Supporting Information

Self-photosensitizing metal complexes for photocatalytic hydrogen evolution

Mingyu Ma [a,†], Zongyang Liu [a,†], Kuo Yuan [a,†], Zheyuan Liu [b,†], Jiaxin Wang [a], Qingqing Lin [b], Di-Chang Zhong [a,*], and Tong-Bu Lu [a,*]

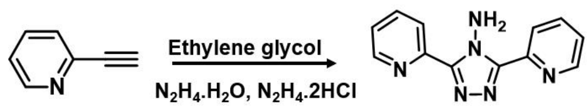
[a]*Institute for New Energy Materials and Low Carbon Technologies, School of Materials Science and Engineering, Tianjin University of Technology, Tianjin 300384, China*

[b]*Key Laboratory of Advanced Materials Technologies, International (Hong Kong Macao and Taiwan) Joint Laboratory on Advanced Materials Technologies, School of Materials Science and Engineering, Fuzhou University, Fuzhou 350108, China*

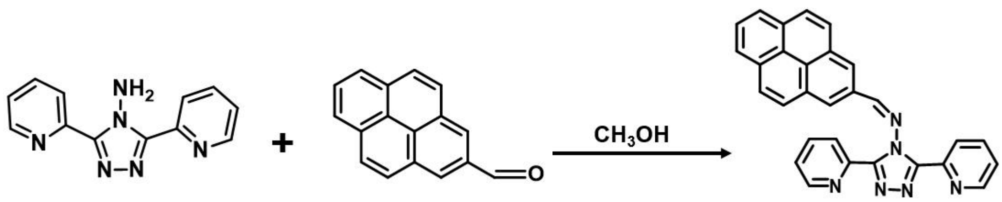
† These authors contributed equally to this work.

* Corresponding author.

E-mail: dczhong@email.tjut.edu.cn (D.-C. Zhong); lutongbu@tjut.edu.cn (T.-B. Lu)



Scheme S1. Synthesis of 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole (L).



Scheme S2. Synthesis of pyrene-L.

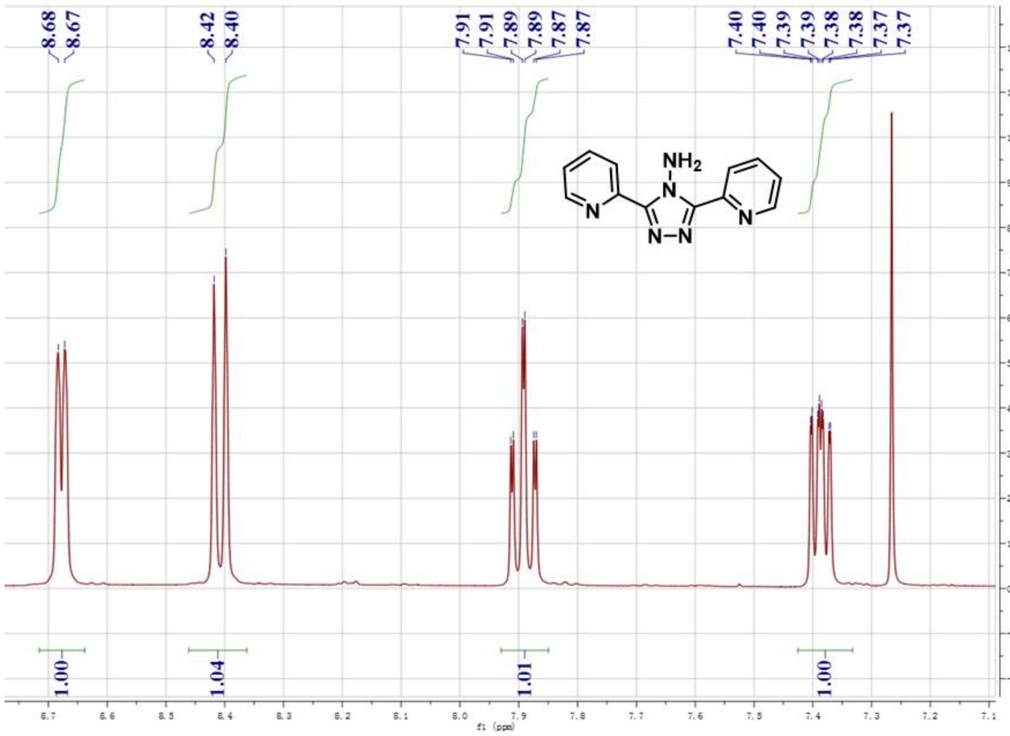


Fig. S1. ^{1}H NMR spectrum of L (4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole).

