

Supplementary Information

P4VP-Ru^{II}(bda) Polyelectrolyte-metal Complex as Water Oxidation Catalyst: On the Unique Slow-Diffusion and Multi-charge Effects of Polyelectrolyte Ligand

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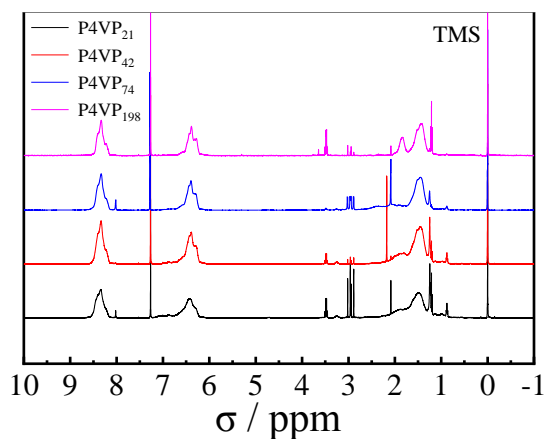


Figure S1. $^1\text{H-NMR}$ spectra of polymeric ligands P4VPs with different chain lengths prepared by RAFT polymerization in CDCl_3 .

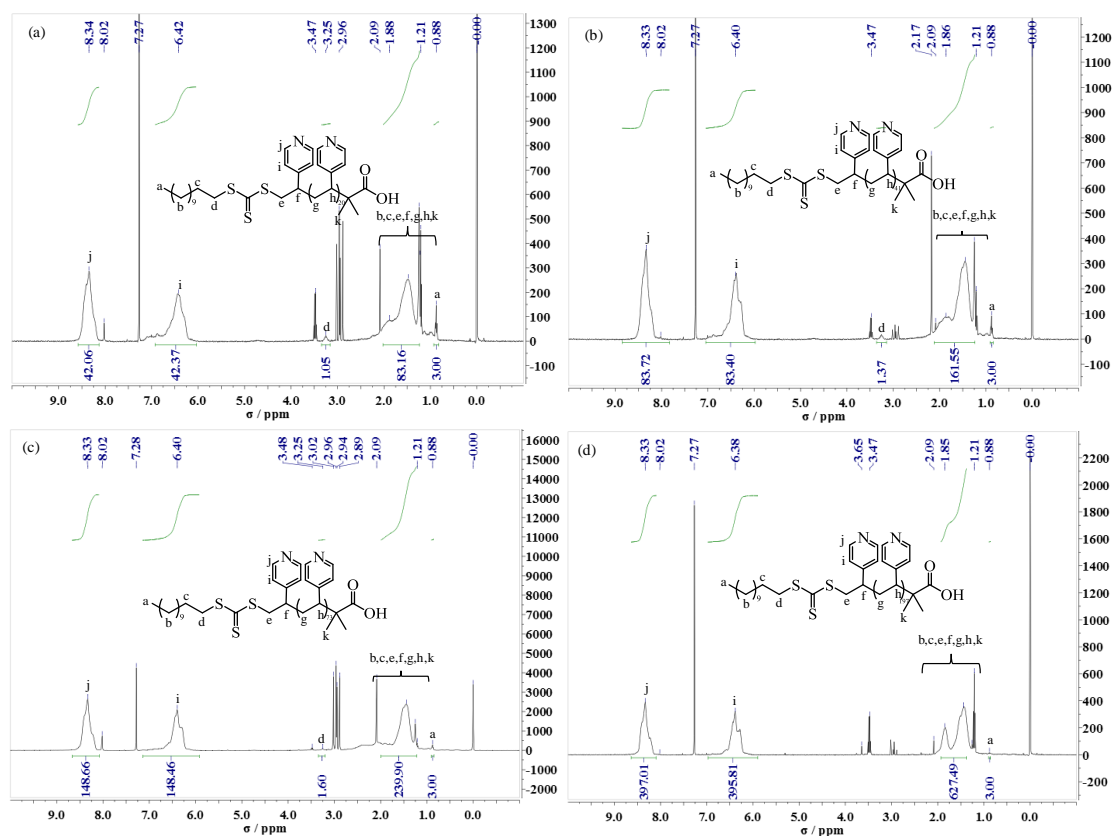


Figure S2. (a)-(d) Original $^1\text{H-NMR}$ spectra of polymeric ligands P4VPs with different chain lengths prepared by RAFT polymerization in CDCl_3 . The relative error during the integration calculation is within $\pm 5\%$.

