Water-Assisted Highly Efficient Photocatalytic Reduction of CO₂ to CO with Noble Metal-Free Bis(terpyridine)iron(II) Complexes and an Organic Photosensitizer

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photocatalytic system, composed of bis(terpyridine)iron(II) complexes and an organic thermally activated delayed fluorescence compound, has been developed for selective reduction of CO₂ to CO with a maximum turnover number up to 6320, 99.4% selectivity, and turnover frequency of 127 min⁻¹ under visible–light irradiation in dimethylformamide/H₂O solution. More than 0.3 mmol CO was generated using 0.05 μ mol catalyst after 2 h of light irradiation. The apparent quantum yield was found to be 9.5% at 440 nm (180 mW cm⁻²). Control experiments and UV–vis–NIR spectroscopy studies further demonstrated that water strongly promoted the photocatalytic

cycle and terpyridine ligands rather than Fe(II) were initially reduced during the photocatalytic process.

INTRODUCTION

Solar-driven reduction of CO₂ to value-added chemical fuels has attracted extensive attention in the past decade.^{1–9} Among various catalysts for CO_2 reduction reaction (CO_2RR), molecular metal complexes have shown promising catalytic efficiencies not only under electrochemical conditions but also upon visible-light irradiation due to their diverse chemical structures via tuning ligands and metals.^{10–18} From the point of view of sustainable development, molecular photocatalysts based on earth-abundant metals are more appealing than noble metal complexes.^{19–26} Recently, non-precious metal complexes such as Fe,^{11,27–29} Co,^{30–33} Ni,^{34–36} Cu,³⁷ and Mn^{38–40} have been widely studied for photocatalytic CO₂RR. However, those non-precious molecular catalysts are usually used together with precious photosensitizers such as $[Ru(bpy)_3]^{2+}$. To construct fully noble metal-free photocatalytic systems for CO_2RR , a few luminescent Cu(I) complexes, Zn(II)complexes, and organic dyes have been developed as efficient photosensitizers for photocatalytic CO2RR.27,41-47 Besides molecular photosensitizers, quantum dots such as CuInS₂ and CdS are also employed as light-absorbing components for photocatalytic CO₂RR by combining molecular metal complexes.^{34,48} However, most noble metal-free photocatalytic systems display a moderate turnover number (TON) less than 3000 under optimal conditions even after longtime irradiation. Therefore, it is still necessary to develop more efficient fully noble metal-free photocatalytic systems.

Tridentate ligands based on 2,2':6',2''-terpyridine (tpy) and their metal complexes have been widely studied in a large range of research fields.⁴⁹⁻⁵² Some terpyridine-based metal

complexes have been developed for CO₂RR. Initially, they were used for electrocatalytic CO₂RR. For example, Meyer and coworkers have utilized novel terpyridine–Ru(II) complexes typically as $[Ru^{II}(tpy)(bpy)(S)]^{2+}$ for electrocatalytic reduction of CO₂ since the 1980s.^{53,54} They found that ligands such as tpy and bpy instead of Ru^{II} were reduced during electrocatalytic processes. Abruna et al. developed a series of terpyridine complexes based on first-row transition metals including Fe(II), Co(II), and Ni(II) in the late 1980s and early 1990s.55 ⁻⁵⁷ Electropolymerized films of metal terpyridine complexes exhibited moderate catalytic efficiencies toward the reduction of CO2. Recently, Fontecave and coworkers investigated the application of $[M(tpy)_2]^{2+}$ complexes (M = Fe, Co, Ni, Cu, Zn, and Mn) for homogeneously electrocatalytic CO₂RR in 2014.⁵⁸ They found that $[Co(tpy)_2]^{2+}$ and $[Ni(tpy)_2]^{2+}$ showed efficient catalytic activity with relatively low Faradic efficiencies, while $[Fe(tpy)_2]^{2+}$ almost exhibited no catalytic efficiency. However, Ortiz-Frade et al. found that Febased tpy complex $[Fe(tpy)_2]^{2+}$ was electrochemically active under a CO₂ atmosphere even though it had no open coordination site in 2017.59 The different results obtained by them are probably due to the different electrochemical potential window they used. Lately, solar-driven CO₂

TON: 6320

TOF: 127 min⁻¹

Seletivity: 99.4%

AQY: 9.5% ter-assisted CO₂RR

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Received: November 30, 2020 Published: February 21, 2021



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ACS Publications

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reduction systems with tpy-based metal complexes have been developed by the group of Reisner, where they combined Ni(II) and Co(II) complexes with CdS QDs and SilTiO₂ in water.^{34,60} The two light-driven systems displayed TONs less than 400. We recently found a terpyridine–Fe(III) complex that showed impressive photocatalytic efficiency with a TON of 2250 when an organic thermally activated delayed fluorescence (TADF) compound **4CzIPN** was employed as the photosensitizer.⁶¹ However, the apparent quantum yield (AQY) is relatively low (2.04%). More importantly, further studies including roles of solvent water and ligands in the photocatalytic cycle are much in demand for designing more efficient photocatalysts.

Herein, we report a noble metal-free photocatalytic system for CO₂ reduction using *bis*(terpyridine)iron(II) complexes as catalysts and an organic TADF dye **4CzIPN** as a photosensitizer in dimethylformamide (DMF)/H₂O (v/v = 3:2) solution (Figure 1). It is found that the Fe(II) complex



Figure 1. Chemical structures of photosensitizer 4CzIPN and bis(terpyridine)iron(II) complexes abbreviated as Fe(Ntpy)₂, Fe-(Htpy)₂, and Fe(Cltpy)₂, respectively.

 $Fe(Ntpy)_2$ bearing electron-donating groups displayed the highest TON up to 6320 with 99.4% selectivity and a TOF of 127 min⁻¹ in the first 20 min. The AQY was estimated to be 9.5%. More importantly, we found that the photocatalytic process was strongly promoted by water and initiated through the reduction of terpyridine ligands. To the best of our knowledge, such a highly efficient non-precious visible-light-driven system for CO₂RR using molecular photocatalysts has rarely been reported.

