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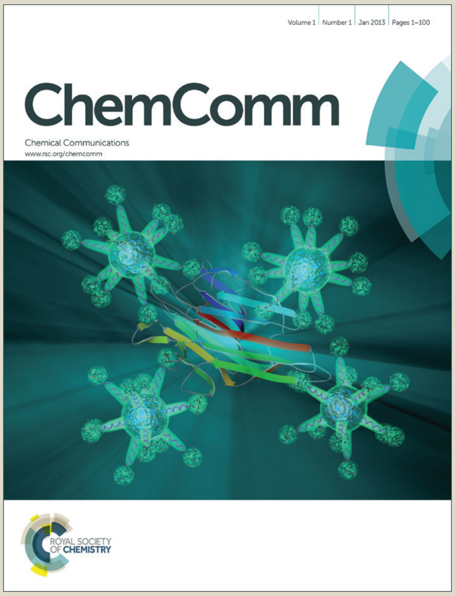

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Photocatalytic water reduction from a noble-metal-free molecular dyad based on a thienyl-expanded BODIPY photosensitizer†

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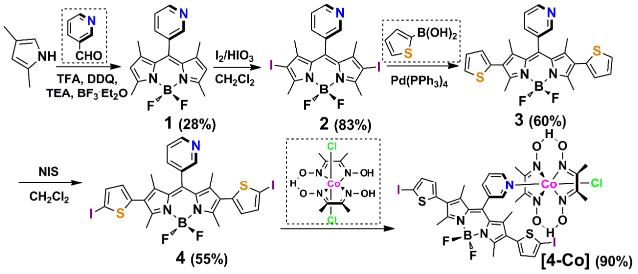
A noble-metal-free molecular dyad was constructed by anchoring a thienyl-expanded BODIPY photosensitizer (PS) to a cobaloxime catalyst, which gives a 2.5 fold increase in the TON, and a 3 fold enhancement in the quantum efficiency as compared to the multicomponent catalytic system for the geneation of hydrogen *via* the reduction of water. The stability of PS was expected to improve by introducing thienyl moiety into the BODIPY core.

Sunlight-driven water splitting into its constituent elements, is a very attractive sustainable approach to produce the fuel H_2 as a carbon-neutral and renewable energy carrier for the future.[1] Since the late 1970s, considerable effort has been devoted to the development of multicomponent homogeneous molecular systems for photodriven hydrogen production that contain a photosensitizer (PS), which absorbs the energy of light, a water reduction catalyst (WRC), and a sacrificial electron donor (SED) coupled or not to an electron mediator.[2] However, these multicomponent systems still need to be improved because many interfacial interactions could affect the intermolecular electron transfer reactions. In contrast with such multicomponent systems, more recently various single-component photocatalysts have been constructed by covalently or coordinately linking a PS and a WRC, which would improve the efficiency of the catalysis by facilitate the intramolecular electron transfer from the PS to the WRC. These include Ru-Pt complexes,[3] Ru-Pd complexes,[4] Ru-Rh complexes[5] and Ir-Co complexes.[6] However, in these systems, the components of PS and WRC are still relied on expensive and unsustainable noble-metal complexes. Absolutely noble-metal-free single-component photocatalysts for H_2 evolution with relatively effective turnover numbers (TONs) are scarcely reported.[7]

In 2014, single-component and multicomponent photocatalytic systems comprising 2,6-dihalogenated boron dipyrromethene (BODIPY) PSs and a cobaloxime WRC have been reported in succession.[8] These halogenated BODIPY compounds are effective PSs for solar H_2 production because of their high molar absorptivity, high intersystem crossing (ISC) efficiency and simple synthesis.[8c] Nevertheless, H_2 production in these systems stalls after 4-5 h Xe light irradiation due to the formation of unstable $PS^{\bullet -}$ radical anions during the course of the reactions, and the durability of PSs needs to be improved. In efforts to develop completely noble-metal-free and robust single-component photocatalysts based on more stable BODIPY chromospheres, we had the idea to attach thienyl moiety to the BODIPY core for this purpose in view of its lower electron delocalization energy barrier in dye-sensitized solar cells (DSSCs).[9] In this context, we describe herein a non-noble metallic PS-WRC molecular dyad [**4-Co**] by directly anchoring a thienyl-substituted BODIPY to a cobaloxime catalyst, which shows more robust for solar-driven water reduction than ever reported absolutely noble-metal-free single-component photocatalysts. The photocatalytic performance of [**4-Co**] was clearly improved as compared to that of the mixture of **4** and cobaloxime components.