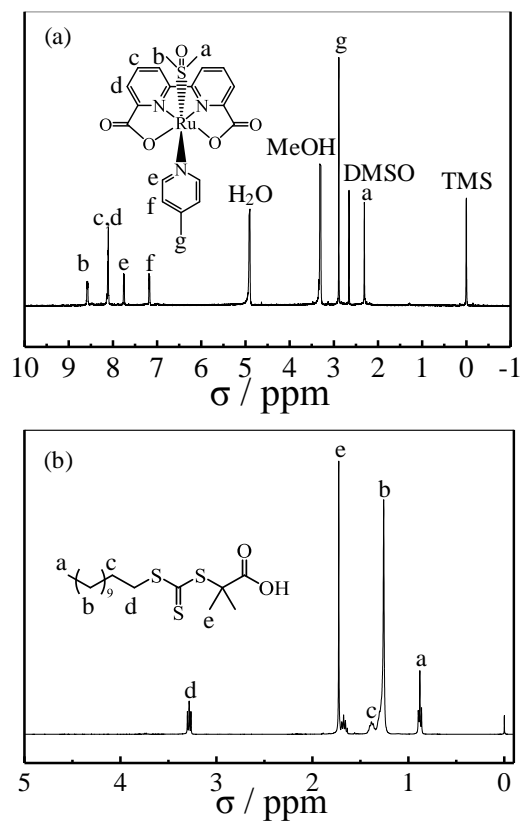


Figure S3. (a) ¹H-NMR spectrum of [Ru(bda)(pic)(DMSO)] (pic = 4-picoline) precursor. (b) ¹H-NMR spectrum of RAFT agent.

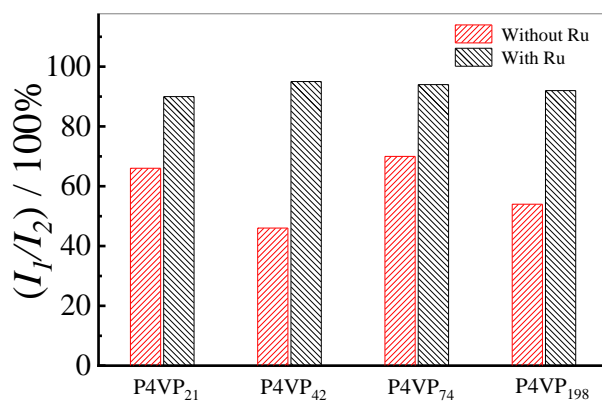


Figure S4. The ratio (I_1/I_2) of peak intensities of carboxylic ester (I_1) and pyridine (I_2) in FTIR spectra for P4VP and P4VP-Ru samples.

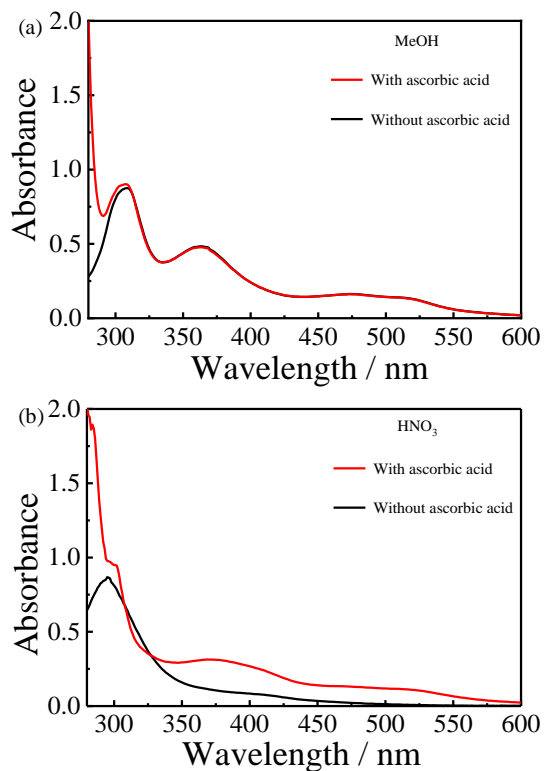


Figure S5. (a) and (b) UV-vis spectra of P4VP-Ru (with or without ascorbic acid) at a fixed concentration in different solvents: (a) MeOH; (b) HNO₃ (pH = 1.0).