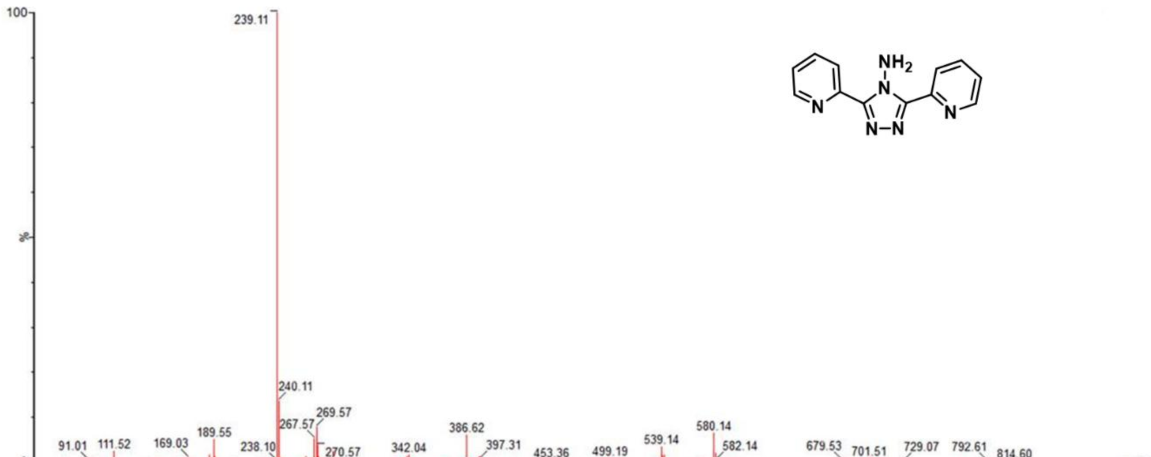


Fig. S2. LC-MS of L in CH_3OH solution, where the peak at *m/z* 239.11 can be assigned to the species of $[L+H^{+}]^{+}$.

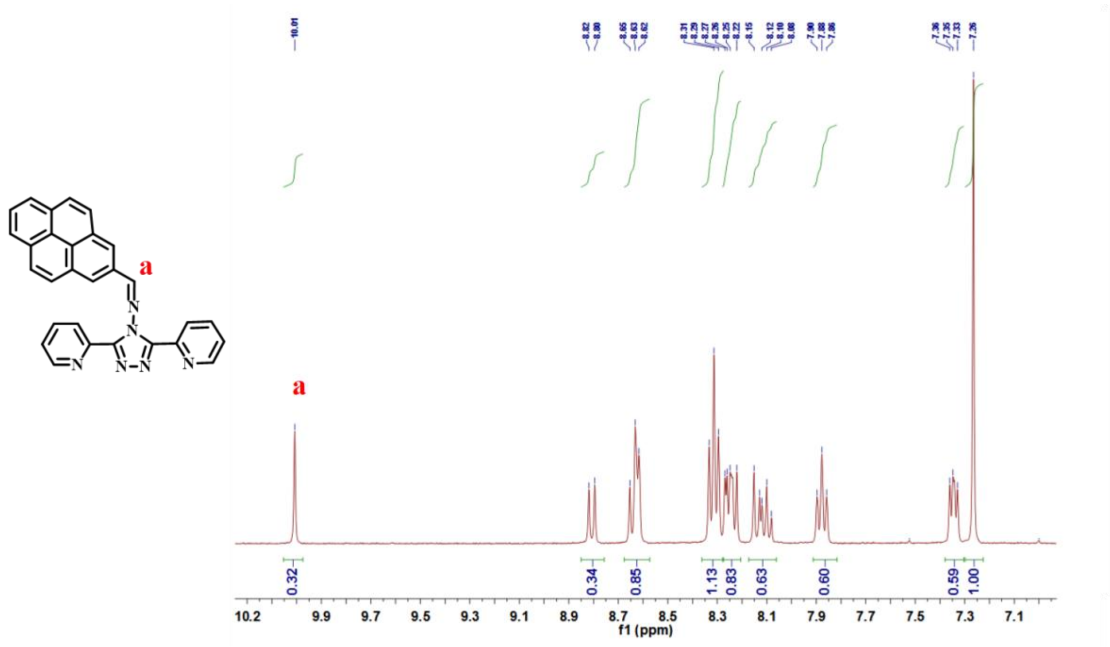


Fig. S3. ^{1}H NMR spectrum of pyrene-L in $CDCl_3$.

