

Coordination of Ruthenium Phthalocyanine with Poly(4-vinylpyridine)

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Synthesis

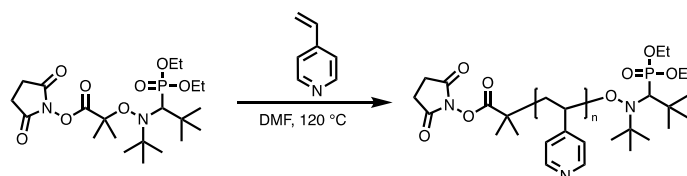
Synthesis of RuPc(CO)

Synthesis of **RuPc(CO)** was adapted from previously reported procedures.³⁸ Phthalocyanine (100 mg, 0.19 mmol) and $\text{Ru}_3(\text{CO})_{12}$ (249 mg, 0.39 mmol) were dissolved in *o*-dichlorobenzene (4 mL) in a sealed tube and heated at 185 °C for 16h. The crude was cooled to room temperature and added to a column chromatography in heptane, going from this solvent to pure CHCl_3 and then to THF, obtaining the product after evaporation as a dark blue powder (95 mg, 76%), that was used in the next reaction without further purification.

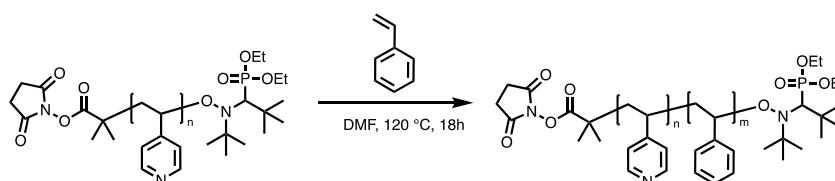
Synthesis of Ru{(t-bu)Pc}(CO)

Synthesis of **t-Bu-RuPc(CO)** was adapted from previously reported.⁴⁶ *t*Bu-phthalocyanine (100 mg, 0.13 mmol) and $\text{Ru}_3(\text{CO})_{12}$ (173 mg, 0.27 mmol) were dissolved in phenol (8 g) in a sealed tube and heated at 185 °C for 16h. The crude was cooled to room temperature and ethanol (30 mL) and water (100 mL) were added. The solid precipitate was filtered under vacuum and washed with 100 mL of a mixture water/MeOH (4:1). The obtained precipitate was purified by column chromatography going from toluene to pure CHCl_3 to obtain the product as a dark blue powder (89 mg, 76%) that was used in the next reaction without further purification.

Synthesis of P4VP



Synthesis of **P4VP** was performed according to literature with modification. In a typical polymerization, NHS-BB (7.3 mg, 20 μmol) and 4VP (1.02 mL, 9.5 mmol) were dissolved in 50 wt% DMF (1.1 mL) and bubbled with $\text{N}_{2(\text{g})}$ in a 6 dr vial for 15 minutes. The reaction mixture was heated at 120 °C under $\text{N}_{2(\text{g})}$ for 1.5 h in a heating block. An aliquot was taken to determine the conversion of the polymerization. Conversion of the 4VP polymerization was determined through $^1\text{H-NMR}$ spectroscopy by comparing one of the vinyl peaks (1H, 5.96 ppm) to one of the aromatic peaks (2H, 6.16-6.48 ppm) giving a conversion of 30%. The polymer was then precipitated in ether (2x). The resulting light pink polymer was dried overnight in a vacuum oven at 80 °C (257 mg, 26%).



Synthesis of P4VP-b-PS

Chain extension of **P4VP** with styrene was performed according to literature with modification.¹⁸ **P4VP** (100 mg, 6.3 μmol , 1 eq) and St (290 μL , 2.5 mmol, 400 eq) were dissolved in 50 wt% DMF (385 μL) and bubbled with $\text{N}_{2(\text{g})}$ in a 6 dr vial for 5 minutes. The reaction mixture was heated at 120 °C under $\text{N}_{2(\text{g})}$ for 18 hr in a heating block. An aliquot was taken to determine the conversion of the polymerization. Conversion of the styrene polymerization was determined through $^1\text{H-NMR}$ spectroscopy by comparing one of the vinyl peaks (1H, 5.77 ppm) to one of the aromatic peaks (3H, 6.87-7.19 ppm) giving a conversion of 60%. The polymer was then precipitated in ether (2x). The resulting light pink polymer was dried overnight in a vacuum oven at 80 °C.

