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# Designing Highly Efficient Cu<sup>I</sup> Photosensitizer for Photocatalytic H<sub>2</sub> Evolution from Water

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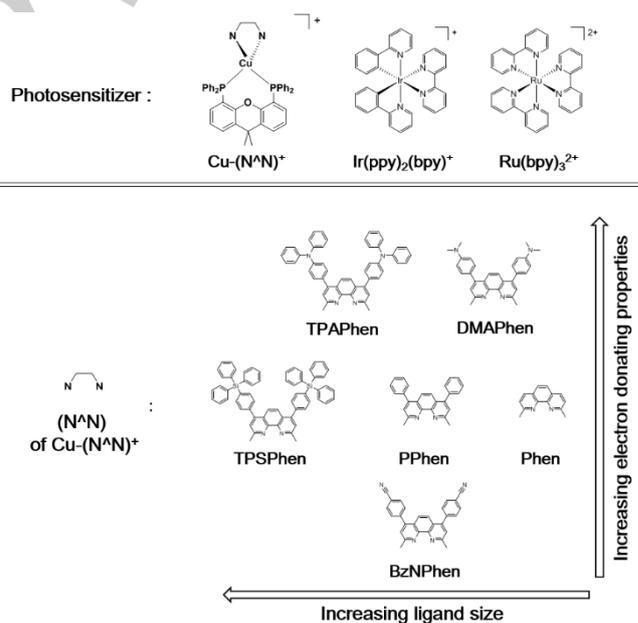
**Abstract:** A series of Cu<sup>I</sup> photosensitizers was synthesized, characterized, and investigated for photocatalytic H<sub>2</sub> evolution from water. The structure-property correlation was made for their catalytic activity and photophysical properties, which was further elaborated by DFT calculation. A novel Cu<sup>I</sup> photosensitizer (Cu-TPA<sup>Phen</sup>) with triphenylamine-substituted phenanthroline ligand showed unprecedentedly high turnover number of 19,000 when tested in combination with triethylamine as a sacrificial reagent and colloidal Pt as a H<sub>2</sub> evolution catalyst. This work paves the way toward cheap metal-based photosensitizers which can replace noble metal complexes in photocatalytic systems.

Catalysis is an important breakthrough for securing future's sustainable energy.<sup>[1]</sup> Photocatalytic H<sub>2</sub> evolution reaction (HER) from water is a highly desirable strategy since it utilizes two of the most abundant resources on earth, solar energy and water.<sup>[2]</sup> In the photocatalytic HER system, the choice of proper photosensitizer performing the initial step of light absorption is of key importance.<sup>[3]</sup>

Historically, Ru<sup>II</sup> complexes have been most commonly used as photosensitizers for photocatalytic HER from water,<sup>[4]</sup> and recently, Ir<sup>III</sup> photosensitizers have also been investigated as superior alternatives.<sup>[5]</sup> Many noble-metal-free complexes have been reported as photosensitizers for HER as well, but few of them showed comparable level of catalytic activities for HER against noble metal based counterparts.<sup>[6]</sup> Recently, Beller group reported a series of [Cu<sup>I</sup>(P<sup>^</sup>P)(N<sup>^</sup>N)]<sup>+</sup> photosensitizers (where P<sup>^</sup>P = diphosphine and N<sup>^</sup>N = phenanthroline-based diimine ligand) and recorded turnover number (TON) of 1,330 of HER, suggesting the potential of the noble metal free system.<sup>[7-9]</sup>

On the other hand, we have recently reported high performance photosensitizers consisting of a [Ir<sup>III</sup>(C<sup>^</sup>N)<sub>2</sub>(bpy-R)]<sup>+</sup> scaffold, where C<sup>^</sup>N is a monoanionic cyclometalating ligand and bpy-R is a 4,4'-disubstituted-2,2'-bipyridyl ligand. By employing tetraphenylsilane as a bulky R moiety, state-of-the-art TON of 17,000 could be achieved with this [Ir<sup>III</sup>(C<sup>^</sup>N)<sub>2</sub>(bpy-R)]<sup>+</sup> photosensitizer.<sup>[10]</sup> Since we learned that the catalytic activities of Ir<sup>III</sup> photosensitizers for HER could be tuned such remarkably

through their ligand modification, we decided to extend our ligand engineering strategy to the complexes based on the first row transition metal of Cu<sup>I</sup> in this work. Copper is a 10<sup>5</sup> times more abundant metal than iridium on earth, which is preferable in terms of monetary expense and scalability of the HER systems. The prerequisites for efficient photosensitizers are strong visible light absorption, long excited state lifetime and high photoluminescence quantum yield.<sup>[5a, 6b]</sup> Herein we attempted to correlate the ligand structure of [Cu<sup>I</sup>(P<sup>^</sup>P)(N<sup>^</sup>N)]<sup>+</sup> photosensitizers with their catalytic performance by incorporating a series of different substituents on phenanthroline-based N<sup>^</sup>N ligand. Six different N<sup>^</sup>Ns were designed and synthesized to give different size and electronic effect on the Cu<sup>I</sup> photosensitizers.



