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A homogeneous molecular system for the photogeneration of hydrogen from water based on a $[Ru^{II}(bpy)_3]^{2+}$ photosensitizer and a phthalycyanine cobalt catalyst

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ABSTRACT

In this contribution, we report an efficient homogeneous system for the visible light-driven H_2 production from aqueous protons. This comprises a macrocyclic phthalycyanine cobalt complex $[Co^{II}Pc(-2)]$ as a hydrogen-evolving catalyst (HEC), $[Ru^{II}(bpy)_3]Cl_2$ (bpy = 2,2′-bipyridine) as a photosensitizer (PS) and triethylamine (TEA) as a sacrificial electron donor (SED). The system gives up to 2400 TON versus the catalyst with an initial TOF as high as 680 TON h^{-1}. Phthalocyanine cobalt and its derivatives are a promising new direction for molecular catalysts readily accessible in a large scale and low-cost achieving the photogeneration of H_2.

Solar light-driven water splitting into molecular dihydrogen (H_2) is one of the most promising scenarios for sustainable energy supply. An efficient photocatalytic molecular system for proton reduction to H_2 generally combined a light-absorbing photosensitizer (PS), a hydrogen-evolving catalyst (HEC) and a sacrificial electron donor (SED) [1]. The development of highly efficient, inexpensive noble-metal-free molecular HECs for the reduction of protons to hydrogen is a prerequisite, but faces many difficult challenges [2]. So far, many macrocyclic cobalt complexes have been explored in the context of photocatalytic H_2 evolution as mechanistic models and functional catalysts, with cobaloximes playing by far the main role in the field [3].

Recently, as one of important cobalt macrocycles, porphyrin cobalt was used as a homogeneous HEC for the photoreduction of water to H_2 in the presence of $[Ru^{II}(bpy)_3]Cl_2$ (bpy = 2,2′-bipyridine) as the PS and ascorbic acid (AA) as the SED, achieving TON (versus the catalyst) up to 725 [4]. The system, however, is limited by its poor stability due to the depletion of the catalyst, which does not exceed 3 h. We are curious to know whether phthalocyanine cobalt structurally related to porphyrin cobalt also catalyzes photogeneration of H_2. Our considerations are highly emboldened from the earlier reports that phthalocyanine cobalt functioned as electrocatalysts for proton reduction [5].

As part of our efforts to construct and examine systems containing noble-metal-free components [6], in this contribution, we report that a phthalycyanine cobalt ($[Co^{II}Pc(-2)]$) can serve as a novel low-cost and efficient visible light-driven catalyst in an artificial photocatalytic system for H_2 evolution in combination with $[Ru^{II}(bpy)_3]Cl_2$ as the PS and triethylamine (TEA) as the SED (Scheme 1). The system gives up to 2400 TON (TON = amount of produced hydrogen/amount of catalyst) with respect to the HEC phthalocyanine cobalt with an initial TOF as high as 680 TON h^{-1}.

In most of previous systems using $[Ru^{II}(bpy)_3]Cl_2$ as the PS for the photogeneration of H_2, ascorbic acid (AA) was often employed as the SED [4,7]. However, when the HEC $[Co^{II}Pc(-2)]$ was initially paired with $[Ru^{II}(bpy)_3]Cl_2$ as the PS and AA as the SED, no hydrogen was detected by GC analysis after 10 h of irradiation with a pH range of 2.0–7.0. Despite the negative results regarding H_2 generation, the reports that phthalocyanine cobalt complexes exhibited efficiently electrocatalytic proton reduction encourage us

