

Probing Co-Assembly of Supramolecular Photocatalysts and Polyelectrolytes Using Isothermal Titration Calorimetry[†]

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Table of Contents

Content	Page
Table of Contents	S1
Materials/Synthesis	S2
Electronic Absorption	S3
Luminescence Spectroscopy	S4
Luminescence Titrations	S5
Excited State Lifetime	S6
Cryogenic Transmission Electron Microscopy	S6
Dynamic Light Scattering	S6
Isothermal Titration Calorimetry	S8
NMR Spectroscopy	S14
Static Light Scattering	S15
References	S16

Experimental

Materials. All chemicals were used as received unless noted otherwise. $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ were purchased from Alfa Aesar. 2,2'-Bipyridine (bpy), 2,3-bis(2-pyridyl)pyrazine (dpp), ascorbic acid, sodium ascorbate, tetrabutylammonium chloride (TBACl) and tetrabutylammonium hexafluorophosphate (TBAPF_6) were purchased from Fluka. Poly(vinyl sulfonate) ($M_w = 10,000$), p-toluene sulfonate and $[\text{Ru}(\text{bpy})_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ were purchased from Aldrich Chemical Company. Spectral grade acetonitrile was purchased from Burdick & Jackson. Poly(4-styrenesulfonate) (PSS) [$M_n = 1.44 \text{ kDa}$ ($\text{PDI} = 1.17$); $M_n = 57.8 \text{ kDa g/mol}$ ($\text{PDI} = 1.18$); $M_n = 1.01 \text{ MDa}$ ($\text{PDI} = 1.18$)] was purchased from scientific polymer products. Ammonium hexafluorophosphate (NH_4PF_6) was purchased from Strem Chemicals. Absolute ethanol, diethyl ether, dimethylformamide, and methylene chloride were purchased from Fischer Scientific. Sephadex[®] LH-20 was purchased from GE Healthcare. Ultrapure water was obtained from a Millipore Milli-Q[®] water purification system. Ultrapure argon and breathing air were purchased from Airgas. The starting material $[(\text{bpy})_2\text{Ru}(\text{dpp})][\text{PF}_6]_2$ was synthesized using previously reported procedures.¹

Synthesis. $[(\text{bpy})_2\text{Ru}(\text{dpp})]_2[\text{RhCl}_2]\text{Cl}_5$. The trimetallic complex $[(\text{bpy})_2\text{Ru}(\text{dpp})]_2[\text{RhCl}_2][\text{PF}_6]_5$ was prepared using a building block approach.² $[(\text{bpy})_2\text{Ru}(\text{dpp})][\text{PF}_6]_2$ (0.30 g, 0.32 mmol) was combined with $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (0.045 g, 0.18 mmol) in a solution of 2:1 ethanol:water. The solution was then refluxed for 2 hours, cooled to room temperature and precipitated by adding dropwise to a saturated aqueous solution of (NH_4PF_6). The product was collected by vacuum filtration and washed with 50 ml H_2O and 150 mL diethyl ether. The resulting product was then isolated using size exclusion chromatography having Sephadex[®] LH-20 as stationary phase and 2:1 ethanol:acetonitrile mobile phase. The trimetallic complex

$[\{(bpy)_2Ru(dpp)\}_2RhCl_2][PF_6]_5$ was converted to the water soluble $[\{(bpy)_2Ru(dpp)\}_2RhCl_2]Cl_5$ through salt metathesis by dissolving 5 g of the complex in acetonitrile and adding dropwise to a saturated solution of TBACl, collected by vacuum filtration, washed with 250 mL of acetonitrile followed by 200 mL of ether, and oven dried overnight.³

Poly(4-styrenesulfonate) Deuteration. Deuteration of the sulfonated polymer for use in NMR studies was carried out in a sealed bomb having a Teflon[®] reaction vessel. The polymer (1 g) was dissolved in deuterium oxide (D₂O) (pH = 10.0, adjusted with NaOD) and heated for 30 days at 200 °C in the presence of 0.250 g Pd/C. The reaction was monitored by removing 100 uL and measuring ¹H NMR in D₂O. Completion of the reaction showed only very small broad peaks throughout the aromatic region.

Methods.

