Influence of Polystyrenesulfonate on Electron Transfer Quenching of Ruthenium Trisbipyridine Luminescence by Viologens: Non-Covalent Assembly and Covalent Tethering of the Ruthenium Complex

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SUPPLEMENTARY MATERIAL

ADDITIONAL EXPERIMENTAL DATA

Table S1-S2
Figures S1-S11

ADDITIONAL THEORETICAL BACKGROUND

Calculation of theoretical bimolecular diffusion-controlled rate constants

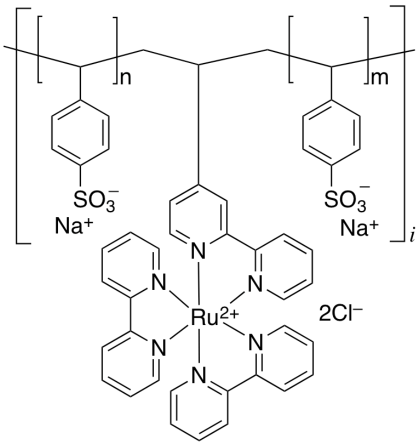
ADDITIONAL EXPERIMENTAL DATA

COMPLEX	**absorption**				**luminescence**					**TA**	
	λ_{max} (aq)	**λ_{max} (PSS)**	**PSS ε shift**	**λ_{isos} /nm**	**λ_{max} (aq)**	**λ_{max} (PSS)**	**I/I_0 air**	**τ/τ_0 air**	**τ/τ_0 Ar**	**λ_{max} (aq)**	**λ_{max} (PSS)**
$[Ru(bpy)_3]^{2+}$	452 nm	456 nm	-5%	465	615 nm	617 nm	1.85	1.75	1.33	363 nm	366 nm
RuB-PSS	-	458 nm	-	-	-	618 nm	1.62	1.73	1.14	-	365 nm

Table S1. Absorption, emission, and transient absorption (TA) characteristics of $[Ru(bpy)_3]^{2+}$ in aqueous solution and in the presence of PSS (PSS/Ru = 50 for $[Ru(bpy)_3]^{2+}$); data in air. For RuB-PSS (PSS/Ru = 19), the enhancement was calculated relative to the same concentration of $[Ru(bpy)_3]^{2+}$ in solution. $\tau_0 = 360$ ns.

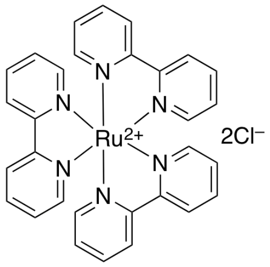
[PSS] / mM	**PSS/Ru**	**τ_1 / ns**	**A_1 / %**	**τ_2 / ns**	**A_2 / %**
0	0	487	100		
0.1	5	570	49	200	51
0.2	10	725	64	210	36
0.4	20	885	75	260	25
0.7	35	1222	59	390	41
1.0	50	1320	62	415	38
2.0	100	1420	62	445	38
3.0	150	1513	63	472	37
5.0	250	1537	65	471	35
10.0	500	1709	60	560	40

Table S2. Double exponential decays of $*[Ru(phen)_3]^{2+}$ in the presence of PSS in air. $[[Ru(phen)_3]^{2+}] = 2\times10^{-5}$ M.

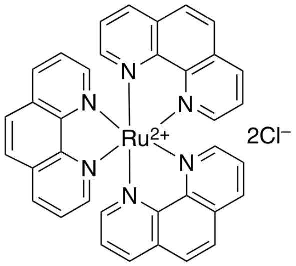


PSS-$[Ru(bpy)_2(bpy')]^{2+}$ (19:1)

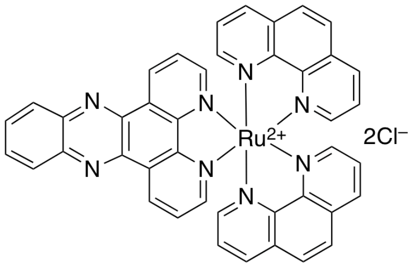
RuB-PSS



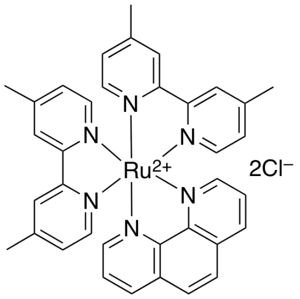
$[Ru(bpy)_3]^{2+}$



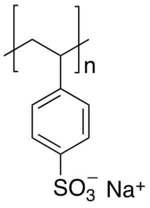
$[Ru(phen)_3]^{2+}$



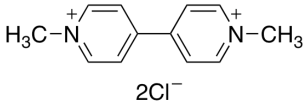
$[Ru(phen)2dppz]^{2+}$



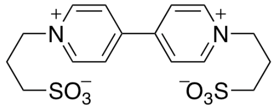
$[Ru(phen)(dmb)_2]^{2+}$



PSS



MV^{2+}



PVS^0

Fig. S1 Structures of all compounds examined in this study.

