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Supporting Information

Towards Comprehensive Insight into Efficient Hydrogen Production by Self-assembled $Ru(bpy)_3^{2+}$-Polymer-Pt Artificial Photosystems

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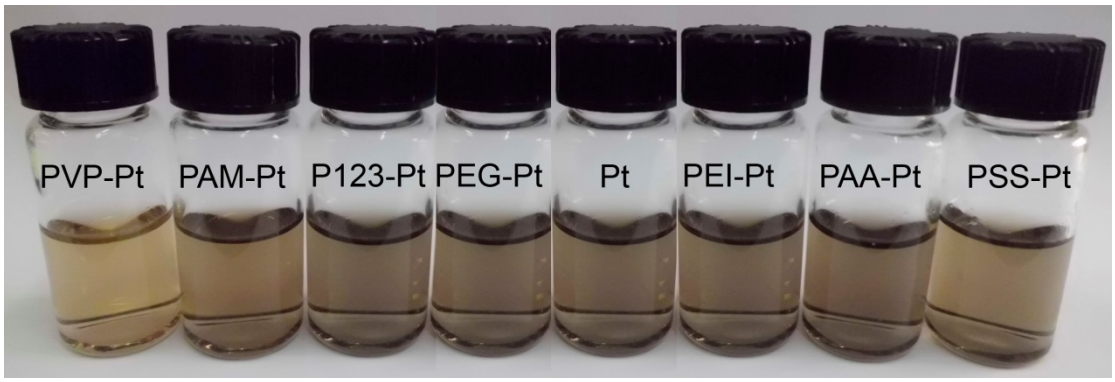

Figure S1 Photographs of PVP-Pt, PAM-Pt, P123-Pt, PEG-Pt, Pt, PEI-Pt PAA-Pt and PSS-Pt colloids.

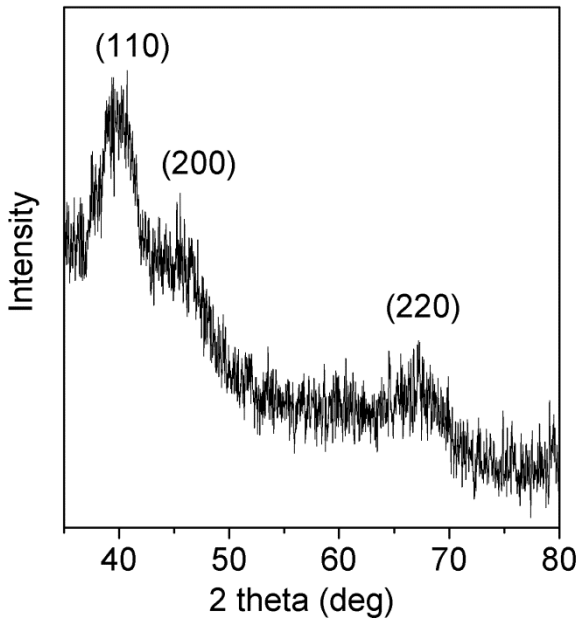

Figure S2 XRD patterns of naked Pt nanoparticles.

