Photochemical oxidation of water and reduction of polyoxometalate anions at interfaces of water with ionic liquids or diethylether

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Abstract

It has been known for some time that photochemical reduction of polyoxometalate anions (POMs) in molecular solvents may occur in the presence of an efficient electron donor such as 2-propanol or benzyl alcohol (1–6). In recent studies, we have found that photoreduction of tetracyanoquinodimethane (TCNQ) to TCNQ− and [P2W18O62]6− to [P2W18O62]7− or more extensively reduced POMs occurs in “wet” ionic liquids (ILs) where water acts as an electron donor and is photo-oxidized to dioxygen (7, 8). Intriguingly, these processes do not occur in wet molecular organicsols or in neat water itself. The net reactions that describe the photo-irradiation of [P2W18O62]6− in wet 1-butyl-3-methylimidazolium tetrafluoroborate [Bmim][BF4] (Fig. S1) are summarized in Eqs. 1 and 2:

\[ 4[P_2W_{18}O_{62}]^{6−} + hν \rightarrow 4[P_2W_{18}O_{62}]^{6−}, \]  

\[ 4[P_2W_{18}O_{62}]^{6−−} + 2H_2O \rightarrow 4[P_2W_{18}O_{62}]^{7−} + O_2 + 4H^+. \]

However, while [P2W18O62]7− is the detected product it is probable that more extensively reduced POMs are generated (8) as intermediates in the overall water oxidation reaction [Eq. 3]:

\[ 2H_2O \rightarrow O_2 + 4H^+ + 4e^−. \]

The modified structure of water present as a solute in ILs relative to that found in bulk water is postulated to facilitate H2O2 acting as an electron donor (7–10). However, while multistep two- and four-electron-proton-coupled reaction schemes have been postulated, full mechanistic details have yet to be established (8).

To date, photochemical reactions have rarely been carried out in ILs even though these low temperature molten salts that consist entirely of ionic species have emerged as an important class of solvent (11–18). Nevertheless, it is known that IL media can provide a favorable solvent polarity effect for photo-induced electron transfer (19). Both protic and aprotic ILs are often sparingly soluble or immiscible in water, so certain mixtures of ILs and water give rise to two phases. Furthermore, on examining ILs as a medium for photooxidation of water (7, 8), it was noted that even if an IL is fully miscible with water, the kinetics of its dissolution are often sufficiently slow that two phases may persist for long periods of time. Consequently, studies on the photochemistry at both thermodynamically stable and unstable water–IL interfaces should be possible in a regime in which significant structural kinetic and thermodynamic differences occur relative to bulk solvents. Consequently, photooxidation of water at interfaces may be even more favorable than in bulk wet ILs.

Solubility issues play an important role in determining which photo-reactions may be studied at water–IL interfaces. Sodium and potassium salts of polyoxometalate anions are often very soluble in aqueous media. In contrast, tetraalkylammonium salts such as [Bmim][P2W18O62] are sparingly soluble in water (or even insoluble) but are reasonably soluble in many ILs. However, dissolution of these salts in highly viscous aprotic ILs is often kinetically slow even though mM concentrations or above are thermodynamically accessible (20–22). Typically, reduced polyoxometalate anions are substantially more soluble in IL media. For example, one-electron reduced [P2W18O62]7− is highly soluble in many aprotic and protic ILs even in the presence of K+ counter ions (23, 24). It is apparent that a water–IL interface with a POM present in either phase can provide an environment where a variety of mass transport outcomes are possible.

