

Supporting Information

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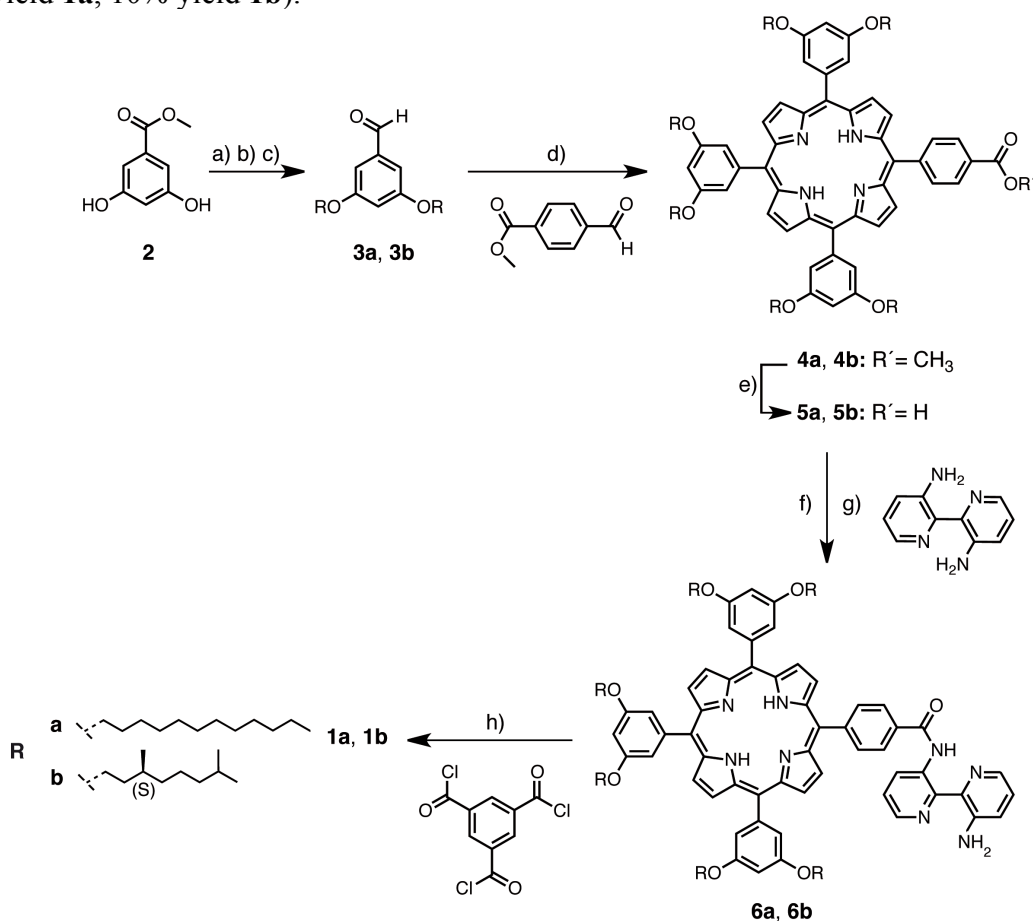
Materials and methods

Reagents were purchased from Sigma-Aldrich, Acros or Fluka and were used without further purification. All solvents were dried by means of standard protocols with sodium and benzophenone as indicator. Column chromatography was carried out on silica gel 60 (Fluka, 40-63 μm). IR spectra were recorded on a Bruker Tensor 27 spectrometer equipped with ATR and reported as wavenumbers in cm^{-1} with band intensities indicated as s (strong), m (medium), w (weak), br (broad). ^1H and ^{13}C NMR spectra were recorded either on a Bruker Avance-300, a Varian Oxford AS 500 MHz or a Bruker Avance AMX-700 and reported as chemical shifts (δ) in ppm relative to tetramethylsilane ($\delta = 0$) at room temperature unless other temperature was indicated. Spin multiplicities are reported as a singlet (s), broad singlet (br s), doublet (d), triplet (t) and quartet (q) with proton-proton coupling constants (J) given in Hz, or multiplet (m). Matrix-assisted laser desorption ionization (MALDI) mass spectrometry (MS) was performed on a Bruker Ultraflex spectrometer using ditranol as matrix. Absorption spectra were recorded with a Varian Cary 50 and 5000 spectrophotometer and UV-3600 Shimadzu UV-vis-NIR Spectrophotometer. CD and fluorescence measurements were carried out on a JASCO J-815 DC spectrometer. Dynamic light scattering measurements were performed on a Malvern mV Zetasizer equipped with an 830 nm laser and processed with a digital correlator that computed intensity-intensity autocorrelation of the scattered light. Measurements were carried out in a 1-cm path-length quartz cell maintained at 298 K.

Scanning Electron Microscopy (SEM): SEM images were acquired using a JEOL JSM 6335F microscope working at 10 kV.

Synthesis

The synthesis of discotics **1a** and **1b** was carried out following a linear strategy (Scheme S1). Achiral and chiral **3a** and **3b** were synthesized in excellent yields (92%) from commercially available methyl 3,5-dihydroxybenzoate (**2**) and respective tosylated alkylating reagents (TsOR), followed by exhaustive reduction to alcohol with LiAlH₄ and selective oxidation to aldehyde with pyridinium chlorochromate (PCC). Condensation of **3a/3b**, methyl 4-formylbenzoate (**7**) and pyrrole afforded porphyrins **4a/4b** in 20% yield. Quantitative saponification of **4a/4b** with KOH and subsequent acyl chloride coupling with 3,3'-diamino-2,2'-bipyridine (**8**) allowed the preparation of **6a/6b** in reasonable yields (74%). Finally, **1a/1b** were obtained via non-optimized coupling conditions between **6a/6b** and commercially available trimesoyl chloride (**9**) (15% yield **1a**, 10% yield **1b**).



Scheme S1. Synthetic route to **1a** and **1b**. Reagents and conditions: a) TsOR, KOH, butanone, Δ , 16h, 98%. b) LiAlH₄, THF, 2h, 98%. c) PCC, DCM, 40 °C, 16h, 96%. d) Pyrrole, Chloranil, DCM, TFA, 16h, 20%. e) KOH, Δ , 16h, 99%. f) Oxalyl chloride, DMF, DCM. g) DCM, TEA, 62%. h) DCM, TEA, 15% (**1a**) and 10% (**1b**).