Scheme 1 Synthetic procedures for thienyl-substituted BODIPY **4** and noble-metal-free molecular dyad **[4-Co]**.

The synthetic route for the preparation of thienyl-expanded BODIPYs is shown in Scheme 1 (the details are provided in ESI†). Compounds **1**-**2** were available from a previous study.[8b] **3** is obtained *via* Suzuki cross coupling reaction, and **4** was obtained in yield 55% *via* an iodination reaction of **3** with N-iodosuccinimide (NIS). The new compounds **3** and **4** were characterized on the basis of their ^1H and ^{13}C NMR spectra and elemental analyses. The structure of **3** was also elucidated by X-ray crystallography (Fig. S1, ESI†). In the crystal structure of **3**, the BODIPY moiety exhibits the expected planar arrangement of the dipyrrin group and nearly tetrahedral geometry about the boron atom. The *meso*-pyridyl group is nearly orthogonal to the indacene plane with a dihedral angle of 89.03°. The perpendicular configuration between *meso*-pyridyl moiety and BODIPY core may facilitate a desirable intramolecular electron transfer from the PS to the WRC unit upon pyridyl group coordinated to the cobaloxime catalyst. The average torsion angle between the indacene plane and thiophene ring is ~51.4°, indicating the presence of limited π-conjugation.

The UV-vis absorption and emission spectra of these PSs (**1**-**4**) are summarized in Table 1 and Fig. S2 (ESI†). The incorporation of thienyl moiety for **3** causes a moderate bathochromic shift of *ca*. 26 nm relative to the parent BODIPY **1** (λ_{max} = 501 nm), which is due to the limited π-conjugation between the BODIPY core and the thienyl moiety. A slight red-shift of ~3 nm is observed when two iodine atoms are added to form **4** to further enhance the rate of ISC.

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† Electronic Supplementary Information (ESI) available: Detailed experimental, Table S1-S4 and Fig. S1-S9. see DOI:10.1039/b000000x.

The emission spectra showing the typical small Stokes shift (10-17 nm) were observed for the unsubstituted BODIPY **1** and bis-iodo-BODIPY **2**. However, much larger Stokes shift of 95 nm and 106 nm were observed for **3** and **4** with the thienyl moieties at 2,6-position of the BODIPY core. The origin of large Stokes shift for the thienyl-substituted BODIPY **4** was rationalized by the concept of the increased geometry relaxation upon photoexcitation, which was supported by theoretical calculations (see the details in Table S1-S2 and Fig. S3, ESI†).

Table 1 Absorption and emission data in CH_3CN at room temperature

compd	absorption	emission		
	λ_{max}, nm (ε, M^{-1} cm^{-1})	λ_{max}, nm	Φ_F[a]	τ_F, ns
1	366 (4547), 475 (16696), 501 (78200)	511	0.75	3.10
2	390 (8711), 507 (20262), 534 (58800)	551	0.01	*b*
3	397 (9223), 527 (53800)	622	0.10	1.45
4	402 (10292), 530 (60800)	636	0.05	1.25
[4-Co]	252 (63163), 409(11312), 536 (56800)	645	–	1.20

[a] Corrected emission spectra were used with 1,3,5,7-tetramethyl-8-phenyl-BODIPY as a standard (Φ_{fl} = 0.72 in tetrahydrofuran). [b] Not determined.

The molecular dyad [**4-Co**] was synthesized in good yield (90%) from **4** and the cobaloxime precursor [Co(dmgH)$(dmgH)_2Cl_2$] in the presence of triethylamine (Et_3N). The absorption spectrum of [**4-Co**] corresponds to the superposition of those of the components in their respective proportions (Fig. S4, ESI†). This superposition confirms that the PS and catalytic centers are largely electronically uncoupled, and indicates the molecular dyad consisting of the nonconjugated bridge BODIPY moiety will maintain the desired photophysical and catalytic properties of each unit.