ILs may act both the solvent and electrolyte, so voltammetric detection of electroactive POM species is possible by careful placement of electrodes in the bulk solution and near the interface. A similar situation applies in an aqueous medium or...
organic solvent phases, provided an electrolyte is added. In principle, voltammetric monitoring of a two-phase system will allow the level of reactivity to be probed in both phases. An organic–aqueous interface provides another scenario to study photochemistry in which the structure of interfacial water is again expected to differ from that in bulk water. In this study we show that photo-oxidation of water in the presence of photoactive \([P_2W_{18}O_{62}]^{6–}\), \([S_2MnO_8O_6]^{4–}\), or \([S_2W_{18}O_{62}]^{4–}\) anions occurs preferentially at water–IL and water–diethylether interfaces. We emphasize the use of electroanalytical techniques of transient and steady-state voltammetry to establish the POM redox level [Eq. 2] and to detect dioxygen and proton concentrations (Eq. 3, the Clark and pH electrodes).

**Results and Discussion**

As noted above, \(K_0\[P_2W_{18}O_{62}\]_s is highly soluble in water but has very limited solubility in the aprotic and protic ionic liquids used in this study. However, the solubility of the reduced species formed in photo-irradiation experiments (8) is significantly higher in the ILs. This is illustrated by cyclic voltammograms obtained when \(K_0\[P_2W_{18}O_{62}\] was adhered to a GC electrode and placed in contact with the IL DEAS (Fig. S1). Increased currents were detected upon repetitive cycling of the potential (Fig. S2), consistent with dissolution of the more soluble reduced salt of \([P_2W_{18}O_{62}]^{7–}\) formed at the electrode surface. The mechanism appears to be analogous to that proposed for a POM-modified electrode in contact with \([Bmim][PF_6]\) (20) and is described by Eqs. 4 and 5:

\[
K_0\[P_2W_{18}O_{62}\]_s + DEA^{+}\text{IL} + e^- \rightleftharpoons [DEA][K_0][P_2W_{18}O_{62}]_s \tag{4}
\]

\[
\text{dissolution} \quad [P_2W_{18}O_{62}]^{6–} + e^- \rightleftharpoons [P_2W_{18}O_{62}]^{7–}\text{IL} + \text{DEA}^{+}\text{IL} + 6 K^{+}\text{IL}. \tag{4}
\]

\[
[P_2W_{18}O_{62}]^{7–}\text{IL} + n e^- \rightleftharpoons [P_2W_{18}O_{62}]^{(n+1)–}\text{IL}. \tag{5}
\]

Scanning to more negative potentials generates \([P_2W_{18}O_{62}]^{8–}\text{IL}, and more highly reduced forms [Eq. 5]. Formation of soluble reduced anions was confirmed visually by the appearance of a blue color in the IL near to the electrode surface.

In order to ascertain if photoreduction of \([P_2W_{18}O_{62}]^{6–}\text{IL could occur at the thermodynamically unstable water–DEAS interface, photochemical experiments were initially undertaken on solutions contained in a soda glass vial with visual monitoring of solution color as a function of time (Fig. 1). In a previous study, it was shown that photoreduction of \([P_2W_{18}O_{62}]^{6–}\text{IL does not occur in either bulk water or bulk DEAS (8). In the present two-phase configuration, the upper phase was water, in which \(K_0\[P_2W_{18}O_{62}\] is highly soluble, and the lower phase was DEAS, in which the salt is essentially insoluble. Even though DEAS is highly miscible in water, the dissolution process (in the absence of convection) is slow, allowing a two-phase system to exist for more than 10 h. However, after sufficient time has elapsed, the upper phase can be described as water-rich and the lower one as DEAS-rich.

