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Orchestrated Photocatalytic Water Reduction Using Surface-Adsorbing Iridium Photosensitizers

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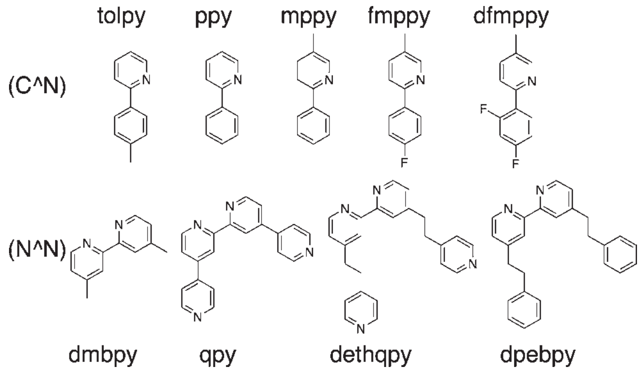
Supporting Information

ABSTRACT: A series of novel Ir(III) luminophores containing pendant pyridyl moieties that allow for adsorption onto metal surfaces has been synthesized. These new photosensitizer compounds have been evaluated for their efficacy in hydrogen-producing photoreactions. The new complexes are shown to significantly outperform the control photosensitizers without adsorbing moieties.

The search for water-splitting photocatalytic systems continues to be of importance in the quest for sustainable solar energy collection and storage.[1−4] To this end, several catalytic systems for solar hydrogen production have been developed.[5−12] Previously, water reduction systems based on an Ir(III) bis-2-phenylpyridine 2,2′-bipyridyl photosensitizer architecture, colloidal platinum catalyst, and triethylamine as a sacrificial reductant have been developed in the Bernhard laboratory.[13,14] However, it has been shown that the performance of this system is limited by photolytic photosensitizer degradation.[14] Specifically, the bipyridyl ligand dissociates from the complex, while the Ir photosensitizer (PS) is in the reduced (PS^-) state due to electrons populating the antibonding LUMO. The free sites on the metal are then occupied by coordinating acetonitrile solvent molecules, forming an ineffectual light absorber. Previous techniques for preventing this deactivation pathway have included switching solvents from acetonitrile to weakly-coordinating tetrahydrofuran and incorporating ligand architectures that prevent dissociative deactivation pathways, such as the $Ir(C^\wedge N^\wedge N)_2$ architecture.[15] It would be desirable, however, to reduce the amount of time the photosensitizer spends in the singly reduced state by increasing the rate of electron transfer from PS^-. An effective method of increasing electron-transfer rates in both synthetic and biological systems is to spatially link electron donors and acceptors.[16,17] Several groups have shown that ionic metal complexes with pendant pyridyl moieties are able to adsorb and form monolayers on platinum surfaces.[18−26] Therefore, we have designed a series of novel iridium photosensitizers with pendant pyridine moieties, which allow these molecules to assemble onto the colloidal platinum catalyst in the photolytic water reduction systems.

Two different 2,2′-bypyridyl ligands with pendant pyridyl moieties were chosen: 4,4′:2′,2″:4″,4‴-quaterpyridyl (qpy) and 4,4′-bis(2-(pyridin-4-yl)ethyl)-2,2′-bipyridine (dethqpy). The novel dethqpy ligand was synthesized by reacting 4,4′-dimethyl-2,2′-bipridyl (dmbpy) with 2 equivalents of lithium diisopropylamide. The resulting dilithiated complex was reacted with 4-chloromethylpyridine to form the desired ligand. The qpy[27] and dpebpy[28] ligands were synthezised according to literature procedures. The dmbpy ligand was chosen as a control ligand to design photosensitizers with photophysical properties similar to those of the dethqpy compounds. These bipyridyl ligands were combined with a series of five cyclometallating ligands that lead to diverse excited-state energies: 2-*p*-tolylpyridine (tolpy), 2-phenylpyridine (ppy), 5-methyl-2-phenylpyridine (mppy), 2-(4-fluorophenyl)-5-methylpyridine (fmppy), and 2-(3,4-difluorophenyl)-5-methylpyridine (dfmpy). Chart 1 shows the structures of the ligands used to synthesize the PS complexes in the $[Ir(III)(C^\wedge N)_2(N^\wedge N)]^+$ architecture.

