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Organocatalytic photoreduction of Zn(II) to zinc metal[†]

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The photoreduction of Zn(ii) to Zn metal catalyzed by 8-hydroxyquinoline derivatives is reported. Structure–activity relationships, ideal reaction conditions, and the reaction kinetics are described and a mechanism involving an *in situ* formed quinolate complex is portrayed.

The photon-driven reduction of metal ions is an unusual but highly useful photosynthetic reaction with potential applications in solar fuels, organic synthesis and metal coatings. For instance, coupling such a process with a complementary OH⁻ oxidation would reverse the discharge chemistry observed in highly efficient metal air batteries¹ and convert solar radiation to stored electrochemical potential. On the other hand, the produced metal particles with pristine surfaces are highly reactive and can also function efficiently in organic reductive coupling reactions of aryls and olefins or in the preparation of arylmetal species.² Additionally, metal photolithographic deposition techniques would allow for the fabrication of low work function electrodes for organic electronics and photovoltaic applications.

These potential uses make the photoreduction of metals an appealing research topic. Earlier studies predominately targeted cations with high reduction potentials or used UV radiation for the photogeneration of base metals. For instance, Ag^+ ($E_{red}(Ag^+/Ag) = +0.80$ V vs. SCE) was photocatalytically reduced to silver metal with $[Ru(bpy)_3]^{2+}$ as the photosensitizer.³ Cations of less noble metals such as $Pb(\pi)$ or $Cd(\pi)$ (e.g. $E_{\rm red}({\rm Cd}^{2+}/{\rm Cd}) = -0.40$ V vs. SCE) were photoreduced in systems that required high-intensity UV radiation, an approach that is incompatible with a solar fuel scheme.⁴ To our knowledge, no molecular photoreactions have been described in the literature that use visible light with an electrochemically highly reactive metal such as Zn, Al, or even Li. The lack of air-stability of lithium and the complex threeelectron redox process required for the photoreduction of aluminum renders Zn(II) the target of choice for exploring this type of reaction. Along these lines, the Bernhard group recently documented the visiblelight driven reduction of $Zn(\pi)$ to zinc metal by an $Ir(\pi)$ photocatalyst

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with triethylamine performing as the sacrificial reductant.⁵ This work describes the substitution of this expensive and toxic noble metal complex with an organocatalyst. It is found that 8-hydroxyquinoline (Hq) derivatives form coordinated Zn species that are responsible for light absorption and catalytic activity. This work uses the vast body of work on Zn-based quinolate complexes⁶ as a guideline for synthetic modification to the ligand framework.

Similarly to the electroluminescence tuning of quinolate LEDs, structure–activity relationships were observed between the 8-hydroxyquinoline ligands and the photocatalytic reduction of Zn(II). Zinc metal was initially observed to be produced when vials containing ZnCl₂, triethylamine (TEA, electron donor) and catalytic quantities of 8-hydroxyquinoline (Hq) were exposed to 465 nm LED light under inert atmosphere in a homemade photoreactor and zinc metal was quantified by established procedure.⁵ The omission of ZnCl₂, TEA, Hq, or light prevented the production of zinc metal. Given the mechanistic evidence observed in this work, a basic reaction scheme involving the reductive quenching of a Zn(II) monoquinolate by TEA and subsequent catalytic reduction of solid ZnCl₂ to afford Zn⁰ *via* a chloride stabilized Zn(I) intermediate is proposed in Fig. 1.

The substitution of different 8-hydroxyquinoline ligands varying at the 5, 7, and 2 positions was found to significantly affect the yield of the desired photoproduct. Fig. 2 illustrates the basic structure and variable positions of the quinoline ligands used in this study while



Fig. 1 General schematic of photocatalyzed Zn(II) reduction.

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Fig. 2 Structure of 8-hydroxyquinoline derivatives.



Fig. 3 Yield of photoreduced zinc metal upon the addition of different 8-hydroxyquinoline ligands after 68 h. Each reaction vial contained 3 μ mol ligand, 3 mmol ZnCl₂, 1 ml TEA, and 9 ml MeCN.