To achieve the thermodynamically unstable two-phase condition, an aqueous solution containing \([P_2W_{18}O_{62}]^{6–}\text{IL was added slowly and dropwise onto the top of the DEAS phase in the soda glass vial using a Pasteur pipette whose tip rested against the edge of the vial, as shown in Fig. 2. This approach minimized mixing of the two solvents by convection: Miscibility was achieved only after standing for more than 10 h (predominantly by diffusion, a very slow process). Water has the lower viscosity (approximately 1 vs. > 4,356 mPa s) and density (1.00 vs. 1.21 g cm\(^{-3}\)) (25–27). Thus, careful dropwise addition of the aqueous solution onto the IL surface was preferred to the alternative of addition of the IL onto water. The addition of water (5 mL) to DEAS (2 mL), in the manner described, leads to the formation of two phases, with the bottom one being the denser IL phase (Fig. L4). Prior to irradiation with white light, clyc voltammetric monitoring of the \([P_2W_{18}O_{62}]^{6–}\text{IL (Fig. 3) confirmed that oxidized \([P_2W_{18}O_{62}]^{6–}\text{IL remained present in the aqueous phase and that its concentration in the DEAS phase was negligible (below the detection limit of 10 \(\mu\text{M}\). Note that electrolyte KCl (0.1 M) was also present in the aqueous phase in experiments involving voltammetric monitoring of the aqueous phase. A single phase was formed rapidly when the two-phase system was shaken vigorously. It follows that partial mixing of the two near liquids must occur in the interfacial region (Fig. 1) in a time-dependent manner.

In photochemical experiments, the initial water–DEAS two-phase system was irradiated from the side with white light (\(\lambda = 275–750\) nm). The light source was located at a distance of 3 cm from the vial in a manner that ensured that both phases were exposed to the same light intensity (Fig. 2A). No change in temperature (\(\pm 0.1^\circ\text{C}\)) was detected during the course of this experiment. Very similar results were obtained using UV light (275–320 nm) because the \([P_2W_{18}O_{62}]^{6–}\text{anion only absorbs weakly in the visible wavelength region.

Initially, both phases were colorless. Five to 10 min of irradiation with white light generated blue coloration solely in the water–DEAS interfacial region (Fig. 1 B and C). The blue color is characteristic of reduced \([P_2W_{18}O_{62}]^{n–}\text{(n > 6). After 10 min, the color diffused slowly into the bulk water phase but not into the DEAS phase (Fig. 1C). Previously, photoreduction of \([P_2W_{18}O_{62}]^{6–}\text{was shown to occur in aqueous media containing DEAS concentrations \(\geq 0.08 \text{M}\) (8). It is likely that these conditions are present in the interfacial region in the present experiment. The time required for blue material to be detected in the aqueous phase decreased with increasing \([P_2W_{18}O_{62}]^{6–}\text{concentration (0.1 to 3 mM), consistent with the extent of photoreduction being dependent on the polyoxometalate anion concentration. After 20 min of irradiation, some blue material was seen to be transported into the DEAS phase (Fig. 1D). Continued photoreduction led to further diffusion of color into the IL phase until, after about 1 h, this phase was uniformly blue (Fig. 1E).
Rent was higher in the bulk aqueous solution than in the region just above the interface (Fig. 4). This reflects the higher concentration of viscous DEAS in the interfacial region and correspondingly lower diffusion coefficient values. The diffusion coefficient for $[P_2W_18O_{62}]^{6-}$ in water–DEAS mixed solvent media is a function of DEAS concentration (Table S1).

The mass transport process is driven by the differential solubilities and distribution coefficients of the reactant and product as well as their diffusion coefficients in the water and IL phases. $K_2 [P_2W_18O_{62}]$ is highly soluble in water but not in the IL; the reduced material is more soluble in the IL than in water. The overall mass transport observations are rationalized by the fact that the diffusion coefficient of $[P_2W_18O_{62}]^{7-}$ in the IL is two orders of magnitude smaller than in molecular solvents (i.e., the product anion diffused into the aqueous phase prior to its extraction into the IL phase). Eventual transfer of $[P_2W_18O_{62}]^{7-}$ to the IL layer was confirmed by cyclic voltammetric experiments (Fig. 5).