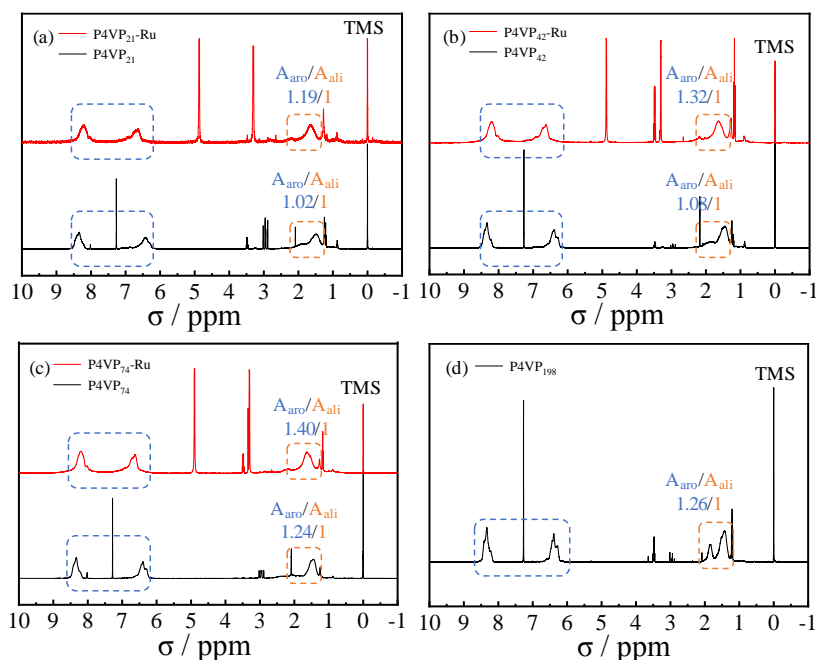


Figure S6. Comparative plots of ¹H-NMR spectra and the experimentally determined values of $A_{\text{aro}}/A_{\text{ali}}$ for P4VPs and P4VPs-Ru with different chain lengths in CDCl₃, where A_{aro} and A_{ali} are the integral areas of ¹H-NMR signals of aromatic protons and aliphatic protons, respectively. The relative error during the integration calculation is within $\pm 5\%$.

