

Photooxidation in Water by New Hybrid Molecular Photocatalysts Integrating an Organic Sensitizer with a Polyoxometalate Core

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Abstract: Hybrid compounds consisting of an organic sensitizer and a polyoxometalate unit were synthesized following two strategies: a) the covalent functionalization of lacunary decatungstosilicate with organosilylfulleropyrrolidines; b) the charge interaction between cationic sensitizers and the polyoxoanions, yielding electrostatic aggregates. These hybrid complexes effect catalytic photooxygenation in water under heterogeneous conditions, 25 °C and O₂ (1 atm), using visible light irradiation ($\lambda > 375$ nm). As representative target substrates, phenol (4 mM) is oxidized in 150 min with a COD loss up to 30% (TON up to

50), while L-methionine methyl ester (15 mM) undergoes selective photooxygenation to the corresponding sulfoxide in 90 min (TON up to 200). The photocatalyst stability has been evaluated on the basis of system recycling along three oxidation runs. The inhibition exerted by sodium azide, a typical ¹O₂ quencher, suggests the occurrence of a Type II photooxidation mechanism.

Keywords: fullerene; photocatalysis; photooxidation; polyoxometalates; singlet oxygen sensitizers

Introduction

The hybrid approach in catalysis aims at the invention of new systems where the merging of organic and inorganic domains produces a functional synergistic effect with the ultimate scope to improve the catalytic performance.^[1] The potential of this method has a major appeal in the field of photoactivated oxygenations where the key step, i.e., dioxygen activation, may be achieved through diverse mechanistic pathways depending on the nature (organic/inorganic) of the photocatalyst.^[2–4] Moreover, due to the urgent need of new sustainable methods for chemical transformations, the design of alternative photooxygenation systems employing visible light, oxygen, and aqueous media at mild temperatures, is a timely field of investigation.^[3–6] Indeed, photocatalytic oxygenation of widely different substrates is of interest either for synthetic procedures, or for advanced oxidation processes applied to wastewater treatment.^[4,7,8] It is especially for wastewater detoxification that photooxygenations hosting multiple activation mechanisms are expected to promote an efficient degradation of the target pollutant. The hybrid way to the photocatalyst design can then be exploited to combine organic and inorganic components with different properties and capabilities. Recently this approach has been exploited for the surface derivatization of TiO₂,

yielding heterogeneous integrated systems with advanced photocatalytic performance.^[3,9] With the same aim, an innovative route may be sought in the molecular functionalization of polyoxometalates, often referred to as the homogeneous analogues of photoactive semiconductor metal oxides.^[3] Polyoxometalates (POM) are inorganic complexes of general formula [M_mO_y]^{p–} or [X_xM_mO_y]^{q–} (M = W, Mo, V, etc. and X = Si, P, As, Sb, etc.) characterized by a rich variety of structures, with different chemical composition, charge and counterion.^[10–12] Their chemistry is of interest in several disciplines including catalysis, materials science and medicinal chemistry. Furthermore, the activity of polyoxotungstates in promoting environmentally benign photocatalytic processes is documented, both in organic solvents and in water.^[13,14]

Polyoxometalate-based hybrids belong to three main classes depending on the linkage between the organic and inorganic components, specifically: (i) weak hydrogen bonding or van der Waals contacts; (ii) electrostatic forces established through Coulombic anion/cation interactions; (iii) covalent bonds.^[15,16] In the first case, polyoxometalates are embedded or adsorbed on supports like polymeric films,^[17] whereas in the second case they form electrostatic aggregates with organic or organometallic groups.^[15] The third way requires the covalent attachment of the organic residue R on the polyoxo-

metalate surface. This strategy is conveniently accomplished by reacting organosilyl groups $[\text{RSi}(\text{OR}')_3]$ or RSiCl_3 , with lacunary polyoxometalates of the Keggin series to obtain $\text{RSi}-\text{O}-\text{M}$ bonds.^[18–20]

