Charge-Modulated Self-Assembly and Growth of Conjugated Polyelectrolytes-Polyoxometalate Hybrid Networks

Electronic Supplementary Information

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1. Experimental Details

1.1 Materials

The polymer poly[(9,9-di(3,3'-*N*,*N*'-trimethylammonium)propylfluorenyl-2,7-diyl)-*alt*-(1,4phenylene)]diiodide salt –end capped with DMP (**PFP**) was purchased from American Dye Source, Inc. with an M_w 10000-15000 g mol⁻¹. The polymer poly[(2,5-bis(2-(*N*,*N*-diethylammonium bromide)ethoxy)-1,4-phenylene)-*alt*-1,4-phenylene] (**NET**) was purchased from Sigma Aldrich and had an $M_w = 1054$ g mol⁻¹, $M_n = 745$ g mol⁻¹ and a PDI = 1.4. Both polymers were used as purchased without further purification. Potassium carbonate (99%) was purchased from Sigma Aldrich and used without further purification. Potassium chloride (99%) was obtained from Riedel-de Haën and used as received. β_2 -K₈SiW₁₁O₃₉ was prepared using as previously reported.¹ Millipore water was used for all syntheses and in the case of solution studies was further filtered using 0.2 µm nylon syringe filter.

1.2 Synthesis and Characterisation of K8[SiW10O36] •xH2O

K₈[SiW₁₀O₃₆]•*x*H₂O (**POM**) was synthesised according to the procedure previously reported.² In brief, a solution of β₂-K₈SiW₁₁O₃₉ in 300 mL water was adjusted to pH 9.1 from the addition of potassium carbonate solution (2 M) and kept at 25 °C. After 15 minutes, K₈[SiW₁₀O₃₆]·*x*H₂O was precipitated from the solution by the addition of potassium chloride (40 g, 0.537 mol). During precipitation, pH 9.1 is maintained by addition of potassium carbonate solution. The precipitate was filtered and air dried under vacuum filtration. Yield: 17.41 g (63%). FTIR v_{max} (cm⁻¹): 3360 (br), 988 (m), 942 (m), 844 (s), 804 (s), 725 (vs). The number of H₂O groups was determined as *x* = 7 by thermogravimetric analysis (TGA) on a Perkin Elmer Pyris 1 TGA thermogravimetric analyzer in the range 30-900 °C under nitrogen (heating rate 10 °C min⁻¹), suggesting some H₂O may be lost during storage to atmosphere (reports show *x* = 12).²

1.3 Instrumentation and Methods

1.3.1 UV/Vis absorption and Photoluminescence Spectroscopy. UV/Vis absorption spectra were recorded at room temperature on a Shimadzu UV2401 PC UV/Vis scanning spectrometer with a scanning slit width of 0.5 nm. Photoluminescence (PL) measurements were performed at room temperature using a Fluorolog-3 (Horiba Jobin Yvon) spectrophotometer. Excitation and emission monochromator slit widths were both maintained at 3/3 nm for **NET**, and 2/2 nm for **PFP** samples. Samples were measured in 1 cm path length quartz cuvettes. Emission and excitation spectra were corrected for the wavelength response of the system using correction factors supplied by the manufacturer.

Titration procedure: **PFP** stock solution $(1.44 \times 10^{-3} \text{ M} (r.u.))$ was prepared in Millipore water/MeCN (75:25% v/v), and **NET** stock solution $(1.84 \times 10^{-3} \text{ M} (r.u.))$ was prepared in Millipore water, both were stirred for at least two days before use. **PFP** $(2.4 \times 10^{-6} \text{ M} (r.u.))$ and **NET** $(5 \times 10^{-6} \text{ M} (r.u.))$ were prepared from these stock solutions. Aliquots of an aqueous **POM** solution (0.04 mM) were added to a fixed volume of the CPE solution across the concentration range $0 - 1.54 \times 10^{-6} \text{ M}$ for **NET** and $0 - 7.2 \times 10^{-7} \text{ M}$ for **PFP**. Dilution effects were accounted for in the absorption and PL spectra and no significant change in pH was observed across the titrations.

