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Supporting Information

Shrink Wrapping Redox-Active Crystals of Polyoxometalate Porous Frameworks with Organic Polymers

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1. General Experimental Section

All of the reagents used were obtained from commercial suppliers and were used without further purification.

Instrumentation

Thermo-gravimetric Analysis (TGA): TGA was performed on A TA Q500 instrument under a nitrogen atmosphere. The heating range was from RT to 500 ^{o}C at 5 ^{o}C per min.

^{1}H NMR: ^{1}H NMR spectra were recorded on a Bruker DPX 400. All □□value

Powder X-Ray diffraction: PXRD patterns were collected on a Philips X-pert diffractometer (λ(CuK$_{\alpha}$) = 1.5405 Å) equipped with PW3710 control unit.

Raman measurements: Raman spectra were recorded on a Horiba Jobin Yvon LabRAM HR800 spectrometer in conjunction with HeNe 20 mW (λ = 532 nm) laser.

Fourier-transform infrared (FT-IR) measurements: FT-IR spectra were recorded on a Shimazu FT-IR 8400S Fourier Transformer Infrared Spectrophotometer fitted with a diamond anvil stage.

2. Experimental Section

Syntheses of 1 and 2: The POM networks (**1** and **2**) were synthesized according to previously reported methods.[3d]

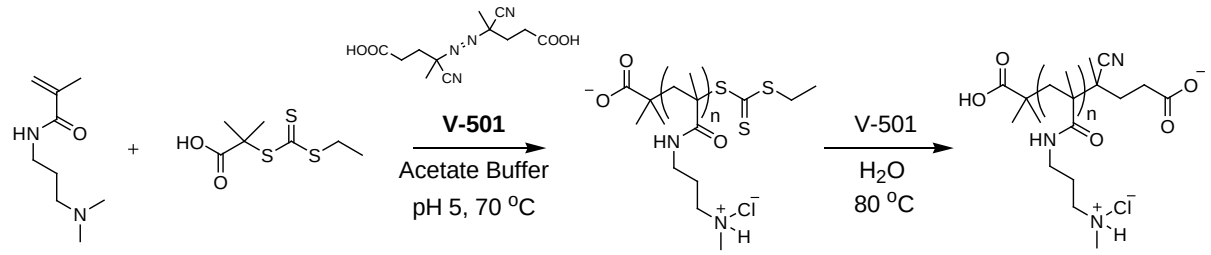
Synthesis of 1-Py: 20 mg of **1** was put in neat pyrrole (1 mL) and the solution was heated at 85 °C for 12 h. The resulting crystals were thoroughly washed with MeOH and then soaked in 10 mL of MeOH for 3 days with fresh MeOH added every 24 h. The crystals were isolated and dried in air.

Synthesis of 1-ANI: The composite was synthesized following the same procedure as **1-Py**.

Typical procedure of guest-exchange reaction with alkyl ammonium bromides: The guest-exchange experiments were carried out in 5 mL of CD_3OD at 50 ^oC, in the presence of four molar equivalents of TMABr (10.5 mg, 68 μmol) in relation to the amount of morpholinium cations in the 10 mg of POMOF crystals. After 24 h, the guest-exchange reaction yields were calculated by integrating the 12H singlet of TMABr against the 4H triplet of morpholine from ^1H NMR spectrum. A control experiment was also carried out simultaneously, whereby the same quantity of crystals was placed in 5 mL of CD_3OD. The control experiment shows negligible quantities of morpholine in the CD_3OD solution after many hours, confirming the crystals stability in this solvent, and that morpholine does not leach with time.

Typical procedure of guest-exchange reaction with guanidine hydrochloride: The guest-exchange experiments were carried out in 5 mL of CD_3OD at room temperature, in the presence of 40 molar equivalents of guanidine hydrochloride (130 mg, 1.36 mmol) in relation to the amount of morpholinium cations contained in the 20 mg of POM network crystals. Tetraheptylammonium bromide (16.7 mg, 34 μmol) was also added to the CD_3OD solution as a marker for quantifying the displacement of morpholinium by guanidinium couterions. The guest-exchange reactions were monitored by ^1H NMR after 1, 2, 4, 8 and 12 h and their reaction yields were calculated by integrating the 4H triplet of morpholine against the methyl protons of tetraheptylammonium bromide.

