Supporting Information

Incorporation of a Molecular $[Ru(dcbpy)(bpy)_2]^{2+}$ Photosensitizer and a $Pt(dcbpy)Cl_2$ Catalyst into Metal-Organic Frameworks for Photocatalytic Hydrogen Evolution from Aqueous Solution

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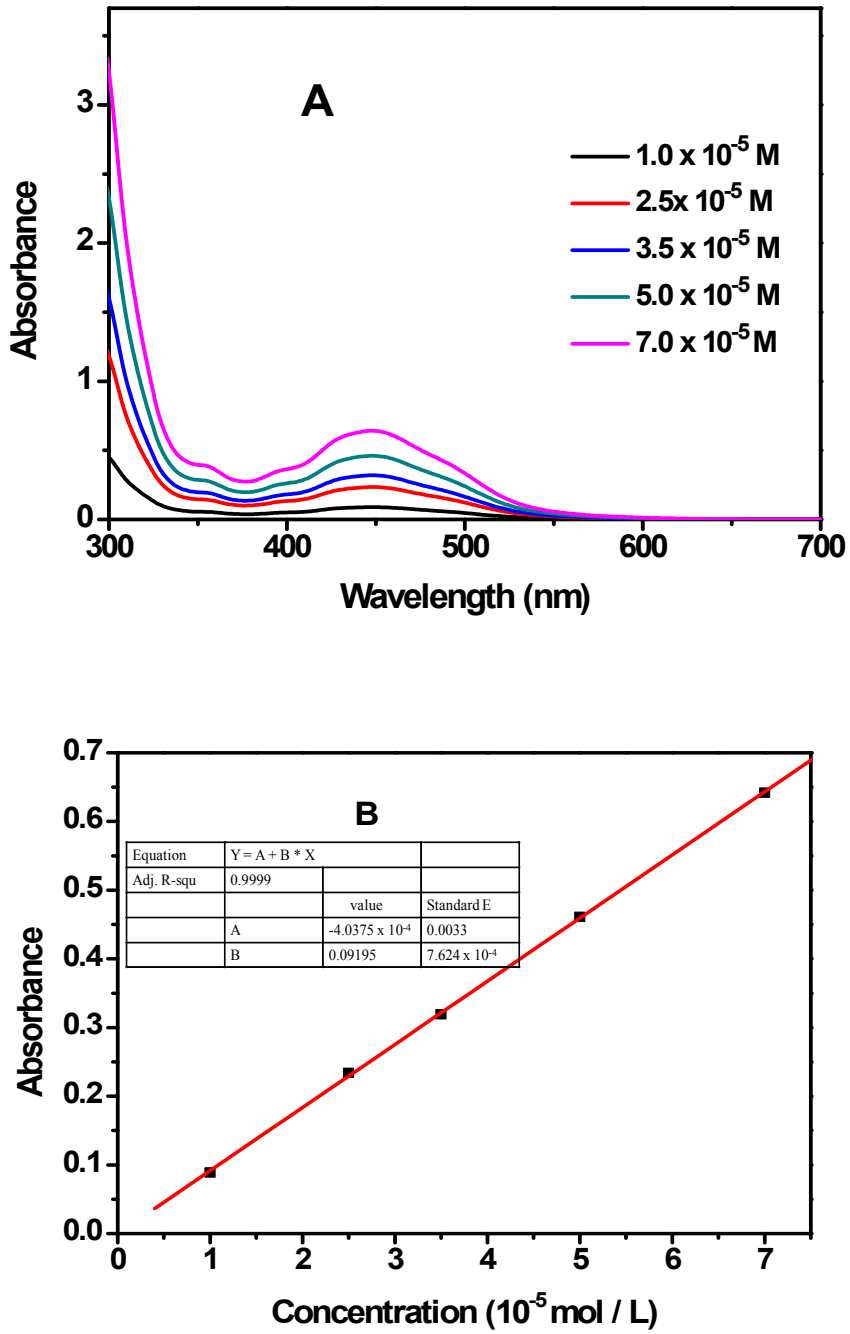

Figure S1. (A) The UV-vis absorption spectra of RuDCBPY at various concentrications in aqueous solution. (B) The absorbance of RuDCBPY at 448 nm as a function of concentration.

