

Robust Cuprous Phenanthroline Sensitizer for Solar Hydrogen Photocatalysis

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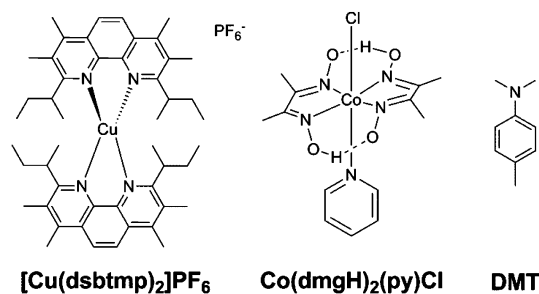
Supporting Information

ABSTRACT: The Cu(I) metal-to-ligand charge-transfer complex, $[\text{Cu}(\text{dsbtmp})_2]^+$ (dsbtmp = 2,9-di(*sec*-butyl)-3,4,7,8-tetramethyl-1,10-phenanthroline), exhibits outstanding stability as a visible-light-absorbing photosensitizer in hydrogen-evolving homogeneous photocatalysis. In concert with the $\text{Co}(\text{dmgH})_2(\text{py})\text{Cl}$ water reduction catalyst and *N,N*-dimethyl-*p*-toluidine sacrificial donor in 1:1 $\text{H}_2\text{O}:\text{CH}_3\text{CN}$, this Cu(I) sensitizer remains active even after 5 days of visible-light-pumped ($\lambda_{\text{ex}} = 452 \pm 10 \text{ nm}$) hydrogen evolution catalysis. Deuteration studies illustrate that the hydrogen produced from this composition does indeed originate from aqueous protons.

Photosynthesis of fuels powered by sunlight represents a sustainable, carbon-neutral approach suitable for future energy challenges.^{1,2} Sunlight-driven water splitting requires sensitizers that can capture and convert solar photons into redox equivalents that are ultimately coupled to catalysts that operate the relevant half-reactions.³ In terms of proton reduction catalysis, significant effort has been dedicated to both photosensitizer (PS) and water reduction catalyst (WRC) design.^{4–7} In the interest of long-term sustainability, an ideal scenario is one where both the molecular PS and the WRC are composed exclusively of earth-abundant elements and the resulting composition exhibits long-term fuel-forming stability.^{8–11} While significant progress has been made in terms of earth-abundant WRCs, only a handful of PSs in this category have been successfully applied to solar fuels photochemistry.^{9–12} During photocatalysis, these main group and transition metal PSs commonly suffer from photobleaching, hydrogenation, ligand scrambling, ligand loss, or solvent coordination, completely inactivating the composition. In this Communication, we demonstrate that a newly conceived Cu(I) PS, $[\text{Cu}(\text{dsbtmp})_2]^+$ (dsbtmp = 2,9-di(*sec*-butyl)-3,4,7,8-tetramethyl-1,10-phenanthroline), exhibits outstanding molecular PS stability, remaining active even after 5 days of visible-light-pumped ($\lambda_{\text{ex}} = 452 \pm 10 \text{ nm}$) hydrogen evolution catalysis in 1:1 $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ at near-neutral pH.

We recently reported the surprising photophysical and electrochemical properties of $[\text{Cu}(\text{dsbtmp})_2]^+$, which possesses an excited-state lifetime of 1.2 μs in degassed 1:1 $\text{CH}_3\text{CN}:\text{H}_2\text{O}$, exhibits completely reversible redox behavior, and is a potent excited-state reductant, $-1.48 \text{ V vs Fc}^{+/0}$.¹³ These desirable PS properties partially result from cooperative steric interactions between the *sec*-butyl and methyl substituents on the

phenanthroline ligands, rendering a fortuitously stable homoleptic Cu(I) complex that does not exhibit significant structural distortion in the metal-to-ligand charge-transfer (MLCT) excited state.¹⁴ Since a vast number of PS performance metrics have been evaluated using the Co(III) diglyoxime WRCs whose mechanism of hydrogen evolution was elucidated, the $\text{Co}(\text{dmgH})_2(\text{py})\text{Cl}$ (dmgH = dimethylglyoximate, py = pyridine) species was selected for the present proof-of-concept experiments using $[\text{Cu}(\text{dsbtmp})_2]^+$.^{8,9,15–21} Additionally, *N,N*-dimethyl-*p*-toluidine (DMT) was chosen as the sacrificial electron source since its associated radical cation DMT^{•+} is known to dimerize instead of engaging in destructive high-energy radical chemistry with the PS and/or WRC.²² The structures of the molecules used in this hydrogen-producing composition are presented below.



