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Prussian Blue Coordination Polymer Nanobox Synthesis using Miniemulsion Periphery Polymerization (MEPP)

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Experimental

Materials: Poly(ethylene glycol)-*b*-poly(propylene glycol)-*b*-poly(ethylene glycol) (PEO₁₂₂PPO₅₆PEO₁₂₂; EPE) triblock copolymer ($M_n \sim 14,000$ g/mol), 4-(dimethylamino)-pyridine (DMAP), pentacyanoamine ferrate ammonium disodium salt pentahydrate (Na₂NH₄[Fe(CN)₅NH₃] \cdot 5H₂O), bromoacetyl chloride, iron (III) chloride, sodium hydrogen carbonate, sodium chloride and sodium sulfate were purchased from Sigma-Aldrich (United Kingdom) and used without further purification, unless otherwise indicated. Toluene (anhydrous; Sigma-Aldrich) dichloromethane (DCM; reagent grade; Fisher Scientific), methanol (MeOH; HPLC grade; Fisher Scientific), diethyl ether (Et₂O; reagent grade; Sigma-Aldrich) and hexadecane (HD; Alfa Aesar) were used without further purification.

Characterization: A transmission electron microscope (TEM; Philips CM-10) with an acceleration voltage of 80 kV was used to take low magnification TEM images. A field emission gun TEM microscope (Philips CM200 FEGTEM; 200kV) equipped with a Gatan GIF200 imaging filter running DigitalMicrograph™ software was used to take higher magnification TEM images and FFT power spectra, and perform elemental mapping. The bright field tilt series was performed on an FEI Tecnai TF20 microscope fitted with a Gatan Orius SC1000 digital camera running DigitalMicrograph™ tomography software. TEM samples were prepared by drying a drop of miniemulsion onto a carbon-coated copper grid under ambient conditions. Grids were rinsed with distilled water to remove excess FeCl₃. The specimens were observed without staining due to the presence of Fe. SEM micrographs were obtained using a LEO 1530 Gemini FEGSEM (3kV). SEM samples were prepared by adhering TEM grids containing a previously dried miniemulsion droplet to aluminium stoppers using double sided carbon tape. SEM specimens were coated with a gold/platinum alloy thin film prior to observation. Wide angle X-ray diffraction (WAXD) measurements were performed using a Philips PW1050 XRD diffractometer equipped with Ni-filtered Cu K α radiation, having a wavelength of 0.154 nm. The diffractometer was scanned over a 2 θ range of 5-50° with a scanning rate of 1.2° min⁻¹.

Miniemulsion samples were prepared for WAXD analysis by the removal of all solvents under reduced pressure at ~50 °C. The addition of diethyl ether after the removal of ~99% water and toluene aided the formation of powder samples. This was subsequently removed under reduced pressure at room temperature and the sample was dried overnight in a vacuum oven. UV spectroscopy measurements were obtained using a Hitachi U3500 at room temperature. Cyclic voltammetry (CV) was conducted using an Autolab PGSTAT 30 System (Ecochemie, The Netherlands). A three-electrode system was employed with a glassy carbon (GC) disk of 3 mm diameter as working electrode, Ag/AgCl as reference electrode and platinum wire as auxiliary electrode. Before each experiment, the GC electrode was polished with decreasing size alumina powder (1, 0.3 and 0.05 μm) until a mirror finish was obtained. Nafion was employed to anchor the PB nanoboxes onto the surface of the GC electrodes. Aliquots of 5 μL of a 4 % PB nanobox solution and a 0.2 % Nafion solution were dropped onto the surface of the GC electrode. The GC electrode was then dried for 23 hours in order to obtain a stable PB nanobox modified electrode.