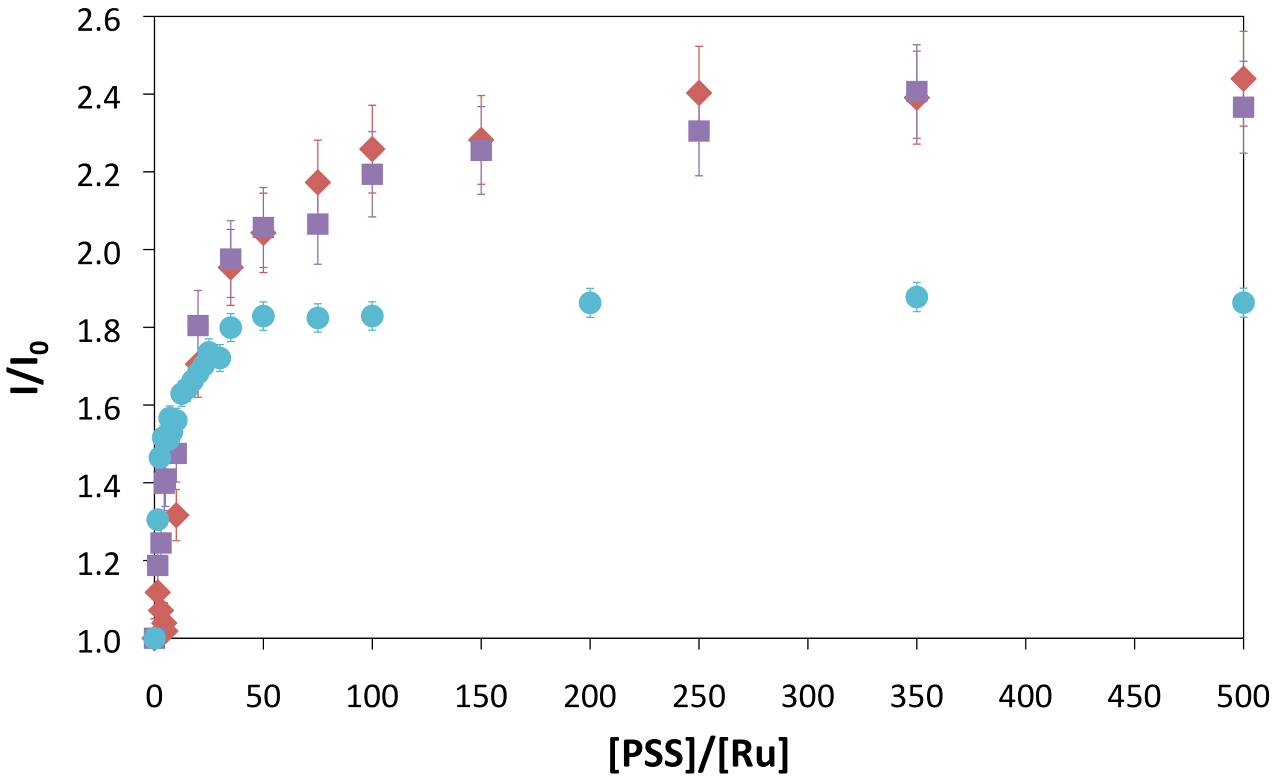


Fig. S2 Increase in the luminescence intensity of $[Ru(L)_3]^{2+}$ on addition of PSS to aqueous solution in air; $[Ru(bpy)_3]^{2+}$ (●), $[Ru(phen)(dmb)_2]^{2+}$ (■), and $[Ru(phen)_3]^{2+}$ (◆). $[[Ru(L)_3]^{2+}] = 2 \times 10^{-5}$ M. Excitation was at isosbestic points.

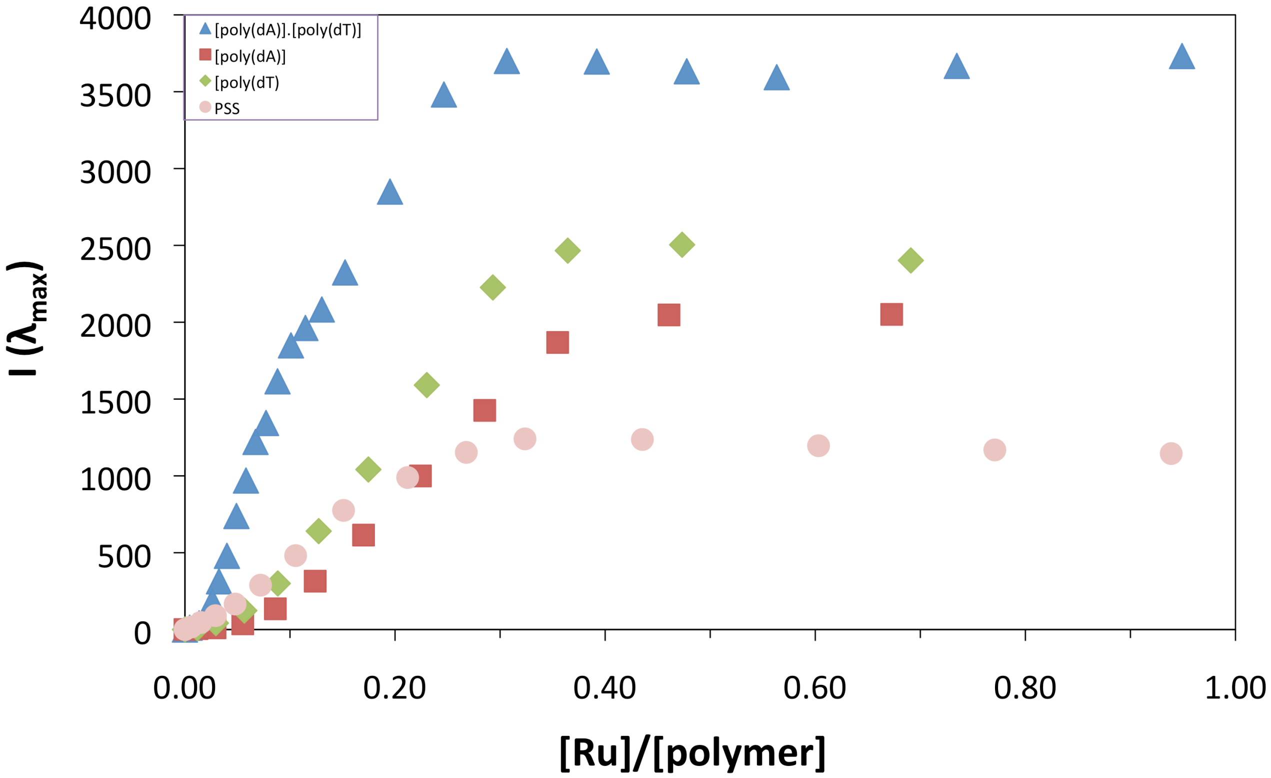


Fig. S3 Increase in the luminescence intensity of Δ-[Ru(phen)$_2$dppz]$^{2+}$ in the presence of PSS and DNA in 5 mM phosphate (pH 6.9) in air. [Ru(phen)$_2$dppz]$^{2+}$ has no measureable emission in aqueous solution in the absence of polymer .[Ru(phen)$_2$dppz]$^{2+}$ is added to polymer and becomes emissive if bound; the emission plateaus at saturation of binding. λ_{ex} = 480 nm. 5 μM [poly(dT)] (◆), 5 μM [poly(dA)] (■), 10 μM [poly(dA)]·[poly(dT)] (▲), and 10 μM PSS (●). Polymer concentrations are expressed as nucleotide concentration for nucleic acids, and as styrene sulphonate concentration for PSS.