3,5-((3*S*),7-dimethyl)octyloxybenzaldehyde (**3b**)

To a solution of methyl 3,5-((3*S*),7-dimethyl)octyloxybenzoate (0.5 g, 1 mmol) in dry ether (20 mL) at 0 °C under argon atmosphere, a solution of LiAlH₄ 1 M (5 mL, 5 mmol) was added. This mixture was stirred at room temperature for 2 h. After this time, isopropanol (15 mL) and HCl 1 M was added to neutralize. Then, the resulting mixture was extracted with CH₂Cl₂ (3 x 20 mL) and the organic phase was dried over Na₂SO₄, filtered and the solvent was removed under reduced pressure giving rise to 3,5-((3*S*),7-dimethyl)octyloxybenzyl alcohol. The resulting alcohol (0.42 g, 1 mmol) was oxidized

without further purification in CH₂Cl₂ (40 mL) by addition of pyridinium chlorochromate (0.63 g, 3 mmol). The solution was stirred to reflux for 16 hours. Then, the solvent was removed under reduced pressure and the product was obtained by silica gel column chromatography using a mixture of hexane: CH₂Cl₂ (3:1) as eluent. The product was obtained as a white oil (0.41, 96%). ¹H NMR (200 MHz, CDCl₃): δ= 9.89 (s, 1H), 6.99 (d, *J* = 2.3 Hz, 2H), 6.69 (t, *J* = 2.3 Hz, 1H), 4.02 (td, *J* = 6.4, 1.2 Hz, 4H), 1.94 – 1.71 (m, 2H), 1.68 – 1.51 (m, 4H), 1.59 – 1.03 (m, 12H), 0.90 (dd, *J* = 14.6, 6.4 Hz, 28H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ= 192.4, 168.1, 138.3, 106.1, 67.2, 39.62, 37.64, 36.46, 33.4, 32.4, 27.4, 22.3 ppm; MALDI-TOF MS: *m/z*: calcd: 418.33; found: 418.35 (M).

5,10,15-Tris-meso-(3,5-dodecyloxyphenyl)-20-meso-(4-metoxycarbonylphenyl)porphyrin 4a:

3a (1.04 g, 2.21 mmol)¹ or **3b** (0.99 g, 2.21 mmol), methyl 4-formylbenzoate (0.12 g, 0.74 mmol) and pyrrole (0.02 g, 2.96 mmol, 0.02 mL) were dissolved in CH₂Cl₂ (350 mL). The mixture was stirred and deoxygenated for 1 h. Under rigorous stirring, TFA (0.2 g, 1.7 mmol, 0.3 mL) was added and the resulting solution was stirring covering to the light during 16 h. After this time, chloranil was added to the solution and heating until reflux for 2 h. Then, the solvent was removed under reduced pressure and the resulting porphyrin mixture was purified and separated using column chromatography (silica, eluent: Hexane:CH₂Cl₂ (2:1) giving a purple oil for **3a** (0.27 g, 20%) and **3b** (0.23 g, 20%). Compound **3a**: ¹H NMR (400 MHz, CDCl₃): δ= 9.09-8.96 (m, 6H), 8.79 (d, *J* = 6 Hz, 2H), 8.53 (d, *J* = 7.9 Hz, 2H), 8.35 (d, *J* = 7.9 Hz, 2H), 7.37 (d, *J* = 2.2 Hz, 6H), 6.89 (s, 3H), 4.15-4.08 (m, 15H), 1.84 (d, *J* = 7.1 Hz, 12H), 1.23 (s, 108H), 0.97 – 0.78 (m, 18H) -2.78 (s, 2H) ppm; ¹³C NMR (175 MHz, CDCl₃): δ= 167.4, 148.1, 147.8, 147.3, 146.8, 142.1, 135.2, 134.3, 133.6, 132.1, 130.9, 129.8, 129.5, 128.9, 127.1, 126.1, 122.3, 121.9, 120.1, 53.3, 33.4, 32.4, 27.4, 22.3, 13.9 ppm; MALDI-TOF MS: *m/z*: calcd: 1777.4; found: 1777.35 (M). Compound **3b**: ¹H NMR (400 MHz, CDCl₃): δ = 9.02-8.95 (m, 6H), 8.76 (d, *J* = 4.9 Hz, 2H), 8.48 – 8.26 (m, 4H), 7.37 (d, *J* = 2.2 Hz, 6H), 6.89 (d, *J* = 2.1 Hz, 3H), 4.25 – 4.05 (m, 15H), 1.92 – 0.65 (m, 114H) -2.75 (s, 2H) ppm; ¹³C NMR (175 MHz, CDCl₃): δ= 168.1, 149.1, 147.8, 147.2, 146.8, 142.1, 135.2, 135.1, 134.6, 133.1, 131.9, 129.3, 128.2, 127.5, 127.1, 126.5, 126.1, 122.3, 121.9, 120.1, 60.3, 34.3, 28.2, 23.4, 14.1 ppm; MALDI-TOF MS: *m/z*: calcd: 1609.16; found: 1610.16 (M)⁺.

5,10,15-Tris-meso-(3,5-dodecyloxyphenyl)-20-meso-(4-benzoic acid)porphyrin 5a:

