

Supplementary Information

Hydrogen Photogeneration Promoted by Efficient Electron Transfer from Iridium Sensitizers to Colloidal MoS₂ Catalysts

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Syntheses. 2(4-trifluoromethylphenyl)pyridine¹, 2-(4-tert-butylphenyl)pyridine¹, 4,4'-dicarboxy-2,2'-bipyridine², 4,4'-bis(hydroxymethyl)-2,2'-bipyridine², [Ru(dmphen)₃](PF₆)₂³, [Co(bpy)₃]Cl₂³, [Rh(dtb-bpy)₃](PF₆)₃⁴ and [Co(dmgH)₂(H₂O)₂]⁵ were synthesized according to a procedure in the literatures. All Ir(III) were prepared by two-step reaction. In the first step, cyclometalated Ir(III) dimers (C[^]N)₂Ir(μ-Cl)₂Ir(C[^]N)₂ were synthesized by the Nomoyama route, by refluxing the cyclometalated ligand with IrCl₃ in 2-ethoxyethanol mixed with water (3:1). The second step is the reaction of [Ir(N[^]C)₂Cl]₂ dimers with auxiliary diimine ligands in present of excessive Na₂CO₃ to afford the final product. The typical procedure is given for complexes **1** and **3**.

[Ir(4CF₃ppy)₂(Hdcbpy)] (1). A solution of [Ir(4CF₃ppy)₂Cl]₂ (0.25 mM) in 10 mL methanol was added to a stirred suspension of the H₂dc bpy (0.55 mM) in 10 mL dichloromethane. Excessive Na₂CO₃ was added to the mixture and was then refluxing overnight under stirring. After the solution cooled to room temperature, the solvent was removed under reduced pressure. The red pure production was obtained through a

silica column with CH₃OH/CH₂Cl₂ (1:1) for the elution. Yield: 88%. ¹H NMR (500 MHz, CD₃COOD): δ 9.33 (2H, s), 8.28 (d, J = 5.5, 2H), 8.22 (d, J = 7.5, 2H), 8.12 (d, J = 6.5, 2H), 8.04 (m, 4H), 7.86 (d, J = 7.5, 2H), 7.40 (d, J = 8.0, 2H), 7.26 (t, J = 7.0, 2H), 6.57 (s, 2H). HRMS Calcd for IrC₃₆N₄H₂₂F₆O₄, 881.1174 ([M+H]⁺); Found, 881.1169. Anal. Calcd for IrC₃₆N₄H₂₁F₆O₄: C 49.15, H 2.41, N 6.37; Found: C 48.45, H 2.95, N 5.91.

[Ir(bq)₂(Hdcbpy)] (2). Complex **2** was isolated as a red powder. Yield: 79%. ¹H NMR (500 MHz, CD₃COOD): δ 8.90 (s, 2H), 8.54 (d, J = 5.5, 2H), 8.04 (s, 2H), 7.99 (d, J = 6.5, 2H), 7.88 (d, J = 7.5, 2H), 7.78 (s, 4H), 7.56 (m, 4H), 7.17 (s, 2H), 6.20 (d, J = 8.0, 2H). Anal. Calcd for IrC₃₈N₄H₂₃O₄: C 57.64, H 2.93, N 7.07; Found: C 58.05, H 2.95, N 6.91.

[Ir(ppy)₂(dhmbpy)](PF₆) (3). In a round-bottomed flask, 0.38 g of dichloro-bridged Ir(III) dimer and 2.2 equiv of the diimine ligand are added in 25 mL of mixed CH₃OH/CH₂Cl₂ (1:1) solution. The mixture was refluxed overnight at nitrogen atmosphere. After cooling to room temperature, counter ion exchange from Cl⁻ to PF₆⁻ was accomplished via a metathesis reaction, the complex were precipitated from the methanol solution with an excess of NH₄PF₆, washed with water and methanol, and dried. Further purification was achieved by column chromatography (silica, CH₃OH/CH₂Cl₂ (1:1)). Complex **3** was isolated as a yellow powder. Yield: 75%. ¹H NMR (500 MHz, DMSO): δ 8.73 (s, 2H), 8.25 (d, J = 6.5, 2H), 7.92 (m, 4H), 7.78 (d, J = 7.5, 2H), 7.62 (t, J = 6.0, 4H), 7.16 (t, J = 7.5, 2H), 7.01 (t, J = 6.5, 2H), 6.90 (t, J = 7.5, 2H), 6.19, (d, J = 7.5, 2H), 5.78 (t, J = 6.5, 2H), 4.75 (d, J = 7.5, 4H); EIMS *m/z*:

717.42 ($[M-PF_6]^+$); Anal. Calcd for $IrC_{34}N_4H_{28}O_2PF_6$: C 47.39, H 3.27, N 6.50; Found: C 47.25, H 4.05, N 6.97.