Electronic Absorption Spectroscopy. Electronic absorption was measured using a Hewlett-Packard 8453 diode array spectrophotometer with 1 nm resolution. Spectra were collected in 1 cm quartz cuvettes (Starna Cells Inc.) in spectrophotometric grade acetonitrile. Extinction coefficients were calculated from the average of three samples.

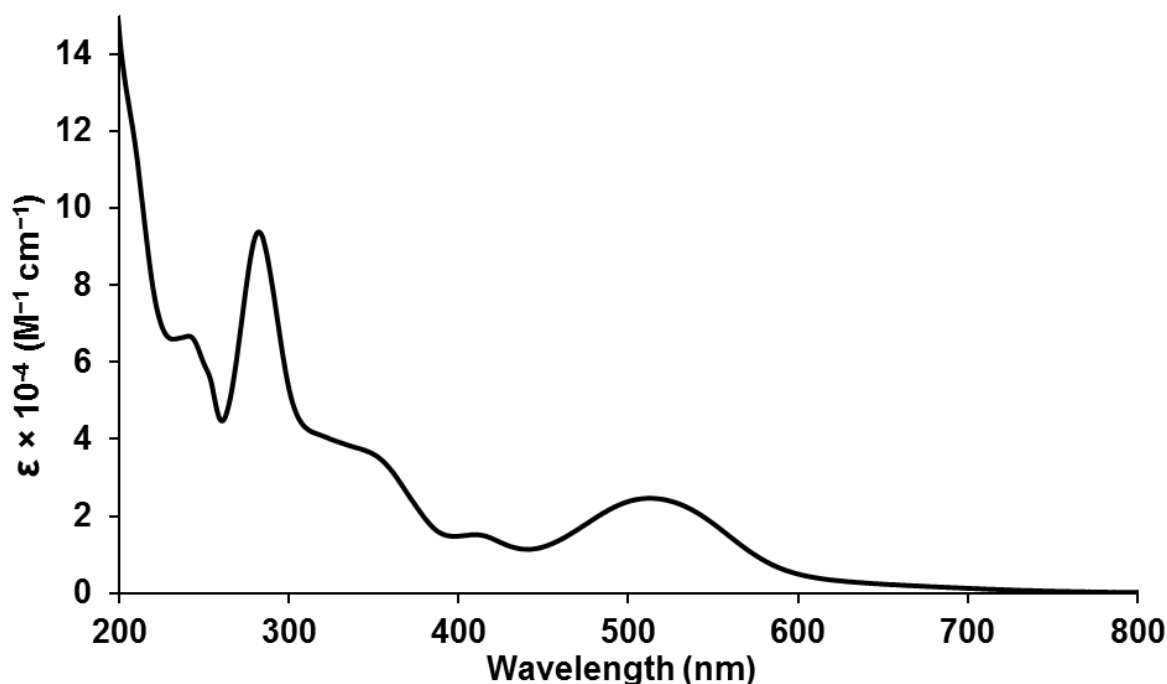


Figure S1. Electronic absorbance spectrum of $[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{RhCl}_2]\text{Cl}_5$ in deoxygenated aqueous solution. (bpy = 2,2'-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine).

Luminescence Spectroscopy. Steady state luminescence spectroscopy of $[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{RhCl}_2]\text{Cl}_5$ (10 μM) was measured in screw-top 1 cm quartz cuvettes (Starnes Cells Inc.). Emission spectra were measured at room temperature in ultrapure water following deoxygenation with argon. Spectra were measured using a Quanta Master QM-200-45E fluorimeter from Photon Technologies International Inc. The samples were excited using a water-cooled 150 W Xenon arc lamp and emission was measured at a 90° angle using a thermoelectrically cooled Hamamatsu R2658 photomultiplier tube operating in photon counting mode. The emission

quantum yields were referenced to $[\text{Os}(\text{bpy})_3]^{2+}$ ($\Phi = 4.62 \times 10^{-3}$) and calculated using the method of Winfield and Williams,^{4,5} using the same instrument settings and correcting for PMT response.