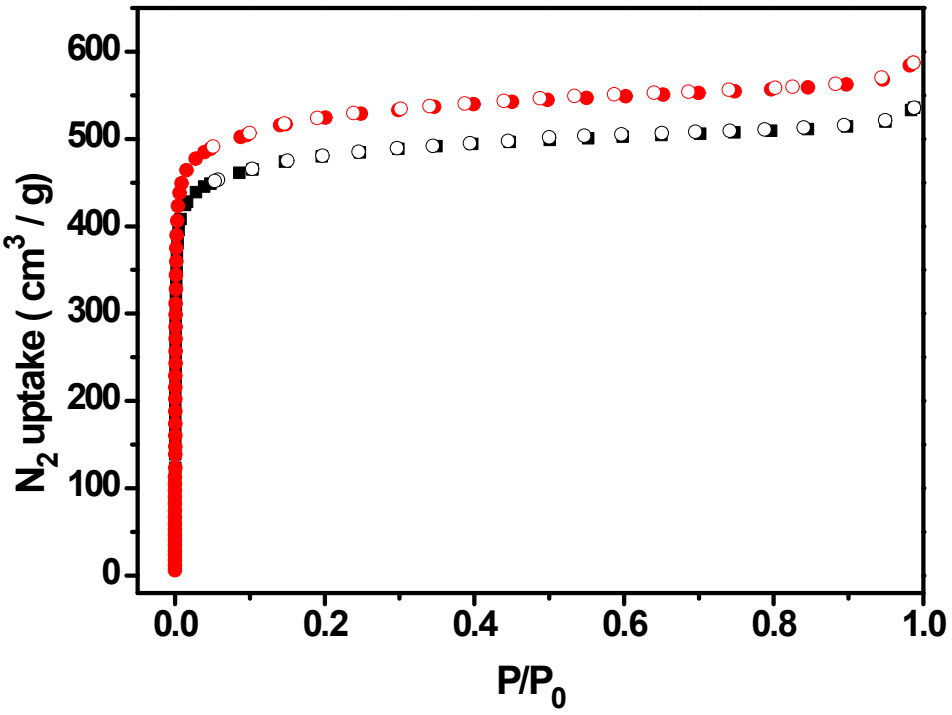

Figure S2. N_2 absorption (filled sympols) and desorption (open sympols) isotherms for Pt-UIO-67 (red) and Ru-Pt@UIO-67 (black).

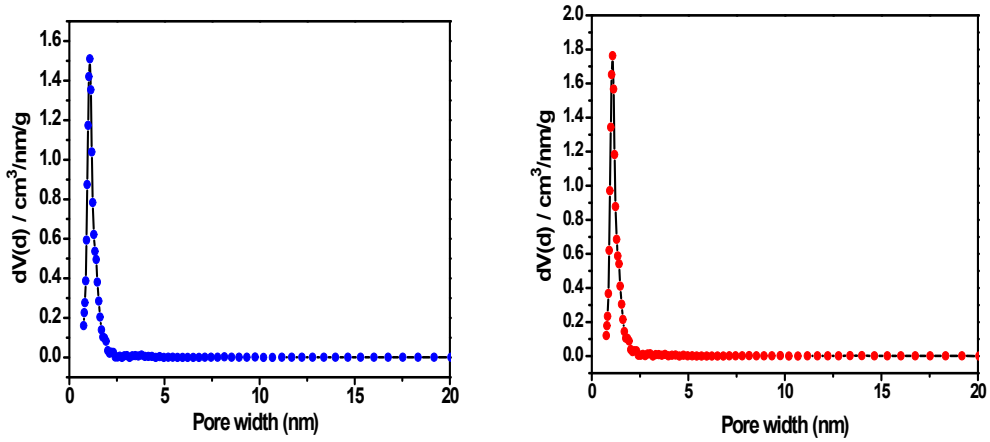

Figure S3. Pore size distribution of Pt-UIO-67 (left) and Ru-Pt@UIO-67 (right) obtained from N_2 gas sorption experiments by DFT calculation.

Table S1. Surface area, pore volume and main pore size of Pt@UIO-67 and Ru-Pt@UIO-67.

Samples	S_{BET}	Pore volume	Main Pore Size
UIO-67	3000 m^2/g	1.05 cm^3/g	8 Å
Pt@-UIO-67	2053.713 m^2/g	0.9083 cm^3/g	8-10 Å
Ru-Pt@UIO-67	1886.130 m^2/g	0.8286 cm^3/g	8-10 Å

