Photocatalytic water reduction from a noble-metal-free molecular dyad based on a thienyl-expanded BODIPY photosensitizer

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Electronic Supplementary Information (ESI)

[Detailed experimental, Table S1-S4 and Fig. S1-S9]

1. Experimental

Characterization

¹H and ¹³C NMR were obtained at room temperature using a Bruker Advance 300 or Bruker PLUS 400 spectrometer with tetramethylsilane (TMS, 0.00 ppm) as an internal standard and $CDCl_3$ as solvent. Chemical shift multiplicities are reported as s = singlet, d = doublet, and br =broad singlet. Coupling constants (J) values are given in Hz. Cyclic voltammetry experiments were carried out with a CHI 650E electrochemical analyzer using a three-electrode system at room temperature. The working electrode was 2 mm Pt with a Pt wire as auxiliary electrode and a 0.01M Ag/AgNO₃ solution reference electrode. All measurements were performed in freshly distilled and deoxygenated dichloromethane with a solute concentrate of ca. 1.0 mM in the presence of 0.1 M tetrabutylammonium hexafluorophosphate (TBAP) as a supporting electrolyte. C, H, and N microanalyses were carried out with a CE instruments EA 1110 analyzer. UV-vis spectra in solution were recorded on a UV-2100 (Shimadzu) spectrophotometer. Steady-state fluorescence spectroscopic studies in solution were performed on a Hitachi F-7000 spectrophotometer with a xenon arc lamp as light source. The slit width was set at 2.5 nm for excitation and 5.0 nm for emission. Fluorescence decay curves of the samples were measured with the time-correlated single-photon-counting (TCSPC) method on FLSP920 Lifespec-ps (Edinburgh) and the data were analyzed by Edinburgh software. The goodness of the fit of the decays as judged by reduced chi-squared (χ^2_R) and autocorrelation function *C*(j) of the residuals was below $\chi^2_R < 1.1$. The fluorescence decay time (τ) was obtained from the slope. Samples for absorption and emission measurements were contained in 1 cm \times 1 cm quartz cuvettes. Measurements were made using optically dilute solutions after deoxygenation by purging with dried N₂. Gas chromatograph/mass spectrometry (GC/MS) analysis was carried out on a GCMS-QP 2010 Plus instrument operated in the electron impact ionization mode. The temperature of ion source was maintained at 180 °C. The type of GC capillary column was Rtx-5MS (30 m \times 0.25 mm id, 0.25 μ m film thickness).

Synthetic Procedures

The syntheses of the unsubstituted BODIPY **1** and bis-iodo-BODIPY **2** were achieved following a reported procedure¹ and characterized by ¹H NMR, ¹³C NMR and elemental analyses to determine their structures. $[Co(dmgH)(dmgH)_2Cl_2]$ and $[Co^{III}(dmgH)_2(Py)Cl]$ were synthesized following literature procedures.^{2,3} The synthesis and characterization of **3**, **4** and **[4-Co]** are described:

2,6-Di(thiephene-2-yl)-4,4-difluoro-1,3,5,7-tetramethyl-8-(3-pyridyl)- 4-bora-3a,4a-diaza-s-indacene (3): To the solution of **2** (210.3 mg, 0.36 mmol) in mixed solvent of toluene (4 mL), ethanol (4 mL) and water (2 ml), thiophene-2-boronic acid (187.0 mg, 1.46 mmol) and Na₂CO₃ (376.1 mg, 3.55 mmol) were added. Then Pd(PPh₃)₄ (5.0 mg) was added under nitrogen atmosphere. The reaction mixture was refluxed for 8 h. After complete consumption of **2**, the solution was evaporated under reduced pressure. The crude product was purified by chromatography on a column packed with flash silica gel, using CH₂Cl₂-hexane (1:2, v/v) as eluent, from which the desired product **3** was obtained as red solid in 60 % yield. ¹H NMR (400 MHz, CDCl₃): δ (ppm)= 8.84 (d, J = 4.1 Hz, 1H), 8.69 (s, 1H), 7.86 (d, J = 7.6 Hz, 1H), 7.62 (dd, J = 7.3, 5.2 Hz, 1H), 7.39 (dd, J = 5.2, 1.0 Hz, 2H), 7.11 (dd, J = 5.1, 3.5 Hz, 2H), 6.89 (dd, J = 3.5, 5.5 Hz, 2

