Oxidation Photocatalysis

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Homogeneous Photocatalytic Oxidation of Alcohols by a Chromophore–Catalyst Dyad of Ruthenium Complexes**

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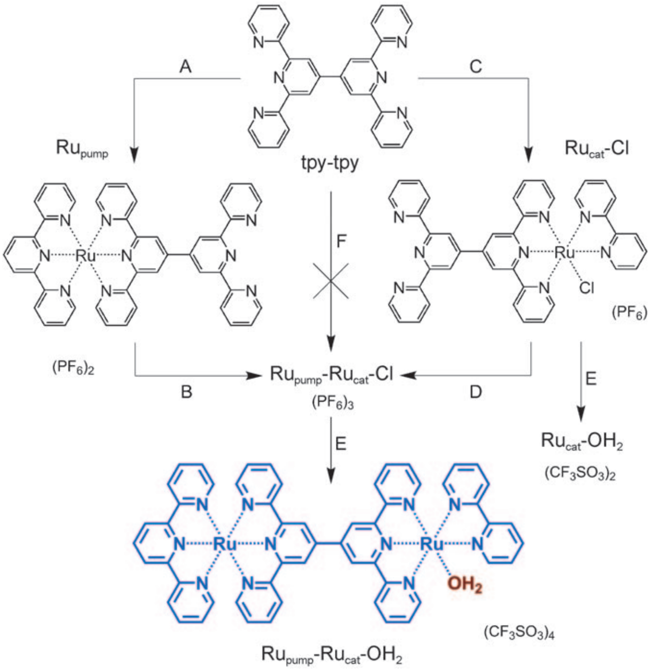
A common challenge in the molecular photocatalysis of water splitting toward artificial photosynthesis[1] has been the realization of modular, multicomponent chromophore–catalyst assemblies that can meet the kinetic and thermodynamic requirements whilst successfully integrating both 1) the charge-transfer photoexcitation and accompanying stepwise transfer of a single electron to/from an acceptor/donor at the chromophoric end, and 2) the proton-coupled, multielectron redox buildup and chemical reactivity of the catalytic unit. Of particular interest to us is the potential utilization of visible sunlight energy to photochemically drive the catalytic oxidation of water into dioxygen. This reaction is highly endergonic and mechanistically complex, and involves a four-electron/four-proton transformation that has been recognized as the bottleneck for the overall water splitting leading to H_2 and O_2 evolution. The photocatalysis of this process remains to be demonstrated in (supra)molecular chemistry.

As a step toward this goal, we have designed and prepared a structurally simple dyad assembly of ruthenium complexes that is capable of catalytically performing the homogeneous visible-light photooxidation of organic compounds at ambient conditions in aqueous solution. As a proof of concept, we chose the dehydrogenation of alcohols, which is a thermodynamically uphill conversion involving a two-electron/two-proton coupled process. Besides their practical importance in organic processes,[2] such transformations are also of relevance to hydrogen-based energy technologies because the anodic liberation of protons and electrons [Eq. (1)] can be coupled with recombination on a cathode for H_2 fuel production in an integrated photoelectrochemical cell.[3]

$$R^1CH(-OH)R^2 \xrightarrow[H_2O,\ 25\,^\circ C,\ 1\ atm]{h\nu} R^1C(=O)R^2 + 2\,H^+ + 2\,e^- \qquad (1)$$

The photocatalyst was constructed from ruthenium polypyridyl building blocks using the synthetic strategy shown in Scheme 1. A key consideration in the design of this assembly was the fact that the $[Ru^{II}(tpy)(bpy)(OH_2)]^{2+}/[Ru^{IV}(tpy)(bpy)(O)]^{2+}$ couple has been extensively explored[4,5] in proton-coupled electron-transfer (PCET) reactions[6] and oxidation of organic substrates upon redox activation by either electrochemistry or chemical oxidants, that is, $H_2O\text{-}Ru^{II} \rightleftarrows O{=}Ru^{IV} + 2\,H^+ + 2\,e^-$. The $[Ru(tpy)_2]^{2+}$ unit is a well known chromophore[7], owing to its efficient metal-to-ligand charge transfer (MLCT) "pump", with a strong absorption in the visible region. $[Ru(tpy)_2]^{2+}$ is a more appealing alternative to the bipyridine $[Ru(bpy)_3]^{2+}$ analogue because substitution at the 4'-position of terpyridine can be used to afford linear, rigid structures favoring electron-transfer directionality.[7,8]