The light-energized Cu(I) PS is oxidatively quenched by $\text{Co}(\text{dmgH})_2(\text{py})\text{Cl}$ ($k_q = 7.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, Figure S1) and cannot be reductively quenched by DMT (Figures S7 and S8). In contrast to most other compositions utilizing the $\text{Co}(\text{dmgH})_2(\text{py})\text{Cl}$ WRC, this reaction initiates exclusively from oxidative quenching of the excited PS by the catalyst, taking Co(III) to Co(II), and then DMT regenerates the resting state of the PS through thermal electron transfer. Under the reaction conditions used ($[\text{DMT}] = 0.07 \text{ M}$), dimerization of the DMT radical cation will necessarily occur prior to other ill-defined chemistry.²² Potentials $E_{\text{Co(II)/Co(I)}}$ and $E_{\text{Cu(II)/Cu(I)}}^*$ are similar (Figure S8), implying that the second reduction likely occurs at a slow rate.¹³ Alternatively, Co(II) might disproportionate $2\text{Co(II)} \rightarrow \text{Co(I)} + \text{Co(III)}$, yielding the desired Co(I) species poised for hydrogen evolution.

In a typical experiment, a 10 mL solution of 1:1 ACN: H_2O containing the appropriate concentration of each component was prepared in an airtight glass vial, and the pH was adjusted

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by addition of HCl. All solutions were degassed by a series of vacuum and argon pressurization cycles, and then the individual samples were illuminated from the bottom using blue LEDs (452 ± 10 nm, 540 mW). The mixtures were maintained at 20°C throughout the illumination period while being constantly agitated at 100 rpm. H_2 production was monitored in real time using pressure transducers, and the final amounts of hydrogen were quantified by both mass spectrometry and gas chromatographic analysis of the reactor headspace. The pH optimization study illustrated that the yield of hydrogen was maximized between 5.5 and 6.5 (Figure S2). In all experiments reported here, the Cu(I) PS and DMT concentrations were fixed at 2.2×10^{-4} M and 0.07 M, respectively, while the cobalt catalyst concentration was varied between 2.2×10^{-4} and 5.0×10^{-4} M; these conditions were determined to be the optimum concentrations in terms of total accumulated hydrogen yield (Figure S3). Control experiments indicated that hydrogen is produced only when all three components are present in solution.

The unparalleled stability of this Cu(I) PS was ascertained through near-complete regeneration of catalysis subsequent to Cu(I) PS precipitation (using pure water) followed by re-dissolution into fresh 1:1 $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ solution containing DMT and $\text{Co}(\text{dmgH})_2(\text{py})\text{Cl}$, Figure 1. It was not surprising

