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Strong Visible Light-Absorbing Cuprous Sensitizers for Dramatically Boosting Photocatalysis

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Abstract: Developing strong visible-light-absorbing (SVLA) earth-abundant photosensitizers (PSs) for significantly improving the utilization of solar energy is highly desirable, yet it remains a great challenge. Herein, we adopt a through-bond energy transfer (TBET) strategy by bridging boron dipyrromethene (Bodipy) and a Cu(I) complex with an electronically conjugated bridge, resulting in the first SVLA Cu(I) PSs (**Cu-2** and **Cu-3**). **Cu-3** possesses an extremely high molar extinction coefficient of 162260 $M^{-1}cm^{-1}$ at 518 nm, over 62 times higher than that of traditional Cu(I) PS (**Cu-1**). Remarkably, the photooxidation activity of **Cu-3** is substantially greater than that of **Cu-1** and noble-metal PSs ($Ru(bpy)_3^{2+}$ and $Ir(ppy)_3^{+}$) for both energy- and electron-transfer reactions. Femto- and nanosecond transient absorption and theoretical investigations demonstrate that a "ping-pong" energy-transfer process in **Cu-3** involving a forward singlet TBET from Bodipy to the Cu(I) complex and a backward triplet-triplet energy transfer greatly contributed to the long-lived and Bodipy-localized triplet excited state.

Introduction

Photosensitizers (PSs) have been widely used as light-harvesting molecules in both natural and artificial photosynthetic systems for efficient solar energy conversion.[1-3] In recent decades, noble-metal complexes have been widely explored as PSs owing to their fascinating photophysical and photochemical properties.[4-9] In this field, Ru(II),[10-15] Ir(III),[16-19] and Pt(II),[20-23] complexes with long-lived excited states have been widely used for intermolecular energy or electron transfers to promote photocatalysis.[24-26] In this field, we have tried to introduce ^{3}IL-type Ir and Ru-PSs with long-lived excited state into photocatalytic systems for boosting H_2 production.[18,25] Unfortunately, their high cost and ultra-low content in Earth's crust make them unsuitable for meeting the requirements of long-term and large-scale applications.[24,27,28] Therefore, increasing attention has been paid to exploring earth-abundant transition-metal PSs.[29-32] Of particular interest are iron and copper due to their low costs and toxicities.[29,33-36] Iron complexes, such as $[Fe(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine) and relevant polypyridyl coordination compounds, have been designed and synthesized; however, they are rarely used as PSs as their ultrashort excited state lifetimes are in the picosecond range.[29,37] Copper(I) complexes, such as copper(I) bis-phenanthroline (Phen) complex, can give a relatively long-lived ^{3}MLCT state (metal-to-ligand charge transfer, $\pi_M \rightarrow \pi_L^*$) up to the μs range via efficient intersystem crossing (ISC), highlighting their potential for photochemical reactions.[38-41] However, these copper PSs usually present weak visible-light-harvesting abilities (< 3000 $M^{-1}cm^{-1}$), leading to much poorer catalytic activities relative to those of traditional noble-metal PSs, such as $Ru(bpy)_3^{2+}$(**Ru-1**) and $Ir(ppy)_3^{+}$(**Ir-1**) (ppy = 2-phenylpyridine).[38-42] Thus, rationally designing and synthesizing highly active copper(I) PSs with strong visible-light-absorbing (SVLA) ability and long excited state lifetimes is an urgent task but it remains a great challenge.

Through-bond energy transfer (TBET) has been regarded as an efficient strategy for intramolecular energy-transfer; it requires an electronically conjugated bridge to link the donor and acceptor in a noncoplanar manner (Scheme 1).[43-45] Remarkably, the TBET process is not limited by spectral overlap, which plays a key role in determining the efficiency of the fluorescence resonance energy-transfer process (FRET).[1,44,45] As a result, TBET can dramatically expand the possible molecular designs with the potential for efficient intramolecular energy transfer.[46] However, TBET has never been applied to enhance the visible-light-harvesting ability of earth-abundant transition-metal PSs. To achieve SVLA PSs with long-lived excited state via a TBET process, the following key factors are essential: (i) a donor with SVLA ability, (ii) an acceptor with efficient ISC ability, (iii) an acceptor with a lower singlet-state energy level compared to that of the donor and (iv) a noncoplanar electronically conjugated bridge between the donor and acceptor (Scheme 1).