RESULTS AND DISCUSSION

The three bis(terpyridine)iron(II) complexes including Fe-(Ntpy)₂, Fe(Htpy)₂, and Fe(Cltpy)₂ were readily available through the reaction between FeCl₂ 4H₂O and corresponding terpyridine ligands such as Ntpy, Htpy, and Cltpy. They were designed to be similar in chemical structure but mainly different in the group at the 4' position of the terpyridine skeleton. This is to explore the substituent effect on the catalytic efficiency of bis(terpyridine)iron(II) complexes. It is worth noting that bis(terpyridine)iron(II) complexes have no open coordination sites, which is different from the terpyridine-Fe(III) complex.⁶¹ We studied electronic transitions of bis(terpyridine)iron(II) complexes at a steady state by UV-vis-NIR spectroscopy. As shown in Figure 2a, these Fe(II) complexes exhibit a ligand-based absorption band around 325 nm and another shoulder band around 370 nm. $Fe(Ntpy)_2$ has a distinctive absorption peak at 406 nm due to intraligand charge transfer (ILCT) transition caused by the N,N-dimethyl group in the ligand Ntpy. The relatively strong bands at 587, 574, and 572 nm are assigned as metal-to-ligand charge transfer (MLCT) (Fe^{II} to terpyridine ligands)



Figure 2. (a) UV-vis-NIR absorption spectra of *bis*(terpyridine)iron(II) complexes $Fe(Ntpy)_2$, $Fe(Cltpy)_2$, and $Fe(Htpy)_2$ in DMF solution at room temperature. CV results of *bis*(terpyridine)iron(II) complexes (b) $Fe(Ntpy)_2$, (c) $Fe(Htpy)_2$, and (d) $Fe(Cltpy)_2$ under N₂ (black line) and CO₂ (red line) atmosphere at 100 mV s⁻¹ scan rate, respectively.

transitions of $Fe(Ntpy)_2$, $Fe(Cltpy)_2$, and $Fe(Htpy)_2$, respectively. The MLCT transitions around 580 nm are similar to other reported *bis*(terpyridine)iron(II) complexes.^{55,56,62-65}

Cyclic voltammetry (CV) experiments were further carried out to examine the catalytic activity of three bis(terpyridine)iron(II) complexes toward the reduction of CO₂. The reducing potentials of bis(terpyridine)iron(II) complexes and corresponding terpyridine ligands are collected in Table 1. As

Table 1. Partial Reducing Potentials of Bis(terpyridine)iron(II) Complexes, Ligands, and 4CzIPN in DMF Using SCE as a Reference^{*a*}

compounds	E (V) [$\Delta E_{\rm p}$ (mV)]	$E_{\rm red}(\rm CO_2)~(V)^b$
Fe(Ntpy) ₂	-1.34 [60], -1.43 [60], -2.15 [irr.]	-1.82
Fe(Cltpy) ₂	-1.22 [60], -1.32 [60], -2.08 [irr.]	-1.75
Fe(Htpy) ₂	-1.24 [60], -1.35 [60], -2.01 [110]	-1.78
Ntpy	-2.13 [90]	
Cltpy	-1.97 [irr.], -2.06 [66]	
Htpy	-2.05 [95]	
4CzIPN	-1.31 [77]	

^{*a*}Standard conditions: 1 mM compounds, 0.1 M Bu₄NPF₆, GC working electrode, Ag/AgCl reference electrode, and platinum plate counter electrode at 100 mV s⁻¹ scan rate at room temperature in N₂-saturated DMF solution. ^{*b*}Experiments were carried out in CO₂-saturated DMF solution.

shown in Figure 2 and Table 1, all *bis*(terpyridine)iron(II) complexes have three similar reducing processes. The potentials of $Fe(Ntpy)_2$ are more negative than those of $Fe(Htpy)_2$ and $Fe(Cltpy)_2$ which have the most positive potentials. This is probably due to the electron-donating *N*,*N*-dimethyl groups in $Fe(Ntpy)_2$ and electron-withdrawing Cl atom in $Fe(Cltpy)_2$. For $Fe(Ntpy)_2$, the potentials at -1.34 and -1.43 V are reversible with $\Delta E_p = 60$ mV, indicating two one-electron electrochemical processes. The two waves are not easy to be recognized through CV, but square wave voltammetry (SWV) experiment clearly confirms the two waves (Figure S1). They are attributed to the reduction of ligand Ntpy in comparison with other metal terpyridine

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Figure 3. Conditions: all reaction solutions were irradiated with visible light (3 W white LEDs, $\lambda = 420-650$ nm) irradiation for 120 min under a CO₂ atmosphere at room temperature. (a) TONs of products CO and H₂ using **Fe**(**Ntpy**)₂ (10 μ M), **4CzIPN** (50 μ M), and TEA (0.28 M) in 5 mL of DMF/H₂O solution with different fractions of water (0–70%). (b) TONs of products CO and H₂ using **Fe**(**Ntpy**)₂ (10 μ M), (c) TONs of products CO and H₂ using **Fe**(**Ntpy**)₂ (40 μ M), (c) TONs of products CO and H₂ using **Fe**(**Ntpy**)₂ (40 μ M), and TEA (0.28 M) in 5 mL of DMF/H₂O (v/v = 3:2) solution with different concentrations of **4CzIPN** (10–150 μ M). (c) TONs of products CO and H₂ using **Fe**(**Ntpy**)₂ (0–40 μ M). (d) TONs of products CO and H₂ with **Fe**(**Ntpy**)₂ (10 μ M), **Fe**(**Cltpy**)₂ (10 μ M), and **Fe**(**Htpy**)₂ (10 μ M) in the presence of **4CzIPN** (100 μ M), TEA (0.28 M) in 5 mL of DMF/H₂O (v/v = 3:2) solution. (e) Time course of TON (CO and H₂) using **Fe**(**Ntpy**)₂ (10 μ M), TEA (0.28 M), and **4CzIPN** (100 μ M, blue) or [Ru(bpy)₃]²⁺ (100 μ M, black) in 5 mL of DMF/H₂O (v/v = 3:2) solution. The blue line was carried out with **Fe**(**Ntpy**)₂ (10 μ M), TEA (0.28 M), and **4CzIPN** (100 μ M) in 5 mL of CH₃CN/H₂O (v/v = 3:2) solution. (f) TON_{CO} of irradiated reaction solution containing **Fe**(**Ntpy**)₂ (10 μ M), TEA (0.28 M), and **4CzIPN** (100 μ M, black bar), **Fe**(**Ntpy**)₂ (10 μ M, red bar), ligand **Ntpy** (20 μ M, blue bar) for another 120 min of light irradiation under a CO₂ atmosphere at room temperature.

complexes.^{54–56,66} They are not likely to be assigned as Fe(II)centered potentials. Additionally, we found the linear relationship between currents and square root of scan rate for the two reducing processes from 100 to 800 mV s⁻¹ (Figure S2). The third irreversible reduction signal at -2.15 V is similar to that of the free ligand Ntpy. Under a CO₂ atmosphere, the current obviously increased at -1.82 V for $Fe(Ntpy)_{2}$, suggesting its catalytic activity toward the reduction of CO₂. The potentials of CO₂ reduction for $Fe(Cltpy)_2$ (-1.75 V) and $Fe(Htpy)_2$ (-1.78 V) are more positive than for $Fe(Ntpy)_2$, in line with their chemical structures. Therefore, all three Fe(II) complexes could be probably used as efficient catalysts for photocatalytic CO₂RR when cooperating with a suitable photosensitizer. Nevertheless, the direct reduction of these *bis*(terpyridine)iron(II) complexes around -1.82 V for photocatalytic CO₂ reduction might be difficult because such strong reducing photosensitizer is really rare under light-driven conditions. More importantly, the ligand could be reduced prior to -1.82V. Hence, a ligand-based reduction process might play an important role when *bis*(terpyridine)iron(II) ligands are utilized for photocatalytic CO₂RR.