0.9 Hz, 2H), 2.64 (s, 6H), 1.40 (s, 6H). ¹³C NMR (400 MHz, CDCl₃): δ (ppm)=156.66, 148.79, 146.99, 140.08, 137.89, 136.72, 133.56, 132.30, 131.24, 128.03, 127.34, 126.36, 124.55, 13.69, 13.63. Anal. Cacld for C₂₆H₂₂BF₂N₃S₂: C, 63.81; H, 4.53; N, 8.59. Found: C, 63.90; H, 4.58; N, 8.52. UV-vis, λ_{max}/nm , (ϵ/L mol⁻¹ cm⁻¹), (CH₃CN): 390 nm (9223), 527 nm (53800).

2,6-Di(5-iodothiephene-2-yl)-4,4-difluoro-1,3,5,7-tetramethyl-8-(3-pyridyl)- 4-bora-3a,4a-diaza-s-indacene (4): To **3** (128.8 mg, 0.26 mmol) in 8 mL of EtOH was added NIS (257.4 mg, 1.04 mmol). This mixture was left stirring at room temperature for 24 h, washed with an aqueous solution of sodium carbonate, and extracted by CH₂Cl₂. Organic layers were combined, dried over Na₂SO₄, and evaporated to dryness under vacuum. Purification was performed by column chromatography on silica gel using CH₂Cl₂-petroleum ether (1:1, v/v) as eluent to obtain the desired product **4** as purple-red solid in 55% yield. ¹H NMR (500 MHz, CDCl₃): δ (ppm)= 8.82 (s, 1H), 8.64 (s, 1H), 7.75–7.68 (m, 1H), 7.56–7.50 (m, 1H), 7.25 (d, J = 3.7 Hz, 2H), 6.56 (d, J = 3.7 Hz, 2H), 2.61 (s, 6H), 1.39 (s, 6H). ¹³C NMR (500 MHz, CDCl₃): δ (ppm)= 156.24, 150.48, 148.30, 140.54, 140.04, 138.39, 137.29, 136.04, 131.39, 129.68, 126.25, 123.96, 73.74, 13.52. Anal. Cacld for C₂₆H₂₀BF₂I₂N₃S₂: C, 42.13; H, 2.72; N, 5.67. Found: C, 42.37; H, 2.80; N, 5.60. UV-vis, λ_{max}/nm , (ε /L mol⁻¹ cm⁻¹), (CH₃CN): 402 nm (10292), 530 nm (60800).

[{Co(dmgH)₂Cl}{2,6-Di(5-iodothiephene-2-yl)-4,4-difluoro-1,3,5,7-tetramethyl-8-(3-pyridyl)-4-bora-3a,4a-diaza-s-indacene}] ([4-Co]): To a stirred solution of Co(dmgH)(dmgH₂)Cl₂ (27.5 mg, 0.076 mmol) in anhydrous CH₃OH (5 mL) was added triethylamine (Et₃N, 10.6 uL, 0.076 mmol). The solution slowly turned into yellow-brown in color. 4 (37.42 mg, 0.05 mmol) in CH₂Cl₂ (3 mL) was then added. The reaction mixture was stirred for 3 h at room temperature. The formed microcrystalline purple precipitate was filtered off and washed with small amounts of ice cold CH₃OH until the filtrate had no residual fluorescence under UV illumination. After drying under high vacuum, a dark purple product was obtained (yield 56.3 mg, 90%). ¹H NMR (400 MHz, CDCl₃) δ 8.45 (d, *J* = 5.8 Hz, 1H), 8.34 (d, *J* = 1.6 Hz, 1H), 7.70 (dt, *J* = 7.8, 1.5 Hz, 1H), 7.50 – 7.43 (m, 1H), 7.26 – 7.24 (m, 2H), 6.55 – 6.54 (m, 2H), 2.58 (s, 6H), 2.38 (s, 12H), 1.02 (s, 6H). UV-vis, λ_{max}/nm , (ε /L mol⁻¹ cm⁻¹), (CH₃CN): 252 nm (63163), 409 nm (11312), 536 nm (56800).