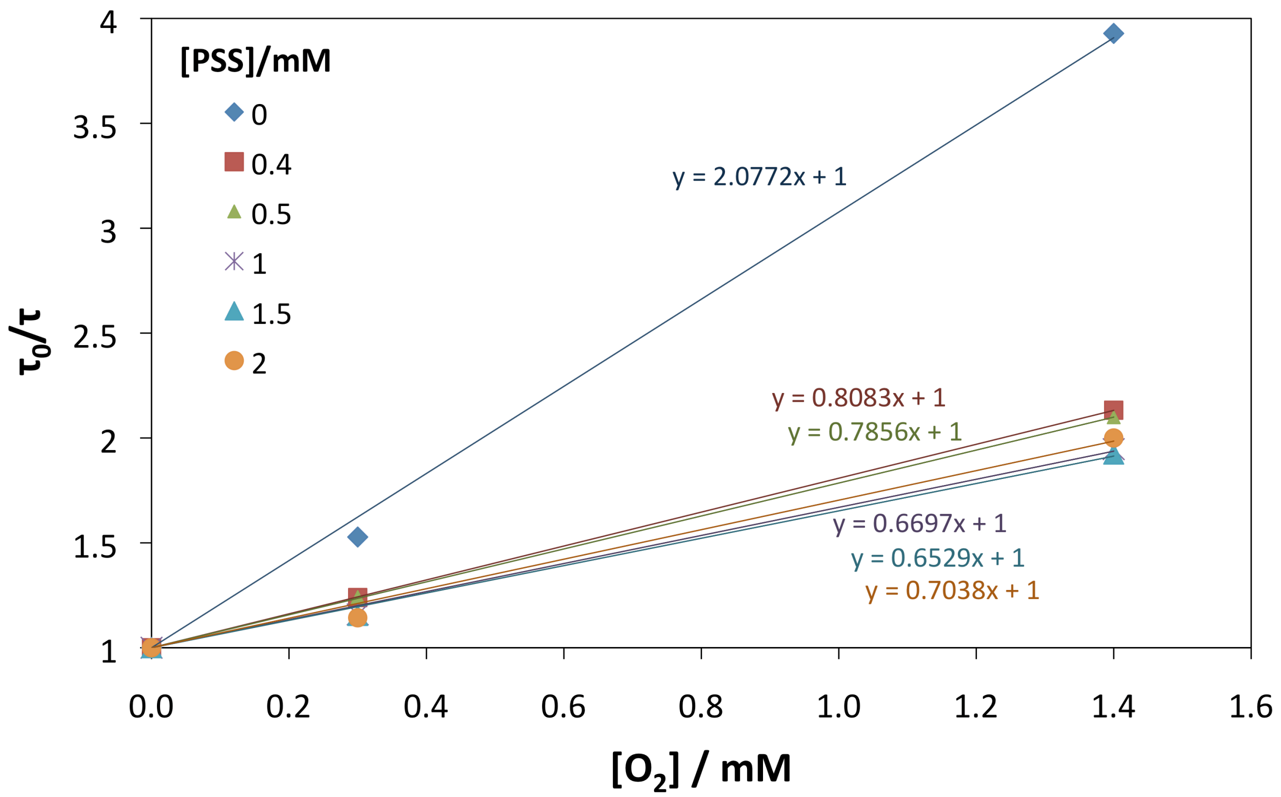


Fig. S4 Stern-Volmer plot for oxygen quenching of $[Ru(bpy)_3]^{2+}$ as a function of added PSS. $[[Ru(bpy)_3]^{2+}] = 2 \times 10^{-5}$ M. The concentration of O_2 in water at ambient atmosphere is assumed to be equal to 3×10^{-4} M, in O_2-saturated water is assumed to be 1.4×10^{-3} M, and in argon-saturated water is assumed to be insignificant [M. Montalti, A. Credi, L. Prodi, M. T. Gandolfi, Handbook of Photochemistry, 3rd edition, CRC, (2006)].

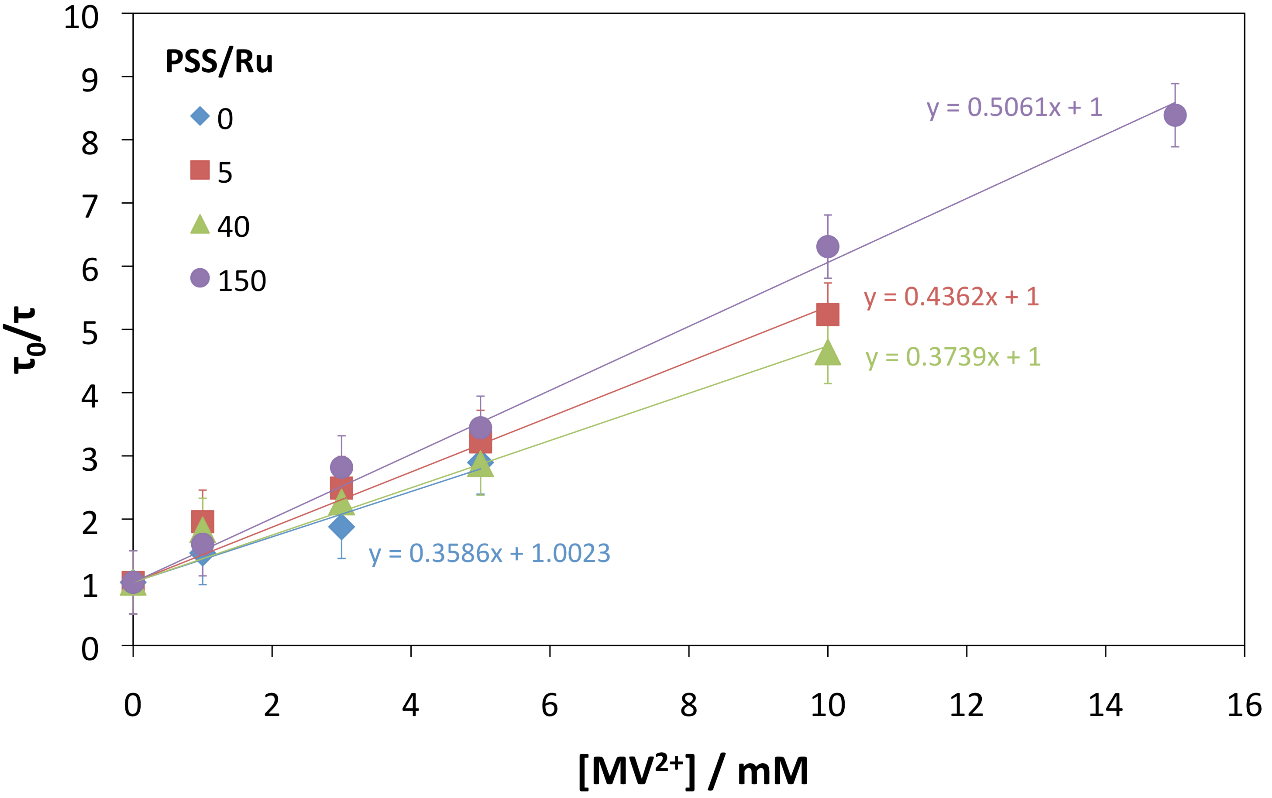


Fig. S5 Effect of PSS on the lifetime quenching of $*[Ru(bpy)_3]^{2+}$ by MV^{2+} in air. $[[Ru(bpy)_3]^{2+}] = 2\times10^{-5}$ M. PSS/Ru values according to legend at right of plot.