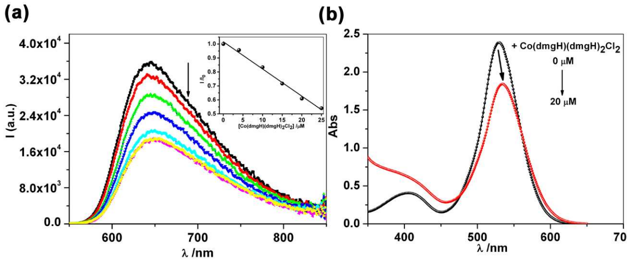

Fig. 1 (a) Fluorescence spectra of **4** in deoxygenated Et_3N/CH_3CN solution in the absence and presence of increasing amounts of [Co(dmgH)$(dmgH)_2Cl_2$]. λ_{ex} = 527 nm, [**4**] = 10 μM, [Co(dmgH)$(dmgH)_2Cl_2$] = 0-25 μM. T = 298 K. Inset: the corresponding Stern–Volmer plot of I_o/I *versus* concentration of [Co(dmgH)$(dmgH)_2Cl_2$]. (b) UV-vis absorption spectra.

When titrated with [Co(dmgH)$(dmgH)_2Cl_2$] in the Et_3N/CH_3CN solution, the emission intensity of **4** was gradually decreased (Fig. 1a). Due to the fact that [Co(dmgH)$(dmgH)_2Cl_2$] does not possess any distinct visible light absorption to overlap the excitation or emission of **4**, which excludes energy transfer process responsible for the reduced fluorescence intensity. To verify the quenching mechanism, the UV-vis absorption spectra were studied. The changes in the absorbance spectra for **4** + [Co(dmgH)$(dmgH)_2Cl_2$] indicate a strong probability of static quenching responsible for the process (Fig. 1b). The lifetime of **4** remained almost unchanged in response to the presence of [Co(dmgH)$(dmgH)_2Cl_2$], further suggesting that the quenching process operated through the static mechanism. On the basis of the Stern-Volmer plot, the observed association constant (K_A) and quenching rate constant (k_q), calculated by the equation: $I_0/I = 1+ K_A[Q] = 1 + k_q\tau_0[Q]$ ([Q] taken as the concentration of the [Co(dmgH)$(dmgH)_2Cl_2$]), was to be 1.1 × 10^4 M^{-1} and 9 × 10^{13} M^{-1} s^{-1}. The value of K_A ensures a moderate amount of complex formation. The k_q is apparently more than 3 orders of magnitude higher than the diffusion-controlled limit under these conditions, ruling out diffusional quenching mechanism (2 × 10^{10} M^{-1} s^{-1}). Overall, the data is well represented by the static quenching model, suggesting that quenching in this system can be attributed to the formation of a ground-state complex [**4-Co**] between the PS **4** and quencher.

Since the thermodynamic analysis based on the redox potentials of [**4-Co**] and **4** shows that intra- and intermolecular electron transfer processes from the reduced $PS^{\bullet-}$ species to the centre of cobalts are energetically feasible (Table S3 of ESI†), we set out to evaluate the activities of the molecular dyad [**4-Co**] and the intermolecular system of **4** with $[Co^{III}(dmgH)_2(Py)Cl]$ for H_2 generation. Photocatalytic H_2 evolution catalyzed by [**4-Co**] was first carried out with triethanolamine (TEOA) as the SED at 298 K using a Xe lamp (300 W) with a cutoff filter (λ > 420 nm). The H_2 yield strongly depends on initial system pH and the concentration of photocatalyst. The pH conditions were selected based on those used for hydrogen photogeneration in previous reports,[8] which have been optimized for the BODIPY PSs. Fig. 2a shows the amount of H_2 produced as a function of the irradiation time for [**4-Co**] at two different pH values of the solution (pH = 7 and 8.5).[10] Reproducible values within ±5% were obtained in repeated experiments. It was found that activity for H_2 evolution increased with the increase of the pH value from 7 to 8.5. After 10 h of irradiation, TON up to ~73 (~880 μmol) was obtained for [**4-Co**] at pH = 8.5. Control experiments suggested that absence of either [**4-Co**] or TEOA yielded an unobservable amount of H_2. The formation of Co colloids as possible catalytically active species in the course of the photocatalysis was ruled out on the basis of mercury-poisoning experiments. Hydrogen production increased almost linearly with the photocatalyst [**4-Co**] in the concentration range of 1.5 × 10^{-5} – 1.2× 10^{-4} M in the presence of TEOA at pH 8.5 (Fig. 2b). This result clearly indicates that, in this range of concentrations, H_2 production is not limited by diffusion, and that efficient intramolecular electron transfer takes place.