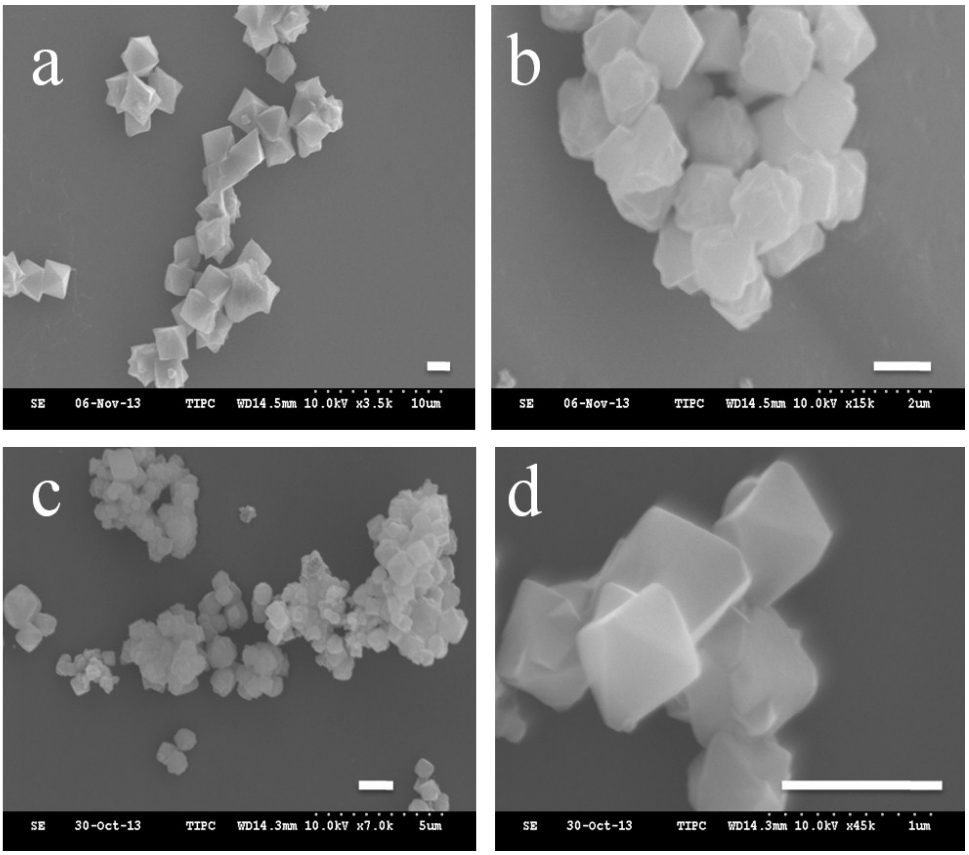

Figure S4. SEM images of (a) UIO-67, (b) Pt@UIO-67 and (c,d) Ru-Pt@UIO-67. Scale bar: 1 μm.

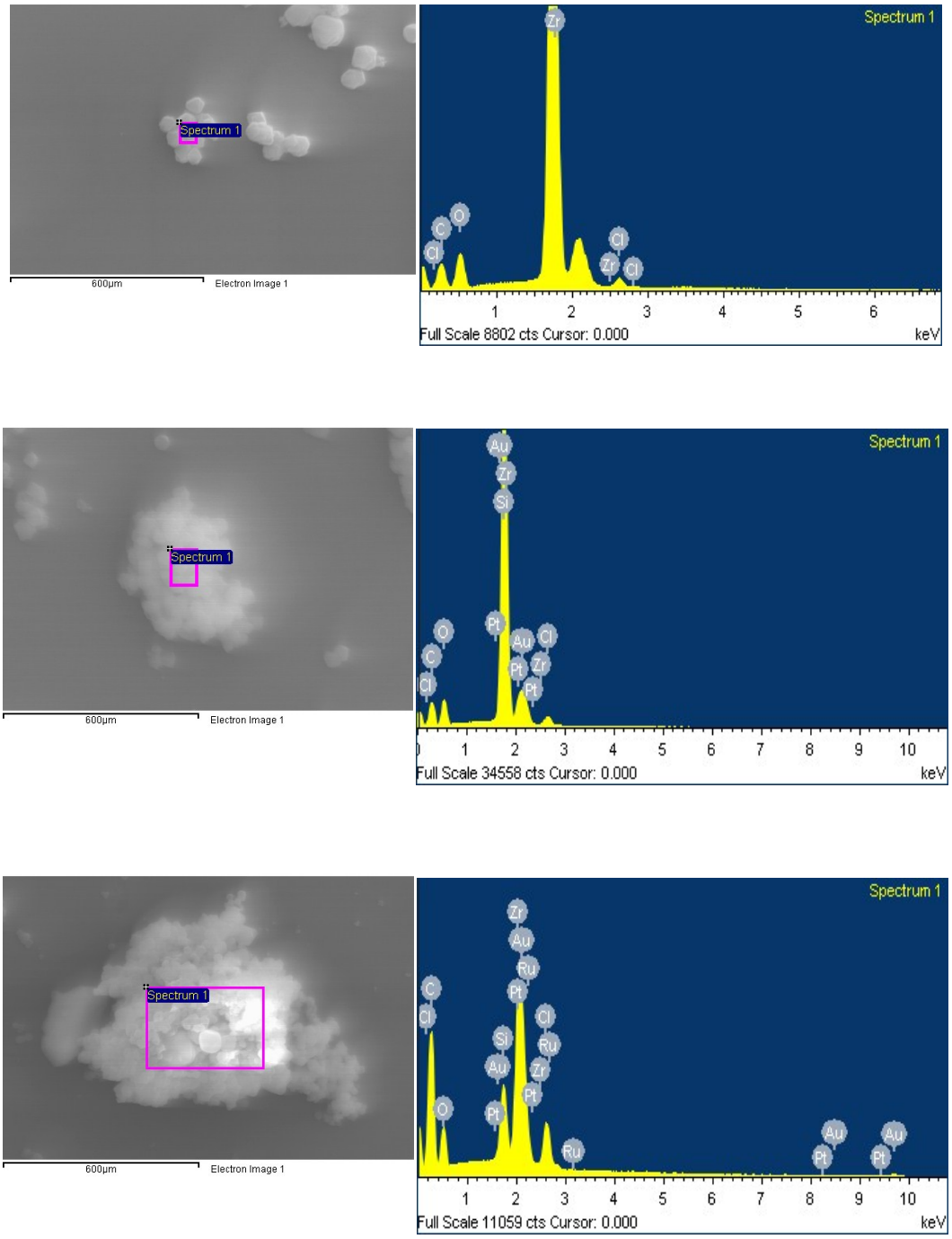

Figure S5. SEM-Energy disperses X-ray (EDX) analysis in random areas of UIO-67, Pt@UIO-67, and Ru-Pt@UIO-67 (from top to bottom).