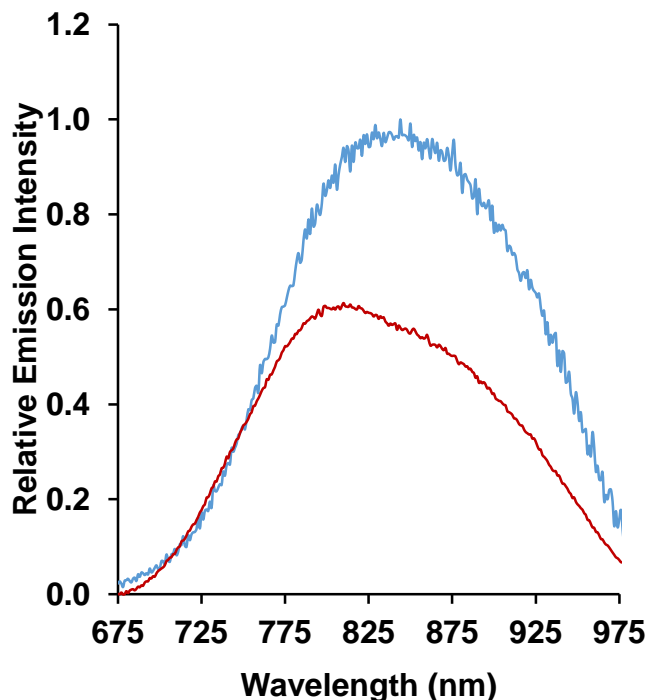


Figure S2. Relative emission intensity of **Ru,Rh,Ru** (10 μM) in the presence (red) and absence (blue) of poly(vinylsulfonate) (PVS) (2.5 mM). Measured in deoxygenated aqueous solutions, corrected for PMT response.

Luminescence Titrations. Steady-state emission spectroscopy of $[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{RhCl}_2\text{Cl}_5$ (10 μM) was measured in screw-top 1 cm quartz cuvettes (Starnes Cells Inc.). Emission spectra were measured at room temperature in ultrapure water following deoxygenation with argon. A deoxygenated solution of PSS (57.8 kDa) was titrated into the cuvette containing the photocatalyst by adding 25 μL injections using a Hamilton syringe. Spectra were measured using a Quanta Master QM-200-45E fluorimeter from Photon Technologies International Inc. The samples were excited using a water-cooled 150 W Xenon arc lamp and emission was measured at a 90° angle using a thermoelectrically cooled Hamamatsu R2658 photomultiplier tube operating in photon counting mode. The emission quantum yields were

referenced to $[\text{Os}(\text{bpy})_3]^{2+}$ ($\Phi = 4.62 \times 10^{-3}$) and calculated using the method of Winfield and Williams,^{4,5} using the same instrument settings and correcting for PMT response.

Excited-State Lifetime Measurements. Time-resolved emission spectroscopy of $[\{(\text{bpy})_2\text{Ru}(\text{dpp})\}_2\text{RhCl}_2]\text{Cl}_5$ (10 μM) was measured in screw-top 1cm quartz cuvettes (Starnes Cells Inc.). Emission spectra were measured at room temperature in ultrapure water following deoxygenation with argon. Time-resolved emission was measured using a PL-2300 nitrogen laser equipped with a PL-201 dye laser. The dye used was coumarin 500 and excitation monochromator was set to 520 nm. The emission was detected at 90° after passing through a monochromator set to 790 nm and measured using a Hamamatsu R928 PMT operating in direct output mode. The emission decay was recorded on a Techtronix TDS3052C oscilloscope. The lifetime was calculated from the average of 300 sweeps. Data was fitted to mono and bi exponential decay functions in the absence and presence of 2.5 mM PSS, respectfully.

Cryogenic Transmission Electron Microscopy. Samples were prepared for TEM by combining $[\{(\text{bpy})_2\text{Ru}(\text{dpp})\}_2\text{RhCl}_2]\text{Cl}_5$ (120 μM) with 57.8 kDa PSS (0.5 mM) in ultrapure water. The samples were deposited on a Qauntafoil[®] grid having 2 μm pores and frozen in liquid ethane at -195°C . The samples were then transferred to a temperature controlled holder maintained at -195°C and analyzed with a JEOL 2100 transmission electron microscope.

Dynamic light scattering. Dynamic light scattering (DLS) was measured on a Malvern Zetasizer Nano ZS. Samples were prepared for DLS by combining $[\{(\text{bpy})_2\text{Ru}(\text{dpp})\}_2\text{RhCl}_2]\text{Cl}_5$ (120 μM) to PSS (0.5 mM) (57.8 kDa) in ultrapure water. Solutions were allowed to equilibrate for 5 minutes prior to analysis measured on a Malvern Zetasizer Nano ZS.