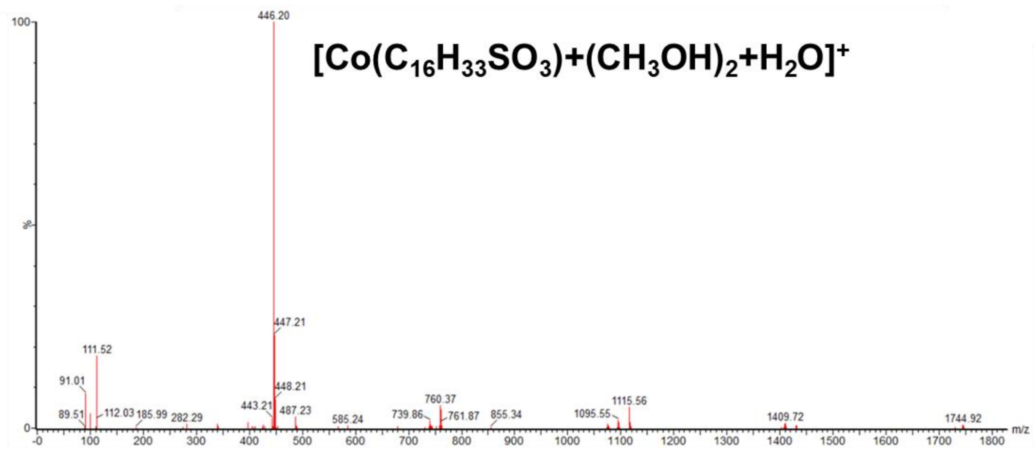


Fig. S4. LC-MS of Cobalt cetylsulfonate in CH_3OH solution, where the peak at *m/z* 446.20 can be assigned to the species of $[Co(C_{16}H_{33}SO_3)+(CH_3OH)_2+H_2O]^+$.

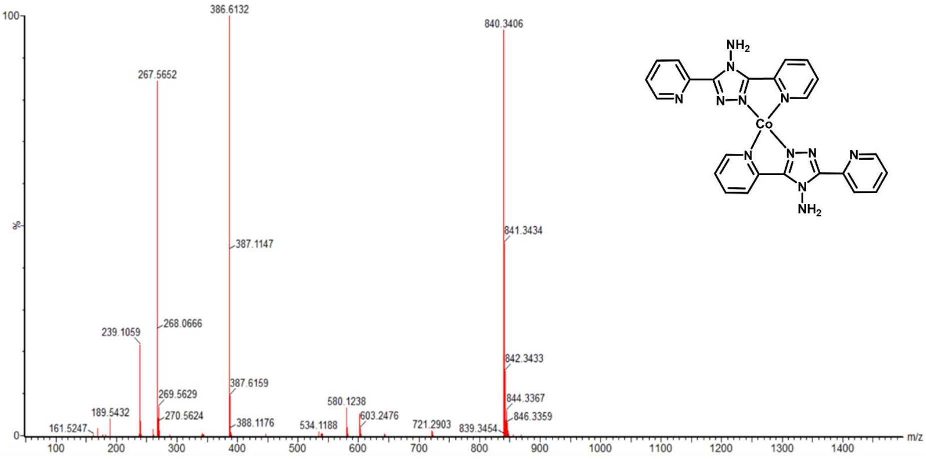


Fig. S5. LC-MS of CoL_2 in CH_3OH solution, where the peak at *m/z* 267.56 can be assigned to the species of $[CoL_2]^{2+}$.

