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Charge Photo-Accumulation and Photocatalytic Hydrogen Evolution Under Visible Light at an Iridium(III)-Photosensitized Polyoxotungstate

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Abstract

Steady-state irradiation under visible light of a covalent Ir(III)-photosensitized polyoxotungstate is reported. In the presence of a sacrificial electron donor, the photolysis leads to the very efficient photoreduction of the polyoxometalate. Successive formation of the one-electron and two-electron reduced species, which are unambiguously identified by comparison with spectroelectrochemical measurements, is observed with a significantly faster rate reaction for the formation of the one-electron reduced species. The kinetics of the photoreduction, which are correlated to the reduction potentials of the polyoxometalate (POM), can be finely tuned by the presence of an acid. Indeed light-driven formation of the two-electron reduced POM is considerably facilitated in the presence of acetic acid. The system is also able to perform photocatalytic hydrogen production under visible light without significant loss of performance over more than 1 week of continuous photolysis and displays higher photocatalytic efficiency than the related multi-component system, outlining the decisive effect of the covalent bonding between the POM and the photosensitizer. This functional and modular system constitutes a promising step for the development of charge photoaccumulation devices and subsequent photoelectrocatalysts for artificial photosynthesis.

Photoconversion of light into chemical fuels is emerging as a major scientific challenge.¹⁻⁴ In the past decades, molecular approaches have mostly focused on one hand on the design of photosensitive systems displaying long-lived photo-induced charge separation states to permit further electron transfers⁵⁻¹⁰ and, on the other hand, on catalysts able to use these photogenerated charges for achieving either oxygen¹¹⁻¹⁸ or hydrogen evolution.¹⁹⁻²⁴ As these two reactions are multi-electronic processes while photosensitizers deliver electrons and holes sequentially, the charges need to be directed to a charge accumulation site.²⁵ However, only a few molecular photoactive systems with a designed charge accumulation site have been described so far.²⁶⁻³⁰ Another requirement is crucial for efficient charge accumulation in such systems: when partially filled, the reservoir should not interfere with the photoactive moiety. Indeed, in classical donor-acceptor (D-A) systems, the electron acceptor, once reduced, potentially becomes an electron donor and often displays light-absorbing properties. Thus it may act, in a subsequent light-driven process, as a deleterious

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quencher of the excited donor D^* by reverse charge transfer (equation 1) or energy transfer (equation 2).



Since they can store several electrons with modest difference in potentials between successive reduction steps,^{31, 32} polyoxometallates (POMs) are attractive candidates to further illustrate charge photoaccumulation. While electrocatalytic reduction of protons by POMs has been thoroughly investigated,³³⁻³⁵ their activity in water photoreduction has been far less developed and only under UV-light excitation,³⁶⁻³⁸ with two recent notable exceptions.^{39, 40} This is in striking contrast with recent but extensive studies on light-driven water oxidation mediated by transition metal substituted POMs. In this context, we recently reported the synthesis and photophysical properties of a series of heteroleptic carbocyclometalated iridium(III)-polyoxometalate conjugates^{41, 42} following mild reaction conditions developed earlier by some of us.⁴³⁻⁴⁶ In such complexes, photoinduced charge-separated excited states of various lifetimes (ranging from nanoseconds to hundreds of nanoseconds) were observed by transient absorption spectroscopy. Most importantly, the functionalization of the heteroleptic cyclometalated iridium(III) on the picolinate ligand provides directionality to the photoinduced electron transfer by enhancing charge separation and delaying charge recombination, which is an asset for preventing reverse charge transfer from proceeding (equation 1). The kinetics of charge separation and charge recombination in these reported POM-[Ir] hybrids were correlated to the redox potential of the POM with the fastest electron transfer rates (both charge separation and charge recombination) observed for the POMs that are the most easily reduced. Among the different POM-[Ir] conjugates we selected the Dawson-type organosilyl hybrid $[P_2W_{17}O_{61}\{O(SiC_3H_7O_2)_2\}]^{6-}$, named **D_{Si}[Ir]**, since it offers the best compromise between efficient charge separation and long-lived charge-separated state. This hybrid, isolated as a tetrabutyl ammonium salt, contains two heteroleptic cyclometalated iridium(III) units connected to the mono-lacunary site of the Dawson-type α_2 - $[P_2W_{17}O_{61}]^{10-}$ through a Si-O-Si anchorage (Scheme 1). In this hybrid, the POM and the chromophore are poorly coupled electronically.