Inspired by the catalytic activities of bis(terpyridine)iron(II) complexes toward CO₂ reduction, we then employed them as photocatalysts for photocatalytic CO₂RR. The organic TADF compound **4CzIPN** was used here as the photosensitizer (P) due to its suitable excited-state lifetime and redox potentials.^{67,68} Triethylamine (TEA) was used as the sacrificial electron donor, which could reduce the excited state of **4CzIPN** (P*) to generate reduced **4CzIPN** (P⁻) under visiblelight irradiation. Light sources are white LEDs (3 W, $\lambda = 420-$ 650 nm). The potential of reduced **4CzIPN** is close to ligandbased potentials of *bis*(terpyridine)iron(II) complexes, which is helpful for electron-transfer process between them. As can be seen from Figure 3a, a higher TON_{CO} could be obtained in the mixed DMF/H_2O solution than in DMF. Therefore, it can be concluded that water strongly promoted the catalytic process and the highest TON_{CO} was reached in the mixed DMF/H₂O (v/v = 3:2) solution. When the fraction of water became higher, we observed insoluble aggregates of the photosensitizer 4CzIPN and the TON_{CO} decreased sharply. The amounts of 4CzIPN and $Fe(Ntpy)_2$ also had a big effect on the catalytic efficiency of the photocatalytic process (Figure 3b,c). It is worth noting that H₂ evolution was very low no matter what the reaction conditions were. The optimal concentration of 4CzIPN was 100 μ M when the used Fe(Ntpy)₂ was 10 μ M. Under optimal conditions, TON_{CO} was estimated to be 6320 and TON of H₂ was 35 upon visible-light irradiation for 120 min. Only a trace amount of formic acid was detected by HPLC. Selectivity of this photocatalytic system was then estimated to be 99.4% (CO over H_2), which is encouraging for fully noble metal-free photocatalytic CO₂RR in the presence of water. Control experiments showed that light, $Fe(Ntpy)_{2}$, 4CzIPN, and TEA are all indispensable for efficient photocatalytic reduction of CO₂ to CO in this work. Isotope labeling experiment with ³CO₂ confirmed the generation of ¹³CO during the photocatalytic process (Figure S3).

 $Fe(Cltpy)_2$ and $Fe(Htpy)_2$ also displayed good selectivity toward CO generation but TONs were found to be 2780 and 4500, respectively (Figure 3d). This seems to contradict the CV potentials of $Fe(Ntpy)_2$, $Fe(Cltpy)_2$, and $Fe(Htpy)_2$ (Table 1). Since $Fe(Cltpy)_2$ has the most positive reduction potentials, it should be more feasible to receive electrons from reduced photosensitizer (P⁻) than $Fe(Ntpy)_2$, spontaneously resulting in higher catalytic efficiency. However, we indeed pubs.acs.org/IC



Figure 4. Conditions: all solutions were irradiated with white LEDs (3 W, $\lambda = 420-650$ nm) at room temperature. (a) UV-vis-NIR absorption spectra of DMF/H₂O (v/v = 3:2) solution containing **Fe**(**Ntpy**)₂ (10 μ M) upon light irradiation for 0–9 min under a N₂ atmosphere. (b) UV-vis-NIR absorption spectra of DMF/H₂O (v/v = 3:2) solution containing **4CzIPN** (50 μ M) and TEA (93 mM) upon light irradiation for 0–120 s under a N₂ atmosphere. (c) UV-vis-NIR absorption spectra of DMF solution containing **Fe**(**Ntpy**)₂ (10 μ M), **4CzIPN** (50 μ M), and TEA (93 mM) upon light irradiation for 0–300 s under a N₂ atmosphere. (d) UV-vis-NIR absorption spectra of DMF/H₂O (v/v = 3:2) solution containing **Fe**(**Ntpy**)₂ (10 μ M), **4CzIPN** (50 μ M), and TEA (93 mM) upon light irradiation for 0–200 s under a N₂ atmosphere. The yellow line is the spectrum of irradiated solution that was put in the dark for another 480 s (e) UV-vis-NIR absorption spectra of DMF solution containing **Fe**(**Ntpy**)₂ (10 μ M), **4CzIPN** (50 μ M), and TEA (93 mM) upon light irradiation for 0–340 s under a CO₂ atmosphere. (f) UV-vis-NIR absorption spectra of DMF/H₂O (v/v = 3:2) solution containing **Fe**(**Ntpy**)₂ (10 μ M), and TEA (93 mM) upon light irradiation for 0–340 s under a CO₂ atmosphere.

found that $Fe(Ntpy)_2$ is much more efficient for CO_2RR . Therefore, we speculate that electron donating *N*,*N*-dimethyl groups in $Fe(Ntpy)_2$ are probably beneficial to enhance the nucleophilicity of Fe(II) center, which is more essential for the whole catalytic cycle.