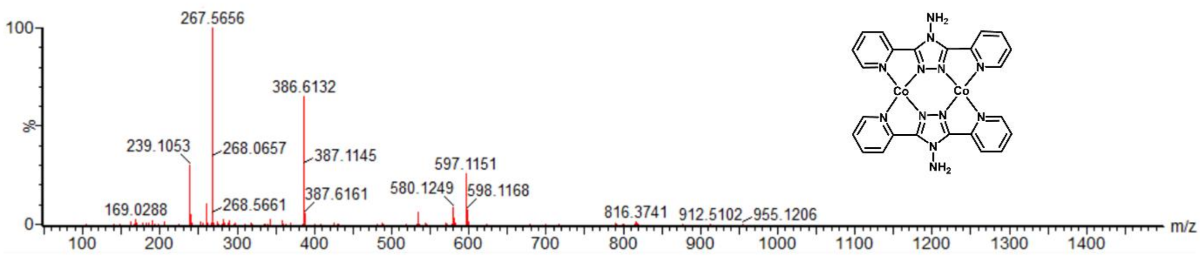


Fig. S6. LC-MS of Co_2L_2 in CH_3OH solution, where the peak at *m/z* 386.6 can be assigned to the species of $[Co_2L_2+(OH^-)_3+(CH_3OH)_2+(CH_3CN)+(Na^+)]^{2+}$.

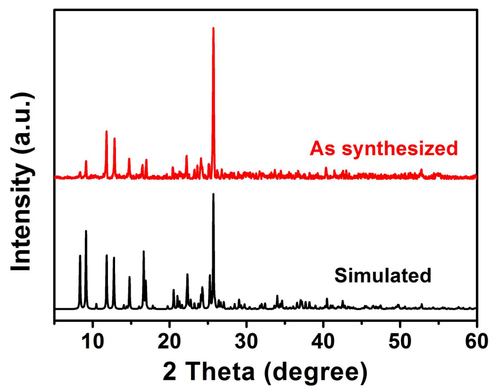


Fig. S7. The powder X-ray diffraction (PXRD) pattern of Co_2L_2.

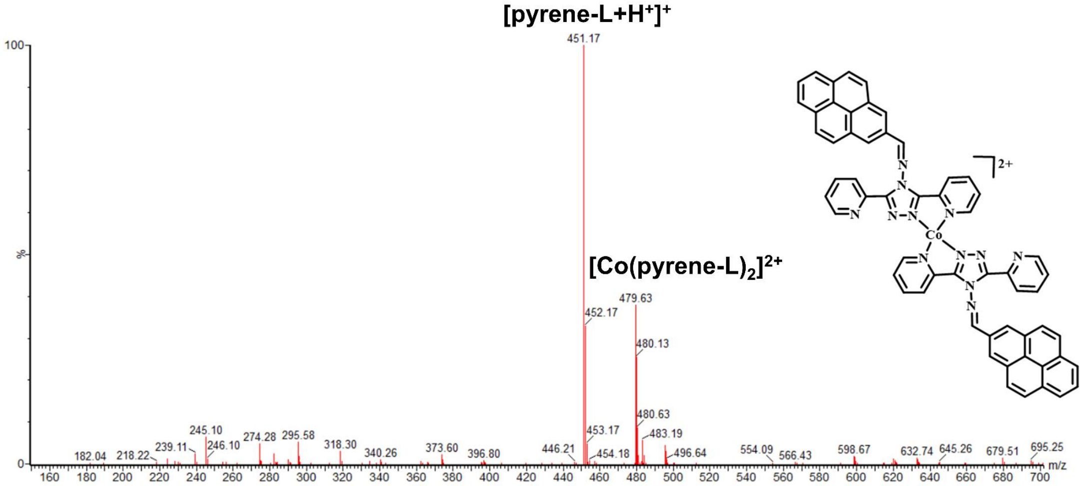


Fig. S8. LC-MS of Co(pyrene-L)$_2$ in CH_3OH solution, where the peak at *m/z* 479.63 can be assigned to the species of $[Co(pyrene\text{-}L)_2]^{2+}$.