As a consequence, in **D_{Si}[Ir]** the POM displays redox properties very similar to those of the hybrid precursor bearing two iodoaryl moieties, named **D_{Si}[I]**.^{47, 48} In the previously mentioned study, transient absorptions measurements only allowed for the characterization of the first photo-induced electron transfer. Charge photo-accumulation studies can be achieved in the presence of an additional electron donor in the solution that can irreversibly quench the charge separation state, regenerate the initial state of the photosensitizer and make a second photo-induced process possible. We herein provide unprecedented evidence of charge accumulation on a polyoxotungstate by visible-light. Furthermore, this system is able to perform direct photocatalytic hydrogen evolution, albeit at low pace, without noticeably decreasing over more than 1 week of continuous photolysis.

The photoreduction reaction of **D_{Si}[Ir]** is easily monitored by electronic spectroscopy since, in their reduced forms, POMs display intense d-d and intervalence charge transfer transitions.⁴⁹⁻⁵² For reference, spectroelectrochemical measurements carried out on the related **D_{Si}[I]** are given in the Supporting Information: electrolysis was followed by rotating disk electrode voltamperometry and UV-Vis spectroscopy to provide the spectroscopic signature of the successively formed one- and two-electron reduced species. The evolution of the electronic spectrum of a degassed DMF solution of **D_{Si}[Ir]** (0.2 mM) under visible

light irradiation ($\lambda > 400$ nm) and in the presence of triethylamine (NEt_3 , 1 M) acting as sacrificial electron donor is shown in Figure 1. First, a large band with a maximum absorption at 840 nm, corresponding to the one-electron reduced POM ($1e^- \text{-D}_{\text{Si}}[\text{Ir}]$), grows.

Then, under prolonged photolysis, an additional absorption appears at 710 nm, attributed to the two-electron reduced POM ($2e^- \text{-D}_{\text{Si}}[\text{Ir}]$). As luminescence of the iridium complex precursor $[\text{Ir}]$ is not affected by the sacrificial donor under similar conditions, we assume that the active species responsible for the oxidation of the triethylamine is more likely the oxidized photosensitizer, in the charge-separated state, rather than the excited form of the photosensitizer itself (Scheme 2). The formation of $1e^- \text{-D}_{\text{Si}}[\text{Ir}]$ is very fast. We measured a half-reaction time constant of $\tau_{1/2} = 43$ s with the setup shown in Figure S1 under continuous visible-light irradiation ($400 \text{ nm} < \lambda < 800 \text{ nm}$) and a quantum yield at 400 nm of $\phi_{400 \text{ nm}} = 10.5 \pm 1\%$. The second reduction to $2e^- \text{-D}_{\text{Si}}[\text{Ir}]$ is significantly slower ($\tau_{1/2} = 270$ s, $\phi_{400 \text{ nm}} = 2.3 \pm 0.5\%$). This can be attributed to incomplete charge-separation in the already one-electron reduced species. Indeed, the second reduction process of $\text{D}_{\text{Si}}[\text{Ir}]$ occurs at a potential 400 mV more negative than the first, slowing down the second photoinduced electron transfer process. However the two-electrons photoreduction observed is much more efficient than that of a previously reported electrostatic $[\text{Ru}(\text{bpy})_3]_2[\text{S}_2\text{M}_{18}\text{O}_{62}]$ system.⁵³ If the quantitative photoreduction of $[\text{S}_2\text{M}_{18}\text{O}_{62}]^{4-}$ at 420 nm has been nicely described, the corresponding tungstate $[\text{S}_2\text{W}_{18}\text{O}_{62}]^{4-}$ led to reduced species that could only be poorly characterized after at least one hour of photolysis. Concomitantly, a decrease of the chromophore absorption was observed, suggesting a significant degradation of the system. By introducing a covalent link between the photosensitizer and the polyoxotungstate, we strongly favour direct charge injection to the POM, and prevent the system from degradation.

Multi-electron processes can be facilitated to a large extent in the presence of protons. In particular, the electrochemical behavior of POMs is drastically affected by the presence of acids.³¹ As shown in Figure 2, in the presence of acetic acid the waves of $\text{D}_{\text{Si}}[\text{Ir}]$ are shifted to higher potential, thus conferring to the POM improved reservoir properties.