It was further evidenced that both photosensitizer and solvent were important to achieve efficient photocatalytic TONs. As shown in Figure 3e, TON_{CO} was only 19 when $[\operatorname{Ru}(\operatorname{bpy})_3]^{2+}$ was used instead of **4CzIPN**. This result suggests that **4CzIPN** could be used as a more efficient photosensitizer than $[\operatorname{Ru}(\operatorname{bpy})_3]^{2+}$. It is probable that the reduced photosensitizer (P⁻) with negative charge may surround the positive complex Fe(Ntpy)₂ through electrostatic interaction, making electron transfer more feasible. When the solvent DMF was replaced by CH₃CN, TON_{CO} decreased to 992. However, CH₃CN has been used as a solvent for efficient photocatalytic CO₂RR with various iron complexes, suggesting that CH₃CN may hinder a certain crucial step of the photocatalytic cycle which still requires further investigation in detail.^{17,69}

Although this photocatalytic system displayed relatively high TON up to 6320, the catalytic reaction mostly ceased after 120 min of irradiation. The TOF was estimated to be 127 min⁻¹ in the first 20 min under optimal conditions (Figure S4). Additionally, the AQY was estimated to be 9.5% under blue light (180 mW cm⁻², 440 nm) irradiation (see the Supporting Information), which is much higher than our previous work.⁶¹ To know more about quick shutoff of this catalytic process, we recorded the UV–vis–NIR spectrum of the irradiated reaction solution and found that the MLCT absorption band of **Fe(Ntpy)**₂ and characteristic absorption band of **Fe(Ntpy)**₂ and **4CzIPN** is responsible for the low durability of this photocatalytic system. However, the MLCT band at 587 nm obviously rose after the ligand **Ntpy** was added again into

the irradiated solution, suggesting that Fe(II) still existed even though the photocatalytic cycle stopped. These assumptions were further confirmed by adding reagents to the irradiated reaction solution for another 120 min of irradiation. As shown in Figure 3f, adding the photosensitizer 4CzIPN into the irradiated solution resulted in a $\mathrm{TON}_{\mathrm{CO}}$ of 36 due to the decomposition of $Fe(Ntpy)_2$. The TON_{CO} was 1021 when $Fe(Ntpy)_2$ was added, indicating that partial photosensitizer remained active after 120 min of irradiation. It should be noted that the addition of ligand Ntpy also rebooted the photocatalytic cycle with a TON_{CO} of 493. This result strongly revealed the existence of Fe(II) after the reaction ceased and the decomposition of $Fe(Ntpy)_2$ was probably caused by the side reaction of ligand Ntpy such as a reduction reaction which made Ntpy lose the ability to coordinate with Fe(II) and accept electrons from the reduced photosensitizer. As a result, we witnessed a higher TON_{CO} of 3667 when both 4CzIPN and ligand Ntpy were added into the irradiated solution together.

To further elucidate the photocatalytic process, UV–vis– NIR absorption spectroscopy was employed to monitor the reaction under a N₂ or CO₂ atmosphere (Figure 4). We recorded the absorption spectra of $Fe(Ntpy)_2$ in DMF and DMF/H₂O (v/v = 3:2), respectively. As shown in Figure 4a, the MLCT absorption band at 587 nm of $Fe(Ntpy)_2$ changed a little after 9 min of irradiation. A new tiny peak was observed at 960 nm in the mixed DMF/H₂O solution, while no such peak appeared in the DMF solution (Figure S6). Hence, it can be assumed that the new peak at 960 nm was originated from the interaction between H₂O and $Fe(Ntpy)_2$. A similar result was found when TEA was added into DMF/H₂O solution of $Fe(Ntpy)_2$, suggesting no redox reaction between $Fe(Ntpy)_2$ and TEA (Figure S7). We then investigated the absorption spectra of photosensitizer **4CzIPN** in the presence of TEA upon visible-light irradiation (Figure 4b). The absorption bands at 368 and 448 nm diminished quickly in 120 s, which was resulted from the reduction of excited-state 4CzIPN by TEA. We next studied UV-vis-NIR spectra of the solution containing $Fe(Ntpy)_2$, 4CzIPN, and TEA under a N_2 atmosphere. In the DMF solution (Figure 4c), the absorption bands decreased significantly below 500 nm, which were majorly due to the reduction of 4CzIPN by comparison with absorption spectra in Figure 4b. The MLCT peak of $Fe(Ntpy)_2$ at 587 nm disappeared and two new absorption bands at a longer wavelength (626 and 810 nm) rose, indicating that the MLCT transition between Fe(II) and neutral ligand Ntpy diminished. The two new bands at 626 and 810 nm are ascribed to $\pi^* - \pi^*$ transitions of radical anion ligand (Ntpy^{•-}) which was generated through the reduction of neutral ligand Ntpy by the photosensitizer P⁻, consistent with the reported spectroelectrochemical experiments and theoretical calculations on $[Fe(tpy) (tpy^{\bullet-})]^+, {}^{64} [Ni(tpy)(tpy^{\bullet-})]^+, {}^{70}$ and $[Cr(tpy)(tpy^{-})]^{2+71}$ complexes by Braterman, Klein, and Wieghardt, respectively. The transformation of neutral ligand (Ntpy) to radical anion ligand (Ntpy^{•-}) upon light irradiation also explains why the MLCT peak of Fe(Ntpy), at 587 nm disappeared. More importantly, this further demonstrates that reduction of Fe(II) to Fe(I) by reduced photosensitizer (P⁻) is not available in this photocatalytic system, which is in accord with the assignments of ligand-based potentials in Figure 2 and Table 1. In the mixed DMF/H₂O (v/v = 3:2) solution (Figure 4d), absorption spectra changed similarly to that in the DMF solution and the MLCT band gradually decreased along with the rising bands at 626 and 810 nm, revealing the reduction of neutral ligand (Ntpy) and simultaneous generation of radical anion ligand (Ntpy^{•-}). It should be noted that the spectrum kept a similar shape and MLCT peak could not recover after the irradiated solution was placed in the dark for another 480 s. Therefore, the radical anion ligand (**Ntpy**^{•-}) is relatively stable and the electron transfer between anion ligand and Fe(II) is negligible.

Under a CO₂ atmosphere, both spectra in DMF and DMF/ H₂O changed less than under a N₂ atmosphere. However, the spectra in DMF are similar for both atmospheres (Figure 4c,e). We could still see the bands assigned to the radical anion ligand (Ntpy^{•-}) at 626 and 810 nm under a CO₂ atmosphere in Figure 4e, suggesting that the electrons located in the anion ligand hardly transferred to reduce CO₂ and the photocatalytic cycle proceeded very slowly in DMF. This was further confirmed by the subsequent analysis of the headspace gas of the irradiated solution in Figure 4e through gas chromatography (GC) and only trace amount of CO was detected. On the contrary, no absorption bands of radical anion ligand (Ntpy^{•–}) were observed in the DMF/H₂O solution under a CO_2 atmosphere (Figure 4f), indicating that the electrons located in the anion ligand (Ntpy^{•-}) transferred to reduce CO₂ and the catalytic cycle proceeded smoothly. In fact, we found a significant generation of CO after analyzing the headspace gas in Figure 4f by GC. Although the MLCT band of Fe(Ntpy), at 587 nm gradually decreased in Figure 4f, it still kept most of the absorbance and did not disappear as shown in Figure 4c-e. The minor diminishment of the MLCT band at 587 nm could be ascribed to the binding with H_2O or CO_2 as well as partial cleavage of the Fe-N bond. The dramatically different results of the control experiments in Figure 4e,f show that water is beneficial for the electron transfer from radical

anion ligand (Ntpy^{•–}) to CO_2 , resulting in efficient reduction of CO_2 .

