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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: ChemSusChem 10.1002/cssc.201701354

Link to VoR: http://dx.doi.org/10.1002/cssc.201701354



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Photocatalytic CO₂-to-CO Conversion by a Copper(II) Quaterpyridine Complex

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Abstract: The invention of efficient systems for the photocatalytic reduction of CO₂ comprising earth-abundant metal catalysts is a promising approach for the production of solar fuels. One bottleneck is to design highly selective and robust molecular complexes able to transform the gas. The Cu(II) quaterpyridine complex $[Cu(qpy)]^{2+}$ (1) is found to be a highly efficient and selective catalyst for visible-light driven CO₂ reduction in CH₃CN using $[Ru(bpy)_3]^{2+}$ as photosensitizer, BIH/TEOA as sacrificial reductant. The photocatalytic reaction is greatly enhanced by the presence of H₂O (1–4% v/v), and a TON of >12,400 for CO production can be achieved with 97% selectivity, which is among the highest of molecular 3d CO₂ reduction catalysts. Results from Hg-poisoning and dynamic light scattering (DLS) experiments suggest that this photocatalysis is homogenous. To the best of our knowledge 1 is the first example of molecular Cu-based catalyst for the photoreduction of CO₂.

In recent years, tremendous efforts have been devoted by chemists to convert solar energy into storable chemical forms.^{[1-} ^{7]} Regarding molecular based catalytic systems, 3d complexes have been widely studied as viable catalysts for solar fuel production by the splitting of water and the reduction of carbon dioxide. A number of carbon dioxide reduction catalysts based on Mn, Fe, Co and Ni have been reported.^[8-32] On the other hand, there are only very few reports on the use of molecular copper complexes for the electrocatalytic reduction of CO2, [33-35] although electrocatalytic, and more recently also photocatalytic, CO2 reduction by Cu heterogeneous materials have been well documented.^[36-40] One example is given by the one electron catalytic CO2-to-oxalate conversion with a dinuclear Cu complex,^[33] and a second one involved the use of a Cu porphyrin deposited on graphite electrode to produce CO along with small amounts of methane and ethane^[35], although in that case demetalation of the catalyst and further formation of Cu particles, which are, as noted above, highly active towards CO₂ reduction. We report herein that the copper(II) complex

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 $[Cu(qpy)]^{2^+}$ (1) of the planar tetradentate ligand 2,2':6',2":6",2":quaterpyridine (qpy) is a highly efficient catalyst for visible-light driven reduction of CO₂ to CO using $[Ru(bpy)_3]^{2^+}$ (**RuPS**) as photosensitizer. To the best of our knowledge, $[Cu(qpy)]^{2^+}$ is also the first example of molecular copper catalyst for the photocatalytic reduction of CO₂.



Scheme 1. Structure of the catalyst 1, photosensitizer (RuPS) and sacrificial reductant (BIH).

The structure of $[Cu(qpy)](NO_3)_2 \cdot 2H_2O$ has been previously reported to consist $[Cu(qpy)(OH_2)(NO_3)]^+$ cation with a distorted tetragonal pyramidal geometry, which bears an axial H₂O ligand (Cu-O = 2.286(3) Å) and a weakly bound $NO_3^ (Cu-O = 2.695(3) \text{ Å}) \cdot ^{[41]}$ We have also determined the X-ray crystal structure of $[Cu(qpy)](CIO_4)_2$, which has a distorted square planar structure with two weakly bound CIO_4^- ions (Cu-O = 2.518(2) Å and 2.470(2) Å) in the axial positions and a bent O– Cu-O angle (169.86(9)°) (Figure S1, Tables S1 and S2).