In this work, for the first time, we adopted the TBET strategy to rationally design and synthesize SVLA cuprous Phen sensitizers by introducing a SVLA boron dipyrromethene (Bodipy) as an energy donor to a Cu(I) complex (Scheme 1). The Bis-(2,9-diphenyl-1,10-Phen) copper(I) complex with efficient ISC (ca. 100 %) ability (triplet state energy level of 1.82 eV), and a low singlet state energy level (ca. 2.10 eV) was used as the ideal spin convertor and energy acceptor. The careful coupling of Bodipy with Cu(I)-Phen results in two SVLA cuprous PSs (**Cu-2** and **Cu-3**). Furthermore, a "ping-pong" energy-transfer process was first observed in these Cu(I) PSs (**Cu-2** and **Cu-3**) with a forward singlet TBET from the Bodipy to the Cu(I) complex and a backward triplet-triplet energy transfer (TTET).[47] This process also contributes substantially to achieving the long-lived excited-states for **Cu-2** and **Cu-3** (27.2 μs for **Cu-3** and 33.8 μs for **Cu-2**), which are approximately 100 and 125 times longer than that of **Cu-1** (0.27 μs for **Cu-1**). As a result, the superior SVLA ability, long-lived excited-state and efficient intramolecular energy transfer of **Cu-3** can facilitate photocatalysis for both energy- and electron-transfer reactions. Its performance for photooxidation of 1,5-dihydroxynaphthalene (DHN) was significantly enhanced, ca. 69.2, 14.8 and 15.7 times higher than those of **Cu-1**, and noble-metal PSs **Ru-1** and **Ir-1**, respectively.

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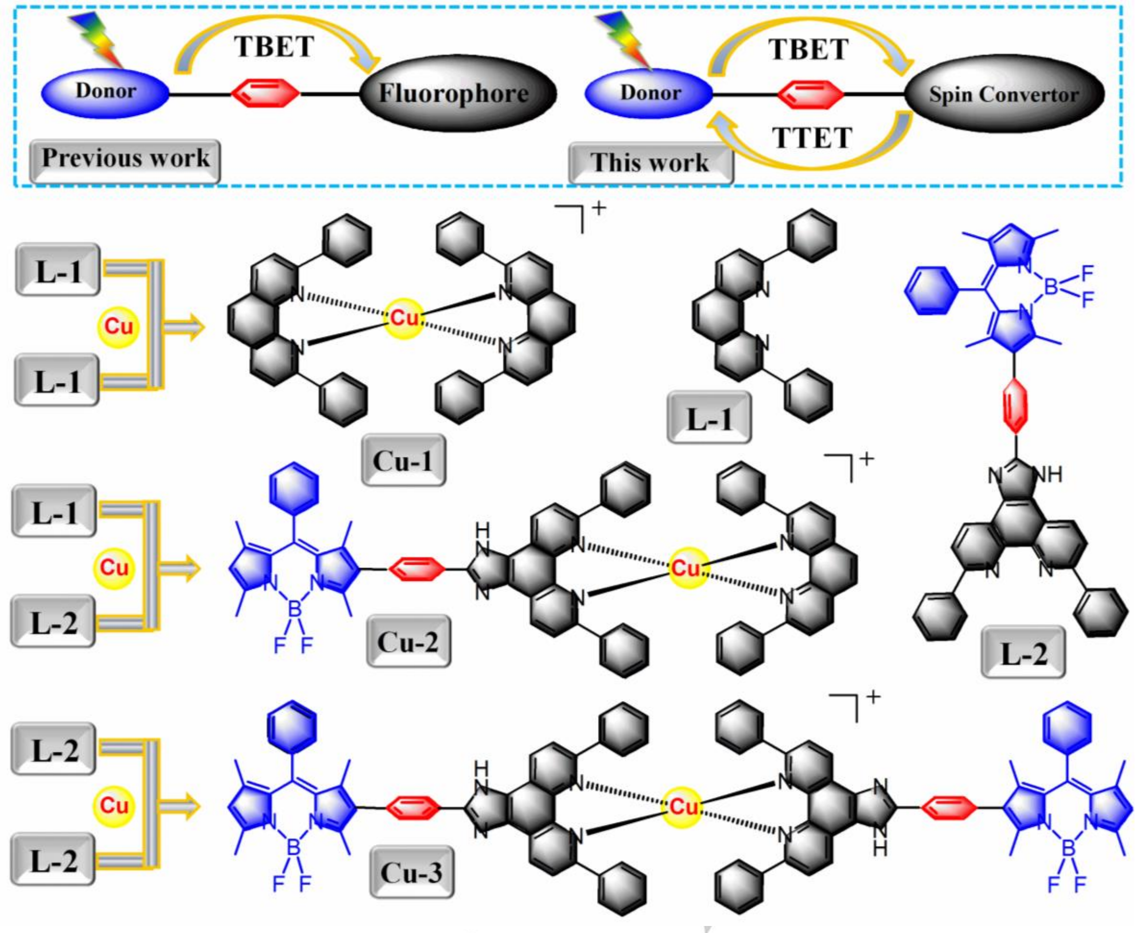

