

Supporting Information

Water Oxidation with a Noble Metal-Free Photoanode Modified with an Organic Dye and a Molecular Cobalt Catalyst

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Materials

All synthetic reactions were carried out under N₂ atmosphere with standard Schlenk techniques. According to standard methods, solvents were dried and purified prior to use. 4-(di-p-tolylamino)benzaldehyde (≥ 98%), bromotrimethylsilane (≥ 98.0%), diethyl cyanomethyl phosphonate (≥ 98%, GC), cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O, 99%) (≥ 99.0%), pyridine (≥ 99.0%) were purchased from Aladdin. 4-Pyridylacetonitrile hydrochloride (≥ 95.0%) were purchased from J&K chemical company. All other chemicals are commercially available. High purity water (18.2 MΩ·cm) supplied by a Milli-Q system (Millipore, Direct-Q 3 UV) was used in all experiments.

Characterization

¹H NMR spectra were collected at 298 K using a Bruker DRX-500 instrument. Electrospray ionization mass spectra were recorded on an LTQ Orbitrap XL Micromass spectrometer (Thermo Scientific, USA). Electrochemical measurements were taken with a CHI 760E electrochemical potentiator (Shanghai Chenhua, China). Photoluminescence spectra were analyzed with a Fluorolog FL-3-22 fluorometer from Horiba-Jobin-Yvon Ltd. equipped with a 450 W Xe lamp and two analyzing monochromators.

X-ray crystallography

Single-crystals of **D1** were obtained by slow diffusion of diethyl ether in **D1** DCM solutions. Intensities were collected on a Bruker SMART APEX CCD diffractometer with graphite monochromator Mo-Kα (λ = 0.71073 Å) using the SMART and SAINT programs. The structure was solved by direct methods and refined on F₂ by full-matrix least-squares methods with SHELXTL version 5.1.37. All non-hydrogen atoms were refined anisotropic ally. All hydrogen atoms were set geometrically and constrained to ride on their carrier atoms. The structure has been deposited to the CCDC with the deposition number 2027522. The detailed crystal data are given in Table S1.

Table S1. Crystallographic Data for **D1**

Compound	CCM-1
Empirical formula	C ₂₈ H ₂₃ N ₃
Formula weight	401.49 g/mol
Temperature	170 K
Crystal system	triclinic
Space group	P -1 (2)
Unit cell dimensions	a = 6.8605(3) Å; α = 92.836° b = 7.6642(3) Å; β = 93.632° c = 20.8113(8) Å; γ = 99.805°
Volume	1074.09(8) nm ³
Z	21
Density (calculated)	1.397 g/cm ³
Absorption coefficient	0.126 mm ⁻¹
F (000)	424
Crystal size	0.5 x 0.5 x 0.5 mm ³
Theta range for data collection	5.404 to 65.278
Index ranges	-9 ≤ h ≤ 10, -11 ≤ k ≤ 11, -30 ≤ l ≤ 28
Reflections collected	25370
Independent reflections	6792 [R _{int} = 0.0585, R _{sigma} = 0.0748]
Completeness to theta = 27.54°	99.5 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6792/0/127
Goodness-of-fit on F ²	1.091
Final R indices [I > 2σ(I)]	R ₁ = 0.1107, wR ₂ = 0.2745
R indices (all data)	R ₁ = 0.1788, wR ₂ = 0.3177
Largest diff. peak and hole	1.03/-0.70 e.Å

Emission spectral fitting procedure

Emission spectra of TiO₂|**D1** and TiO₂|**D2** were first converted to intensity units of quanta per second with the x-axis expressed as wavenumbers and then fit using a single-mode Franck-Condon analysis, equation S1

$$I(\tilde{\nu}) = \sum_{\nu=0}^{10} \left\{ \left(\frac{E_0 - \nu \hbar \omega}{E_0} \right)^3 (S^\nu) \times \exp \left[-4 \ln \left(\frac{2}{\Delta \tilde{\nu}_{0,1/2}} \right) \left(\frac{\tilde{\nu} - E_0 + \nu \hbar \omega}{\Delta \tilde{\nu}_{0,1/2}} \right)^2 \right] \right\} \quad (\text{Equation S1})$$

In this equation, $\hbar\omega$ is the quantum vibrational energy spacing of the single acceptor mode of medium frequency, the value of $\hbar\omega$ was obtained by previously described method.¹ S is the Huang-Rhys factor. The fitting was performed in MATLAB (version R2018a) with 11 vibrational levels included in the summation.

O₂ Measurements

Faradaic efficiencies (FE) for O₂ evolution were evaluated by the use of a previously described collector–generator (C-G) technique. The technique was carried out at room temperature by using a CHI 760E electrochemical analyzer, two working electrodes were positioned in parallel at a separation distance of 1 mm. At a constant bias of 0.6 V vs. NHE with illumination above 400 nm (100 mW cm⁻²) photoelectrochemical O₂ generation at the generator was monitored at a fluorine-doped tin oxide (FTO) collector cathode with a pre-established collection efficiency of 70%. The FE for O₂ formation was calculated from current–time plots by using equation S2. In this equation, Q_{Coll} is the integrated charge passed at the collector electrode and Q_{Gen} the total charge passed at the generator electrode.

$$FE(\%) = \frac{Q_{\text{Coll}}/Q_{\text{Gen}}}{70\%} \times 100\% \quad (\text{Equation S2})$$

Table S2. Time coefficients and relative amplitudes of TR-PL decay traces in Figure 2

Sample	τ_1 , ns	A_1	τ_2 , ns	A_2	τ_3 , ns	A_3	$\langle\tau\rangle_{av}^{a)}$, ns
Al ₂ O ₃ D1	0.13	0.66	0.59	0.28	2.4	0.06	0.39
TiO ₂ D1	0.01	0.71	0.11	0.27	0.48	0.04	0.056
Al ₂ O ₃ D2	0.16	0.60	0.64	0.37	2.0	0.04	0.40
TiO ₂ D2	0.02	0.92	0.13	0.08	0.75	0.01	0.04

a) The values of $\langle\tau\rangle_{av}$ were determined with $\langle\tau\rangle_{av} = A_1\tau_1 + A_2\tau_2 + A_3\tau_3$.