Results and Discussion

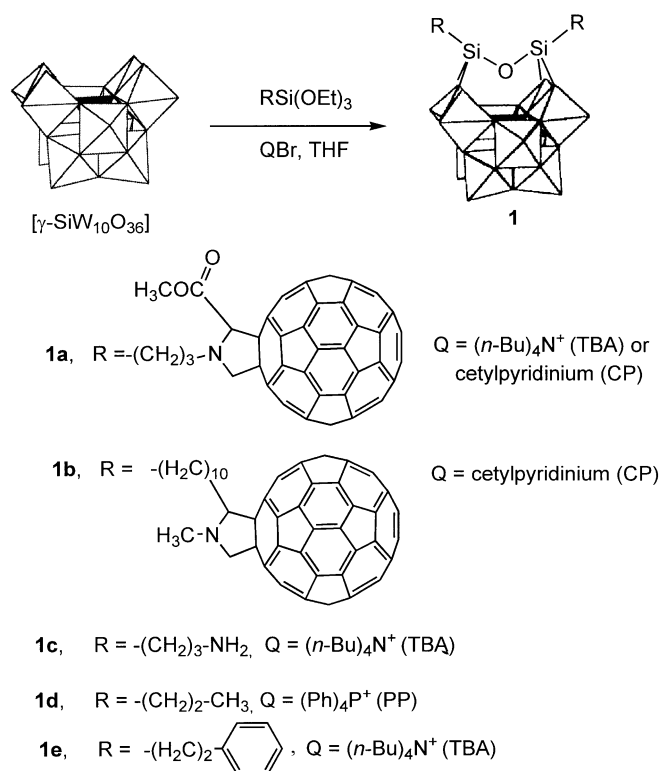
This work describes the synthesis, characterization and photocatalytic activity of new polyoxometalate-based hybrids incorporating: (a) fulleropyrrolidines linked through the covalent functionalization of the divacant decatungstosilicate $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$; (b) cationic sensitizers, namely methylene blue (MB^+) and tris(2,2'-bipyridine)ruthenium (II) ($[\text{Ru}(\text{bpy})_3]^{2+}$) in electrostatic adducts with two polyanions: decatungstate $[\text{W}_{10}\text{O}_{32}]^{4-}$ and hexamolybdate $[\text{Mo}_6\text{O}_{19}]^{2-}$.^[21]

Synthesis of Fullerene-Containing Hybrids

Fullerene-based sensitizers can promote photooxidations both in organic and aqueous media.^[22] Such molecules display excitation with visible light ($\lambda > 375$ nm), high quantum yield (≈ 1 for $^1\text{O}_2$ generation) and resistance to oxidative degradation.^[22] Despite these advantages, their use is severely hampered by the low solubility and tendency to form non-active aggregates. The hybrid combination with polyanions aims to provide a platform to tune the physicochemical behavior as a function of the inorganic component and of its counterion.

To this aim, *N*-[3-(triethoxysilyl)propyl]-2-carbomethoxy-3,4-fulleropyrrolidine, **1a**^[23] and *N*-methyl-2-[10-(triethoxysilyl)decyl]-3,4-fulleropyrrolidine, **1b**,^[24] bearing a silicon-alkoxide moiety, were used to graft the [60]fullerene sensitizer to the four nucleophilic surface oxygen atoms of $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$. The synthetic protocol (Scheme 1)^[18] requires the addition of two equivalents of the organosilane derivative to a lipophilic salt of the lacunary polyanion, (either isolated or formed *in situ* in the presence of a phase-transfer agent), followed by acidification with HCl.

With the same procedure, three model triethoxysilanes $\text{RSi}(\text{OEt})_3$ with $\text{R} = n$ -propylamino (**1c**), $\text{R} = n$ -propyl (**1d**) and $\text{R} =$ phenethyl (**1e**) react yielding the expected complexes having C_{2v} symmetry with formula $[\gamma\text{-SiW}_{10}\text{O}_{36}(\text{RSi})_2\text{O}]^{4-}$ (**1c–e**) as confirmed by NMR characterization.^[18] In all cases, the ^{29}Si NMR spectra exhibit two signals in a ratio of 2:1 at *ca.* $\delta = -63$ (RSiO_3) and -88 (SiO_4) while ^{183}W NMR provides the typical set of three resonances, at *ca.* $\delta = -108$ (2W), -134 (1W), -140 (2W), which demonstrate the grafting of the dimeric siloxane unit.^[18] For these complexes, the elemental analysis and FT-IR spectroscopic characterization are also in agreement with the proposed structure and correspond closely to that of [60]fullerene-POM hybrids



Scheme 1. Synthesis of hybrid complexes **1** by functionalization of $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ with $\text{RSi}(\text{OEt})_3$.