To a solution of **4a** (0.2 g, 0.11 mmol) or **4b** (0.2 g, 0.12 mmol) in THF (10 mL), KOH (0.07 g, 1.2 mmol) was added and heated under refluxing for 16 h. Then, HCl was added to neutralize the solution. The mixtures were extracted with CH₂Cl₂ (3 x 20 mL) and the solvent was removed under reduced pressure. The resulting porphyrin was purified and separated using column chromatography (silica, eluent: CH₂Cl₂:CH₃OH (20:1) giving a purple oil for **5a** (0.17 g, 99%) and **5b** (0.19 g, 99%). Compound **5a**: ¹H NMR (400 MHz, CDCl₃): δ= 9.02 – 8.93 (m, 6H), 8.79 (d, *J* = 4.8 Hz, 2H), 8.53 (d, *J* = 8.0 Hz, 2H), 8.35 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 2.2 Hz, 6H), 6.89 (s, 3H), 4.11 (t, *J* = 6.6 Hz, 12H), 1.84 (d, *J* = 7.3 Hz, 12H), 1.23 (s, 108H), 0.98 – 0.70 (m, 18H) -2.81 (s, 2H) ppm; ¹³C NMR (175 MHz, CDCl₃): δ= 710.2, 150.3, 148.8, 147.3, 146.8, 142.1, 135.2, 134.3, 133.6, 131.9, 130.4, 129.8, 129.2, 128.9, 127.6, 126.1, 122.3, 121.9, 120.1, 33.4, 33.1, 30.4, 22.3, 13.5 ppm; MALDI-TOF MS: *m/z*: calcd: 1763.41; found: 1763.45 (M). Compound **5b**: ¹H NMR (400 MHz, CDCl₃): δ= 9.01 – 8.95 (m, 6H), 8.79 (d, *J* = 4.8 Hz, 2H), 8.52 (d, *J* = 8.1 Hz, 2H), 8.34 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* =

2.1 Hz, 6H), 6.89 (t, $J = 2.3$ Hz, 3H), 4.23 – 4.07 (m, 12H), 1.92 (td, $J = 11.7, 9.7, 5.0$ Hz, 12H), 1.79 – 1.59 (m, 12H), 1.50-1.05 (m, 36H), 0.95 (d, $J = 6.4$ Hz, 36H), 0.84 (d, $J = 6.4$ Hz, 18H) -2.82 (s, 2H) ppm; ^{13}C NMR (175 MHz, CDCl_3): $\delta = 170.1, 149.1, 147.8, 147.2, 146.8, 142.1, 135.2, 135.1, 134.6, 133.1, 132.9, 130.3, 128.2, 127.5, 127.1, 126.5, 126.1, 122.3, 121.7, 120.5, 34.3, 28.2, 23.4, 14.0$ ppm; MALDI-TOF MS: m/z : calcd: 1596.12; found: 1596.15 (M).

5,10,15-Tris-meso-(3,5-dodecyloxyphenyl)-20-meso-(4-benzoylamino)porphyrin-2,2'-bipyridine-3-amine 6a:

To a solution of compound **5a** (0.05 g, 0.03 mmol) or **5b** (0.05 g, 0.03 mmol) in distilled dichloromethane (5 mL), oxalyl chloride (0.015 mL, 0.02g, 0.13 mmol) and DMF (1 drop) were added. The mixture was stirring for 2 h at room temperature. The solution was concentrated in vacuo and dried thoroughly on a high vacuum line for 2h. Then, a solution of acid chloride in dichloromethane (10 mL) was added dropwise under an argon atmosphere to an ice-cooled solution of 2,2'-bipyridine-3,3'-diamine (0.015 g, 0.08 mmol) and triethylamine (TEA) (0.2 mL) in dry dichloromethane (5 mL). After complete addition, the ice bath was removed, and the mixture was stirred and covered the light at room temperature for 16 h. The mixture was concentrated in vacuo and purified by column chromatography (SiO_2 ; eluent: dichloromethane:hexane (10:1)). **6a** and **6b** was obtained as purple oil (0.04 g, 62%). Compound **6a**: ^1H NMR (400 MHz, CDCl_3): $\delta = 9.48$ (dd, $J = 8.4, 1.6$ Hz, 1H), 9.04 – 8.92 (m, 6H), 8.84 (d, $J = 4.9$ Hz, 2H), 8.52 – 8.33 (m, 5H), 8.18 (t, $J = 3.0$ Hz, 1H), 7.49 – 7.34 (m, 7H), 7.21 – 7.14 (m, 2H), 6.89 (s, 3H), 6.68 (s, 2H), 4.11 (t, $J = 6.6$ Hz, 12H), 1.84 (d, $J = 7.3$ Hz, 12H), 1.23 (s, 108H), 0.98 – 0.70 (m, 18H) -2.83 (s, 2H) ppm; ^{13}C NMR (175 MHz, CDCl_3): $\delta = 165.5, 158.2, 143.6, 142.7, 141.3, 134.2, 132.1, 127.6, 124.8, 123.4, 77.2, 76.8, 68.4, 31.9, 30.7, 30.2, 29.9, 29.7, 29.6, 26.7, 25.3, 22.6, 14.2$ ppm; MALDI-TOF MS: m/z : calcd: 1931.42; found: 1931.41 (M). Compound **6b**: ^1H NMR (400 MHz, CDCl_3): $\delta = 9.48$ (dd, $J = 8.4, 1.6$ Hz, 1H), 9.04 – 8.92 (m, 6H), 8.84 (d, $J = 4.9$ Hz, 2H), 8.52 – 8.33 (m, 5H), 8.18 (t, $J = 3.0$ Hz, 1H), 7.49 – 7.34 (m, 7H), 7.21 – 7.14 (m, 2H), 6.89 (s, 3H), 6.68 (s, 2H), 4.23 – 4.07 (m, 12H), 1.92 (td, $J = 11.7, 9.7, 5.0$ Hz, 12H), 1.79 – 1.59 (m, 12H), 1.50-1.05 (m, 36H), 0.95 (d, $J = 6.4$ Hz, 36H), 0.84 (d, $J = 6.4$ Hz, 18H) -2.82 (s, 2H) ppm; ^{13}C NMR (175 MHz, CDCl_3): $\delta = 163.1, 157.5, 142.6, 140.5, 134.5, 132.1, 125.8, 124.8, 124.4, 120.1, 77.2, 76.8, 68.4, 67.2, 66.8, 66.3, 31.8, 29.6, 26.1, 26.0, 24.5, 24.4, 23.5, 22.5, 13.24$ ppm; MALDI-TOF MS: m/z : calcd: 1763.25; found: 1763.22 (M).