We then investigated the photoreduction reaction of $\text{D}_{\text{Si}}[\text{Ir}]$ in the presence of acetic acid (0.1 M). The study of the stability of the heteroleptic iridium(III) complex covalently linked to the POM showed that in DMF or MeCN solutions, the presence of strong acid (HCl, trifluoroacetic acid) leads to an irreversible loss of picolinate ancillary ligands as recently described elsewhere.⁵⁴ However, we checked that, even in large excess (500 equiv) of acetic acid (AcOH), $\text{D}_{\text{Si}}[\text{Ir}]$ is stable for few days (Figure S4). We note that AcOH ($\text{pK}_a = 13.5$ in DMF) is unable to protonate NEt_3 ($\text{pK}_a = 9.2$ in DMF) under these conditions⁵⁵ and thus does not significantly influence the apparent pH value of the reaction medium.⁵⁶ The presence of the acid barely modifies the initial evolution of the absorption spectra. The initial one-electron reduced POM, has an absorption maximum at 845 nm and the absorption of the two-electron reduced POM is centred at 695 nm. While the formation of $1e^- \text{-D}_{\text{Si}}[\text{Ir}]$ is only slightly faster compared to the photoreduction in the absence of AcOH ($\tau_{1/2} = 37$ s), formation of $2e^- \text{-D}_{\text{Si}}[\text{Ir}]$ is drastically accelerated ($\tau_{1/2} = 60$ s) in the presence of acid. Again, the photoreduction kinetics seems to be correlated to the redox properties of the POM. Indeed, the presence of AcOH affects more significantly the redox potential of the second reduction of the POM than the first one (see Figure 2; $\Delta E_1 = 60$ mV, $\Delta E_2 = 280$ mV). As a consequence, in the presence of acetic acid, the light-driven formation of the two-electron reduced POM is considerably facilitated, while the kinetics of formation of the one-electron reduced POM is almost unchanged. We have previously described how the structure-related redox potentials of the POM impacts the kinetics of the charge separation/recombination steps.⁴¹ Further tunability is thus addressable through the acid dependence of

the reduction processes. This makes POMs unique for the design of finely controlled molecular electron reservoirs.

As POMs are known to catalyze proton reduction under certain conditions,^{31, 33, 34, 38} we thus wonder whether the POM moiety in **D_{Si}[Ir]** could act both as an electron reservoir and as a H₂-evolving catalyst under photolysis conditions. Gas chromatography monitoring of the photolysis of **D_{Si}[Ir]** in the presence of NEt₃ and acetic acid in DMF shows that H₂ continuously accumulates in the headspace of the reaction vessel. After an initial induction period, H₂ evolution was sustained for days with a turnover frequency (TOF) of *ca.* 0.25 h⁻¹. Up to 41 turnovers (calculated vs the POM) are formed within a 7-days experiment (Figure 3). No H₂ could be detected when NEt₃ was omitted or when **D_{Si}[Ir]** was replaced by the reference compound **D_{Si}[I]**. Only traces of H₂ were detected when a mononuclear carbocyclometalated picolinate iridium(III) complex, **[Ir]**, was used instead of **D_{Si}[Ir]**. Interestingly, the turnover frequency for hydrogen evolution is twice lower for the multicomponent system consisting of **D_{Si}[I]** and 2 equiv of **[Ir]** under the same conditions, emphasizing again the beneficial effect of the covalent tether between the photosensitizer and the POM (See inset in Figure 3).

We have thus demonstrated that upon steady-state visible irradiation and in the presence of a sacrificial electron donor, the carbocyclometalated iridium(III)-polyoxometalate conjugate **D_{Si}[Ir]** is capable of photo-accumulating two electrons on the POM in a very efficient manner. This all-integrated system offers unique advantages for charge photo-accumulation since it fulfills the previously mentioned requisites.