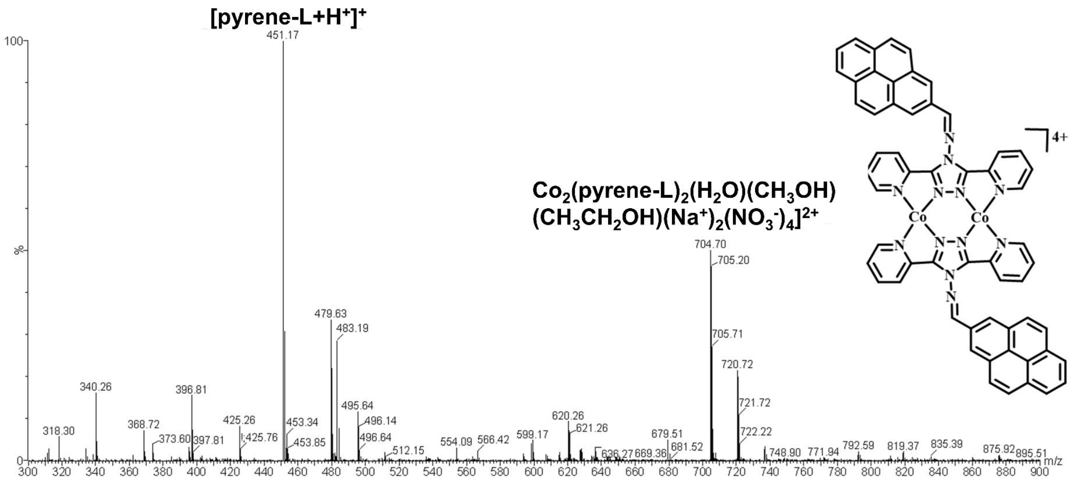


Fig. S9. LC-MS of Co_2(pyrene-L)$_2$ in CH_3OH solution, where the peak at *m/z* 451.17, and 704.70 can be assigned to the species of $[pyrene\text{-}L+H^+]^+$, $[Co_2(pyrene\text{-}L)_2(H_2O)(CH_3OH)(CH_3CH_2OH)(Na^+)_2(NO_3^-)_4]^{2+}$, respectively.

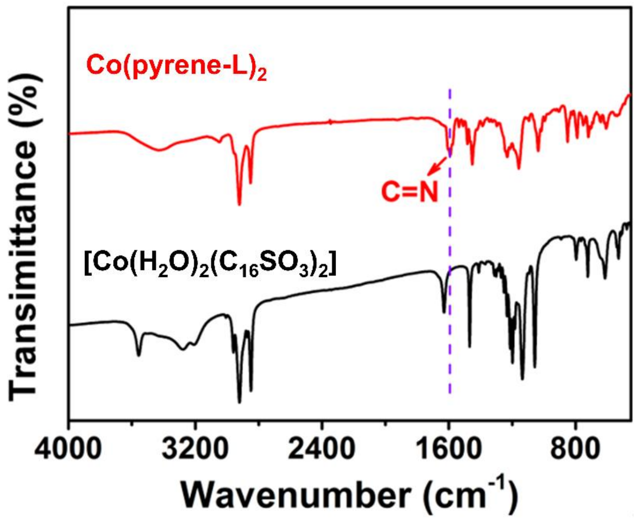


Fig. S10. FT-IR spectra of Co(pyrene-L)$_2$ and [Co(H_2O)$_2$($C_{16}SO_3$)$_2$].

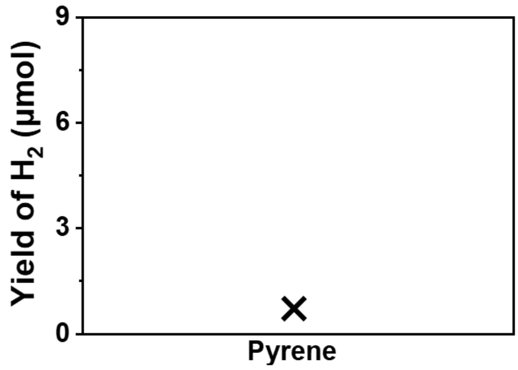


Fig. S11. Results of photocatalytic H_2 evolution by pyrene after illumination for 12 h.