Synthesis of bromide-terminated poly(ethylene glycol)-*b*-poly(propylene glycol)-*b*-poly(ethylene glycol) triblock copolymer (EPE-Br)

The following represents a variation on that reported previously by our group¹ and allows for more rigorous yet facile purification. Poly(ethylene glycol)-*b*-poly(propylene glycol)-*b*-poly(ethylene glycol) triblock copolymers (7.3 g, 0.5 mmol), were dried using azeotropic distillation at 110 °C under N₂ from their anhydrous toluene solution (150 ml). Anhydrous toluene was added at room temperature to bring the total toluene content to ~ 70ml before cooling to 0 °C using an ice bath. Subsequently, 1.0 ml (12 mmol) bromoacetyl chloride was added drop-wise to the prepared solution under a N₂ atmosphere. Afterwards, the cooling bath was removed and the reaction mixture was stirred at 70 °C overnight, with a N₂ atmosphere maintained throughout. On cooling, approximately 90% of the toluene was removed under vacuum. The resultant concentrated mixture was then precipitated into ~300 ml of cold Et₂O. The precipitated polymer was collected by filtration and further purified by 3 or 4 cycles of dissolving in a small amount of DCM (~15mls) and precipitation into cold Et₂O. Further purification to ensure the absence of any hydrolysis (acid) products was conducted by dissolution in ~300mls DCM and washing of said solution three times with ~100 ml of a saturated aqueous solution of sodium hydrogen carbonate. A spatula tip of sodium chloride was added if necessary to aid separation of the layers. The DCM solution of polymers was then dried over anhydrous sodium sulfate prior to a final precipitation into cold Et₂O, followed by filtration and drying overnight under vacuum at ambient temperature. Bromo-functionality was calculated to be >90% by comparison of the BrCH₂ ¹H NMR peak @ 4.03 ppm with the OCH₂CH(CH₃) peak @ 1.15 ppm.

¹H NMR (MeOD, 500 MHz): 4.33 (m, 4H from COOCH₂), 4.03 (s, 4H from BrCH₂), 3.65 (m, 972H from OCH₂CH₂O), 3.55 (m, 112H from OCH₂CH(CH₃)), 3.49 (m, 56H from OCH₂CH(CH₃)), 1.15 (m, 168H from OCH₂CH(CH₃)).

Synthesis of pentacyano(4-(dimethylamino)-pyridine)ferrate ammonium disodium salt (Fe-DMAP)

The following synthesis exhibits deviations from that used previously to prepare pentacyano(4-(dimethylamino)-pyridine)ferrate trisodium salt.¹ The current strategy represents an improved purification regime applicable to both the ammonium disodium salt discussed herein and its trisodium counterpart. In a typical run, a solution of 2.0 g (16 mmol) DMAP in 150 ml methanol (HPLC grade) was heated to 40 °C. Then 2.0 g (5.5 mmol) of Na₂NH₄[Fe(CN)₅NH₃].5H₂O was added to the solution to yield a dark purple colour immediately. The suspension was stirred overnight at 40 °C under N₂ atmosphere. The solution was then filtered through celite to remove unreacted Na₂NH₄[Fe(CN)₅NH₃].5H₂O (green insoluble solid). The resultant solution was then concentrated to approximately 5ml under vacuum and precipitated as a fine dark blue solid by addition to ~250ml DCM. The above filtration and precipitation purification regime was repeated at least three times. Finally, the dark blue product was collected and dried under vacuum at ambient temperature (yield ~40%).

¹H NMR (MeOD, 500 MHz): 7.95 (d, 2H), 6.52 (d, 2H), 2.90 (s, 6H). **Note:** Product exhibits limited solubility in MeOD as exemplified by low intensity of NMR product peaks relative to solvent peaks.

Synthesis of poly(ethylene glycol)-*b*-poly(propylene glycol)-*b*-poly(ethylene glycol) terminated with pentacyano(4-(dimethylamino)-pyridine)ferrate ammonium disodium salt (EPE-Fe)

Bromide-terminated poly(ethylene glycol)-*b*-poly(propylene glycol)-*b*-poly(ethylene glycol) triblock copolymer (EPE-Br; 1.0 g, 0.07 mmol) was dissolved in 5 ml methanol (HPLC grade) and heated to 50 °C. To this solution was added 0.130 g (0.42mmol) Fe-DMAP. The reaction vessel was then sealed under N₂ and stirred at 50 °C for 72 hours. On cooling, the majority of solvent (~90%) was removed under vacuum to yield a viscous dark purple crude product. To precipitate out excess Fe-DMAP, ~100 ml of DCM was added at this stage. The insoluble solids were then filtered off using a celite containing filter and the purple solution was collected. Again the majority of the solvent was removed before addition to cold Et₂O, which resulted in a purple precipitate of EPE-Fe. The solvent was then removed under reduced pressure and the resultant dark purple EPE-Fe was dried overnight under vacuum at room temperature. The degree of terminal ferrate functionality attained in EPE-Fe was measured by comparing the UV-vis absorbance (@ 662 nm) of a known concentration of EPE-Fe aqueous solution versus a UV calibration curve prepared by plotting absorbance vs. concentration for aqueous solutions of Fe-DMAP in the range of 0 – 0.2 mg/ml. The degree of functionality was calculated to be 94% for the EPE-Fe polymers.