(1) The iridium complex, because of its heteroleptic character, favors charge transfer to the POM and slows down backward electron transfer. This prevents the reduced POM from acting as a deleterious quencher of the excited iridium complex by reverse charge transfer (i.e. equation 1). (2) The absorbance of both one-electron and two-electron reduced POMs, although important in the lower energy part of the visible spectrum is modest to weak at *ca.* 510 nm (emission maximum wavelength of the iridium complex)⁵⁷ disfavoring energy transfer from the excited iridium complex to the reduced POM (i.e. equation 2). (3) The presence of acid leads to proton-assisted reduction of the POM, which provides the POM with improved reservoir properties and enhances the rate of photoproduction of the two-electron reduced POM. Finally, the system displays promising photocatalytic activity for hydrogen evolution. Further studies are required to establish the catalytic mechanism at work and eventually identify the catalytic active species formed *in situ* during the induction period.⁵⁸ While the catalytic rate is modest, the deceleration over seven days of continuous photolysis is very low, which establishes the robustness of the system upon turn-over. Indeed, monitoring of the ³¹P NMR signals of **D_{Si}[Ir]** under irradiation indicates that the POM framework of the hybrid is maintained (Figure S4). We are currently working on the improvement of photocatalytic activity for hydrogen evolution of the system. This implies optimization of the photocatalytic conditions (solvent, electron donor...), improvement of the robustness of the photoactive complex towards acid and design of multicomponent POM-[Ir]/electrocatalyst systems.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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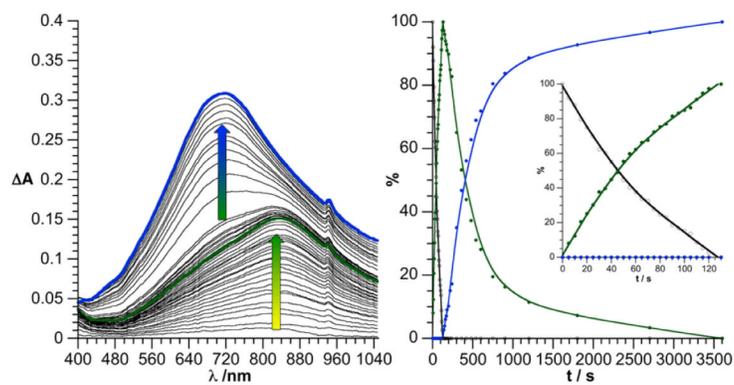


Figure 1. Left: evolution of the differential visible absorption spectrum of a solution of $D_{SI}[Ir]$ (0.2 mM) in DMF containing NEt_3 (1 M) during photoirradiation under visible light (green $t = 130$ sec., blue $t = 1$ hour). For clarity purpose, the blank corresponds to the absorption of the initially yellow solution before photolysis. Right: distribution of the different reduction states of $D_{SI}[Ir]$ during the photolysis. Legend: non-reduced $D_{SI}[Ir]$ (colorless circle), $1e^-$ - $D_{SI}[Ir]$ (green circle) and $2e^-$ - $D_{SI}[Ir]$ (blue circles).

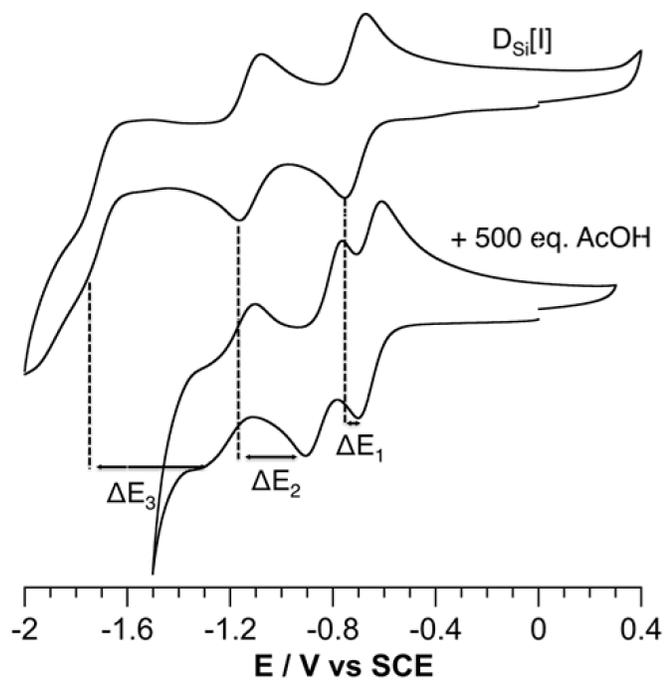


Figure 2. Evolution of cyclic voltammograms of a 10^{-3} M solution of the reference POM hybrid $D_{Si}[I]$ in DMF containing 0.1 M TBAPF₆ upon addition of 500 equiv AcOH. Working electrode : glassy carbon; reference electrode, SCE.