The production of dioxygen via Eq. 2 in the upper aqueous phase in the water–DEAS system was monitored by a Clark-type electrode located 1 cm above the interface. The aqueous phase containing $[P_2W_18O_{62}]^{6-}$ was initially degassed for 10 min with dinitrogen to minimize the dioxygen concentration. This solution was then added to dinitrogen-degassed DEAS using the procedure described in Fig. 2A. The vial was then sealed from the atmosphere (8). No significant change in $[O_2]$ from the background level of about 120 μM was apparent initially but a significant increase occurred after about 6 min of irradiation with white light (Fig. 6). The delay is attributed to the time required for diffusion of $O_2$ to the Clark electrode. After prolonged photolysis, the oxygen concentration reached a maximum value and then decreased slowly (Fig. 6). $[P_2W_18O_{62}]^{7-}$ reacts very slowly with $O_2$ to regenerate $[P_2W_18O_{62}]^{6-}$. Clearly, if this reaction were fast, $[P_2W_18O_{62}]^{7-}$ would not be detected. More highly reduced anions react rapidly with $O_2$ so $[P_2W_18O_{62}]^{7-}$ is the “sink” (28).

Two-phase irradiation experiments were also carried out under the conditions described above but with [Bmim][PF$_6$] as the IL. Water is only sparingly soluble in this aprotic IL and the system now represents a thermodynamically stable two-phase scenario. However, photoreduction again occurred preferentially at the interface with initial diffusion of $[P_2W_18O_{62}]^{7-}$ into the aqueous phase followed by subsequent extraction into the IL phase.

**Fig. 2.** Schematic representation of the cell arrangement for photochemical experiments at a water–IL interface. (A) Dropwise addition of the aqueous phase onto the IL phase; (B) in situ voltammetric monitoring.

Steady-state microelectrode voltammetric measurements on the $[P_2W_18O_{62}]^{6-}/7-$ couple were undertaken in the aqueous phase after 20 min of irradiation by using the photoelectrochemical cell shown in Fig. 2B. Results are displayed in Fig. 4. Close to the interface, the anion was found to be at the one electron-reduction level $[P_2W_18O_{62}]^{7-}$. In the bulk phase, $[P_2W_18O_{62}]^{7-}$ was still the major component but with a significant concentration of $[P_2W_18O_{62}]^{6-}$ still present. The magnitude of the limiting current was higher in the bulk aqueous solution than in the region near the interface with initial diffusion of $[P_2W_18O_{62}]^{7-}$ into the aqueous phase followed by subsequent extraction into the IL phase.

**Fig. 3.** Cyclic voltammograms ($v = 0.15$ V s$^{-1}$) obtained at a GC electrode before irradiation with white light in (A) the aqueous phase ($K_2 [P_2W_18O_{62}]$, 0.3 mM; KCl, 0.1 M) and (B) the DEAS phase of the thermodynamically unstable two-phase system.

**Fig. 4.** Steady-state voltammograms (GC microelectrode; $d = 15$ μm); $v = 0.002$ V s$^{-1}$) obtained in the aqueous phase ($K_2 [P_2W_18O_{62}]$, 0.3 mM; KCl, 0.1 M) after 20 min of irradiation of the water–DEAS two-phase system. Voltammograms obtained just above the interface (−) and in the bulk region (−) of the aqueous solution phase.
preferentially at the interface to produce all cases, photoreduction of the polyoxometalate anion occurred (5). Again, at longer times, the reduced anions were transferred to the water-acetonitrile phase (0.1 M Bu$_4$NPF$_6$) after 2 h irradiation and (C) after 4 h irradiation. The increase in faradic current is primarily due to the transfer of photo-generated [P$_2$W$_{18}$O$_{62}$]$_{5-}$ into the IL phase.