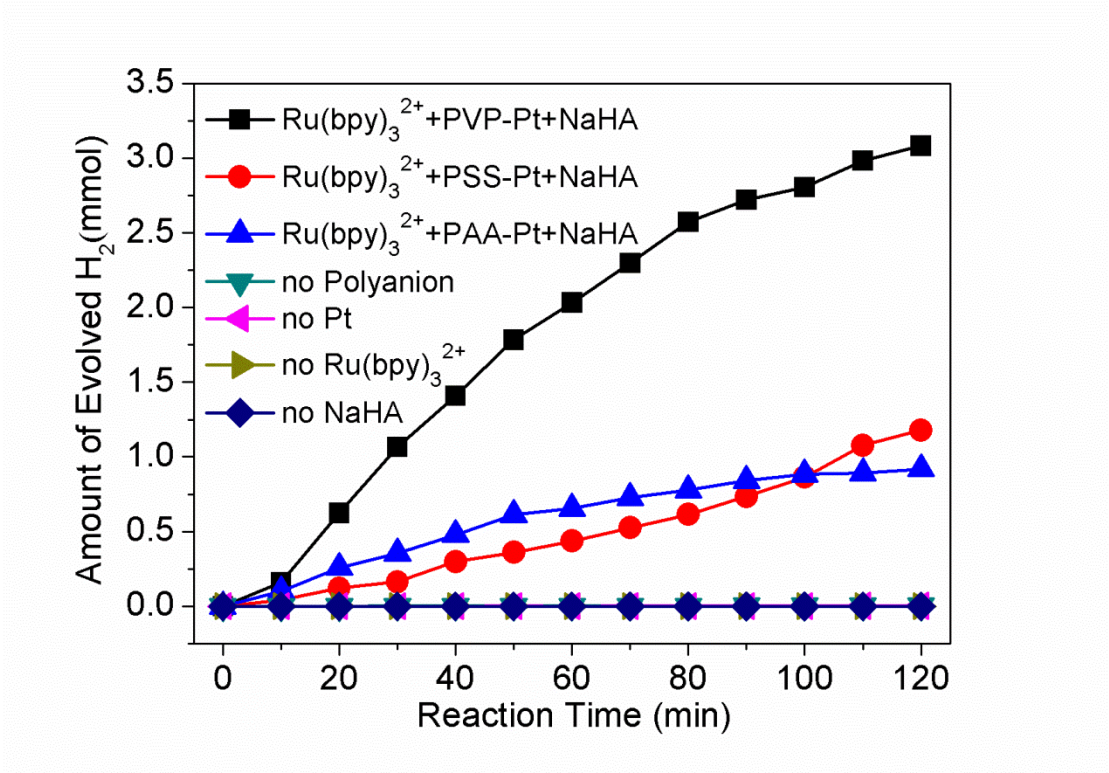

Figure S3 Photocatalytic H_2 evolution at pH=4 in a deaerated ethylene glycol and H_2O [1:5 (v/v)] mixed solution (150 mL); Sample concentration: $Ru(bpy)_3Cl_2$ (66.7μM), NaHA (50 mM), Pt (167 μM) and PVP or PSS or PAA (8.33 mM as a monomeric unit); the control experiments were operated at the same concentration with one component absent.

Table S1 Preparation Conditions and Average Diameter of PVP-Pt_n

Entry	Sample Name	NaOH (mM)	Average Diameter (nm) [a,b]
1	PVP-Pt_{60}	12	1.2 ± 0.2
2	PVP-Pt_{75}	10	1.3 ± 0.3
3	PVP-Pt_{95}	8	1.4 ± 0.2
4	PVP-Pt_{115}	7.2	1.5 ± 0.3
5	PVP-Pt_{276}	4	2.0 ± 0.3

[a] The diameter of particles was measured after H_2O was added into the as-prepared colloids (in a 5:1 ratio with EG, v/v).

[b] The number of Pt atoms of clusters were calculated using the equation $n = \left(\frac{d_{Pt}}{1.105 \times d_{atom,Pt}} \right)^3$, where n was the number of Pt atoms, d_{Pt} was diameter of the Pt nanoparticle, and $d_{atom,\ Pt}$ was the atomic diameter of Pt ($d_{atom,\ Pt}$=0.278 nm).[1]

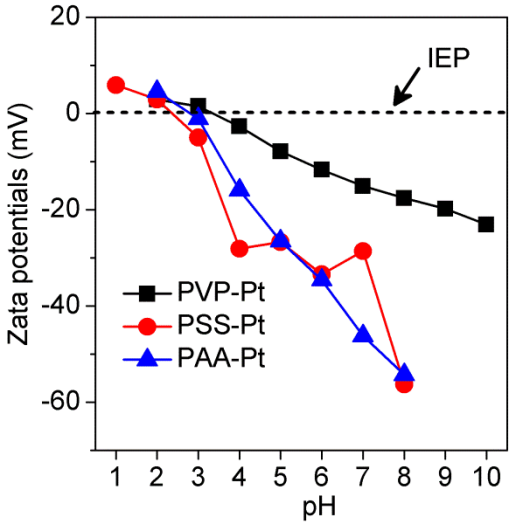

Figure S4 Zeta potentials of PVP-Pt, PSS-Pt, PAA-Pt colloids as a function of pH.