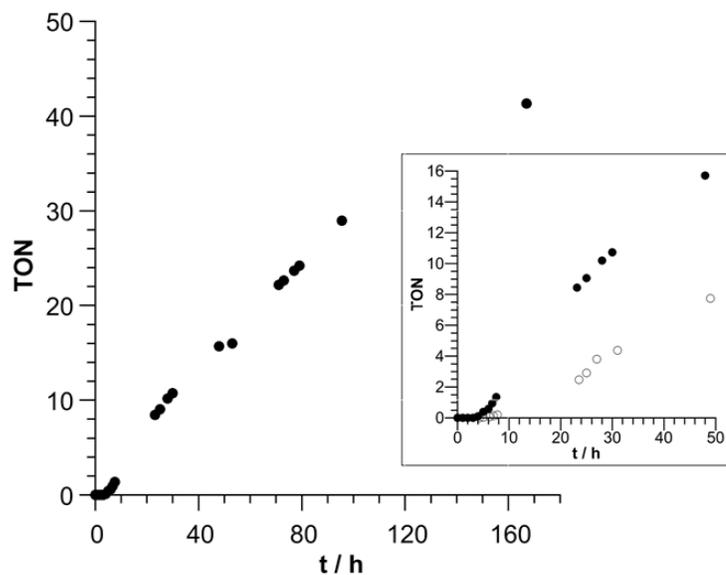
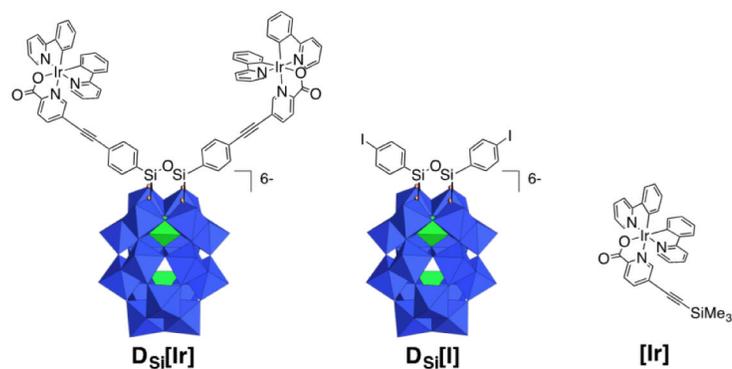
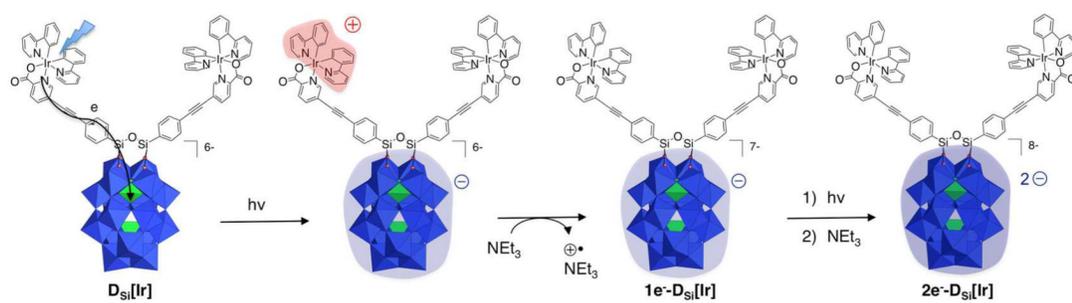


Figure 3. Photochemical production of hydrogen from DMF solutions (10 mL) of NEt_3 (1 M) and AcOH (0.1 M) catalyzed by $\text{D}_{\text{Si}}[\text{Ir}]$ (0.2 mM). Comparison with the multicomponent system consisting of $\text{D}_{\text{Si}}[\text{I}]$ (0.2 mM) and 2 equiv. of $[\text{Ir}]$ (0.4 mM) is shown in the inset (colorless dots). In these experiments, one turnover corresponds to $2 \mu\text{mol}$ ($48 \mu\text{L}$) H_2 evolved.

**Scheme 1.**

Molecular representation of the photoactive POM-based hybrid **D_{Si}[Ir]**, reference POM **D_{Si}[I]** and reference iridium complex **[Ir]** described in this study. In the polyhedral representation, the WO₆ octahedra are depicted with oxygen atoms at the vertices and metal cations buried inside. Color code: WO₆ octahedra, blue; PO₄ tetrahedra, green.

**Scheme 2.**

Charge photo-accumulation occurring in the $D_{Si}[Ir]$ dyad.