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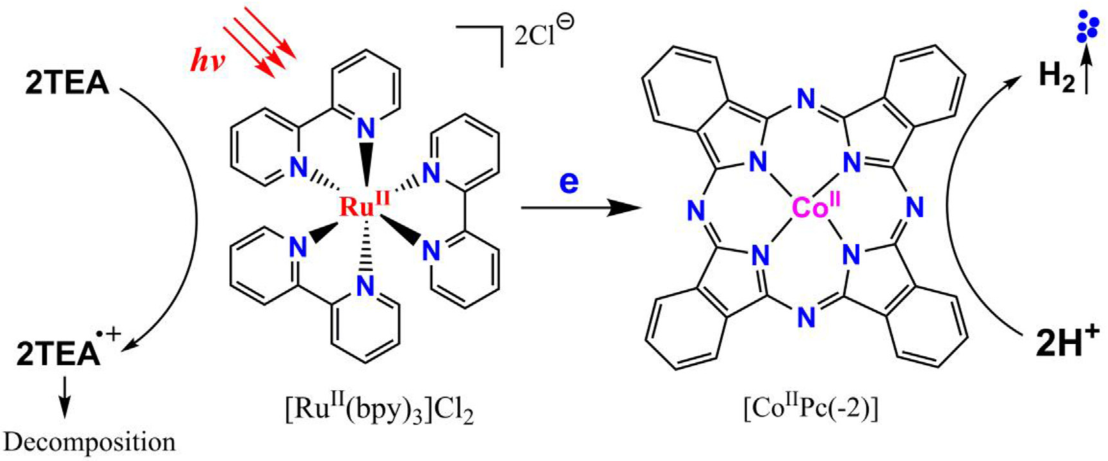
to explore the system in the basic solutions by employment of different SED components. Triethanolamine (TEOA) and triethylamine (TEA) are two kinds of SEDs that have been previously utilized in the basic solutions for the photocatalytic water reduction systems [2]. We evaluated the use of these two SEDs, and the kinetic traces in Fig. 1a show the aliphatic amine TEA gives a two-fold increase in total hydrogen production compared to TEOA. Thus, all subsequent studies were conducted using TEA as the SED. It should be noteworthy that when employing TEA as the SED, the net reaction being driven photochemically can be expressed by the equation (*Eq. 1*: $NEt_3 + H_2O \rightarrow H_2 + HNEt_2 + CH_3CHO$). Thermochemical data indicate that the overall reaction is a thermodynamically unfavorable reaction and must be driven by light energy [8].

The influence of solvents on the H_2-evolving reaction was explored with the system of $[Co^{II}Pc(-2)]$ (2×10^{-5} M), $[Ru^{II}(bpy)_3]Cl_2$ (2×10^{-4} M) and TEA (0.36 M) at pH 9.0 within 10 h of visible-light irradiation ($\lambda > 420$ nm). It is well known that solvents have an apparent influence on the photoinduced H_2 production [6,9]. As shown in Fig. 1b, when the mixture of CH_3CH_2OH/H_2O (4:1, v/v) was used as solvent, more than 300 μmol H_2 was produced, corresponding to 150 TON with respect to the catalyst. In contrast, 130 and 80 TON were obtained, respectively, in the mixed solvents of CH_3OH/H_2O (4:1) and CH_3CN/H_2O (4:1), while DMF/H_2O (4:1) or THF/H_2O (4:1) resulted in no hydrogen production. The solvent dependence for hydrogen production probably may be ascribed to many factors including solvent polarity, stabilization of reduction intermediates and Co(II/I) reduction potential necessary for hydrogen generation [6a,9].

The pH value significantly affected the interaction of PS and HEC, the state of PS and TEA, and the subsequent driving force for photocatalytic H_2 evolution in the photocatalytic system. The $[Ru^{II}(bpy)_3]Cl_2/[Co^{II}Pc(-2)]$/TEA photocatalytic system functioned between pH 8.0 and pH 11.0, with a maximum catalytic activity at pH 10.0 (Fig. S1, in the Supporting Information). It sharply decreased in a more acidic or more basic medium. The great decrease in TONs at lower pH values was probably because of the protonation of TEA, which resulted in poor electron-donating ability. In higher pH values, the decreased concentrations of proton will lead to a deceleration of efficiency of photogenerated hydrogen. Control experiments showed that the absence of PS or TEA led to no significant H_2 production. However, weak H_2 production was observed from solutions containing only the PS $[Ru^{II}(bpy)_3]Cl_2$, which is in agreement with previous observations [10]. The amount of H_2 only produced from $[Ru^{II}(bpy)_3]Cl_2$, which cannot be neglected, was subtracted from the total H_2 produced, to calculate the corrected TON.