Coordination of RuPc to P4VP

To prepare **4VP-RuPc**, **RuPc(CO)** (5 mg, 7.8 μmol) and **4VP** (0.84 μL , 7.9 μmol) were heated in DMF or THF (500 μL) at 50 °C for 5h. Subsequently, the reaction mixture was rotovaped to remove the solvent and excess unreacted **4VP**. No further purification was performed. $\delta = 9.42\text{--}9.25$, (*broad multiplet*, 8H, $H^{\text{RuPC arom}}$), 8.15–8.12, (*broad multiplet*, 4H, $H^{\text{RuPC arom}}$), 5.47–5.40 (*dd*, $J=5.44$ Hz, 1H, H^{4VP}), 4.92–4.87 (*d*, $J=4.90$ Hz, 1H, H^{4VP}), 4.82–4.79 (*d*, $J=4.80$ Hz, 1H, H^{4VP}), 2.95–2.88 (*d*, $J=2.92$, 1H, H^{4VP}), 1.95–1.93 (*m*, 2H, H^{4VP}), 1.78–1.77 (*broad multiplet*, 36H, C(CH₃)₃).

Similarly, **P4VP-RuPc** and **P4VP-b-PS-RuPc** was prepared by heating **RuPc(CO)** (5 mg) with **P4VP (20 mg)** or **P4VP-b-PS-RuPc(20 mg)** in DMF (200 μL) at 50 °C for 5h. The resulting reaction mixture was pipetted onto a watch glass and placed in a vacuum oven at 120 °C overnight (18 h) to yield a dark blue film.

Characterization

Compound Characterization

Ferrocene voltammograms were recorded as standards to estimate HOMO and LUMO levels, using the empirical correlation E_{HOMO} (eV) = $-(E_{\text{ox,onset}} - E_{\text{oxFc/Fc+,onset}}) - 4.80$.

Electrochemical Characterization

Cyclic voltammetry was performed using a Bioanalytical Systems Inc. (BASi) Epsilon potentiostat with C3 cell stand, a glass cell and recorded using BASi Epsilon EC software (V 2.13.77 (c) 2013BASi). Platinum wires were used for the working and counter, and a silver rod and used as the pseudo-reference electrode. The measurements were performed in a dry THF solution under nitrogen, using a 0.1 M tetrabutylammonium hexafluorophosphate (Aldrich) as the supporting electrolyte with a scan rate of 200 mV s⁻¹. All measurements were referenced to the Fc/Fc+redox couple (+0.48 V vs. SCE) as an internal standard.

Optoelectronic Characterization

UV-vis and Fluorescence spectra were measured using an Agilent Technologies Cary 7000 UV-Vis-NIR spectrophotometer and an Agilent Technologies Cary Eclipse Fluorescence spectrophotometer, respectively. Absorbance measurements were collected at ambient temperature in solution with DMF within the range of 250–800 nm, and using a solid state adapter with thin films deposited onto glass substrates within a range of 300–800nm. Fluorescence measurements were collected at ambient temperature using a solid state adapter with thin films deposited onto glass substrates within the range of 400–800 nm using λ_{max} of the absorbance spectrum as the excited wavelength.

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) of POTbc collected using a TA Waters TGA5500 instrument under air at atmospheric pressure using a temperature ramp of 20 °C/min⁻¹ from 30–900 °C.