Synthesis of p(DMAPMAm)



DMAPMAm **CTA** **p(DMAPMAm)-RAFT** **p(DMAPMAm)**

N-[3-(dimethylamino)propyl] methacrylamide (**DMAPMAm**) (3.68 g, 21.6 mmol), 2-(ethylthiocarbonothioylthio)-2-methylpropanoic acid (**CTA**) (16.4 mg, 73.1 µmol) and V-501 (2.66 mg, 9.49 µmol) were dissolved in Acetate Buffer (11.6 mL, 10 mM, pH 5.5) and the final pH re-adjusted to 5 using HCl (1M). The polymerization was carried out overnight (23 h, 98% conversion). **p(DMAPMAm)-RAFT** was purified by precipitating into acetone (2x) and dialysis against water and recovered as a light yellow powder (2.83 g, 74%) after freeze-drying from water (dark, 2 days). **p(DMAPMAm)-RAFT** (2.83 g, 49.9 µmol) was then dissolved in H_2O (40.0 mL) and V-501 (495 mg, 1.77 mmol) was added. Reaction was carried out overnight. The title compound **p(DMAPMAm)** was purified by dialysis against NaCl (2 x) and water (2 x) and recovered as a white powder (985 mg, 35%) after freeze-drying from water (dark, 2 days) ^{1}H-NMR (D_2O, 400 MHz) δ (ppm) 4.0-3.1 (m, 4H, CH_2-N DMAPMAm), 2.90 (s, 6H, CH_3-N DMAPMAm), 2.1-1.9 (m, 3H, CH_3 MAm), 1.9-1.6 (m, 2H, CH_2 DMAPMAm), 1.2-0.8 (m, 2H, CH_2 MAm backbone) Mn (GPC) 22828, PDI (GPC) 2.49, DP 217.

Isolation of coated polymers from 1-Py or 1-ANI. 100 mg of **1-Py** or **1-ANI** were digested in 5 mL of water with sonication. Then, the insoluble organic polymers were recovered by centrifugation. After washing with 5 ml of water three times, they were dried in air and obtained as black powder.