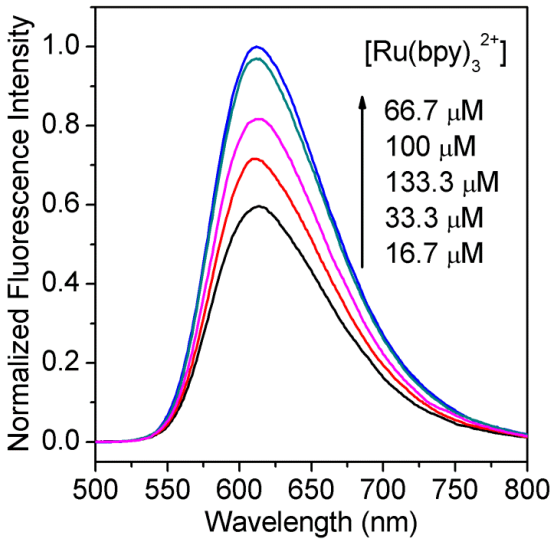

Figure S5 Normalized fluorescence spectra of $Ru(bpy)_3Cl_2$ with various concentration in ethylene glycol and H_2O [1:5 (v/v)] mixed solution excited at 450nm at room temperature.

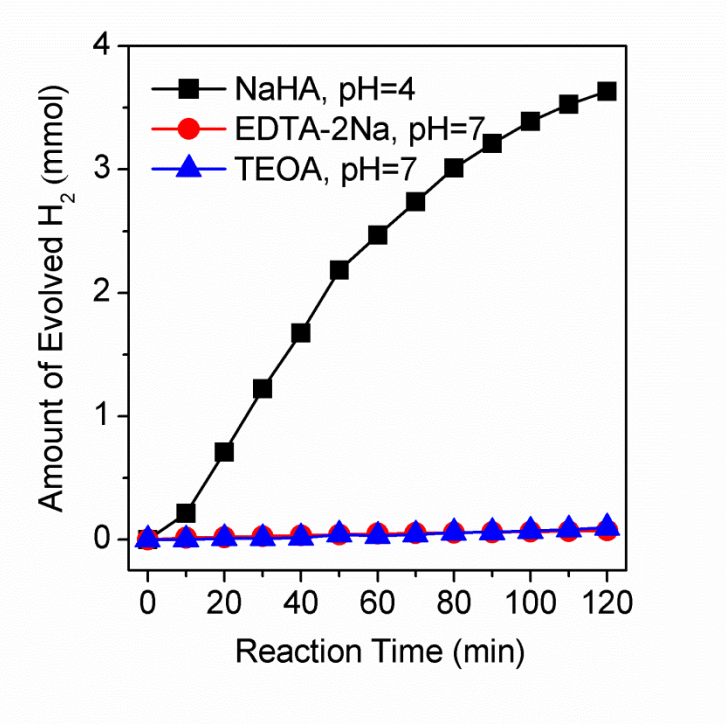

Figure S6 Time course of hydrogen evolution under photoirradiation ($\lambda \geq 420$ nm) of a deaerated ethylene glycol and H_2O [1:5 (v/v)] mixed solution (150 mL) containing $Ru(bpy)_3Cl_2$ (66.7 μM), Pt (167 μM) and PVP (8.35 mM as a monomeric unit) and various electron donors (50 mM; (black) NaHA at optimal pH 4, (red) EDTA-2Na at optimal pH 7; (blue) TEOA) at optimal pH 7.

Table S2A Calculation details for the amount of surface Pt atoms [1-3]

Sample	d_{Pt}[a] /nm	N_{total} [b] /-	m[c] /-	$N_{surface}$ [d] /-	$n_{surface}$[e] /μmol
PVP-Pt	1.4	95	3.5	65	17.4
PSS-Pt	2.0	276	4.8	146	13.2
PAA-Pt	2.1	320	5.1	170	13.3

[a] Average diameter of Pt particles determined by TEM observations.

[b] The number of total Pt atoms per particle,

$$N_{total} = \left(\frac{d_{Pt}}{1.105 \times d_{atom,Pt}} \right)^3 (d_{atom,Pt} = 0.278nm)$$

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[c] The number of shells, $N_{total} = \frac{10m^3 - 15m^2 + 11m - 3}{3}$.

[d] The number of surface Pt atoms per particle, $N_{surface} = 10m^2 - 20m + 12$.