**Scheme 1.** Chemical structures of photosensitizers. N<sup>^</sup>N of Cu-(N<sup>^</sup>N)<sup>+</sup> stands for the 4,7-disubstituted-2,9-dimethyl-1,10-phenanthroline ligand: TPA = triphenylamine; DMA = dimethylaniline; TPS = tetraphenylsilane; P = phenyl group; BzN = benzonitrile; Phen = 2,9-dimethyl-1,10-phenanthroline. Ru(bpy)<sub>3</sub><sup>2+</sup> and Ir(ppy)<sub>2</sub>(bpy)<sup>+</sup> were used as reference complexes representative of noble metal-based photosensitizers.

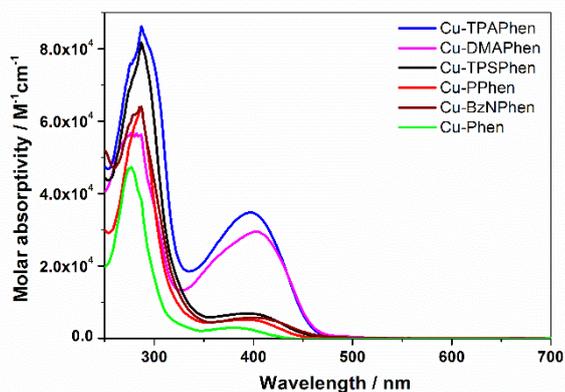
Scheme 1 illustrates the chemical structure of photosensitizers investigated in this work. The 4,7 positions of 2,9-dimethyl-1,10-phenanthroline (Phen) ligands were modified as follows: i) *tert*-amines and benzonitrile substituents were selected to give electron donating and withdrawing effects, respectively; ii) different number of phenyl groups were incorporated to give different size effects; iii) tetraphenylsilane (TPS) was introduced

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## COMMUNICATION

to give extreme bulkiness without significant electronic effect. Conventional noble metal-based photosensitizers of  $\text{Ir}(\text{ppy})_2(\text{bpy})^+$  and  $\text{Ru}(\text{bpy})_3^{2+}$  were also prepared for the comparative study. All the photosensitizers, with a same counter anion of  $\text{PF}_6^-$ , were synthesized according to the standard procedures described in Supporting Information (SI).



**Figure 1.** Absorption spectra of  $\text{Cu}^{\text{I}}$  photosensitizers in Ar-saturated mixed solution (10  $\mu\text{M}$ ) of THF:H<sub>2</sub>O 8:2 v/v.

**Table 1.** Photophysical properties of  $\text{Cu}^{\text{I}}$  photosensitizers.

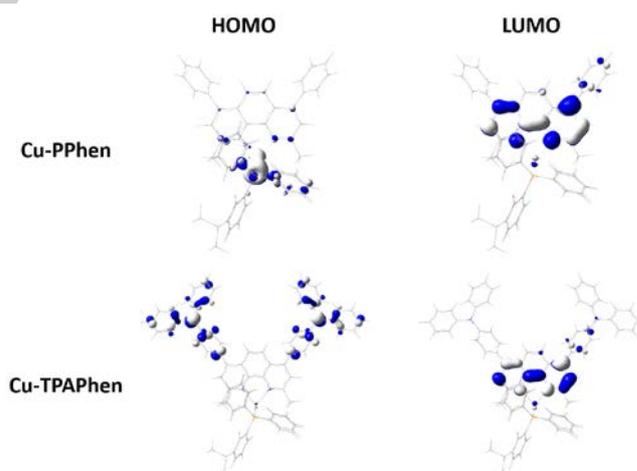
Photosensitizers	$\lambda_{\text{abs,max}}^{\text{[a]}}$ / nm	$\epsilon^{\text{[a]}}$ / $\text{M}^{-1}\text{cm}^{-1}$	PLQY <sup>[b]</sup> / %	$\tau^{\text{[c]}}$ / $\mu\text{s}$
Cu-TPAphen	397	34,700	10.0	88
Cu-DMAphen	403	29,400	6.2	120
Cu-TSPphen	394	6,800	2.1	0.82
Cu-Pphen	391	5,200	3.1	1.3
Cu-BzNphen	400	5,700	0.2	0.22
Cu-phen	380	2,900	2.6	1.1

[a] Absorption maxima ( $\lambda_{\text{abs,max}}$ ) and molar absorptivity ( $\epsilon$ ) from absorption spectra of 10  $\mu\text{M}$  solution in Ar-saturated mixed solution of THF:H<sub>2</sub>O 8:2 v/v. [b] Relative photoluminescence quantum yield (See SI). [c] Intensity-averaged lifetimes from bi-exponential fits.