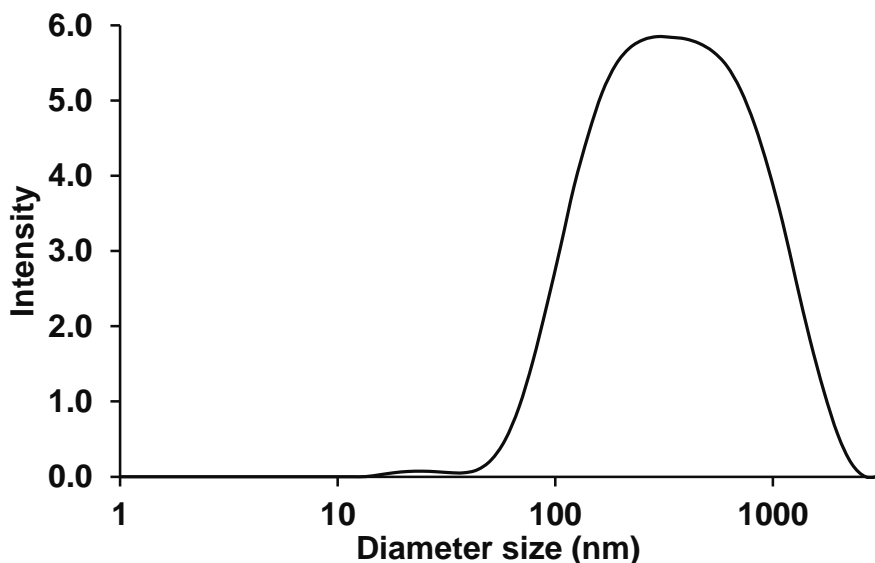


Figure S3: Size distribution of polymer:catalyst aggregates in aqueous solutions containing $[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{RhCl}_2\text{Cl}_5$ and PSS from dynamic light scattering studies. bpy = 2,2'-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine

Isothermal Titration Calorimetry. Isothermal titration calorimetry was carried out on a TA Instruments-Waters LLC NanoITC[®] titration calorimeter. Solutions of the Ru,Rh,Ru complex were titrated into the cell (0.170 mL) containing polyelectrolyte using an automated buret equipped with a 0.050 mL Hamilton syringe. Approx. 36 injections of 0.00143 mL were performed with 300 s between injections to allow for heat signals to return to baseline intensity. Control titrations of the complex titrated into ultrapure water and titration of ultrapure water into polyelectrolyte were subtracted from the heats obtained. Experiments were performed in triplicate and fitted with TA NanoAnalyze[®] software and the values averaged to obtain binding parameters reported herein. The heats obtained are related to the enthalpy of binding (ΔH), binding stoichiometry (n), binding affinity (K), reaction volume (V), and the free ligand concentration (L) using equation 1. The heats obtained can also be related to the total ligand concentration (L_T) using equation 2 and the concentration of ligand bound (L_B) using equation 3.⁶ Fitting of the two-stage thermogram was

performed using the method of Kim.⁷ Both stages of the thermogram were fit with an independent site model, the first stage (NDH1) was a function of parameters N_1 , ΔH_1 , and K_1 while the second stage (NDH2) was a function of N_3 , ΔH_1 , K_1 , N_2' , $\Delta H_2'$, K_2' . The second endothermic binding stage near the end of the titrations was fit with an additional function (Equation 4) which represented the fractional coverage of the collapsed polymer and was incorporated into the model to correct the mole ratio (N_2) due to the previous binding event. The equations (NDH1, NDH2) were fit simultaneously and the sum of NDH1 and NDH2 related to the experimental integrated heats using least squares analysis. The true stoichiometry (N_2) of the second binding event (endothermic) was calculated by subtracting the n value obtained using equation 4 (N_3) and the n value obtained from the independent site model (N_2').

$$Q = V[M] \frac{n\Delta H K [L]}{1 + K [L]} \quad (1)$$

$$Q = \frac{(1 + [M]nK + K[L_T]) - [(1 + [M]nK + K[L_T])^2 - 4[M]nK^2[L_T]]^{\frac{1}{2}}}{\frac{2K}{V\Delta H}} \quad (2)$$

$$[L_B] = \frac{Q}{V\Delta H} \quad (3)$$

$$\theta_{collapsed} = ABS[\frac{(\Delta H_1 - \frac{\Delta Q}{\# \text{ moles titrant}})}{\Delta H_1}] \quad (4)$$