On the basis of the above results, it can be proposed that the photosensitizer 4CzIPN is reduced by electron donor TEA upon light irradiation. The reduced 4CzIPN is a moderate reductant which could further reduce terpyridine-based ligands in bis(terpyridine)iron(II) complexes. For example, the ligand Ntpy is reduced to generate radical anion Ntpy^{•-}, which is consistent with UV-vis-NIR absorption spectra in Figure 4ce. The electron localized on the reduced ligand may be further consumed for the reduction of CO₂. Such phenomenon that electrons on the reduced ligands were consumed for the reduction process has been studied in electrocatalytic CO₂ reduction reactions with polypyridyl-Ru(II) complexes by Meyer and coworkers.⁵³ The significance of water was revealed by replacing H₂O with D₂O in the photocatalytic reaction (Figure S8). We found the TOF in DMF/H_2O is a little higher than that in DMF/D_2O (TOFH₂O/TOFD₂O = 1.38). However, more experiments are required to elucidate the reaction mechanism in detail.

CONCLUSIONS

In summary, we have developed a noble metal-free photocatalytic system for the selective reduction of CO₂ to CO using bis(terpyridine)iron(II) complexes and an organic TADF photosensitizer in DMF/H2O solution. It is found that Fe(Ntpy)₂ bearing electron-donating groups is most efficient $(TON_{CO} = 6320, TOF_{CO} = 127 \text{ min}^{-1}, 99.4\%$ selectivity, and AQY = 9.5% at 440 nm) under optimal conditions, demonstrating substituent effect on the catalytic efficiency of molecular photocatalysts for CO₂ reduction. The TADF compound 4CzIPN was proved to be a promising photosensitizer and showed much better performance than the popular ruthenium photosensitizer $[Ru(bpy)_3]^{2+}$ in this work. We believe TADF photosensitizers will contribute more to the development for photocatalytic CO₂ reduction in the future. Terpyridine-based ligands were found to be reduced during photocatalytic process. It is also revealed that the catalytic reaction is strongly promoted by water. These results shed new light on designing molecular photocatalysts for CO₂ reduction.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c03503.

Experimental details; general synthetic route for bis-(terpyridine)iron(II) complexes $Fe(Ntpy)_{2}$, $Fe(Htpy)_{2}$, and $Fe(Cltpy)_{2}$; SWV result and CVs of $Fe(Ntpy)_{2}$ in DMF under a N₂ atmosphere; isotopic labeling experiment with ¹³CO2; TOF determination for photocatalytic CO₂RR with $Fe(Ntpy)_{2}$; UV–Vis–NIR absorption spectra; ¹H NMR spectrum of $Fe(Ntpy)_{2}$ in DMSO– d₆, $Fe(Htpy)_{2}$ in DMSO–d₆, and $Fe(Cltpy)_{2}$ in DMSO–d₆; and HR–ESI–MS spectrum of $Fe(Ntpy)_{2}$, $Fe(Cltpy)_{2}$, and $Fe(Htpy)_{2}$ (PDF).

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (21605013) and Natural Science Foundation of Ningbo (202003N4077).

REFERENCES

(1) Gao, W.; Bai, X.; Gao, Y.; Liu, J.; He, H.; Yang, Y.; Han, Q.; Wang, X.; Wu, X.; Wang, J.; Fan, F.; Zhou, Y.; Li, C.; Zou, Z. Anchoring of black phosphorus quantum dots onto WO₃ nanowires to boost photocatalytic CO_2 conversion into solar fuels. *Chem. Commun.* **2020**, *56*, 7777–7780.

(2) Zhou, J.; Cui, J.-X.; Dong, M.; Sun, C.-Y.; You, S.-Q.; Wang, X.-L.; Zhou, Z.-Y.; Su, Z.-M. Synergetic effect of H^+ adsorption and ethylene functional groups of covalent organic frameworks on the CO₂ photoreduction in aqueous solution. *Chem. Commun.* **2020**, *56*, 7261–7264.

(3) Dalle, K. E.; Warnan, J.; Leung, J. J.; Reuillard, B.; Karmel, I. S.; Reisner, E. Electro- and Solar-Driven Fuel Synthesis with First Row Transition Metal Complexes. *Chem. Rev.* **2019**, *119*, 2752–2875.

(4) Ma, B.; Chen, G.; Fave, C.; Chen, L.; Kuriki, R.; Maeda, K.; Ishitani, O.; Lau, T.-C.; Bonin, J.; Robert, M. Efficient Visible–Light–Driven CO_2 Reduction by a Cobalt Molecular Catalyst Covalently Linked to Mesoporous Carbon Nitride. *J. Am. Chem. Soc.* **2020**, *142*, 6188–6195.

(5) Cheng, X.; Zhang, J.; Tan, X.; Zheng, L.; Tan, D.; Liu, L.; Chen, G.; Wan, Q.; Zhang, B.; Zhang, F.; Su, Z.; Han, B.; Zhang, J. Improved photocatalytic performance of metal–organic frameworks for CO₂ conversion by ligand modification. *Chem. Commun.* **2020**, *56*, 7637–7640.

(6) Ji, S.; Qu, Y.; Wang, T.; Chen, Y.; Wang, G.; Li, X.; Dong, J.; Chen, Q.; Zhang, W.; Zhang, Z.; Liang, S.; Yu, R.; Wang, Y.; Wang, D.; Li, Y. Rare-Earth Single Erbium Atoms for Enhanced Photocatalytic CO₂ Reduction. *Angew. Chem., Int. Ed.* **2020**, *59*, 10651–10657.

(7) Wang, Z. J.; Song, H.; Liu, H.; Ye, J. Coupling of Solar Energy and Thermal Energy for Carbon Dioxide Reduction: Status and Prospects. *Angew. Chem., Int. Ed.* **2020**, *59*, 8016–8035.

(8) Roy, S.; Reisner, E. Visible–Light–Driven CO₂ Reduction by Mesoporous Carbon Nitride Modified with Polymeric Cobalt Phthalocyanine. *Angew. Chem., Int. Ed.* **2019**, *58*, 12180–12184.

(9) Lei, K.; Wang, D.; Ye, L.; Kou, M.; Deng, Y.; Ma, Z.; Wang, L.; Kong, Y. A Metal–Free Donor–Acceptor Covalent Organic Framework Photocatalyst for Visible–Light–Driven Reduction of CO_2 with H₂O. *ChemSusChem* **2020**, *13*, 1725–1729.

