Supporting Information

Dual Lanthanide Role in the Designed Synthesis of Hollow Metal Coordination (Prussian Blue Analogue) Nanocages with Large Internal Cavity and Mesoporous Cage

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Scheme S1: Synthetic protocol for ester-linked pyridyl pentacyanoferrate terminated poly(ethylene glycol)-*b*-poly(propylene glycol)-*b*-poly(ethylene glycol) (EPE-Py-Fe)



Figure S1: UV-vis absorption spectrum showing the charge transfer band of EPE-Py-Fe in H₂0 ($\lambda_{max} = 406$ nm)



Figure S2: FT-IR spectra of a) crude EPE-Py-Fe (**black**; note the large CN (cyano) absorption band at ~2065 cm⁻¹ corresponding to pentacyano ferrate (both polymer coordinated and residual uncoordinated)); b) purified EPE-Py-Fe (**red**; the large CN band has decreased to reveal two smaller distinct CN bands corresponding to the axial and equatorial vibrations of the polymer coordinated pentacyano end group. See also the carbonyl ester stretch at 1729 cm⁻¹ as discussed in maintext); c) solids recovered on addition of MeOH solution of crude EPE-Py-Fe to 10-fold volume of EtOH, followed by centrifugation and drying (**blue**; note the dominant CN band. The cyano band has shifted to ~2047 cm⁻¹ indicating a different coordination environment to the polymer coordinated pentacyano groups in the purified EPE-Py-Fe and d) pentacyano ferrate salt (Na₂NH₄[Fe(CN)₅NH₃]·5H₂O) starting material (**green**). **Note:** There is some evidence of residual EPE polymer in the spectrum of the removed residual ferrate salt (**blue**; CH band ~2900 cm⁻¹). This is due to residual levels of the EtOH/MeOH solution of purified EPE-Py-Fe retained in the centrifuge tube on decanting.



Figure S3: UV-vis absorption spectra illustrating the slight blue shift on the addition of Gd(NO₃)₃ (red and blue; 7 and 19 fold excesses respectively; $\lambda_{max} = 397$ nm) and Er(NO₃)₃ (green and pink; 7 and 19 fold excesses respectively; $\lambda_{max} = 397$ nm) to miniemulsions prepared using EPE-Py-Fe as stabiliser (black; $\lambda_{max} = 406$ nm).



Figure S4: Photographs showing sample vials containing a miniemulsion comprised of EPE-Py-Fe metallo-surfactant and Gd^{3+} (left) and Gd@PB Prussian blue analogue coordination polymer nanocages after precipitation of an aliquot of the miniemulsion in a large volume (~10 fold) of methanol (right). Notice how the coloured coordination polymer material has precipitated and rested to the bottom leaving a clear supernatant on top.



Figure S5: Spot EDX spectra of single Gd@PB (top) and Er@PB (bottom) Prussian Blue analogue coordination polymer organo-nanoshells prior to precipitation and purification to remove EPE surfactant and excess lanthanide salts. **Note**: Unassigned peaks between 3 and 4 keV in Er@PB correspond to K, presumably attributable to impurities in either the pentacyanoferrate salt and/or the water used to prepare the miniemulsions. This impurity is largely removed from the purified nanocages (see Figure S11).



Figure S6: High magnification HRTEM images of the surface of Gd@PB (left) and Er@PB (right) Prussian Blue analogue coordination polymer nanoshells. Note the absence of crystalline fringes.



Figure S7: High resolution TEM image of a single Er@PB Prussian Blue analogue coordination polymer nanoshell (a) and energy filtered TEM (EFTEM) elemental maps (b, iron ($L_{2,3}$ -edge); c, carbon (K-edge); d, erbium ($N_{4,5}$ edge)) of the same nanoshell. Lighter coloured regions denote high concentrations of the element being mapped. Scale bars = 100nm. Note higher carbon concentrations at the periphery (c) due to EPE surfactant and presence of excess erbium (d) external to the nanoshell.



Figure S8: FT-IR spectra of EPE-Py-Fe (**black**) and the precipitated and purified Prussian Blue analogue metal coordination nanocages (red; Er@PB and green; Gd@PB) obtained using EPE-Py-Fe as the stabiliser in the MEPP process. Note the distinct absence of surfactant peaks in the nanocages, most notably at 2863 cm⁻¹. The CN absorption band shifted from 2065 cm⁻¹ (EPE-Py-Fe) to 2053 cm⁻¹ (Er³⁺) and 2054 cm⁻¹ (Gd³⁺) on occurrence of the coordination polymerization and ester hydrolysis.



Figure S9: SEM image of Er@PB Prussian Blue analogue coordination polymer nanocages prepared after precipitation of nanoshells followed by repeated centrifugation/washing cycles to remove EPE surfactant and excess $Er(NO_3)_3$. Scale $bar = 2 \mu m$.



Figure S10: TEM image of a number of hollow Er@PB Prussian Blue analogue coordination polymer nanocages aggregated together after precipitation and purification to remove EPE surfactant and excess salts. Note hollow nature of individual nanocages.



Figure S11: Spot EDX spectra of single Gd@PB (top) and Er@PB (bottom) Prussian Blue analogue coordination polymer nanocages after precipitation and purification to remove EPE surfactant and excess salts. The atomic ratio compositions of the nanocages were calculated as 1Gd: 1Fe (Gd@PB) and 2Er : 3Fe (Er@PB) respectively.



Figure S12: Wide angle X-ray diffraction (WAXD) data indicating the amorphous nature of the PB analogue coordination polymer nanocages (Er@PB; top and Gd@PB; bottom). **N.B.** WAXD analysis was conducted after precipitation and purification.



Figure S13: FT-IR spectra of EPE-Py (**black**) and solid retained from the dried supernatant after precipitation of Er@PB (red) and Gd@PB (green) PB analogue coordination polymer nanocages in methanol. Note the presence of the distinctive ester carbonyl stretch in EPE-Py (**black**) at 1729 cm⁻¹ and the C-H stretch absorption band of EPE at ~2863 cm⁻¹ in all spectra.