Transmission Electron Microscopy

Images of annealed **P4VP-RuPc** and **P4VP-b-PS-RuPc** were obtained using transmission electron microscopy. Samples were prepared by drop-casting 125 mg/mL polymer/DMF solution onto a watch-glass and left in a vacuum oven at 120 °C until solvent evaporated. The dried, cast polymer samples were left to cool overnight. Liquid N₂ was then poured over the annealed-polymer coated watch-glasses; the cast polymer was cracked, lifted from the watchglass, and collected. Sections were cut on a Leica UCT ultramicrotome (Leica Microsystems, Leica UCT Ultramicrotome) equipped with a diamond blade, placed onto copper grids. TEM imaging was performed on the prepared samples using a FEI Titan 80-300.

Gel Permeation Chromatography

GPC of the polymers was performed using the multi-detector Malvern OMNISEC GPC. It included an OMNISEC Resolve pump, an autosampler (CHR7100), two D6000M columns, an OMNISEC Reveal (CHR6000) differential refractive index, a diode-array-based UV/Vis spectrometer, and a Viscotek SEC-MALS 20 multi-angle light scattering detector. An HPLC grade DMF at 40 °C was used as the mobile phase (flow rate 1.0 mL min⁻¹). A triple detection calibration was performed on the instrument using a narrow MW polystyrene (Malvern). Samples were dissolved in

HPLC grade DMF at 2.0 mg/mL concentration and filtered using a syringe filter with 0.2 μ M PTFE membrane (VWR international) prior to analysis. The dn/dc for the sample was determined on-line using the OMNISEC software, which assumes 100% of the injected sample mass elutes from the column (dn/dc=0.1546). The number average molecular weights (M_n) and dispersities ($\mathcal{D} = M_w/M_n$) were determined using the OMNISEC software.

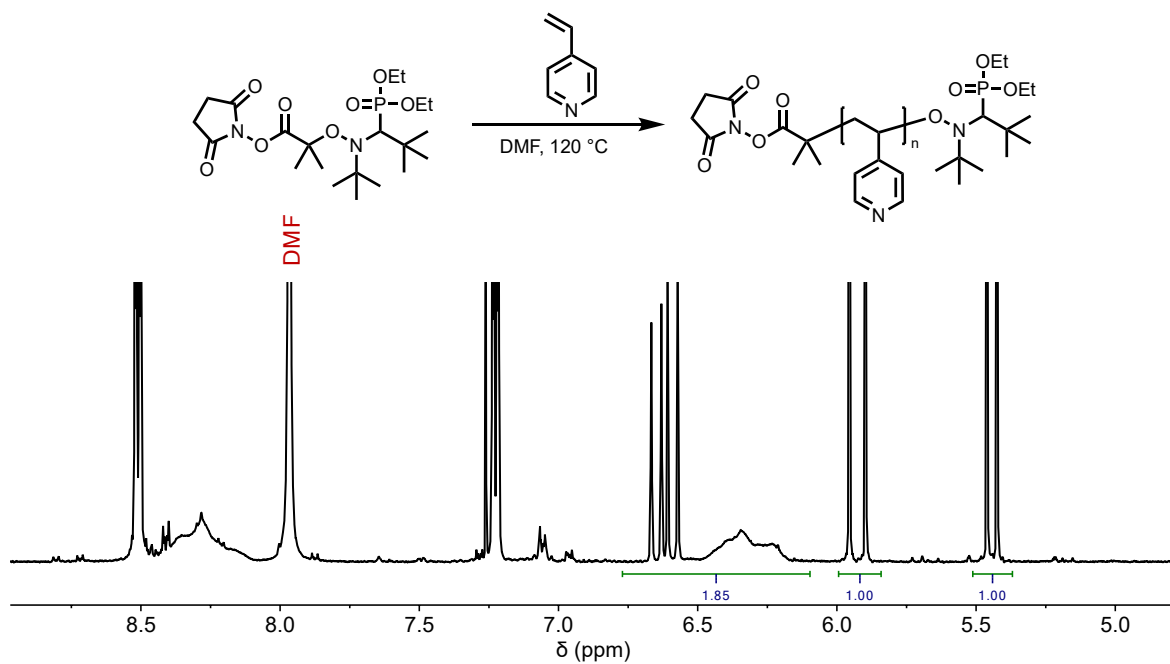


Figure S1. ¹H-NMR of **4VP** polymerization after 90 min (CDCl₃).