An induction period with no detectable H_2 evolution in the first half an hour from the reaction profile is observed. Generally, the appearance of induction phase may be ascribed to the formation of Co^I species or cobalt colloids produced from the photodecomposition of molecular Co catalysts. Consequently, mercury-poisoning experiments are carried out to determine if colloidal cobalt is possibly formed and responsible the activity of H_2 evolution. The addition of a large excess of mercury has no significant effect on the catalytic activity of $[Co^{II}Pc(-2)]$ (Fig. S2, in the Supporting Information), excluding the formation of metal colloids during the photocatalytic reaction. Experiments with D_2O in place of water while keeping other conditions identical are conducted. The large deuterium incorporation into the gaseous hydrogen products provides strong evidence that the only hydrogen source in the produced hydrogen gas is water (Fig. S3, in the Supporting Information).

To investigate the catalytic activity of the complex $[Co^{II}Pc(-2)]$, we studied the effect of the relative concentration of $[Co^{II}Pc(-2)]$ and $[Ru^{II}(bpy)_3]Cl_2$ on the H_2 production. The catalyst is most active at low concentrations, and hydrogen evolution is observed using $[Co^{II}Pc(-2)]$ as low as 2×10^{-6} M. Fig. 2a shows the effect of varying catalyst concentration on the rate and overall yield of hydrogen generation under continuous irradiation. Increasing the concentration of $[Co^{II}Pc(-2)]$ increases the overall rate of H_2 generation and the total amount of hydrogen evolved for the system. The initial rates for hydrogen evolution are obtained from the linear portion of each curve and indicate a first order dependence on catalyst concentration for this system. When the catalyst concentration is fixed at 2×10^{-6} M and the PS $[Ru^{II}(bpy)_3]Cl_2$ concentration increases from 2×10^{-4} to 6×10^{-4} M, TON_{cat} between 1300 and 2400 are obtained, corresponding to a TOF_{cat} of 310 and 680 h^{-1}, respectively (Fig. 2b). The apparent quantum efficiency of the H_2-evolving system at 420 nm can be calculated to be 4.20% [11]. In the previous report, porphyrin cobalt was used as molecular photocatalyst to reduce protons into H_2 in the presence of $[Ru^{II}(bpy)_3]Cl_2$ (bpy = 2,2′-bipyridine) as the PS and ascorbic acid (AA) as the SED. Though the system achieves TON (versus the catalyst) up to 725, the catalytic activity quickly decomposes after only 2 h of irradiation [4]. For comparison, the longevity of the hydrogen-generating system with the complex phthalycyanine cobalt can be increased. Furthermore, re-addition of the same quantity of fresh HEC



Scheme 1. Photocatalytic H_2-production system using $[Co^{II}Pc(-2)]$ as HEC, $[Ru^{II}(bpy)_3]Cl_2$ as PS and TEA as SED.