Photocatalytic CO₂ reduction by **1** was investigated in CH₃CN (MeCN) by using [Ru(bpy)₃]²⁺ (RuPS) as photosensitizer and BIH/TEOA as sacrificial reductant (Scheme 1). BIH is an efficient reductive quencher for the excited state of RuPS, while TEOA (triethanolamine) mainly functions as proton acceptor of BIH⁺⁺.^[42,43] As shown in Figure 1 and in Table 1 (entry 4), CO is produced upon visible light irradiation ($\lambda > 420$ nm). The amount of CO increases with irradiation time and then levels off after 3.5 h, with a turnover number (TON) of 2425. H₂ is also produced with a TON of 620, while only a trace amount of formate could be detected (TON = 8). Hence the selectivity for CO production is 80%. In the absence of BIH (Table 1, entry 6), the TON for CO is much lower (210), while that of H_2 is not much affected (590), and there is a slightly larger amount of formate (TON 66). No CO was detected in the absence of TEOA. Replacing TEOA with triethylamine (TEA) resulted in immediate formation of a white precipitate, probably BI⁺, and CO was not produced. On the other hand, if 1 was omitted (Table 1, entry 1), essentially no CO or H₂ could be detected within the same irradiation time. When 1 was replaced by a simple Cu^{2+} salt such as $Cu(ClO_4)_2$ (Table 1, entry 8), no CO or formate was detected, and only H₂ was produced (TON = 141). This result indicates that catalytic CO production is not due to Cu2+ ion that may arise from demetalation of 1. Since Cu nanoparticles are known to be CO₂ photoreduction catalysts,^[36] catalysis was also performed in the presence of mercury, which may form inactive amalgam with any Cu(0) present. The yield of CO was found to be decreased by around 10% (Figure 1 and Table 1). Dynamic light scattering experiments did not reveal the formation of any particles during photocatalysis (Figure S4). We conclude from all these results that photocatalytic reduction of CO_2 by this system is predominately homogeneous.

As shown in Figure 2 and Table 1 (entries 2-4, 9), both the rate and CO yield increase with catalyst concentration. The initial rate shows a linear correlation with [1] (Figure S5), suggesting that the rate-limiting step for CO₂ reduction involves a single Cu site. The photolysis was also investigated using ¹³C-labelled CO₂ and ¹³CO was detected by GC-MS (Figure S6), indicating the CO produced originates from the reduction of CO₂.



Figure 1. Plot of CO amount and TON versus time during irradiation of a) 1 (5 μ M)/RuPS (2 mM)/TEOA (15% v/v)/BIH (0.1 M) in CO₂-saturated MeCN, b) 0.1 mL Hg added, c) no BIH added and d) Cu(ClO₄)₂ (5 μ M) used as catalyst instead of 1.



Figure 2. Time trace of CO evolution during irradiation of 1/RuPS (2 mM)/BIH(0.1 M)/TEOA (15% v/v) in CO₂-saturated MeCN at various [1] (1.0 – 7.5 μ M).



Figure 3. Time trace of CO evolution during irradiation of 1 (1.0 μ M)/RuPS (2 mM)/BIH (0.1 M)/TEOA (15% v/v) in CO₂-saturated MeCN containing various concentrations of H₂O (1 – 10 % v/v).

The production of CO was found to be greatly enhanced by the presence of a few % (v/v) of water (Figure 3 and Table S3). Both the yield and rate for CO generation increased when H₂O was added (1-4%). At 1 µM of 1, an optimum CO yield of 31.2 µmol (TON = 12,400) was observed with 3% H_2O after 3 h of irradiation, and the yield of H₂ has also increased similarly by approx. four folds (1.0 µmol, TON = 410, Table S3) as compared to dry MeCN, leading to a selectivity of 97% for CO production. No CO was detected in the absence of 1, but some CO (TON = 664) was obtained with 3% H₂O in the absence of TEOA. Further increase in the amount of water added resulted in lower CO production; the CO TON became 850 when 10% H₂O was added. On the other hand, the yield of H₂ increased steadily with [H₂O], and at 10% H₂O the yield is over 10 times higher than without adding H₂O. However, similar H₂ yields were also obtained in control experiments without 1 (Table S3). Thus, the suppressed CO production at $[H_2O] > 4\%$ may be partly due to competitive H_2 generation by RuPS. As discussed and analyzed in details elsewhere, $^{\left[44,45\right] }$ adding a weak acid like e.g. $H_{2}O$ could boost the CO₂ binding step to the metal center by providing thermodynamic stabilization of the intermediate through H-bonds and/or protonation. It may also favor the cleavage of the C-O bond leading to the release of CO and a water molecule. However, when the concentration (or the strength) of the added acid increases, competition for H₂ evolution may occur, leading to an optimized concentration for CO₂ selective reduction. Similar enhancement of photocatalytic CO2-to-CO conversion by weak acid has been reported in several cases.[44-46] The photocatalysis in the presence of H₂O was also found to be homogeneous, as indicated by Hg⁰ poisoning and DLS results (Figure S7 and S8). The quantum yield (Φ_{CO}) for CO production in optimized conditions (3% water) has been determined to be 1.2% by ferrioxalate actinometry (λ = 460 nm). The quenching rate constant (k_q) of the ruthenium excited state **RuPS**^{*} by **1** was found to be 2.15 $\times 10^8$ M⁻¹ s⁻¹ by Stern-Volmer plot (Figure S9), which is much lower than that by BIH (4.0 x 10⁹ M⁻¹ s⁻¹).^[19] Since in addition BIH is more than 10 times more concentrated than 1 (see Table 1), reductive quenching of **RuPS**^{*} by BIH should