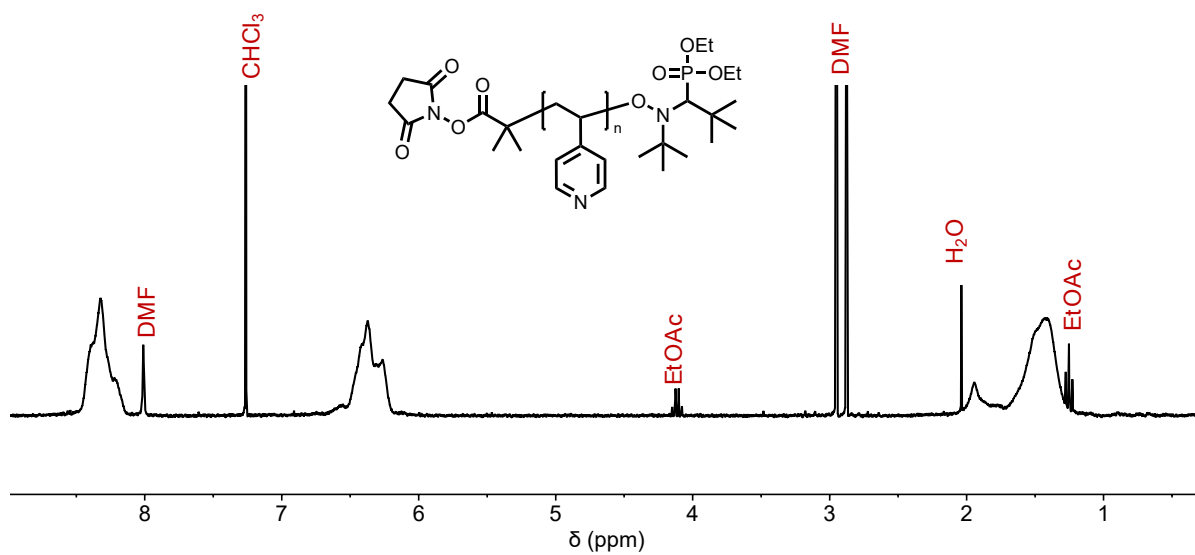


Figure S2. ¹H-NMR of **P4VP** (CDCl₃).