Scheme 1. Through-bond energy transfer cassettes (up) and the assembly process (down) of **Cu-1 - Cu-3** and the structure of **L-1** and **L-2**.

Results and Discussion

The details of the synthetic process are shown in Scheme 1 and scheme S1. In this process, **Cu-1**, **Cu-2** and **Cu-3** can be facilely prepared by reactions of $Cu(CH_3CN)_4PF_6$ with **L-1**, the mixture of **L-1** and **L-2**, and **L-2**, respectively. Both intermediates (**L-1** and **L-2**) and the Cu(I) complexes (**Cu-1**-**Cu-3**) were well defined and characterized by NMR spectroscopy and mass spectrometry (Figure S1-S21). Notably, a benzene ring was used as the electronically conjugated bridge to link the Bodipy and Cu(I) complex (for **Cu-2** and **Cu-3)**. The ground-state structures of these Cu(I) PSs, optimized by DFT calculations, show significant torsion between Bodipy and the Phen ligand around the Cu(I) center, which would allow efficient TBET from Bodipy to the Cu(I) complex (Figure S22).

In recent decades, much attention has been paid to exploring visible-light-harvesting copper complexes to enhance the utilization of solar energy.[48,49] Herein, Cu(I) PSs with SVLA ability were first achieved with high molar extinction coefficients of 79876 $M^{-1}cm^{-1}$ for **Cu-2** and 162260 $M^{-1}cm^{-1}$ for **Cu-3** at 518 nm, and these are 30.8 and 62.5-fold higher than that of **Cu-1** (2595 $M^{-1}cm^{-1}$ at 443 nm), respectively (Figure 1, S23 and Table S1-S2). To evaluate their intramolecular energy-transfer efficiencies, the ground-state absorption and photoluminescence spectra of **Cu-1**, **Cu-2**, **Cu-3** and **L-2** were compared in detail (Figure 1a, 1b and S24). As shown in Figure 1b, **L-2** exhibits a strong fluorescence emission peak at 550 nm, and this peak is almost completely quenched in **Cu-2** and **Cu-3** under the same conditions, which indicates an efficient energy or electron transfer from Bodipy to the Cu(I) coordination center. Furthermore, the emission intensities of **Cu-2** and **Cu-3** at 700 nm obviously increase with the introduction of Bodipy upon selective excitation of the Bodipy ligand, which preliminarily confirmed the efficient energy transfer from Bodipy to the Cu(I) center (Figure S25), demonstrating efficient TBET processes in these two complexes. Furthermore, the emission of **Cu-2**, phenyl-Bodipy (**Ph-Bodipy**), and the mixture of **Cu-1**/**Ph-Bodipy** were compared with optically matched solutions at the same absorbance (Figure S25). As shown in Figure S25, both Bodipy and the mixed system show a strong emission peak with similar emission intensity at around 539 nm, however, the emission of Bodipy part in **Cu-2** was almost quenched completely. This result further confirmed that the excitation energy of the Bodipy unit could be efficiently transferred to Cu(I) coordination center in **Cu-2**. This conclusion was further supported by the well-matched absorption and excitation spectra of **Cu-2** and **Cu-3** (Figure S26).

Femtosecond transient absorption experiments were further performed to track the TBET process of **Cu-3** (Figure 1c). Upon excitation at 510 nm, the bleaching peak at approximately 519 nm for **L-2** went back to zero, and its recovery was fitted to 1.3 ns, which has the same order of magnitude as that of the Bodipy chromophore, and this recovery can be attributed to the depletion of its ground state (Figure S27-S28). For **Cu-3**, the

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decay of the bleaching peak at 519 nm was determined to be 33.6 ps, which is much faster than that of **L-2**. In addition, the weak bleaching at approximately 472 nm emerged, which could be attributed to the formation of a singlet state in the Cu(I) center. The TBET process thus provides a viable pathway for efficient and fast singlet energy transfer, which will facilitate the use of all the excitation energy.