(vv). Inadiation time – 5.5 m (white light, x > 420 mm). Tons obtained in the presence of catalyst are listed without background conection.									
	[Cu(qpy) ²⁺]/ µM	H ₂		СО		НСООН			
		Yield/µmol	TON	Yield/µmol	TON	Yield/µmol	TON		
1	0	0.3		0		0	0		
2	1	0.2	93	7.4	2939	0	0		
3	2.5	3.0	490	23.3	3730	0	0		
4	5	7.8	623	30.3	2425	0.1	8		
5 ^[a]	5	0.18	14	0	0	0	0		
6 ^[b]	5	7.4	592	2.6	210	0.83	66		
7 ^[c]	5	0.44	35	29	2317	0	0		
8 ^[d]	5	1.76	141	0	0	0	0		
9	7.5	15.3	814	29.7	1582	0	0		

Table 1. Table Caption. Yields of H₂, CO and HCOOH under various photocatalytic conditions in acetonitrile using **RuPS** (2 mM), BIH (0.1M) and 15% TEOA (v/v). Irradiation time = 3.5 h (white light, $\lambda > 420$ nm). TONs obtained in the presence of catalyst are listed without background correction.

[a] under Ar. [b] no BIH. [c] with 0.1 mL Hg^0 . [d] 1 replaced by 5 μ M Cu(ClO₄)₂.

predominate and be the first step of the process. To explore the reason for catalysis leveling off, fresh reagents were added in different combinations after 120 min irradiation so as to identify the limiting reagents (Figure S14). Addition of RuPS/BIH/TEOA/H₂O produced essentially no CO during the second photocatalysis experiment, pointing to decomposition of 1 into an inactive species. When 1 alone was added, only a small amount of CO was produced (TON = 116) during the second photocycle, showing that other components have been depleted. Addition of 1/RuPS/TEAO together with H₂O or BIH resulted in a TON of CO <50% as compared to the first photocycle. When 1/BIH/H₂O were added together with RuPS or TEOA more than 80% (TON > 2,200) of the original catalytic activity was restored. All together, these results indicate that the main limiting factor of the photocatalysis is related to the deactivation of 1, as well as to the consumption of both BIH and H_2O .

Electrospray ionization mass spectrometry (ESI/MS) of a blue solution of 1 in CH₃CN exhibits peaks at m/z 187 and 207 in the mass spectrum, which are assigned to [Cu(qpy)]²⁺ and [Cu(qpy)(CH₃CN)]²⁺, respectively (Figure S10). Upon addition of excess of BIH to 1, these peaks disappeared and new peaks at m/z 223 and 373 appeared (Figure S11), which are assigned to BI⁺ and [Cu₂(qpy)₂]²⁺, respectively. The UV/Vis spectrum of the solution containing 1 and BIH also shows the presence of a new species with λ_{max} at 432 and 545 nm (Figure S12), which is identical to that obtained upon direct one-electron electrochemical reduction of 1 (Figure S13). That [Cu(qpy)]²⁺ is spontaneously reduced by BIH is also confirmed by the observation of its first electrochemical reduction (Figure 4). Without added BIH, the Cu^{II} species is reduced at +0.1 V vs. SCE and then dimerizes (note that the CO₂ reduction occurs at more negative potentials (onset potential at ca. -1.4 V vs. SCE) following a second reduction, see Figures S2 and S3). The dimer is further reoxidised at +0.41 V vs. SCE on the oxidative scan (Figure 4A). Upon adding 0.05 M BIH, the reduction wave of the Cu^{II} species disappears (Figure 4B). These results indicate that the Cu^{II} initial species ($[Cu(qpy)]^{2+}$) is reduced to a Cu^I species by BIH before irradiation, probably $[Cu_2(qpy)_2]^{2+}$. Note that redox induced formation of binuclear Cu^I complexes with functionalized quaterpyridine have been reported.^[47] We thus propose that under photocatalytic conditions the dimeric species formed upon spontaneous reduction by BIH is further reduced to Cu⁰(qpy) or Cu^I(qpy⁻), which is the active species for CO₂ reduction.