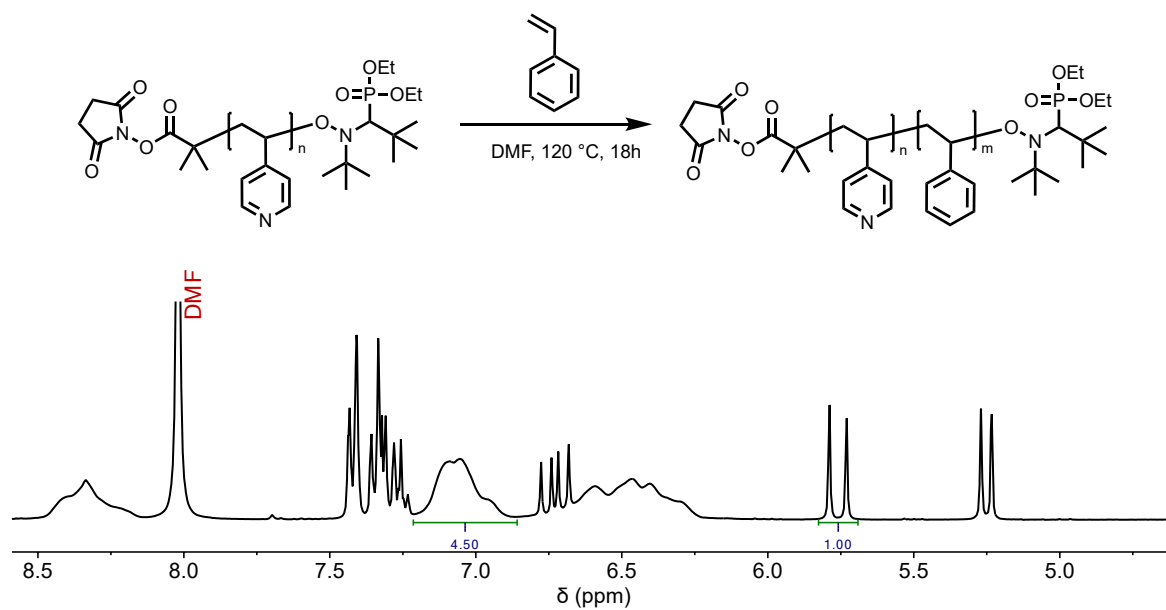


Figure S3. ¹H-NMR of **P4VP** chain extension with styrene after 18h (CDCl₃).

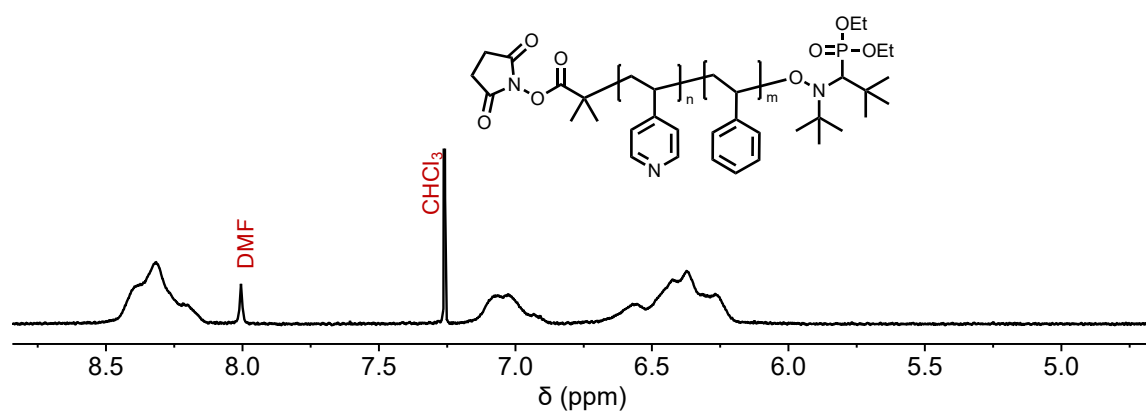


Figure S4. ¹H-NMR of **P4VP-b-PS** (CDCl₃).