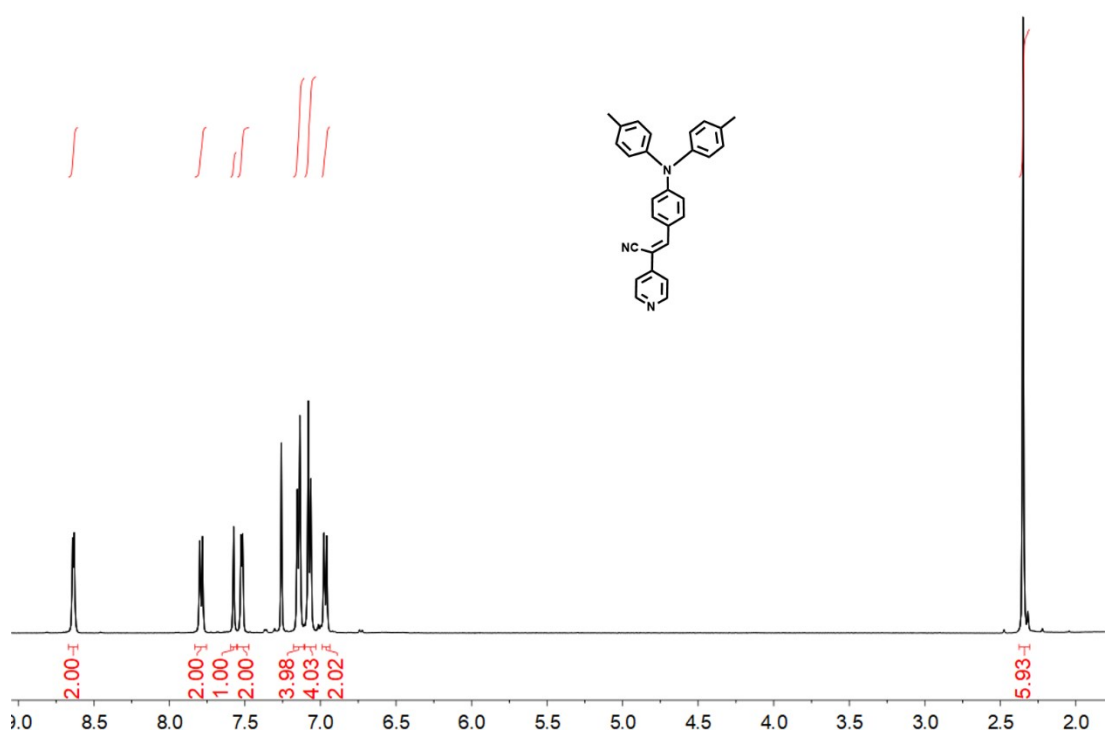


Fig.S1 ¹H NMR spectrum of complex **D1** in CDCl₃.

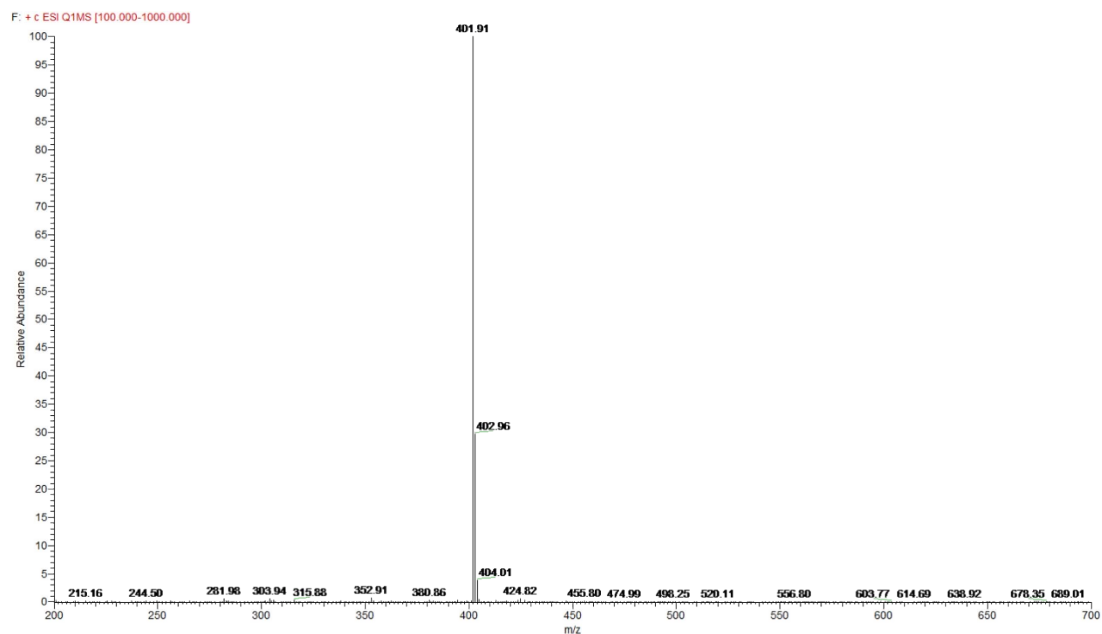


Fig. S2 ESI-MS spectrum of complex D1 in CH₃OH.