$[Ir(4CF_3ppy)_2(dhmbpy)](PF_6)$ (4). Complex **4** was isolated as a yellow powder. Yield: 76%. 1H NMR (500 MHz, DMSO): δ 8.79 (s, 2H), 8.47 (d, $J = 7.5$, 2H), 8.18 (d, $J = 7.5$, 2H), 8.09 (t, $J = 7.5$, 2H), 7.80 (d, $J = 8.5$, 2H), 7.76 (d, $J = 7.0$, 2H), 7.65 (d, $J = 6.0$, 2H), 7.38 (d, $J = 6.5$, 2H), 7.32 (t, $J = 7.5$, 2H), 6.34 (s, 2H), 5.78 (m, 2H), 4.77, (d, $J = 7.0$, 4H); EIMS m/z : 853.25 ($[M-PF_6]^+$); Anal. Calcd for $IrC_{36}N_4H_{26}F_6O_2PF_6$: C 43.33, H 2.63, N 5.62; Found: C 43.25, H 3.05, N 5.81.

$[Ir(4Buppy)_2(dhmbpy)](PF_6)$ (5). Complex **5** was isolated as a yellow powder. Yield: 84%. 1H NMR (500 MHz, DMSO): δ 8.74 (s, 2H), 8.20 (d, $J = 7.5$, 2H), 7.91 (t, $J = 7.0$, 2H), 7.79 (d, $J = 6.5$, 2H), 7.73 (d, $J = 6.0$, 2H), 7.67 (d, $J = 6.5$, 2H), 7.63 (d, $J = 5.5$, 2H), 7.16 (t, $J = 6.5$, 2H), 7.05 (d, $J = 7.5$, 2H), 6.23 (s, 2H), 5.75 (t, $J = 7.5$, 2H), 4.75 (d, $J = 8.5$, 4H), 1.05 (s, 18H); EIMS m/z : 829.50 ($[M-PF_6]^+$); Anal. Calcd for $IrC_{42}N_4H_{44}O_2PF_6$: C, 51.79, H, 4.55, N, 5.75. Found: C, 51.25, H, 4.65, N, 5.91.

$[Ir(ppy)_2(dmbpy)](PF_6)$ (6). Complex **6** was isolated as a yellow powder. Yield: 79%. 1H NMR (500 MHz, DMSO): δ 8.23 (d, $J = 7.0$, 2H), 7.92 (t, $J = 7.5$, 2H), 7.86 (d, $J = 6.5$, 2H), 7.73 (d, $J = 6.0$, 2H), 7.32 (s, 2H), 7.24 (t, $J = 7.5$, 2H), 7.18 (d, $J = 7.0$, 2H), 7.04 (s, 4H), 6.95 (t, $J = 6.5$, 2H), 6.83, (t, $J = 8.5$, 2H), 6.58 (d, $J = 7.0$, 2H), 6.18 (d, $J = 7.0$, 2H); EIMS m/z : 687.42 ($[M-PF_6]^+$); Anal. Calcd for $IrC_{32}N_6H_{26}PF_6$: C 46.21, H 3.15, N 10.10; Found: C 46.25, H 3.35, N 10.31.

Colloidal MoS_2 NPs. Colloidal MoS_2 was prepared via a one-step solvothermal reaction of $(NH_4)_2MoS_4$ and hydrazine hydrate in a methanol solution according to a

previously reported method. 10 μmol $(\text{NH}_4)_2\text{MoS}_4$ was added to 20 mL of methanol, the solution was sonicated at room temperature for approximately 20 min until a clear solution was achieved. After that, 0.1 mL of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ and an appropriate amount of PVP was added, the reaction solution was transferred to a 25 mL Teflon-lined autoclaves. A colloidal MoS_2 solution was obtained after it was heated at 150 $^\circ\text{C}$ for 3 h, the solution was directly used for hydrogen evolution reaction. Reference samples were prepared without PVP in methanol or in aqueous solution with PVP under the same reaction condition.

