Organic & Biomolecular Chemistry

Reversible Morphological Changes of Assembled Supramolecular Amphiphiles Triggered by pH-Modulated Host-Guest Interactions

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Supporting Information

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Table of Contents

1.	Materials and General Methods	S 3
2.	Variable Concentration Conductivity Analysis	S4
3.	Calculation of the Free Energies of Micellisation	S4
4.	Synchrotron Small-Angle X-ray Analysis and Modelling	S 5
5.	Full ¹ H-NMR Spectra of Acid-Base Switching	S7
6.	Single Crystal X-ray Crystallography	S 8
7.	References	S10

1. Materials and General Methods

Starting materials and reagents were purchased from commercial suppliers and used as received. Compounds 1^{4+} and tri(ethylene glycol)-disubstituted 1,5-diaminonaphthalene (DAN-TEG) were synthesised following procedures reported^{S1,S2} in the literature. Deuterated solvents including NaOD and DCl (Cambridge Isotope Laboratories) for NMR spectroscopic analyses were used as received. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer. Chemical shifts are calibrated relative to the residual signal of the solvent (D_2O : δ 4.79 ppm). UV-Vis spectra were recorded on a Varian CARY 100BIO temperature-controlled spectrophotometer in a quartz cuvette with a 1 mm path length at 298 K. Dynamic laser light scattering (for the determination of the hydrodynamic diameter $(D_{\rm H})$ and the diffusion coefficient (D₀)) measurements were performed using a Malvern Nano Series Zetasizer Nano-ZS at a scattering angle of (θ) of 173°. All solvents used for dynamic laser light scattering were filtered through a Whatman Anotop 25 inorganic membrane filter with a 0.02 µm pore size prior to sample preparation. Conductivity measurements were performed on a Thermo Orion 550 equipped with a conductivity cell. Care was taken during the drop-wise addition of base to the samples to prevent the existence of high local concentrations of base in the sample which could potentially lead to nucleophilic attack at the bipyridinium group. Towards this end all acid-base switching experiments were carried out with the slow and gentle drop wise addition of acid or base to a vigorously stirring solution and allowed to equilibrate following the addition. Synchrotron small angle X-ray scattering intensities were measured at the Argonne National Laboratory's advanced photon source (APS). Single crystal X-ray diffraction was performed by the X-ray facility of the Department of Chemistry at the University of Houston.

2. Variable-concentration Conductivity



Fig. S1 Variable-concentration conductivity plots illustrating the CMC for 1^{4+} (red) and the CMC for 1^{4+} with 1 equivalent of DAN-TEG (green) as well as the CMC for 1^{4+} with 2 equivalents of DAN-TEG (blue) at 298 K in water.

3. Calculation of the Free Energies of Micellisation

Free energies of micellisation were calculated using the method described by Zana^{S3} and are reported (Table S1) per hydrophobic tail. The following equation was used for all free energy calculations: $\Delta G_{\rm M}^{\rm o} = RT \left(\frac{1}{j} + \beta \frac{i}{j} \frac{|z_{\rm s}|}{|z_{\rm s}|} \right) \ln \operatorname{cmc} + RT \left(\frac{j}{j} \frac{|z_{\rm s}|}{|z_{\rm s}|} - \frac{\ln j}{i} \right)$

where *R* is the gas constant, *T* is the temperature in Kelvin, *i* is the number of charged groups in the molecule, *j* is the number of hydrophobic tails in the molecule, *zs* is the charge per charged group, *zc* is the charge per counterion, the degree of counterion binding $\beta = (m_1 - m_2)/(m_1)$ where *m*₁ is the slope of the graph of conductivity versus concentration (Fig. S1) below the critical micelle concentration, *m*₂ is the slope of the graph of conductivity versus concentration (Fig. S1) above the critical micelle concentration, and cmc is the critical micelle concentration.

Spacios	CMC ^{<i>a</i>}	β^b	ΔG° m cmc c	
species	[mM]		[kcal mol ⁻¹]	
1 ⁴⁺	8.2 ± 1.4	0.35 ± 0.01	-3.27 ± 0.13	
1^{4+} w/ 1 eq DAN-TEG	7.1 ± 0.9	0.48 ± 0.04	-4.08 ± 0.22	
1^{4+} w/ 2 eq DAN-TEG	6.7 ± 0.2	0.59 ± 0.01	-4.71 ± 0.06	

Table S1: Critical Micelle Concentrations Obtained by Variable-Concentration Conductivity and the Corresponding Gibbs' Free Energies of Micellisation (ΔG°_{M}) and Degree of Counterion Binding (β) for Compound 1⁴⁺ in the Presence and Absence of DAN-TEG at 298 K

^{*a*} Critical micelle concentrations obtained by variable-concentration conductivity measurements in water. ^{*b*} The values for β and ΔG°_{M} were obtained by the method described by Zana^{S3} using variable-concentration conductivity data and represent the free energy of transferring over a single hydrophobic chain from water to the micellar pseudophase. For the purposes of comparison, the free energies reported here for the two-tailed gemini surfactant $\mathbf{1}^{4+}$ are for a single chain transfer. Doubling of ΔG°_{M} for compound $\mathbf{1}^{4+}$ will yield a more accurate measure for the whole molecule.

4. Synchrotron Small-Angle X-ray Analysis and Modelling

All SAXS data was analyzed and modeled using Wavemetrics' Igor Pro 6.2 software running both the IRENA package and the NIST Center for Neutron Research SANS package macros.



Fig. S2 Synchrotron small angle X-ray scattering (SAXS) scattered intensity profiles for a 1×10^{-2} M solution of 1^{4+} untemplated fitted^{S4} to an oblate ellipsoid of rotation form factor combined with a screened-Coulomb structure factor ^{S5} (black trace).