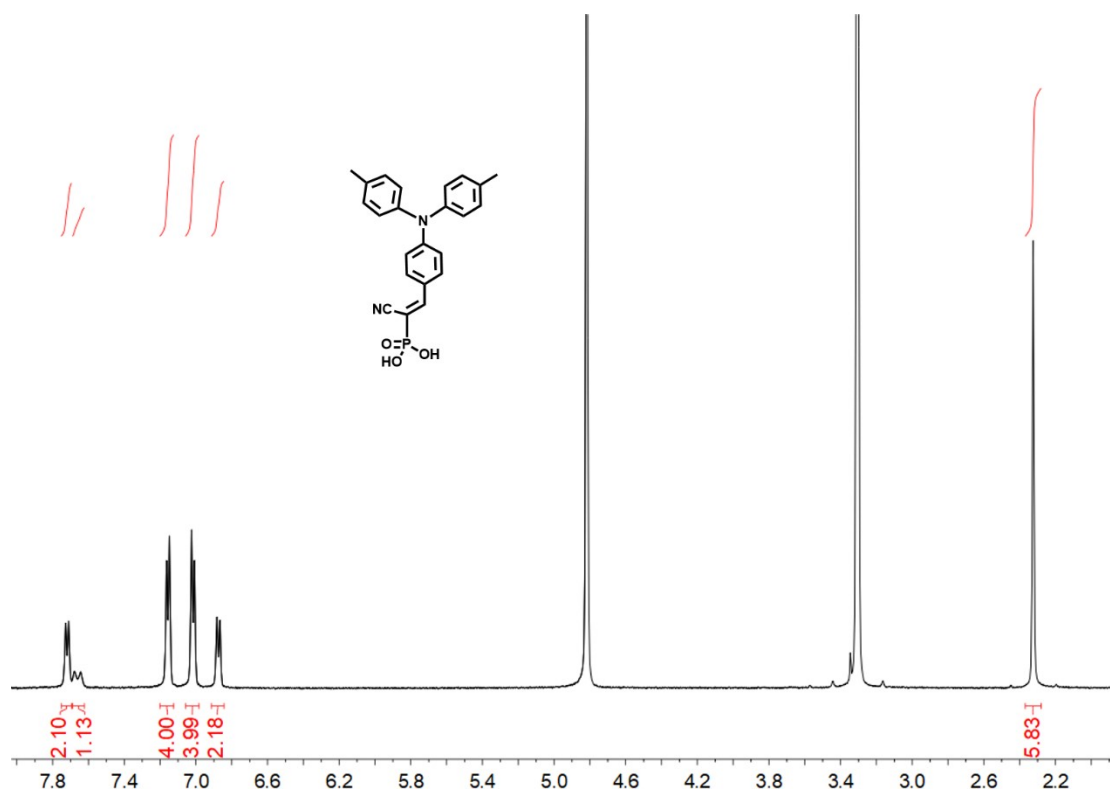


Fig. S3 ¹H NMR spectrum of complex D2 in CD₃OD.

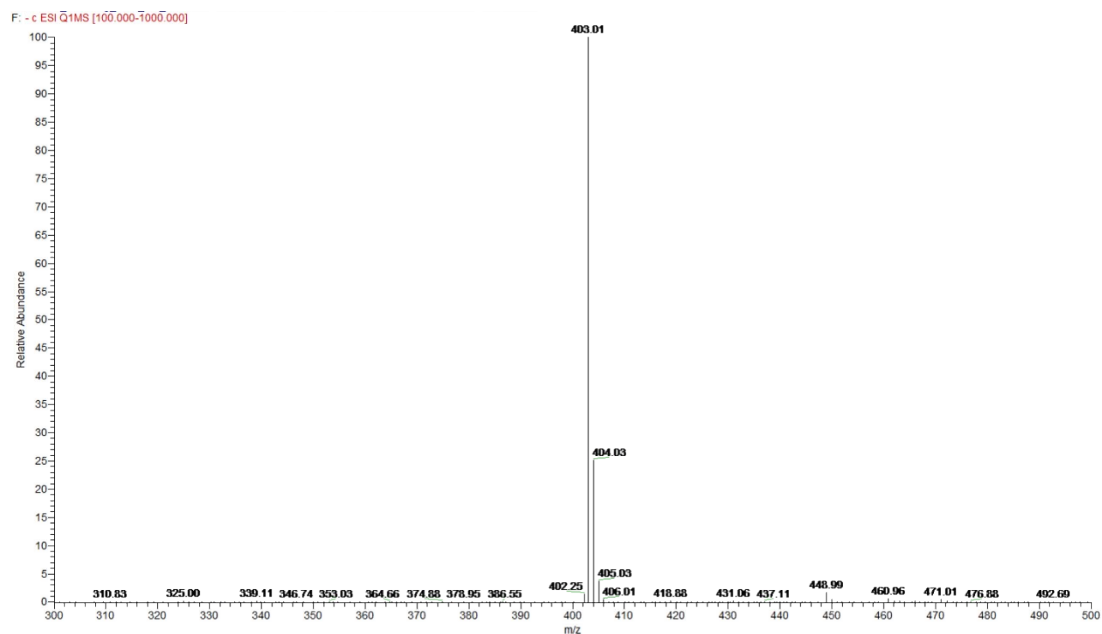


Fig S4 ESI-MS spectrum of complex **D2** in CH_3OH .