Scheme 1. Synthetic strategy for the preparation of the dyad assembly and its monometallic precursors/components: A) $[Ru(tpy)(dmso)Cl_2]$ (0.8 equiv) in *N*,*N*-dimethylformamide, reflux; isolation, then NH_4PF_6 (excess) in water. B) *cis*-$[Ru(bpy)(dmso)_2Cl_2]$ (1.0 equiv) in methanol, reflux; then NH_4PF_6 (excess). C) *cis*-$[Ru(bpy)(dmso)_2Cl_2]$ (0.7 equiv) in *N*,*N*-dimethylformamide, reflux; isolation, then NH_4PF_6 (excess) in water. D) *cis*-$[Ru(tpy)(dmso)Cl_2]$ (1.0 equiv) in methanol, reflux; then excess NH_4PF_6. E) ion-exchange resin (Cl^- form) in water; separation, then addition of $Ag(CF_3SO_3)/K(CF_3SO_3)$. F) Single-pot reaction in *N*,*N*-dimethylformamide, stoichiometric amounts of *cis*-$[Ru(tpy)(dmso)Cl_2]$ and *cis*-$[Ru(bpy)(dmso)_2Cl_2]$.

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The simplest approach to coupling the catalyst to the chromophore without dramatically perturbing their referential redox and spectral features was to introduce a single covalent bond between the two units. We found that two methods were successful (Scheme 1), both starting from the "back-to-back" bridging terpyridine ligand 6′,6″-bis(2-pyridyl)-2,2′:4′,4″:2″,2‴-quaterpyridine (tpy-tpy). This bridging ligand was then capped in a stepwise manner with terminal metal–tpy/bpy units. In one route (Scheme 1, A and B), the chromophore fragment, or charge-transfer "pump" (Ru_{pump}), was used as an intermediate to the dyad, whereas in the other (Scheme 1, C and D), the dyad was prepared from the catalytic fragment (Ru_{cat}). Although both methods gave good amounts of the chloro dyad (Ru_{pump}-Ru_{cat}-Cl), synthesis from Ru_{cat} afforded the higher yield. The single-pot reaction (Scheme 1, F) gave only trace amounts of the target product. In the final step (Scheme 1, E), the chloro species isolated as a hexafluorophosphate salt was converted into the aquo form of the dyad as a triflate salt (Ru_{pump}-Ru_{cat}-OH_2) by removal of the Cl^- ligand using Ag^+ ions in aqueous solution.

All compounds in Scheme 1 were fully characterized by mass spectrometry, NMR spectroscopy, and elemental analysis.[9] The ESI mass spectrum of Ru_{pump}-Ru_{cat}-Cl showed a single charge state at $m/z = 1381.92$, which is consistent with the formulation of the tricationic complex plus two PF_6^- counterions; the ESI mass spectrum of Ru_{pump}-Ru_{cat}-OH_2 revealed a double charge state at $m/z = 676.5$, which is consistent with the tetracationic complex plus two $CF_3SO_3^-$ counterions. All of the compounds are diamagnetic and had well-resolved ^{1}H NMR spectra that exhibited the typical aromatic resonances associated with polypyridyl ligands; the spectrum of the aquo dyad, Ru_{pump}-Ru_{cat}-OH_2, showed two distinct singlets at $\delta = 9.38$ and 9.27 ppm that are readily assigned to two sets of 3′,5′-protons at the tpy-tpy bridge.