¹H NMR (MeOD, 500 MHz): 8.11 (d, 4H), 7.00 (d, 4H), 3.65 (m, 972H from OCH₂CH₂O), 3.55 (m, 112H from OCH₂CH(CH₃)), 3.49 (m, 56H from OCH₂CH(CH₃)), 3.27 (s, 12H from NCH₃), 1.15 (m, 168H from OCH₂CH(CH₃)).

Preparation of miniemulsion and coordination polymer nanoboxes: To prepare the nanoboxes toluene (0.5 g) was first mixed with hexadecane (HD) (20 mg). This organic phase was then added to the aqueous phase consisting of distilled water (9.08 g), 0.255g of EPE-Fe and 0.145g of EPE-Br under vigorous stirring. After 45 min, the resulting mixture was sonicated (Bandelin Sonopuls HD2200, 60% power) for a period of 15 mins. The resultant miniemulsion was stable for a period of weeks. To prepare coordination polymer nanoboxes, approximately 5 molar excess iron (III) chloride (FeCl_3) (relative to EPE-Fe and -Br end groups; 48mg in this case) was added to the above miniemulsion in 0.5 mls of H_2O to induce coordination polymerization. The mixture was then stirred for 72 hours at room temperature.

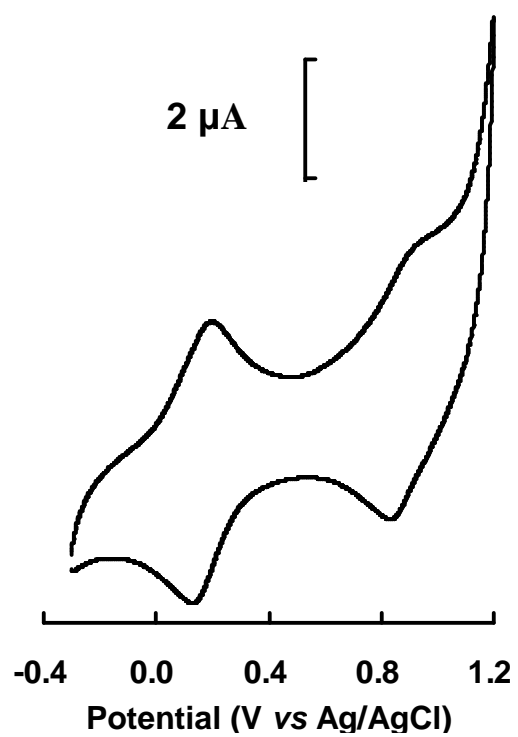


Figure S1: Cyclic voltammogram of the PB nanoboxes immobilised on glassy carbon (GC) electrodes in aqueous KCl solution

