Electronic Supplementary Information (ESI):

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Organocatalytic Photoreduction of Zn(II) to Zinc Metal

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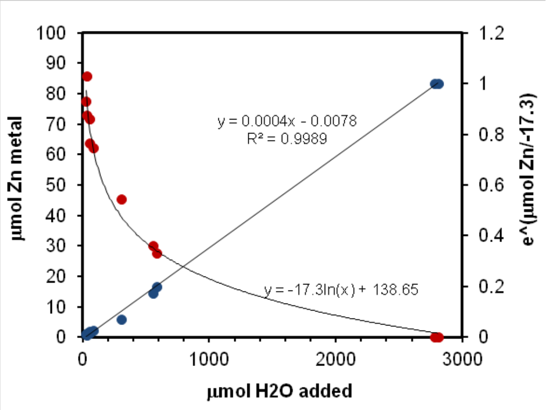
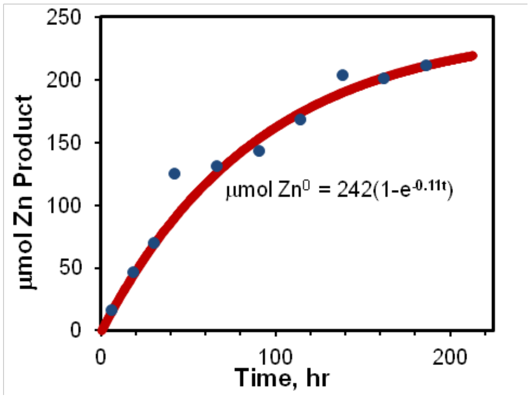
Effect of H_2O on Photoreduction of Zn(II)

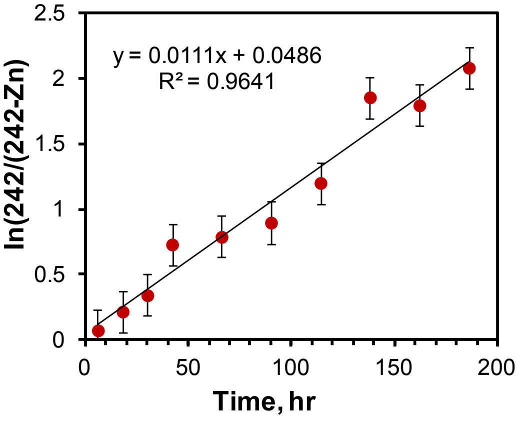
Zinc chloride purchased from Sigma-Aldrich was of an unspecified degree of hydration and used as received for all other photoreactions. In this experiment, the $ZnCl_2$ was heated and dried in a vacuum oven overnight. 420 mg of this $ZnCl_2$ was used per vial, in addition to our standard reaction conditions of 300 µM 5,7-dCl-Hq, 1 ml of TEA and 9-x ml of MeCN, where x = ml of H_2O also added to the vial. An exponential fit was successfully applied. The results are below. Water may displace MeCN coordinated to Zn(II) and therefore shift the reduction potential of Zn(II) more negative and decrease yield of zinc metal product.



Kinetics Studies

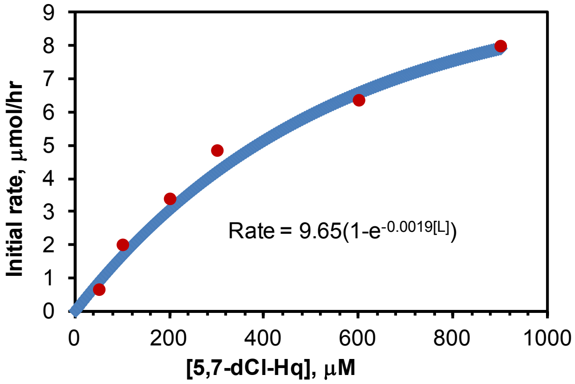
Unless otherwise stated, reaction conditions were as follows: 420 mg $ZnCl_2$, 1 ml TEA, 9 ml MeCN, and 300 µM 5,7-dCl-Hq per vial. Decrease in the zinc production shows a first order fit due to catalyst deterioration.