Preparation of 1-sensitized MoS_2 NPs.

The MoS_2 nanoparticles (20 mg) were added into 25 mL of 0.1 mM CH_3CN solution of complex **1**. The mixture was stirred in the dark at room temperature for about 12 h. After filtered and washed with acetonitrile (5 mL) for three times, the product was dried under vacuum at 100 $^\circ\text{C}$ overnight for further characterization.

Characterization. ^1H spectra were recorded on a Bruker AMX 500 (500 MHz) FT NMR spectrometer. Analyses for C, H and N were conducted on a Perkin-Elmer 240C element analyzer. Absorption spectra were recorded on a Varian Cary 50 UV-Vis spectrophotometer. Emission spectra and luminescence quenching experiments were performed on a Varian Cary Eclipse fluorescence spectrophotometer. Mass spectra were obtained using a thermo LCQ Fleet ESI Mass Spectrometer. Electrochemical measurements were performed under a nitrogen atmosphere, and the electrolyte used was 0.1 M n-tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile with a PARSTAT-2273 advanced

electrochemical system with a standard three-electrode system consisting of Ag/AgCl as the reference electrode, a platinum sheet as counter electrode, a glassy carbon disk as the working electrode. Emission Lifetimes of Ir(III) complexes were measured using Horiba Jobin-Yvon FluoroMax-4-TCSPEC spectrometer. Samples were prepared in a glove box under a nitrogen atmosphere within a quartz cell. GC-MS analysis were carried out using an Agilent Technology 6890N gas chromatograph coupled to an Agilent 5975 mass selective spectrometer. The product was identified by comparing the mass spectra with authentic ones in the NIST 02 library. The X-ray photoelectron spectrometer (XPS) was performed by ESCALAB 250 apparatus, using monochromated Al $K\alpha$ radiation at 150 W in the pass energy model (PE = 50 eV). The nanoscale image of MoS₂ was obtained using transmission electron microscopy (TEM, JEOL3010, Japan) and scanning electron microscope (SEM, NOVA NANOSEM230, FEI, USA).

Apparent quantum yield (AQY). The apparent quantum yield (AQY) can be calculated from the ratio of the number of reacted electrons ($n_{\text{electrons}}$) involved in the photocatalytic reaction to the injected photons (n_{photons}) as the following equations:

$$n_{\text{photons}} = \frac{P\lambda}{hc} \times t \quad (1)$$

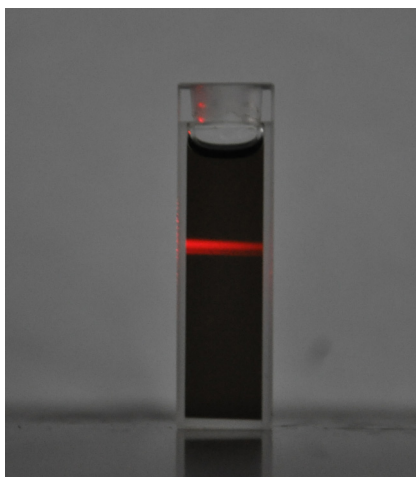
$$\begin{aligned} \text{AQY}[\%] &= \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100 \\ &= \frac{2 \times \text{number of evolved H}_2 \text{ molecules}}{\text{number of incident photons}} \times 100 \quad (2) \end{aligned}$$

The $n_{\text{electrons}}$ number was double the quantity of molecular H₂ that was detected by gas chromatography. The total number of photons was calculated according to the eq 1, in which λ is the wavelength of the monochromatic light; P is the input optical