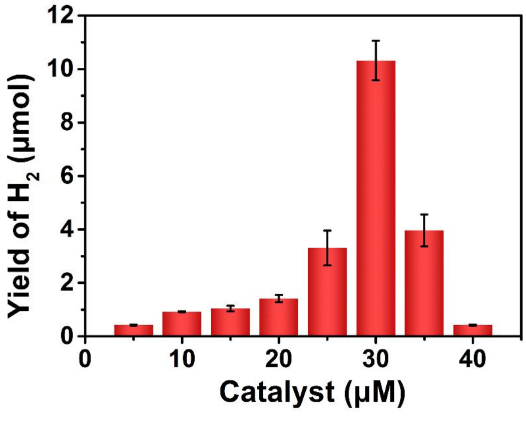


Fig. S12. Results of photocatalytic H_2 evolution by Co$_2$(pyrene-L)$_2$ at different concentrations after illumination for 12 h.

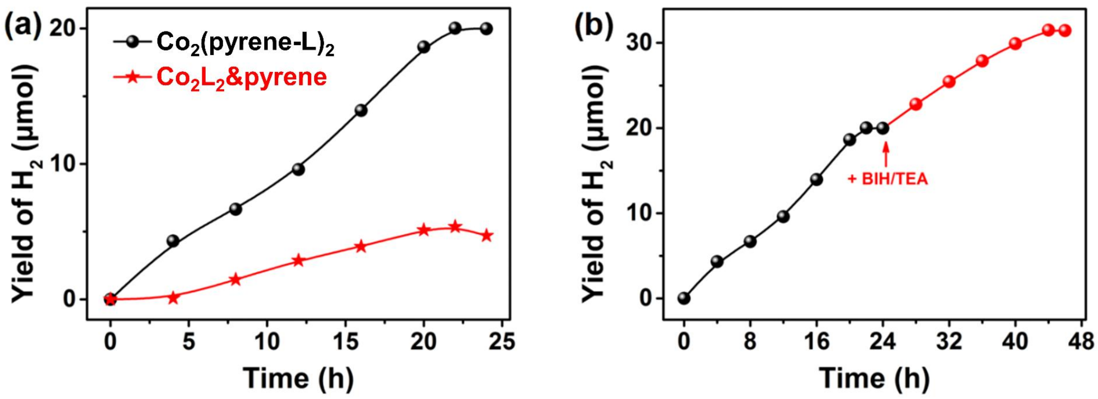


Fig. S13. (a) Photocatalytic H_2 evolution of Co_2(pyrene-L)$_2$ and Co_2L_2&pyrene. (b) Photocatalytic H_2 evolution of Co_2(pyrene-L)$_2$ by the addition of fresh BIH and TEA in 24 h.

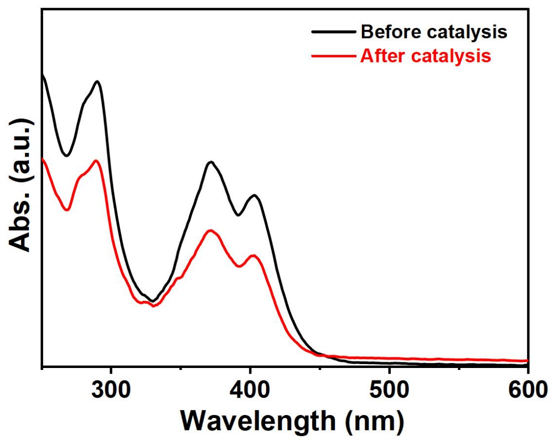


Fig. S14. UV-Vis spectra of Co_2(pyrene-L)$_2$ before and after catalysis.

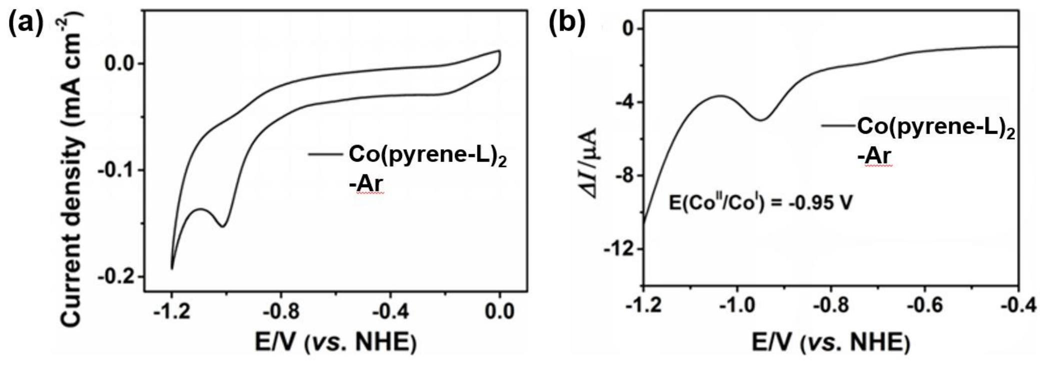


Fig. S15. (a) CV curves for 50 μM Co(pyrene-L)$_2$; (b) Differential pulse voltammetry (DPV).