Chart 1



The efficacies of the PS compounds for water reduction were evaluated in parallel on our home-built 16-well photoreactor.[13] Photoreaction mixtures contained 1.00 μmol of PS, 0.500 μmol of K_2PtCl_4, 1.0 mL of triethylamine (TEA), 1.5 mL of H_2O, and 7.5 mL of THF. The Pt salt has been shown to form a colloid *in situ*.[13] The total electron turnover numbers for all 15 PS compounds are graphed in Figure 1. The presence of pendant pyridyl moieties on the qpy and dethqpy complexes leads to a dramatic increase in catalytic activity of the system with respect to the analogous dmbpy complexes. This increase in activity is apparent despite arguably inferior photophysics of the complexes that contain linking ligands.

Radiative quantum yields (ϕ_r) for the photosensitizers were measured at 450 nm in THF/H_2O mixtures (85% THF by volume) to mimic photoreaction conditions and are graphed in Figure 2. The dmbpy complexes had the highest quantum yields for all C^N ligands with the exception of dfmppy luminophores.

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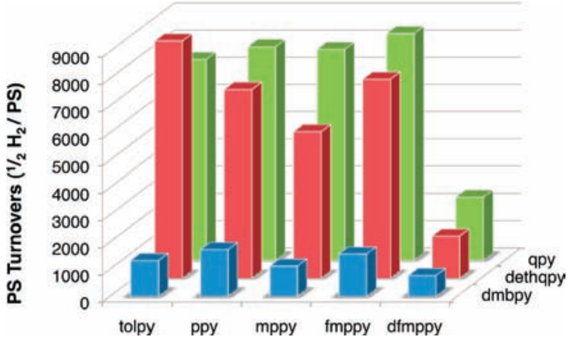

Figure 1. Electron turnovers for the various Ir PS complexes. Photoreaction mixtures contained 1.00 μmol of PS, 0.500 μmol of K_2PtCl_4, 1.0 mL of TEA, 1.5 mL of H_2O, and 7.5 mL of THF. Reactions were run for 75 h.

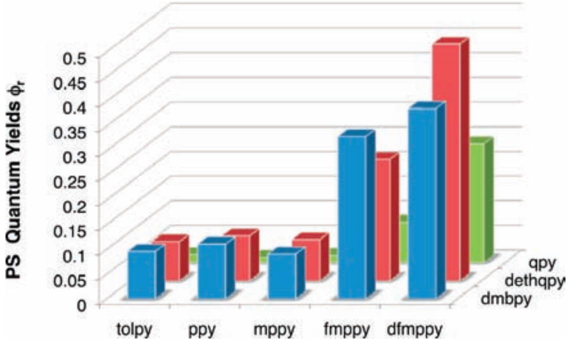

Figure 2. Comparison of the radiative quantum yields (ϕ_r) for the various PS complexes. Emission spectra were measured at 450 nm excitation, and quantum yields were calculated relative to $[Ru(bpy)_3]PF_6$.

The dethqpy quantum yields are similar to those of the dmbpy compounds but slightly lower. This is to be expected: the greater conformational freedom of the dethqpy ligand increases the likelihood of nonradiative decay in these complexes. In contrast, the larger π system of the qpy ligand leads to dramatic changes in the photophysical properties compared to those of the dmbpy and dethqpy complexes. The quantum yields are generally reduced and the phosphorescence is red-shifted relative to those of the dmbpy and dethqpy compounds. Nevertheless, the qpy and dethqpy complexes significantly outperform the dmbpy complexes in hydrogen evolution reactions. It is likely that this increase in performance can be attributed to the spatial linking of the photosensitizer to the platinum colloid surface, but the very low concentration of platinum in the photoreactions makes analysis of the colloidal surface unfeasible. Such a PS/colloid ensemble would render the electron-transfer step no longer diffusion dependent. As a consequence, the photosensitizer is more likely to transfer its reducing electrons to the colloidal catalyst, and the aforementioned decomposition of the reduced Ir complex through ligand dissociation will be prevented.

Figure 3 shows kinetic traces for hydrogen evolution reactions of the $[Ir(ppy)_2(N^\wedge N)]^+$ complexes. The $[Ir(ppy)_2(dethqpy)]^+$ and $[Ir(ppy)_2(qpy)]^+$ compounds have longer catalytic lifetimes and a 4-fold increase in turnover numbers compared with $[Ir(ppy)_2(dmbpy)]^+$. A second control molecule, incorporating 4,4′-diphenethyl-2,2′-bipyridine (dpebpy) as its ancillary ligand, was chosen. $Ir(ppy)_2(dpebpy)^+$ was analyzed for hydrogen production.