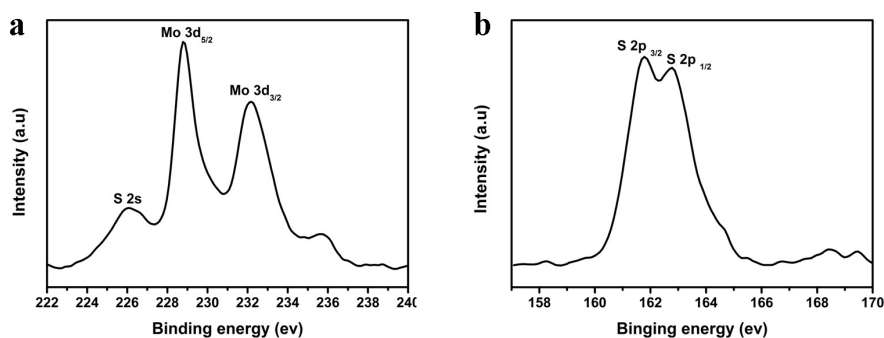
power, which was measured by a Newport Model 840 optical power meter with a 1 cm² photodiode detector; h is Planck's constant; c is the speed of light; and t is the illumination time. The AQY was calculated according to eq 2. The photocatalytic hydrogen reactions were performed for 4 h using monochromatic light irradiated at the following wavelengths: 350, 380, 400, 420, 440 and 480 nm. The light source was a Xe lamp equipped with various band-pass filters.

Computational Details: Density functional theory calculations (B3LYP/LANL2DZ) were performed using GUASSIAN 09. The numerical calculations in this paper were performed on the IBM Blade cluster system at the High Performance Computing Center (HPCC) of Nanjing University.

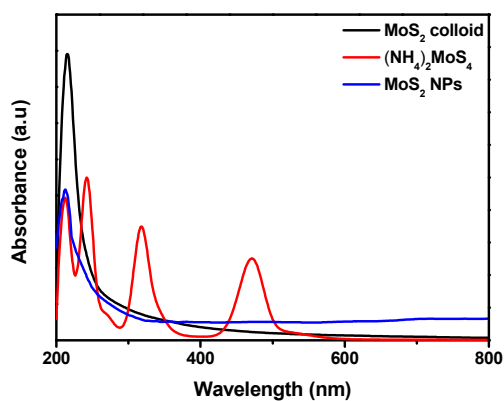
- 1 Beeby, A. *et al.* A new precatalyst for the Suzuki reaction—a pyridyl-bridged dinuclear palladium complex as a source of mono-ligated palladium(0). *New. J. Chem.* **28**, 600-605 (2004).
- 2 Gillaizeau-Gauthier, I. *Et al.* Phosphonate-based bipyridine dyes for stable photovoltaic devices. *Inorg. Chem.* **40**, 6073-6079 (2001).
- 3 Goldsmith, J. I., Hudson, W. R., Lowry, M. S., Anderson, T. H. & Bernhard, S. Discovery and high-throughput screening of heteroleptic iridium complexes for photoinduced hydrogen production. *J. Am. Chem. Soc.* **127**, 7502-7510 (2005).
- 4 Cline, E. D., Adamson, S. E. & Bernhard, S. Homogeneous catalytic system for photoinduced hydrogen production. *Inorg. Chem.* **47**, 10378-10388 (2008).
- 5 Natali, M., Argazzi, R., Chiorboli, C., Iengo, E. & Scandola, F. Photocatalytic hydrogen evolution with a self-assembling reductant–sensitizer–catalyst system. *Chem. Eur. J.* **19**, 9261-9271 (2013).



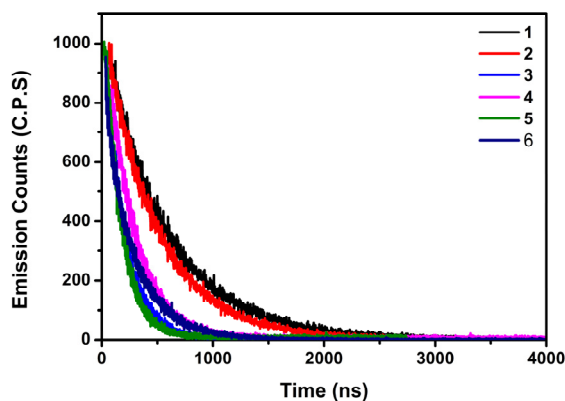
Supplementary Figure S1. Tyndall phenomenon for colloidal MoS₂ in methanol solution.