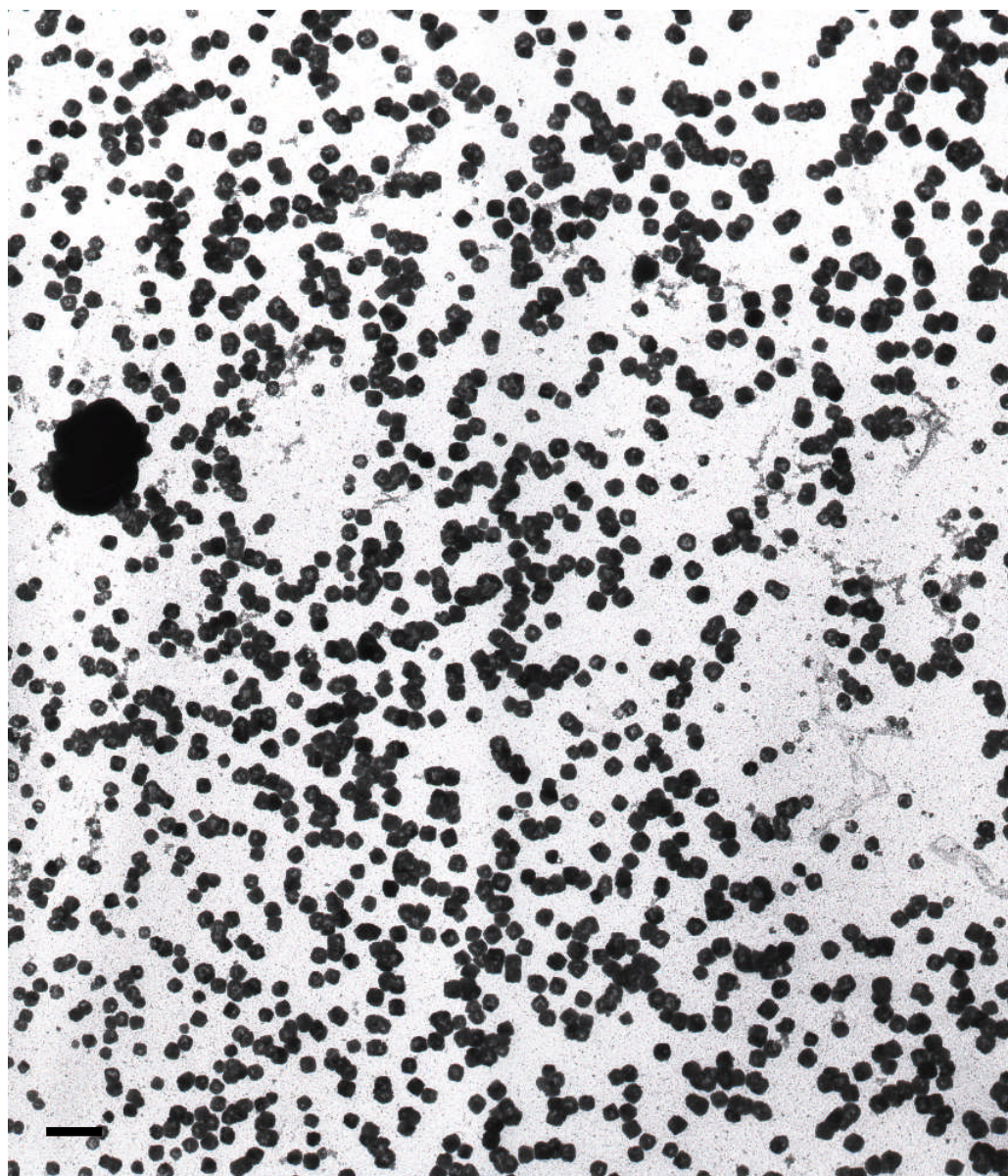


Figure S2: Lower magnification TEM image of the PB nanoboxes in Figure 1 illustrating the uniformity of size and shape of the nanoboxes (Scale bar = 500 nm)

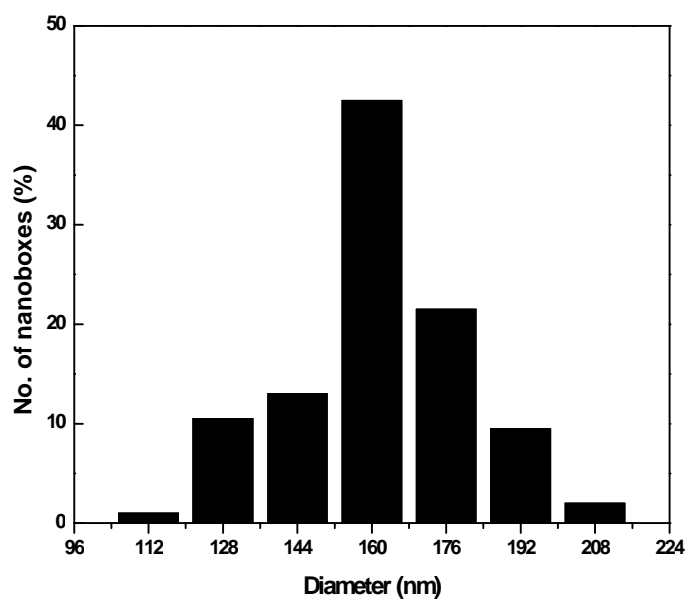


Figure S3: Histogram of the size distribution of the PB nanoboxes as calculated by measuring the sizes of 200 nanoboxes in Figure S1.