1.3.2 Dynamic Light Scattering (DLS). Particle size was determined by DLS using a Zetasizer Nano series nano-ZS (Malvern Instruments, U.K). The apparatus is equipped with a He-Ne laser emitting at 633 nm and with a 4.0 mW power source. The instrument uses a backscattering configuration where detection is done at a scattering angle of 175°.

Titration procedure: Solutions of **PFP** (7.20 × 10⁻⁶ M (r.u.)) and **NET** (9.18 × 10⁻⁶ M (r.u.)) were prepared in filtered Millipore water. Aliquots of a filtered aqueous **POM** solution (0.04 mM) were added to the CPE solution across the concentration range $0 - 3.17 \times 10^{-6}$ M for **NET** and $0 - 2.26 \times 10^{-6}$ ⁶ M for **PFP**. All measurements were performed at 20 °C. The pathlength of the light was automatically adjusted by the apparatus in accordance with the sample turbidity. However, we note that the solutions were not visibly turbid, nor was any precipitation observed. The hydrodynamic radius (r_h) was calculated by assuming that the diffusing particles were monodispersed spheres. The hydrodynamic radius was averaged from 3 runs of approximately 20 measurements each. The autocorrelation function G1 was calculated from the fluctuation of the scattering intensity with time. Cumulants analysis, which is a fit of the logarithm of the correlation function, gave a mean value for the size (Z-average) and width parameter of the distribution, the polydispersity index (PDI).

1.3.3 Linear Dichroism (LD). LD spectra were recorded on a Jasco J-815 CD spectrometer. Solutions were loaded into 1 mm path length Couette flow cells. Baseline line spectra were recorded as the LD spectra of the sample in the Couette flow cell with no spin. These baselines were subtracted from the spectra recorded during a spin rate of approximately 3600 rpm. All measurements were recorded at 25 °C. For both CPEs a starting concentration was chosen which gave an optical density of approximately 1.1. Aqueous **POM** solution (0.04 mM) was then added to obtain a **POM**/CPE charge ratio of 1.

1.3.4 Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM). Samples for AFM and SEM were prepared in the same way. Millipore water was filtered through 0.2 µm nylon syringe filters prior to sample preparation. Concentrations for the blank samples were [**POM**] = 5×10^{-7} M, [**NET**] = 6.4×10^{-7} M (r.u.) and [**PFP**] = 5×10^{-7} M (r.u.) (for AFM, [**PFP**] = 5×10^{-8} M (r.u.)). In

preparation of **POM**/CPE hybrids, the concentration for both CPEs was fixed at [**CPE**] = 5×10^{-7} M (r.u.). The concentration of **POM** was varied to obtain the different charge ratios desired. Specifically, to obtain a **POM**/**NET** charge ratio of 1, [**POM**] = 5×10^{-7} M, and to obtain a **POM**/**PFP** charge ratio of 0.5 the [**POM**] = 6.25×10^{-8} M. For AFM sample preparation, these stocks were diluted by a further factor of 10. The **POM**/CPE films were prepared by drop-casting 20 µL aliquots onto freshly cleaved mica for AFM measurements and cut silicon wafers for SEM. In both cases, films were left to dry at room temperature.

AFM measurements were performed using an Asylum Research MFP-3D[™] Atomic Force Microscope mounted on an anti-vibration plinth, in the tapping mode at room temperature under ambient conditions. The silicon cantilevers used were 125 µm in length and had a resonance frequency of approximately 150 kHz. All raw AFM images were visualised and analysed using the Gwyddion 2.31 software.