To uncover the properties of the triplet excited states, nanosecond time-resolved transient absorption spectra of Cu(I) PSs were acquired (Figure 1d, 1e and S29). Upon pulsed laser excitation at 532 nm, **Cu-1** presents a bleaching band between 420 nm and 480 nm and a positive absorption band between 480 nm and 650 nm, which indicates that **Cu-1** has a typical ^{3}MLCT excited state.[48] Both **Cu-2** and **Cu-3** exhibit a bleaching peak at 518 nm, consistent with the ground-state absorption of Bodipy, and two positive peaks at approximately 445 and 680 nm, corresponding to the triplet state absorption of Bodipy, indicating a Bodipy-localized triplet state for **Cu-2** and **Cu-3**. Notably, as the triplet state of Cu PSs switched from the ^{3}MLCT to ^{3}IL state, this process also contributes substantially to achieve the long-lived excited states for **Cu-2** and **Cu-3** (27.2 μs for **Cu-3** and 33.8 μs for **Cu-2**), which can efficiently promote intermolecular energy / electron transfer for efficient photocatalysis (Figure 1f and S29-S30).

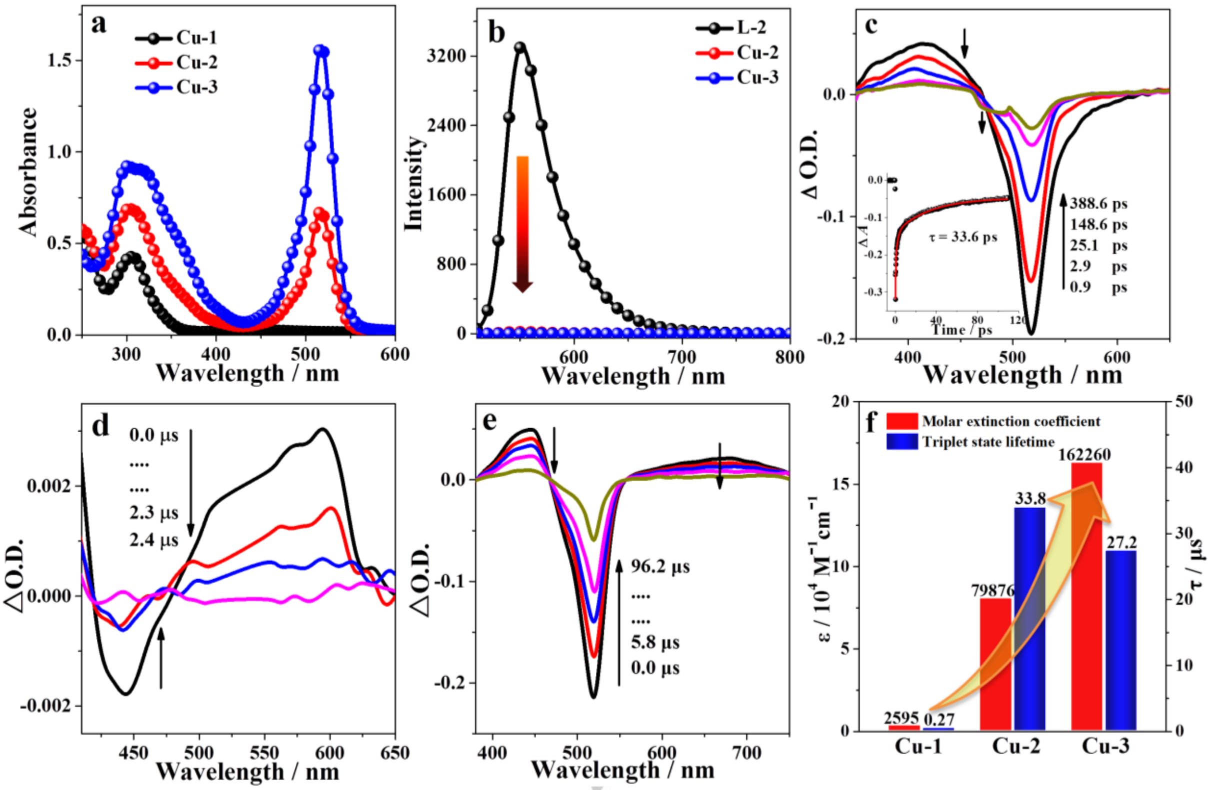

Figure 1. a) Ground-state absorption of **Cu-1**–**Cu-3**, b) Photoluminescence spectra of **L-2**, **Cu-2** and **Cu-3** with an excitation wavelength (λ_{ex}) of 500 nm, c) Femtosecond transient absorption spectra show the map of **Cu-3** and its decay (inset) at 519 nm, λ_{ex} = 532 nm. Nanosecond transient absorption spectra show the map of d) **Cu-1**, λ_{ex} = 532 nm and e) **Cu-3**, λ_{ex} = 532 nm, f) Comparison of the molar extinction coefficients and triplet state lifetimes of **Cu-1–Cu-3**.