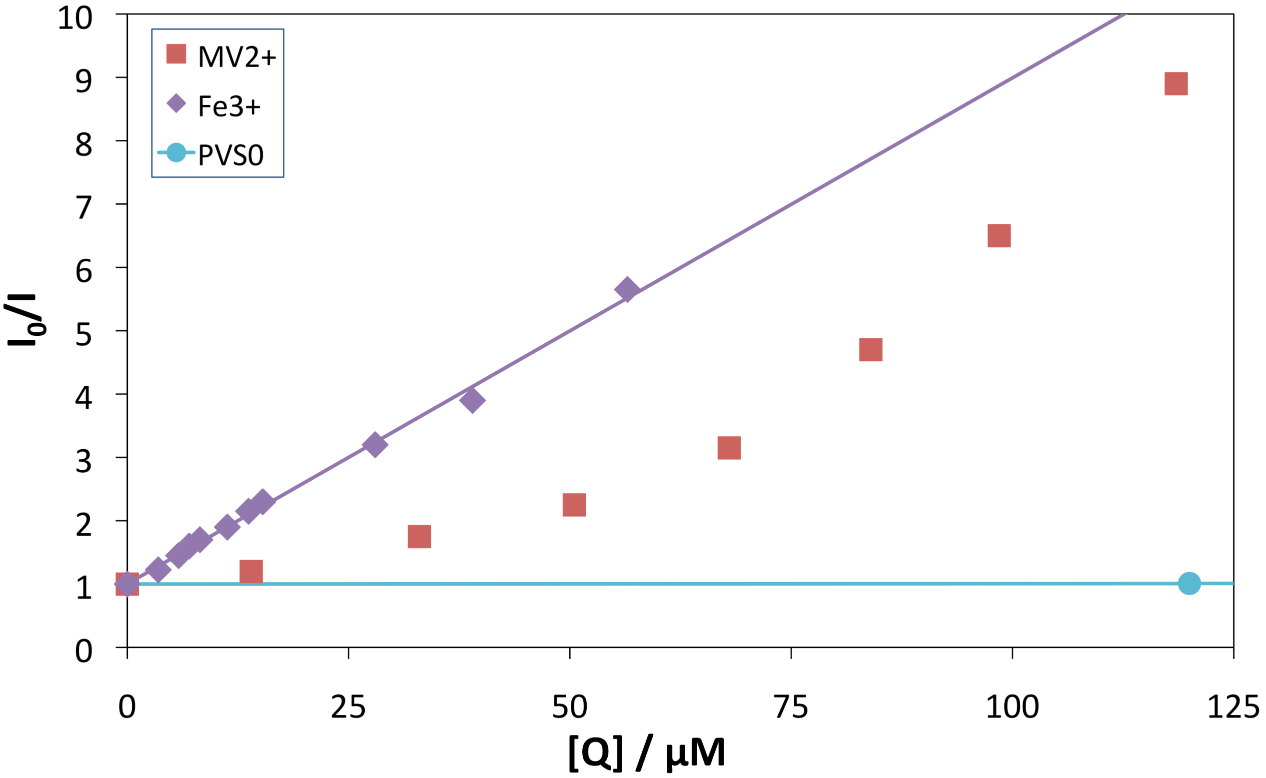
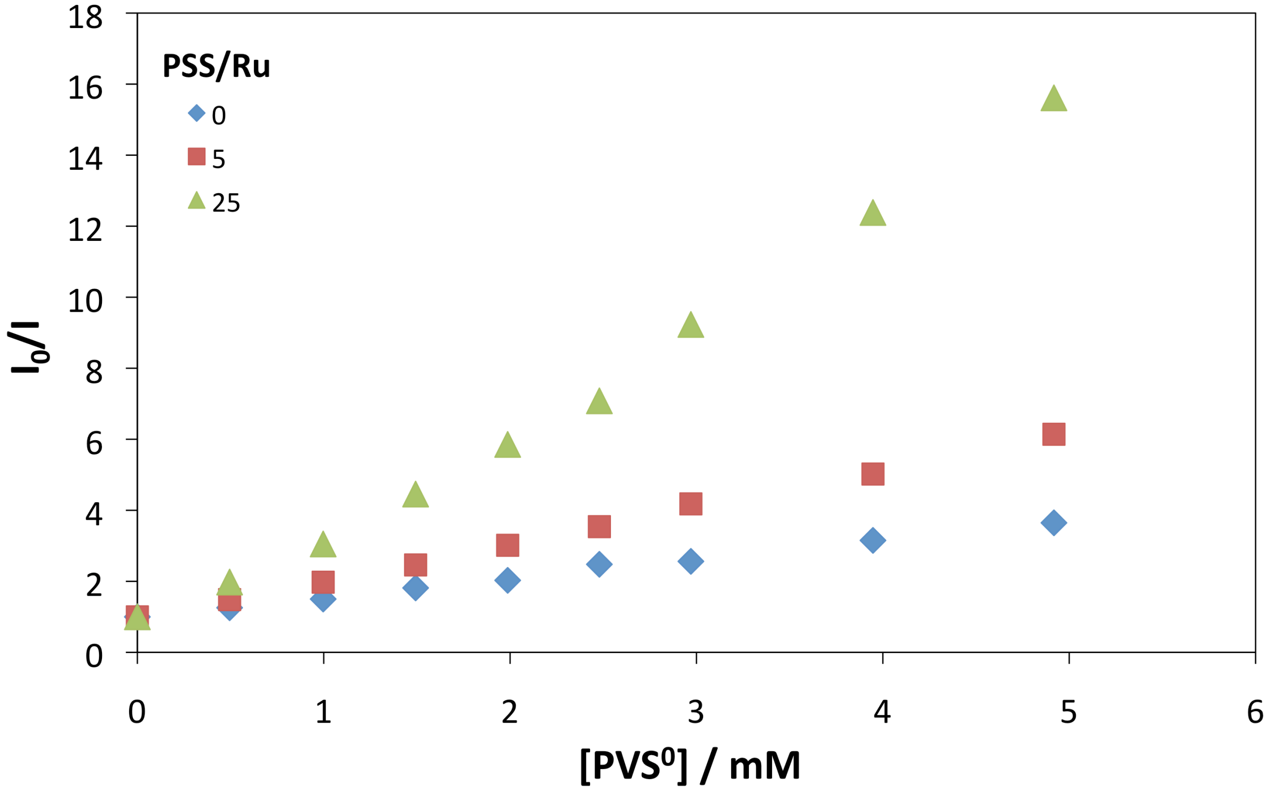


Fig. S6 Quenching of RuB-PSS luminescence in air. Fe^{3+} (◆); MV^{2+} (■); PVS^{0} (●). $[[Ru(bpy)_3]^{2+}] = 2\times10^{-5}$ M.