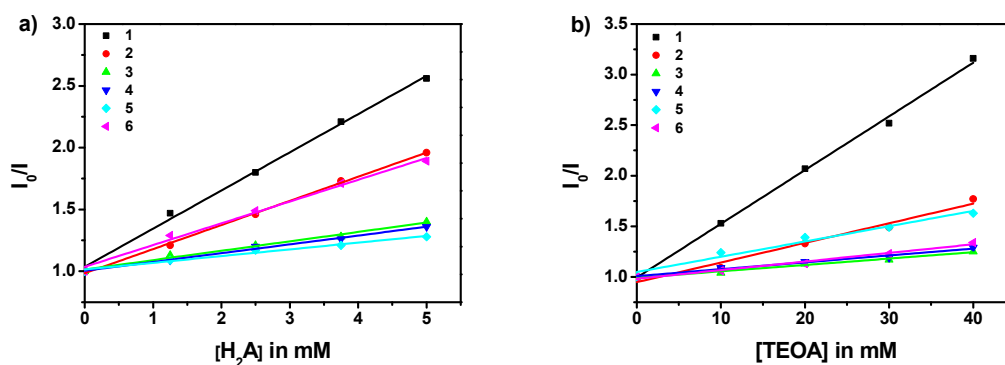
Supplementary Figure S2. XPS spectra of MoS₂ (a) Mo 3d and S 2s peaks, and (b) S 2p peaks. The MoS₂ sample for XPS was prepared by evaporating the methanol solvent.



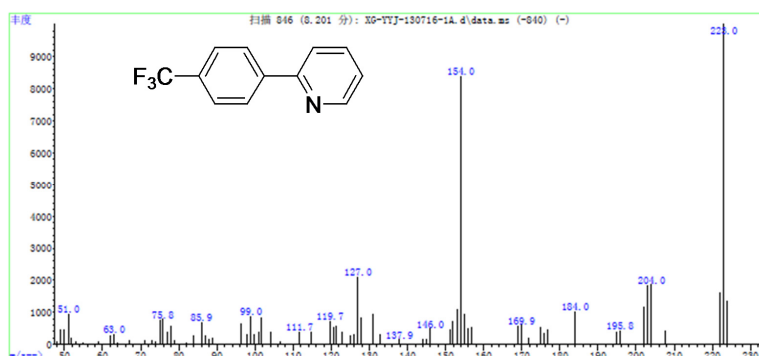
Supplementary Figure S3. Absorption spectra of MoS₂ colloid, MoS₂ NPs, and (NH₄)₂MoS₄ in methanol solution.



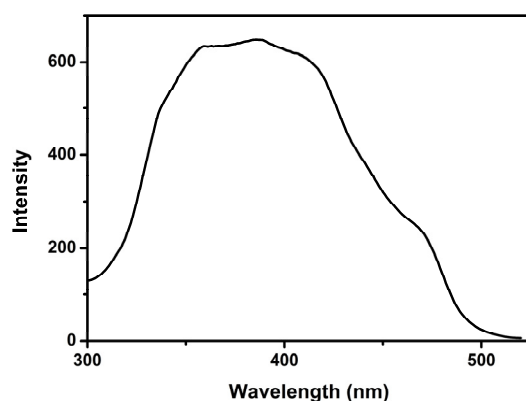
Supplementary Figure S4. Emission decay kinetics for complexes 1-6 measured in nitrogen-saturated CH_2Cl_2 at room temperature.



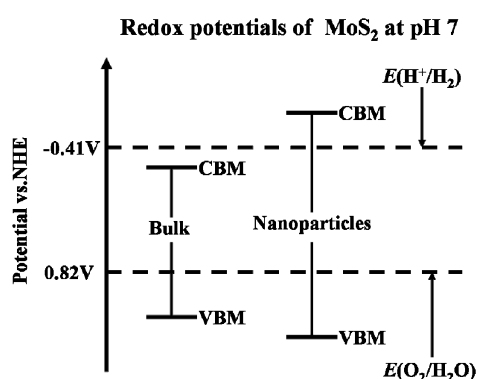
Supplementary Figure S5. Stern-Volmer plot for emission quenching of Ir(III) complexes 1-6 by H_2A (a) and TEOA (b).