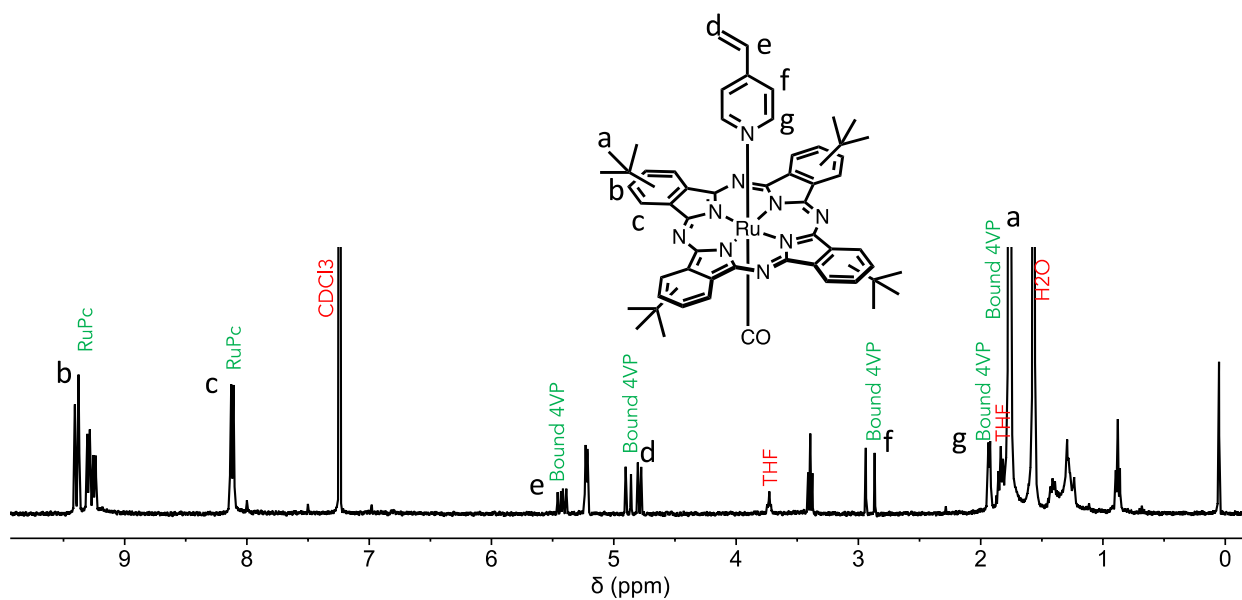


Figure S5. $^1\text{H-NMR}$ of $\text{Ru}\{(\text{t-bu})_4\text{PC}\}(\text{CO})(\mathbf{4VP})$ in CDCl_3 .