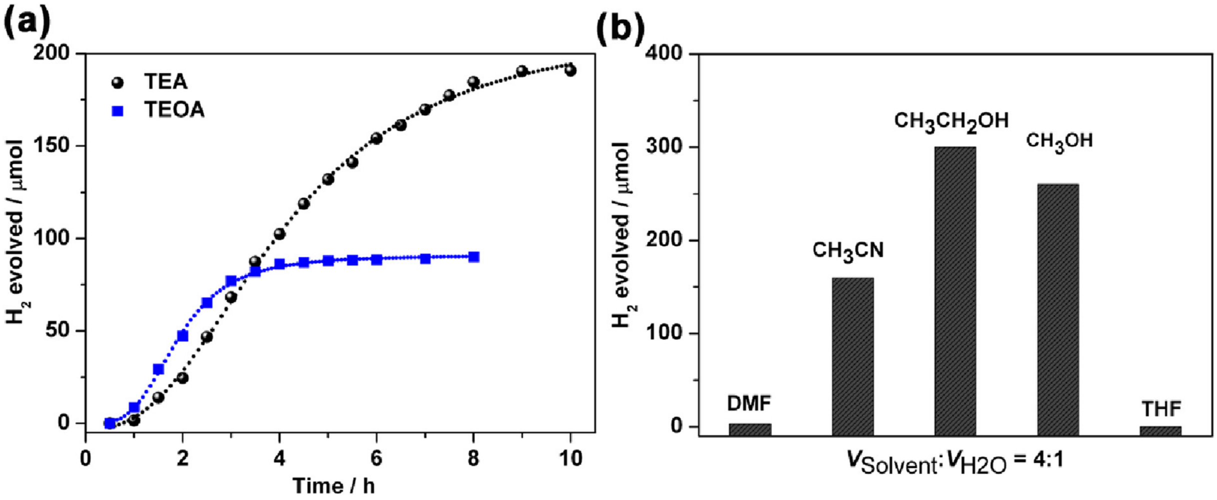


Fig. 1. (a) Photoinduced H_2 evolution vs. time using TEOA or TEA as SED with [Co^{II}Pc(-2)] (2×10^{-5} M) and [Ru^{II}(bpy)$_3$]Cl$_2$ (2×10^{-4} M) in CH_3CN/H_2O (4:1 v/v) at pH 9.0. (b) Comparison of H_2 production using different solvent:water (4:1, v/v) with 2×10^{-5} M [Co^{II}Pc(-2)], 2×10^{-4} M [Ru^{II}(bpy)$_3$]Cl$_2$, 0.36 M TEA at pH 9.0.

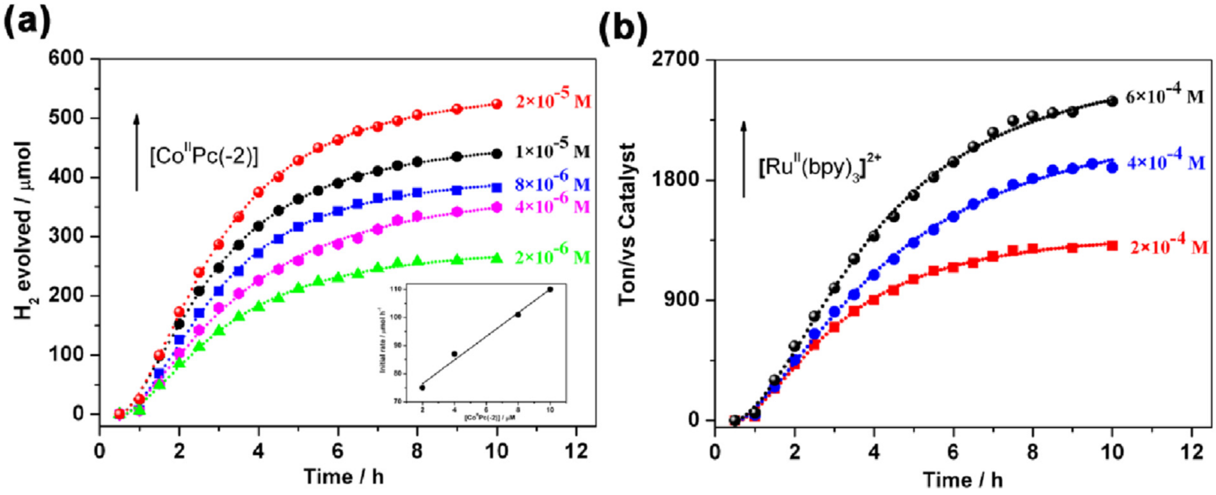


Fig. 2. Photocatalytic H_2 production with 0.36 M TEA in 4:1 CH_3CH_2OH/H_2O solution at pH 10.0 as a function of time under irradiation ($\lambda > 420$ nm) in the presence of (a) [Ru^{II}(bpy)$_3$]Cl$_2$ (2×10^{-4} M) and [Co^{II}Pc(-2)] at various concentrations, and (b) [Co^{II}Pc(-2)] (2×10^{-6} M) and [Ru^{II}(bpy)$_3$]Cl$_2$ at various concentrations. Left inset: the initial rate of hydrogen production.

[Co^{II}Pc(-2)] partly resumed the production of H_2, suggesting the present three-component system was thought to be largely limited by the stability of the HEC and PS.