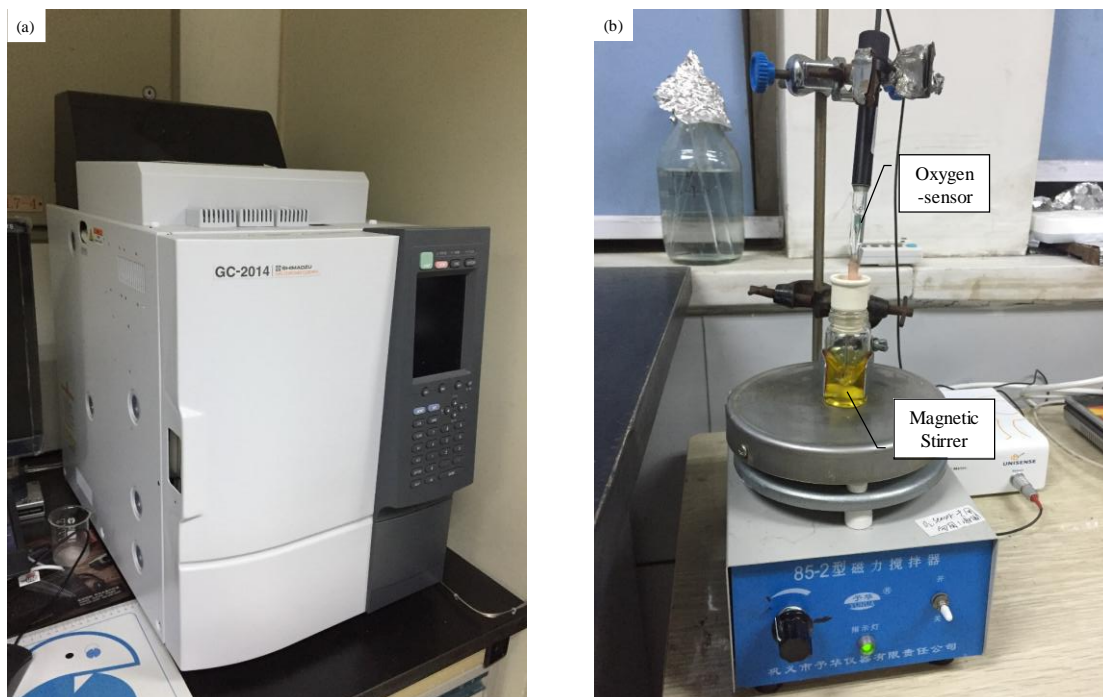


Figure S7. (a) Gas chromatography (GC-2014ATF + SPL) produced by Shimadzu. (b) The experimental setup of oxygen sensor measurement.

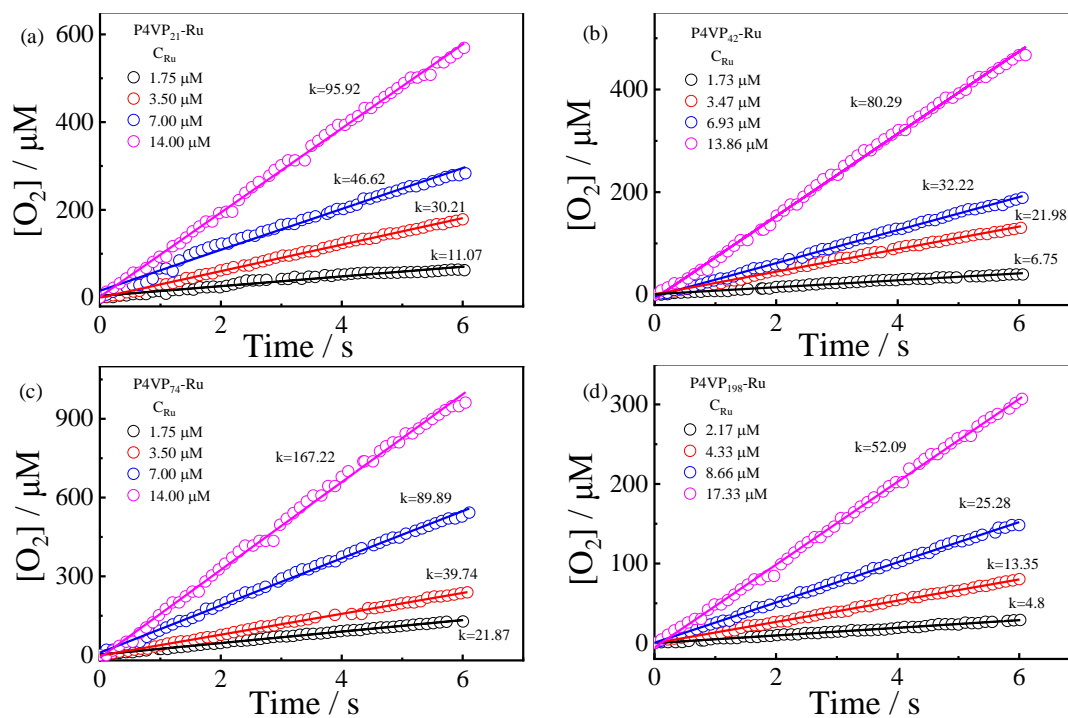


Figure S8. (a)-(d) Reaction time (t) dependence of the oxygen concentration ($[O_2]$) in solution phase by using four kinds of P4VP-Ru complexes as catalysts at different molar concentrations of Ru.