To in-depth understand the excited state properties and intramolecular energy transfer process of these Cu(I) PSs, Gaussian calculations were performed using the DFT and time-dependent DFT (TDDFT) methods. The spin-density surfaces of Cu(I) PSs were calculated to reveal their triplet state population. As shown in (Figure 2), the triplet state of **Cu-1** was localized on the Cu-Phen coordination unit and that of **Cu-2** and **Cu-3** was mainly populated on the Bodipy ligand, which matched well with the results of transient absorption spectra (Figure 1 and S29).

In order to further unveil photophysical processes of **Cu-3**, UV–vis absorption and triplet excited state were rationalized based on optimized ground-state geometry by TDDFT method (Figure 3, S31-S32 and Table S3-S5). Two main transitions of the calculated UV−vis absorption were determined as $S_0 \rightarrow S_7$ and $S_0 \rightarrow S_{12}$, locating at 493 nm and 442 nm, respectively. In view of the analysis of molecular orbitals, the transitions of $S_0 \rightarrow S_7$ and $S_0 \rightarrow S_{12}$ were distributed on Cu(I) coordination center and Bodipy ligands in **Cu-3**, and the corresponding oscillator strengths (*f*) were estimated as 0.0062 and 1.4894, respectively. These results indicate the poor visible light absorption ability for Cu(I) center and SVLA ability for Bodipy ligands, which was well consistent with the experimental absorption spectra (Figure 1a and S23). Then the singlet excited state of **Cu-3** was populated via a vibrational relaxation (VR) process. The singlet excited state of Cu center was lower than that of Bodipy ligand, which was confirmed by emission spectra (Figure S24). Therefore, it's reasonable to transfer singlet excited state energy from Bodipy ligand to Cu(I) center via a TBET process. Owing to the heavy atom effect of Cu, an ISC process proceeded to afford the triplet state (T_7), which was localized at Cu(I) center.

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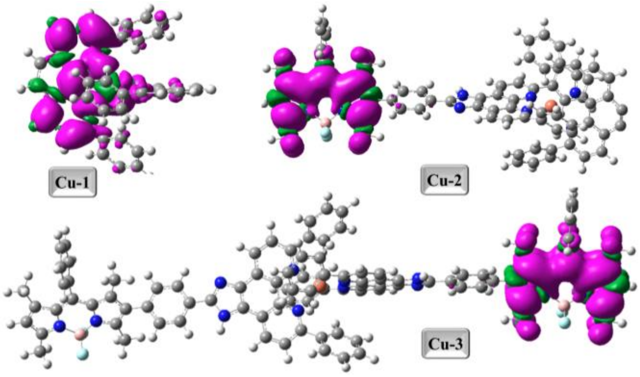

Figure 2. Spin-density surface of **Cu-1**-**Cu-3** at the triplet state, calculated at B3LYP/6–31G /LanL2DZ level with Gaussian 09W.

In addition, the T_1 and T_2 states were mainly populated on two Bodipy ligands, respectively, which were degenerate due to their similar energy level (1.53 eV for T_1 and 1.53 eV for T_2). The energy level of T_1 and T_2 was much lower than that of T_7, signifying that the triplet state energy transfer from Cu(I) center to Bodipy is feasible to afford a Bodipy localized triplet state. This result was in line with spin density surfaces and transient spectrum of **Cu-3** (Figure 1e and 2). As a result, the intramolecular photophysical processes of **Cu-3** were well clarified, revealing a forward TBET process from Bodipy to Cu(I) center and a backward TTET from Cu(I) center to Bodipy.Ultimately, the triplet state of **Cu-3** was populated on the Bodipy part, which further initiated the electron transfer for efficient redox reactions.