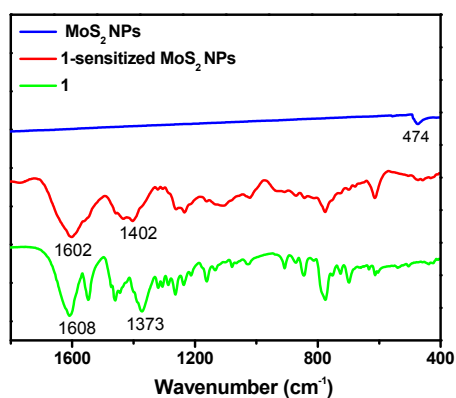
Supplementary Figure S6. GC-MS of decomposition product of Ir(III) PS. The production was collected from the reaction mixture of **1**- MoS_2 - H_2A after 20 h of irradiation, which clearly revealed that 2-(4-trifluoromethylphenyl)pyridine ($m/z = 223$) dissociated from complex **1**.



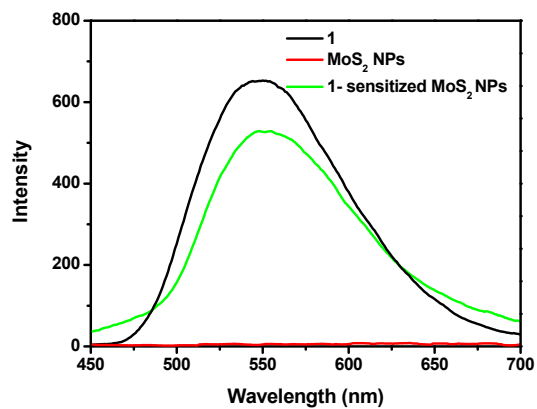
Supplementary Figure S7. Excitation spectra of complex 1 in methanol.



Supplementary Figure S8. Energy diagrams of the conduction and valence band edges vs normal hydrogen electrode (NHE) for MoS₂ of various sizes. The valence band maximum (VBM) shifted-positively with the decreasing particle size, and conduction band minimum (CBM) shifted-negatively with the decreasing particle size.

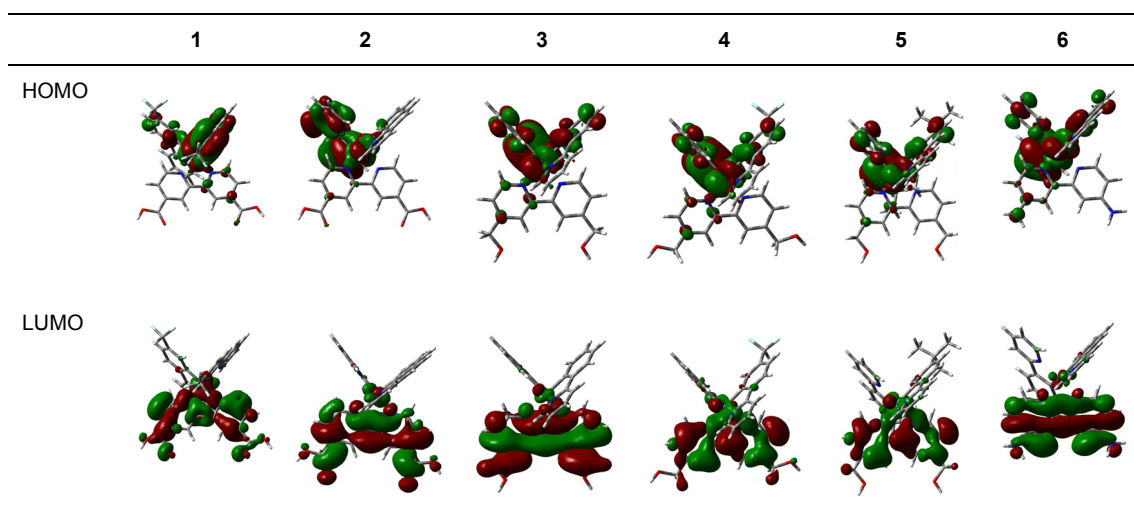


Supplementary Figure S9. FTIR spectra of MoS₂ NPs, PS 1 and 1-sensitized MoS₂.