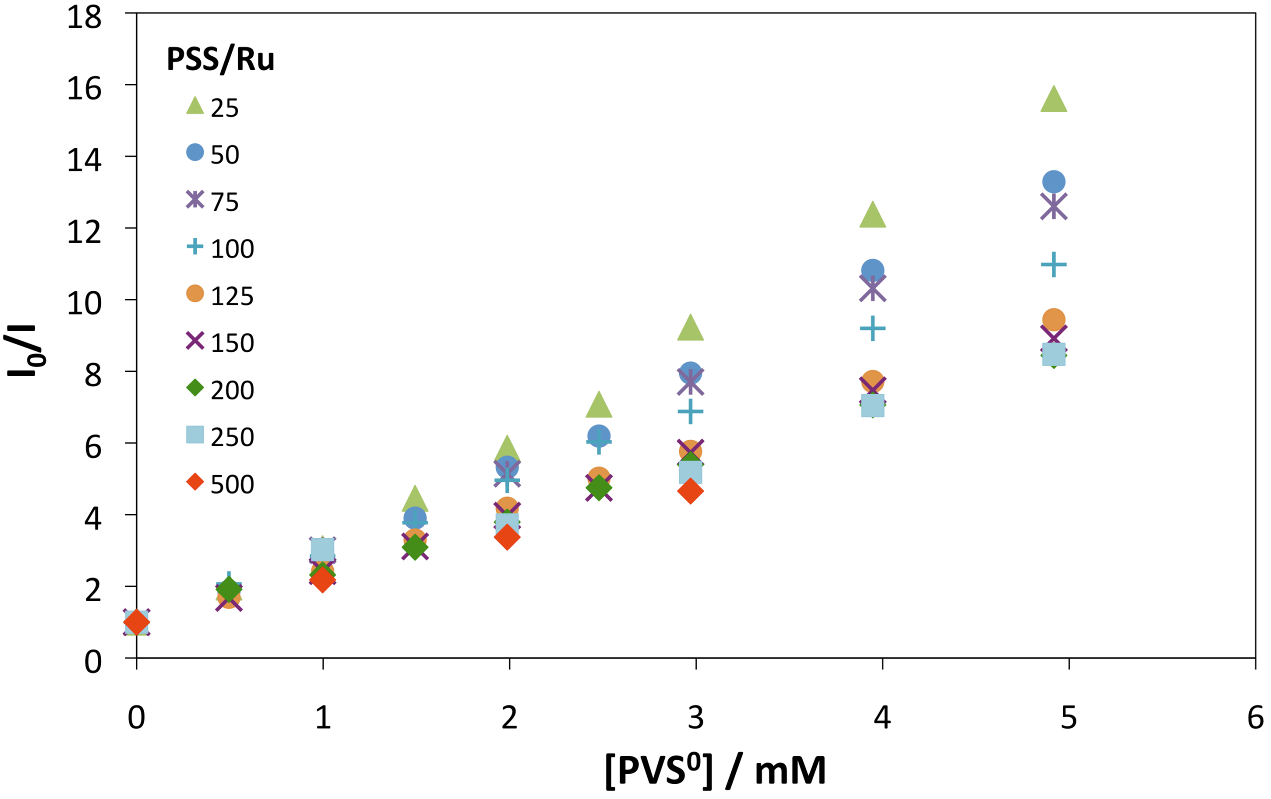


Fig. S7 Effect of PSS on the quenching of *[Ru(bpy)$_3$]$^{2+}$ by PVS^0 in air. [[Ru(bpy)$_3$]$^{2+}$] = 2×10^{-5} M. PSS/Ru are given in the legend on the right of the plot. (top) PSS/Ru < 25; (bottom) PSS/Ru < 25.

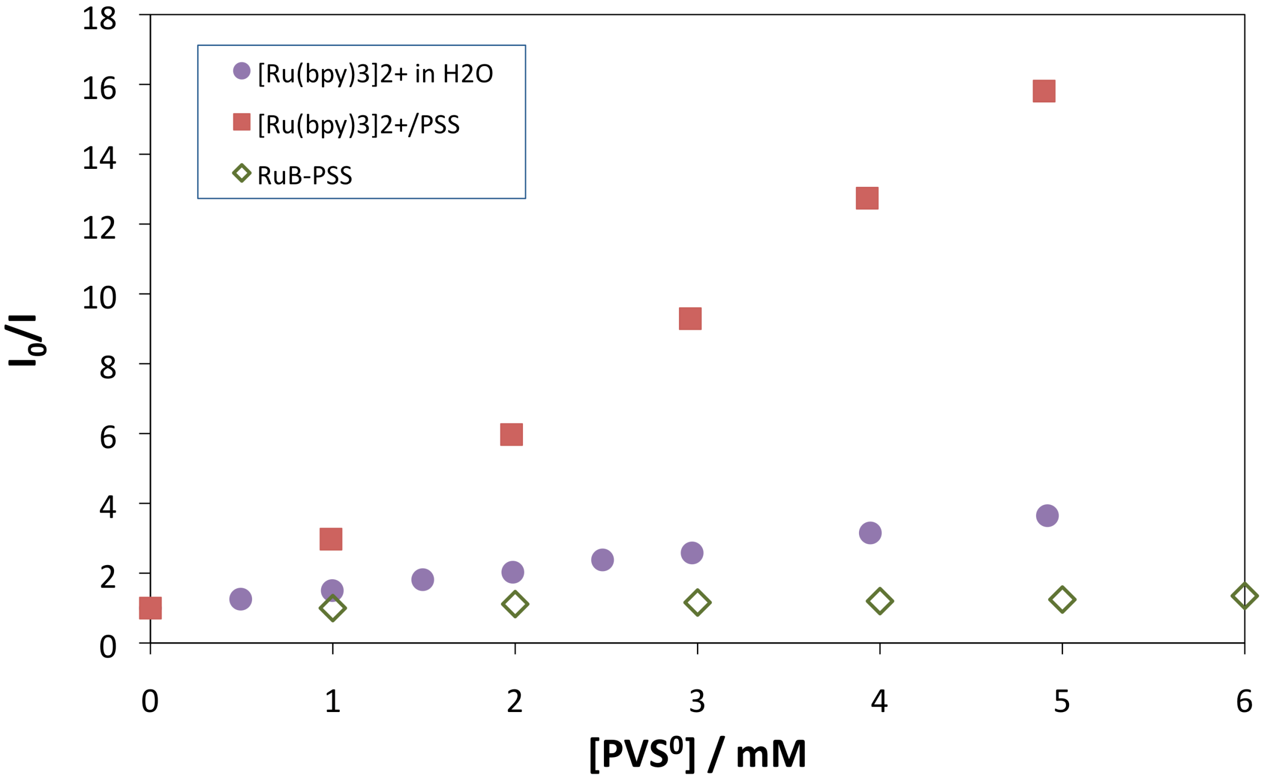


Fig. S8 Comparative quenching of *$[Ru(bpy)_3]^{2+}$ by PVS^0 in different environments in air. In water (●), *$[Ru(bpy)_3]^{2+}$/PSS (PSS/Ru = 50) (■) and *RuB-PSS (PSS/Ru = 19) (◇). $[[Ru(bpy)_3]^{2+}] = 2\times10^{-5}$ M.

ADDITIONAL THEORETICAL DETAILS AND IMAGES

Molecular Modelling and Molecular Dynamics with *Accelrys Molecular Dynamics 4.3*

Ru + PSS structures

1.Forcite Geometry Optimisation calculation.
Quality – ultra fine
Forcefield – universal
Charges charge with QEq

-Discover Setup.
Forcefield – esff
non-bond*: apply setting to – coulomb*
Summation method – Atom based
Quality = ultra fine
Cuttoff distance = 15.50 Å
Spline width = 5.00 Å
Buffer width 2.00 Å
Relative dielectric – 77.73

2. Discover Minimizer.
Method – smart minimizer
Convergence level – ultra fine (for 20 mer) maximum of 20000 iterations
– fine (for 60, 100 mer) maximum of 10000 iterations

3. Discover Dynamics *Quick.*
Ensemble – NVT
Temperature – 298k
Number of steps – 5000
Time step – 1 fs
Dynamic time – 5 ps
Trajectory: *Save-coordinates*
Frame output every 50 steps

4. Discover Dynamics *Longer.*
Ensemble – NVT
Temperature – 298k
Number of steps – 50000
Time step – 1 fs
Dymnamic time – 50 ps
Trajectory*: Save coordinates*
Frame output every 500 steps

NB: Using esff forcefield for the Ru polymers failed to automatically assign a forcefield type to the ruthenium atom. To enable the calculation to run, these forcefield types were manually assigned as a 6 coordinate Ruthenium in the "typing" menu of Discover Setup.