[e] The amount of surface Pt atoms of Pt colloids,

$$n_{surface} = \frac{N_{surface}}{N_{total}} \times n_{total} (n_{total} = 25.6\mu mol)$$

Table S2B Calculation detail for mole ratio of PS/polymer/surface Pt atoms

photosystem	n $[Ru(bpy)_3^{2+}]$ /μmol	n (poly) /μmol	n (Pt) /μmol	Ratio /-
$Ru(bpy)_3^{2+}$-PVP-Pt	10	100	17.4	1: 10 : 1.7
$Ru(bpy)_3^{2+}$-PSS-Pt	10	25	13.2	1: 2.5 : 1.3
$Ru(bpy)_3^{2+}$-PAA-Pt	10	200	13.3	1: 20 : 1.3

1 Y. Shiraishi, D. Tsukamoto, Y. Sugano, A. Shiro, S. Ichikawa, S. Tanaka and T. Hirai, *ACS Catalysis*, 2012, **2**, 1984-1992.

2 R. E. Benfield, *Journal of the Chemical Society, Faraday Transactions*, 1992, **88**, 1107-1110.

3 O. M. Wilson, M. R. Knecht, J. C. Garcia-Martinez and R. M. Crooks, *Journal of the American Chemical Society*, 2006, **128**, 4510-4511.