Fig. S3 Synchrotron small angle X-ray scattering (SAXS) scattered intensity profiles for a 1×10^{-2} M solution of 1^{4+} template with 1 molar equivalent of **DAN-TEG** fitted^{S4} to a lamellar form factor ^{S5c} (black trace).





Fig. S4 Synchrotron small angle X-ray scattering (SAXS) scattered intensity profile for a 1×10^{-2} M solution of 1^{4+} untemplated (a) fitted ^{S4} to a Guineir-Porod empirical model ^{S6} (black trace). Fitting parameters: Guinier scale = 1.29594; dimension variable (s) = 0.489816; radius of gyration (Rg) = 245.785 Å, Porod exponent = 2.15503; background = -0.0467919. SAXS scattered intensity profile for a 1×10^{-2} M solution of 1^{4+} template with 1 equivalent of DAN-TEG (b) fitted ^{S4} to a Guineir-Porod empirical model ^{S6} (black trace). Fitting parameters: Guinier scale = 0.0248709; dimension variable (s) = 1.90413; radius of gyration (Rg) = 3616.46 Å, Porod exponent = 2.94434; background = 0.0163568.



5. Full ¹H-NMR Spectra of Acid-Base Switching

Fig. S5 Stacked ¹H-NMR spectra of 1×10^{-2} M 1⁴⁺ (300 MHz, D₂O, 298 K): Spectrum of 1⁴⁺ with peak assignments, (b) with the addition of 2 equivalents of DAN-TEG, (c) with the addition of 2 equivalents of DCl, (d) with the addition of 2 equivalents of NaOD, and (e) with another 2 equivalents of DCl. Gradual broadening of the proton signals is expected as the ionic strength continually increases with each successive neutralisation of acid and base. Increasing ionic strength screens the Coulombic repulsion among charged head groups favoring micelle formation.



6. Single Crystal X-ray Crystallography

Fig. S6 (a) A space-filling representation of the solid-state crystal superstructure packing of methyl viologen with DAN-TEG illustrating the face-to-face intermolecular donor-acceptor $[\pi-\pi]$ interactions between the DAN recognition unit (pink) and the bipyridinium unit of methyl viologen (blue) (glycol chains and hydrogens omitted for clarity). (b) With glycol chains present. (c) A ball-and-stick representation overlaid with the solvent accessible surface of the solid-state superstructure packing of methyl viologen with DAN-TEG illustrating the face-to-face intermolecular donor-acceptor $[\pi-\pi]$ interactions between the DAN recognition unit (pink) and the bipyridinium unit of methyl viologen with DAN-TEG illustrating the face-to-face intermolecular donor-acceptor $[\pi-\pi]$ interactions between the DAN recognition unit (pink) and the bipyridinium unit of methyl viologen (blue) (glycol chains and hydrogens omitted for clarity). (d) Looking down the axis of the $[\pi-\pi]$ donor-acceptor stack. (Top right) Molecular formulae depicting the non-covalent donor-acceptor $[\pi-\pi]$ interactions between methyl viologen and DAN-TEG.

Crystal Data for Methyl Viologen : DAN-TEG Donor Acceptor Stack

All measurements were made with a Siemens SMART platform diffractometer equipped with a 4K CCD APEX II detector. A hemisphere of data (1271 frames at 6 cm detector distance) was collected using a narrow-frame algorithm with scan widths of 0.30% in omega and an exposure time of 35 s/frame. The data were integrated using the Bruker-Nonius SAINT program, with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. A psi scan absorption correction was applied based on the entire data set. Redundant reflections were averaged. Final cell constants were refined using 3508 reflections having I>10\s(I), and these, along with other information pertinent to data collection and refinement, are listed below. The Laue symmetry was determined to be -1, and the space group was shown to be either P1 or P-1. The asymmetric unit consists of one-half 1,5-disubstituted naphthalene and one-half methyl viologen cation situated about inversion centers, and a PF₆ anion in a general position.

Empirical formula	$C_{34}H_{48}F_{12}N_4O_6P_2$		
Formula weight	$898.70 \text{ g mol}^{-1}$		
Temperature	223 K		
Wavelength	0.71073 Å		
Crystal system	Triclinic		
Space group	P-1		
Unit cell dimensions	$a = 8.1218(9) \text{ Å}$ $\alpha = 79.387(1)^{\circ}$		
	$b = 11.2172 (12) \text{ Å}$ $\beta = 79.478 (1)^{\circ}$		
	$c = 11.2671 (12) \text{ Å}$ $\gamma = 107.320(3)^{\circ}$		
Volume	989.55(19) Å ³		
Z	1		
Absorption coefficient	0.215		
F(000)	466		
Crystal size	$0.40 \times 0.30 \times 0.15 \text{ mm}^3$		
Theta range for data collection	1.85° to 25.0°		
Index ranges	$-9 \le h \le 9, -12 \le k \le 13, 0 \le 1 \le 13$		
Reflections collected	5054		
Independent reflections	3465		
Absorption correction	Empirical		
Max. and min. transmission	0.9984 and 0.8533		
Refinement method	Full-matrix least-squares on F ²		
Data / restraits /parameters	3465 / 1 / 264		
Good-of-fit on F^2	1.028		
Final R indices $[I>2\sigma(I)]$	$R_1 = 0.0547, wR_2 = 0.1418$		
R indices (all data)	$R_1 = 0.0618, wR_2 = 0.1489$		

Crystallographic Data deposition: Crystallographic data (excluding structure factors) for the structures have been deposited in the Cambridge Structural Database, Cambridge Crystallographic Data Centre, www.ccdc.cam.ac.uk/, Cambridge CB2 1EZ, United Kingdom (CSD reference no. 950629).

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