SEM measurements were performed using a Zeiss-Ultra Scanning Electron Microscope at an accelerating voltage of 2-5 kV using an In-Lens detector. Each silicon wafer was mounted onto a carbon disc and a connection made between wafer and stage with Ag-DAG paint.

1.3.5 ¹H Nuclear Magnetic Resonance (NMR), Fourier Transform Infrared (FTIR) spectroscopy and Thermogravimetric Analysis (TGA)

¹H NMR spectroscopy was performed on a Bruker DPX 400 NMR instrument at 400 MHz. All samples were dissolved in *d*-DMSO (~4 mg/mL).

FTIR spectra were recorded on a Perkin-Elmer Spectrum 100 FTIR spectrometer using a universal ATR sampling accessory. All spectra were recorded at room temperature between 4000-650 cm⁻¹ with a resolution of 4 cm⁻¹. To obtain a reasonable signal to noise ratio the average of 32 scans was taken. For the case of the **POM**/CPE=1 complexes, the sample was dried in an oven at 70 °C over 48 hours to ensure removal of excess solvent.

TGA was performed on a Perkin Elmer Pyris 1 TGA thermogravimetric analyser in the range 30-900 °C in a nitrogen atmosphere using a heating rate of 3 °C/min.

2. Supporting Data



Figure S1. Chemical structures for (a) $poly[(2,5-bis(2-(N,N-diethylammonium bromide)ethoxy)-1,4-phenylene)-alt-1,4-phenylene](NET)and(b)<math>poly[(9,9-di(3,3'-N,N'-trimethylammonium)propylfluorenyl-2,7-diyl)-alt-(1,4-phenylene)](PFP).(c) View looking down and(d) side-on projection of the lacunary <math>[SiW_{10}O_{36}]^{8-}$ fragment (POM).



Figure S2. (a) UV/Vis absorption and (b) PL spectra of **NET** in water $(5 \times 10^{-6} \text{ M} (r.u.))$ on addition of **POM** (0+1.54 × 10⁻⁶ M). Inset: Corresponding Stern-Volmer plot (red dashed line indicates **POM**/CPE=1). * indicates an isosbestic point.



Figure S3. UV/Vis absorption spectrum of POM in aqueous solution (2.4×10^{-6} M).



Figure S4. UV/Vis absorbance maximum of (a) **NET** at 360 nm in aqueous solution (5×10^{-6} M (r.u.)) on **POM** addition ($0 - 1.72 \times 10^{-6}$ M) and (b) **PFP** at 415 nm in aqueous solution (2.4×10^{-6} M (r.u.)) on **POM** addition ($0 - 7.2 \times 10^{-7}$ M), plotted as a function of charge ratio.



Figure S5. Z-average radii determined by DLS of (a) **NET** in aqueous solution $(9.18 \times 10^{-6} \text{ M} (r.u.))$ on addition of **POM** $(0 - 3.17 \times 10^{-6} \text{ M})$, (b) **PFP** in aqueous solution $(7.20 \times 10^{-6} \text{ M} (r.u.))$ on addition of **POM** $(0 - 2.26 \times 10^{-6} \text{ M})$, plotted against charge ratio.

NB: r_h is determined from a polynomial fit of the logarithm of the correlation function using the cumulants method. This method becomes less reliable for multimodal distributions and as such only qualitative observations regarding the change in r_h can be made.



Figure S6. ¹H NMR spectra of NET and POM/NET=1 in *d*-DMSO (400 MHz).

Upon addition of **POM** to **NET** the ¹H NMR signals remain in the same position, which is expected since no formal chemical bonding occurs between the two species. The broad peak at 9.68 ppm is assigned to the N-H proton (9). Upon addition of **POM** the intensity of this peak decreases and sharp spikes appear, which is attributed to electrostatic bonding between the anionic **POM** to the positively-charged nitrogen on the CPE. This is expected to weaken and lengthen the N-H bond, thereby enabling the hydrogen to rotate more freely, resulting in slightly sharper peaks in the NMR spectrum, as shown in the inset of (b) [(i) = NET, (ii) = POM/NET=1].