To assess the reliability of the theoretical results, Gaussian calculations were further performed with M06 (Figure S31 and S32, Table S4).[50] As a result, the theoretical results obtained with M06 were similar to that obtained with B3LYP, confirming that both the computational functions are reasonable in these multicomponent Cu-based complexes(Table S5).[30]

These advantages, including the superior SVLA ability, long excited lifetime and efficient intramolecular energy transfer, of **Cu-2** and **Cu-3** indicate their great potential for boosting photocatalysis. The sensitizing abilities of these earth-abundant Cu(I) PSs (**Cu-1** - **Cu-3**) were examined in the photooxidation of DHN to juglone (Figure 4, S33-S39, and Table S2). Juglone, an important moiety in drug molecules, irreversibly inhibits peptidyl-prolyl cis/trans isomerases in the parvulin family.[19] As shown in Fig. S33, upon excitation with a 175 W xenon lamp, the triplet state of **Cu-3** was populated via a series of intramolecular photophysical processes. Then, O_2 is sensitized into singlet oxygen ($^1O_2$) through a TTET process between **Cu-3** and O_2, which is highly dependent on the triplet lifetime of PSs. In the photooxidation reaction, the intensity of the absorption peak at 301 nm of DHN gradually decreased, and a new peak corresponding to the formation of juglone began to grow in at 427 nm.

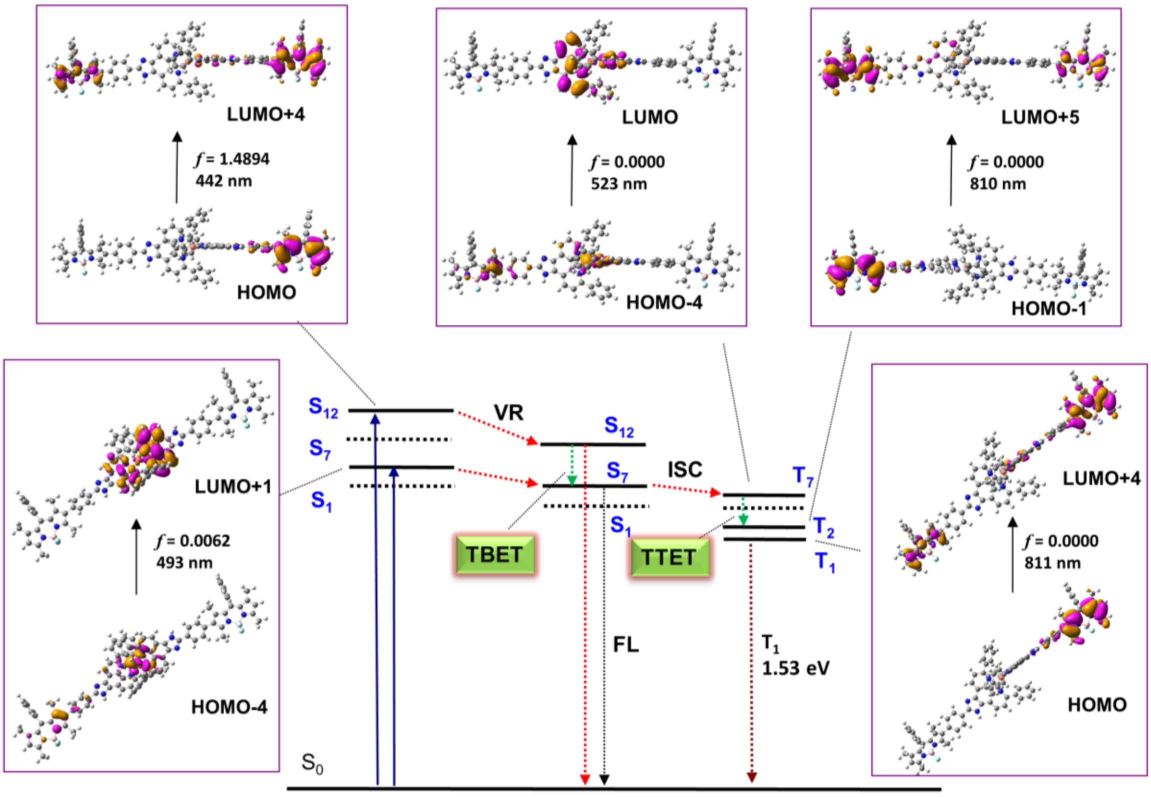

Figure 3. Selected frontier molecular orbitals involved in the excitation and triplet excited state of **Cu-3**. VR stands for vibrational relaxation. The left column is UV–vis absorption (based on ground state geometry), the middle column is the fluorescence emission, and the right column is the triplet excited state (based on ground state geometry). For clarity, only selected excited states are presented.

