A5 – Additional Supplementary data (Chapter 5.3.1)

- **Supporting data for Chapter 5.3.1 OPE1, OPE2 aggregation**

Experimental spectral images were provided by the collaborating experimentalists from the following publication:

D. S. Philips, K. K. Kartha, A. T. Politi, T. Kruger, R. Q. Albuquerque and G. Fernandez, *Angew. Chem. Int. Ed.*, 2019, **58**, 4732-4736.

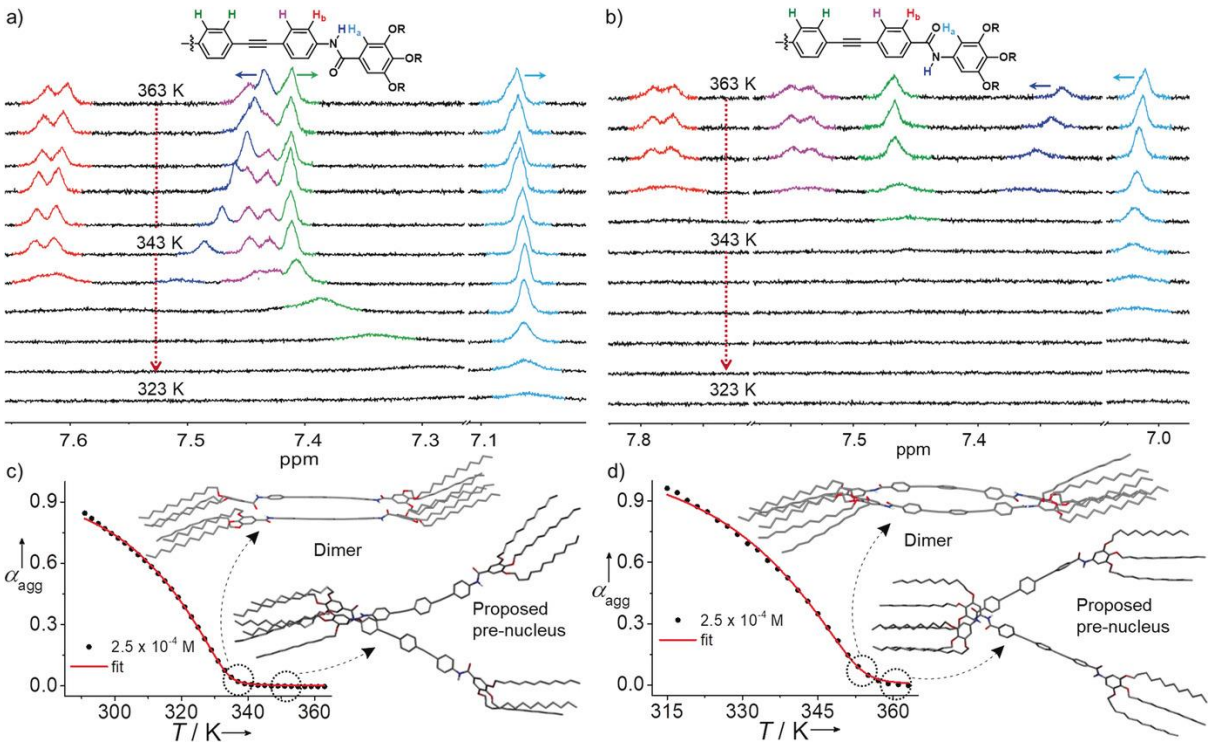
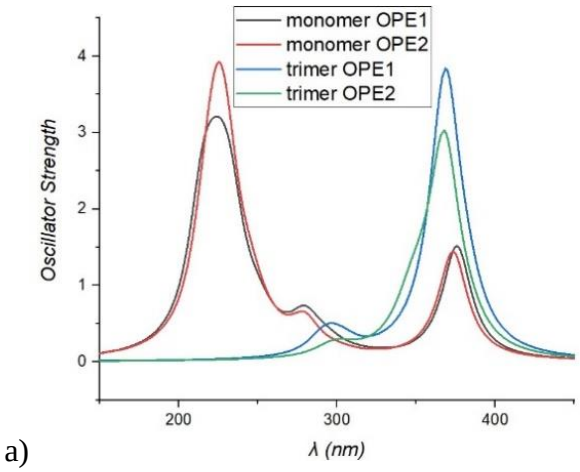
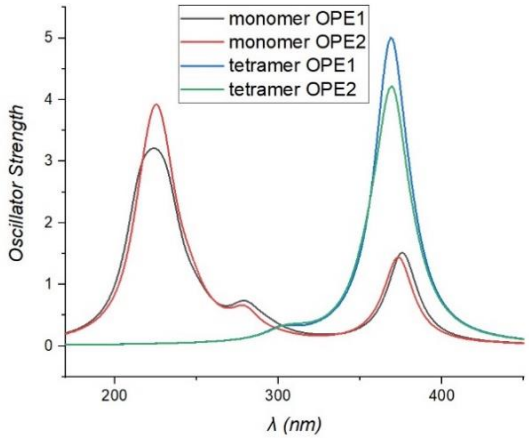