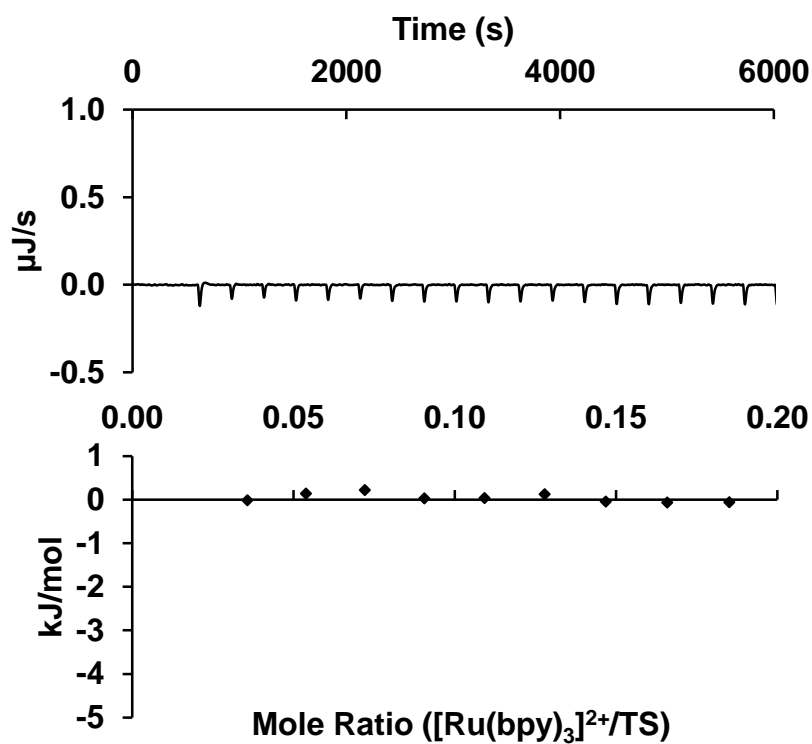


Figure S4. Thermograms for the isothermal titration of 2.0 mM [Ru(bpy)₃]Cl₂ into 1.1 mM p-toluenesulfoante (TS). Measured in aqueous solution, corrected for dilution response. bpy = 2,2'-Bipyridine

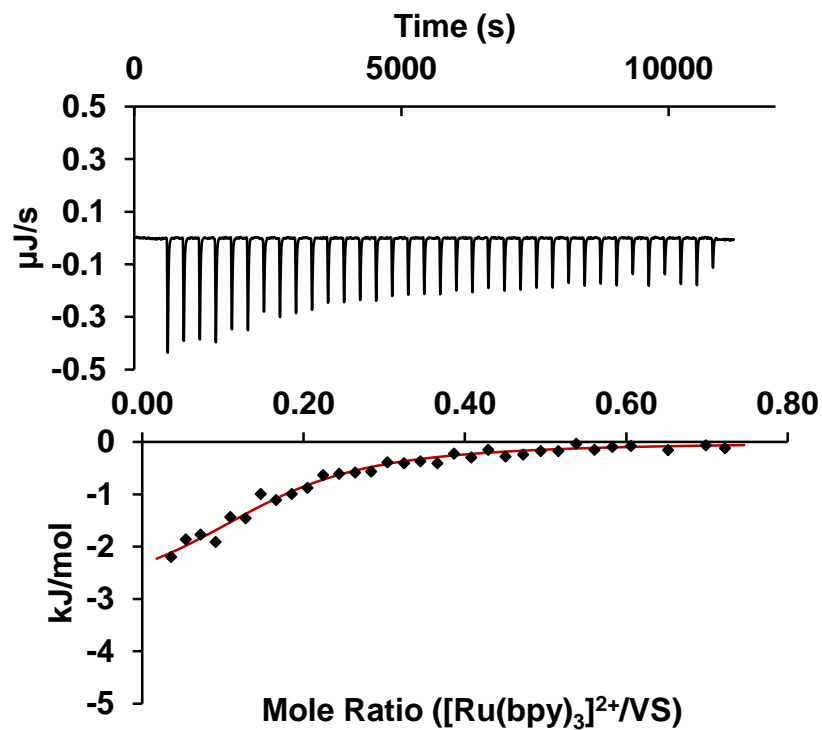


Figure S5. Thermograms and single-site fit for the isothermal titration of 2.0 mM $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ into 1.0 mM poly(vinylsulfonate) (PVS). Measured in aqueous solution, corrected for dilution response. bpy = 2,2'-Bipyridine

