Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Noble-metal-free nickel(II) phthalocyanine as a stable catalyst for visible-light-driven hydrogen evolution from water

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Experimental section

Reagents and materials.

Commercially available chemical reagents were used without purification. Neutral nickel phthalocyanine complex was purchased from Alfa Aesar China (Tianjin) Co., Ltd, which was used as hydrogen evolution reaction catalyst without purification. $[Ni(bpy)_3](PF_6)_2$ was prepared according to the literature procedure.[1] ^1H NMR spectra were recorded on a Bruker AMX 500 (500 HZ) FT NMR spectrometer. Analyses of the C, H and N content were conducted on a Perkin-Elmer 240C element analyzer. The emission spectra and the luminescence quenching experiments were performed on a Varian Cary Eclipse fluorescence spectrophotometer. The emission lifetimes of the iridium complexes were measured using the integrating sphere on an FLS920 fluorescence spectrophotometer (Edinburgh Instruments Ltd., UK) with a hydrogen-filled lamp as the excitation source.

Synthesis of IrPS

2-(3,4-difluorophenyl)pyridine was synthesized by a classical Pd-Catalyzed cross-coupling reaction according to previous report.[2] The iridium photosensitizer was prepared through a two-step reaction according to a previous reported.[3] Iridium trichloride hydrate (0.32 g, 1 mmol) and 2-(3,4-difluorophenyl)pyridine (0.42 g, 2.20 mmol) were reacted at 130 ^oC for 24 h in 40 mL degassed 2-ethoxyethanol/water (3:1 v/v). After cooling to room temperature, 50 mL of water was added and the yellow suspension was filtrated. The pure $[Ir_2(dfppy)_4Cl_2]$ was obtained through column chromatography on silica gel using n-hexane/ethyl acetate (4:1 v/v) as the eluent. Then $[Ir_2(dfppy)_4Cl_2]$ (0.42 g, 0.30 mmol) and H_2dcbpy (0.08 mmol) were added in CH_3OH/CH_2Cl_2 (30 mL, 1:1, v/v). Excessive Na_2CO_3 was added to the mixture which was then refluxing overnight under stirring. The resulting precipitate was filtered as crude product which was purified by column chromatography on silica gel (CH_3OH/CH_2Cl_2, 1/1). Yield: 465 mg (92%). ^1H NMR (500 MHZ, CD_3COOD)：δ 8.75 (2H, J = 8.5, d), 8.11（2H, J = 8.0, t), 8.03 (2H, dd), 7.95 (2H, dd), 7.85 (2H, J = 7.5, t), 7.77 (2H, dd), 7.67 (4H, s), 7.01 (2H, J = 7.5, d). Anal. Found for

$C_{34}H_{19}F_4IrN_4O_4$: C, 50.26; H, 2.56; N, 6.67; Calcd for $C_{34}H_{19}F_4IrN_4O_4$: C, 50.06; H, 2.35; N, 6.87.

Photocatalytic hydrogen production

Photocatalytic hydrogen production experiments were carried out in a Pyrex top-irradiation reaction vessel, which was connected to a closed gas-circulation lation glass system. In a typical hydrogen production experiment, 100 ml of 8:2 acetone/water solution containing of 20 μM NiPS, 100 μM IrPS and 0.2 M TEOA system was evacuated several times to remove air completely, the mixture solution was then irradiated by a white LED lamp (COB, 30 W) equipped with a cut-off filter ($\lambda > 420$ nm) and under gentle magnetic stirring. The reaction solution was maintained at room temperatures by a flow of cooling water during the measurements. The evolving hydrogen was periodically detected by a gas chromatograph (Shimadzu GC-1690, argon as a carrier gas) equipped with a thermal conductivity detector. The apparent quantum yield (AQY) of H_2 evolution system was measured in 8:2 acetone-water solution containing of 20 μM NiPc, 100 μM IrPS and 0.2 M TEOA at pH 10 by using low power LED (GS-UV, 3 W, 420 nm) (Shenzhen Warner JPLED Co. Ltd. China) as light source. The AQY was calculated according to the following equations:

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

$$\begin{aligned} \mathrm{AQY}[\%] &= \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100 \\ &= \frac{2 \times \text{number of evolved } H_2 \text{ molecules}}{\text{number of incident photons}} \times 100 \qquad (2) \end{aligned}$$

where P is the input optical power; λ (360 nm) is the wavelength of the monochromatic light; h is Planck's constant; c is the speed of light; and t is the illumination time.

Reference

[1] C. Ruiz-Pérez, P. A. L. Luis, F. Lloret and M. Julve, *Inorg. Chim. Acta.* 2002, **336**, 131-136.

[2] A. Beeby, S. Bettington, I. J. S. Fairlamb, A. E. Goeta, A. R. Kapdi, E. H. Niemelä and A. L. Thompson, *New. J. Chem.* 2004, **28**, 600-605.

[3] W. L. Jiang, Y. Gao, Y. Sun, F. Ding, Y. Xu, Z. Q. Bian, F. Y. Li, J. Bian and C. H. Huang, *Inorg. Chem.* 2010, **49**, 3252-3260.