3. Raman spectra

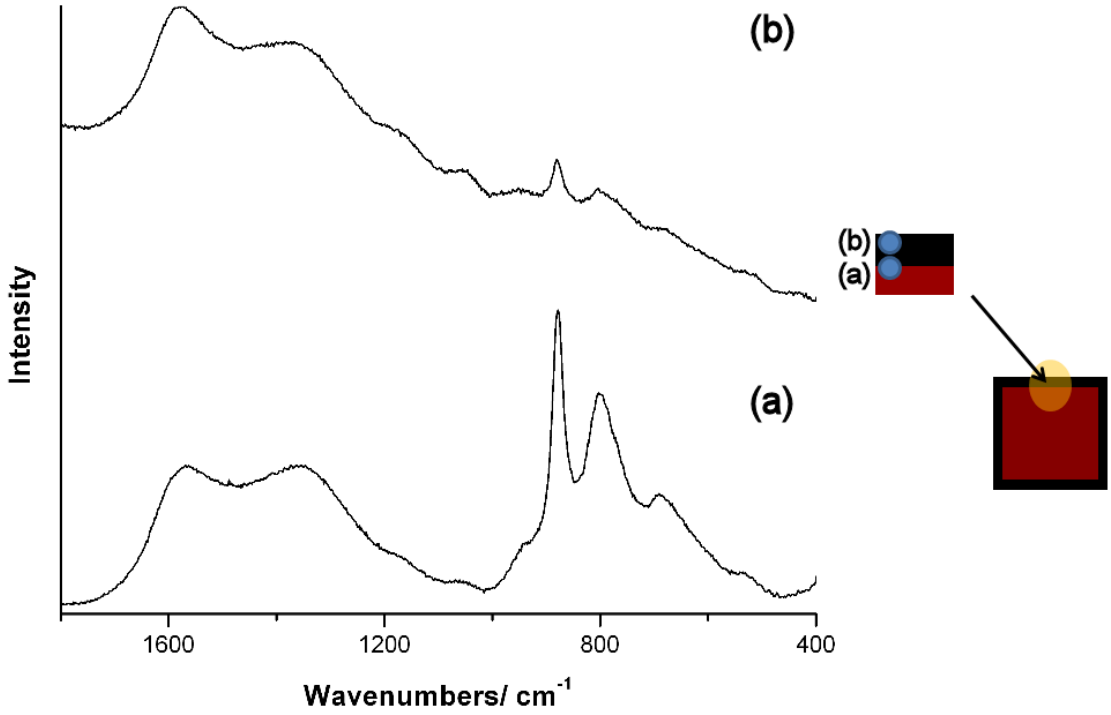


Figure S1. Raman spectra obtained from **1-Py** at specific positions. The positions were indicated with blue points on the cartoon shown right side.

4. IR spectra

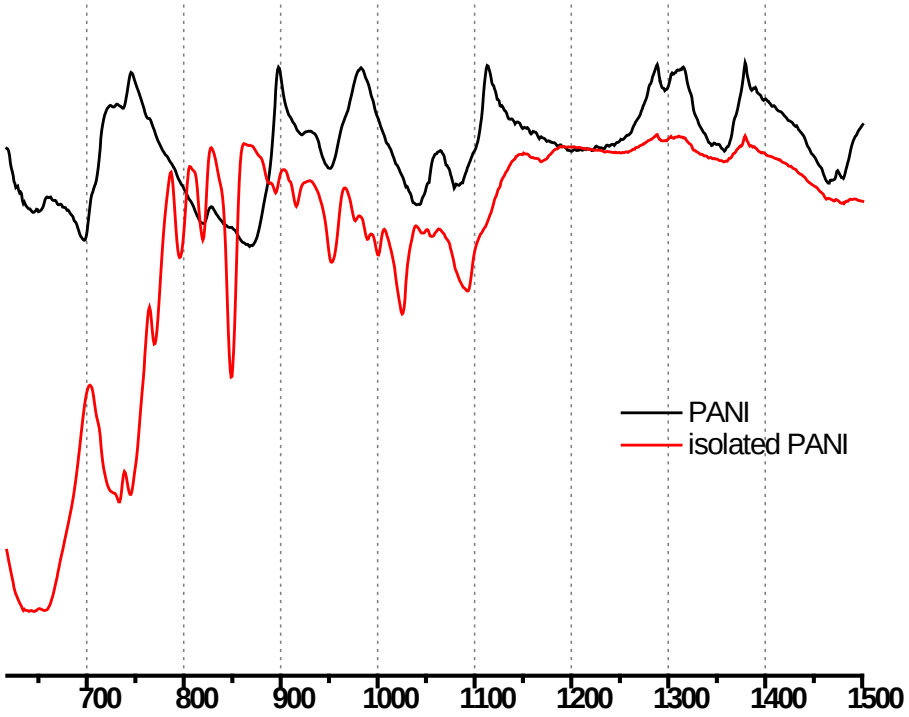


Figure S2. IR spectra of bulk polyaniline (black) and polyaniline isolated from **1-ANI** (red).