1a, b (Figure 1), whose still low solubility hampers an exhaustive NMR characterization.^[25]

In particular, FT-IR analysis provides evidence of: (i) the isostructural features of the polyoxometalate framework for complexes **1**, characterizing the low-wavenumber spectral region ($< 1000\text{ cm}^{-1}$), (ii) the introduction of the organosilyl groups on the polyoxometalate surface, giving rise to new stretching bands in the range $1150\text{--}1000\text{ cm}^{-1}$ (ν_{CSi} , ν_{SiO}) and to a distinctive modification of the stretching bands in the region $950\text{--}735\text{ cm}^{-1}$ ($\nu_{\text{W=O}}$, ν_{WOW});^[18,26] (iii) the contemporary presence in **1a, b** of the domains pertaining to the polyoxotungstate and to the fulleropyrrolidine characterized by the sharp band at 525 cm^{-1} .^[23,24] Accordingly, the UV-Vis spectra of hybrids **1a, b** contain the visible trace of the fulleropyrrolidine-based sensitizer with an extended ground state absorption in the range $400\text{--}800\text{ nm}$ and transitions at 430 and 740 nm .^[23,24]

Synthesis of Hybrid Salts

For this class of hybrid materials, two cationic sensitizers, i.e., methylene blue (MB^+) and tris(2,2'-bipyridyl)ruthenium(II) $[\text{Ru}(\text{bpy})_3\text{Cl}_2]$ have been used as counterions of the $[\text{W}_{10}\text{O}_{32}]^{4-}$ and $[\text{Mo}_6\text{O}_{19}]^{2-}$ polyoxoanions. Thus, three different adducts have been isolated through

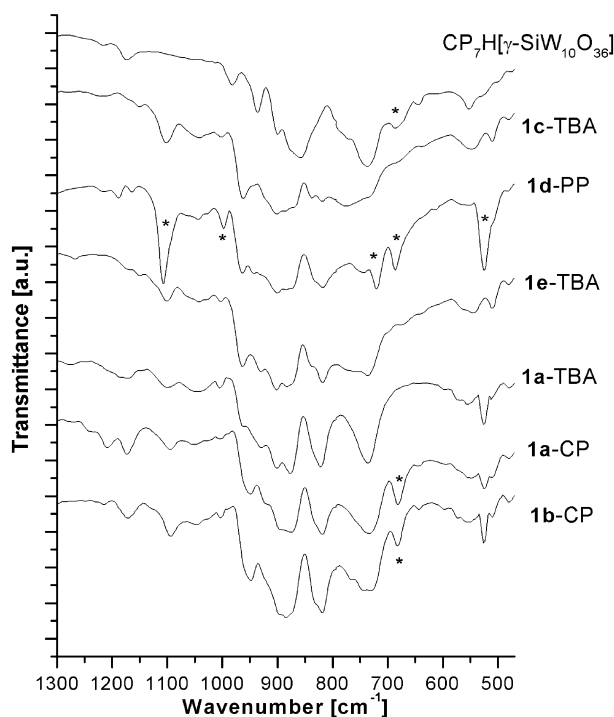


Figure 1. Comparison between low-wavenumber FT-IR spectra (KBr pellets) of lacunary $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ and hybrids **1**. From the top: $\text{CP}_7\text{H}[\gamma\text{-SiW}_{10}\text{O}_{36}]$, **1c** (TBA salt), **1d** (PP salt), **1e** (TBA salt), **1a** (TBA salt), **1a** (CP salt), **1b** (CP salt). Counterion bands are marked with a star (CP = cetylpyridinium, TBA = $n\text{-Bu}_4\text{N}^+$, PP = Ph_4P^+). The vertical axis is given in arbitrary units (a.u.).