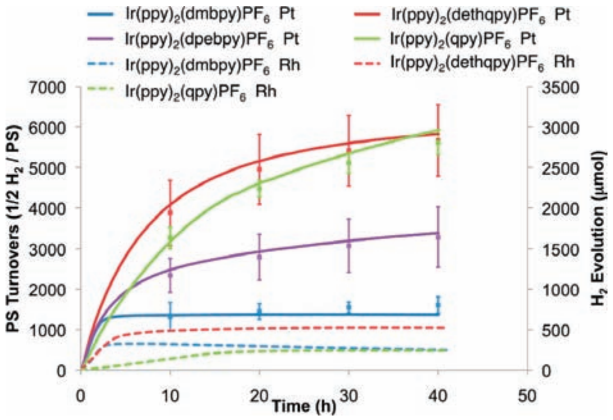

Figure 3. Representative kinetic traces of hydrogen evolution photoreactions containing $[Ir(ppy)_2(N^\wedge N)]^+$ photosensitizers with both Pt and Rh catalysts. Photoreactions contained 1.00 μmol of PS, 1.0 mL of TEA, 1.5 mL of H_2O, 7.5 mL of THF, and either 0.500 μmol of K_2PtCl_4 (solid lines) or 0.50 μmol of $[Rh(bpy)_2Cl_2]Cl$ (dashed lines). Error bars represent $\pm 1\sigma$ ($n = 6$), centered around the average turnover number at that time point.

This compound was evaluated because it has the same structure as the $[Ir(ppy)_2(dethqpy)]^+$ photosensitizer but omits the nitrogen heteroatoms in the pendant aromatic rings. This complex allows for a structural analogue of the dethqpy complex but without the adsorbing moiety. The $[Ir(ppy)_2(dethqpy)]^+$ complex shows a 2-fold increase in hydrogen evolution relative to $[Ir(ppy)_2(dmbpy)]^+$, but it is, in turn, outperformed by the complexes with pendant pyridyl groups. It has been shown, however, that metal complexes with large aliphatic and aromatic groups can adsorb onto metal surfaces due to London dispersion and hydrophobic interactions, without adsorbing nitrogen moieties.[29] It is possible that the performance of the $Ir(ppy)_2(dpebpy)^+$ photosensitizer is due to this weaker adsorption effect.

The error bars on the kinetic traces represent one standard deviation ($n = 6$) above and below the mean hydrogen evolution of the reactions after 10, 20, 30, and 40 h. While some of the photosensitizers showed considerable variance between reactions, the relative hydrogen production of the different photosenstizers remained the same. The complexes with pendant pyridyl groups consistently outperformed the control molecules.

Figure 3 also shows kinetic traces for reactions in which the platinum catalyst has been replaced with 0.50 μmol of $[Rh(bpy)_2Cl_2]Cl$, which has been shown to act as a molecular catalyst for water reduction.[6] With this molecular catalyst, the pendant pyridyl moieties do not provide a clear advantage over the control PS in terms of reaction rate or catalytic lifetime. In the case of the molecular rhodium catalyst, the linking pyridyl moieties do not bind to the catalyst as they do with the colloidal catalyst. In this case, the electron-transfer step of the hydrogen production reaction will still be diffusion dependent, and a large increase in hydrogen production is not observed relative to the control PS.

In order to confirm that water was acting as the proton source in the hydrogen evolution reactions, photoreactions were carried out with the $[Ir(ppy)_2(N^\wedge N)]^+$ complexes, using the same conditions as above but substituting D_2O in place of the water. Analysis of the photoreaction headspaces is summarized in Table 1. The large percentage of D_2 in the products of all three reactions confirms that water is reduced in the reactions.

Table 1. Analysis of Products from the D_2O Photoreactions

	$[Ir(ppy)_2(dmbpy)]^+$	$[Ir(ppy)_2(dethqpy)]^+$	$[Ir(ppy)_2(qpy)]^+$
% H_2	5.1	7.6	5.2
% HD	22.4	35.0	28.6
% D_2	72.5	57.4	66.2
total % D	83.7	74.9	80.5

The rates of the photoreactions carried out in H_2O and D_2O were compared. Differences in reaction rates were observed but found to be within experimental error, and no conclusive kinetic isotope effect could be determined.

In conclusion, we report the synthesis of a series of novel iridium photosensitizer complexes. These compounds incorporate pendant pyridyl moieties to allow the complexes to adsorb on platinum surfaces. These photosensitizers were evaluated in water reduction photoreactions and were found to exhibit higher stability than photosensitizers that exhibited similar photophysical properties but lacked adsorbing moieties.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Detailed experimental and spectroscopic procedures; excited-state lifetimes of PS; and synthesis and characterization of the dethqpy ligand and novel iridium compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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