The photophysical properties of the  $\text{Cu}^{\text{I}}$  photosensitizers are summarized in Table 1. All the measurements were carried out in THF:H<sub>2</sub>O 8:2 v/v mixtures to mimic the photocatalytic reactions, *vide infra*. It is notable that the *tert*-amine containing complexes, Cu-TPAphen and Cu-DMAphen, show peculiar photophysical properties totally different from the other  $\text{Cu}^{\text{I}}$  complexes. These two complexes show one order of magnitude higher molar absorptivities ( $\epsilon$ ) in the visible region and significantly higher photoluminescence quantum yields (PQLYs) compared to the other complexes (see Figure 1 and Table 1). Particularly, the photoluminescence (PL) lifetimes ( $\tau$ ) of these two complexes are extremely long (88  $\mu\text{s}$  and 120  $\mu\text{s}$ , respectively), suggesting their

superior performance as the photosensitizer. While such long PL lifetime of  $[\text{Cu}^{\text{I}}(\text{P}^{\wedge}\text{P})(\text{N}^{\wedge}\text{N})]^+$  complexes has been known to be attributed to the thermally activated delayed fluorescence (TADF),<sup>[11]</sup> significantly different absorption and emission behaviors of *tert*-amine containing complexes from those of other  $\text{Cu}^{\text{I}}$  complexes should be rationalized.

The origin of such unique photophysical properties of the *tert*-amine containing  $\text{Cu}^{\text{I}}$  complexes was explored by density functional theory (DFT) based quantum chemical calculations. Figure 2 shows optimized geometry and molecular orbital contour diagrams of Cu-Pphen and Cu-TPAphen. The  $\text{Cu}^{\text{I}}$  complex without *tert*-amine moiety, Cu-Pphen, follows metal to ligand charge transfer (MLCT) transition upon photoexcitation, where the highest occupied molecular orbital (HOMO) is localized on the  $\text{Cu}^{\text{I}}$  center and the lowest unoccupied molecular orbital (LUMO) is localized on the phenanthroline moiety. As for this MLCT transition, it is reported that tetrahedral coordination geometry of  $\text{Cu}^{\text{I}}$  complex is distorted upon transition because  $\text{Cu}^{\text{I}}$  is oxidized to  $\text{Cu}^{\text{II}}$  which prefers square planar geometry. Generally, such molecular distortion accompanying the electronic transition activates the non-radiative deactivation pathway to lower the PLQY and shorten the photoluminescence lifetime.<sup>[7-9,12-14]</sup> On the other hand, the HOMO of Cu-TPAphen is localized in the amine moieties and the electronic transition can be assigned to intra-ligand charge transfer (ILCT). Thus, there is no change in the oxidation state of  $\text{Cu}^{\text{I}}$  upon transition, which effectively prevents the distortion of coordination axes to give higher PLQY and longer PL lifetime as shown in Table 1. In addition, the ILCT character renders the stronger absorption features (larger molar absorptivities, see Table 1) of Cu-TPAphen compared to Cu-Pphen with  $d-\pi^*$  transition. Similarly Cu-DMAphen showed ILCT transition behavior, while all the other four  $\text{Cu}^{\text{I}}$  complexes showed MLCT transition behavior (See SI).

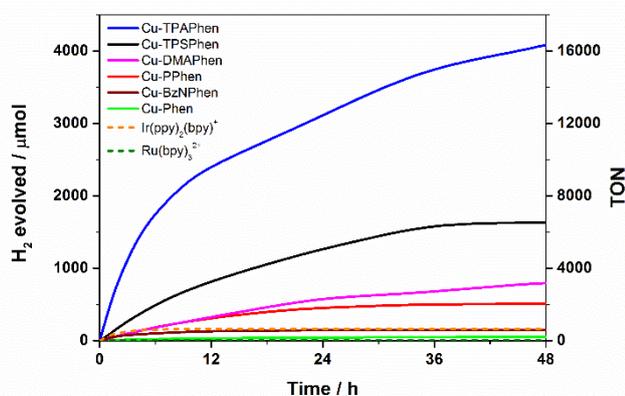


**Figure 2.** Molecular orbital contour diagrams of Cu-Pphen and Cu-TPAphen.

The photocatalytic hydrogen production efficiencies with  $[\text{Cu}^{\text{I}}(\text{P}^{\wedge}\text{P})(\text{N}^{\wedge}\text{N})]^+$  photosensitizers were evaluated by visible light irradiation; the system incorporated colloidal Pt as a hydrogen

