Supporting Information

Enhanced Photocatalytic H₂ Production on CdS Nanorods with Simple

Molecular Bidentate Cobalt Complexes as Cocatalysts under Visible

Light

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Table S1. Rate of H₂ production over different photocatalytic systems. Experiments were performed under visible light ($\lambda > 420$ nm) using 0.02 mM complex **1**, 0.5 M ascorbic acid in 20 mL water at pH 4.

| Photocatalytic system | $H_2 (\mu mol h^{-1} mg^{-1})$ |
|---|--------------------------------|
| Complex 1/CdS in solution without ascorbic acid | 0.0 |
| Complex 1 in ascorbic acid solution | 0.0 |
| CdS in ascorbic acid solution | 12 |
| Complex 1/CdS in ascorbic acid solution | n 550 |

Table S2. Rate of H₂ production using different sacrificial reagents. Experiments were performed under visible light ($\lambda > 420$ nm) using 1 mg CdS and 0.02 mM complex 1 in 20 mL water.

| Sacrificial reagents | Conditions | H ₂ (μmol.h ⁻¹ .mg ⁻¹) | |
|---|-------------------|--|--|
| Methanol | 25 % v/v | 0.0 | |
| TEA | 5 % v/v | 18 | |
| TEOA | 5 % v/v | 40 | |
| NaI | 0.1 M | 0.0 | |
| EDTA | 0.1 M | 1.2 | |
| $Na_2S_2O_4$ | 0.5 M | 0.0 | |
| Na ₂ S | 0.5 M | 120 | |
| Na ₂ S and Na ₂ SO ₃ | 0.75 M and 1.05 M | 335 | |
| Ascorbic acid | 0.5 M, pH 4 | 540 | |

| Table S3. Comparison of turnover numbers (TONs) and apparent quantum yield (AQY) | of |
|--|----|
| different photocatalytic systems based on cobalt complexes as molecular cocatalysts. | |

| Cocatalyst | TONs | AQY (%) | Reference |
|---|---------|--------------|--------------|
| Co bidentate complexes | 15,200 | 27 (420 nm) | Present work |
| Cobaloximes | 171 | 9.1 (420 nm) | S 1 |
| Cobaloximes | 273 | 16 (412 nm) | S2 |
| Cobaloximes | 900 | 4 (520 nm) | S3 |
| Cobalt bipyridyl complexes | | 13 (450 nm) | S4 |
| Cobalt dithiolenes | 2700 | | S5 |
| Cobalt dithiolenes | 300,000 | 24 (520 nm) | S6 |
| Cobalt salen complexes | 64,700 | 29 (420 nm) | S7 |
| Cobalt tetraaza- macrocyclic complex | 1000 | | S8 |



Figure S1. TEM image of complex 1/CdS NRs (2.4 wt % of Co in the composite).



Figure S2. The estimated band gap of the CdS NRs, complex 1 and complex 1/CdS NRs.



Figure S3. The photographs of complexes **1-4** (0.02 mM) in aqueous solutions at pH 4. Complexes **1** and **3** are good soluble while **2** and **4** show low solubility at room temperature.



Figure S4. UV-vis absorption spectra of complexes 1-4 (2×10^{-5} M) in water.



Figure S5. (a) Photocatalytic H₂ production of pure CdS NRs in 0.5 M ascorbic acid solution at pH 4 under visible light irradiation ($\lambda > 420$ nm). (b) Time course H₂ production of 0.02 mM cobalt complex 1 under visible light ($\lambda > 420$ nm) at pH 4. Photocatalytic system contained 1.0 mg CdS NRs and 0.5 M ascorbic acid in 20 mL water.



Figure S6. Powder XRD patterns of CdS before (red plot) and after (black plot) 10 hours of visible light irradiation ($\lambda > 420$ nm).



Figure S7. (a) TEM image of CdS NRs after 10 h of photocatalytic reaction (b) after 10 h of photocatalytic reaction (enlarged) (c) EDX spectrum of CdS NRs washed by ethanol and water after 10 h of irradiation, in which no cobalt species were found.



Figure S8. Hydrogen production under different concentrations of complex **1**. The reaction mixtures contain 0.5 M ascorbic acid, 1.0 mg CdS at pH 4 in 20 mL water.



Figure S9. ¹H NMR of 3-formyl-4-hydroxybenzoic acid.



Figure S10. ¹H NMR of ligand L-1.



Figure S11. ¹H NMR of ligand L-2.



Figure S12. ¹H NMR of ligand L-3.



Figure S13. ¹H NMR of ligand L-4.

References.

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