCH<sub>3</sub>), 1.30-1.50 (m, 18H, CH<sub>2</sub>), 1.65 (m, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.80-1.88 (m, 6H, OCH<sub>2</sub>CHH, CHCH<sub>3</sub>), 2.04 (m, 3H, OCH<sub>2</sub>CHH), 2.21 (quint, 2H, NCH<sub>2</sub>CH<sub>2</sub>), 4.15 (m, 4H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N, NCH<sub>2</sub>), 4.28 (m, 6H, OCH<sub>2</sub>), 7.09 (d, 2H, ArH), 7.24 (d, 2H, ArH), 7.28 (d, 4H, ArH), 8.04 (d, 2H, ArH), 8.10 (d, 2H, ArH), 8.13 (d, 4H, ArH), 8.71 (br, 2H, CONH), 8.85 (d, 2H, β-pyrrole), 8.90 (s, 6H, β-pyrrole). <sup>13</sup>C-NMR: δ 19.8, 22.7, 24.8, 27.5, 28.0, 30.1, 36.4, 37.4, 39.4, 39.9, 65.8, 66.6, 112.6, 112.67, 112.71, 119.6, 119.9, 134.4, 134.8, 135.6, 147.6, 148.9, 158.2, 158.9. IR (UATR): ν (cm<sup>-1</sup>) = 3317, 3210, 3097, 2952, 2924, 2868, 1746, 1694, 1606, 1573, 1508, 1466, 1410, 1399, 1381, 1365, 1350, 1283, 1240, 1173, 1107, 1046, 1020, 982, 965, 878, 840, 798, 762, 732, 709, 668. MALDI-TOF MS (MW=1268.69): m/z = 1269.81 [M]<sup>+</sup>. Anal. Calcd. for C<sub>80</sub>H<sub>97</sub>N<sub>7</sub>O<sub>7</sub> (%): C, 75.74; H, 7.71; N, 7.73. Found: C, 74.88; H, 7.54; N, 7.78. mp = 191.0 °C.



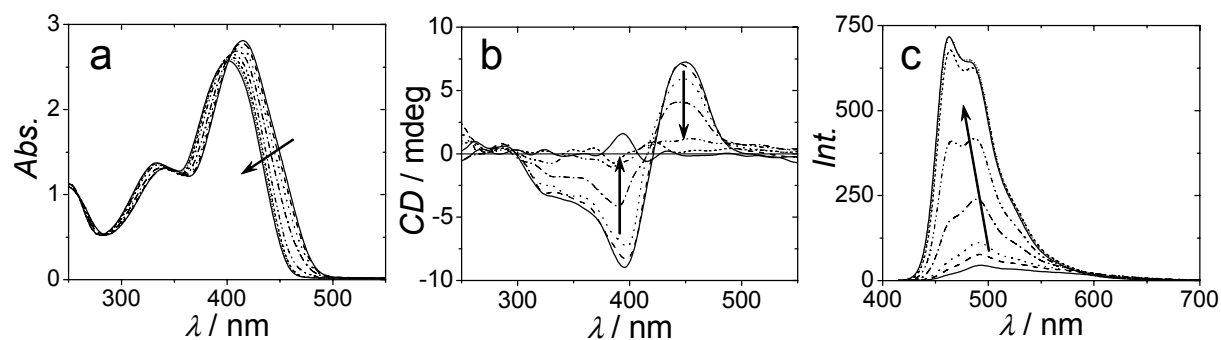
**Fig. S1** Temperature-dependent (a) UV/Vis (b) CD and (c) fluorescence studies on **CN-Por** in MCH ( $2 \times 10^{-5}$  M). The arrows indicate a temperature increase from (a, c) 0 °C to 80 °C and to (b) 0 °C to 60 °C. The transition temperature for this system is 42 °C.