Figure S7. FTIR spectra for (a) NET, (b) POM/NET=1, (c) PFP and (d) POM/PFP=1.

The presence of typical aliphatic v_{C-H} stretching modes (2940-2990 cm⁻¹), aromatic v_{C-H} stretching (3010-3030 cm⁻¹ (weak)), aromatic δ_{C-C} bending (1460-1530 cm⁻¹) modes and characteristic **POM** bands at 1630, 840, 804 and 725 cm⁻¹ confirm the presence of both CPE and **POM** in the 1:1 complex. For **NET**, the v_{N-H} stretching mode at 3384 cm⁻¹ shifts to 3374 cm⁻¹ upon binding to the **POM**, providing further evidence for electrostatic interaction between **NET** and **POM** *via* the N-H group.



Figure S8. TGA thermograms (a) NET, (b) POM/NET=1, (c) PFP and (d) POM/PFP=1 in N₂.

The onset decomposition temperature, T_{onset} for **NET** is 265 °C (inflection point at 286 °C) with large weight loss of 42.7%. The initial weight loss 100 °C is associated with residual surface solvent molecules on the oligomer. **PFP** exhibits a similar decomposition profile, with $T_{\text{onset}} = 258$ °C (inflection point at 276 °C), with a weight loss of 46.0%. Both CPEs continue to decompose, leaving an amorphous carbon residue due to the anoxic environment.

For the **POM**/CPE=1 complexes the onset decomposition temperatures are consistent with the parent CPEs ($T_{onset} = 259$ °C for **POM**/**NET**=1 and $T_{onset} = 263$ °C for **POM**/**PFP**, respectively). The large mass of residual material remaining at 900 °C is attributed to **POM**, confirming the presence of both species in the complex.



Figure S9. Linear dichroism spectrum of PFP (2.14×10^{-5} M (r.u.)) and POM/PFP=0.5.



Figure S10. AFM amplitude of (a) **POM** (5×10^{-7} M), (c) **NET** (6.4×10^{-7} M (r.u.)), (e) **PFP** (5×10^{-8} M (r.u.)) drop-cast onto freshly cleaved mica. SEM images of (b) **POM** (5×10^{-7} M), (d) **NET** (6.4×10^{-7} M (r.u.)), (f) **PFP** (5×10^{-7} M (r.u.)) drop-cast onto silicon wafers.



Figure S11. AFM (a) height, (b) amplitude and (c) phase images of **POM/NET** = 1 charge ratio ([**POM**] = 1.25×10^{-8} M, [**NET**] = 5×10^{-8} M (r.u.)). SEM (d), (e), and (f) images ([**POM**] = 1.25×10^{-7} M, [**NET**] = 5×10^{-7} M (r.u.)). (g) AFM amplitude image of **POM/PFP** = 1 ([**POM**] = 1.25×10^{-8} M, [**PFP**] = 5×10^{-8} M (r.u.)). AFM (h) height and (i) amplitude images of **POM/NET** = 0.5 ([**POM**] = 6.25×10^{-9} M, [**NET**] = 5×10^{-8} M (r.u.)) and SEM (j) and (k) images ([**POM**] = 6.25×10^{-8} M, [**PFP**] = 5×10^{-7} M (r.u.)).



Figure S12. AFM (a) height, (b) amplitude and (c) phase images of **POM/PFP=5** ([**POM**] = 6.25×10^{-8} M, [**PFP**] = 5×10^{-8} M (r.u.)) drop-cast onto freshly cleaved mica.



Figure S13. AFM (a) height, (b) amplitude and (c) phase images of **POM/NET**=5 ([**POM**] = 7.5×10^{-7} M, [**NET**] = 6×10^{-7} M (r.u.)) drop-cast onto freshly cleaved mica.

3. References

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