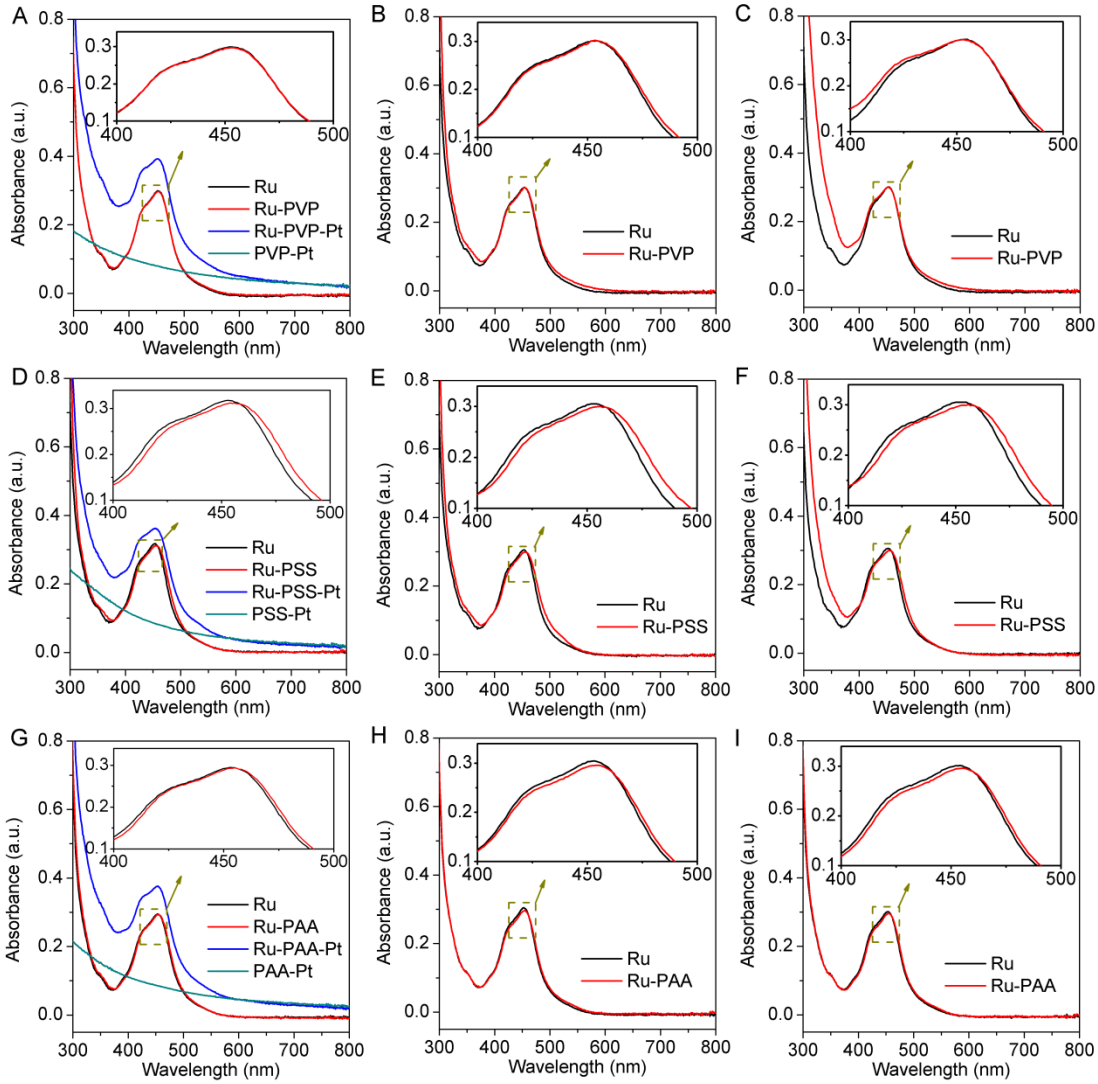

Figure S7 UV-vis absorption spectrums of $Ru(bpy)_3Cl_2$ (abbr.: Ru), Ru-polymer, Ru-polymer-Pt, polymer-Pt [PVP (A), PSS (D), PAA (G)]. Conditions: $Ru(bpy)_2Cl_3$ (2.5×10^{-5} M), polymer (8.0×10^{-4} M), Pt (4.0×10^{-4} M). And UV-vis absorption spectrums of $Ru(bpy)_2Cl_3$ (2.5×10^{-5} M) in absence or in the presence of various concentrations polymers (B: 8.0×10^{-3} M PVP, C: 8.0×10^{-2} M PVP, E: 8.0×10^{-3} M PSS, F: 8.0×10^{-2} M PSS, H: 8.0×10^{-3} M PAA, I: 8.0×10^{-2} M PAA)