In related experiments, two-phase systems were formed with acetonitrile (9% water) as the phase containing dissolved K$_2$[P$_2$W$_{18}$O$_{62}$], [Bu$_4$N]$_4$[S$_2$W$_{18}$O$_{62}$] or [Bu$_4$N]$_4$[S$_2$Mo$_{18}$O$_{62}$] and 0.1 M Bu$_4$NPF$_6$ as the supporting electrolyte. The IL phases tested were DEAS, DEAP, [Bmim][BF$_4$], or [Bmim][PF$_6$]. In all cases, photo-reduction of the polyoxometalate anion occurred preferentially at the interface to produce [P$_2$W$_{18}$O$_{62}$]$_{7-}$, [S$_2$Mo$_{18}$O$_{62}$]$_{5-}$, or [S$_2$W$_{18}$O$_{62}$]$_{5-}$ followed by diffusion into the water-acetonitrile phase (0.1 M Bu$_4$NPF$_6$, voltammetric detection). Again, at longer times, the reduced anions were transported into the IL phase. [S$_2$Mo$_{18}$O$_{62}$]$_{5-}$ is further reduced to [S$_2$Mo$_{18}$O$_{62}$]$_{6-}$ on longer light exposure times. Unlike the other POM anions, [S$_2$Mo$_{18}$O$_{62}$]$_{4+}$ is photochemically reduced very slowly to [S$_2$Mo$_{18}$O$_{62}$]$_{5-}$ in wet acetonitrile, confirming that the role of reversible potential also is significant (8, 28). In general terms the overall reaction is represented by Eq. 6:

$$4\text{POM} + 2\text{H}_2\text{O} + \nu \rightarrow 4\text{POM}^- + 4\text{H}^+ + \text{O}_2.$$  

[6]

The significance of the interfacial region was supported by data obtained in analogous experiments involving a thermodynamically stable (immiscible) aqueous-organic solvent two-phase system. A biphasic system consisting of an aqueous solution of K$_2$[P$_2$W$_{18}$O$_{62}$] (0.3 mM; 0.1 M KCl) in contact with diethyl ether phase was examined; on this occasion the diethyl ether phase is on top (p = 0.7134 vs. 1.0000 g cm$^{-3}$ for water) (26). Irradiation with white light for 10 min gave the outcome shown in Fig. 7. Steady-state voltammograms were obtained with a GC microelectrode placed at three different locations (A–C) in the aqueous phase (Fig. 8). All voltammograms exhibit similar total limiting currents but reveal differences in the redox level in the three zones; the oxidation current is higher for the locations closer to the interface, indicating increased proportions of reduced anion [P$_2$W$_{18}$O$_{62}$]$_{7-}$. No extraction into the ether phase occurred in this system as the POM salts are insoluble in ether, irrespective of redox level.

In addition, a decrease of pH from 6.35 to 3.90 occurred in region A during the experiment shown in Fig. 7. This is consistent with production of protons via Eq. 3. Dioxygen evolution was detected by a Clark-type electrode experiment. A control reaction involving irradiation of a suspension of K$_2$[P$_2$W$_{18}$O$_{62}$] in diethyl ether did not change color over 2 h. Photodegradation does not occur for the salt dissolved in neat water.

It is apparent that the interface between the liquid phases plays a key role in photoreduction of the POM anion. This was again apparent in the experiment of Fig. S3 where reduced anion can be detected at the water–diethyl ether interface after irradiation with sunlight for 3 min. Longer exposure times led to diffusion of reduced product into the aqueous phase. Equivalent changes occurred in the water–DEAS system upon exposure to sunlight; as with white light, diffusion into the aqueous phase occurred initially, then, after 4 h, the products extracted into the IL phase.

Photoreduction was also observed when solid polyoxometalate salts were in contact with water vapor. Soda glass vials containing powdered salts were used for these experiments. A micro droplet of water was adhered to the vial edge and immediately sealed from the atmosphere. It was placed on a hot plate so that evaporation of water occurred followed, upon cooling, by uniform condensation over the solid. Controls lacking the droplet and subjected to high vacuum were treated equivalently. The vials were exposed to sunlight (23–31 °C for 12 h per day) and the color changes monitored over a two-week period. Surface color

![Fig. 5. Cyclic voltammograms obtained at a GC working electrode (v = 0.15 V s$^{-1}$) in photo-irradiation experiments of a water–DEAS two-phase system initially containing K$_2$[P$_2$W$_{18}$O$_{62}$] (0.2 mM) in the aqueous phase. The electrode was located in the DEAS ionic liquid phase (see Fig. 2B). (A) Before irradiation with white light; (B) after 2 h irradiation and (C) after 4 h irradiation. The increase in faradic current is primarily due to the transfer of photogenerated [P$_2$W$_{18}$O$_{62}$]$_{7-}$ into the IL phase.](image)