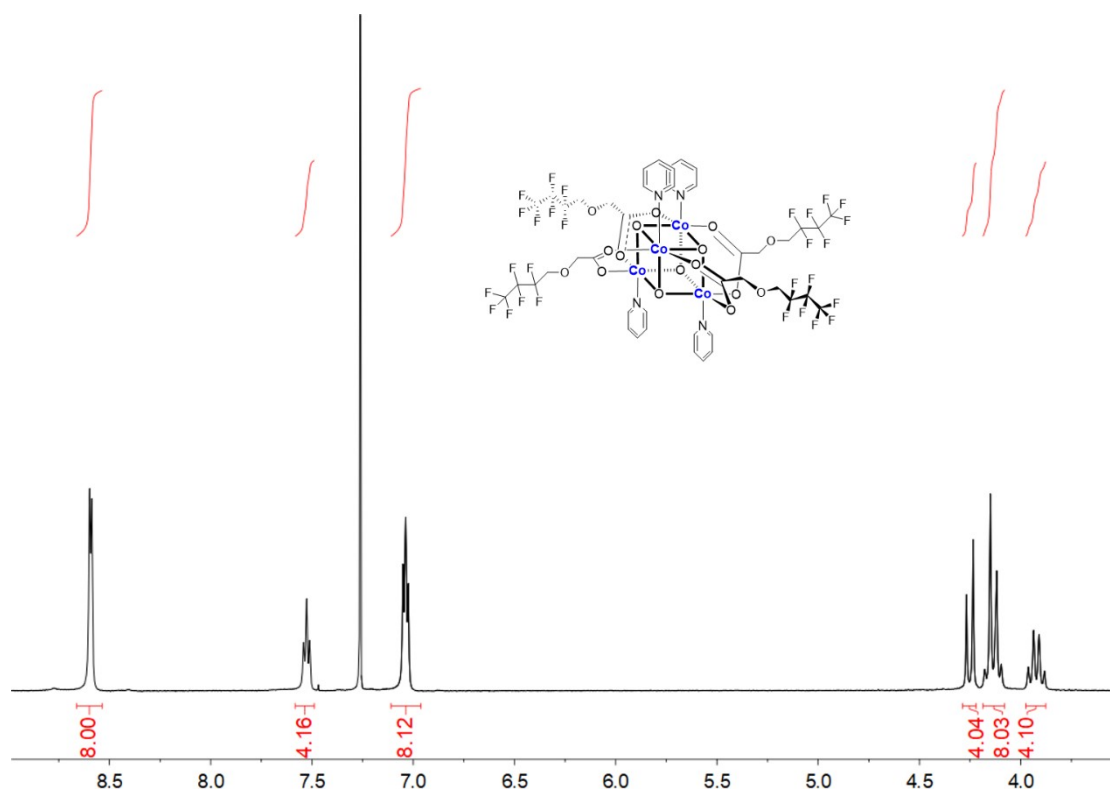


Fig S5 ^1H NMR spectrum of complex **CoF** in CDCl_3 .

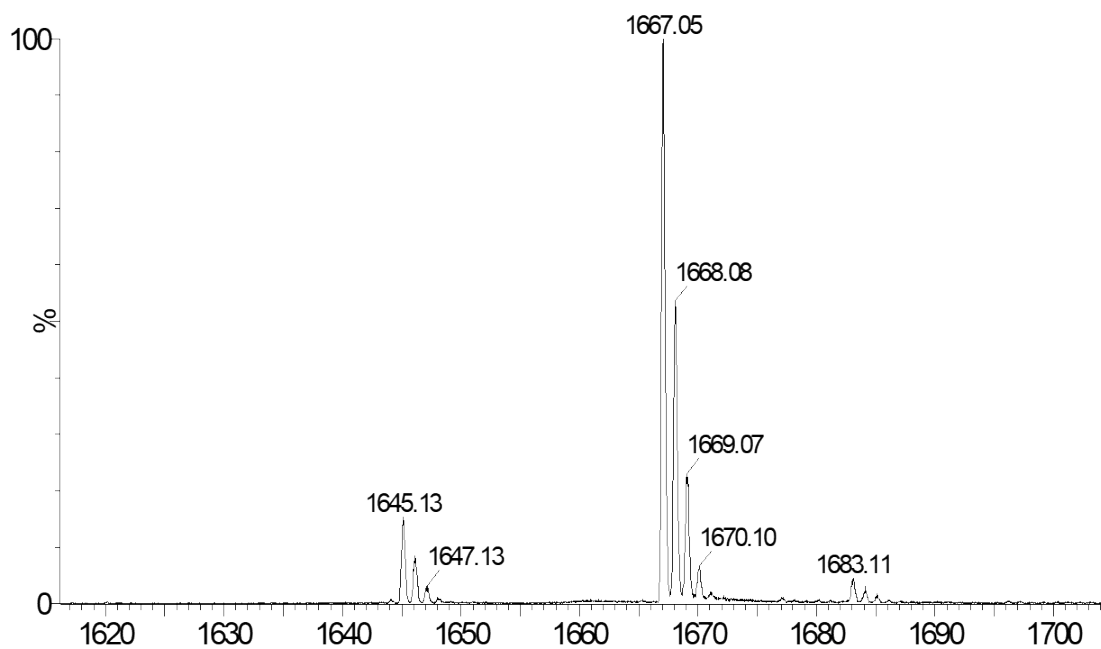


Fig. S6 ESI-MS spectrum of complex **CoF** in CH_3OH .