(10) Marianov, A. N.; Jiang, Y. Covalent ligation of Co molecular catalyst to carbon cloth for efficient electroreduction of CO_2 in water. *Appl. Catal., B* **2019**, *244*, 881–888.

(11) Sakaguchi, Y.; Call, A.; Cibian, M.; Yamauchi, K.; Sakai, K. An noble-metal-free system for light-driven CO₂ reduction to CO

using a pyridinophane iron catalyst. *Chem. Commun.* **2019**, *55*, 8552–8555.

(12) Wang, X.; Goudy, V.; Genesio, G.; Maynadié, J.; Meyer, D.; Fontecave, M. Ruthenium-cobalt dinuclear complexes as photocatalysts for CO₂ reduction. *Chem. Commun.* **2017**, *53*, 5040–5043.

(13) Rohacova, J.; Ishitani, O. Rhenium(I) trinuclear rings as highly efficient redox photosensitizers for photocatalytic CO_2 reduction. *Chem. Sci.* **2016**, *7*, 6728–6739.

(14) Elgrishi, N.; Chambers, M. B.; Wang, X.; Fontecave, M. Molecular polypyridine-based metal complexes as catalysts for the reduction of CO_2 . *Chem. Soc. Rev.* **2017**, *46*, 761–796.

(15) Brown, C. M.; Auvray, T.; DeLuca, E. E.; Ezhova, M. B.; Hanan, G. S.; Wolf, M. O. Controlling photocatalytic reduction of CO_2 in Ru(II)/Re(I) dyads via linker oxidation state. *Chem. Commun.* **2020**, *56*, 10750–10753.

(16) Burks, D. B.; Davis, S.; Lamb, R. W.; Liu, X.; Rodrigues, R. R.; Liyanage, N. P.; Sun, Y.; Webster, C. E.; Delcamp, J. H.; Papish, E. T. Nickel(II) pincer complexes demonstrate that the remote substituent controls catalytic carbon dioxide reduction. *Chem. Commun.* **2018**, *54*, 3819–3822.

(17) Chai, X.; Huang, H.-H.; Liu, H.; Ke, Z.; Yong, W.-W.; Zhang, M.-T.; Cheng, Y.-S.; Wei, X.-W.; Zhang, L.; Yuan, G. Highly efficient and selective photocatalytic CO_2 to CO conversion in aqueous solution. *Chem. Commun.* **2020**, *56*, 3851–3854.

(18) Khadhraoui, A.; Gotico, P.; Boitrel, B.; Leibl, W.; Halime, Z.; Aukauloo, A. Local ionic liquid environment at a modified iron porphyrin catalyst enhances the electrocatalytic performance of CO_2 to CO reduction in water. *Chem. Commun.* **2018**, *54*, 11630–11633. (19) Kuehnel, M. F.; Sahm, C. D.; Neri, G.; Lee, J. R.; Orchard, K. L.; Cowan, A. J.; Reisner, E. ZnSe quantum dots modified with a Ni(cyclam) catalyst for efficient visible–light driven CO2 reduction in water. *Chem. Sci.* **2018**, *9*, 2501–2509.

(20) Boutin, E.; Merakeb, L.; Ma, B.; Boudy, B.; Wang, M.; Bonin, J.; Anxolabéhère-Mallart, E.; Robert, M. Molecular catalysis of CO_2 reduction: recent advances and perspectives in electrochemical and light–driven processes with selected Fe, Ni and Co aza macrocyclic and polypyridine complexes. *Chem. Soc. Rev.* **2020**, *49*, 5772–5809.

(21) Liu, W. J.; Huang, H. H.; Ouyang, T.; Jiang, L.; Zhong, D. C.; Zhang, W.; Lu, T. B. A Copper(II) Molecular Catalyst for Efficient and Selective Photochemical Reduction of CO₂ to CO in a Water-Containing System. *Chem.—Eur. J.* **2018**, *24*, 4503–4508.

(22) Bonin, J.; Maurin, A.; Robert, M. Molecular catalysis of the electrochemical and photochemical reduction of CO_2 with Fe and Co metal based complexes. Recent advances. *Coord. Chem. Rev.* 2017, 334, 184–198.

(23) Luo, Y.-H.; Dong, L.-Z.; Liu, J.; Li, S.-L.; Lan, Y.-Q. From molecular metal complex to metal–organic framework: The CO_2 reduction photocatalysts with clear and tunable structure. *Coord. Chem. Rev.* **2019**, 390, 86–126.

(24) Liu, Y.; Guo, J.-H.; Dao, X.-Y.; Zhang, X.-D.; Zhao, Y.; Sun, W.-Y. Coordination polymers with a pyridyl-salen ligand for photocatalytic carbon dioxide reduction. *Chem. Commun.* **2020**, *56*, 4110–4113.

(25) Kamada, K.; Jung, J.; Wakabayashi, T.; Sekizawa, K.; Sato, S.; Morikawa, T.; Fukuzumi, S.; Saito, S. Photocatalytic CO₂ Reduction Using a Robust Multifunctional Iridium Complex toward the Selective Formation of Formic Acid. *J. Am. Chem. Soc.* **2020**, *142*, 10261– 10266.

(26) Cancelliere, A. M.; Puntoriero, F.; Serroni, S.; Campagna, S.; Tamaki, Y.; Saito, D.; Ishitani, O. Efficient trinuclear Ru(II)-Re(I) supramolecular photocatalysts for CO_2 reduction based on a new tris-chelating bridging ligand built around a central aromatic ring. *Chem. Sci.* **2020**, *11*, 1556–1563.

(27) Rao, H.; Bonin, J.; Robert, M. Visible–light Homogeneous Photocatalytic Conversion of CO_2 into CO in Aqueous Solutions with an Iron Catalyst. *ChemSusChem* **2017**, *10*, 4447–4450.

(28) Rao, H.; Bonin, J.; Robert, M. Non-sensitized selective photochemical reduction of CO_2 to CO under visible light with an iron molecular catalyst. *Chem. Commun.* **2017**, *53*, 2830–2833.

(29) Chen, L.; Qin, Y.; Chen, G.; Li, M.; Cai, L.; Qiu, Y.; Fan, H.; Robert, M.; Lau, T.-C. A molecular noble metal-free system for efficient visible light-driven reduction of CO_2 to CO. *Dalton Trans.* **2019**, 48, 9596-9602.

(30) Wang, F. Artificial Photosynthetic Systems for CO_2 Reduction: Progress on Higher Efficiency with Cobalt Complexes as Catalysts. *ChemSusChem* **2017**, *10*, 4393–4402.