Table S1. The summary of photocatalytic activity of Co_2(pyrene-L)$_2$ and corresponding catalysts.[a]

Samples	H_2 yield (μmol)
Co_2(pyrene-L)$_2$	10.32
Co(pyrene-L)$_2$	1.07
Co_2L_2&pyrene	3.15
Co_2L_2&[Ru(phen)$_3$](PF$_6$)$_2$	1.83

[a] Irradiation for 12 h, Ar atmosphere, 25 ºC, catalyst (30 μM), BIH (0.025 M), TEA (0.3 M), and 5 mL $CH_3CN/CH_3OH/H_2O$ (*v/v/v* = 3:1:1) solution.

Table S2. The summary of photocatalytic activity of Co_2(pyrene-L)$_2$ and corresponding catalysts.[a]

Sample	H_2 yield (μmol)
30 μM Co_2(pyrene-L)$_2$	10.32
30 μM Co_2L_2&600 μM pyrene	5.03

[a] Irradiation for 12 h, Ar atmosphere, 25 ºC, BIH (0.025 M), TEA (0.3 M), and 5 mL $CH_3CN/CH_3OH/H_2O$ (*v/v/v* = 3:1:1) solution.

Table S3. The summary of photocatalytic activity of Co_2(pyrene-L)$_2$ and corresponding catalysts.[a]

Sample	Concentration (μM)	H_2 yield (μmol)
Co(pyrene-L)$_2$	30	1.07
	60	2.36

[a] Irradiation for 12 h, Ar atmosphere, 25 ºC, BIH (0.025 M), TEA (0.3 M), and 5 mL $CH_3CN/CH_3OH/H_2O$ (*v/v/v* = 3:1:1) solution.

Table S4. The summary of self-photosensitizing metal complexes performance in photocatalytic hydrogen evolution.

Entry	Photocatalyst	Light Source	TON	Reference
1	$[RuPt]^{2+}$	$\lambda \geq 350$ nm	4.8 (10 h)	1
2	$[PtCl(terpy)]Cl\cdot 2H_2O$	550 nm $\geq \lambda \geq$ 350 nm	3 (7 h)	2
3	$[PtCl_2(4,4'\text{-MV2})]^{4+}$	$\lambda \geq 400$ nm	14 (12 h)	3
4	$[PtCl_2(4,4'\text{-MV4})]^{8+}$	$\lambda \geq 400$ nm	18 (12 h)	3
5	$[PtCl_2(5,5'\text{-MV4})]^{8+}$	$\lambda \geq 400$ nm	27 (12 h)	3
6	$[PtCl_2(4,4'\text{-MP1})]^{+}$	$\lambda \geq 400$ nm	2.7 (6 h)	3
7	$[PtCl_2(4,4'\text{-MP2})]^{2+}$	$\lambda \geq 400$ nm	3.2 (6 h)	3
8	$[PtCl_2(5,5'\text{-MP2})]^{2+}$	$\lambda \geq 400$ nm	3.8 (6 h)	3
9	$[PtCl(tpy)]^{+}$	800 nm > λ > 400 nm	0.1 (10 h)	4
10	$Pt_2(bpia)Cl_3$	800 nm > λ > 400 nm	93 (104 h)	4
11	Pt(bpca)Cl	800 nm > λ > 400 nm	1.1 (34 h)	4
12	$Rhz(dfpma)_3Cl_2(PPh_3)$	$\lambda > 338$ nm	130 (12 h)	5
13	*cis*-$[Rh_2(DPhF)_2(bncn)_2](BF_4)_2$	LED $\lambda = 670$ nm	170 (24 h)	6
14	$[Rh_2(DToIF)_2(L)(p)][BF_4]_2$	LED $\lambda = 655$ nm	23 (24 h)	7
15	*cis*-$[Rh_2(DTolF)_2(bpnp)(L)]^{2+}$	LED $\lambda = 670$ nm	16 (24 h)	8
16	CuAA	LED $\lambda = 450$ nm	6820 (20 d)	9
17	CuPP	LED $\lambda = 450$ nm	3738 (12 d)	9
18	CuAHA	LED $\lambda = 450$ nm	2240 (8 d)	9
19	$[HFe_2(pdt)(CO)_4(dppv)]^{+}$	$\lambda \geq 400$ nm	4 (4 h)	10
20	$Mn(bpy)(CO)_3Br$	Xe lamp	3400 (72 h)	11
21	$W(pyNHC)(CO)_4$	780 nm > λ > 380 nm	17.2 (3 h)	12
22	$Co_2(pyrene\text{-}L)_2$	$\lambda \geq 320$ nm	68.8 (12 h)	This work