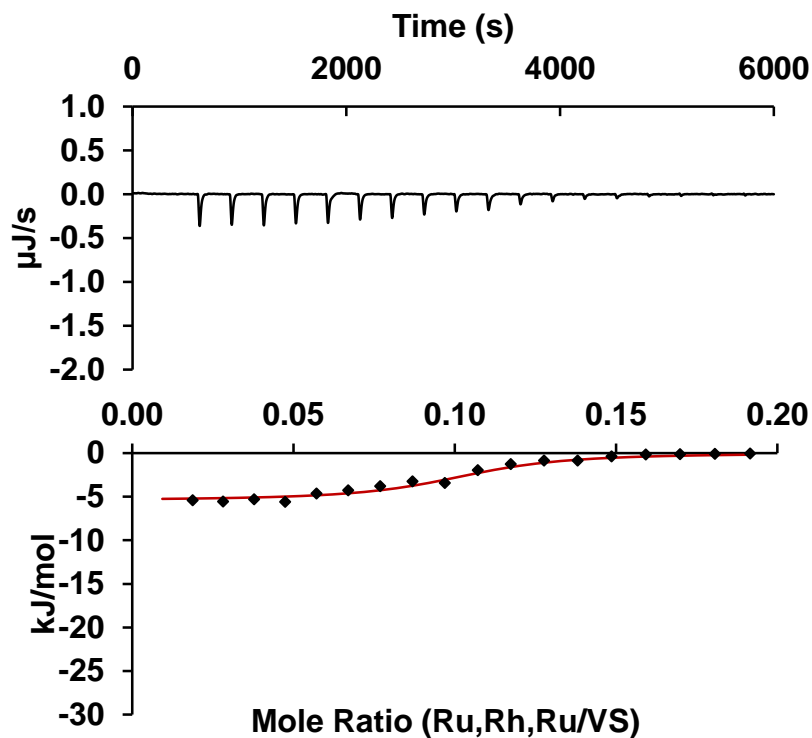


Figure S6. Thermograms and single-site fit for the isothermal titration of 1.18 mM $[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{RhCl}_2]\text{Cl}_5$ into 1.31 mM poly(vinylsulfonate) (PVS). Measured in aqueous solution, corrected for dilution response. bpy = 2,2'-Bipyridine, dpp = 2,3-Bis(2-pyridyl)pyrazine