The redox potentials were then determined by cyclic voltammetry (CV); the $E_{1/2}$ values (Table 1) confirmed that the electronic properties of the metal centers are only weakly perturbed in the bimetallic assembly by comparison with their monometallic components. The observed shifts of nearly −0.5 V from the all-polypyridyl species ($[Ru(tpy)_2]^{2+}$ and Ru_{pump}) to the chloro intermediates, and about +0.3 V from these to the aquo products, are typical of these type of complexes and follow the trend predicted by comparison of the corresponding ligand electrochemical parameters ($E_L(L) = 0.25$ V, −0.24 V, and 0.04 V for py, Cl^-, and H_2O respectively).[10]

The CVs of the Ru_{pump}-Ru_{cat}-OH_2 dyad in water exhibited two closely spaced, reversible oxidations at 0.54 and 0.59 V versus SCE (Figure 1). The fact that these processes correspond to the successive PCET couples (H_2O-Ru^{II}/HO-Ru^{III} and HO-Ru^{III}/O$=$$Ru^{IV}$, with a constant overall charge of $+2$) was demonstrated by the dependence of $E_{1/2}$ on pH and the corresponding Pourbaix diagram,[9] which followed the predicted Nernstian behavior[5] over the pH range 1–13. Similar behavior was observed for the monometallic fragment Ru_{cat}-OH_2; however, in this case, the two PCET processes collapsed into a single, unresolved pair of CV waves with average potentials at 0.57 V. The assignment of these two overlapping, stepwise proton-coupled redox processes ($2e^-/2H^+$ overall) was confirmed by the comparative analysis of their relative current intensities (integrated areas) with a known $1e^-/1H^+$ process for the couple $[Ru^{II}(edta)(OH_2)]^{2-}/[Ru^{III}(edta)(OH)]^{2-}$[11] under identical conditions (pH 8.5). The narrow $E_{1/2}$ separations, or overlap, indicate a very efficient redox potential leveling[12] in these systems, with the two-electron/two-proton activation and the catalyst cycling from

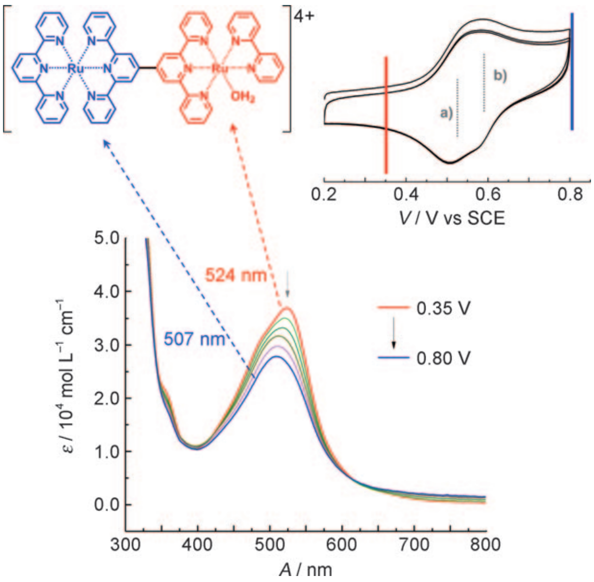


Figure 1. Visible absorption spectra showing the spectroelectrochemical oxidation of the Ru^{II}_{pump}-Ru^{II}_{cat}-OH_2 dyad (red) into its Ru^{II}_{pump}-$Ru^{IV}_{cat}$$=$O form (blue). The applied potentials are noted in the corresponding cyclic voltammogram (in water at pH 6.8; 0.1 M phosphate buffer).[9] The $E_{1/2}$ of the chromophore center is above 1.2 V and therefore Ru^{II}_{pump} is unchanged throughout (a) and (b) for the H_2O-Ru^{II}/HO-Ru^{III} and HO-Ru^{III}/O$=$$Ru^{IV}$ couples; the dyad remains strongly absorbing upon oxidation of the Ru_{cat} unit, owing to the "MLCT pump" capability of Ru^{II}_{pump}.

