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Supporting Information
Chiral Perylene Materials by Ionic Self-Assembly

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Table of Contents

1. Experimental Details.................................................................................................................. 2
  1.1 General Considerations........................................................................................................... 2
  1.2 Synthesis Procedures and Analytical Data ............................................................................. 2
2. Tables S1 – S2 – Photophysical Characterisation................................................................. 5
3. Figures S1 – S4 – Photophysical Characterization................................................................. 5
4. Figure S5 – Polarised Light Microscopy ................................................................................... 8
5. Figures S6 – S11 – Mixed Solvent Systems ............................................................................. 8
6. Figure S12 – Mixed Solvent System – Control Experiments .................................................. 11

References .................................................................................................................................... 11
1. Experimental Details

1.1 General Considerations

Materials: Surfactants were purchased from Sigma Aldrich and used as received without further purification. All other chemicals were purchased from Aldrich or Acros Organics and used as received unless otherwise specified. N,N’-bis(2-(trimethylammonium)-3-(phenyl)propyl-perylene diimide, (1) was synthesised using a procedure which has been published previously.

Equipment: $^1$H and $^{13}$C NMR spectra were recorded on a Jeol ECP(Eclipse) 400 spectrometer using the proton signal of TMS or the deuterated solvent as internal standard. All samples were recorded at 20°C. ESI-mass spectrometry analyses of the samples were performed on a QStar XL Applied Biosystems spectrometer.

![Scheme S1](image)

**Scheme S1.** The synthesis of chiral tecton N,N’-bis(2-(trimethylammonium)-3-(phenyl)propyl perylene diimide BTPPP, (1) is published elsewhere.$^1$

1.2 Synthesis Procedures and Analytical Data

**General procedure for the synthesis of complexes 1-SDS:** 1 (40mg, 0.04 mmol) was dissolved in deionised water (4 ml) to give a 1 wt% solution using heating at 65°C and brief sonication. Sodium dodecyl sulphate (SDS) (27.9 mg, 0.08 mmol) was dissolved in deionised water (2.79 ml) to give a 1 wt% solution. Both solutions were heated to 65°C, then the surfactant was added dropwise to 1 over ten minutes. The mixture was allowed to stir at 65°C
for 1h, then the temperature was then reduced to R.T, and the mixture was allowed to stir overnight.

The precipitated complex was obtained by centrifugation and washed with deionised water to remove unbound ions (3 x 30 ml). The resulting purified complex was dried at 60°C overnight to remove residual solvent. Yield: 74%

$^1$H NMR (400 MHz, d6-DMSO) δ: 0.85 (t, 6 H, J= 6.8 Hz, CH$_3$), 1.22 - 1.26 (br. m, 36 H, CH$_2$), 1.43 – 1.51 (m, 4 H, CH$_2$), 2.92 (dd, 2 H, J= 14.7, 9.4 Hz pery CH$_2$), 3.55 (br. dd, 2 H, J=15.4 Hz, pery CH$_2$), 3.66 (t, 4 H, J= 6.7 Hz, CH$_2$), 4.48 – 4.57 (m, 4 H, pery CH$_2$), 4.73 - 4.81 (m, 2 H, pery CH), 6.64 (t, 2 H, J= 7.9 Hz, pery H$_{PHE}$), 6.79 (t, 4 H, J= 7.7 Hz, pery H$_{PHE}$), 7.09 (d, 4 H, J= 7.5 Hz pery H$_{PHE}$), 8.46 (d, 4 H, J= 7.6 Hz pery aromatic CH) and 8.92 (d, 4 H, J= 8.2 Hz pery aromatic CH). MS (ESI): m/z 1296.61 [M-Na]$^+$; m/z 1007.5 [M]$^+$ (calc. minus one molecule of surfactant)

**General procedure for the synthesis of 1-SDBS:** 1 (40mg, 0.04 mmol) was dissolved in Borax buffer solution (pH = 9, 4 ml) to give a 1 wt% solution using heating at 65°C and brief sonication. 4-Dodecylbenzenesulfonic acid (26.2 mg, 0.08 mmol) was dissolved in Borax buffer solution (pH = 9, 2.62ml) to give a 1 wt% solution. Both solutions were heated to 65°C, then the surfactant was added dropwise to 1 over ten minutes and the mixture was allowed to stir at 65°C for 1h. The temperature was then reduced to R.T, and the mixture was allowed to stir overnight.