Fig. 3 documents their activity. Most noticeable is the increased yield of zinc metal with halide-substituted quinoline ligands.

The electron withdrawing halides are located on the phenol moiety of the quinoline ligand where the HOMO resides.^{6d} The lower energy HOMOs that result cause enhanced luminescence quenching of halogenated quinolates by TEA and, as a consequence, higher yields of Zn⁰. Among these ligands, 5,7-dCl-Hq exhibits the highest catalytic turnover numbers (TONs), and it was therefore employed for the rest of the studies.

Beyond the structure of the quinoline ligand, other photoreaction conditions were manipulated in order to understand the involved mechanism. The use of zinc halide salts as a starting reagent was found to afford significantly more zinc metal than when salts with acetate, sulphate, or tetrafluoroborate anions were employed (Fig. 4). Zinc halide salts are likely more successful due to their ability to stabilize a short lived Zn(i) intermediate, as postulated earlier.⁵ Indeed, the preferential use of ZnCl₂ in the synthesis of aryl-diimine and Cp* stabilized Zn(i)–Zn(i) complexes suggest Cl⁻ may help mediate Zn(ii) reduction.^{7,8}

The originally used acetonitrile (MeCN) solvent environment proved to be optimal; reactions performed in alcohols, ethers, esters, and hydrocarbons exhibit far inferior metrics compared to acetonitrile. In fact, addition of a small percentage of acetonitrile dramatically improves the Zn yield in ethyl acetate, toluene, and heptanes (Fig. 5). Acetonitrile has been shown to positively shift the reduction potential of Zn(π); the resulting increased ΔE between the LUMOs of Zn(π) and the photocatalyst makes MeCN the most effective solvent.⁵ Water was shown to inhibit Zn(π) photoreduction at concentrations above 300 mM but it was also found that the use of anhydrous ZnCl₂ failed to produce any zinc metal under otherwise identical reaction



Fig. 4 Dependence of the yield of photoreduced zinc metal on the zinc salt starting material. Reactions conditions included 3 μ mol 5,7-dCl-Hq ligand, 2.95 mmol Zn(II) salt, 1 ml TEA, and 9 ml MeCN per vial.

conditions. Stoichiometric quantities of H_2O are required in the subsequent oxidative degradation of the ammonium radical cation generated by sacrificial TEA oxidation.⁹ It is also important to note that heptanes and toluene were the most effective solvents when 10% MeCN was added. These nonpolar solvents are non-coordinating and will thus not compete with MeCN for any open coordination sites on Zn(II) or any intermediate. The success of nonpolar solvents despite the limited solubility of $ZnCl_2$ is also consistent with a heterogeneous reaction, an observation that is corroborated on later in this article with the kinetic evidence.

The reaction mechanism was further investigated in an attempt to identify the active catalytic quinolate species. *In situ* catalyst ligation is likely due to the widely known chelation of Zn(II) by 8-hydroxyquinolines.¹⁰ Fig. 6 plots the relative quinolate concentrations derived from peak integration areas of ¹H NMR spectra *versus* an increasing ligand to zinc(II) ratio. A single compound, likely a mono-substituted [Zn(5,7-dCl-q)L_n] (where L = H₂O, OH⁻, Cl⁻ or MeCN) complex is the dominant quinolate species when ZnCl₂ is in excess of 5,7-dCl-Hq, such as under typical photoreduction conditions. Cyclic voltammetry excludes the formation of Zn(5,7-dCl-q)₂ when Zn(II) is in excess of ligand due to the lack of a second



Fig. 5 Effect of solvent on Zn(11) photoreduction. There was in each vial 3 μ M 5,7-dCl-Hq, 420 mg ZnCl₂, 1 ml TEA, and 9 ml solvent.