General procedure for photocatalysis

Photocatalytic water splitting experiment was performed in a Pyrex top-irradiation reaction vessel connected to a glass closed gas circulation system (Labsolar-IIIAG photocatalytic system, Beijing Perfectlight Co., Ltd.). In a typical experiment, 1.2×10^{-4} M solutions of **[4-Co]** was prepared in a mixture of acetonitrile-water 4:1 (v/v), containing 0.38 M of triethanolamine (TEOA). The pH value of the solution was adjusted by addition of hydrochloric acid as required and measured on a DENVER UB-7 pH meter. The obtained reactant solution was put into a 250 mL Pyrex flat-bottomed reaction vessel and vigorously stirred in the dark for 0.5 h. The reaction system was evacuated three times with half an hour each time to remove air completely prior to light illumination. The reaction solution was irradiated using an external light source comprising a 300 W Xe arc lamp (MICROSOLAR 300, Beijing Perfectlight Co., Ltd.) with an optical filter employed to cut off light with wavelengths below 420 nm. During the water photochemical reaction, the reaction mixture was mixed using a magnetic stirring bar and the temperature of the reactant solution was maintained at room temperature by a flow of cooling water. The amount of H₂ gas produced in the reaction system was measured with a gas chromatograph (GC 7900, Shanghai Techcomp Instrument Ltd.) with a thermal conductivity detector (TCD), a 5 Å

molecular sieve column (4 mm(OD) × 3mm(ID) × 3m), and with N₂ as carrying gas. Each photocatalysis experiment was conducted three times with the reported µmol hydrogen being the average of the trials. The hydrogen dissolved in solution was neglected and the amounts of hydrogen were quantified by external standard method. Apparent quantum efficiency (AQE) of H₂ generation was calculated from the ratio of the number of reacted electrons during hydrogen evolution to the number of incident photons according to eq: AQE[%] = (number of reacted electrons/number of incident photos) × 100 = (2 × number of evolved H₂ molecules/number of incident photos) × 100. For the deuteration experiments, water is replaced by deuterium oxide, and quantitative gas mixture analysis was performed using MS.

Determination of pH values in mixed solvent systems

Any pH values reported in the manuscript correspond to the pH of the aqueous solution of the TEOA before mixing with CH₃CN, also known as *w* wpH. The pH of the mixed solvent can be measured directly to give a value for *s* wpH. A more accurate value of pH can be calculated for the solvent mixture (*s* spH) by a previously outlined procedure,⁴ where the conversion parameter $\delta = s$ wpH - *s* spH = -0.9. Thus, for the *w* wpH values of 8.5 and 7, the *s* wpH values obtained in 4:1 CH₃CN:H₂O were 8.3 and 6.9, respectively, corresponding to *s* spH values of 9.2 and 7.5, respectively.

Quantum chemical calculations

Theoretical calculations have been performed with the Gaussian 09 software package.⁵ Geometries were optimized under the DFT level of theory using the hybrid functional B3LYP, which combines Becke's 3-parameter exchange functional⁶ and Lee, Yang, and Parr's correlation functional.⁷ The polarizable continuum model (PCM)⁸ of acetonitrile was used in all calculations. **4** was optimized using the 6-31+G(d) basis set,⁹ for which $3-21G^{10}$ was used for iodine while the 6-31G(d) was used for the remaining atoms. All geometries were deemed minima, as no negative frequencies were found. TDDFT¹¹ using the optimized geometrical parameters and the same basis set was performed to compute the vertical transition energies. All molecular orbitals were visualized with the software *GaussView* 5.0.