N,N',N''-Tris{[3(3'-5,10,15-Tris-meso-(3,5-dodecyloxyphenyl)-20-meso-(4-benzoylamino)porphyrin-2,2'-bipyridyl)]benzene-1,3,5-tricarbanamide (1a):

A solution of 1,3,5-benzenetricarbonyl trichloride (0.008 g, 0.03 mmol) in dry CH_2Cl_2 was added dropwise at 0°C under an argon atmosphere to a solution of **5a** (0.173 g, 0.09 mmol) or **5b** (0.158 g, 0.09 mmol) and TEA (0.3 mL). The mixture was covered and stirred until room temperature was reached. The mixture was concentrated in vacuo and purified by column chromatography (SiO_2 ; eluent: dichloromethane:hexane (50:1)). **1a** (0.026 g, 15%) and **1b** (0.016 g, 10%) were obtained as purple oil. Compound **1a**: ^1H NMR (400 MHz, CDCl_3): $\delta = 15.76$ (s, 3H), 15.23 (s, 3H), 9.80 – 9.69 (m, 6H), 9.43 (s, 3H), 9.23 (s, 3H), 9.06-9.03 (m, 18H), 8.90 (d, $J = 4.7$ Hz, 6H), 8.70 (s, 3H), 8.52 (dt, $J = 55.3, 7.0$ Hz, 12H), 7.70 (ddd, $J = 48.1, 8.5, 4.7$ Hz, 6H), 7.42 (d, $J = 5.3$ Hz, 18H), 6.93 (s, 9H), 4.15 (t, $J = 6.9$ Hz, 36H), 1.89 (qq, $J = 10.3, 6.6$ Hz, 36H), 1.53 (dq, $J = 15.1, 7.8, 6.2$ Hz, 36H), 1.44 – 1.01 (m, 144H), 0.88 (ddt, $J = 25.1, 17.6, 8.6$ Hz, 54H), -2.76 (s, 6H) ppm; ^{13}C NMR (175 MHz, CDCl_3): $\delta = 166.5, 164.2, 158.2, 141.6, 140.7,$

134.5, 130.1, 125.8, 124.8, 124.4, 114.42, 100.9, 77.2, 77.0, 76.8, 68.4, 31.9, 30.7, 30.2, 29.9, 29.7, 29.6, 29.4, 29.2, 28.9, 26.7, 26.1, 25.3, 22.6, 14.2 ppm; MALDI-TOF MS: m/z: calcd: 5954.22; found: 5956.17 (M). Compound **1b**: ^1H NMR (400 MHz, CDCl_3): δ = 15.71 (s, 3H), 15.16 (s, 3H), 9.80 – 9.69 (m, 6H), 9.43 (s, 3H), 9.19 (s, 3H), 9.06-9.03 (m, 18H), 8.86 (d, J = 4.7 Hz, 6H), 8.70 (s, 3H), 8.52 (d, J = 7.2 Hz, 6H), 8.45 (d, J = 7.2 Hz, 6H), 7.70 (ddd, J = 48.1, 8.5, 4.7 Hz, 6H), 7.39 (d, J = 5.3 Hz, 18H), 6.93 (s, 9H), 4.15 (t, J = 6.9 Hz, 36H), 2.39 – 2.15 (m, 36H), 2.07 – 1.83 (m, 18H), 1.56-1.25 (m, 126H), 0.96 (d, J = 6.0 Hz, 54H), 0.85 (dd, J = 14.1, 6.8 Hz, 108H), -2.76 (s, 6H) ppm; ^{13}C NMR (175 MHz, CDCl_3): δ = 165.8, 164.3, 158.5, 141.6, 140.7, 134.5, 130.1, 125.8, 124.8, 124.4, 120.1, 114.4, 100.9, 77.2, 77.0, 76.8, 68.4, 67.2, 66.8, 66.3, 31.8, 29.6, 26.1, 26.0, 24.5, 24.4, 24.0, 22.5, 13.4 ppm; MALDI-TOF MS: m/z: calcd: 5445.60; found: 5445.95. (M).

Supplementary Figures

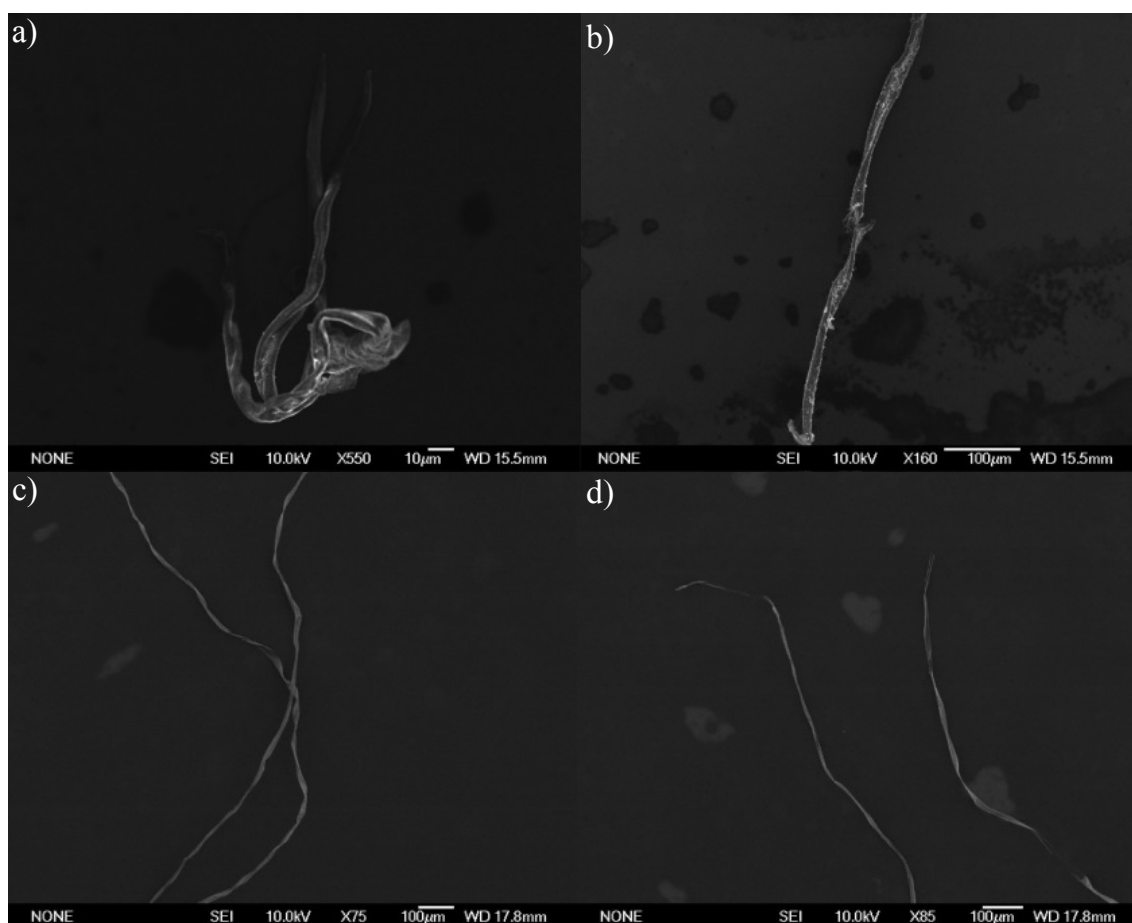


Figure S1. SEM images for **1b** (a, b) and **1a** (c, d) (1mg/ml, n-heptane)