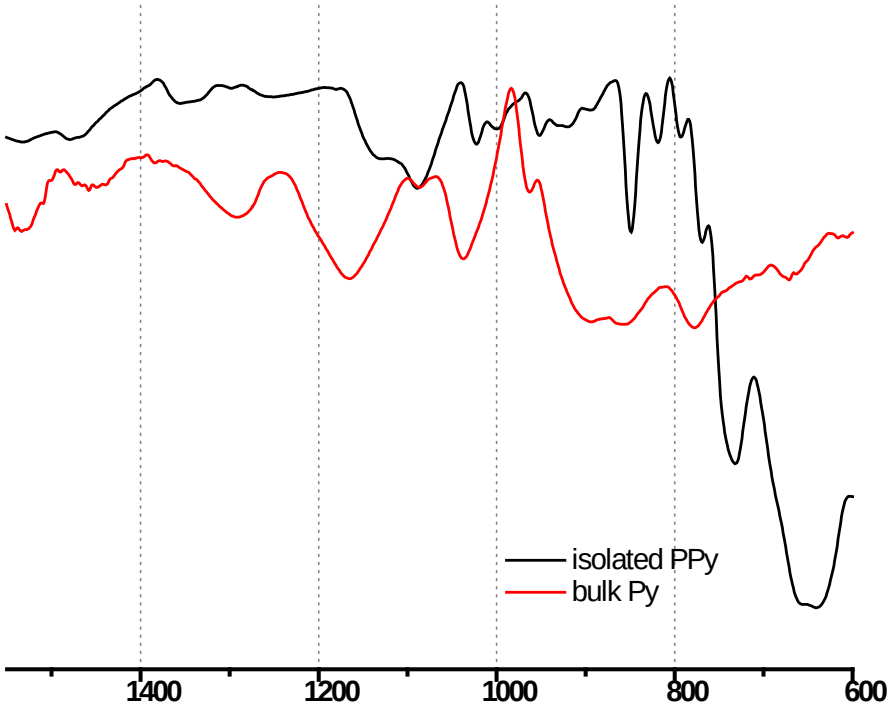


Figure S3. IR spectra of bulk bulk polypyrrole (red) and polypyrrole isolated from **1-Py** (black).

5. ^{1}HNMR spectra

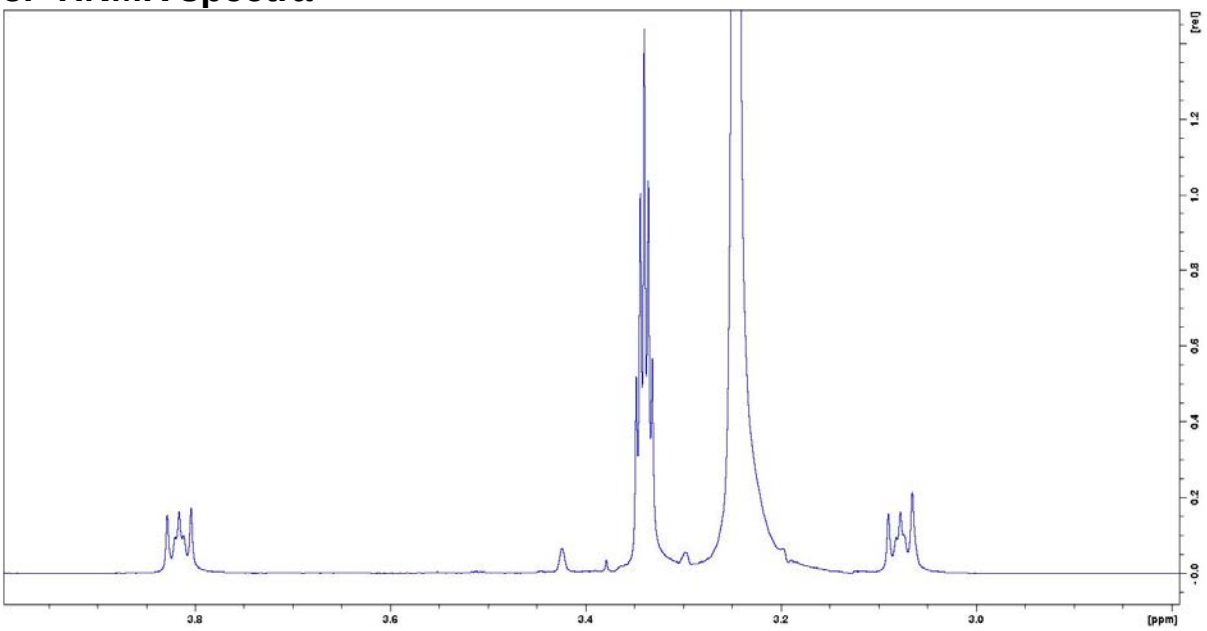


Figure S4. ^{1}H NMR spectra showing the exchange of morpholinium counterions in **1** with TMA counterions. Morpholine signals at 3.83 and 3.15 ppm and TMA signal at 3.25 ppm.