PSS alone

The calculation was carried out exactly the same as for Ru + PSS except that the forcefield used in Discover Setup was set to *compass* not *esff.*

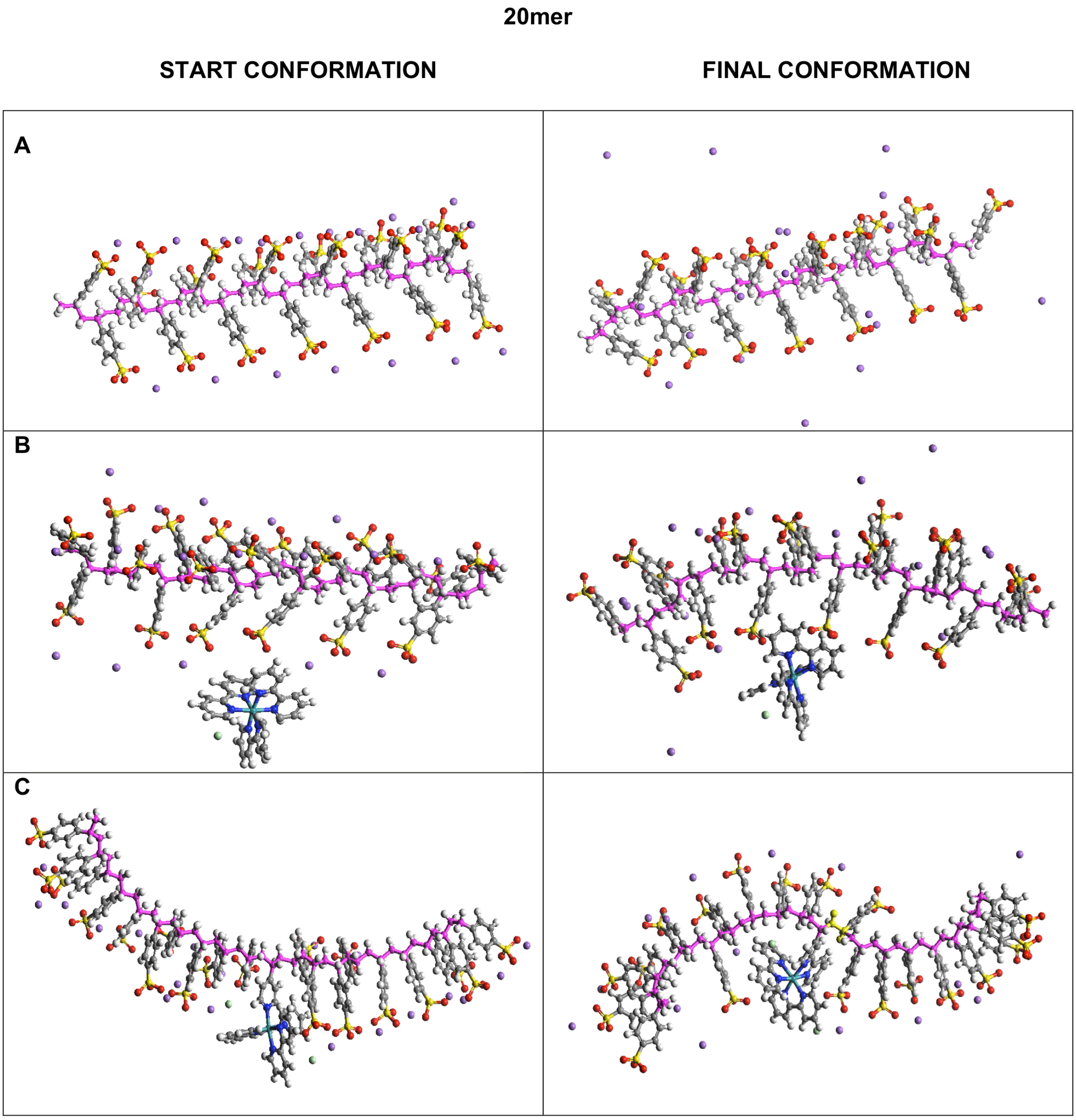


Fig. S9 Calculated MM/MD conformation of (A) 20mer PSS chain; (B) 20mer PSS chain complexed with $[Ru(bpy)_3]^{2+}$; (C) 20mer RuB-PSS (19:1) copolymer.

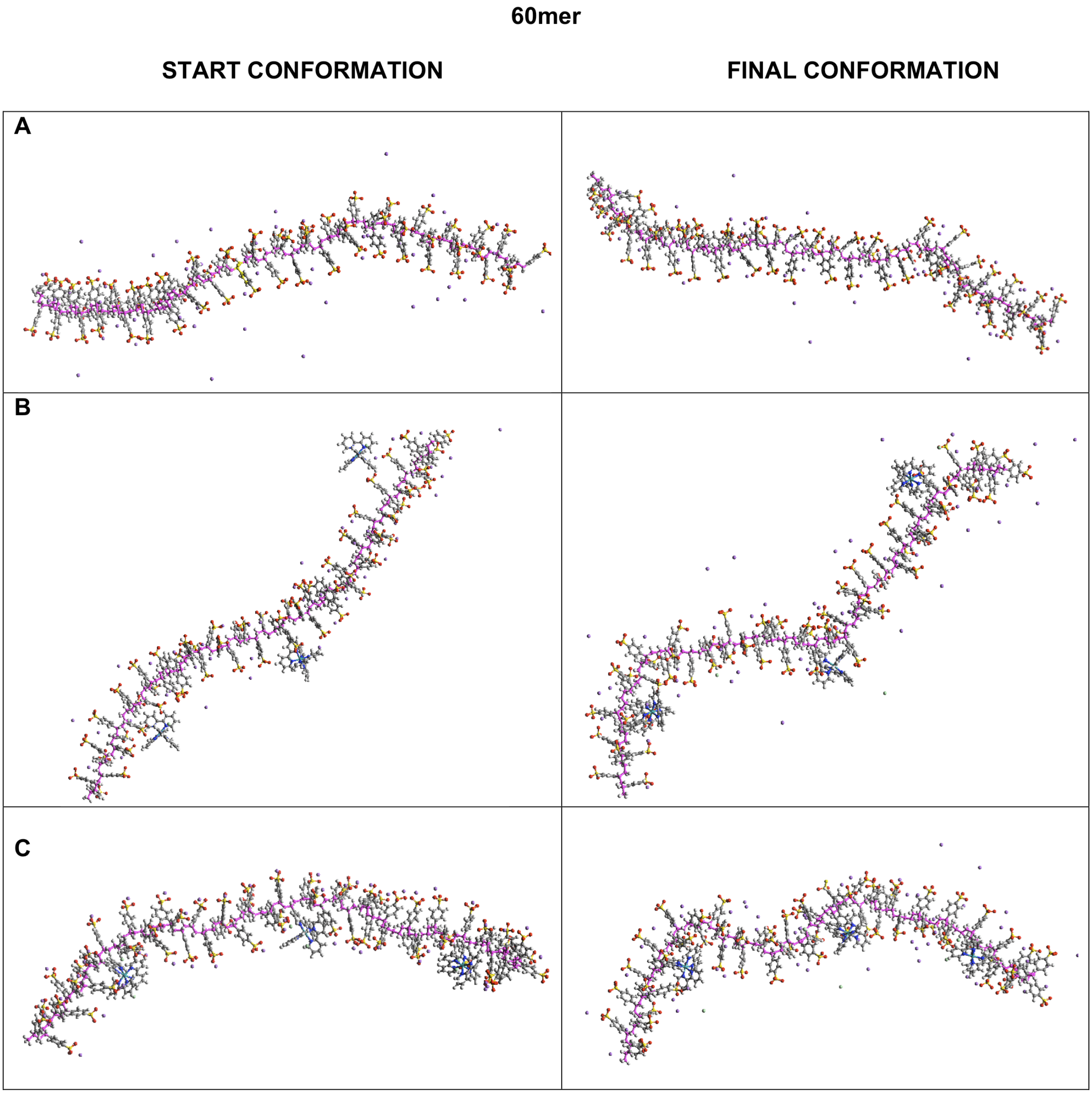


Fig. S10 Calculated MM/MD conformation of (A) 60mer PSS chain; (B) 60mer PSS chain complexed with $[Ru(bpy)_3]^{2+}$; (C) 60mer RuB-PSS (19:1) copolymer.