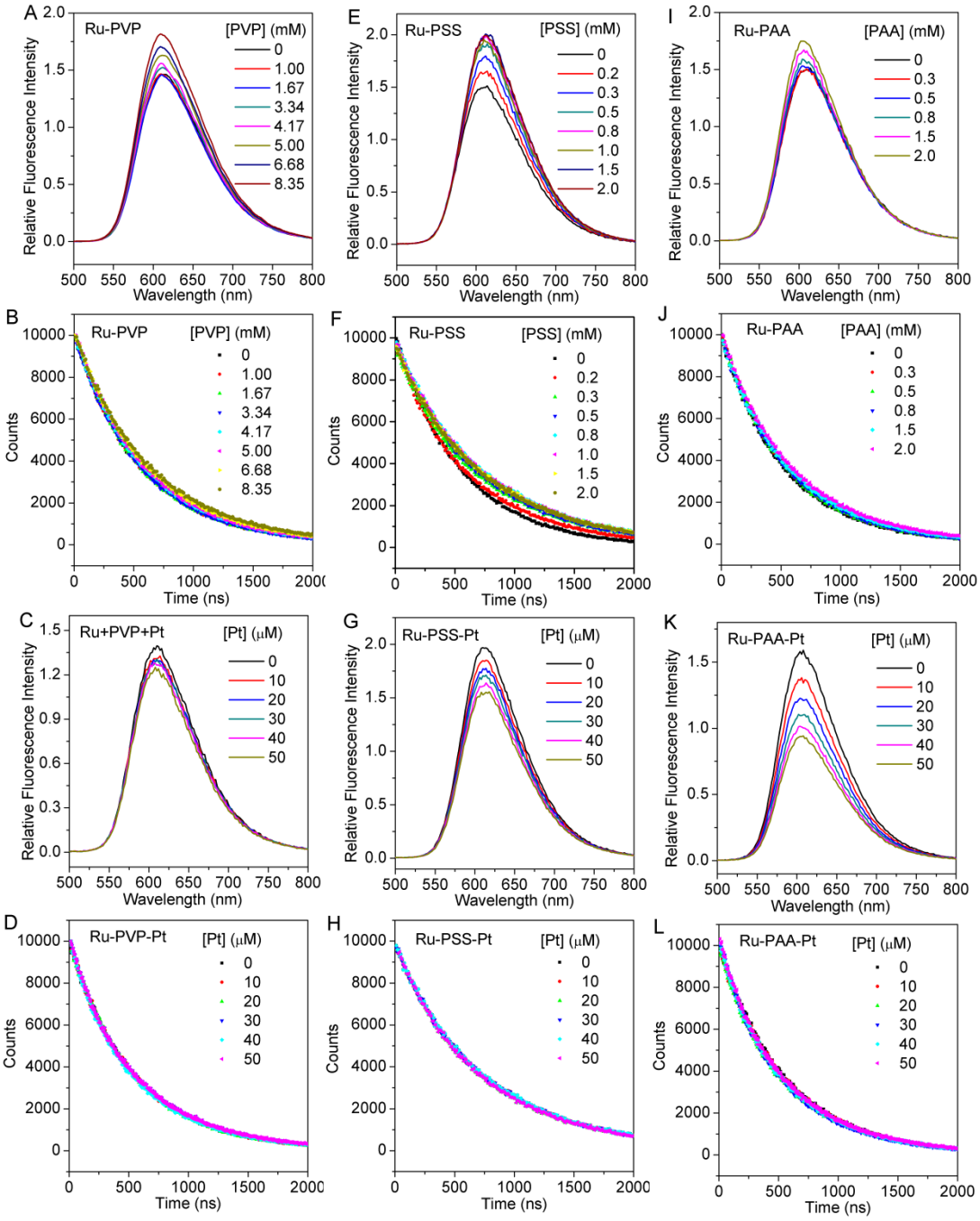

Figure S8 Relative emission spectra and time-resolved fluorescence decays at 613 nm of the de-aerated $Ru(bpy)_3Cl_2$ (2.5×10^{-5} M) solution in present of various concentrations polymer (PVP: A and B; PSS: E and F; PAA: I and J) at pH=4. Relative emission spectra and time-resolved fluorescence decays at 613 nm of the de-aerated $Ru(bpy)_3^{2+}$-Polymer (PVP: C and D; PSS: G and H; PAA: K and L) solution in the presence of various concentrations Pt colloids. Condition: $Ru(bpy)_3^{2+}$ (2.5×10^{-5} M), poly (8.0×10^{-4} M)

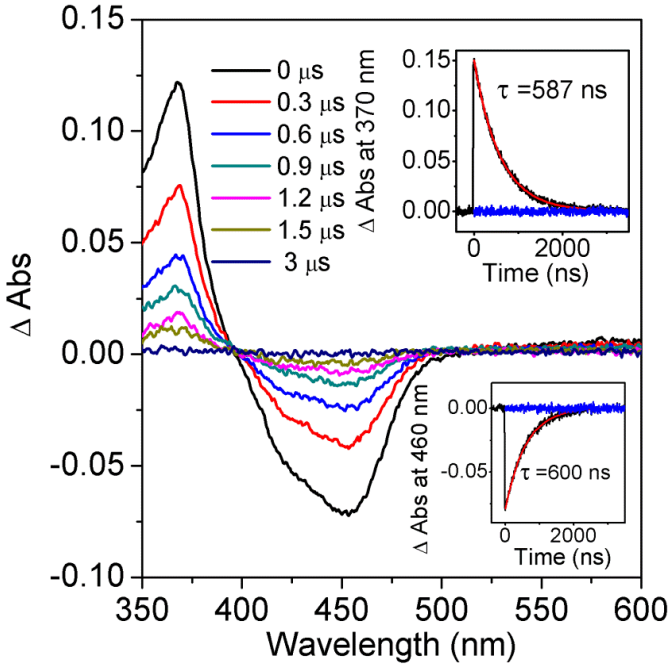

Figure S9 Transient absorption of $Ru(bpy)_3^{2+}$ (2.5×10^{-5} M) in water, excited with a 450 nm laser Nd: YAG (~ 5 mJ/pulse). Inset (up): Excited state absorption decay at 370 nm. Inset (down): Ground-state bleach recovery measured at 460 nm. The blue data points represent the residual of the exponential decay fit.