The first light-driven step of the photocatalytic mechanism with the system [Ru^{II}(bpy)$_3$]Cl$_2$/[Co^{II}Pc(-2)]/TEA (or TEOA) can be a reductive quenching of *[Ru^{II}(bpy)$_3$]Cl$_2$ by TEA (or TEOA) leading to the reduced form of [Ru^{II}(bpy)$_2$(bpy$^{\bullet-}$)]$^+$ (*Eq. 2*: *[Ru^{II}(bpy)$_3$]Cl$_2$ + TEA → [Ru^{II}(bpy)$_2$(bpy$^{\bullet-}$)]$^+$ + TEA$^{\bullet-}$), or an oxidative quenching of *[Ru^{II}(bpy)$_3$]Cl$_2$ by [Co^{II}Pc(-2)] yielding the oxidized form of [Ru^{III}(bpy)$_3$]$^{3+}$ (*Eq. 3*: [Ru^{II}(bpy)$_3$]Cl$_2^*$ + [Co^{II}Pc(-2)] → [Ru^{III}(bpy)$_3$]$^{3+}$ + [Co^{I}Pc(-2)]$^-$). According to the electrochemical and photophysical data ($E^*_{1/2}$[Ru^{II}(bpy)$_3$]Cl$_2$/[Ru^{II}(bpy)$_2$(bpy$^{\bullet-}$)]$^+$ = 0.67 V, $E_{1/2}$[Ru^{III}(bpy)$_3$]$^{3+}$/*[Ru^{II}(bpy)$_3$]Cl$_2$ = −0.76 V, $E_{1/2}$[Co^{II}Pc(-2)]/[Co^{I}Pc(-2)]$^-$ = −0.48 V, E_{ox}(TEOA) = 0.90 V and E_{ox}(TEA) = 0.73 V, respectively, vs. SCE) [5,12,2c], the driving force of the reductive quenching of *[Ru^{II}(bpy)$_3$]Cl$_2$ by TEOA (or TEA) and of the oxidative quenching of [Ru^{II}(bpy)$_3$]Cl$_2^*$ by [Co^{II}Pc(-2)] were estimated to be $\Delta G_0 = 0.23$ (or 0.06 eV) and −0.25 eV, respectively. The calculated free-energy ΔG_0 suggested that the [Co^{II}Pc(-2)]/[Ru^{II}(bpy)$_3$]Cl$_2$/TEOA or [Co^{II}Pc(-2)]/[Ru^{II}(bpy)$_3$]Cl$_2$/TEA system should proceed by oxidative quenching of *[Ru^{II}(bpy)$_3$]Cl$_2$ by [Co^{II}Pc(-2)] to generate the reduced form [Co^{I}Pc(-2)]$^-$ species, because the reductive quenching of *[Ru^{II}(bpy)$_3$]Cl$_2$ by TEOA or TEA is not exergonic.

In order to check for these possibilities, the interaction between *[Ru^{II}(bpy)$_3$]Cl$_2$ and [Co^{II}Pc(-2)] was investigated through emission quenching experiments. As shown in Fig. 3a, the PS [Ru^{II}(bpy)$_3$]Cl$_2$ gave a strong emission band as expected in the range of 500–800 nm with a maximum peak at 610 nm upon excitation at 460 nm in CH_3CH_2OH/H_2O (4:1, v/v) at room temperature. The luminescence intensity of [Ru^{II}(bpy)$_3$]Cl$_2$ gradually is decreased upon increasing the concentration of [Co^{II}Pc(-2)] in the [Ru^{II}(bpy)$_3$]Cl$_2$ solution. After carefully correcting for inner filter effects, on the basis of the Stern-Volmer plot (Fig. 3b) [13], the quenching constant k_q, calculated using the equation $I_0/I = 1 + K_{sv}[Q] = 1 + k_q\tau_0[Q]$, was 1.6×10^{10} M^{-1} s^{-1} for [Co^{II}Pc(-2)], which was at the diffusion-controlled limit. Interestingly, as shown in Fig. 3c or 3d, it was found that the emission quenching of [Ru^{II}(bpy)$_3$]Cl$_2$ in CH_3CH_2OH/H_2O (4:1, v/v) was not observed when an excess of TEOA or TEA was added to the photocatalytic system. It is notable that neither TEOA