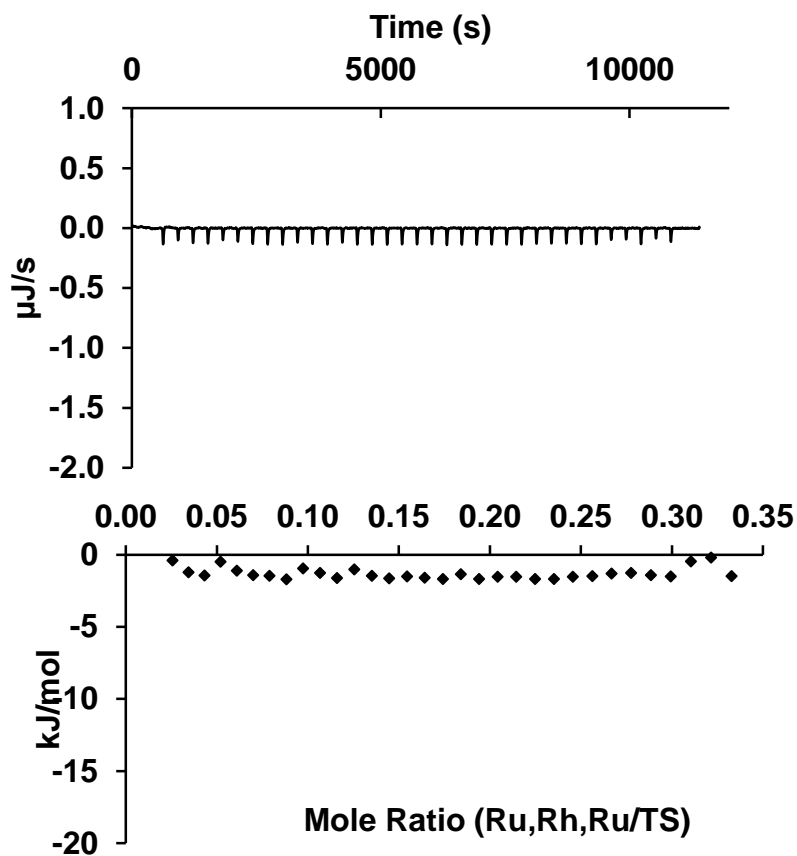


Figure S7. Thermograms for the isothermal titration of 1.18 mM $[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{RhCl}_2\text{Cl}_5$ into 1.3 mM toluenesulfonate (TS). Measured in aqueous solution, corrected for dilution response. bpy = 2,2'-Bipyridine, dpp = 2,3-Bis(2-pyridyl)pyrazine)

NMR Spectroscopy. NMR spectroscopy was carried out on solutions containing 5 mM $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ in 50 mM poly(styrenesulfonate) (57.8 kDa), poly(vinylsulfonate) or p-toluenesulfonate TS in ultrapure water using an Agilent 400 MHz NMR spectrometer.

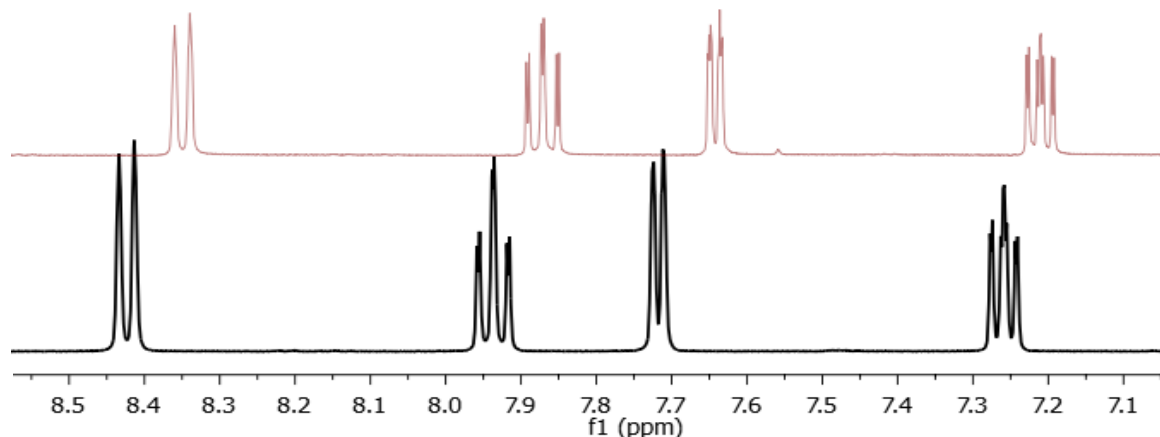


Figure S8. ^1H NMR (400 MHz) spectrum of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ (5 mM) in the absence (black) and presence of deuterated p-toluenesulfonate ($\text{d}_7\text{-TS}$) (50 mM) in D_2O . bpy = 2,2'-bipyridine