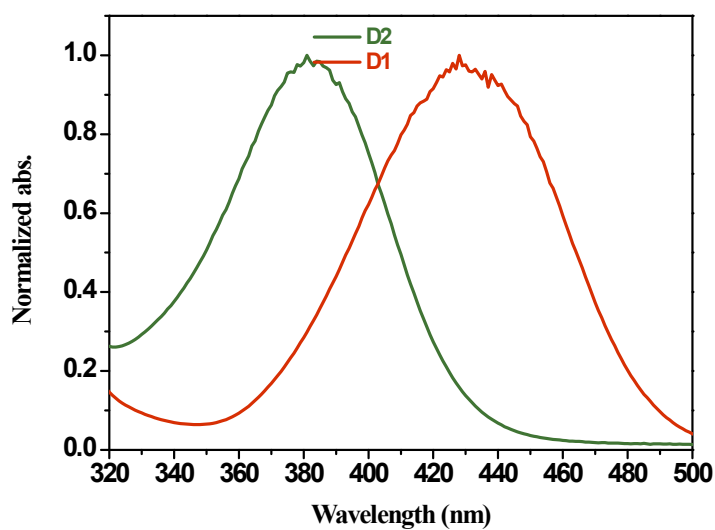


Fig. S7 Normalized UV-Vis absorption spectra for **D1** (red) and **D2** (green) in THF.

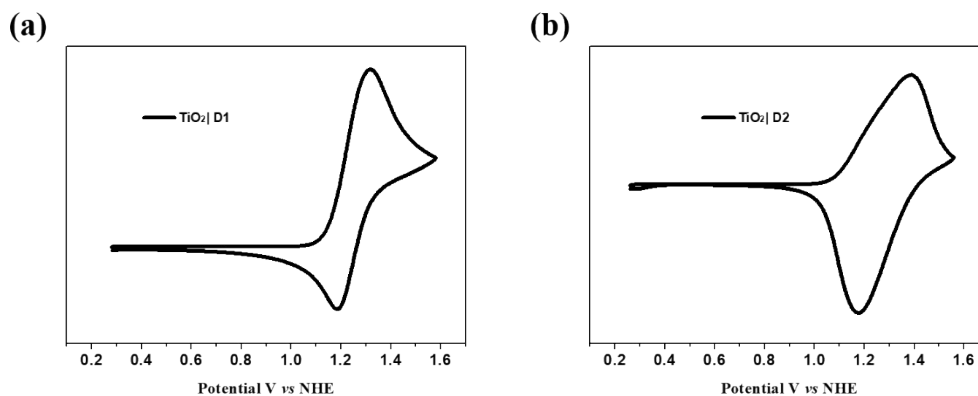
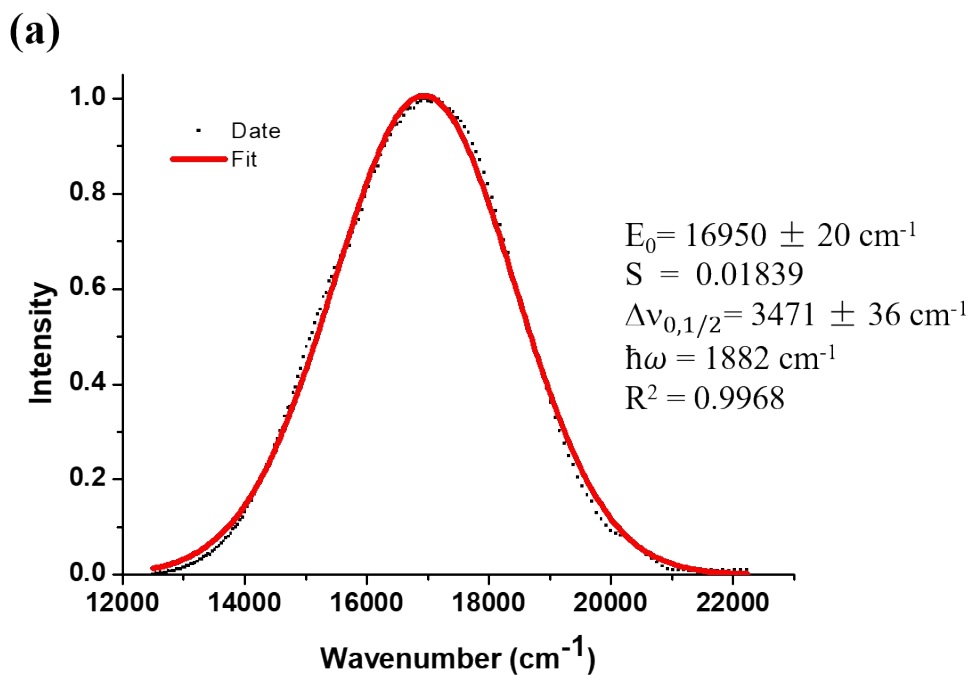


Fig. S8 Cyclic voltammograms for **D1** (a) and **D2** (b) on TiO₂ in acetonitrile with 0.1 M TBAPF₆ and a scan rate of 50 mV s⁻¹ (calibrated with Fc/Fc⁺ as an external reference and converted to NHE by addition of 0.63 V).



(b)

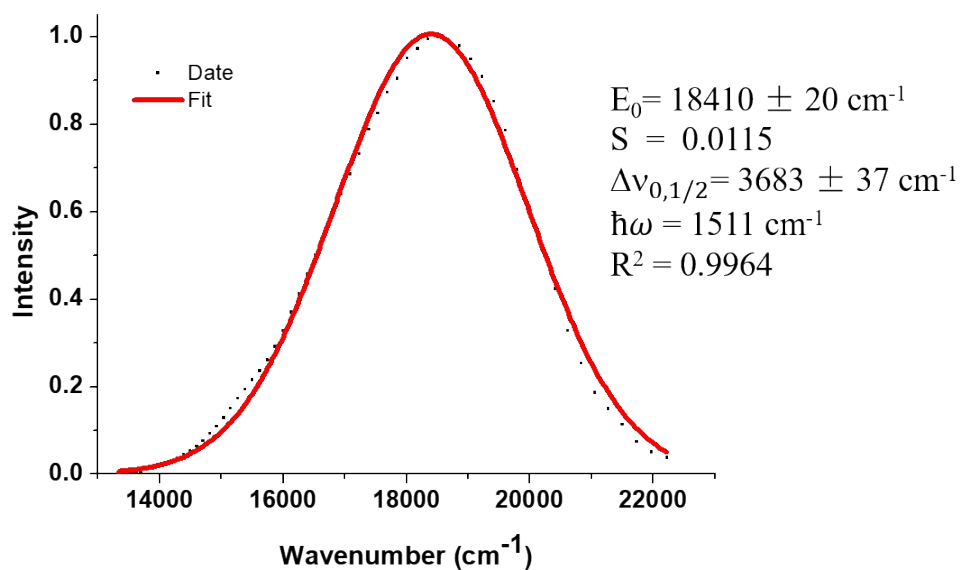


Fig. S9 Emission spectra of **D1** (a) and **D2** on TiO_2 (b) immersed in pH 7 phosphate buffer and fitting thereof.