Figure A5.1 Partial variable temperature 1H-NMR measurement of 1 (a) and 2 (b) in MCH-d14 at 2.5 x 10-4 M. c,d) Cooling curves determined from VT-UV measurements at 2.5 x 10-4 M for 1 (c) and 2 (d) obtained by monitoring the absorbance at 385 nm and 380 nm, respectively. The geometries of the proposed prenuclei and dimer structures shown in c) and d) are the initial (pre-nucleus) and optimized (dimer) structures obtained from PM7 calculations.



a)



b)

Figure A5.2 The computed UV spectrum using the ZINDO method for the OPE1 and 2. Comparing their monomers and trimers in and monomers and tetramers in b).

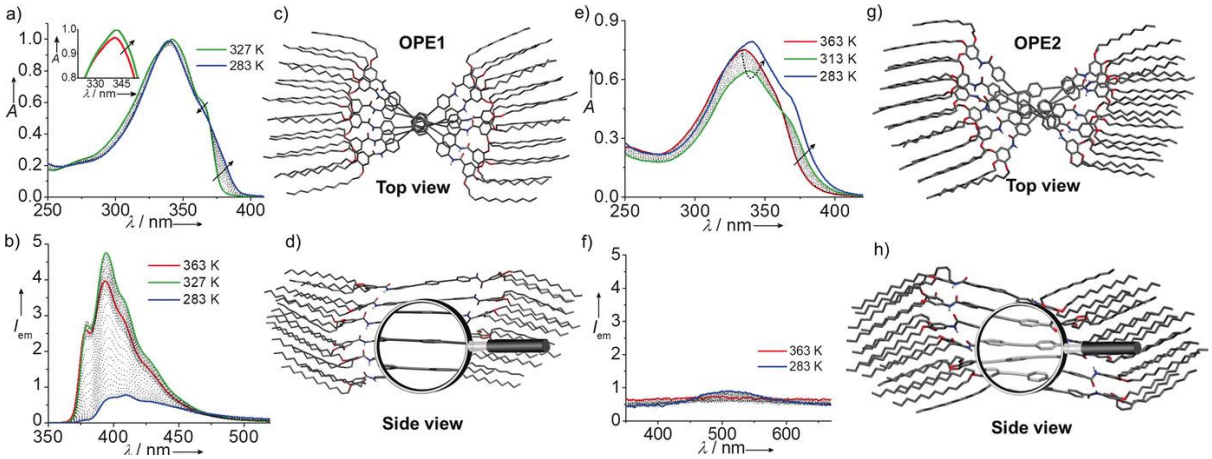


Figure A5.3 Temperature-dependent absorption (a, e) and emission (b, f) studies of 1 and 2 (c=1×10^{-4} M, MCH), respectively. The inset shows the increase in absorbance of 1 upon cooling from 363 K (red) to 327 K (green). Top and side views of PM7-optimized hexamers of 1 (c, d) and 2 (g ,h).

Table A5.1 Thermodynamic parameters for 1-4 at varied concentrations. The values of degree of cooperativity (σ), Knucl and Kel are determined at 298 K.