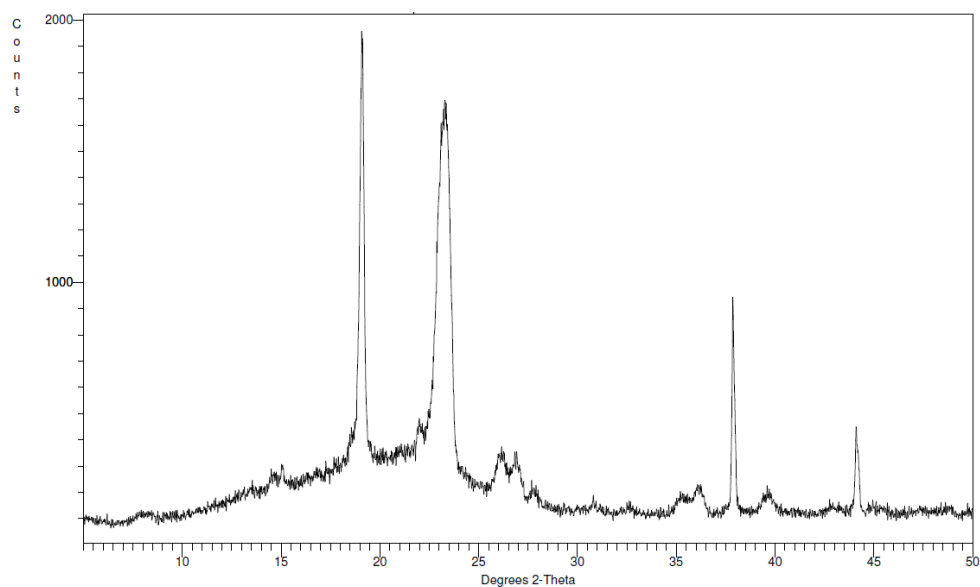
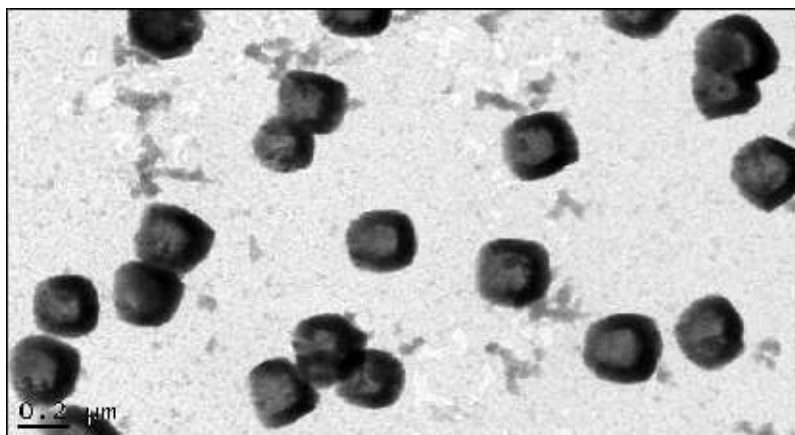


Figure S4: WAXD pattern of the nanoboxes. Diffraction peaks at approximately 19.3° , 23.3° and 26° can be assigned to the (120), (112) and (240) diffractions of the PEO segments,² while those at 35.5° and 39° can be assigned to the (400) and (420) diffractions of PB.³ The peaks due to PB at lower angles are overlapped by those of the PEO segments which are the major component. Peaks at 38° and 44° are reflections from the sample holder.⁴

Tilt Series



Multimedia S1: Tilt series from 42° to -50° of the nanoboxes in Figure 1. Note the change in diffraction contrast (“sparkling”) at the surface of the particles which indicates the presence of crystallinity. The video can be viewed (or downloaded for viewing here) at <http://www.chem.leeds.ac.uk/RMH/>

References

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