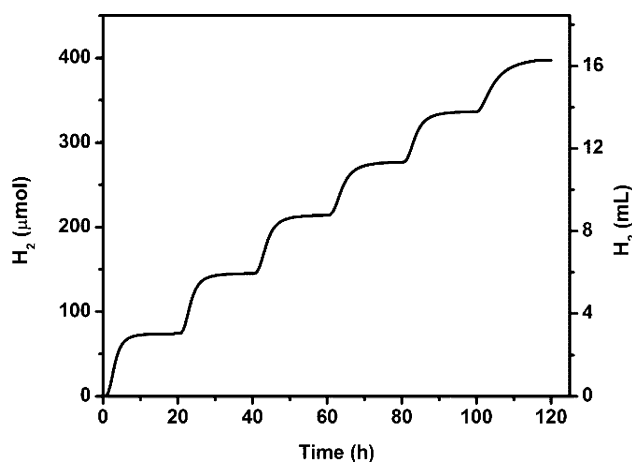


Figure 1. Photocatalytic hydrogen production utilizing 2.2×10^{-4} M $[\text{Cu}(\text{dsbtmp})_2]\text{PF}_6$, 0.07 M DMT, and 2.2×10^{-4} M $\text{Co}(\text{dmgH})_2(\text{py})\text{Cl}$ in 1:1 $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ at pH 6.0 ($\lambda_{\text{ex}} = 452 \pm 10$ nm, 540 mW). At intervals of 20 h, the Cu(I) PS was precipitated by the addition of water, isolated by vacuum filtration, and then dissolved into fresh 1:1 $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ containing DMT and Co catalyst at their initial concentrations, and the photocatalysis was resumed.

that the catalyst was the least stable moiety in the composition, as it has been shown to be quite labile in numerous photocatalytic H_2 -producing schemes.^{8,15,23} Note that the PS is not decomposed under photocatalytic conditions, as ascertained by identical MLCT absorption for the precipitated Cu(I) samples after the end of a given hydrogen-producing cycle compared to the same solution maintained in the dark (Figure S4). Due to this less than quantitative precipitation procedure, it was found that the Cu(I) PS could be isolated with $83 \pm 9\%$ yield (Figure S5) after each cycle; the experimental conditions ensured near-complete absorption of the blue incident photons in each cycle. The UV-vis (Figure S5) and ESI-MS (Figure S6) taken before and after 5 days of catalysis clearly indicated that $[\text{Cu}(\text{dsbtmp})_2]^+$ remains intact

under the photocatalytic conditions, suggesting further application of this first-row transition metal sensitizer in related energy conversion schemes. As in other schemes using the Co-dmg platform,^{8,15,23} the TON was a mere 35 (H_2/Co) on average, calculated after the end of each catalytic cycle, and the TOF was 5 (TON/h). It is important to note that 40% of the Cu(I) PS was recovered after six consecutive long-term photocycles (Figure S5), and most of the Cu(I) PS loss can be attributed to the non-ideal precipitation procedure performed after each cycle (Figures S4–S6). We believe that the small quantum yield of hydrogen production ($\sim 0.3\%$) as well as the TONs can be significantly optimized in the future by utilizing superior hydrogen-evolving catalysts and alternative electron donors. When $[\text{Cu}(\text{dsbtmp})_2]^+$ was replaced with $[\text{Ru}(\text{bpy})_3]^{2+}$, the catalyst also limited the performance, with a TON of 31 (H_2/Co) and a TOF of 17 (TON/h) (Figure S9). The faster rate of hydrogen production was attributed to reductive quenching of $[\text{Ru}(\text{bpy})_3]^{2+*}$ by DMT ($k_q = 3.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, Figure S10), which yields a strongly reducing and long-lived $[\text{Ru}(\text{bpy})_3]^+$ species thermodynamically capable of performing both Co(III)/Co(II) and Co(II)/Co(I) reductions (Figure S11).

The molecular nature of the hydrogen-producing photocatalysis from $\text{Co}(\text{dmgH})_2(\text{py})\text{Cl}$ was previously ascertained using the mercury poisoning test,²¹ and it was verified here by no detectable formation of nanoparticles beyond 1 nm through dynamic light scattering experiments.

Finally, deuterated water was used in place of H_2O to glean insight into the source of protons reduced by this photocatalytic composition. H_2 was the sole gaseous product formed in the headspace of the reaction mixture in 1:1 $\text{H}_2\text{O}:\text{CH}_3\text{CN}$ as ascertained by MS (Figure 2a). The origin of H_2 is believed to be aqueous protons since D_2 constituted the major product when D_2O was substituted for H_2O (Figure 2b). This strongly suggests that neither is H_2 a direct byproduct of DMT dehydrogenation, nor does it originate from the CH_3CN co-solvent. The large deuterium incorporation into the gaseous hydrogen products (0.5% H_2 , 4.5% HD , 95% D_2) provides strong evidence that molecular H_2 is indeed derived from water in this photocatalytic composition.