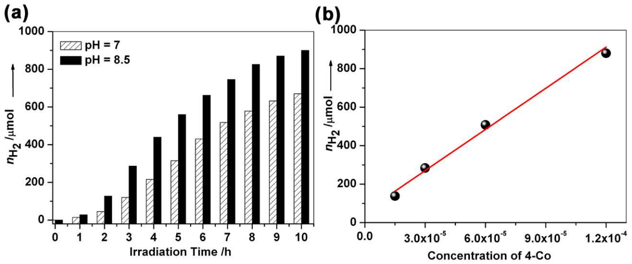

Fig. 2 (a) Photocatalytic hydrogen generation upon Xe irradiation (λ > 420 nm) at two different pH values for the one-component system [**4-Co**] (0.12 mM) in CH_3CN/H_2O (4:1, v/v) in the presence of TEOA (5%, v/v). (b) Photocatalytic hydrogen production as a function of the concentration of [**4-Co**].

To make a comparison of intra- and intermolecular catalytic systems, a three-component system was assembled in a solution of acetonitrile/water (4:1, v/v) containing **4** (0.12 mM), $[Co^{III}(dmgH)_2(Py)Cl]$ (0.12 mM), and TEOA (0.38 M) at a pH value lower than the pK_a of TEOA (pH = 8.5). As shown in Fig. 3a, hydrogen production is observed only after a longer induction period of 2 h with the initial hydrogen production rate and TON (~27/10 h) being considerably slower and lower than when [**4-Co]** was used as both PS and H_2-generating catalyst under the same conditions. Apparent quantum efficiency (AQE) for these H_2-evolving systems at 420 nm can be calculated by AQE = $2\Delta(H_2)/\Delta(hv)$ where $\Delta(H_2)$ is the H_2 generation rate, and the factor of 2 accounts for the requirement of two electrons per H_2 molecule. The AQE of 0.94% is obtained for the three-component system, and the AQE reaches 2.89% when using [**4-Co**] as H_2-generating system. These observations indicate that the attachment of thienyl-substituted BODIPY to the catalyst in [**4-Co**] offers a strong benefit in H_2 generation when compared to that of the separate **4** and cobaloxime components. The intramolecular electron transfer efficiency from PS to the catalyst could improve quantum yields of catalyst reduction compared to those obtained *via* diffusion-limited intermolecular electron transfer in the three-component systems.

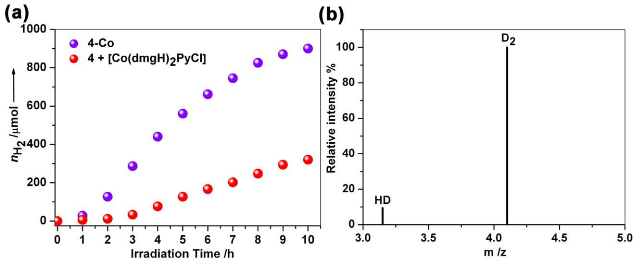

Fig. 3 (a) Comparison of the H_2-evolving efficiencies of single-component [**4-Co**] (0.12 mM) and multicomponent system with **4** (0.12 mM) and [$Co^{III}(dmgH)_2(Py)Cl$] (0.12 mM) in CH_3CN/H_2O (v/v = 4/1) solution in the presence of TEOA (0.38 M) at pH 8.5. (b) Mass spectrometry analysis of the headspace from reaction containing CH_3CN/D_2O (v/v = 4/1) at pH 8.5 utilizing 0.12 mM [**4-Co**] and 0.38 M TEOA.

To ensure that the source of liberated hydrogen is water, experiments with deuterated water (D_2O) in place of water were carried out. When D_2O was used, formation of D_2 was detected in the GC/MS (Fig. 3b). The large deuterium incorporation into the gaseous hydrogen products provides strong evidence that molecular H_2 is indeed derived from water in this photocatalytic composition. Thus, the origin of H_2 is believed to be aqueous protons since D_2 constituted the product when D_2O was substituted for H_2O.