![Fig. 6. Concentration of dioxygen in the aqueous phase in a sealed glass vial. Dioxygen was detected by a Clark-type electrode as a function of irradiation time during photoliumination with white light of the two-phase water–DEAS system. K$_2$[P$_2$W$_{18}$O$_{62}$] (0.3 mM) and KCl (0.1 M) was present in the initial aqueous phase.](image)

![Fig. 7. Two phases water-diethyl ether system after irradiation with white light for 10 min. The ether phase is at the top with the aqueous phase at the bottom. K$_2$[P$_2$W$_{18}$O$_{62}$] (0.3 mM) and KCl (0.1 M) was present in the initial aqueous phase. Steady-state voltammograms were obtained at the indicated positions (A, B, C) in order to evaluate the redox level of the polyoxometalate after irradiation (see Fig. 8).](image)
changes to green/blue were seen after a few hours for (Bu₄N)₄[SiMo₉O₃2] and after a few days for K₆[P₂W₁₈O₆₄]₄. The controls exhibited no change in color. The observations are consistent with photo-oxidation of the salts and oxidation of water. Similar experiments under 2-propanol vapour produced color changes within 1 h.

This work demonstrated that photooxidation of [P₂W₁₈O₆₄]₄⁻, [S₂Mo₉O₃2]⁴⁻, and [SiW₁₈O₆₄]₄⁻ anions occurred at the interfaces of two-phase systems under conditions in which water acts as the electron donor. It is proposed that photo-oxidation of water is facilitated at an interface where the structure of water is different from that in neat H₂O or when water is dissolved in a molecular organic solvent. In particular, hydrogen bonding is expected to be weaker when water is present in the gas phase or at an interface. While the electrochemical methodology used in this study provides qualitative information on the overall reaction, quantitative photochemical data and the photophysics of the reactions are yet to be established. Thus, while Eq. 6 is written as an overall one-electron reduction step with formation of final product POM⁻, it is probable that multi-electron reduced anions are produced as intermediate photo products arising directly from oxidation of water. They would then be expected to react with oxidized anion, H⁺, or O₂ to generate POM⁻ as the detected final product (8).

Quantum yields, ground and excited state potentials, plus the activity of H⁺ at the interface are needed to quantify the photochemistry. The present study raises a series of important photochemical, photophysical, and interfacial questions that are in general beyond the scope of electrochemical methodology. It is relevant that studies in acid-base behavior and catalysis in emulsions have also revealed the role that differences in structure play in the chemistry of water at interfaces (29–32).

**Materials and Methods**

Reagents. K₆[P₂W₁₈O₆₄]·14H₂O, [Bu₄N]₆[S₂Mo₉O₃2], and [Bu₄N]₆[SiW₁₈O₆₄]·14H₂O were synthesized according to literature procedures (28, 33–35). The aprotic 18-crown-6 ether solution used was provided by ChemBion. Details of all reagents are provided in SI Text.

**Photochemistry.**

In most cases, the POM salt was dissolved in the solvent of interest. Voltammetric experiments in single-phase solutions were conducted at (20 ± 1) °C according to the procedure described before (8). For photochemistry in two-phase environments, a specially designed electrochemical cell arrangement was developed for voltammetric monitoring of reactions taking place upon irradiation with light in a two-phase water/IL system (Fig. 2B). Detailed electrochemical procedures are described in SI Text.

**Photochemistry.**

Both phases and the interfacial regions of aqueous–IL or aqueous–diethylether systems were irradiated with white light (275–750 nm) using a Rofin Polillight PL6 Xe source placed 3 cm from the side wall of the soda glass vial (see Fig. 2A). The oxygen concentration and pH values in aqueous media were estimated with a Clark-type gas sensor and a pH Meter. Further details of the light source, Clark sensor, and pH Meter are provided in ref. 8.