ChemComm



Fig. 6 Relative quinolate concentrations derived from ¹H NMR spectra as 300 µM 5,7-dCl-Hq is titrated with ZnCl₂ in 9:1 MeCN: TEA.

irreversible reduction peak generally observed for Znq2.11 Indeed, ¹H NMR of dissolved solids in a typical photoreaction reveal only one quinolate species, with another-likely the degraded or active catalystforming after light exposure (ESI⁺). The two other quinolates in Fig. 6 correspond to 5,7-dCl-q and Zn(5,7-dCl-q)₂, the latter of which was synthesized by established procedure for reference purposes.¹² The formation of $[Zn(5,7-dCl-q)L_n]$, and $Zn(5,7-dCl-q)_2$ were reversible; K_{eq} values of formation were calculated be 1026 M⁻¹ and 257 M⁻¹ respectively. The parent 5,7-dCl-Hq is fully deprotonated in the TEA environment and does not absorb 465 nm light, rendering both its presence and participation in the photoreduction process unlikely.

Fluorescence quenching was employed to confirm that a monosubstituted zinc quinolate is the active, zinc(II) reducing photocatalyst. The sacrificial electron donor TEA is oxidized at +0.934 V vs. SHE¹³ and is thus incapable of reducing neither a ground state zinc quinolate nor unligated Zn(II) directly. As a consequence, reductive luminescence quenching is necessary. While quenching by TEA was not detected in 5,7-dCl-q nor Zn(5,7-dCl-q)₂, it was observed in $[Zn(5,7-dCl-q)L_n]$, indicating that it is the active catalyst. The quenching effect only follows a linear Stern-Vollmer relationship at TEA concentrations below 0.25% v/v and no additional quenching is observed beyond 1% v/v TEA (ESI⁺).

Catalyst durability and kinetics were also investigated to gain a greater understanding of the Zn(II) photoreduction mechanism. It was found that at 300 μ M 5,7-dCl-Hq, Zn(π) reduction largely ceases after 200 h and fits a first order decay model with $R^2 = 0.96$. After 10 days an average of 242 µmol zinc was produced, equivalent to 81 TONs (ESI[†]). This constitutes roughly 10% of the Zn present in the vial and the increasing coating of the vessel with light-blocking Zn metal could be a contributing factor to this decrease in reactivity.

Rate studies were also performed, and over the first 8 h a dependence of the zinc production rate on the concentrations of both ZnCl₂ and 5,7-dCl-Hq were measured. Similar to our earlier work with an Ir(m) catalyst, a minimum concentration of $ZnCl_2$ is required for the reaction to proceed, represented as the x intercept in Fig. 7. Interestingly, the x intercept roughly corresponds with the solubility of ZnCl₂ in the reaction mixture, which strongly suggests a heterogeneous reaction pathway. It can be observed that the initial reaction rates increase with the addition of more ZnCl₂ until it plateaus and then decreases at very high loadings. This decrease in



Fig. 7 Dependence of initial rate of Zn(II) on ZnCl₂ per reaction vial. Each vial contained 3 µmol ligand, 1 ml TEA, 9 ml MeCN and ZnCl₂.

yield is likely due to the limited solubility of ZnCl₂, which blocks light absorption. A first order dependence of the reaction rate on ligand concentration was also found. The rate of photoreduction initially is proportional to concentration, but levels off at higher loadings due to the saturation of light absorption of the photoactive catalyst species. A R^2 value of 0.99 is observed for the logarithmic fit derived from Beer-Lambert's law, which indicates that light absorption is saturated at higher catalyst concentrations (ESI⁺).

To summarize, this work presents the photoreduction of $Zn(\pi)$ to zinc metal by a zinc quinolate catalyst that is formed in situ. The highest yields of zinc metal were obtained using ZnCl₂ and 5,7-dichloro-8-hydroxyquinoline in acetonitrile. The active catalyst was identified as a mono-substituted zinc quinolate by ¹H NMR and luminescence quenching. Future work will focus on the replacement of TEA for nonsacrificial Zn(II) photoreduction. The authors would like to acknowledge support from the National Science Foundation through CHE-1055547.

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Communication

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