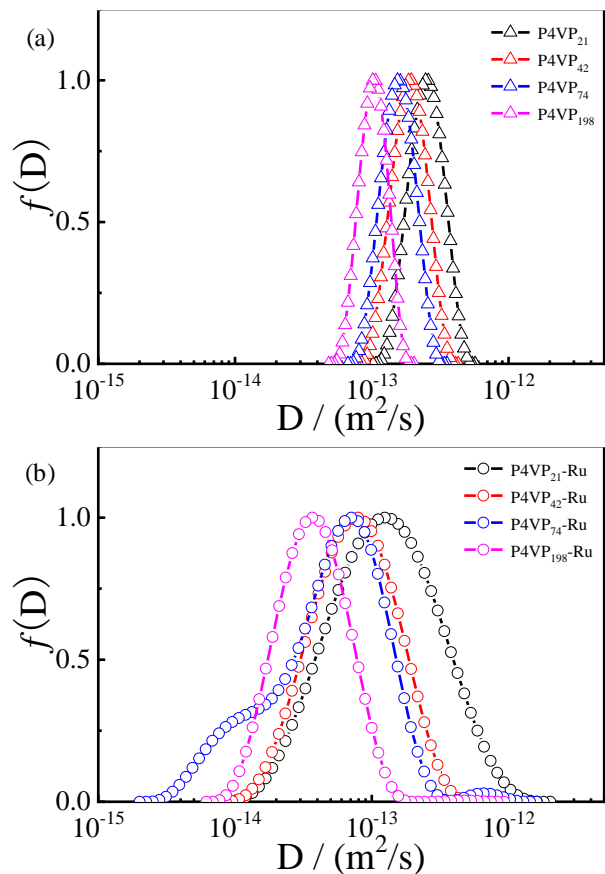


Figure S9. (a) and (b) Diffusion coefficient distributions ($f(D)$) of P4VP-Ru complexes and their corresponding P4VP precursors in MeOH at $T = 25$ °C, where D can be converted into R_h (hydrodynamic radius) via the Stokes-Einstein equation, $R_h = (k_B T / 6\pi\eta_0) / D$, where k_B , T and η_0 are the Boltzmann constant, the absolute temperature and the solvent viscosity, respectively.

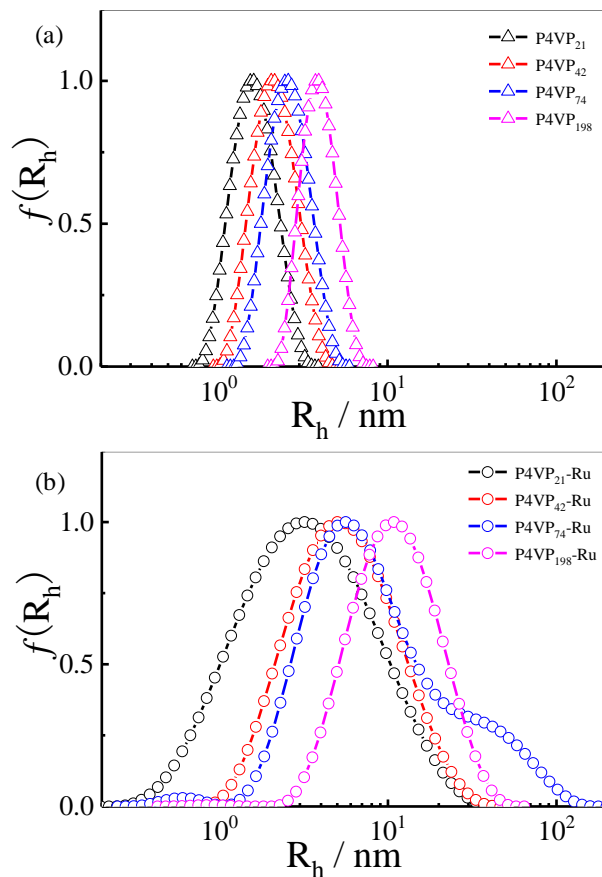


Figure S10. (a) and (b) Hydrodynamic radius distributions ($f(R_h)$) of P4VP-Ru complexes and their corresponding P4VP precursors in MeOH at $T = 25$ °C.