A water-compatible homogeneous photocatalytic composition made up of all earth-abundant elements has been developed to drive solar hydrogen production. Excited-state oxidative quenching of the Cu(I) PS by the molecular cobalt catalyst initiates the photocatalytic cycle, and the PS is ultimately regenerated by sacrificial donation of one electron by DMT. The DMT radical is believed to rapidly engage in bond-forming chemistry, yielding a DMT dimer that can also serve as a sacrificial donor possessing a redox potential almost identical to that of DMT itself.²² Within this hydrogen-producing composition, the Cu(I) PS displayed unprecedented photostability under visible-light illumination for 5 days without losing structural integrity. Deuteration studies performed on the composition leave little doubt that the hydrogen produced from visible-light excitation originates from aqueous protons. These results represent important findings toward the development of sensitizers composed of earth-abundant elements intended for homogeneous and perhaps heterogeneous solar fuels photocatalysis. Similarly, we believe that $[\text{Cu}(\text{dsbtmp})_2]^+$ could potentially serve as a PS in organic synthesis.²⁴

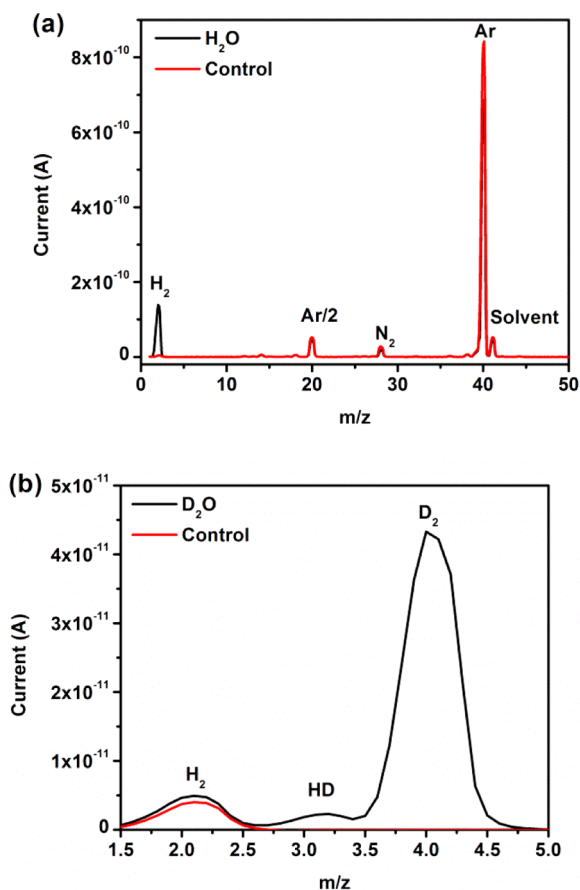


Figure 2. Mass spectrometry analysis of the headspace from reactions containing 1:1 (a) $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ or (b) $\text{CH}_3\text{CN}:\text{D}_2\text{O}$ at pH 6.5 utilizing 2.2×10^{-4} M $[\text{Cu}(\text{dsbtmp})_2]\text{PF}_6$, 0.07 M DMT, and 5×10^{-4} M $\text{Co}(\text{dmgH})_2(\text{py})\text{Cl}$. The control vial contained 0.07 M DMT dissolved in 1:1 $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ at pH 6.5, intended to measure the background signal resulting from the solvent mixture and spectrometer outgassing. All samples were deaerated by purging with ultra-high-purity argon gas.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details, sensitizer luminescence quenching, hydrogen production optimization, UV-vis spectra, ESI-MS spectra before and after photocatalysis, and pertinent energy level diagrams. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Bard, A. J.; Fox, M. A. *Acc. Chem. Res.* **1995**, *28*, 141–145.
- (2) Faunce, T.; Styring, S.; Wasielewski, M. R.; Brudvig, G. W.; Rutherford, A. W.; Messinger, J.; Lee, A. F.; Hill, C. L.; deGroot, H.; Fontecave, M.; MacFarlane, D. R.; Hankamer, B.; Nocera, D. G.; Tiede, D. M.; Dau, H.; Hillier, W.; Wang, L.; Amal, R. *Energy Environ. Sci.* **2013**, *6*, 1074–1076.