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2. Table S1-Table S4

Table S1. Selected parameters for the vertical excitation (UV-vis absorptions) and the emission of **4**. Electronic excitation energies (eV) and oscillator strengths (*f*) configurations of the low-lying excited states of the compounds. The calculation of the $S_0 \rightarrow T_1/T_2$, $T_1 \rightarrow S_0$ energy gaps are based on the optimized ground state geometries (UV-vis absorption) and the optimized T_1 excited state geometries (phosphorescence emission). Calculated by DFT/TDDFT//B3LYP/6-31G(d)/LanL2DZ with Gaussian 09.

Compound		Electronic	TDDFT//B3LYP/6-31g(d)/LanL2DZ			
Compound		transitions ^a	Excitation energy	f^{b}	Composition ^c	CI ^d
4	Absorption ^e	с.т	1.40 ov (834 nm)	0.0000 H	H-2→L	-0.2523
		$S_0 \rightarrow I_1$	1.49 ev (834 mm) 0.0000 H→L	H→L	0.6660	
		C . T	2 38 ov (522 nm)	0 0000	H-2→L	0.5732
		$S_0 \rightarrow I_2$	2.38 eV (322 mm) 0.0000 H→L	0.2341		
	Emission ^f	$T_1 \rightarrow S_0$	1.19 ev (1042 nm)	0.0000	H→L	-0.6868

^{*a*} Only the selected low-lying excited states were presented. The numbers in parentheses are the excitation energy in wavelength. ^{*b*} Oscillator strength. No spin-orbital coupling was considered in the calculation thus the oscillators are zero. ^{*c*} H stands for HOMO and L stands for LUMO. Only the main configurations are presented. ^{*d*} Coefficient of the wavefunction for each excitation. The CI coefficients are in absolute values. ^{*e*} The calculation is based on the optimized ground state geometry. ^{*f*} The calculation is based on the optimized S₁ state geometry.

Table S2. Selected parameters for the vertical excitation (UV-vis absorptions) and the emission of **4**. Electronic excitation energies (eV) and oscillator strengths (*f*) configurations of the low-lying excited states of the compounds. The calculation of the $S_0 \rightarrow S_1/S_3$, $S_1 \rightarrow S_0$ energy gaps are based on the optimized ground state geometries (UV-vis absorption) and the optimized S_1 excited state geometries (fluorescence emission). Calculated by DFT/TDDFT//B3LYP/6-31G(d)/LanL2DZ with Gaussian 09.

Compound		Floctronic	TDDFT//B3LYP/6-31g(d)/LanL2DZ			Z
Compound		transitions ^a	Excitation energy	f ^b	Composition ^c	CI ^d
4	Absorption ^e	$S_0 \rightarrow S_1$	2.58 ev (480 nm)	0.4816	H-2→L H→L	0.3093 0.6330
		$S_0 \rightarrow S_3$	3.13 ev (397 nm)	0.5752	H-2→L H→L	0.6323 -0.3141
	Emission ^f	$S_1 \rightarrow S_0$	1.88 ev (659 nm)	0.2371	H→L	-0.6914

^{*a*} Only selected excited states were presented. The numbers in parentheses are the excitation energy in wavelength. ^{*b*} Oscillator strength. ^{*c*} H stands for HOMO and L stands for LUMO. Only the main configurations are presented. ^{*d*} Coefficient of the wavefunction for each excitation. The CI coefficients are in absolute values. ^{*e*} The calculation is based on the optimized ground state geometry. ^{*f*} The calculation is based on the optimized S₁ state geometry.