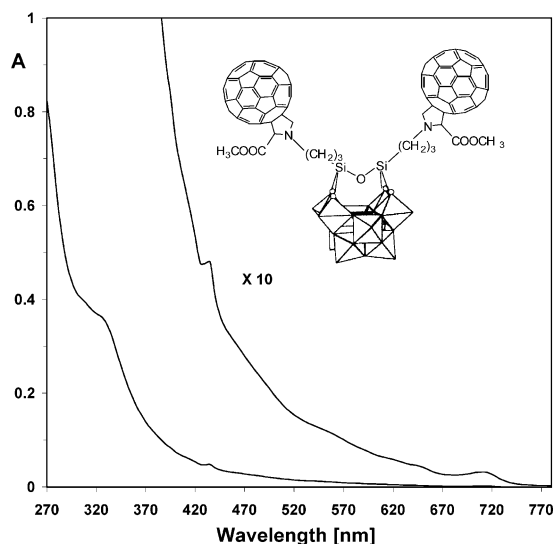


Figure 2. Proposed structure and ground state UV-Vis spectrum of **1a** (TBA salt) in DMF, 3 μM , path length 1 cm.

metathesis exchange in $\text{CH}_3\text{CN-H}_2\text{O}$. Their composition has been checked with elemental analysis and corresponds to the formula $\text{Ru}(\text{bpy})_3[\text{Mo}_6\text{O}_{19}]$ (**2**); $[\text{Ru}(\text{bpy})_3]_2[\text{W}_{10}\text{O}_{32}]$ (**3**) and $(\text{MB})_4[\text{W}_{10}\text{O}_{32}]$ (**4**). For all com-

plexes, FT-IR and UV-Vis analyses confirm the integrity of the inorganic core and the successful incorporation of the organic sensitizer which maintains its absorbance features allowing photoexcitation with $\lambda > 375\text{ nm}$ (see Experimental Section).

Sensitized Heterogeneous Photooxidation in Water by Hybrid POM-Based Complexes

The activity of hybrid photocatalysts **1–4** has been assessed in water under heterogeneous conditions at 25 °C, using visible light ($\lambda > 375\text{ nm}$) and oxygen (1 atm).^[27] To investigate the potential of the method for wastewater treatment, we performed the photooxygenation of an aqueous phenol solution (pH = 10.5). In this respect, the photocatalyst performance has been evaluated in terms of both substrate conversion/oxidation rates and chemical oxygen demand loss (% ΔCOD) of the aqueous solution after photoirradiation (Table 1). Moreover, the actual stability of the heterogeneous photocatalyst has been estimated on the basis of system recycling (I–III oxidation runs in Table 1).^[28] For comparison purposes, Table 1 includes data concerning a minor uncatalyzed process (entry 1 in Table 1) as well as the homogeneous photooxidations with $\text{Na}_4\text{W}_{10}\text{O}_{32}$ and the organic sensitizers $\text{Ru}(\text{bpy})_3\text{Cl}_2$ and MB^+ (entries 15–17 in Table 1).

In all cases, the photocatalyst loading has been chosen, according to its composition, in order to provide the different systems with an equal amount of the integrated organic sensitizer ($3.7 \times 10^{-4}\text{ mmol}$). Under the conditions adopted, phenol oxidation occurs generally in 150 min with a decrease in the COD content in the range 10–30%. Inspection of data in Table 1 raises some key points concerning both the nature of the organic component and that of the inorganic framework. In particular, the covalent grafting of the [60]fullerene sensitizer in hybrid **1b** yields a more efficient and robust system when compared to **1a** (entries 2 and 3). While the oxidations proceed with expected similar initial rates, the discrepancy between the COD loss is likely due to the decomposition of **1a** in solution. Indeed, **1b** can be recycled in three runs with a minor decrease of activity and a total turnover number (TON) > 100 (entries 3–5). The superior stability of **1b** may be ascribed both to the placement of the organosilyl anchor on the fulleropyrrolidine ring (carbon 2) and to the longer $-(\text{CH}_2)_{10}$ -alkyl spacer separating the sensitizer core from the polyanion surface.