- (3) Chanon, M., Ed. *Homogeneous Photocatalysis*; John Wiley & Sons: Chichester, UK, 1997.
- (4) Artero, V.; Chavarot-Kerlidou, M.; Fontecave, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 7238–7266.
- (5) Tinker, L. L.; McDaniel, N. D.; Bernhard, S. J. *Mater. Chem.* **2009**, *19*, 3328–3337.
- (6) Du, P.; Eisenberg, R. *Energy Environ. Sci.* **2012**, *5*, 6012–6021.
- (7) Thoi, V. S.; Sun, Y.; Long, J. R.; Chang, C. J. *Chem. Soc. Rev.* **2013**, *42*, 2388–2400.
- (8) McCormick, T. M.; Calitree, B. D.; Orchard, A.; Kraut, N. D.; Bright, F. V.; Detty, M. R.; Eisenberg, R. *J. Am. Chem. Soc.* **2010**, *132*, 15480–15483.
- (9) Lazarides, T.; McCormick, T.; Du, P.; Luo, G.; Lindley, B.; Eisenberg, R. *J. Am. Chem. Soc.* **2009**, *131*, 9192–9194.
- (10) Han, Z.; McNamara, W. R.; Eum, M.-S.; Holland, P. L.; Eisenberg, R. *Angew. Chem., Int. Ed.* **2012**, *51*, 1667–1670.
- (11) Luo, S.-P.; Mejía, E.; Friedrich, A.; Pazidis, A.; Junge, H.; Surkus, A.-E.; Jackstell, R.; Denurra, S.; Gladiali, S.; Lochbrunner, S.; Beller, M. *Angew. Chem., Int. Ed.* **2013**, *52*, 419–423.
- (12) Edel, A.; Marnot, P. A.; Sauvage, J. P. *Nouv. J. Chim.* **1984**, *8*, 495–498.
- (13) McCusker, C. E.; Castellano, F. N. *Inorg. Chem.* **2013**, *52*, 8114–8120.
- (14) Cunningham, C. T.; Cunningham, K. L. H.; Michalec, J. F.; McMullin, D. R. *Inorg. Chem.* **1999**, *38*, 4388–4392.
- (15) Probst, B.; Guttentag, M.; Rodenberg, A.; Hamm, P.; Alberto, R. *Inorg. Chem.* **2011**, *50*, 3404–3412.
- (16) Hawecker, J.; Lehn, J. M.; Ziessel, R. *Nouv. J. Chim.* **1983**, *7*, 271–277.
- (17) Fihri, A.; Artero, V.; Pereira, A.; Fontecave, M. *Dalton Trans.* **2008**, *0*, 5567–5569.
- (18) Dempsey, J. L.; Winkler, J. R.; Gray, H. B. *J. Am. Chem. Soc.* **2010**, *132*, 1060–1065.
- (19) Dempsey, J. L.; Brunschwig, B. S.; Winkler, J. R.; Gray, H. B. *Acc. Chem. Res.* **2009**, *42*, 1995–2004.
- (20) Du, P.; Knowles, K.; Eisenberg, R. *J. Am. Chem. Soc.* **2008**, *130*, 12576–12577.
- (21) Wang, X. H.; Goeb, S.; Ji, Z. Q.; Pogulaichenko, N. A.; Castellano, F. N. *Inorg. Chem.* **2011**, *50*, 705–707.
- (22) Rees, N. V.; Klymenko, O. V.; Compton, R. G.; Oyama, M. J. *Electroanal. Chem.* **2002**, *531*, 33–42.
- (23) McCormick, T. M.; Han, Z.; Weinberg, D. J.; Brennessel, W. W.; Holland, P. L.; Eisenberg, R. *Inorg. Chem.* **2011**, *50*, 10660–10666.
- (24) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. *Chem. Rev.* **2013**, *113*, 5322–5363.