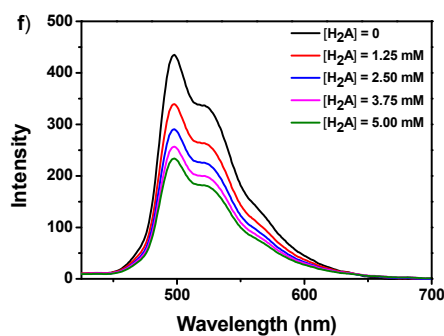
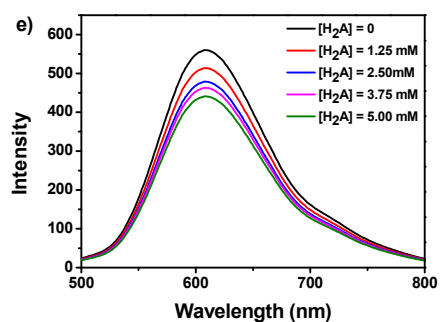
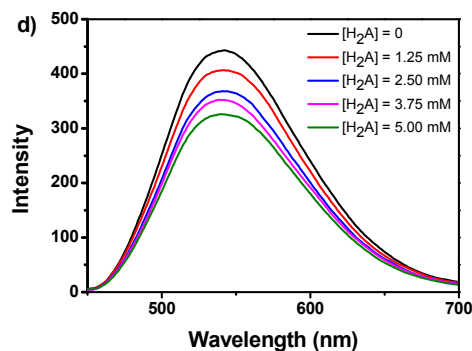
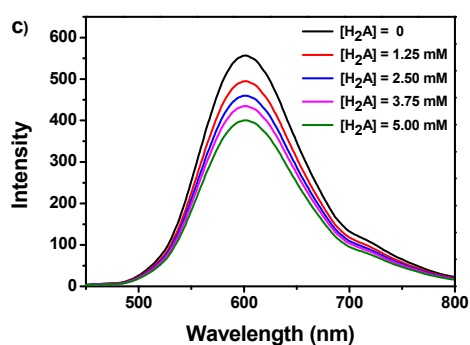
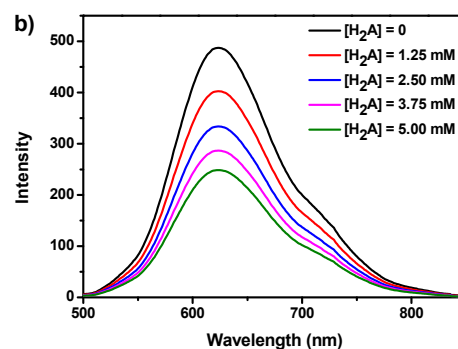
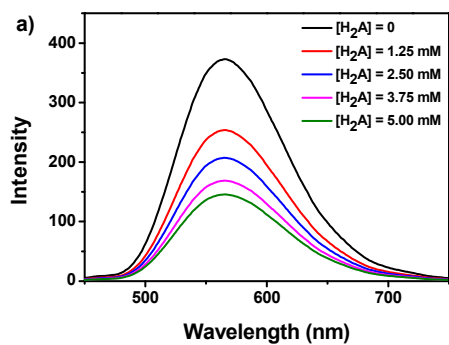


Supplementary Figure S10. Emission spectra of complex 1 (in CH₂Cl₂ solution), MoS₂ NPs (in solid state) and 1-sensitized MoS₂ (in solid state).