On the contrary, the reactivity of hybrid salts, in the order **2** $>$ **3** $>$ **4** (entries 6, 9, 12), seems to depend mainly on the global charge of the polyanion which influences the stoichiometry of the electrostatic adducts and the assembly of the charge compensating sensitizer on its surface. This latter aspect may indeed promote aggregation, self-quenching phenomena or undesired self-induced bleaching. This observation accounts for the su-

Table 1. Photooxidation of phenol by hybrid POM-based complexes under heterogeneous conditions in water.^[a]

Entry	Photocatalyst ^[b] [mol %]	Run ^[c]	Conversion [%] ^[d]	$R_0 \times 10^{-7} [\text{M}^{-1} \text{s}^{-1}]^{\text{[e]}}$	TON ^[f]	$\Delta\text{COD} [\%]^{\text{[g]}}$
1	–	I	17	1	–	4
2	1a [1.8]	I	88	6.2	47	12
3	1b [1.8]	I	89	8.3	42	32
4		II	90	7.4	48	31
5		III	87	6.2	46	20
6	2 [3.7]	I	100	11	27	29
7		II	100	15	27	29
8		III	100	12	27	33
9	3 [1.8]	I	84	7.5	45	29
10		II	63	2.9	34	22
11		III	77	3.6	41	23
12	4 [0.9]	I	42	2.2	44	13
13		II	45	2.2	47	13
14		III	49	2.2	52	12
15 ^[h, i]	$\text{Na}_4\text{W}_{10}\text{O}_{32}$ [37.5]	I	43	2.7	1.1	40
16 ^[h, j]	$\text{Ru}(\text{bpy})_3\text{Cl}_2$ [3.7]	I	100	123	27	–
17 ^[h, j]	MB^+ [3.7]	I	100	50	27	–

^[a] Phenol ($4 \times 10^{-3} \text{ M}$), H_2O (2.5 mL, pH=10.5) $\text{pO}_2=1 \text{ atm}$, $\lambda > 375 \text{ nm}$, reaction time=150 min.

^[b] Photocatalyst legend: **1** = $\text{CP}_4[\gamma\text{-SiW}_{10}\text{O}_{36}(\text{RSi})_2\text{O}]$ (**a**, $\text{R} = N\text{-propyl-2-carbomethoxy-3,4-fulleropyrrolidine}$; **b**, $\text{R} = N\text{-methyl-2-decyl-3,4-fulleropyrrolidine}$); **2** = $\text{Ru}(\text{bpy})_3[\text{Mo}_6\text{O}_{19}]$; **3** = $[\text{Ru}(\text{bpy})_3]_2[\text{W}_{10}\text{O}_{32}]$; **4** = $\text{MB}_4[\text{W}_{10}\text{O}_{32}]$.^[27]

^[c] Recycling experiments (see text).

^[d] Substrate conversion determined by quantitative HPLC analysis.

^[e] Initial rate of photooxidation (see Experimental Section).

^[f] Total turnover number (TON)=moles of substrate converted per mole of photocatalyst.

^[g] Chemical oxygen demand (COD) % loss.

^[h] Reaction performed under homogeneous conditions.

^[i] pH=2, $\lambda > 345 \text{ nm}$.

^[j] Reaction time < 20 min.

perior performance of the one-to-one adduct $\text{Ru}(\text{bpy})_3[\text{Mo}_6\text{O}_{19}]$, **2** (entries 6–8), while a decreased reactivity and stability is indeed registered in the case of the analogous decatungstate salt, **3** (entries 9–11), carrying two molecules of the ruthenium sensitizer. Furthermore, the scarce activity displayed by **4** (entries 12–14), is only partially explained by the intrinsic gap of reactivity exhibited by the homogeneous sensitizers (entries 16, 17), while, considering its molecular composition, it may as well derive from a too crowded detrimental surface distribution of the photoactive sites. In general, heterogeneous photocatalysts display a markedly reduced efficiency with respect to their homogeneous counterparts.^[4,17] This is also the case for the systems under examination (entries 16, 17). Nevertheless, the ease of recovery, recycling and the potential flexibility of application in different media, represent a noticeable advantage outweighing this shortcoming.