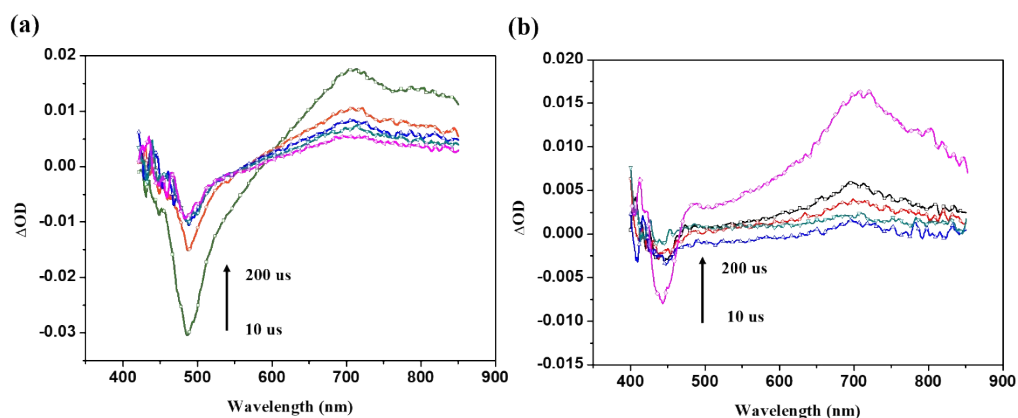


Fig. S10 Transient absorption difference spectra following 532 nm pulsed laser excitation of TiO_2 |**D1** (a) and **D2** (b) in pH 7 phosphate buffer from 10 to 200 μs .

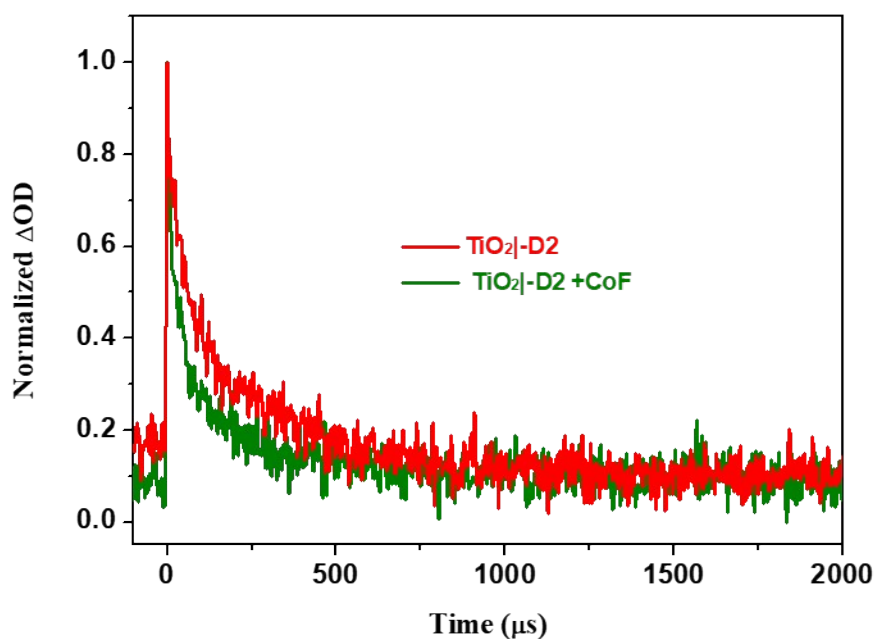


Fig.S11 Normalized transient absorption time traces at 700 nm comparing on TiO₂|D1 (red) and on TiO₂|D1 CoF (green), at a constant bias of 0.4 V vs. NHE immersed in pH 7 phosphate buffer.

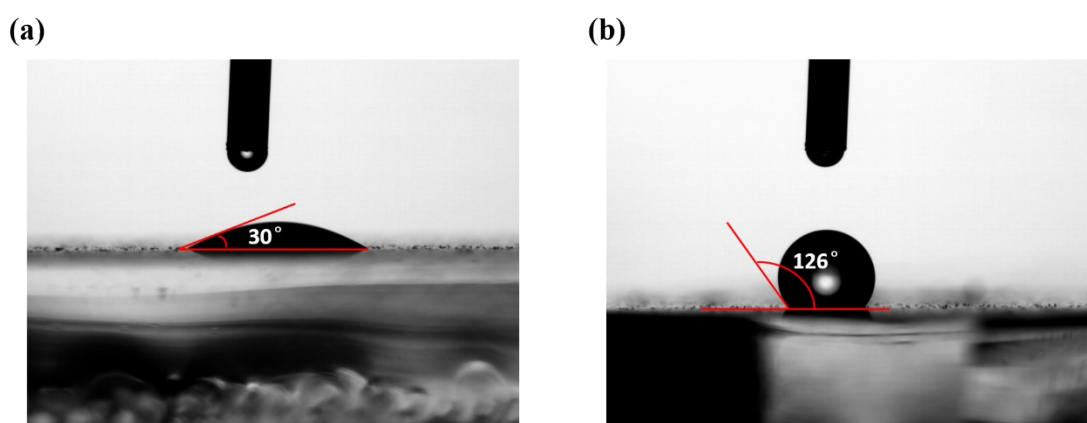


Fig.S12 Wettability of TiO₂|D1 surface (a); Wettability of TiO₂|D1 CoF surface (b).