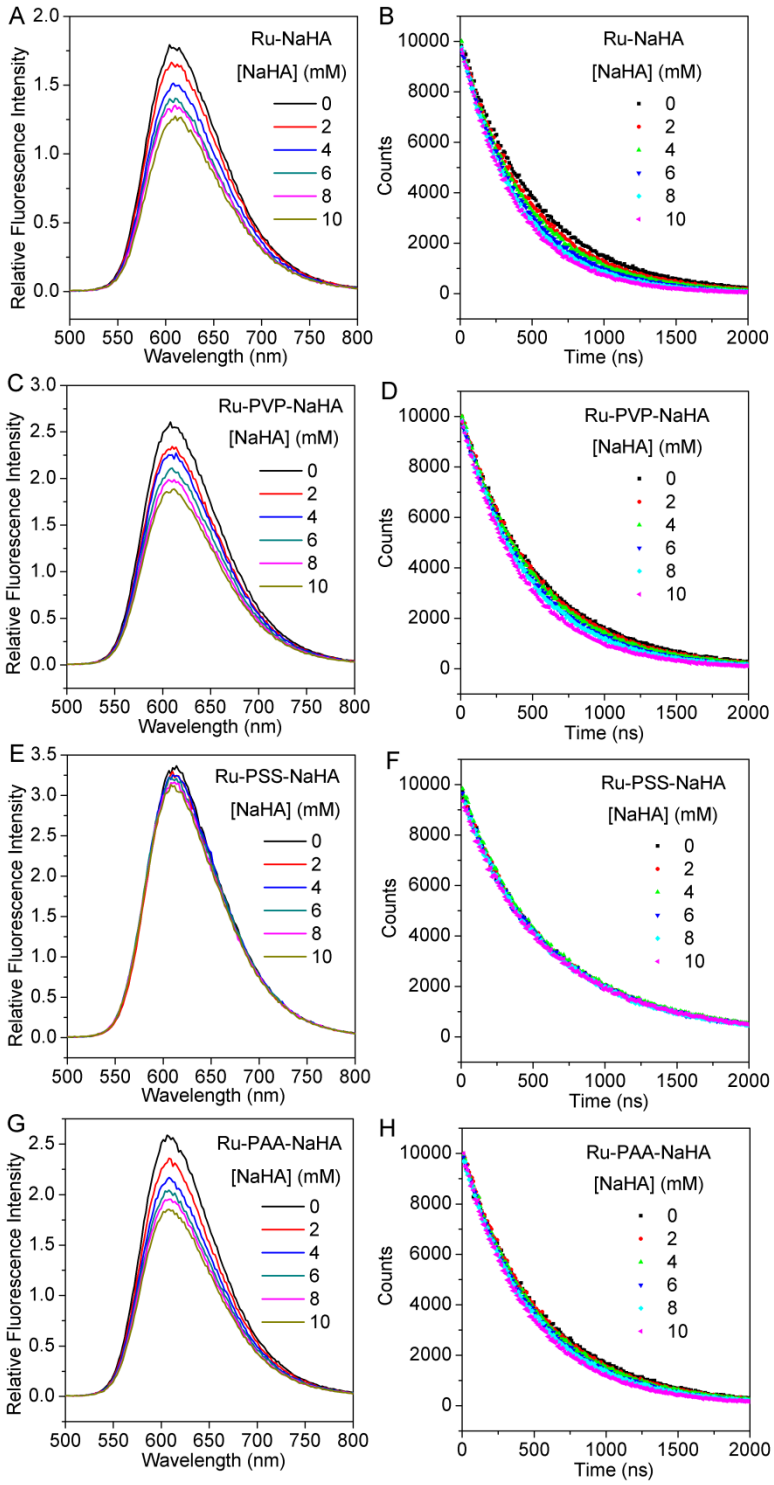

Figure S10 Relative emission spectra and time-resolved fluorescence decays at 613 nm of the de-aerated $Ru(bpy)_3^{2+}$ (A and B) and $Ru(bpy)_3^{2+}$-Polymer (PVP: C and D; PSS: E and F; PAA: G and H) solution in the presence of various concentrations (0 mM, 2 mM, 4 mM, 6 mM, 8 mM, 10 mM) of NaHA. Condition: $Ru(bpy)_3^{2+}$ (2.5×10^{-5} M), polymer (8.0×10^{-4} M)