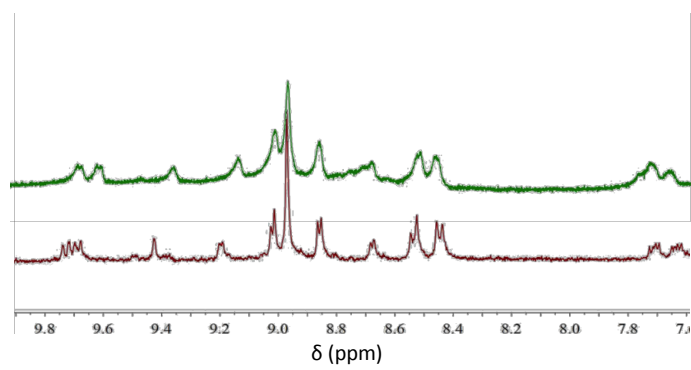
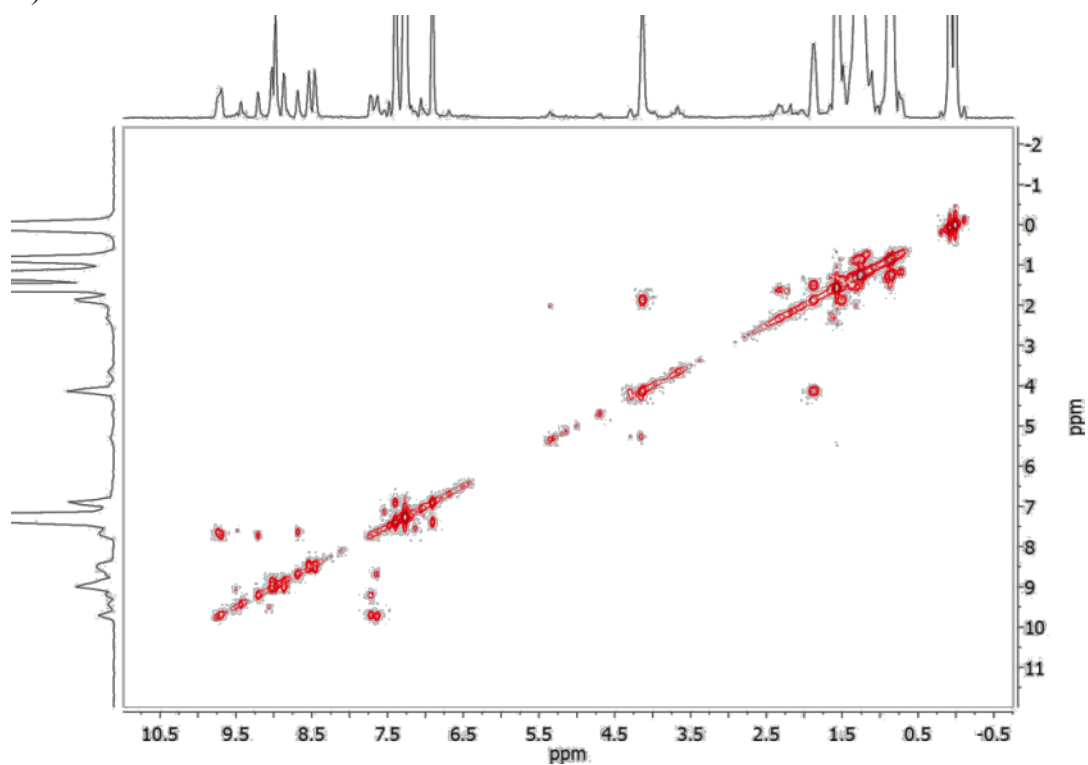


Figure S2. ¹H NMR spectra of **1a** at 4 mM (green) and 0.4 mM (red) in CDCl₃.

a)



b)