Table 1: Metal-centered redox potentials ($E_{1/2}$ vs SCE) for dyads and monometallic components in organic and aqueous solutions.

Complex	MeCN[a] Ru^{II}/Ru^{III}	Acetone[a] Ru^{II}/Ru^{III}	Water[b] H_2O-Ru^{II}/HO-Ru^{III}; HO-Ru^{III}/O$=$$Ru^{IV}$
$[Ru(tpy)_2]^{2+}$	1.28	1.32	–
$[Ru(tpy)(bpy)(Cl)]^+$	0.81	0.84	–
$[Ru(tpy)(bpy)(H_2O)]^{2+}$	–[c]	1.15	0.50; 0.61[d]
Ru_{pump}	1.31	1.35	–
Ru_{cat}-Cl	0.83	0.86	–
Ru_{cat}-OH_2	–[c]	1.16	0.57[e]
Ru_{pump}-Ru_{cat}-Cl	0.86, 1.34	0.88, 1.37	–
Ru_{pump}-Ru_{cat}-OH_2	–[c]	1.19, 1.38	0.54; 0.59[f]

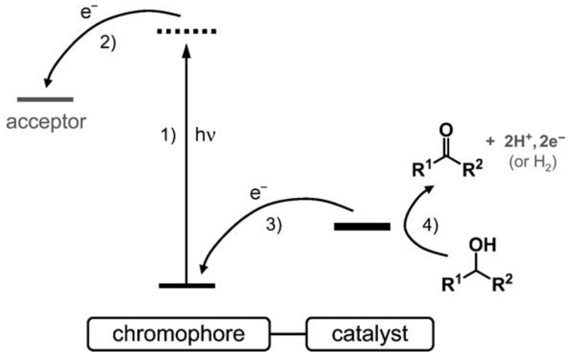
[a] 0.1 M Bu_4NPF_6; Pt electrode. [b] 0.1 M phosphate buffer (pH 6.8); activated glassy carbon electrode. [c] Acetonitrile is coordinating and replaces the water ligand. [d] Reported values are 0.49 and 0.62 versus SSCE.[5] [e] Average potential for the two overlapped proton-coupled redox processes. [f] $E_{1/2}$ values correspond to processes a) and b) in Figure 1, both for the catalytic unit; $E_{1/2}$ of the chromophore center is outside the potential range (> 1.2 V).

ruthenium(II) to ruthenium(III) to ruthenium(IV) occurring essentially at the same potential.

The electronic spectra of the Ru_{pump}-Ru_{cat}-OH_2 dyad in acetone or water showed strong, broad absorptions in the visible region (Figure 1);[9] these absorptions arise from the metal-to-ligand charge transfer (MLCT) transitions on each moiety, that is, dπ(Ru)→π*(tpy/tpy-tpy). These spectra revealed two main components, which were assigned using spectroelectrochemistry in aqueous solution (pH 6.8) as follows: the band with maximum at 524 nm ($\varepsilon \approx 1.1 \times 10^4\,\text{M}^{-1}\,\text{cm}^{-1}$) originates at the catalytic unit and disappears as H_2O-Ru^{II} is oxidized into HO-Ru^{III}/O=Ru^{IV} (in which MLCT transitions are absent); at applied potentials between 0.60 V and 1.2 V vs SCE, only the intense absorption of the Ru^{II} chromophoric moiety (MLCT "pump") is maintained (507 nm; $\varepsilon = 2.8 \times 10^4\,\text{M}^{-1}\,\text{cm}^{-1}$). An analogous pattern was seen for the chloro dyad system Ru_{pump}-Ru_{cat}-Cl in organic solvent, but with the lower-energy MLCT component further red-shifted owing to the strongly π-donating ability of Cl^-, which causes a decrease in the dπ→π* energy gap. The same electronic trend was observed for the monometallic fragments,[9] which is consistent with the redox behavior shown in the electrochemistry data.