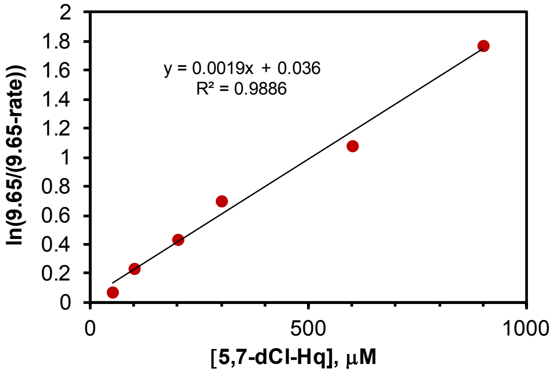




Kinetics Studies continued

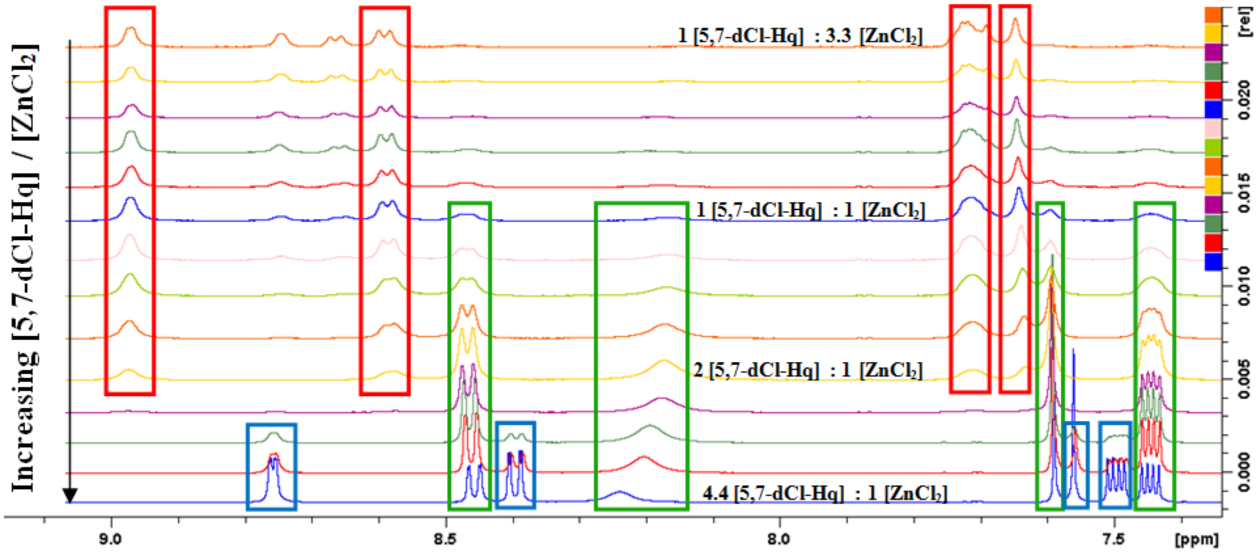
The rate of Zn formation follows Beer-Lambert's law and indicates a saturation of light absorption at higher ligand concentrations.





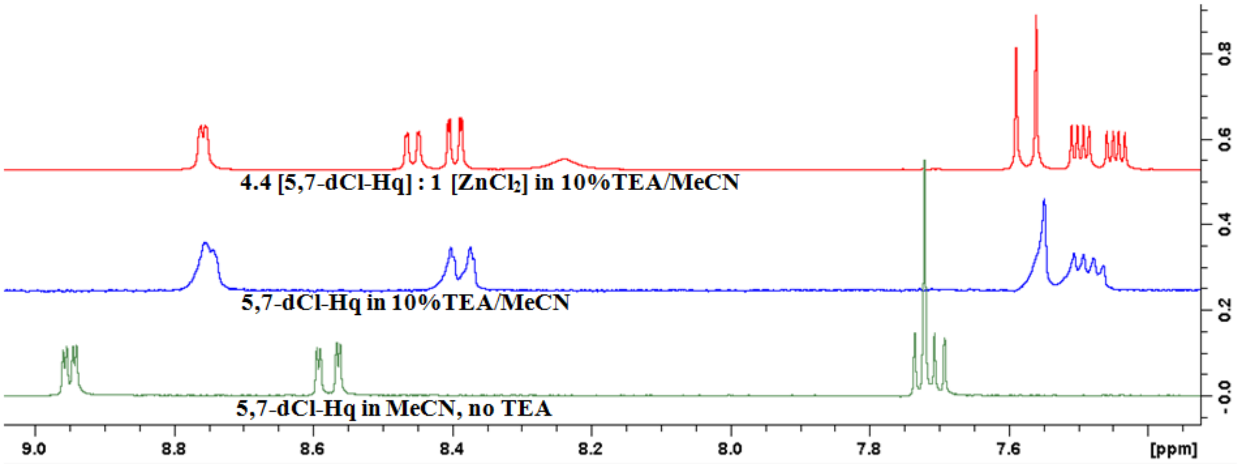
^{1}HNMR Titration Spectra

Peak areas were used to calculate relative concentrations of the quinolate species. While it can be seen that several quinolate signals do overlap, four distinct sets of peaks can be attributed to three different quinolates. Peaks at 8.45, 8.23, 7.59, and 7.44 ppm correspond with Zn(5,7-dCl-q)$_2$ (green boxes), peaks at 8.75, 8.39, 7.56 and 7.49 ppm correspond with 5,7-dCl-q (blue boxes), and peaks at 8.97, 8.58, 7.71 and 7.65 ppm correspond with [Zn(5,7-dCl-q)L$_n$] (red boxes). In the spectra shown below, the greatest ligand to zinc ratio ([5,7-dCl-Hq]/[ZnCl$_2$]) is the bottom blue spectrum, with the relative concentration of 5,7-dCl-Hq decreasing with each subsequent spectra.