To address the photooxidation mechanism and the nature of the active oxidant formed upon irradiation,^[2] the reactions mediated by the representative photocatalysts **1b** and **3**, have been performed in D_2O , where singlet oxygen has a longer lifetime (20 μs instead of 2 μs in H_2O), and in the presence of sodium azide, a known $^1\text{O}_2$ quencher. Under the conditions adopted, the photo-

oxidation rate was found to be insensitive to D_2O . This kinetic probe depends drastically on the concentration of the substrate and on its reactivity and may be inadequate at high substrate concentration.^[29] On the contrary, experiments with sodium azide (30 mM), resulted in a strong depletion of phenol conversion (< 20%), indicating the intervention of $^1\text{O}_2$ in both systems (*cf.* entries 3 and 9).^[6,22] Consistently, 1,4-benzoquinone was the only detectable intermediate observed during photooxidation,^[4,6] at variance with the photocatalytic behavior of homogeneous decatungstate (entry 17), affording 1,2-dihydroxybenzene as major intermediate and an extensive phenol degradation even at low conversion ($\Delta\text{COD}=40\%$).^[14] Although these preliminary experiments do not allow us to address the photooxidation mechanism in detail, this evidence speaks against the occurrence of a synergistic interaction between the two photocatalytic domains in hybrids **1–4**, whose reactivity appears to be dominated by the singlet oxygen pathway.

To assess the potential of the method for synthetic applications, the photocatalytic behavior of hybrids **1a** and **3** has been also evaluated in the selective photooxygenation of L-methionine methyl ester (L-Met-OMe) to the corresponding sulfoxide. The reaction occurs quantitatively in 90 min with turnover number up to 200.^[6]

Conclusions

Thus, the suitability of POM-based hybrids for aqueous photocatalysis is particularly encouraging, and future work aims at improving the design of these composite materials with a twofold purpose: (i) to fine-tune the balance of the hydrophilic-hydrophobic components so as to provide discrete molecular species which can be characterized in solution and used for mechanistic studies; (ii) to develop new systems for environmentally benign photocatalytic synthetic applications.

Experimental Section

General Remarks

Commercially available reagents were used as received without further purification. MilliQ-deionized water was used as solvent. $(n\text{-Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{19}]$,^[30] $(n\text{-Bu}_4\text{N})_4[\text{W}_{10}\text{O}_{32}]$,^[31] $\text{Na}_4\text{W}_{10}\text{O}_{32}$,^[32] $\text{K}_8[\gamma\text{-SiW}_{10}\text{O}_{36}] \cdot 12 \text{H}_2\text{O}$,^[33] N -(3-triethoxysilylpropyl)-2-carboxy-3,4-fulleropyrrolidine,^[23] N -methyl-2-(10-decyltriethoxysilyl)-3,4-fulleropyrrolidine,^[24] were prepared following literature procedures.

$(\text{CP})_7\text{H}[\gamma\text{-SiW}_{10}\text{O}_{36}]$ was prepared from the potassium salt by metathesis exchange with cetylpyridinium chloride (1.2 equivs.). IR (KBr): $\nu = 3126$ (w), 3053 (w), 2919 (s), 2850 (s), 1632 (m), 1486 (m), 1465 (m), 1175 (w), 981 (m), 936 (s), 899 (s), 858 (s), 737 (br s), 685 (s), 644 (m), 552 cm^{-1} (m); anal. calcd. for $\text{C}_{147}\text{H}_{266}\text{N}_7\text{O}_{36}\text{SiW}_{10}$: C 38.60, H 5.86, N 2.14; found: C 38.24, H 6.02, N 2.02.