Compound	$E_{\rm ox}, V$	$E_{\rm red},{ m V}$	$\Delta G_1(eV)^b$	$\Delta G_2(eV)^c$
4	0.91, 1.43	-1.30, -1.43	0.43	-0.42
[4-Co]	0.57, 1.12	-0.85, -1.32	0.64	-0.57
[Co ^{III} (dmgH) ₂ (Py)Cl]	0.74	-1.01	-	-

Table S3 Summary of oxidation and reduction potentials from cyclic voltammograms^a

a) In deoxygenated acetonitrile. b) $\Delta G_1 = E(\mathbf{PS}^+/\mathbf{PS}) - E(\mathrm{Co}^{\mathrm{II}}/\mathrm{Co}^{\mathrm{II}}) - E(^3\mathbf{PS}^*), E(^{3*}\mathbf{PS}) = 1.49 \text{ eV}$ obtained from TDDFT calculations. c) $\Delta G_2 = E(\mathbf{PS}^+/\mathbf{PS}) - E(\mathrm{Co}^{\mathrm{II}}/\mathrm{Co}^{\mathrm{II}}).$

Table S4 The HOMO,	LUMO energy le	evels and chemical	hardness (n)) for 2 and 4
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	2-	(eV)	4 - (eV)		
	α electron	β electron	α electron	β electron	
$E_{ m LUMO}$	-2.09	-1.80	0.86	0.82	
$E_{ m HOMO}$	-3.07	-2.82	-0.75	-2.26	
$\eta = 1/2(E_{\text{LUMO}} - E_{\text{HOMO}})$	0.49	0.51	0.81	1.54	

3. Fig. S1-Fig. S9



Fig. S1 View of the molecular structure of **3**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths and bond angles: B1-N1 = 1.558(9) Å, B1-N2 = 1.549(9) Å, B1-F1 = 1.389(8) Å, B1-F2 = 1.383(8) Å, C22-N1 = 1.323(9) Å, C25-N2 = 1.341(9) Å, N1-C24 = 1.400(8) Å, N2-C26 = 1.413(8) Å; F1-B1-F2 = $108.9(6)^{\circ}$, N1-B1-N2 = $107.6(5)^{\circ}$, N1-B1-F1 = $108.6(6)^{\circ}$, N1-B1-F2 = $110.6(6)^{\circ}$, N2-B1-F1 = $109.7(6)^{\circ}$, N2-B1-F2 = $111.5(6)^{\circ}$. Other data can be obtained from The Cambridge Crystallographic Data Centre *via* CCDC number 1400078.

(a)



Fig. S2 Normalized absorbance and emission spectra of **3** (a) and **4** (b). $c = 1.0 \times 10^{-5}$ M in CH₃CN, at room temperature.



Fig. S3 Rationalization of the absorption-emission and the large stokes shift of **4**. The frontier molecular orbitals (MOs) involved in the vertical excitation (i.e. UV-vis absorption, the left column), the fluorescence emission (the middle column) and the phosphorescence emission (the right column) of **4**. The vertical excitation related calculations are based on the optimized ground state geometry (S₀ state), the emission related calculations were based on the optimized excited state geometry (S₁ and T₁ state). Note the energy levels of the HOMO and LUMO at S₁ state and T₁ state are different from that at the S₀ state (which indicates geometry relaxation). CT stands for conformation transformation. Excitation and radiative process are marked as solid lines and the non-radiative processes are marked by dashed lines. Calculated by DFT/TDDFT//B3LYP/6-31G(d)/LanL2DZ with Gaussian 09.



Fig. S4 Absorbance spectra of **[4-Co]**. $c = 1.0 \times 10^{-5}$ M in CH₃CN, at room temperature.



Fig. S5 Emission spectra of systems containing (a) **4** + [Co^{III}(dmgH)₂(Py)CI]; and (b) **4** + TEOA.



Fig. S6 Frontier molecular molecular orbitals of **4**⁻⁻ obtained through DFT calculations (UB3LYP), since the anion dye has an unpaired electron. The alpha/beta molecular orbitals were all defined due to the negative charge the open-shell system adopted.



(b)



Fig. S7 Fluorescence decay histograms of 3 (a) and 4 (b).



Fig. S8 (a) ¹H NMR and (b) ¹³C NMR spectrum of 3.



Fig. S9 (a) 1 H NMR and (b) 13 C NMR spectrum of 4.