(31) Wang, J.-W.; Huang, H.-H.; Sun, J.-K.; Ouyang, T.; Zhong, D.-C.; Lu, T.-B. Electrocatalytic and Photocatalytic Reduction of CO_2 to CO by Cobalt(II) Tripodal Complexes: Low Overpotentials, High Efficiency and Selectivity. *ChemSusChem* **2018**, *11*, 1025–1031.

(32) Ouyang, T.; Hou, C.; Wang, J.-W.; Liu, W.-J.; Zhong, D.-C.; Ke, Z.-F.; Lu, T.-B. A Highly Selective and Robust Co(II)–Based Homogeneous Catalyst for Reduction of CO₂ to CO in CH_3CN/H_2O Solution Driven by Visible Light. *Inorg. Chem.* **2017**, *56*, 7307–7311.

(33) Guo, Z.; Cheng, S.; Cometto, C.; Anxolabéhère-Mallart, E.; Ng, S.-M.; Ko, C.-C.; Liu, G.; Chen, L.; Robert, M.; Lau, T.-C. Highly Efficient and Selective Photocatalytic CO₂ Reduction by Iron and Cobalt Quaterpyridine Complexes. *J. Am. Chem. Soc.* **2016**, *138*, 9413–9416.

(34) Kuehnel, M. F.; Orchard, K. L.; Dalle, K. E.; Reisner, E. Selective Photocatalytic CO_2 Reduction in Water through Anchoring of a Molecular Ni Catalyst on CdS Nanocrystals. *J. Am. Chem. Soc.* **2017**, *139*, 7217–7223.

(35) Hong, D.; Kawanishi, T.; Tsukakoshi, Y.; Kotani, H.; Ishizuka, T.; Kojima, T. Efficient Photocatalytic CO_2 Reduction by a Ni(II) Complex Having Pyridine Pendants through Capturing a Mg^{2+} Ion as a Lewis–Acid Cocatalyst. *J. Am. Chem. Soc.* **2019**, *141*, 20309–20317.

(36) Hong, D.; Tsukakoshi, Y.; Kotani, H.; Ishizuka, T.; Kojima, T. Visible–Light–Driven Photocatalytic CO₂ Reduction by a Ni(II) Complex Bearing a Bioinspired Tetradentate Ligand for Selective CO Production. J. Am. Chem. Soc. **2017**, 139, 6538–6541.

(37) Guo, Z.; Yu, F.; Yang, Y.; Leung, C.-F.; Ng, S.-M.; Ko, C.-C.; Cometto, C.; Lau, T.-C.; Robert, M. Photocatalytic Conversion of CO2 to CO by a Copper(II) Quaterpyridine Complex. *ChemSusChem* **2017**, *10*, 4009–4013.

(38) Grills, D. C.; Ertem, M. Z.; McKinnon, M.; Ngo, K. T.; Rochford, J. Mechanistic aspects of CO_2 reduction catalysis with manganese–based molecular catalysts. *Coord. Chem. Rev.* **2018**, 374, 173–217.

(39) Woo, S.-J.; Choi, S.; Kim, S.-Y.; Kim, P. S.; Jo, J. H.; Kim, C. H.; Son, H.-J.; Pac, C.; Kang, S. O. Highly Selective and Durable Photochemical CO_2 Reduction by Molecular Mn(I) Catalyst Fixed on a Particular Dye–Sensitized TiO₂ Platform. *ACS Catal.* **2019**, *9*, 2580–2593.

(40) Steinlechner, C.; Roesel, A. F.; Oberem, E.; Päpcke, A.; Rockstroh, N.; Gloaguen, F.; Lochbrunner, S.; Ludwig, R.; Spannenberg, A.; Junge, H.; Francke, R.; Beller, M. Selective Noble-metal-free System for CO₂ Reduction: Comparing Photoand Electrocatalytic Processes. *ACS Catal.* **2019**, *9*, 2091–2100.

(41) Feng, X.; Pi, Y.; Song, Y.; Brzezinski, C.; Xu, Z.; Li, Z.; Lin, W. Metal–Organic Frameworks Significantly Enhance Photocatalytic Hydrogen Evolution and CO₂ Reduction with Noble–metal–free Copper Photosensitizers. J. Am. Chem. Soc. **2020**, 142, 690–695.

(42) Kuramochi, Y.; Fujisawa, Y.; Satake, A. Photocatalytic CO_2 Reduction Mediated by Electron Transfer via the Excited Triplet State of Zn(II) Porphyrin. *J. Am. Chem. Soc.* **2020**, *142*, 705–709.

(43) Bonin, J.; Robert, M.; Routier, M. Selective and efficient photocatalytic CO_2 reduction to CO using visible light and an iron–based homogeneous catalyst. *J. Am. Chem. Soc.* **2014**, *136*, 16768–16771.

(44) Rao, H.; Lim, C.-H.; Bonin, J.; Miyake, G. M.; Robert, M. Visible–Light–Driven Conversion of CO_2 to CH_4 with an Organic Sensitizer and an Iron Porphyrin Catalyst. *J. Am. Chem. Soc.* **2018**, 140, 17830–17834.

(45) Takeda, H.; Ohashi, K.; Sekine, A.; Ishitani, O. Photocatalytic CO_2 Reduction Using Cu(I) Photosensitizers with a Fe(II) Catalyst. *J. Am. Chem. Soc.* **2016**, 138, 4354–4357.

(46) Zhang, X.; Cibian, M.; Call, A.; Yamauchi, K.; Sakai, K. Photochemical CO₂ Reduction Driven by Water–Soluble Copper(I) Photosensitizer with the Catalysis Accelerated by Multi–Electron Chargeable Cobalt Porphyrin. *ACS Catal.* **2019**, *9*, 11263–11273.

(47) Call, A.; Cibian, M.; Yamamoto, K.; Nakazono, T.; Yamauchi, K.; Sakai, K. Highly Efficient and Selective Photocatalytic CO_2 Reduction to CO in Water by a Cobalt Porphyrin Molecular Catalyst. *ACS Catal.* **2019**, *9*, 4867–4874.

(48) Lian, S.; Kodaimati, M. S.; Weiss, E. A. Photocatalytically Active Superstructures of Quantum Dots and Iron Porphyrins for Reduction of CO_2 to CO in Water. ACS Nano **2018**, 12, 568–575.

(49) Winter, A.; Schubert, U. S. Metal-Terpyridine Complexes in Catalytic Application–A Spotlight on the Last Decade. *ChemCatChem* **2020**, *12*, 2890–2941.

(50) Housecroft, C. E.; Constable, E. C. The terpyridine isomer game: from chelate to coordination network building block. *Chem. Commun.* **2020**, *56*, 10786–10794.