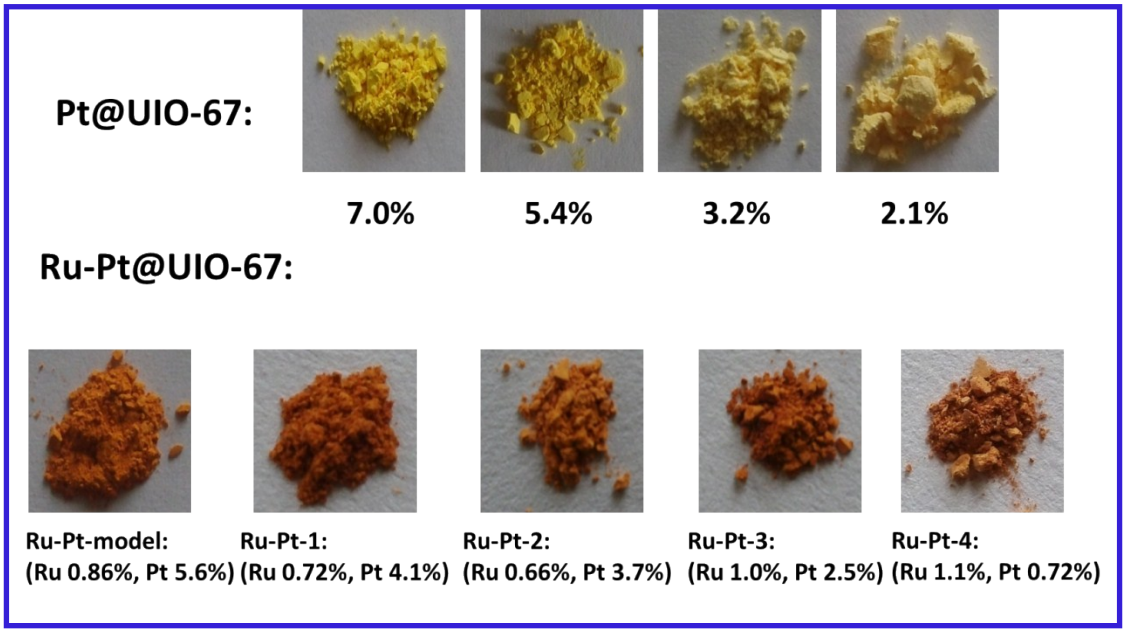

Figure S6. Photographs of Pt@UIO-67 and Ru-Pt@UIO-67 MOFs with various doping concentrations under natural light.

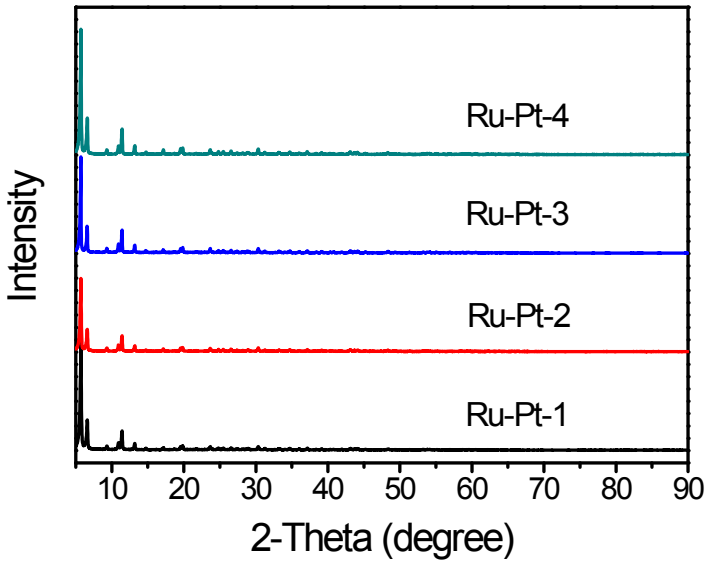

Figure S7. The XRD patterns of Ru-Pt@UIO-67 MOFs.