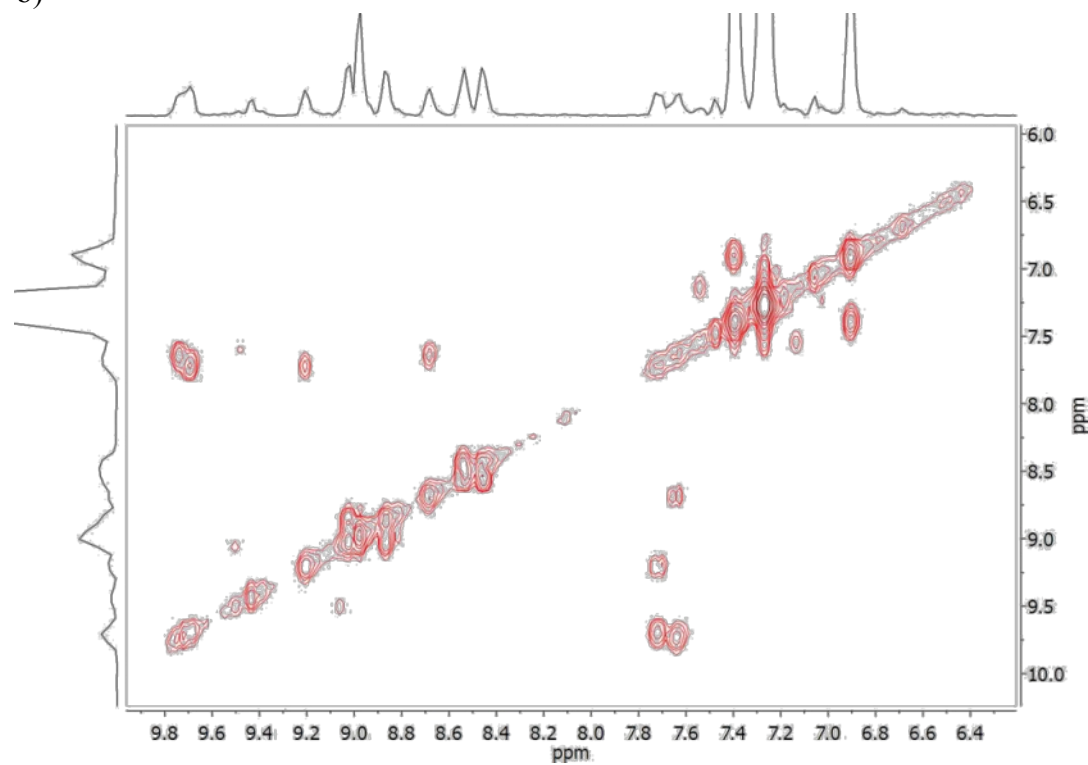


Figure S3. Dimensional-Correlation Spectroscopy (2D-COSY) in CDCl_3 for **1a** (a) and zoom of aromatic zone (b).

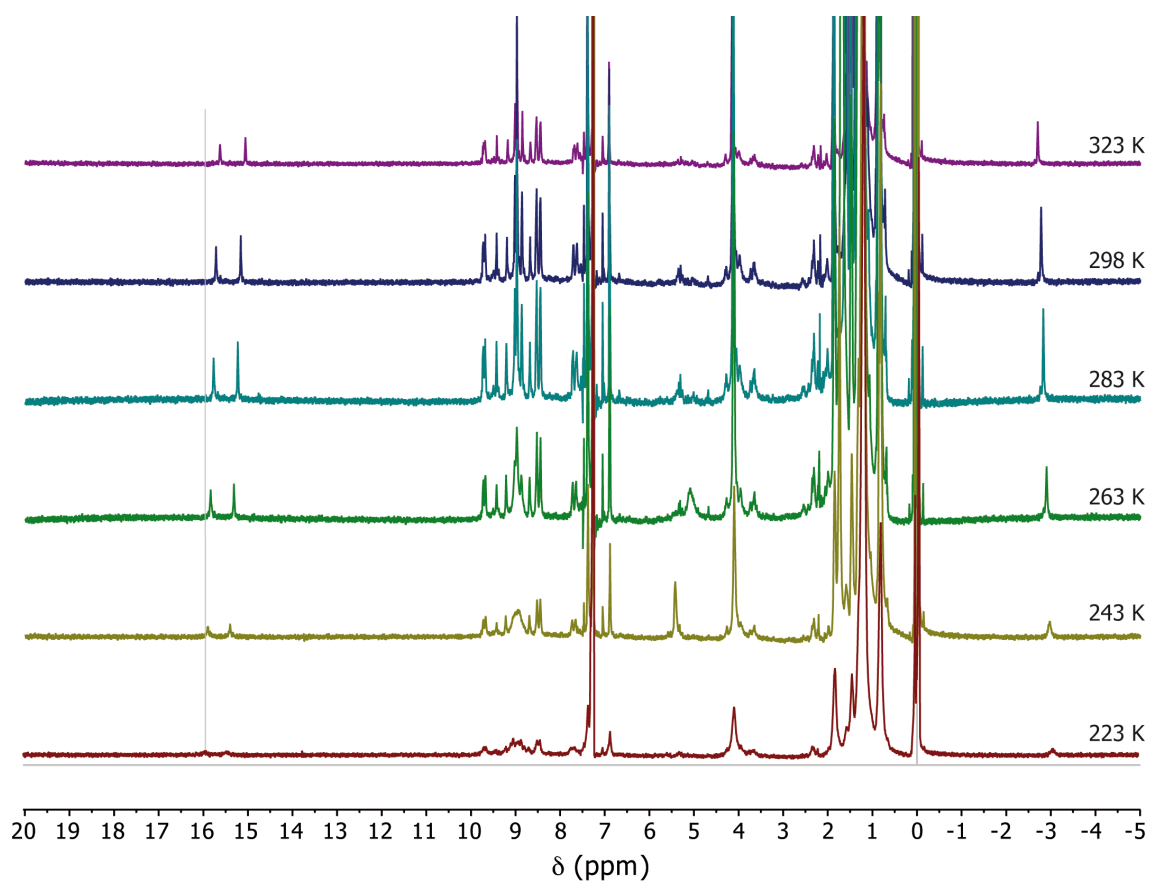


Figure S4. Temperature Dependent (TD) ^1H NMR measurements for compound **1a** (4×10^{-4} M in CDCl_3).