The precipitated complex was obtained by centrifugation and washed with deionised water to remove unbound ions (3 x 30 ml). The resulting purified complex was dried at 60°C overnight to remove residual solvent. Yield: 72%

$^1$H NMR (400 MHz, d6-DMSO) δ : 0.73 -0.88 (br. M overlapping, 10 H, CH$_3$ and CH$_2$), 0.92 – 1.29 (br. m, 32 H, CH$_2$), 1.39 – 1.63 (br. m, 8 H, CH$_2$), 2.86 – 2.98 ( br. m, 2 H, pery
CH$_2$), 3.50 – 3.59 (br. m overlapping with solvent peak, 2 H, CH$_2$), 4.44 – 4.57 (m, 4 H, pery CH$_2$), 4.71 – 4.83 (m, 2 H, pery CH), 6.59 – 6.66 (m, 2 H, pery H$_{PHE}$), 6.73 – 6.82 (m, 4 H, pery H$_{PHE}$), 7.023 – 7.14 (overlapping m, 8 H, pery H$_{PHE}$ (4 H) and surfactant H$_{BZ}$ (4 H)), 7.46 – 7.54 (m, 4 H, surfactant H$_{BZ}$) 8.41 (d, 4 H, J = 7.1 Hz, central aromatic H$_{PERY}$), 8.85 (d, 4 H, J = 6.5 Hz, central aromatic H$_{PERY}$). MS (ESI): m/z 1067.5 [M]$^+$ (calc. minus one molecule of surfactant)

**Mixed-solvent self-assembly method**

Self-assembly of the complexes was carried out using a solution-injection method. The required volume of concentrated EtOH solution (0.74mM) was pipetted rapidly into the required volume of deionised water and EtOH (to give the desired final ratio of EtOH:Water), followed by vigorous mixing of the sealed vial. Preparation of the mixed solvent system was usually accompanied by a colour change from orange to purple. The samples were then allowed to age for 48 h under ambient conditions. Samples for TEM were prepared by casting the aged solution onto copper grids and allowing this to dry at RT.
2. **Tables S1 – S2 – Photophysical Characterisation**

| Complex $A_{0.0}/A_{0.1}$ | $1 \times 10^{-6}$ M | $1 \times 10^{-5}$ M | $1 \times 10^{-4}$ M |
|-----------------------------|----------------------|----------------------|----------------------|
| EtOH                        |                      |                      |                      |
| 1-SDS                       | 1.43                 | 1.43                 | 1.10                 |
| 1-SDBS                      | 1.57                 | 1.55                 | 1.09                 |

**Table S1.** Concentration dependence of $A_{0.0}/A_{0.1}$ absorption ratios for the complexes in EtOH.

| Complex $A_{0.0}/A_{0.1}$ | $1 \times 10^{-5}$ M | $1 \times 10^{-4}$ M | $1 \times 10^{-3}$ M |
|-----------------------------|----------------------|----------------------|----------------------|
| THF                         |                      |                      |                      |
| 1-SDS                       | 0.98                 | 0.73                 | 0.70                 |
| 1-SDBS                      | 0.58                 | 0.58                 | 0.57                 |

**Table S2.** Concentration dependence of $A_{0.0}/A_{0.1}$ absorption ratios for the complexes in THF solvent.

3. **Figures S1 – S4 – Photophysical Characterization**

![Photophysical Characterization](image)
**Figure S1** Concentration-dependent UV measurements a) 1-SDBS in EtOH, b) 1-SDS in THF.

**Figure S2** – Concentration-dependent CD measurements for 1-SDBS in EtOH
Figure S3 – Concentration-dependent fluorescence spectra for 1-SDS in THF

Figure S4 – a) UV of complex films cast from THF, b) CD of complex films cast from EtOH. Thin films of the complexes were prepared by drop casting 1 x 10^{-3} M solutions of each complex onto quartz plates
4. **Figure S5 – Polarisied Light Microscopy**

![Figure S5](image)

**Figure S5.** PLM image of a) 1-SDS and b) 1-SDBS cast from THF. All images at 200x magnification and shown under crossed polarizers. Scale bar = 50 µm

5. **Figures S6 – S11 – Mixed Solvent Systems**

![Figure S6](image)

**Figure S6.** TEM of self-assembled structures of 1-SDS obtained from films cast from solution (c =7 x 10⁻⁴ M) a) EtOH, b) THF.
**Figure S7** – TEM of self-assembled structures of 1-SDBS obtained from films cast from solution ($c = 7 \times 10^{-4}$ M) a) EtOH b) THF.

**Figure S8** – TEM/SEM of self-assembled structures of 1-SDBS obtained from EtOH:Water solvent systems: a) 20/80, b) 80/20 (inset TEM).
Figure S9 – TEM of self-assembled structures of 1-SDS obtained from EtOH:Water solvent systems: a) 20/80, b) 80/20.

Figure S10 – UV spectroscopy of films cast from 50:50 EtOH:Water solvent systems a) 1-SDS, b) 1-SDBS.
**Figure S11** – CD of films cast from 50:50 EtOH:Water solvent systems a) 1-SDS, b) 1-SDBS.

6. **Figure S12 – Mixed Solvent System – Control Experiments**  

**Figure S12** – SEM of self-assembled structures of parent compound 1 obtained from EtOH:Water mixed solvent systems: a) 4/96, b) 20/80, c) 50/50 d) 80/20.

7. **References**

1. Echue, G.; Lloyd-Jones, G. C.; Faul, C. F. J., Chiral Perylene Diimides: Building Blocks for Ionic Self-Assembly. *Chemistry - A European Journal* **2015**, *21* (13), 5118-5128.