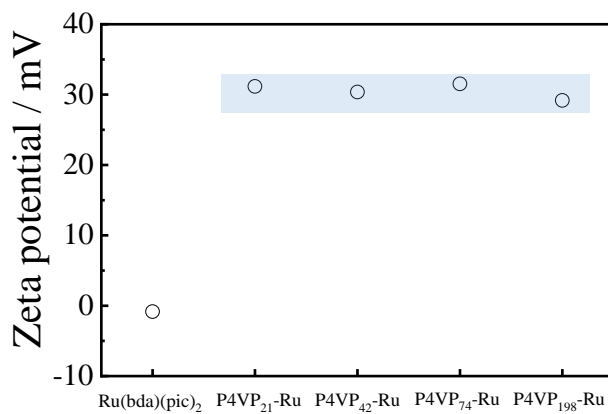


Figure S11. Measured Zeta potentials of four P4VPs-Ru and small-molecule [Ru(bda)(pic)₂], where the polymer concentration is 1.0 g/L and pH = 2.0.

Table S1. The ratio (I_1/I_2) of peak intensities of carboxylic ester (I_1) and pyridine (I_2) in FTIR spectra for P4VP and P4VP-Ru samples.

Sample	I_1/I_2
P4VP ₂₁	0.66/1
P4VP ₂₁ -Ru	0.90/1
P4VP ₄₂	0.46/1
P4VP ₄₂ -Ru	0.95/1
P4VP ₇₄	0.70/1
P4VP ₇₄ -Ru	0.94/1
P4VP ₁₉₈	0.54/1
P4VP ₁₉₈ -Ru	0.92/1

Table S2. The experimentally determined and theoretically calculated values of $A_{\text{aro}}/A_{\text{ali}}$ for P4VP and P4VP-Ru samples, where A_{aro} and A_{ali} are the integral areas of $^1\text{H-NMR}$ signals of aromatic protons and aliphatic protons, respectively.

Sample	$A_{\text{aro}}/A_{\text{ali}}$	
	Theoretical value	Measured value
P4VP ₂₁	1/1.01	1/1.02
P4VP ₂₁ -Ru	1/1.06	1/1.19
P4VP ₄₂	1/1.15	1/1.08
P4VP ₄₂ -Ru	1/1.29	1/1.32
P4VP ₇₄	1/1.22	1/1.24
P4VP ₇₄ -Ru	1/1.39	1/1.40
P4VP ₁₉₈	1/1.29	1/1.26
P4VP ₁₉₈ -Ru	1/1.45	---

Molecular Dynamics Simulation. The molecular dynamics simulation model was constructed based on the previous work of Chremos and Douglas,¹⁻³ which could serve as an effective model for the quantification of the charged species surrounding polyelectrolyte structure. The simulation details can be found in the experimental section.

In the simulation, the two neighboring Ru centers (red and blue beads in Figure 10a)

were designed to be separated by 20 positively charged monomer units, and we define that a collision event can occur only when the distance between two approaching Ru centers is shorter than a critical distance (r_{AB}). Note that the Ru-O-O-Ru dimer intermediate state has to be established if the water oxidation reaction goes in the I2M pathway, therefore, we define $r_{AB} = 0.45$ nm as the critical distance by considering the Ru-O-O-Ru bond length in the intermediate dimer structure.

The calculation of the electrostatic potential (U_e) is based on Debye-Hückel theory:

$$U_E = Z_i Z_j l_B \frac{\exp(-r_{ij}/l_D)}{r_{ij}} \quad (1)$$

where Z_i and Z_j are the valences of the charges, l_B is the Bjerrum length taken as 0.714 nm in aqueous solution at room temperature, and l_D is the Debye screening length, which is set to be 3.0 nm at the ionic concentration of 0.1 M.⁴

References and Notes

1. Chremos, A.; Douglas, J. F. Influence of higher valent ions on flexible polyelectrolyte stiffness and counter-ion distribution. *J. Chem. Phys.* **2016**, *144*, 164904.
2. Chremos, A.; Douglas, J. F. Counter-ion distribution around flexible polyelectrolytes having different molecular architecture. *Soft Matter* **2016**, *12*, 2932-2941.
3. Chremos, A.; Douglas, J. F. Impact of Monovalent Counter-ions on the Conformation of Flexible Polyelectrolytes Having Different Molecular Architectures. *MRS Adv.* **2016**, *1*, 1841-1846.
4. Chodanowski, P.; Stoll, S. Polyelectrolyte Adsorption on Charged Particles in the Debye-Hückel Approximation. A Monte Carlo Approach. *Macromolecules* **2001**, *34*, 2320-2328.