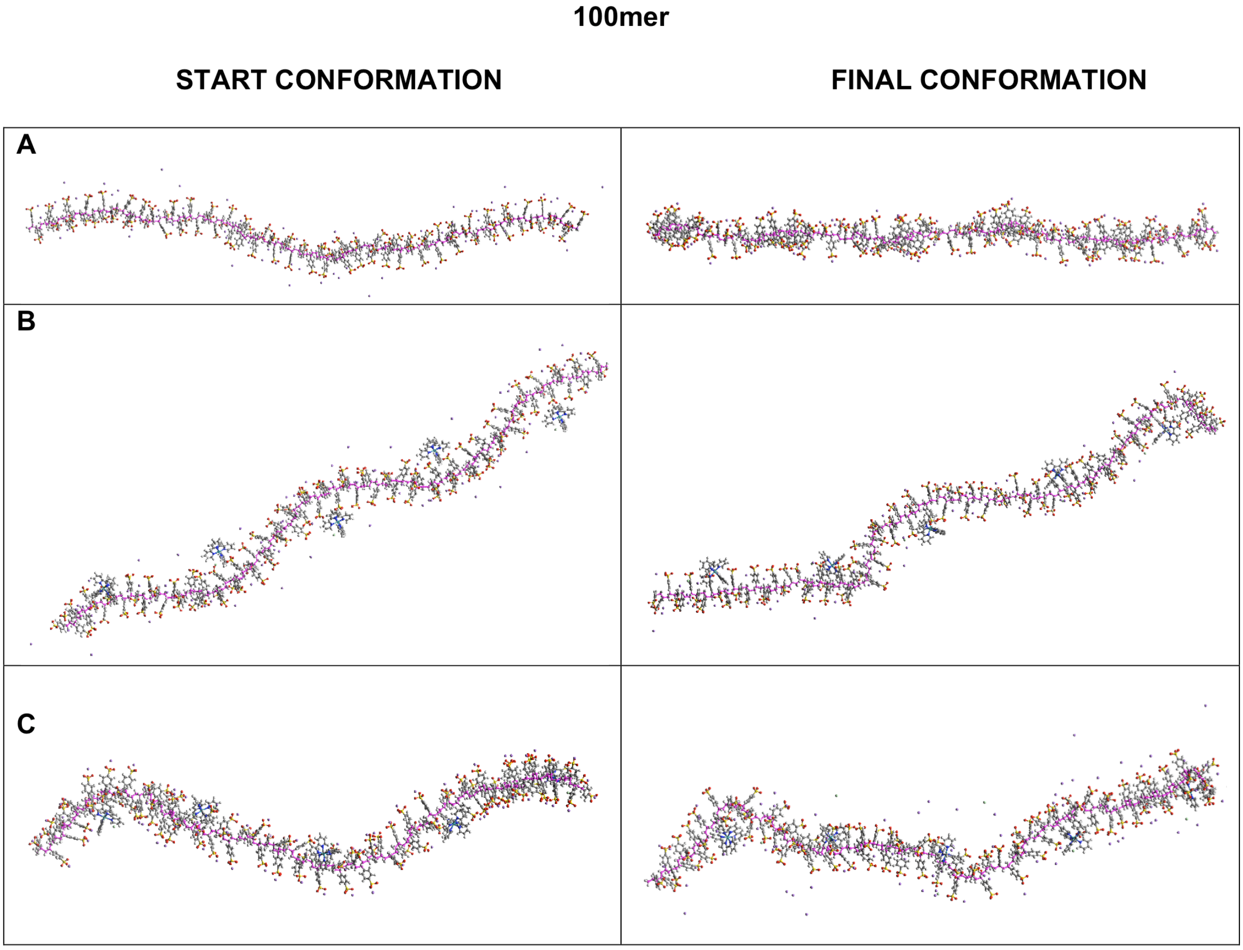


Fig. S11 Calculated MM/MD conformation of (A) 100mer PSS chain; (B) 100mer PSS chain complexed with $[Ru(bpy)_3]^{2+}$; (C) 100mer RuB-PSS (19:1) copolymer.

ADDITIONAL THEORETICAL BACKGROUND

Calculation of theoretical bimolecular diffusion-controlled rate constants

For diffusion-controlled bimolecular collision between an excited state *A and a quencher B, the rate is given as:

$$\frac{d[{}^*\mathrm{A}]}{dt} = k_d[{}^*\mathrm{A}][\mathrm{B}]$$

and the diffusion-controlled rate constant is calculated as:

$$k_d = 4\pi\left(R_A + R_B\right)\left(D_A + D_B\right)N_A$$

Where R_x is the collision radius of species x, D_x is its diffusion coefficient, and N_A is Avogadro's constant. Approximating the species as spherical particles, the diffusion coefficient in a given medium can be calculated as:

$$D_A = \frac{k_B T}{6\pi\eta R_A}$$

where η is the viscosity of the medium.

Constants for calculations

$R(O_2) = 1.2 \times 10^{-10}$ m
$R([\mathrm{Ru(bpy)_3}]^{2+}) = 5.5 \times 10^{-10}$ m
$\eta(H_2O) = 0.894$ cP $= 8.94 \times 10^{-4}$ kg m^{-1} s^{-1} at 298 K
η(PSS) = 150 cP = 0.15 kg m^{-1} s^{-1} at 298 K [N. J. Turro and T. Okubo, *J. Am. Chem. Soc.*, 1982, **104**, 2985-2988.]
$k_B = 1.38065 \times 10^{-23}$ m^2 kg s^{-2} K^{-1}
$N_A = 6.02214 \times 10^{23}$ mol^{-1}
$D([\mathrm{Ru(bpy)_3}]^{2+}/\mathrm{PSS}) \approx 0$ m^2 s^{-1}

Calculated diffusion coefficient of O_2 in PSS at 25 °C

$$D_{O_2} = \frac{k_B T}{6\pi\eta R_A} = \frac{\left(1.38065\times10^{-23}\ \mathrm{m^2\ kg\ s^{-2}\ K^{-1}}\right)\left(298\ \mathrm{K}\right)}{6\pi\left(8.94\times10^{-4}\ \mathrm{kg\ m^{-1}\ s^{-1}}\right)\left(1.2\times10^{-10}\ \mathrm{m}\right)} = 2.03\times10^{-9}\ \mathrm{m^2\ s^{-1}}$$