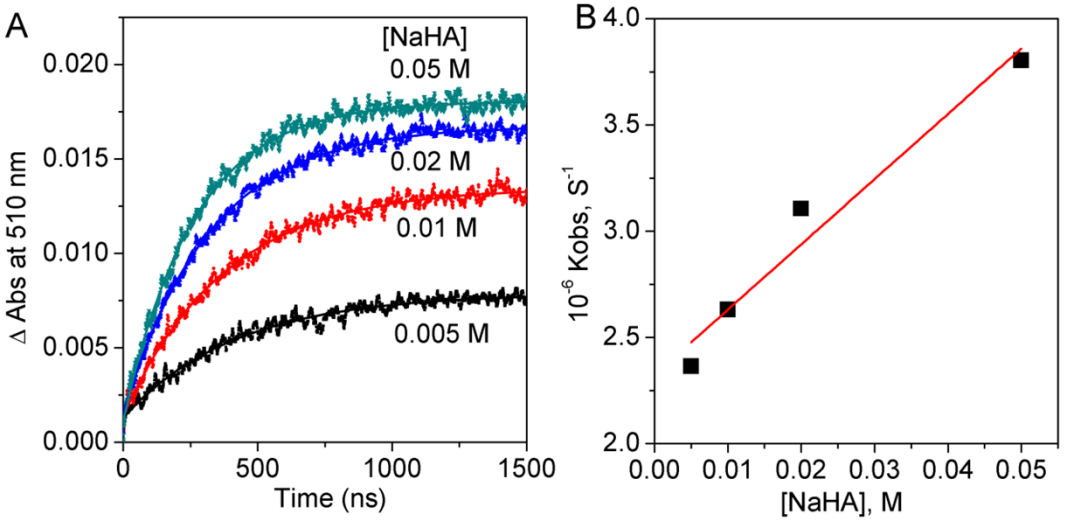

Figure S11 (A) Time profiles of the absorption at 510 nm due to $Ru(bpy)_3^{+}$ at various concentrations of NaHA (green, 0.05 M; bule, 0.02 M; red, 0.01 M; black, 0.005 M) in the presence of $Ru(bpy)_3^{2+}$ (2.5×10^{-5} M) at pH=4. (B) Plot of the pseudo-first-order rate constant (kobs) for electron transfer from NaHA to $Ru(bpy)_3^{2+}$ vs [NaHA].

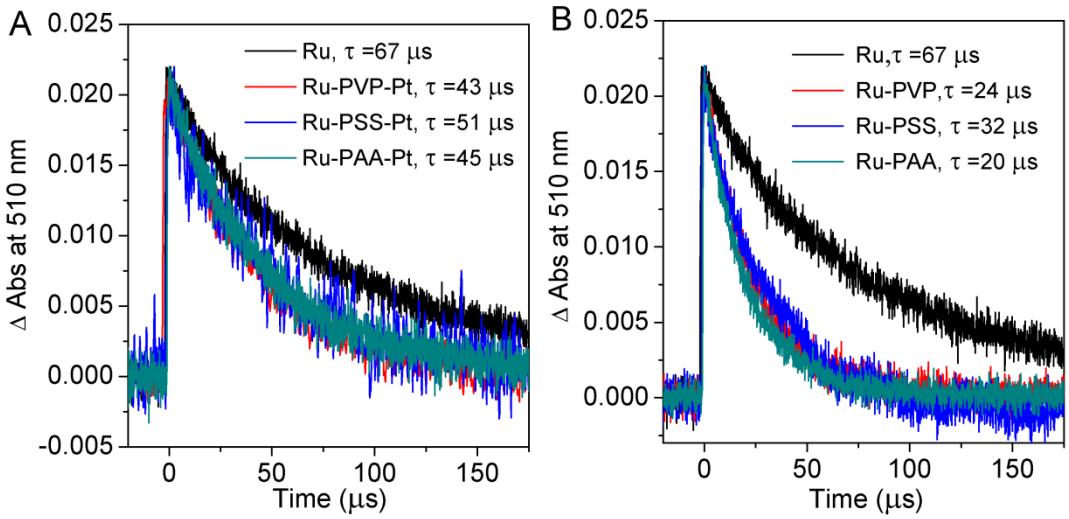

Figure S12 (A) Time profiles of the absorption at 510 nm due to $Ru(bpy)_3^{+}$ in the presence of $Ru(bpy)_3^{2+}$,NaHA and polyanion (PVP, PSS and PAA)-Pt at pH=4. Condition: $Ru(bpy)_3^{2+}$ (2.5×10^{-5} M), NaHA (0.05 M), polyanion (8.0×10^{-4} M), Pt (2.0×10^{-4} M). (B) Time profiles of the absorption at 510 nm due to $Ru(bpy)_3^{+}$ in the presence of $Ru(bpy)_3^{2+}$ and polyanion (PVP, PSS and PAA) at pH=4. Condition: $Ru(bpy)_3^{2+}$ (2.5×10^{-5} M), NaHA (0.05 M), polyanion (8.0×10^{-4} M).