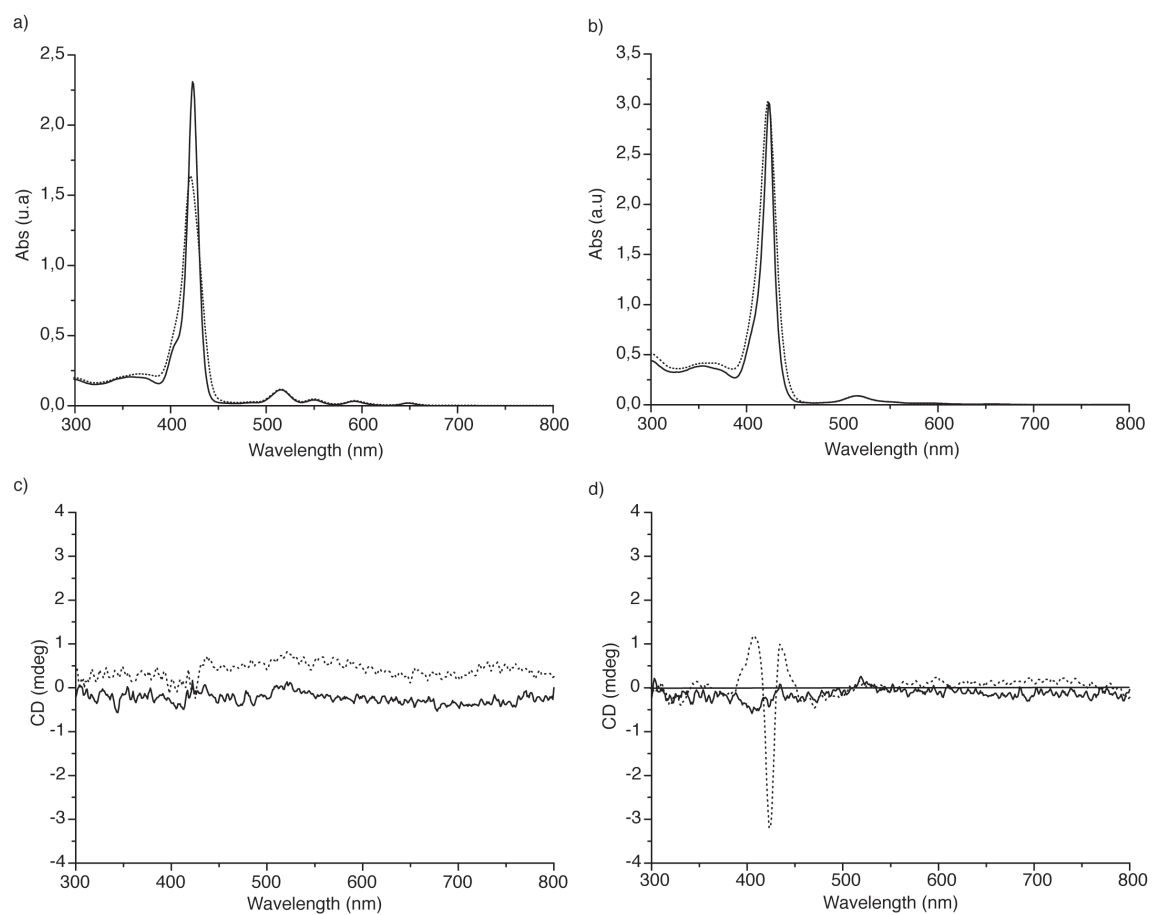


Figure S5. UV and CD spectra of **1a** (a,c)/**1b**(b,d) in toluene (solid line) and MCH (dot line).

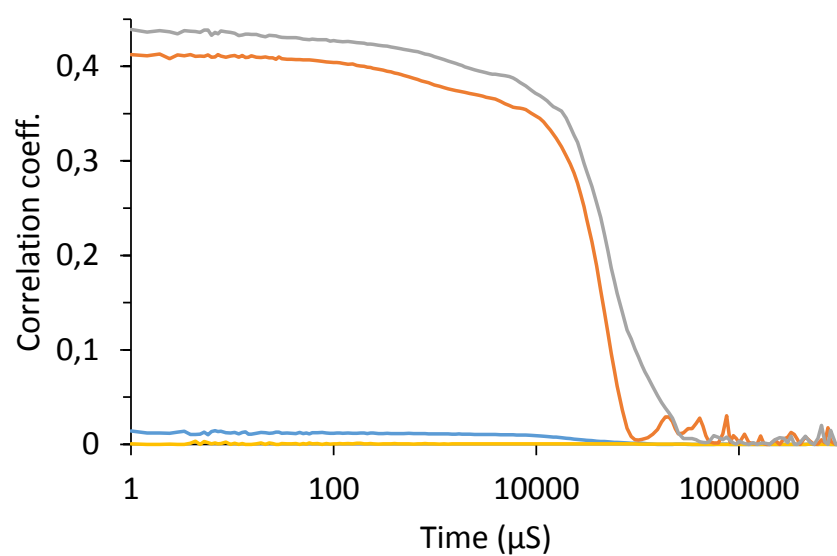


Figure S6. DLS spectra of **1a** in different solvents: chloroform (Blue), Toluene (yellow), MCH (Orange) and n-heptane (grey)

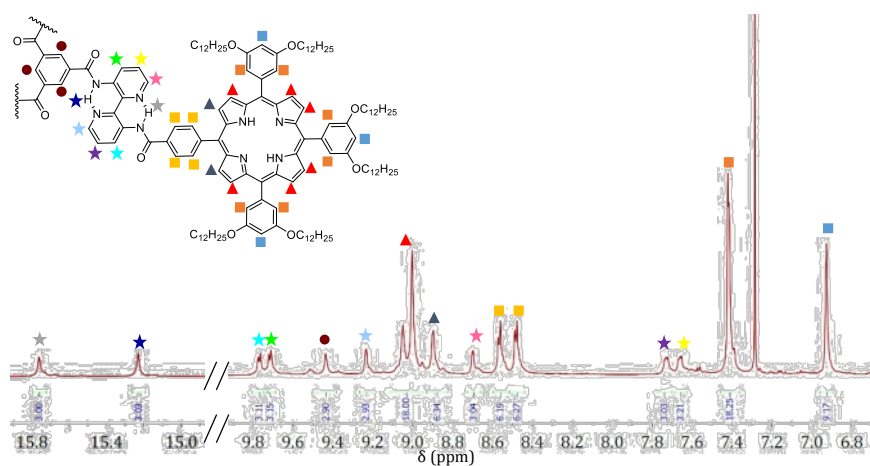


Figure S7. ^1H NMR spectra for compound **1a** (4×10^{-4} M in CDCl_3).

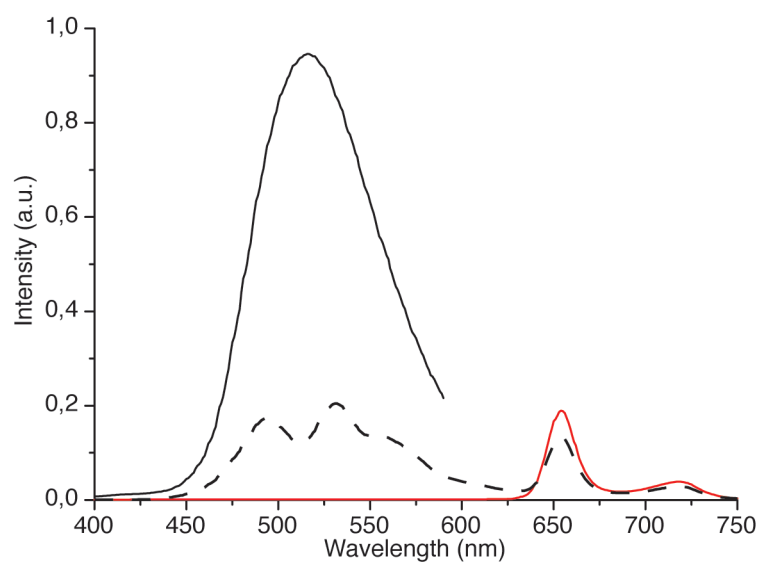


Figure S8. Fluorescence spectra of BTA-Bipy-C₁₂ (black line), **5a** (red line) and BTA-Bipy-C₁₂/**5a** (1:1) (dash black line) $\lambda_{\text{exc}} = 380 \text{ nm}$.