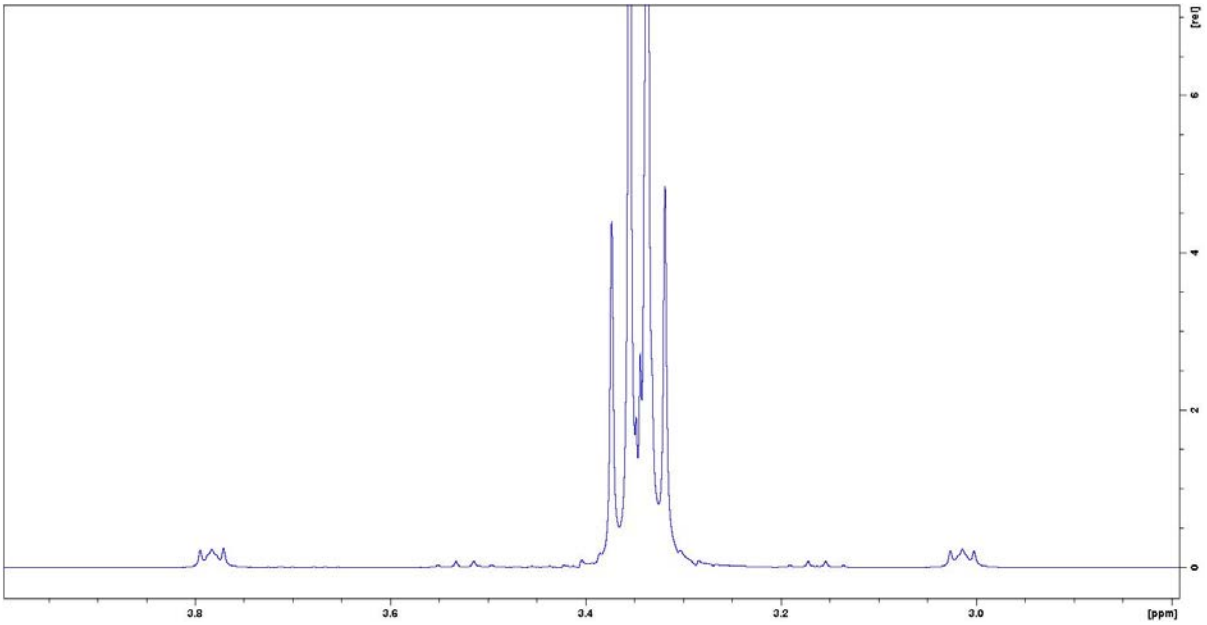


Figure S5. ^{1}H NMR spectra showing the exchange of morpholinium counterions in **1** with TEA counterions.