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evolution catalyst (HEC) and triethylamine (TEA) as a sacrificial reagent. To evaluate the intrinsic efficacy of the  $[\text{Cu}^{\text{I}}(\text{P}^{\wedge}\text{P})(\text{N}^{\wedge}\text{N})]^+$  photosensitizer while excluding complicated side effect of other components,<sup>[9, 13]</sup> highly efficient and robust platinum catalyst was chosen as a HEC in this work. The experiments were carried out by continuously irradiating a 12 mL mixed solution of THF:H<sub>2</sub>O:TEA (8:2:2 v/v/v) containing photosensitizer (0.5 μmol) and HEC (0.5 μmol) until the H<sub>2</sub> evolution ceased (See SI). Figure 3 shows time-dependent H<sub>2</sub> evolution traces during the catalytic process, from which turnover frequencies (TOFs) and turnover numbers (TONs) of the photosensitizers are evaluated as summarized in Table 2. Most remarkably, Cu-TPAphen showed highest catalytic activity with a turnover number (TON) of 19,000 and a turnover frequency (TOF) of 1,800 h<sup>-1</sup>, which is most likely attributed to its superior molar absorptivity and exceptionally long lifetime of ILCT excited states. It is particularly noteworthy that the TON of Cu-TPAphen is 3-4 orders of magnitude higher than those of noble metal based-photosensitizers, Ir(ppy)<sub>2</sub>(bpy)<sup>+</sup> (TON of 650) or Ru(bpy)<sub>3</sub><sup>2+</sup> (TON of 39) evaluated at the identical conditions in this work. In spite of its comparable level of molar absorptivity and PL lifetime, Cu-DMAphen showed somewhat lower catalytic activity than that of Cu-TPAphen to give TON of 3,200 and a TOF of 130 h<sup>-1</sup>. This result can be explained by the different energetics for photo-induced reductive electron transfer: Cu-DMAphen has smaller thermodynamic driving force for electron transfer from TEA since the reduction potential of excited state of Cu-DMAphen is more negative (by 0.04 V) compared to that of Cu-TPAphen (see SI for details). In contrast to such high TON values of ILCT transition Cu<sup>I</sup> complexes, those of Cu-Pphen, Cu-BzNphen, and Cu-phen with MLCT transition characters are significantly low (TON = 2000, 590, and 200, respectively) which is based on their lower PLQY and shorter PL lifetime. On the other hand, Cu-TPSphen also showed quite decent performance (TON of 6,500) in spite of its MLCT excited state, which is consistent with the beneficial role of bulky steric effect previously demonstrated in the case of  $[\text{Ir}^{\text{III}}(\text{C}^{\wedge}\text{N})_2(\text{bpy-R})]^+$  photosensitizer.<sup>[10]</sup> According to the size effect, the TON of phenyl-substituted Cu-Pphen (2000) is quite smaller than that of Cu-TPSphen, while it is still much higher than that of the unfunctionalized Cu<sup>I</sup> complex of Cu-phen (TON = 200).



**Figure 3.** H<sub>2</sub> evolution curve by using photosensitizer with K<sub>2</sub>PtCl<sub>4</sub> as a precursor of HEC and TEA as a sacrificial reagent in a mixed solution of

THF:H<sub>2</sub>O 8:2 v/v (41.67 μM of photosensitizer and K<sub>2</sub>PtCl<sub>4</sub>). TON = n(H<sub>2</sub>)/n(photosensitizer). For the HER conditions, see the experimental section in the SI.

**Table 2.** Results for the photocatalytic H<sub>2</sub> evolution using each photosensitizer.

Photosensitizer	TOF / h <sup>-1</sup>	Time / h	TON
Cu-TPAphen	1,800	96	19,000
Cu-TPSphen	330	46	6,500
Cu-DMAphen	130	48	3,200
Cu-Pphen	130	46	2,000
Cu-BzNphen	160	24	590
Cu-phen	20	43	200
Ru(bpy) <sub>3</sub> <sup>2+</sup>	30	6	39
Ir(ppy) <sub>2</sub> (bpy) <sup>+</sup>	310	17	650

In summary, we have successfully synthesized a series of  $[\text{Cu}^{\text{I}}(\text{P}^{\wedge}\text{P})(\text{N}^{\wedge}\text{N})]^+$  photosensitizers to find that the *tert*-amine substitution on N<sup>^</sup>N ligand generated ILCT excited states to give outstanding absorption and excited state lifetime, which cooperatively increased the photocatalytic HER activity. Remarkable TON value of 19,000 was demonstrated for the Cu-TPAphen which is even better than those of the noble metal complex sensitizers reported so far.

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**Keywords:** hydrogen production • copper • photocatalysis • photosensitizer • water reduction

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