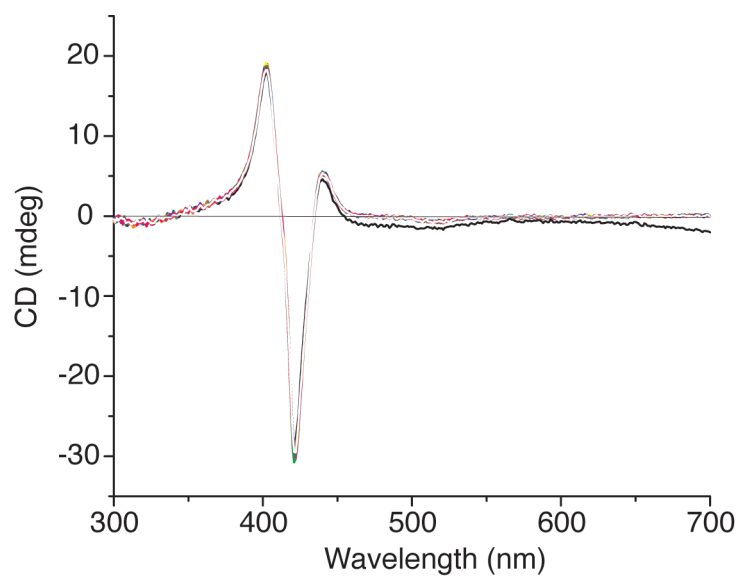


Figure S9. CD spectra of **1b** after heating up to 80 °C for 12 hours.

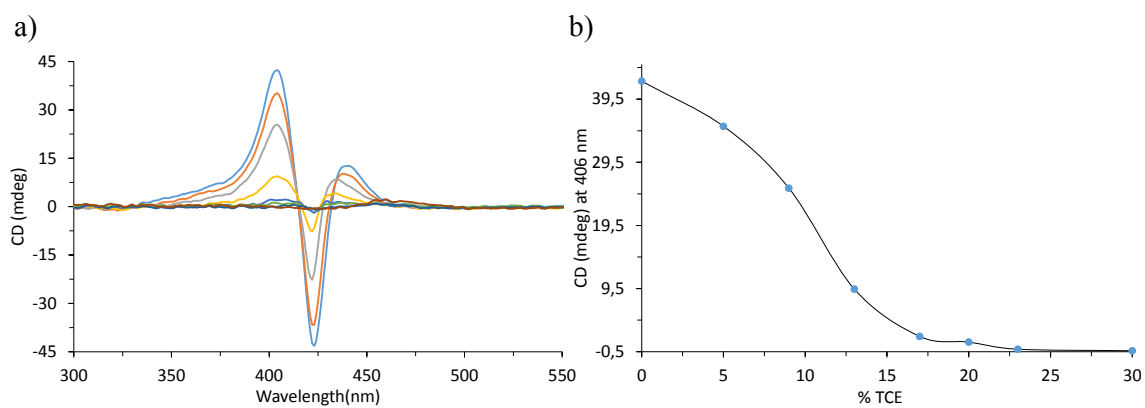


Figure S10. a) **Denaturation** process in CD using a few amount of 1,1,2,2-tetrachloroethylene. b) Plots of the percentage of TCE versus the maximum intensity peaks in the CD spectra at 406 nm.

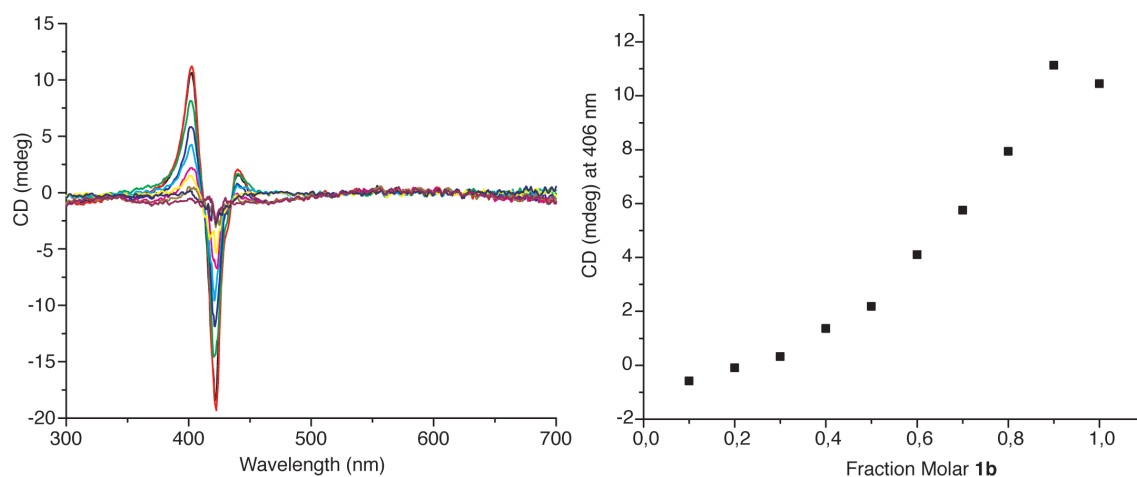


Figure S11. a) CD spectra of the “sergeant and soldiers” experiment in which solutions of varying concentrations of **1a** and **1b** in heptane. b) Plots of the molar fraction of **1b** versus the maximum intensity peaks in the CD spectra at 406 nm.

REFERENCE

1. R. Balasaravanan, A. Silva, *New. J. Chem.* **2016**, *40*, 5099-5106.