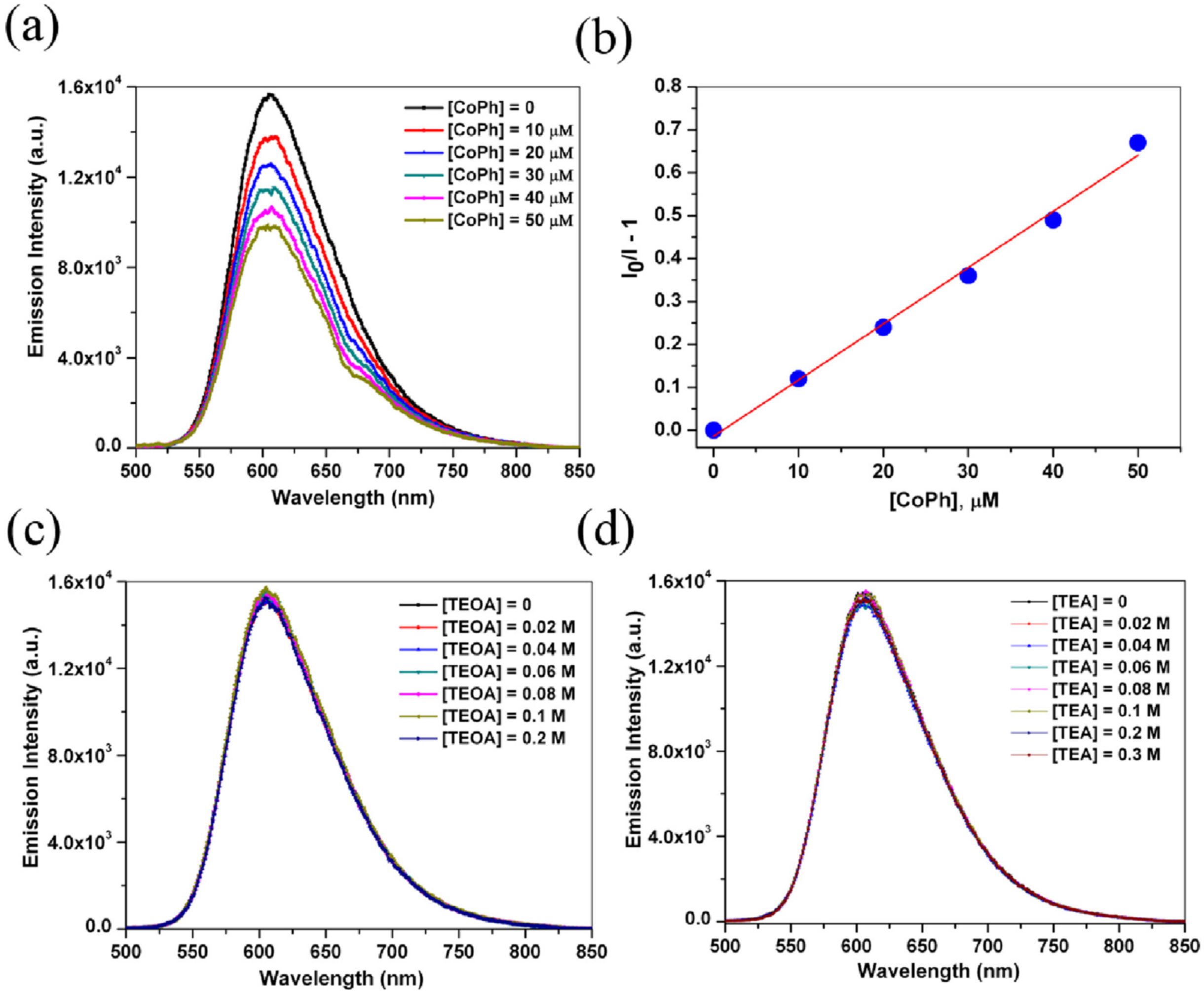


Fig. 3. (a) Fluorescence quenching of $[Ru^{II}(bpy)_3]Cl_2$ solution in 8:2 CH_3CH_2OH/H_2O in pH 10.0 after the sequential additions of $[Co^{II}Pc(-2)]$, inner filter correction applied. (b) Stern-Volmer analysis of the integrated intensity yields a bimolecular quenching rate constant of $k_q = 1.6 \times 10^{10}\ M^{-1}\ s^{-1}$. Photoluminescence spectra of solution containing $[Ru^{II}(bpy)_3]Cl_2$ after addition of different aliquots of TEOA (c) or TEA (d).