To confirm these conclusions, the $[Cu_2^{l}(qpy)_2]^{2+}$ dimer was synthesized (see Experimental Section and Supporting Information for details) and its photocatalytic activity was investigated in acetonitrile with 3% H₂O. CO was produced and then leveled off after 3.5 h of irradiation, similarly to what has been observed for 1. The amount of CO produced (TON = 23,000 vs $[Cu_2^l(qpy)_2]^{2+}$ or 11,500 per Cu center) is twice that obtained using the same mole amount of 1 (Figure S15), in accordance with the initial conversion of $[Cu(qpv)]^{2+}$ to $[Cu_2(qpy)_2]^{2+}$, the latter complex being further reduced to the active catalyst species. Remarkably, 1 appears as one of the most efficient molecular CO2-to-CO photocatalyst. Catalysts based on earth abundant metals have been carefully reviewed recently^[7,32] and mainly include cyclams, polypyridines and their derivatives (Ni, Co, Fe), porphyrins (Co, Fe) as well as carbonyl complexes (Mn, Fe). From these data (see Table 2 in Ref. 7 and Table S1 in Ref. 32) it appears that 1 is one of the most efficient catalysts reported to date in terms of both selectivity for CO formation (97%) and turnover number (12,400).

In conclusion, $[Cu(qpy)]^{2+}$ is a very efficient homogeneous catalyst for the photocatalytic reduction of CO₂ to CO in CH₃CN

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using $Ru(bpy)_3^{2+}/BIH/TEOA$. The yield of CO is significantly enhanced by the addition of 1-4 % water, and a TON of 12,400 can be achieved. To the best of our knowledge, **1** is the first example of Cu molecular catalyst for CO₂ photoreduction, showing that molecular species including copper as metal and a simple, easily synthesized ligand could serve as competent, selective catalysts for CO₂ catalytic reduction. Finally, **1** gives top catalytic performance among molecular 3d metal catalysts reported so far.



Figure 4. CVs of the first reduction (Cu^{II} to Cu^{II} species) wave of **1** (1mM) in Ar-saturated ACN solution + 0.1M $^{n}Bu_{4}NPF_{6}$ (A) and after addition of 0.05 M BIH (B, red trace).

Experimental Section

Synthesis and materials: The ligand 2,2':6',2'':6'',2'''-quaterpyridine (qpy) was prepared by a literature method.^[48] BIH was synthesized using a reported procedure.^[49] [Cu^{II}(qpy)](ClO₄)₂ was prepared by the addition of a chloroform (8 mL) solution of qpy (84 mg, 0.27 mmol) to a stirring solution of Cu(ClO₄)₂·6H₂O (100 mg, 0.27 mmol) in methanol (10 mL). The mixture was stirred for 2 h at room temperature and the resulting pale blue solid was filtered, washed with methanol and chloroform, and then dried under vacuo. [Cu^I₂(qpy)₂](ClO₄) was prepared similarly by adding a chloroform (8 mL) solution of qpy (61 mg, 0.20 mmol) into a stirring acetonitrile (10 mL) solution of [Cu^I(CH₃CN)₄]ClO₄ (64 mg, 0.20 mmol) under an Ar atmosphere. The reddish brown solid formed after 1 h was filtered, washed with chloroform and acetonitrile, and dried under vacuum. All other chemicals were obtained commercially and used without further purification unless otherwise stated. Detailed experimental procedures can be found in the supporting information.

Acknowledgements

The work described in this project was supported by the Hong Kong Research Grants Council (project number 28300014,

18300715), the Hong Kong University Grants Committee Area of Excellence Scheme (AoE/P-03-08) and the Education University of Hong Kong (RG95/2015-2016). PhD fellowship to C. C. from Université Sorbonne Paris Cité (USPC) is gratefully acknowledged. We thank Dr. Shek-Man Yiu for collecting the crystal data.

Keywords: Photocatalysis • carbon dioxide reduction• transition metals • homogeneous catalysis • copper catalyst

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