(51) Sarkar, R.; Xie, T.-Z.; Endres, K. J.; Wang, Z.; Moorefield, C. N.; Saunders, M. J.; Ghorai, S.; Patri, A. K.; Wesdemiotis, C.; Dobrynin, A. V.; Newkome, G. R. *J. Am. Chem. Soc.* **2020**, *142*, 5526–5530.

(52) Hampson, E.; Cameron, J. M.; Amin, S.; Kyo, J.; Watts, J. A.; Oshio, H.; Newton, G. N. Asymmetric Hybrid Polyoxometalates: A Platform for Multifunctional Redox–Active Nanomaterials. *Angew. Chem., Int. Ed.* **2019**, *58*, 18281–18285.

(53) Kang, P.; Chen, Z.; Brookhart, M.; Meyer, T. J. Electrocatalytic Reduction of Carbon Dioxide: Let the Molecules Do the Work. *Top. Catal.* **2014**, *58*, 30–45.

(54) Chen, Z.; Kang, P.; Zhang, M.-T.; Meyer, T. J. Making syngas electrocatalytically using a polypyridyl ruthenium catalyst. *Chem. Commun.* **2014**, *50*, 335–337.

(55) Ramos Sende, J. A.; Arana, C. R.; Hernandez, L.; Potts, K. T.; Keshevarz-K, M.; Abruna, H. D. Electrocatalysis of CO₂ Reduction in Aqueous Media at Electrodes Modified with Electropolymerized Films of Vinylterpyridine Complexes of Transition Metals. *Inorg. Chem.* **1995**, *34*, 3339–3348.

(56) Arana, C.; Yan, S.; Keshavarz-K, M.; Potts, K. T.; Abruna, H. D. Electrocatalytic reduction of carbon dioxide with iron, cobalt, and nickel complexes of terdentate ligands. *Inorg. Chem.* **1992**, *31*, 3680–3682.

(57) Guadalupe, A. R.; Usifer, D. A.; Potts, K. T.; Hurrell, H. C.; Mogstad, A. E.; Abruna, H. D. Novel chemical pathways and charge– transport dynamics of electrodes modified with electropolymerized layers of $[Co(v-terpy)_2]^{2^+}$. J. Am. Chem. Soc. **1988**, 110, 3462–3466. (58) Elgrishi, N.; Chambers, M. B.; Artero, V.; Fontecave, M. Terpyridine complexes of first row transition metals and electrochemical reduction of CO₂ to CO. Phys. Chem. Chem. Phys. **2014**, 16, 13635–13644.

(59) Rebolledo-Chávez, J. P. F.; Cruz-Ramírez, M.; Patakfalvi, R.; Tenorio Rangel, F. J.; Ortiz-Frade, L. Insight on the mechanism of molecular catalysis of CO_2 reduction with Fe(II)–polypyridine complexes. *Electrochim. Acta* **2017**, 247, 241–251.

(60) Leung, J. J.; Warnan, J.; Ly, K. H.; Heidary, N.; Nam, D. H.; Kuehnel, M. F.; Reisner, E. Solar-driven reduction of aqueous CO_2 with a cobalt bis(terpyridine)-based photocathode. *Nat. Catal.* **2019**, *2*, 354–365.

(61) Wang, Y.; Gao, X.-W.; Li, J.; Chao, D. Merging an organic TADF photosensitizer and a simple terpyridine–Fe(III) complex for photocatalytic CO₂ reduction. *Chem. Commun.* **2020**, *56*, 12170–12173.

(62) Zhang, J.; Campolo, D.; Dumur, F.; Xiao, P.; Fouassier, J. P.; Gigmes, D.; Lalevée, J. Visible–light–sensitive photoredox catalysis by iron complexes: Applications in cationic and radical polymerization reactions. *J. Polym. Sci., Polym. Chem. Ed.* **2016**, *54*, 2247–2253.

(63) Munzert, S. M.; Schwarz, G.; Kurth, D. G. Kinetic Studies of the Coordination of Mono- and Ditopic Ligands with First Row Transition Metal Ions. *Inorg. Chem.* **2016**, *55*, 2565–2573.

(64) Braterman, P. S.; Song, J. I.; Peacock, R. D. Electronic absorption spectra of the iron(II) complexes of 2,2'-bipyridine, 2,2'-

bipyrimidine, 1,10-phenanthroline, and 2,2':6',2"-terpyridine and their reduction products. *Inorg. Chem.* **1992**, 31, 555-559.

(65) Rao, J. M.; Macero, D. J.; Hughes, M. C. Dual role of paraphenyl substituents in aromatic imine ligand complexes of cobalt and iron. *Inorg. Chim. Acta* **1980**, *41*, 221–226.

(66) Lee, S. K.; Kondo, M.; Nakamura, G.; Okamura, M.; Masaoka, S. Low-overpotential CO₂ reduction by a phosphine-substituted Ru(II) polypyridyl complex. *Chem. Commun.* **2018**, *54*, 6915–6918.

(67) Uoyama, H.; Goushi, K.; Shizu, K.; Nomura, H.; Adachi, C. Highly efficient organic light–emitting diodes from delayed fluorescence. *Nature* **2012**, 492, 234–238.

(68) Ishimatsu, R.; Matsunami, S.; Kasahara, T.; Mizuno, J.; Edura, T.; Adachi, C.; Nakano, K.; Imato, T. Electrogenerated chemiluminescence of donor-acceptor molecules with thermally activated delayed fluorescence. *Angew. Chem., Int. Ed.* **2014**, *53*, 6993–6996.

(69) Qin, Y.; Chen, L.; Chen, G.; Guo, Z.; Wang, L.; Fan, H.; Robert, M.; Lau, T.-C. A highly active and robust iron quinquepyridine complex for photocatalytic CO_2 reduction in aqueous acetonitrile solution. *Chem. Commun.* **2020**, *56*, 6249–6252.

(70) Hamacher, C.; Hurkes, N.; Kaiser, A.; Klein, A.; Schüren, A. Electrochemistry and spectroscopy of organometallic terpyridine nickel complexes. *Inorg. Chem.* **2009**, *48*, 9947–9951.

(71) Scarborough, C. C.; Lancaster, K. M.; DeBeer, S.; Weyhermüller, T.; Sproules, S.; Wieghardt, K. Experimental fingerprints for redox-active terpyridine in $[Cr(tpy)_2](PF_6)n (n = 3-0)$, and the remarkable electronic structure of $[Cr(tpy)_2]$. *Inorg. Chem.* **2012**, *51*, 3718–3732.