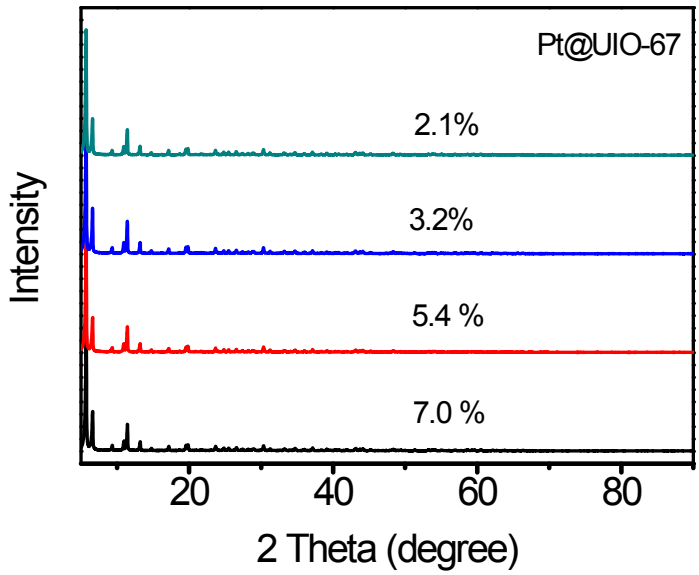

Figure S8. The XRD patterns of Pt@UIO-67 MOFs.

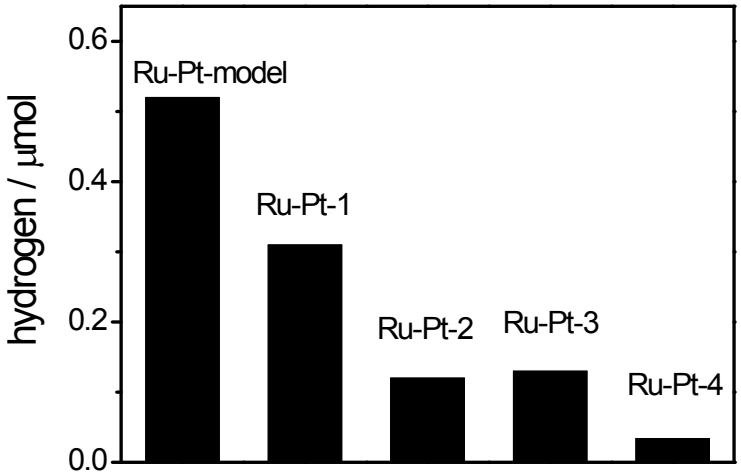

Figure S9. Photocatalytic hydrogen production after 5 h of irradiation from an acetate buffer solution (pH = 5.0) of EDTA-2Na and Ru-Pt@UIO-67 (5 mg). Light source: LED $\lambda > 420$ nm, 30×1 W.

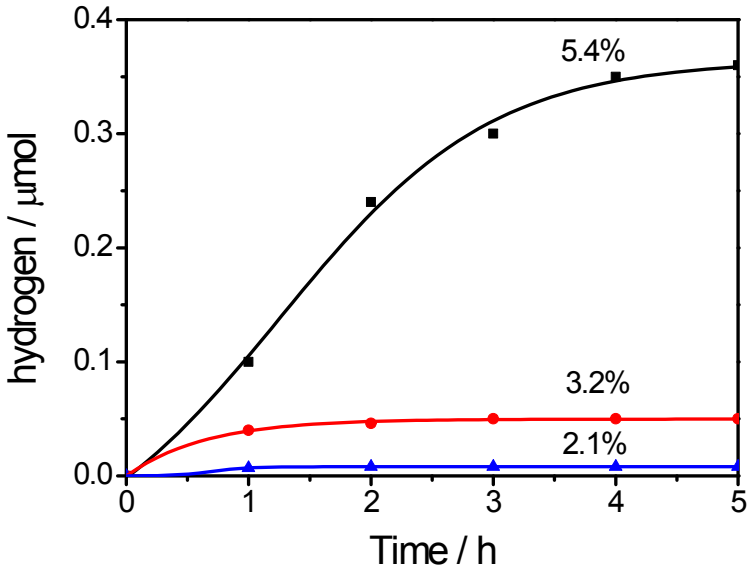

Figure S10. Photocatalytic hydrogen production from an acetate buffer solution (pH = 5.0) of EDTA-2Na and Pt@UIO-67 (~1.47 μmol Pt). Light source: LED λ > 420 nm, 30 × 1 W.