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As shown in (Figure 4), the change in the absorption peaks of DHN in the presence of **Cu-3** was much faster than that with **Cu-1**, indicating a much greater enhancement of the sensitizing ability with **Cu-3**. For comparison, the sensitizing ability of **Cu-2**, noble-metal PSs **Ru-1** and **Ir-1** and long triplet lifetime PS tetraphenylporphyrin (TPP) were also studied under the same conditions (Figure S34 and S35). Specifically, the conversion rate (K_{obs}) of **Cu-3** was as high as 5.2 × 10^{-2} min^{-1}, 69.2 times faster than that of **Cu-1**, and much higher than that of the noble-metal (**Ru-1**, **Ir-1)** and benchmark PSs (**TPP)**. The yield of juglone with **Cu-3** as PS can reach to over 80 % within 60 min, representing the highest yield among the above PSs (Figure 4d). In addition, singlet oxygen quantum yield of **Cu-3** was determined to be 0.85 with Rose Bengal as standard ($\Phi_\Delta = 0.80$). This value is higher than the benchmark PSs, such as Rose Bengal ($\Phi_\Delta = 0.80$) and TPP ($\Phi_\Delta = 0.62$), indicating that **Cu-3** is the state-of-the-art PS for $^1O_2$ generation. Notably, the absorption spectra of **Cu-1** - **Cu-3** or DHN alone remained constant throughout 1 h irradiation with a 175 W xenon lamp (Figure S37). These results indicate that complexes **Cu-1** - **Cu-3** exhibit an excellent photostability in the presence of dioxygen (Figure S37). Thus, these compounds are sufficiently stable under the catalytic conditions and **Cu-3** is indeed an efficient PS for driving this energy-transfer reaction.

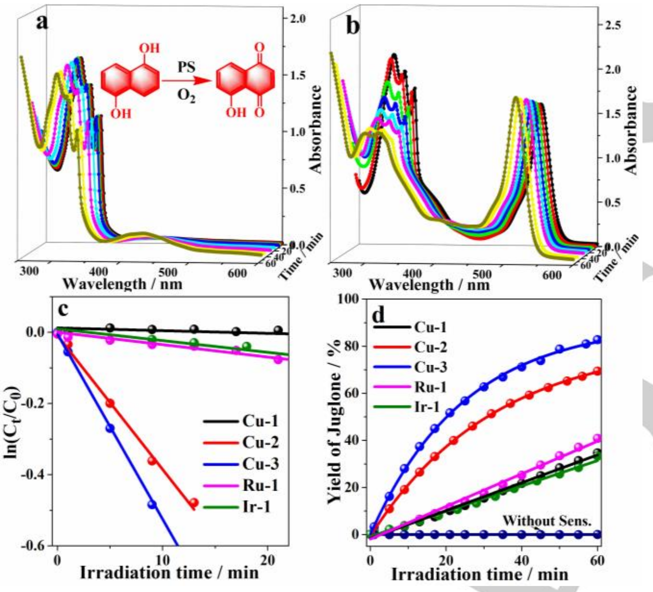

Figure 4. UV-vis absorption spectral changes in the photooxidation of DHN (0.15 mM) using a) **Cu-1** and b) **Cu-3** as singlet O_2 sensitizers, c) plot of $ln(C_t/C_0)$ against irradiation time (t), and d) the yields of juglone during 1 h irradiation with different PSs. c_{PS} = 10.0 μM (6.7 mol% vs DHN) in CH_2Cl_2/MeOH (9/1, v/v). Irradiated with a 175 W Xe lamp (17 mW•cm^2).

The photocatalytic aerobic oxidation of aromatic boronic acids to produce phenols represents a typical electron-transfer reaction,[51] and it was employed here to evaluate the sensitizing activity of these Cu-PSs (Figure 5 and S40-S41). As shown in Figure S40, the excited PSs accepted an electron from N,N-diisopropylethylamine (DIPEA) and then delivered the electron to O_2 to produce $O_2^{\bullet-}$. The efficiency of this reaction was determined by the visible-light-harvesting ability, excited-state lifetime and redox potential of each PS (Figure S42 and Table S6). Under ambient atmospheric conditions, the photocatalytic reaction of 4-formylphenyl boronic acid in the presence of **Cu-3** can efficiently produce 4-formylphenol in 97% yield within 4 h, and this yield is 4 times higher than that with **Cu-1** (20%). A trace amount of 4-formylphenol can be detected in the absence of Cu PSs, DIPEA, O_2 or light, indicating that all the above components are essential for the efficient photocatalytic aerobic oxidation of aromatic boronic acids (Figure 5a). Remarkably, **Cu-3** exhibits a broad substrate scope with over 80% yield for different aromatic boronic acids and borates, and it significantly outperformed the noble-metal PSs **Ru-1** and **Ir-1** (Figure 5b). As a result, **Cu-3** represents a state-of-the-art Cu(I) PSs for both energy- and electron-transfer reactions.