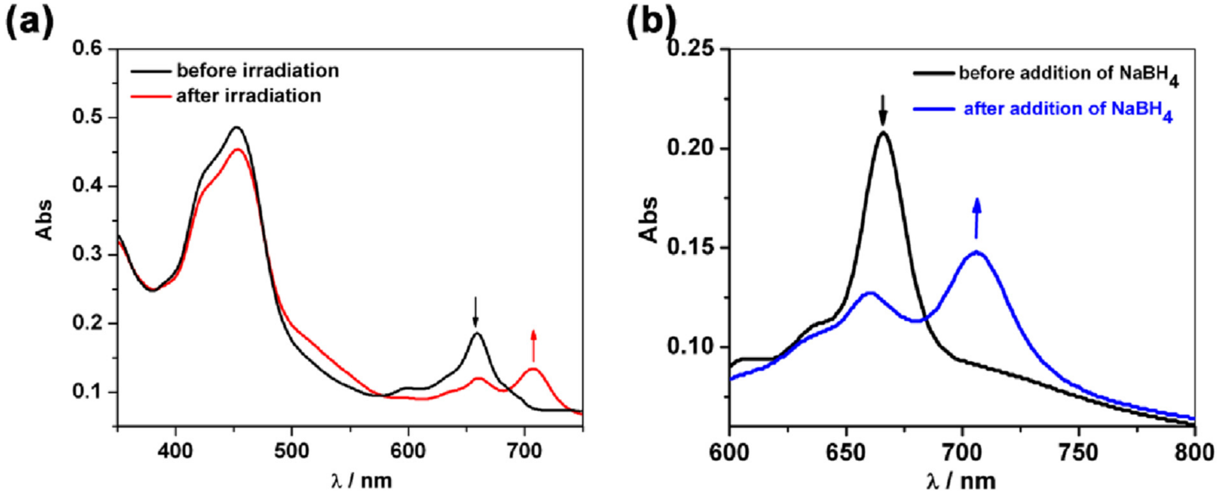


Fig. 4. (a) Absorption spectra of systems containing $[Ru^{II}(bpy)_3]Cl_2$ and TEA (5%, v/v) in $EtOH/H_2O$ (4:1) at pH 10.0 before and after 0.5 h irradiation with $[Co^{II}Pc(-2)]$. (b) UV–vis spectra of $[Co^{II}Pc(-2)]$, and $CoPc^-$ generated after the addition of $NaBH_4$ to$[Co^{II}Pc(-2)]$.

nor TEA can quench $[Ru^{II}(bpy)_3]Cl_2$, which is in accordance with the published work [14].

The above excited quenching experiments suggested that intermolecular quenching was at nearly diffusion-controlled and