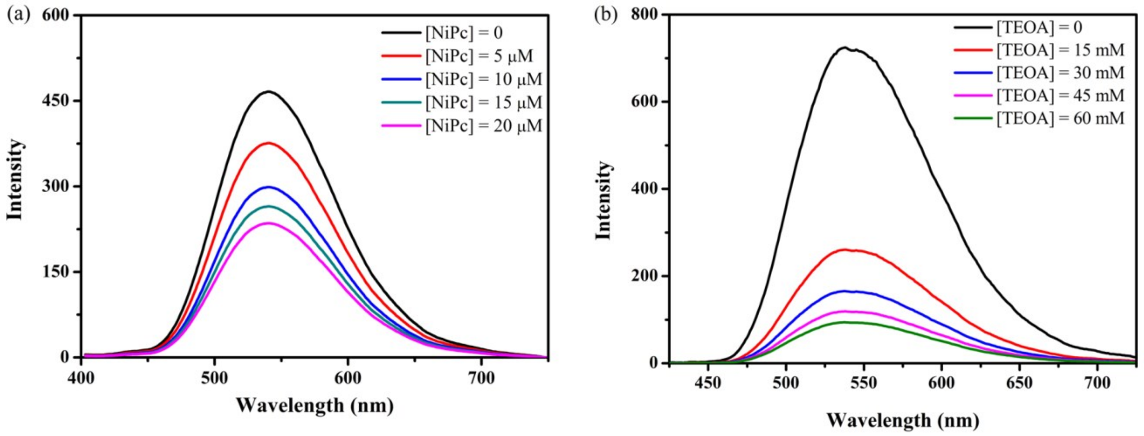

Figure S1. Emission spectra of IrPS* in acetone/water (8:2) by changing the concentration of NiPc (a) or TEOA (b) (the concentration of complex **IrPS** was 20 μM).

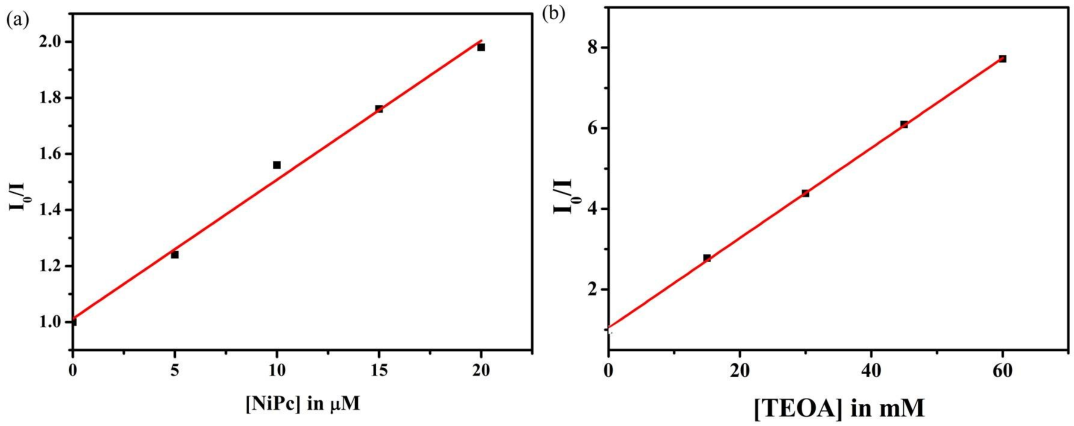

Figure S2. Stern-Volmer plot for emission quenching of Ir(III) complex by NiPC (K_q =1.61 $\times 10^{10}$ M^{-1} s^{-1}) or TEOA ($K_q = 1.80 \times 10^8$ M^{-1} s^{-1}).

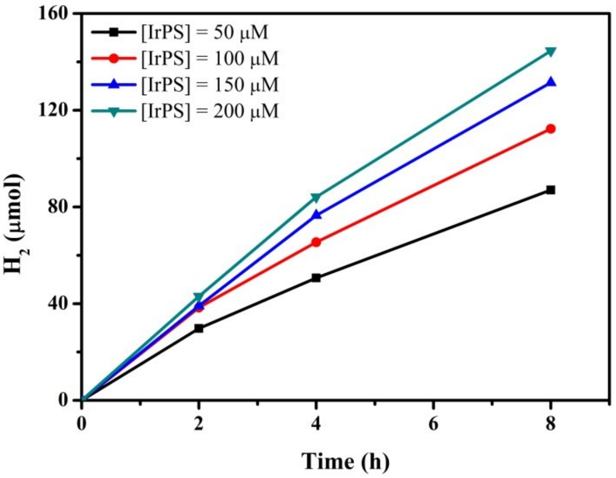

Figure S3. Solar H_2 production traces with different initial concentrations of NiPc in 8:2 acetone/water solution containing 50~200 μM IrPS, 20 μM NiPc and 0.2 M TOEA under visible light irradiation (λ > 420 nm) at pH 10.

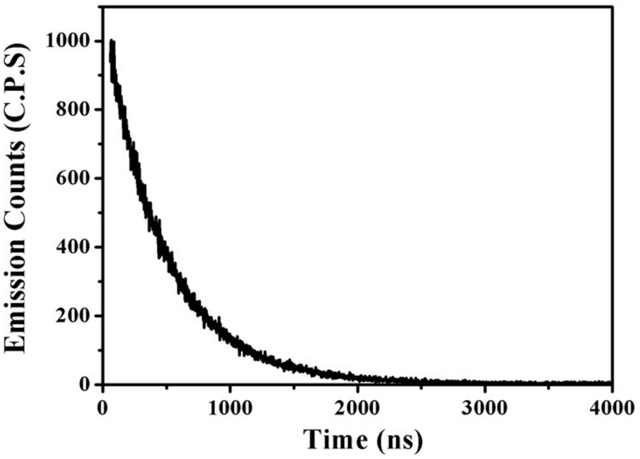

Figure S4. Emission decay kinetics for IrPS measured in nitrogen-saturated CH_2Cl_2 at room temperature, $\tau = 0.62 \mu s$.