Calculated diffusion coefficient of $[Ru(bpy)_3]^{2+}$ in PSS at 25 °C

$$D_{[Ru(bpy)_3]^{2+}} = \frac{k_B T}{6\pi\eta R_B} = \frac{\left(1.38065\times10^{-23}\ \mathrm{m^2\ kg\ s^{-2}\ K^{-1}}\right)\left(298\ \mathrm{K}\right)}{6\pi\left(8.94\times10^{-4}\ \mathrm{kg\ m^{-1}\ s^{-1}}\right)\left(5.5\times10^{-10}\ \mathrm{m}\right)} = 0.444\times10^{-9}\ \mathrm{m^2\ s^{-1}}$$

Theoretical diffusion-controlled rate constant for collision of $[Ru(bpy)_3]^{2+}$ and O_2 in PSS at 25 °C

$$k_d = 4\pi\left(R_A + R_B\right)\left(D_A + D_B\right)N_A$$

$$k_d = 4\pi\left((1.2+5.5)\times10^{-10}\ \mathrm{m}\right)\left((2.03+0.444)\times10^{-9}\ \mathrm{m^2\ s^{-1}}\right)\left(6.02214\times10^{23}\ \mathrm{mol^{-1}}\right)$$

$$k_d = 4\pi\left(6.7\times10^{-10}\ \mathrm{m}\right)\left(2.474\times10^{-9}\ \mathrm{m^2\ s^{-1}}\right)\left(6.02214\times10^{23}\ \mathrm{mol^{-1}}\right) = 12.54\times10^{6}\ \mathrm{m^3\ mol^{-1}\ s^{-1}}$$

$$k_d = 12.54\times10^{9}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}} = 1.3\times10^{10}\ \mathrm{M^{-1}\ s^{-1}}$$

Theoretical diffusion-controlled rate constant for collision of PSS-bound $[Ru(bpy)_3]^{2+}$ and O_2 in water at 25 °C

$$k_d = 4\pi\left(R_A + R_B\right)\left(D_A + D_B\right)N_A$$

$$k_d = 4\pi\left((1.2+5.5)\times10^{-10}\ \mathrm{m}\right)\left((2.03+0)\times10^{-9}\ \mathrm{m^2\ s^{-1}}\right)\left(6.02214\times10^{23}\ \mathrm{mol^{-1}}\right)$$

$$k_d = 4\pi\left(6.7\times10^{-10}\ \mathrm{m}\right)\left(2.03\times10^{-9}\ \mathrm{m^2\ s^{-1}}\right)\left(6.02214\times10^{23}\ \mathrm{mol^{-1}}\right) = 10.29\times10^{6}\ \mathrm{m^3\ mol^{-1}\ s^{-1}}$$

$$k_d = 10.29\times10^{9}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}} = 1.0\times10^{10}\ \mathrm{M^{-1}\ s^{-1}}$$

Therefore, a diffusion-controlled reaction between $[Ru(bpy)_3]^{2+}$ and O_2 when $[Ru(bpy)_3]^{2+}$ is bound to PSS and the viscosity of the medium equals that of water is expected to have a rate constant about 75% the value in aqueous solution.

Calculated diffusion coefficient of O_2 in water at 25 °C

$$D_{O_2} = \frac{k_B T}{6\pi\eta R_A} = \frac{\left(1.38065\times10^{-23}\ \mathrm{m^2\ kg\ s^{-2}\ K^{-1}}\right)\left(298\ \mathrm{K}\right)}{6\pi\left(0.15\ \mathrm{kg\ m^{-1}\ s^{-1}}\right)\left(1.2\times10^{-10}\ \mathrm{m}\right)} = 1.21\times10^{-11}\ \mathrm{m^2\ s^{-1}}$$

Calculated diffusion coefficient of $[Ru(bpy)_3]^{2+}$ in water at 25 °C

$$D_{[Ru(bpy)_3]^{2+}} = \frac{k_B T}{6\pi\eta R_B} = \frac{\left(1.38065\times10^{-23}\ \mathrm{m^2\ kg\ s^{-2}\ K^{-1}}\right)\left(298\ \mathrm{K}\right)}{6\pi\left(0.15\ \mathrm{kg\ m^{-1}\ s^{-1}}\right)\left(5.5\times10^{-10}\ \mathrm{m}\right)} = 0.265\times10^{-11}\ \mathrm{m^2\ s^{-1}}$$

Theoretical diffusion-controlled rate constant for collision of $[Ru(bpy)_3]^{2+}$ and O_2 in water at 25 °C

$$k_d = 4\pi\left(R_A + R_B\right)\left(D_A + D_B\right)N_A$$

$$k_d = 4\pi\left((1.2+5.5)\times10^{-10}\ \mathrm{m}\right)\left((1.21+0.265)\times10^{-11}\ \mathrm{m^2\ s^{-1}}\right)\left(6.02214\times10^{23}\ \mathrm{mol^{-1}}\right)$$

$$k_d = 4\pi\left(6.7\times10^{-10}\ \mathrm{m}\right)\left(1.475\times10^{-11}\ \mathrm{m^2\ s^{-1}}\right)\left(6.02214\times10^{23}\ \mathrm{mol^{-1}}\right) = 7.48\times10^{4}\ \mathrm{m^3\ mol^{-1}\ s^{-1}}$$

$$k_d = 7.48\times10^{7}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}} = 7.5\times10^{7}\ \mathrm{M^{-1}\ s^{-1}}$$

Theoretical diffusion-controlled rate constant for collision of PSS-bound $[Ru(bpy)_3]^{2+}$ and O_2 in water at 25 °C

$$k_d = 4\pi\left(R_A + R_B\right)\left(D_A + D_B\right)N_A$$

$$k_d = 4\pi\left((1.2+5.5)\times10^{-10}\ \mathrm{m}\right)\left((1.21+0)\times10^{-11}\ \mathrm{m^2\ s^{-1}}\right)\left(6.02214\times10^{23}\ \mathrm{mol^{-1}}\right)$$

$$k_d = 4\pi\left(6.7\times10^{-10}\ \mathrm{m}\right)\left(1.21\times10^{-11}\ \mathrm{m^2\ s^{-1}}\right)\left(6.02214\times10^{23}\ \mathrm{mol^{-1}}\right) = 6.14\times10^{4}\ \mathrm{m^3\ mol^{-1}\ s^{-1}}$$

$$k_d = 6.14\times10^{7}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}} = 6.1\times10^{7}\ \mathrm{M^{-1}\ s^{-1}}$$

Therefore, a diffusion-controlled reaction between $[Ru(bpy)_3]^{2+}$ and O_2 when $[Ru(bpy)_3]^{2+}$ is bound to PSS and the viscosity equals that proposed for PSS [N. J. Turro and T. Okubo, *J. Am. Chem. Soc.*, 1982, **104**, 2985-2988.] is expected to have a rate constant about 2-3 orders of magnitude lower than the value in aqueous solution.