In the photocatalytic experiments, sealed vials containing 5.0 mL of an aqueous (H_2O or D_2O) argon-degassed solution at pH 6.8 (0.10 M phosphate buffer) with 0.02 mM Ru_{pump}-Ru_{cat}-OH_2, 10 mM substrate, and 20 mM $[Co(NH_3)_5(Cl)]Cl_2$ (as acceptor)[13] were exposed to simulated visible sunlight irradiation ($\lambda >$ 390 nm) for 24 h. All experiments were performed at room temperature and atmospheric pressure; the reaction products were characterized by ^{1}H NMR spectroscopy and confirmed with GC-MS analysis (for details, see the Supporting Information). All the benzyl alcohols were converted into their corresponding benzyl aldehydes with turnover numbers (TONs) in the range of 150–175 cycles. Moreover, the catalytic reactivity was also highly selective, with no over-oxidized products formed. In the case of aliphatic alcohols, the secondary alcohol 2-propanol was converted into acetone with a TON of 110 cycles (Table 2). However, no activity was observed for the photooxidation of aliphatic primary alcohols. From the kinetic plots of TON versus time, the initial turnover frequencies (TOF) for isopropyl alcohol and benzyl alcohol were estimated to be 14 h^{-1} and 20 h^{-1}, respectively.[9]

The activation of the catalyst occurs upon sequential photoexcited electron transfers from a chromophore-centered ^{3}MLCT state to the sacrificial acceptor[14] (Scheme 2, steps 1–3). Oxidation of the substrate then takes place, coupled with catalyst recycling (Scheme 2, step 4). Here, the acceptor plays a surrogate role for the semiconductor (e.g. TiO_2) in a dyad-sensitized photoelectrochemical scheme in which the released protons provide the route to generate H_2 at the cathode.



Scheme 2. The main putative steps involved in the oxidation of alcohols (4) upon photoactivation of the resting Ru_{pump}-Ru^{II}_{cat}-OH_2 dyad to its catalytic state Ru_{pump}-Ru^{IV}_{cat}=O accompanying a sequential repetition of the photoexcitation and electron transfer process (1)–(3).

Although photophysical and kinetic studies are required to elucidate the mechanistic details of this (photo)chemical cycle, the remarkable photocatalytic activity shown here for a simple dyad assembly is a promising result toward the development of molecular systems for solar, multielectron photooxidation of organics (and, ultimately, water) in combination with H_2 fuel production.

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Table 2: Catalytic photooxidation of alcohols by Ru_{pump}-Ru_{cat}-OH_2.[a]

Substrate	Product[b]	TON[c]
benzyl alcohol	benzaldehyde	150
4-methylbenzyl alcohol	4-methylbenzaldehyde	158
4-chlorobenzyl alcohol	4-chlorobenzaldehyde	166
4-methoxybenzyl alcohol	4-methoxybenzaldehyde	174
1-phenylethanol	acetophenone	132
2-propanol	acetone	110
1-propanol	–	–
ethanol	–	–

[a] Aqueous solution, pH 6.8 (0.1 M phosphate buffer); [catalyst] = 0.02 mM; [substrate] = 10 mM; [acceptor] = 20 mM; Xe lamp source (300 W). [b] No products detected from control experiments in the absence of one of the following: light, catalyst, or acceptor. [c] TON (turnover number) after 24 h.

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[14] The $[\mathrm{Co^{III}(NH_3)_5(Cl)}]^{2+}$ complex ($E_{\mathrm{red}} = -0.3$ V vs SCE; pH 6.8) is the acceptor of choice because, following single-electron reduction by electron transfer from the donor (i.e., photoexcited dyad; $E^* \approx -0.7$ V), it undergoes a fast, irreversible decomposition into $[\mathrm{Co^{II}(H_2O)_6}]^{2+}$. The oxidation potential of this aquo cation (about $+1.8$ V) is far more positive than that required for the re-reduction of the ruthenium centers, and thus back electron transfer to the oxidized dyad photocatalyst is prevented (see, for example, Ref. [13]).