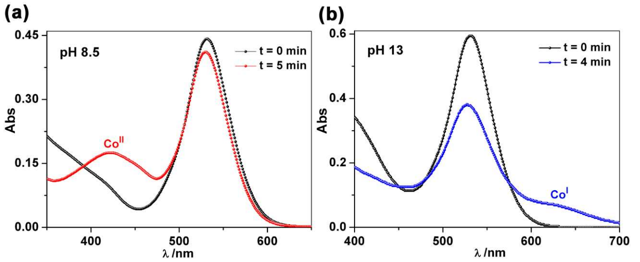

Fig. 4 Time-dependent UV-vis spectra at pH 8.5 (a) and pH 13 (b) before and after irradiation of degassed solution (4:1 acetonitrile-water) containing **4** (1.0×10^{-5} M), [$Co^{III}(dmgH)_2(Py)Cl$] (1.0×10^{-4} M) and TEOA (1.0×10^{-3} M).

To shed light on the photochemical H_2 evolution by the system composed of **4** + [$Co^{III}(dmgH)_2(Py)Cl$] + TEOA, the time-resolved UV-vis absorption spectra for it were acquired at both pH 8.5 and 13 before and after irradiation with visible (λ > 420 nm) (Fig. 4). Before irradiation, the absorption spectra are simply the sums of the individual components. After 5 min of irradiation at pH 8.5 under H_2 producing conditions, peak at λ = ~430 nm corresponding to the Co^{II} species begins to appear in the UV-vis spectrum.[11] When the same experiment is conducted at pH 13, where H_2 formation is greatly suppressed, a new lower energy absorption is observed within 4 min at ~625 nm, which may be assigned to the accumulation of a Co^{I} species.[11] In addition, the intensity of **4** absorption band at pH 13 visibly decreases, implying decomposition of the PS **4** at basic pH is more easily. Addition of 10 equivalents of [$Co^{III}(dmgH)_2(Py)Cl$] or TEOA into a solution of **4** in CH_3CN-H_2O (4:1, v/v) at pH 8.5 results in no appreciable fluorescence quenching (Fig. S5, ESI†), indicating that the singlet excited state of **4** does not take part in the electron transfer reaction due to its short lifetime (τ_F = 1.25 ns in CH_3CN). These results are consistent with what was observed in previous homogeneous photocatalytic hydrogen-generating systems, which showed that a reaction pathway involving reductive electron transfer occurs *via* the triplet excited state of PS.[12]

The duration of the hydrogen-generating systems with **4** as PS (>10 h) can be prolonged compared to the previous systems with PS **2** (4-5 h) under the same conditions.[8b] The stability of the present compositions appears to correlate to the ability for PS$^{\bullet-}$ to electron transfer to the catalyst prior to its decomposition in addition to instabilities related to the catalyst. To better elucidate the relative stability of the radical anion PS$^{\bullet-}$, molecular orbital calculations were performed at the density functional theory (DFT) level for **4**$^{\bullet-}$ and **2**$^{\bullet-}$, respectively. The results of some physicochemical properties such as HOMO, LUMO energies and chemical hardness (η) are listed in Table S4 of ESI†. η is useful to rationalize the relative stability and reactivity of chemical species.[13] Computed value of η increases in the sequence **2**$^{\bullet-}$ < **4**$^{\bullet-}$, indicating that **4**$^{\bullet-}$ appears to be more stable than **2**$^{\bullet-}$. Furthermore, computed frontier molecular orbitals (FMOs) of **4**$^{\bullet-}$ are spread over both the BODIPY core and thienyl moieties as compared to **2**$^{\bullet-}$ (Fig. S6, ESI†), suggesting the π-conjugation between the thienyl moiety and the BODIPY core also makes **4**$^{\bullet-}$ more stable.

In summary, a noble-metal-free molecular dyad [**4-Co**], has been developed as an efficient photocatalyst for photoinduced H_2 generation. The molecular dyad shows higher H_2 generation efficiency than the corresponding multicomponent counterpart with the identical component concentrations. The stability of PS was improved by introducing thienyl moiety into BODIPY core. To our knowledge, the longevity of [**4-Co**] for H_2 evolution (> 10 h) under the irradiation of Xe lamp is the most robust system reported for completely noble-metal-free supramolecular photocatalysts.[7,14]

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Graphical Abstract

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