Entries [1-15]: Noble-metal molecular photocatalysts for HER in the literatures.
Entries [16-21]: Noble-metal free molecular photocatalysts for HER in the literatures.

Table S5. The summary of photocatalytic performance.[a]

Photocatalytic condition.	**H_2 yield (μmol)**
Normal[a]	10.32
No Co_2(pyrene-L)$_2$	0
No Light	0
No BIH and TEA	0.06

[a] Irradiation for 12 h, Ar atmosphere, 25 ºC, BIH (0.025 M), TEA (0.3 M), and 5 mL $CH_3CN/CH_3OH/H_2O$ (*v/v/v* = 3:1:1) solution.

Table S6. Multi-exponential fitting parameters for the time-resolved PL decay traces in Fig. 3f after excitation at 375 nm.

Sample	**τ_1 (ns) (A_1)**	**τ_2 (ns) (A_2)**	**τ_3 (ns) (A_3)**	**τ_{ave} (ns)**
Co_2(pyrene-L)$_2$	0.062 (84.57%)	0.321 (14.84%)	2.000 (0.59%)	0.112
Co_2L_2&pyrene	16.000 (11.59%)	3.000 （17.39%）	13.000 （71.02%）	11.609

$A_1+A_2+A_3=1$; The calculation formula of average lifetime $\tau_{ave} = \Sigma\tau_i*A_i$.

References

[1] H. Ozawa, M.-a. Haga, K. Sakai, *J. Am. Chem. Soc.*, **2006**, 128, 4926–4927.

[2] R. Okazaki, S. Masaoka, K. Sakai, *Dalton Trans.*, **2009**, 6127–6133.

[3] K. Kitamoto, K. Sakai, *Angew. Chem. Int. Ed*., **2014**, 53, 4618–4622.

[4] T. Kunikubo, R. Castañeda, M. Murugesu, J. L. Brusso, K. Yamauchi, H. Ozawa, K. Sakai, *Angew. Chem. Int. Ed.*, **2025**, *64*, e202418884.

[5] A. F. Heyduk, D. G. Nocera, *Science*, **2001**, 293, 1639–1641.

[6] T. J. Whittemore, C. Xue, J. Huang, J. C. Gallucci, C. Turro, *Nat. Chem.*, **2020**, 12, 180–185.

[7] A. Millet, C. Xue, C. Turro, K. Dunbar, *Chem. Commun*., **2021**, 57, 2061–2064.

[8] M. T. Fortunato, C. E. Moore, C. Turro, *J. Am. Chem. Soc.*, **2023**, 145, 27348–27357.

[9] H. Yuan, M. Ming, S. Yang, K. Guo, B. Chen, L. Jiang, Z. Han, *J. Am. Chem. Soc.*, **2024**, 146, 31901–31907.

[10] W. Wang, T. B. Rauchfuss, *J. Am. Chem. Soc.*, **2012**, 134, 4525–4528.

[11] H. Shirley, S. Parkin, J. H. Delcamp, *Inorg. Chem.*, **2020**, 59, 11266−11272.

[12] A. J. Huckaba, H. Shirley, R. W. Lamb, S. Guertin, S. Autry, H. Cheema, K. Talukdar, T. Jones, J. W. Jurss, A. Dass, N. I. Hammer, R. H. Schmehl, C. E. Webster, J. H. Delcamp, *ACS Catal.*, **2018**, 8, 4838−4847.