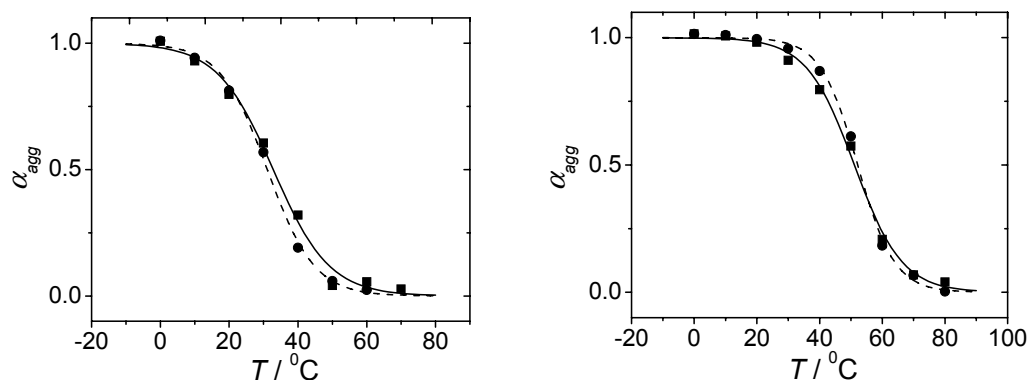
**Fig. S2** Temperature-dependent (a) UV/Vis (b) CD and (c) fluorescence studies on 1:2 **CN-Por/OPV3T** in MCH ( $[OPV3T] = 4 \times 10^{-5}$  M). The arrows indicate a temperature increase from (a, c) 0 °C to 80 °C and from (b) 0 °C to 60 °C. The transition temperature for this system is 48 °C.



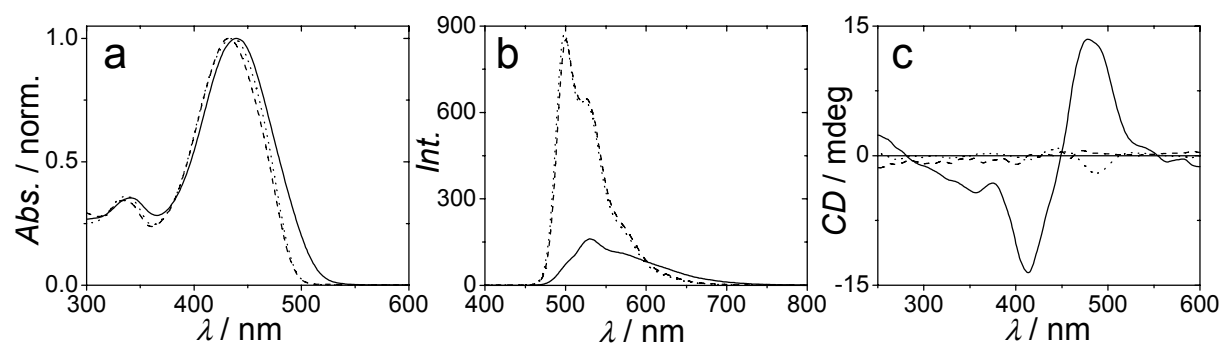
**Fig. S3** Temperature-dependent (a) UV/Vis (b) CD and (c) fluorescence studies on 1:2 **CN-1/OPV4T** in MCH ( $[OPV4T] = 4 \times 10^{-5}$  M). The arrows indicate a temperature increase from 0 °C to 80 °C. The transition temperature for this system is 33 °C.



**Fig. S4.** Temperature-dependent (a) UV/Vis (b) CD and (c) fluorescence studies on 1:2 CN-1/OPV3T in MCH ( $[\text{OPV3T}] = 6 \times 10^{-5} \text{ M}$ ). The arrows indicate a temperature change from (a, c) 0 °C to 70 °C and from (b) 0 °C to 60 °C. The transition temperature for this system is 31 °C.



**Fig. S5.** Transition curves in MCH for (left) 1:2 CN-1/OPVnT; OPV4T (squares, solid line) and OPV3T (rounds, dashed line) and (right) 1:2 CN-Por/OPVnT; OPV4T (squares, solid line) and OPV3T (rounds, dashed line). These results are based on temperature-dependent (left) CD spectroscopy and (right) fluorescence measurements. Lines to guide the eye.



**Fig. S6** Comparison of (a) UV/vis (b) CD and (c) fluorescence curves for OPV4T (dotted line), 1:1 CN-2/OPV4T (dashed line) and 1:2 CN-1/OPV4T (solid line) in MCH at room temperature ( $[\text{OPV4T}] = 4 \times 10^{-5} \text{ M}$  in all cases).

**Fig. S7** Fluorescence quenching behaviour for the energy transfer experiment depicted in Fig. 4b. The initial quenching is fitted with the Stern-Volmer equation.