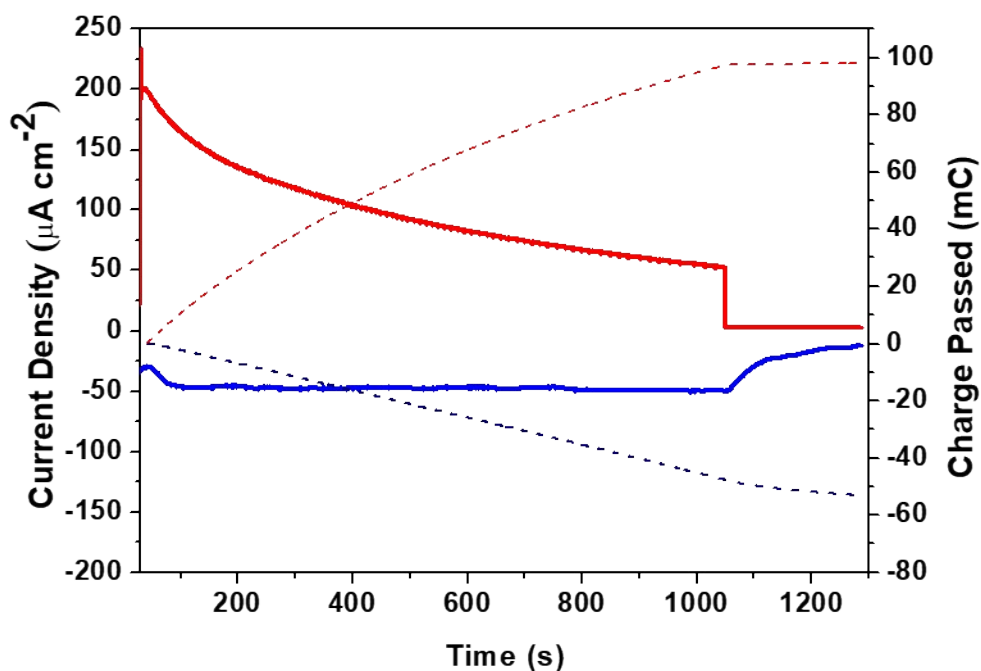


Fig.S13 Current density and charge passed from a collector–generator cell, TiO₂|D1 CoF, pH 7 phosphate buffer (0.1 M Na₂HPO₄/NaH₂PO₄, 0.4 M NaClO₄) under ~100mW cm⁻² white light (< 400nm) illumination for 1000 s with an applied bias of 0.6 V vs. NHE. The solid traces show photocurrents, and the dashed lines show the charge passed for the generator (red) and collector (blue) electrodes.

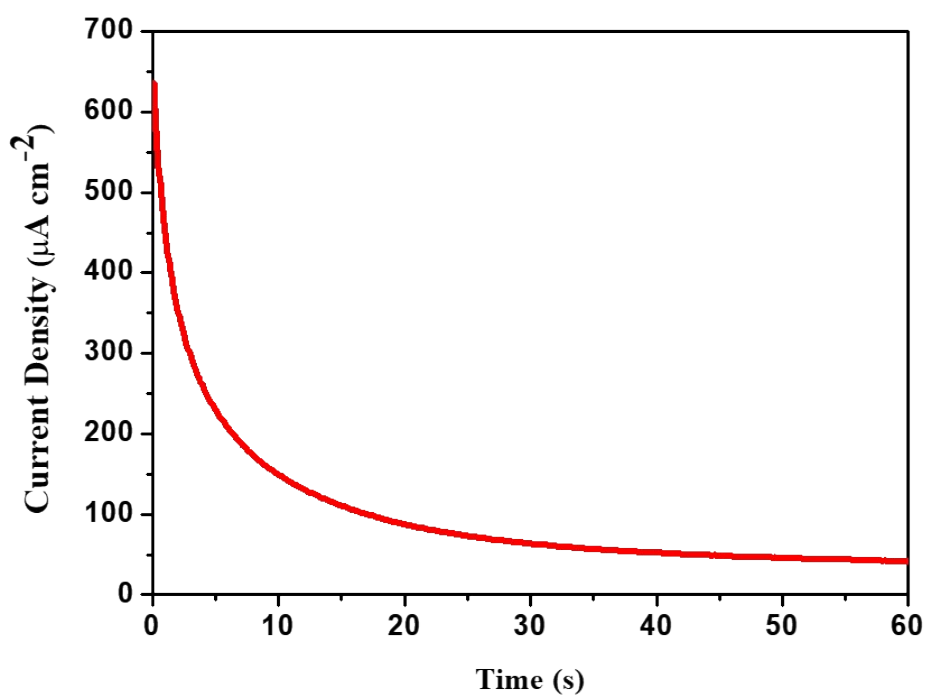


Fig. S14 Current density-time traces for TiO₂|RuP, CoF with illumination above 400 nm at 100 mW cm⁻² in a pH 7 0.1 M phosphate buffer containing 0.5 M NaClO₄ at a constant bias of 0.6 V vs. NHE.