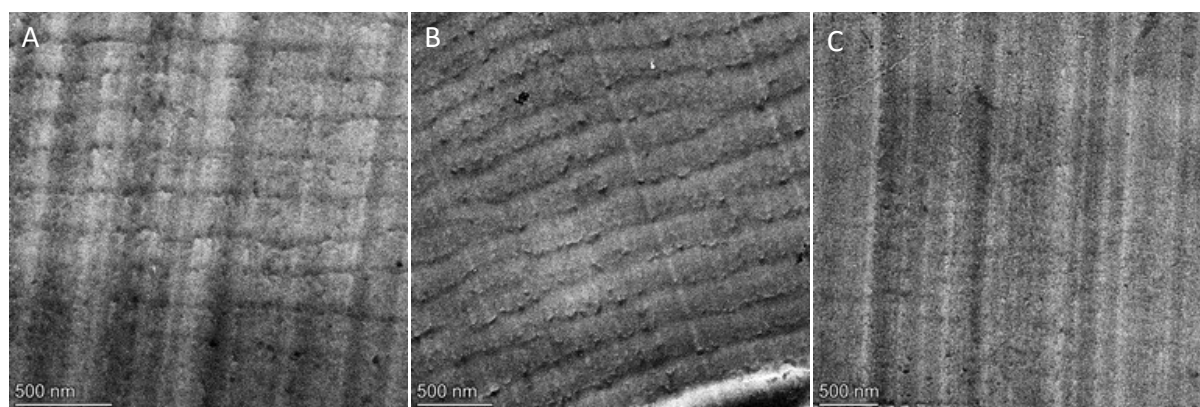


Figure S6. Additional TEM images of $\mathbf{P4VP}$ -RuPC film

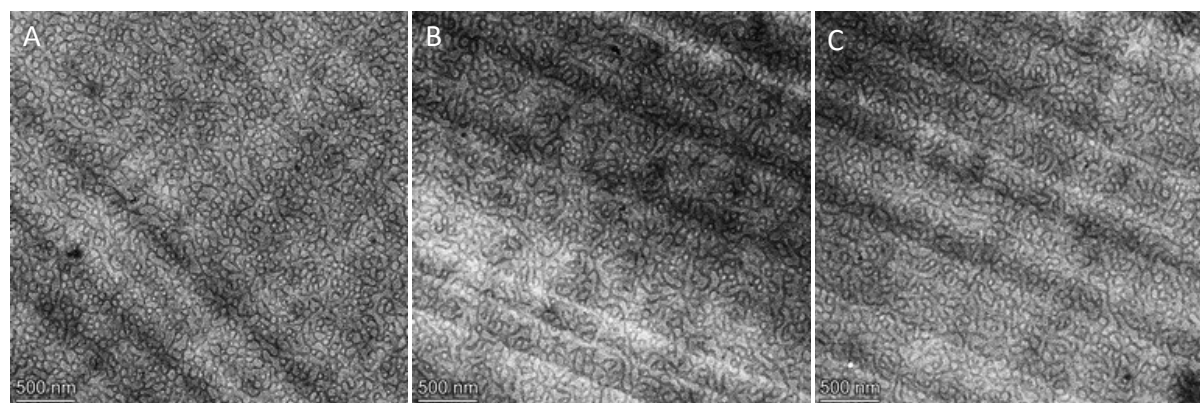


Figure S7. Additional TEM images of $\mathbf{P4VP-b-PS}$ -RuPC film

Figure S8. Gel permeation chromatogram of **4VP** polymerization by NMP

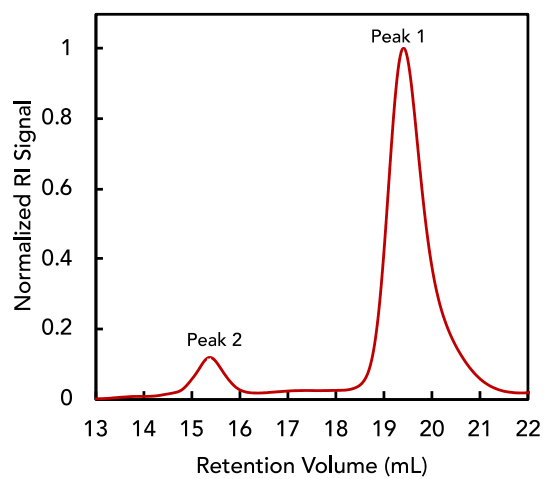


Table S1. M_n and PDI of **P4VP**

Peak	M_n (kDa)	PDI
1	37.0	1.19
2	734.7	3.06

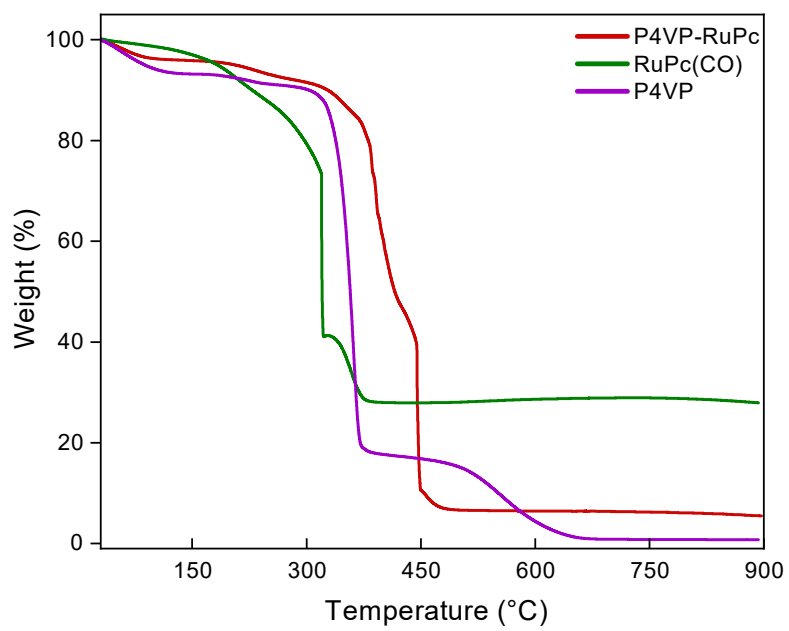


Figure S9. Thermogravimetric analysis (TGA) of P4VP-RuPc, RuPc(CO), and P4VP collected under air at atmospheric pressure using a temperature ramp of 20 °C/min⁻¹ from 30-900 °C.