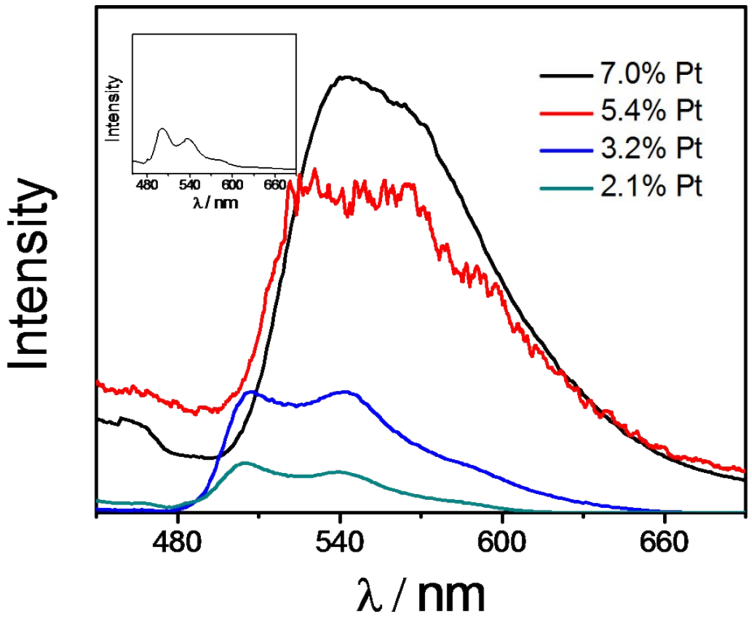

Figure S11. Emission spectra of Pt@UIO-67 MOFs with various doping concentrations at 77 K (λ_{ex} = 365 nm). Inset: The emission spectrum of Pt(dcbpy)Cl_2 in glassy MeOH/EtOH (1:4) solution at 77 K (λ_{ex} = 365 nm).

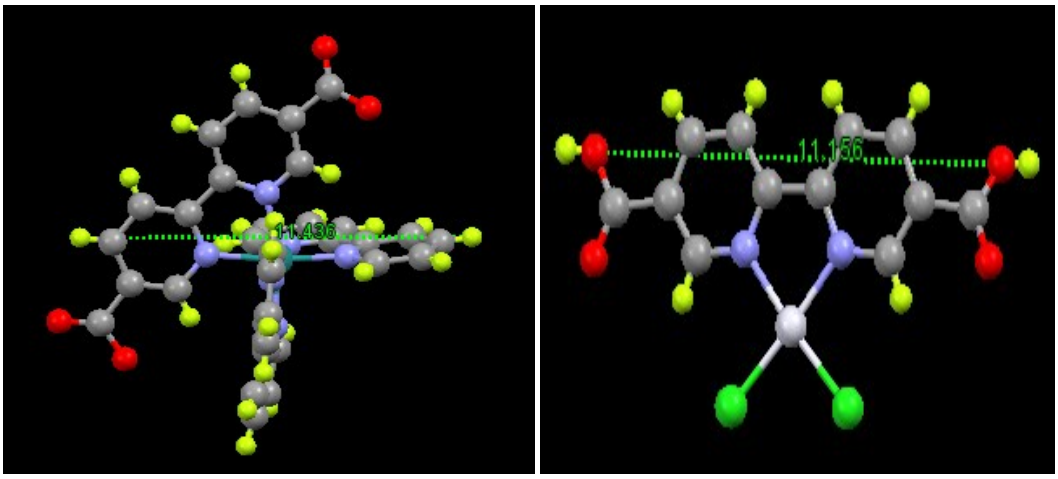

Figure S12. The diameters of RuDCBPY and PtDCBPY molecules.

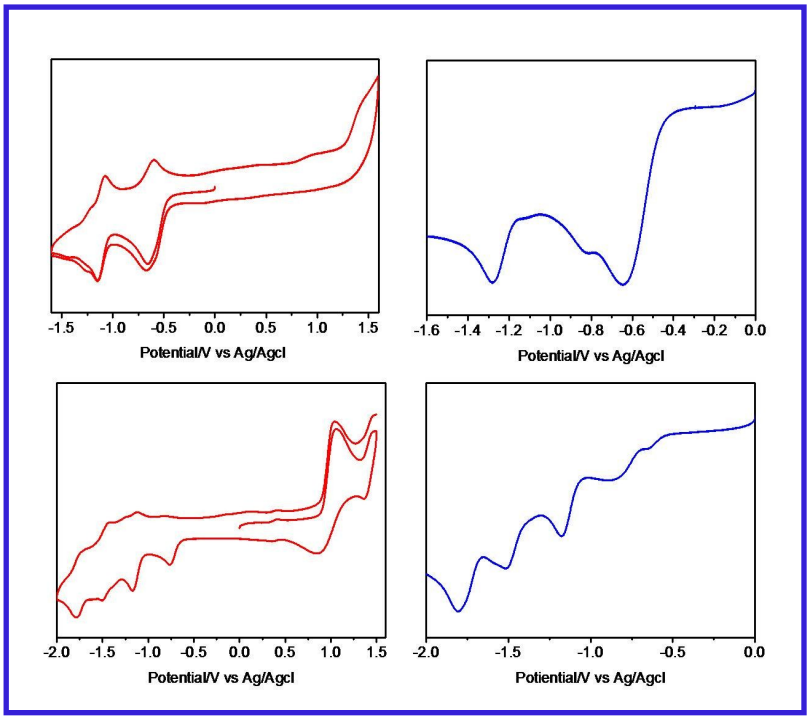

Figure S13. The cyclic voltammograms (CV) and linear sweep voltammograms (LSV) of 0.1 mM PtDCBPY (top) and 0. 1 mM RuDCBPY (bottom) in DMF solution.

Table S2. Spectral data and electrochemical potentials ($E_{1/2}$ vs Ag/AgCl)[a] of RuDCBPY and PtDCBPY.