OPE	ΔH^0 (kJ/mol)	ΔS^0 (kJ/mol)	ΔH^0_{nucl} (kJ/mol)	K_{nucl} (M^{-1})	K_{el} (M^{-1})	σ
1	-79.30 ± 2.788	-0.1767 ±0.009	-6.34 ± 0.498	3.43×10^3	4.44×10^4	7.72×10^{-2}
2	-88.59 ± 2.792	-0.1885 ± 0.008	-7.16 ± 0.548	2.60×10^4	4.73×10^5	5.55×10^{-2}
3	-58.96 ± 1.364	-0.0872 ± 0.004	-15.89 ± 0.601	1.00×10^3	6.10×10^5	1.64×10^{-3}
4	-118.56 ± 3.563	-0.2560 ± 0.010	-20.76 ± 1.719	2.71×10^3	11.1×10^6	2.45×10^{-4}

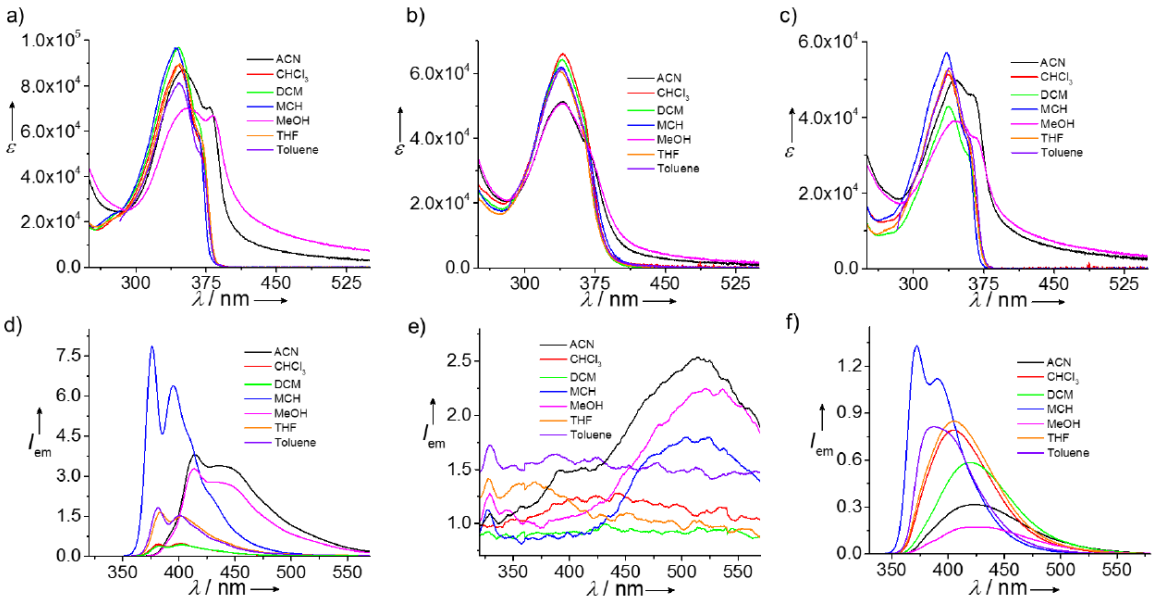


Figure A5.4 Solvent dependent absorption and emission experiments of 1 (a, d) 2 (b, e) and OPEM (c, f) (c = 1 x 10^{-5} M, λ_{ex} = 300 nm).

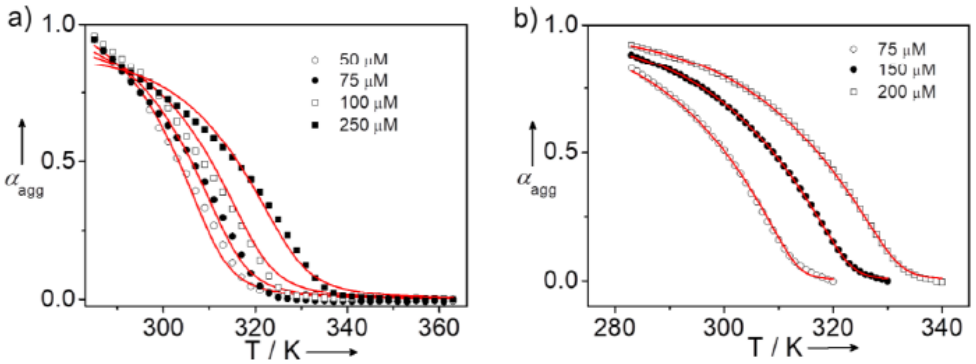


Figure A5.5 Global fitting analysis for the cooperativity factor σ, simultaneous fitting of cooling curves at different concentrations for 1 a) and 2 b).