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Experimental Details for Electrochemical Measurement in the Two-Phase System. The cell consisted of a soda glass vial that is transparent to UV and visible light. A silver wire RE and a platinum wire CE were introduced, each being in contact with both phases. In the water–IL scenario, two glassy carbon WEs ($d = 3$ mm) were also usually present, with one solely in contact with the IL phase (introduced before the addition of the aqueous 0.1 M KCl electrolyte solution), and the second only in contact with the aqueous phase. Voltammetric studies in both phases were possible when the GC WE in either phase was replaced with a microelectrode ($d = 15 \mu m$). These experiments were carried out under slow scan rate and near-steady-state conditions in order to evaluate the redox level of the POM anion in the bulk aqueous or IL phases and near the interface. In the case of water-diethylether experiments, voltammetric monitoring was possible only in the aqueous phase because the resistance in diethylether phase was too high.

In one series of experiments, microcrystals of $K_6[P_2W_18O_{62}]$ were attached mechanically to the surface of the GC working electrode. A few milligrams of powdered salt was placed on filter paper. The electrode was then pressed onto and rubbed over the solid in order that a small quantity was transferred to the electrode surface.

Diffusion coefficients ($D$) were calculated by application of the Randles–Sevcik equation using cyclic voltammetry.

**Fig. S1.** Structures of [Bmim][BF$_4$], [Bmim][PF$_6$], DEAS, and DEAP.

**Fig. S2.** Cyclic voltammograms ($\nu = 0.15$ V s$^{-1}$) obtained for the $[P_2W_18O_{62}]^{6-}/7^-$ and $[P_2W_18O_{62}]^{7-}/8^-$ processes when a GC electrode with adhered $K_6[P_2W_18O_{62}]$ solid is placed in contact with DEAS. The increased current on the second and third cycles confirms dissolution of the salt.
Fig. S3. Color changes in the aqueous phase during photo-irradiation with sunlight of a soda glass vial containing a two-phase water-diethylether system. $K_{i}[P_2W_{18}O_{62}]$ (0.2 mM) was present in the initial aqueous phase. Results are shown after (A) 3, (B) 7, and (C) 35 min exposure to sunlight. $T = 28^\circ$C.

Table S1. $E_f^{\circ}$ values* for the $[P_2W_{18}O_{62}]^{6-/7-}$ and $[P_2W_{18}O_{62}]^{7-/8-}$ processes, diffusion coefficients† ($D$), and pH values in aqueous 0.1 M KCl as a function of DEAS concentration

<table>
<thead>
<tr>
<th>[DEAS] M (pH value)</th>
<th>$E_f^{\circ}$ for designated process (mV vs. Ag/AgCl)</th>
<th>$D \times 10^{6}$ (cm$^2$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (pH = 6.29)</td>
<td>$57$</td>
<td>$-110$</td>
</tr>
<tr>
<td>0.03 M (pH = 3.98)</td>
<td>$59$</td>
<td>$-107$</td>
</tr>
<tr>
<td>0.20 M (pH = 3.00)</td>
<td>$67$</td>
<td>$-105$</td>
</tr>
<tr>
<td>0.64 M (pH = 2.74)</td>
<td>$65$</td>
<td>$-101$</td>
</tr>
<tr>
<td>1.31 M (pH = 2.63)</td>
<td>$58$</td>
<td>$-110$</td>
</tr>
</tbody>
</table>

* $E_f^{\circ}$ is the formal reversible potential determined from cyclic voltammograms as the average of the oxidation and reduction peak potentials at a scan rate of $100$ mV s$^{-1}$ using a glassy carbon electrode. Calculated from a plot of reduction peak current vs. scan rate (20 to $200$ mV s$^{-1}$) for the $[P_2W_{18}O_{62}]^{6-/7-}$ process and use of the Randles–Sevcik relationship.

† Calculated.