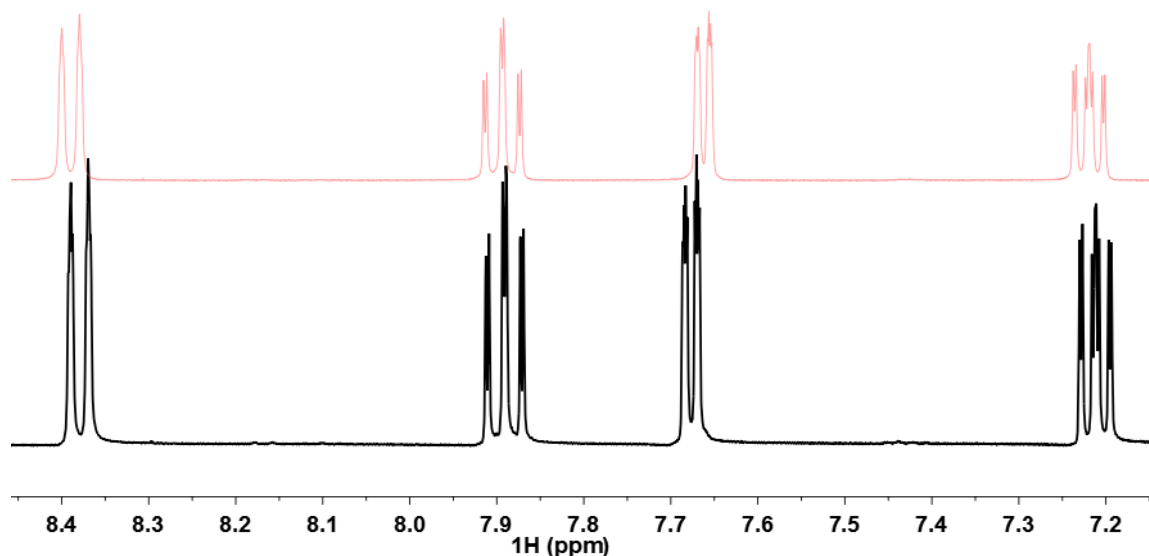


Figure S9. ^1H NMR (400 MHz) spectrum of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ (5 mM) in the absence (black) and presence of poly(vinylsulfonate) (PVS) (50 mM) in D_2O . bpy = 2,2'-bipyridine

Static Light Scattering. Steady state light scattering of $[\{(bpy)_2Ru(dpp)\}_2RhCl_2]Cl_5$ in PSS (57.8 kDa)solutions was measured in screw-top 1 cm quartz cuvettes (Starnes Cells Inc.). Scattering intensity was measured at room temperature in ultrapure water. Spectra were measured using a Quanta Master QM-200-45E fluorimeter from Photon Technologies International Inc. The samples were excited ($\lambda = 600$ nm) using a water-cooled 150 W Xenon arc lamp and scattering measured at a 90° angle using a thermoelectrically cooled Hamamatsu R2658 photomultiplier tube operating in photon counting mode.

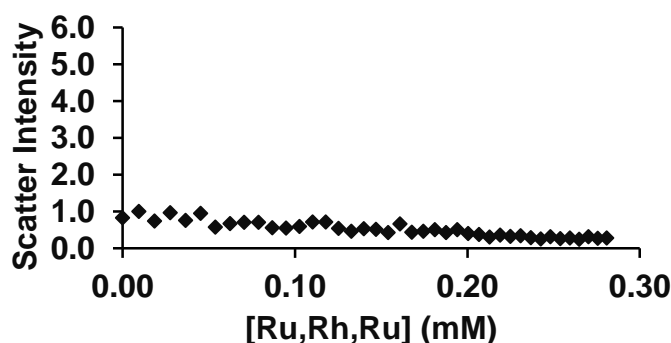


Figure S10. Scattering intensity measured at 90° angle from source ($\lambda = 600$ nm) for the titration of 1.18 $[\{(bpy)_2Ru(dpp)\}_2RhCl_2]Cl_5$ into ultrapure water at $25^\circ C$. Measured in aqueous solution at $25^\circ C$. bpy = 2,2'-Bipyridine, dpp = 2,3-Bis(2-pyridyl)pyrazine)

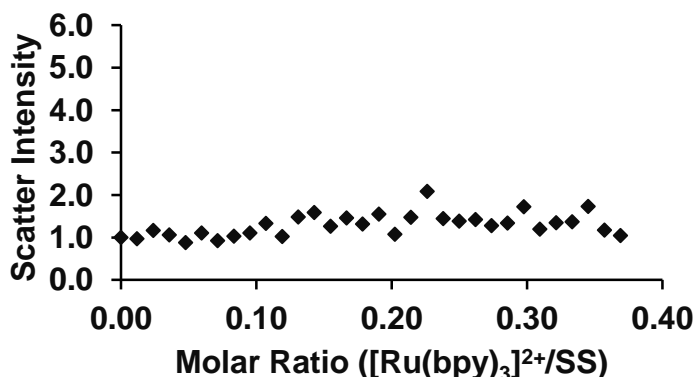


Figure S11. Scattering intensity measured at 90° angle from source ($\lambda = 600$ nm) for the titration of 0.55 $[Ru(bpy)_3]Cl_2$ into 1.1 mM poly(4-styrenesulfonate) (PSS) at $25^\circ C$. Measured in aqueous solution at $25^\circ C$. bpy = 2,2'-Bipyridine, dpp = 2,3-Bis(2-pyridyl)pyrazine

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