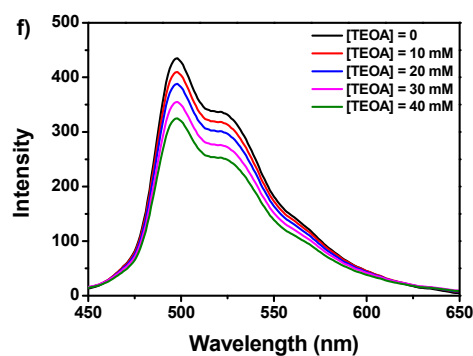
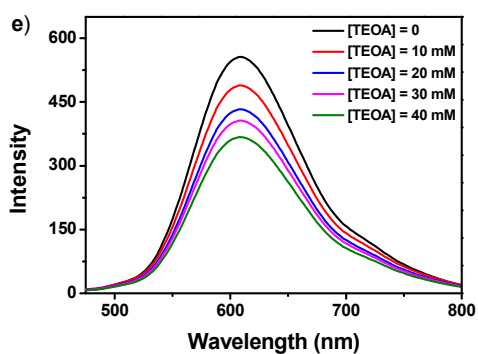
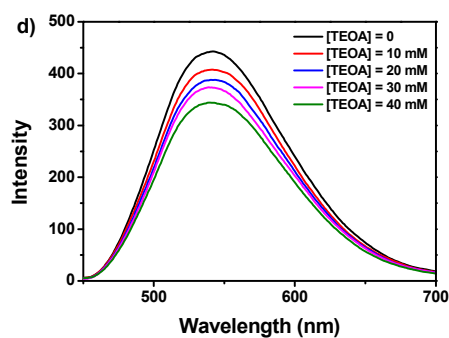
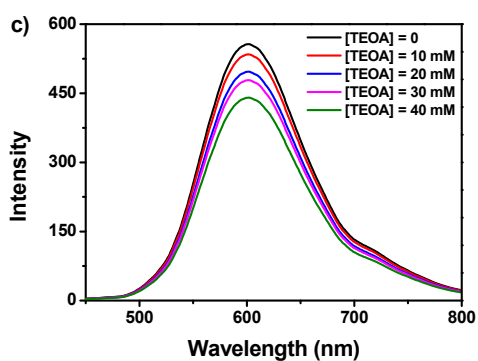
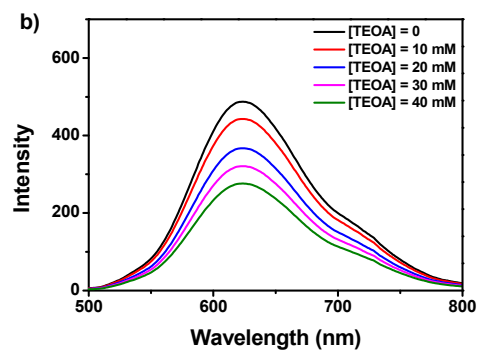
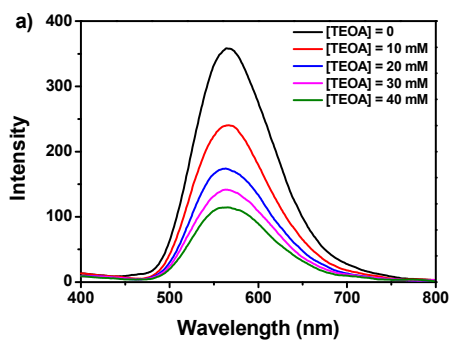
Supplementary Table S1. HOMO and LUMO Distributions for Ir(III) complexes 1-6.



Supplementary Table S2. Emission spectra of Ir(III) complex 1(a), 2(b), 3(c), 4(d), 5(e) and 6(f) in methanol/water (1:1) solution. The emission intensity of Ir(III) complex in methanol solution was measured by changing the concentration of H₂A (the concentration of Ir(III) complex was 2×10^{-5} M).



Supplementary Table S3. Emission spectra of Ir(III) complex 1(a), 2(b), 3(c), 4(d), 5(e) and 6(f) in methanol/water (1:1) solution. The emission intensity of Ir(III) complex in methanol solution was measured by changing the concentration of TEOA (the concentration of Ir(III) complex was 2×10^{-5} M).



Supplementary Table S4. Quenching Kinetics for Ir(III) Complexes 1-6. In all samples, quenching rate constants (k_q) was determined using the Stern-Volmer equation $I_0/I = 1 + k_q\tau[Q]$, where I_0 is the emission intensity in absence of quencher, I is the value in presence of a quencher, τ is the excited-stated lifetime in the absence of a quencher, and $[Q]$ is the molar concentration of the quencher.

| PS | $K_q\text{H}_2\text{A}$ ($\text{M}^{-1}\text{s}^{-1}$) | $K_q\text{TEOA}$ ($\text{M}^{-1}\text{s}^{-1}$) |
|----|--|---|
| 1 | 4.47×10^8 | 0.77×10^8 |
| 2 | 3.77×10^8 | 0.36×10^8 |
| 3 | 2.48×10^8 | 0.23×10^8 |
| 4 | 1.94×10^8 | 0.22×10^8 |
| 5 | 2.74×10^8 | 0.73×10^8 |
| 6 | 6.37×10^8 | 0.31×10^8 |