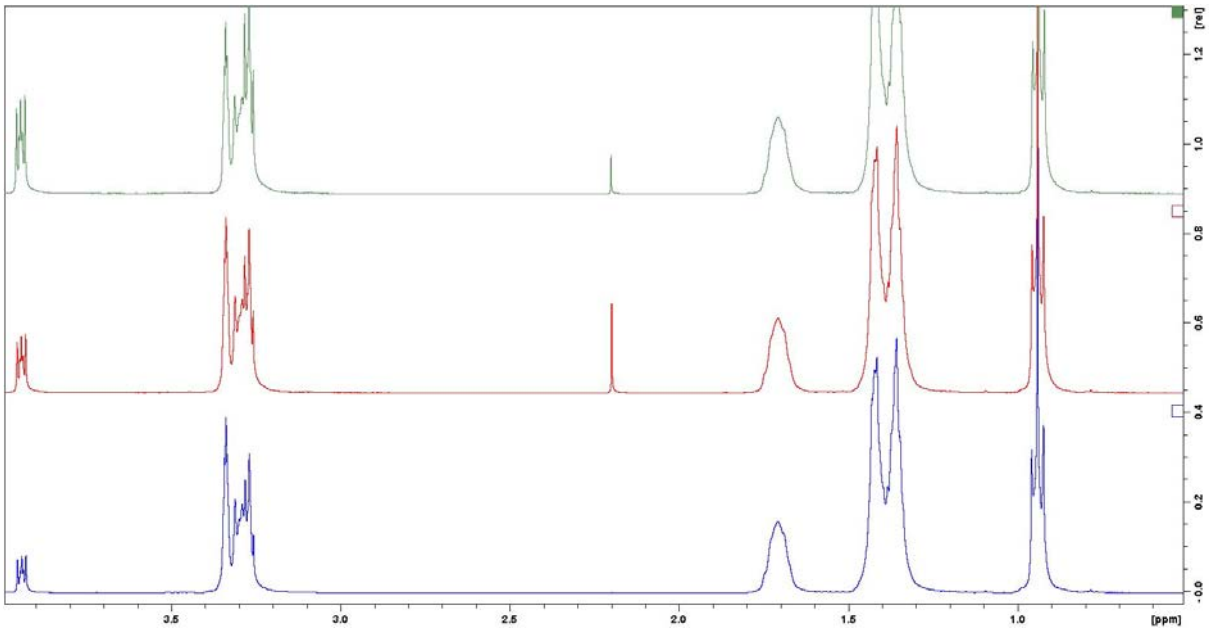


Figure S6. ^{1}H NMR spectra showing the exchange of morpholinium counterions in **1** with guanidinium counterions with a clear increase in the relative peak intensity of the morpholinium signal at 3.90 ppm in relation to the methyl protons of tetraheptylammonium bromide at 0.93 ppm. Sampling intervals, Blue = 1 hour, Red = 2 hours, Green = 12 hours.

6. Tube Growth

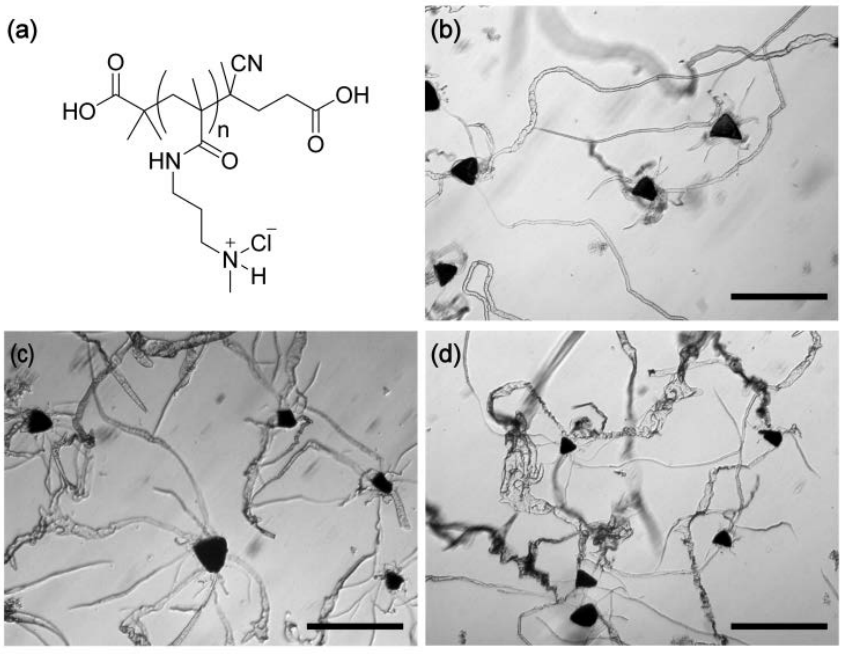


Figure S7. (a) Chemical formula of p(DMAPMAm). Image of microtube grown from (b) crystals of **1**, (c) crystals of **1-ANI** and (d) crystals of **1-Py** following the addition of 0.15 mL of a 1 mmolL^{-1} aqueous solution of p(DMAPMAm). The black scale bar is 200 microns long.

7. References

1. a) C. Ritchie, C. Streb, J. Thiel, S. G. Mitchell, H. N. Miras, D.-L. Long, T. Boyd, R. D. Peacock, T. McGlone and L. Cronin, *Angew. Chem.* 2008, **120**, 6987; *Angew. Chem. Int. Ed.* 2008, **47**, 6881; b) J. Thiel, C. Ritchie, C. Streb, D.-L. Long and L. Cronin, *J. Am. Chem. Soc*. 2009, **131**, 4180.