The calculated structures

D1

C	-3.14810900	-1.23316300	-0.00384900
C	-2.88426100	-2.29456800	0.86564000
C	-3.69993200	-3.41945200	0.85857100
C	-4.80461400	-3.51140900	0.00835900
C	-5.06634300	-2.43462400	-0.84212200
C	-4.24863300	-1.31145200	-0.86003900
C	-2.96299000	1.20130200	-0.01605800
C	-2.53168900	2.20261700	-0.89010000
C	-3.16844100	3.43706200	-0.90192600
C	-4.25716900	3.70191200	-0.06700900
C	-4.68841300	2.68497300	0.78749300

C	-4.04910000	1.45165800	0.82479200
N	-2.32761100	-0.07161700	-0.00014500
C	-0.93456200	-0.17679700	-0.00756800
C	-0.13389400	0.84049300	0.54468900
C	1.24499000	0.74954000	0.53007800
C	1.89405500	-0.36630600	-0.03061400
C	1.08281700	-1.38648700	-0.55713100
C	-0.29671900	-1.30086400	-0.55946300
C	-5.67269000	-4.74291500	-0.00718600
C	-4.92745100	5.05131600	-0.07256400
C	3.33386200	-0.55735300	-0.09630300
C	4.36220000	0.29425600	0.13541200
C	5.78227200	-0.11928100	0.02029400
C	6.18121200	-1.44981400	0.18299500
C	7.52365200	-1.77546600	0.03164100
N	8.48188300	-0.89041100	-0.25102500
C	8.09813600	0.38029700	-0.38444700
C	6.78336300	0.81554400	-0.25752500
C	4.15138800	1.68050500	0.45026500
N	4.03417500	2.80763200	0.69276900
H	-2.03911400	-2.22934200	1.54393100
H	-3.48344200	-4.23662200	1.54152500
H	-5.92221100	-2.47889500	-1.51031800
H	-4.46105300	-0.48290700	-1.52831400
H	-1.69660000	2.00637800	-1.55538100
H	-2.82161400	4.20664100	-1.58630600
H	-5.53530500	2.86404400	1.44442400
H	-4.39113300	0.67105600	1.49704700
H	-0.60921600	1.70329000	0.99733300
H	1.81708600	1.54973600	0.98268200
H	1.55457000	-2.26223500	-0.99518800
H	-0.89113800	-2.09721600	-0.99222200
H	-5.67656100	-5.23655400	0.96756500
H	-6.70451800	-4.49660200	-0.26874200
H	-5.31046300	-5.46860300	-0.74294900
H	-4.90235700	5.50134100	-1.06804500
H	-5.97101400	4.97638900	0.24184800
H	-4.42418900	5.74106700	0.61299800
H	3.62843500	-1.55472300	-0.41753900
H	5.46944600	-2.22188200	0.45381000
H	7.84651200	-2.80649700	0.15638800
H	8.88501500	1.09705400	-0.60688800
H	6.54209800	1.86672200	-0.37678800

D2			
C	3.01847000	-1.18798300	-0.01930000
C	2.76319400	-2.23446500	-0.90633800
C	3.60563700	-3.34108500	-0.93802800
C	4.72711000	-3.42389700	-0.11202700
C	4.97832600	-2.36001500	0.76037000
C	4.13638000	-1.25823700	0.81692000
C	2.78337300	1.23988800	0.04033200
C	2.37194200	2.21070000	0.95692300
C	2.98782700	3.45572000	0.97394600
C	4.03585700	3.76024200	0.10137900
C	4.44830200	2.77273900	-0.79600500
C	3.82909700	1.52934900	-0.83777200
N	2.17121500	-0.04520800	0.02035200
C	0.78369500	-0.17937500	0.05967700
C	-0.05130500	0.84308000	-0.43322500
C	-1.42603600	0.71922900	-0.39255500
C	-2.03497600	-0.43365900	0.13857500
C	-1.19224200	-1.45035000	0.62114300
C	0.18407100	-1.33587600	0.59002200
C	5.64585100	-4.61767000	-0.15063000
C	4.68311400	5.12079200	0.11316000
C	-3.46465200	-0.65766800	0.22685300
C	-4.51439400	0.12351000	-0.13038900
P	-6.15913900	-0.52681600	0.16514700
O	-6.15928200	-1.84447700	0.82856500
O	-6.98198100	0.60284800	0.97425600
O	-6.81793500	-0.38871300	-1.28617900
C	-4.42264100	1.42780000	-0.70677800
N	-4.38454400	2.49042200	-1.16850700
H	1.90235200	-2.17712700	-1.56533000
H	3.39316000	-4.14981000	-1.63175800
H	5.84510700	-2.40111300	1.41495500
H	4.33837900	-0.44070400	1.50184700
H	1.56895300	1.98229100	1.65091800
H	2.65757500	4.20190100	1.69161500
H	5.26394400	2.98320700	-1.48244100
H	4.15560500	0.77114200	-1.54261300
H	0.39497100	1.73396900	-0.85978200
H	-2.02927600	1.52495400	-0.79307700
H	-1.63751300	-2.34731000	1.04315700
H	0.80641600	-2.13168200	0.98229200
H	5.32577100	-5.33894600	-0.90541200
H	6.67186000	-4.31784500	-0.38348800

H	5.66700500	-5.12915000	0.81648000
H	4.68115500	5.55104600	1.11761200
H	5.71749800	5.07021700	-0.23462700
H	4.14717800	5.81431800	-0.54315300
H	-3.75389100	-1.61794800	0.65387900
H	-7.03655000	0.37268500	1.91125500
H	-7.78173200	-0.46224200	-1.27310900

references

1 M. S. Eberhart, D. Wang, R. N. Sampaio, S. L. Marquard, B. Shan, M. K. Brennaman, G. J. Meyer, C. Dares and T. J. Meyer, *J. Am. Chem. Soc.*, 2017, 139, 16248–16255.