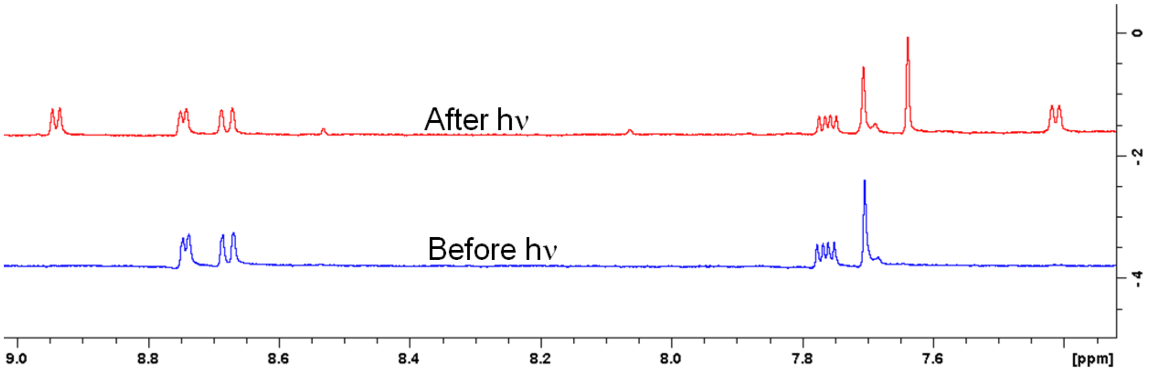
^{1}HNMR Titration Spectra continued

The peaks highlighted in blue boxes on the previous page only appear when the concentration of 5,7-dCl-Hq exceeds twice that of $ZnCl_2$ and can be attributed to deprotonated ligand, 5,7-dCl-q, due to correlation of their ^{1}HNMR spectra. This can be seen below in the stacked ^{1}HNMR spectra of 4.4 [5,7-dCl-Hq] : 1 [$ZnCl_2$] and pure 5,7-dCl-Hq, each in deuterated MeCN with 10% TEA. The absence of free ligand when $ZnCl_2$ is in excess indicates that a zinc quinolate species is likely the active catalyst in the photoreduction of Zn(II). The spectrum of 5,7-dCl-Hq without TEA is depicted at the bottom for reference. The change in solvent environment upon addition of TEA is not limited to an unidirectional shift, but the signal positions are displaced relative to each others, indicating the appearance of a new species which is likely the deprotonated form of the ligand.



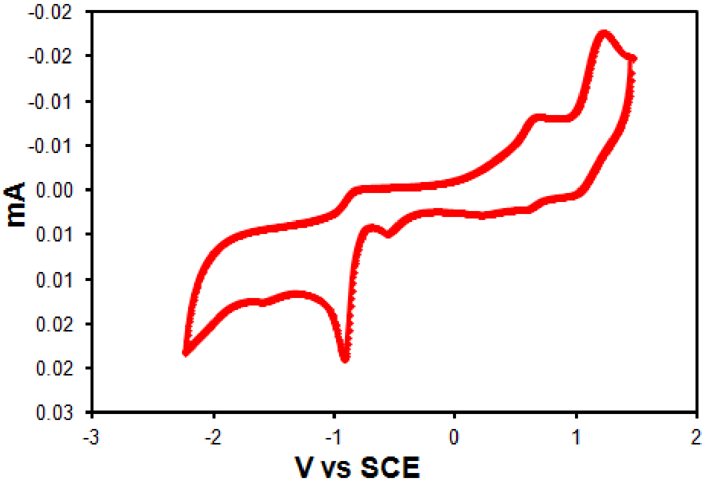
Photoreaction ^{1}HNMR

Photoreactions containing 3μmol 5,7-dCl-Hq, 420 mg $ZnCl_2$, 1 ml TEA and 9 ml MeCN were filtered and dried before and after light exposure. The resulting spectra shown below were taken for each of the dried solids.



Cyclic Voltammetry

Below is a cyclic voltammagram of 3 mM $Zn(BF_4)_2$ and 0.5 mM 5,7-dCl-Hq in MeCN with 100mM tetrabutyl ammonium hexafluorophosphate electrolyte. A glassy carbon working electrode, platinum counter electrode, and silver wire pseudoreference electrode were employed and ferrocene was used as in internal standard. $Zn(BF_4)_2$ was utilized preferentially to $ZnCl_2$ because of superior solubility in acetonitrile, which was required to obtain a clear voltammagram with high signal to noise. An additional benefit was the redox stability of the BF_4^- counterion. The 6 to 1 excess of Zn(II) to ligand was used to simulate photoreaction conditions in which Zn(II) is in excess of the ligand and a mono-substituted zinc quinolate is formed. The in situ formation of such a mono-substituted zinc quinolate is confirmed by the presence of only once reduction peak at -0.91 V before solvent breakdown. In contrast, the bis-subsituted Znq_2 is known to show two irreversible reduction peaks.



Fluorescence Quenching

Stern-Vollmer plot of quenching of $[Zn(5,7\text{-dCl-q})L_n]$ by TEA. The solvent was acetonitrile with 10 mM of both $ZnCl_2$ and 5,7-dCl-Hq.