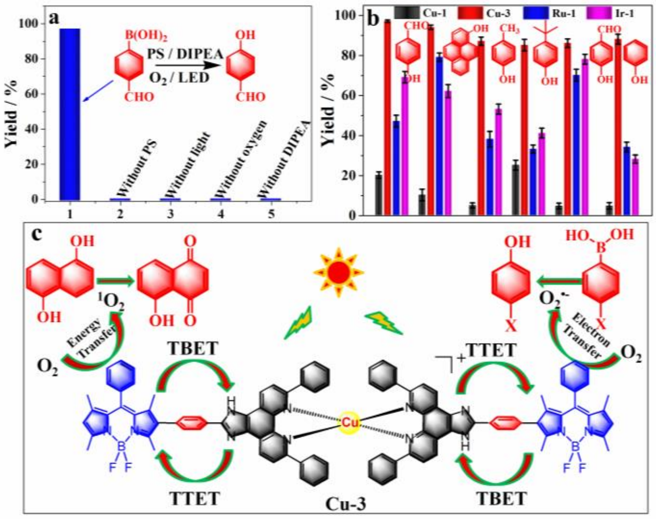

Figure 5. a) Photocatalytic oxidative hydroxylation of arylboronic acids to produce phenols. b) Yields of phenols obtained from different arylboronic acids in the presence of **Cu-1**, **Cu-3**, **Ru-1** and **Ir-1** upon irradiation with a 525 nm LED (23 mW•cm^{-2}). c_{PS} = 20.0 μM (0.12 mol% vs substrates). c) The "ping-pong" energy-transfer process in **Cu-3** for both energy- and electron-transfer reactions.

Conclusion

In this work, a TBET strategy was first extended to construct earth-abundant transition-metal PSs with SVLA ability and long excited-state lifetimes. Bodipy was carefully integrated into a Cu(I) complex to afford the first Cu-based PSs with SVLA abilities (**Cu-2** and **Cu-3**). Upon light irradiation, the SVLA Bodipy in **Cu-3** can harvest visible light to reach its singlet excited state and then efficiently deliver excitation energy to the Cu(I) coordination center via a TBET process. Then, an ISC process produces the triplet excited state of the Cu(I) center, which can further deliver energy to the Bodipy ligand by a back TTET process (Figure 5c). These advantages, the SVLA ability, long excited-state lifetime and efficient intramolecular energy transfer, of **Cu-2** and **Cu-3** can synergistically enhance photocatalysis. The catalytic performance of the earth-abundant PS **Cu-3** for both energy- and electron-transfer reactions significantly outperforms the **Cu-1** and noble-metal PSs **Ru-1** and **Ir-1**. Especially for the photooxidation of DHN, the conversion rate (K_{obs}) with **Cu-3** was 69.2, 14.8 and 15.7 times faster than those of **Cu-1**, **Ru-1** and **Ir-1**, respectively. This work provides a new strategy for developing earth-abundant multicomponent arrays with SVLA ability and long-lived excited states to facilitate photocatalysis for enhancing the solar energy utilization.

Acknowledgements

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Keywords: Cu(I) photosensitizier • strong visible light absorption • through-bond energy transfer • long-lived triplet state • photocatalysis

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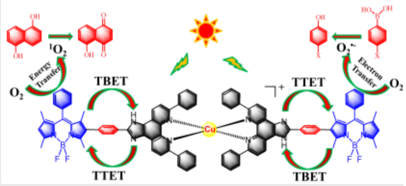
RESEARCH ARTICLE

Through-bond energy transfer strategy was first employed to construct low-cost copper(I) photosensitizer (PS) with strong visible light harvesting ability and long-lived excited state. Their performance for energy and electron-transfer reactions both dramatically outperforms that of traditional Cu-PS and noble-metal PSs ($Ru(bpy)_3^{2+}$ and $Ir(ppy)_3^{+}$).



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Strong Visible Light-Absorbing Cuprous Sensitizers for Dramatically Boosting Photocatalysis