Compound	λ_{max}(nm)		λ_{em}(nm)		$E_{1/2}^{ox}$(ΔE)	$E_{1/2}^{red}$(ΔE)
	H_2O	DMF	H_2O	DMF		
Ru-DCBPY	448	462	650	625	0.97(169)	-1.19(42), -1.46(75), -1.77(66)
Pt-DCBPY	415				1.13^{ir}	-1.25(34), -0.65(37)

[a] Measured with a glassy carbon working electrode, a Ag/AgCl reference electrode, and a platinum plate counter electrode in DMF solution containing $^{n}Bu_4NPF_6$ (0.1 M) at a scan rate of 100 mV/s; ir = irreversible. $E_{1/2} = (E_{pa} + E_{pc})/2$ in volts, and $\Delta E = E_{pa} - E_{pc}$ in mV.

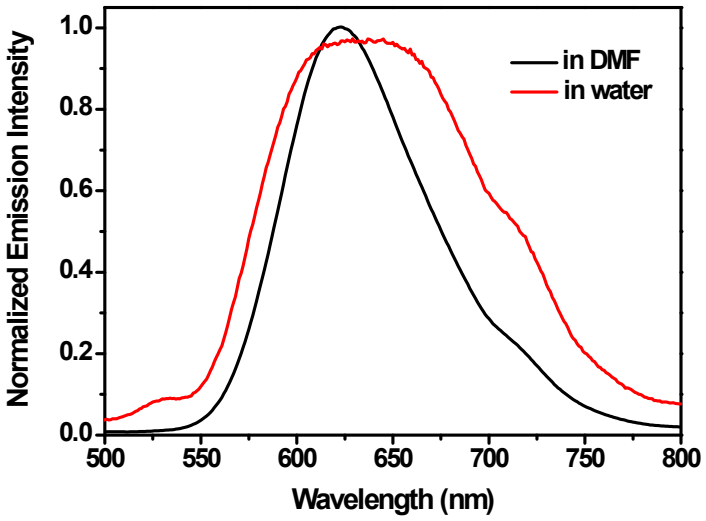

Figure S14. The emission spectra of RuDCBPY in DMF and in water.

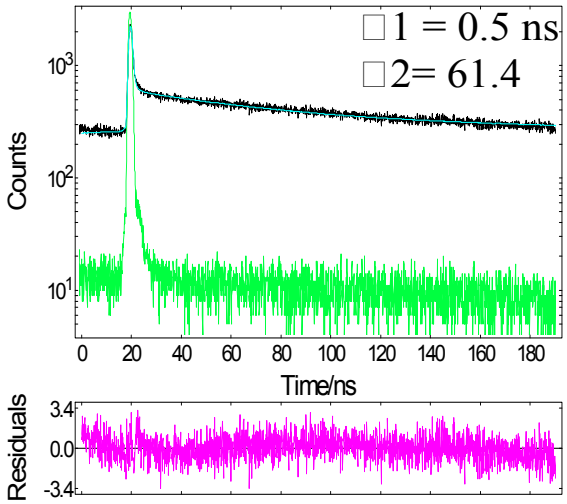

Figure S15. Emission lifetime decays obtained at room temperature for Ru-Pt@UIO-67.

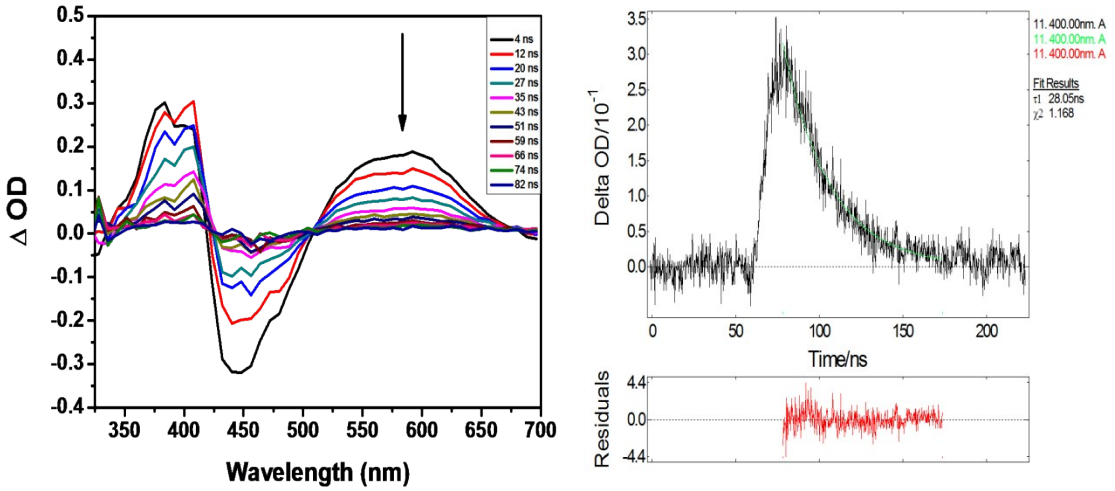

Figure S16. The nanosecond transient absorption spectra and the corresponding nanosecond recovery kinetics of transient bleaching recovery (monitored at 400 nm upon laser excitation at 355 nm) for EDTA-2Na (30 mM) + $[Ru(dcbpy)(bpy)_2]^{2+}$(1.5×10^{-4} M) in pH 5.0 solution.