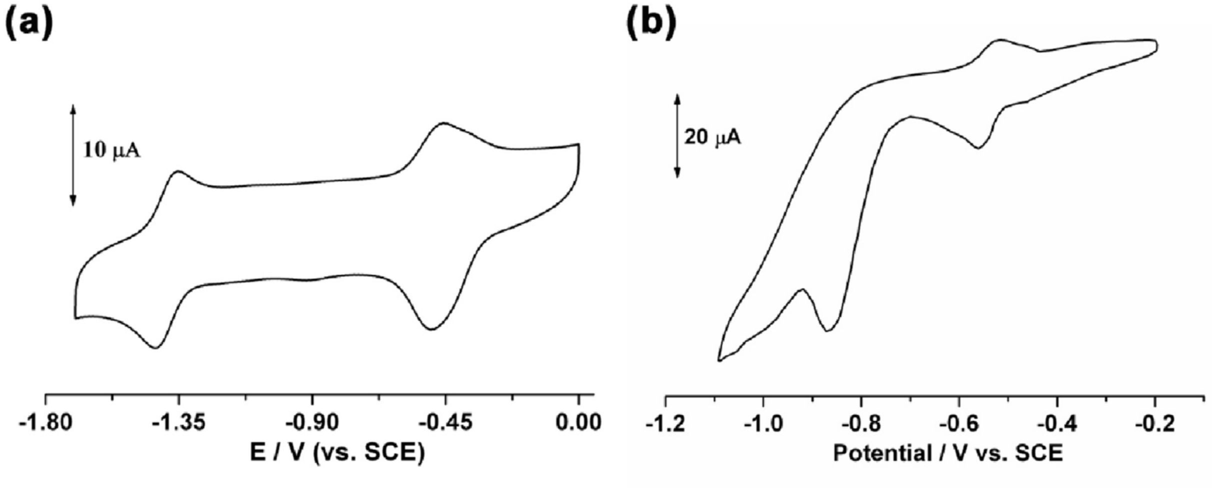


Fig. 5. (a) CV of [Co^{II}Pc(-2)] in Ar-saturated DMSO solution containing 0.1 M $TBAPF_6$ as the supporting electrolyte at the scan rates 0.6 V s^{-1}. (b) CV of [Co^{II}Pc(-2)] after addition of TFA.

the initial reaction is an oxidative (not a reductive) quenching of the excited PS by the formation of [$Ru^{III}(bpy)_3]^{3+}$ and [Co^{I}Pc(-2)]$^-$ through a photo-induced electron transfer from *[$Ru^{II}(bpy)_3]Cl_2$ to [Co^{II}Pc(-2)]. The formation of [Co^{I}Pc(-2)]$^-$ can be observed by following the UV−vis absorption spectra for the [Co^{II}Pc(-2)]/[$Ru^{II}(bpy)_3]Cl_2$/TEA photosystem under H_2-producing conditions. As shown in Fig. 4a, before irradiation, the absorption spectra are simply the sums of the individual components. After 0.5 h illumination (λ > 420 nm), a significant bathochromic shift of the Q band for phthalocyanine cobalt from 667 to 707 nm is observed. The absorbance well matches the reported spectrum [15] of [Co^{I}Pc(-2)]$^-$ and also matches the spectrum of [Co^{I}Pc(-2)]$^-$ generated from CoPc and $NaBH_4$ (Fig. 4b) [16].

Electrochemical studies were further carried out to get insight into the possible catalytic protonation mechanism. As shown in Fig. 5a, cyclic voltammograms (CVs) of [Co^{II}Pc(-2)] in DMSO containing 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) showed two reduction waves from 0 to −1.80 V vs. SCE in the absence of available protons. The first reversible phthalocyanine ring reduction was observed at $E_{1/2} = -0.48$ V. The second reversible redox wave at $E_{1/2} = -1.37$ V was ascribed to Co^{II}/Co^{I}. When trifluoroacetic acid (TFA) is added to a solution of [Co^{II}Pc(-2)], the first wave of redox process remains practically unchanged while the onset of a catalytic irreversible wave is observed at *ca.* -0.9 V (Fig. 5b). The results indicate that the formed Co^{I} species further reacts with a proton to produce a postulated Co^{III}-hydride, which releases molecular hydrogen via a homo- or heterolytic pathway. Further studies including theoretical calculations to identify the exact mechanisms for H_2 evolution catalyzed by cobalt phthalocyanine are in progress.

To conclude, we described herein a phthalocyanine cobalt ([Co^{II}Pc(-2)]) molecular catalyst that is active for the photocatalytic reduction of protons when paired with [$Ru^{II}(bpy)_3]Cl_2$ as the PS and TEA or TEOA as the SED. The HEC achieves 2400 TON (versus [Co^{II}Pc(-2)]) after 10 h of illumination with an initial TOF as high as 680 TON h^{-1}. Owing to the obvious possibilities of tuning the redox properties by modifying the phthalocyanine macrocycle, phthalocyanine cobalt and its derivatives are a promising new direction for molecular catalysts that achieve the photocatalytic generation of H_2.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jallcom.2017.05.040.

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