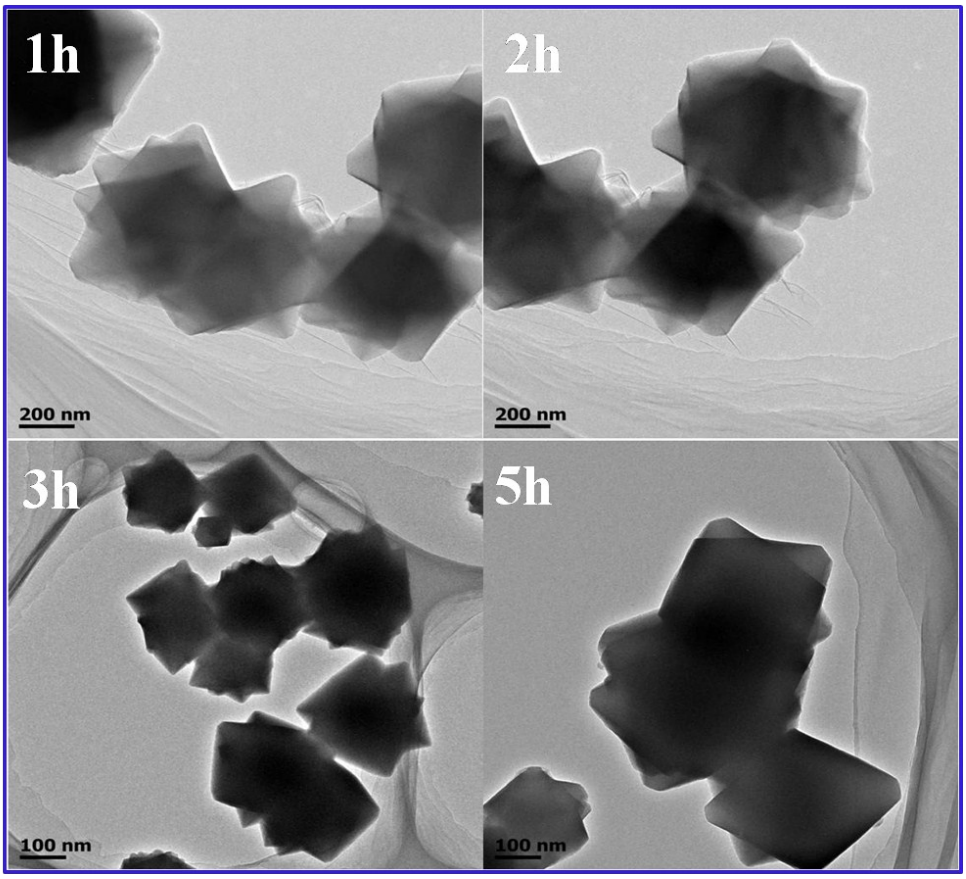

Figure S17. TEM images of Ru-Pt@UIO-67 obtained at different reaction time.

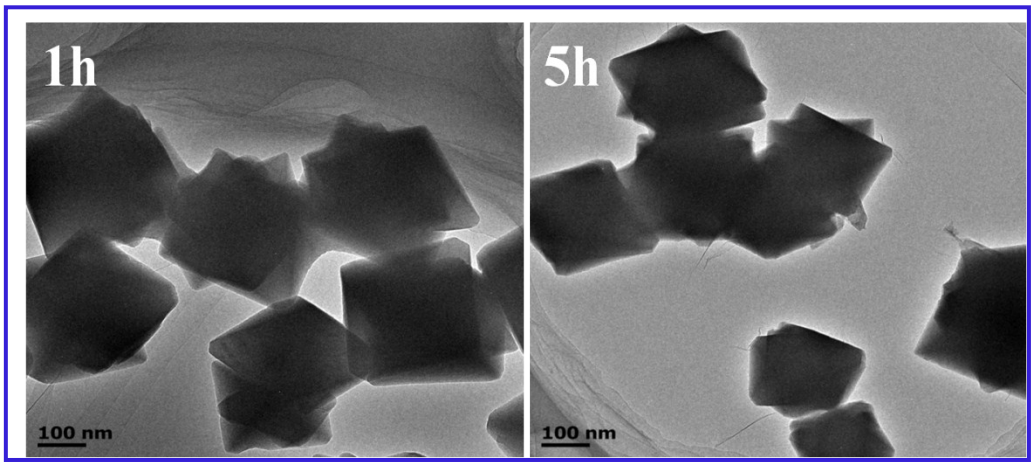

Figure S18. TEM images of Pt@UIO-67 obtained at different reaction time.