FT-IR spectra were recorded with Perkin Elmer 1720X or 1600 instruments; UV-Vis spectra were recorded with Perkin Elmer Lambda 16 or Lambda 45 spectrophotometers, using 1 mm or 1 cm path length quartz cells; ^1H NMR spectra were recorded with a Bruker AC 250 spectrometer, ^{183}W NMR and ^{29}Si NMR spectra were obtained at 16.7 and 59.6 MHz, respectively, with Bruker Avance DRX 400 (10-mm tubes) and DRX 300 spectrometers, and referenced to Na_2WO_4 (D_2O , 2 M) and TMS (CDCl_3 , 50% v/v) solutions. For photooxidation experiments, irradiation was performed with a light source housing (Oriol Instruments), equipped with a 500-W Hg-Xe arc lamp, 200–500 W power supply, F/1.5 UV grade fused silica condenser, liquid (water) filter to absorb IR radiations, a secondary focusing lens to maximize the incident light and cut-off filter allowing irradiation at $\lambda > 375$ nm. The lamp features a continuous emission spectrum from 250 nm to the near IR, to which the discontinuous emission spectrum of Hg, in the UV field, is overlapped; (see Oriol Instrument – The Book of the Photon tools). HPLC analyses were performed on a Spectra-system P2000 instrument equipped with a photodiode array detector (Spectrasystem UV6000LP, Thermo Separation Products) or with a UV SPD-6A detector plus CR-3A integrator (Shimadzu) and using a reverse phase column (Lichrosphere RP18 Alltech). Chemical oxygen demand (COD) analyses were performed with the standard Cr(VI)/ H_2SO_4 kit Idrimeter by Carlo Erba.

General Procedure for the Synthesis of Hybrids 1

$(\text{CP})_7\text{H}[\gamma\text{-SiW}_{10}\text{O}_{36}]$ or $\text{K}_8[\gamma\text{-SiW}_{10}\text{O}_{36}] \cdot 12 \text{H}_2\text{O}$ with a phase transfer reagent ($n\text{-Bu}_4\text{NBr}$ or Ph_4PBr) were suspended in THF (10–20 mL) in the presence of $\text{RSi}(\text{OEt})_3$ derivatives (2 equivs.) and of 12 M HCl (6 equivs.). The solution was stirred for 15 h and the product was isolated by centrifugation or by solvent evaporation and washed with water, CH_3CN or toluene and finally with diethyl ether. Products were dried for 10 h under high vacuum to obtain yields in the range 40–70%.

$(n\text{-Bu}_4\text{N})_4[\gamma\text{-SiW}_{10}\text{O}_{36}[\text{N}-(3\text{-silylpropyl})-2\text{-carboxy-3,4-fulleropyrrolidine}]_2\text{O}]$ (1a-TBA salt): ^1H NMR ($\text{DMSO}-d_6$): $\delta = 0.72$ (m, 4H), 0.93 (m, 48H), 1.31 (m, 32H), 1.56 (m, 32H), 2.01 (m, 4H), 3.05 (m, 4H), 3.16 (m, 32H), 3.77 (m, 6H), 4.38 (m, 2H), 5.06 (m, 2H), 5.23 (m, 2H); IR (KBr): $\nu = 2959$ (s), 2930 (s), 2871 (m), 1734 (m), 1629 (m), 1461 (m), 1378 (w), 1171 (w), 1099 (m), 1043 (m), 1004 (m), 929 (s), 901 (s), 876 (s), 821 (s), 735 (s), 555 (m), 526 cm^{-1} (s); UV-Vis ($\lambda > 350$ nm): 433.6 nm ($\epsilon = 16 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$), 710 nm ($\epsilon = 1.0 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$); anal. calcd. for $\text{C}_{198}\text{H}_{168}\text{N}_6\text{O}_{41}\text{Si}_3\text{W}_{10}$: C 45.64, H 3.25, N 1.61; found: C 45.61, H 2.34, N 1.35.

$(\text{CP})_4[\gamma\text{-SiW}_{10}\text{O}_{36}[\text{N}-(3\text{-silylpropyl})-2\text{-carboxy-3,4-fulleropyrrolidine}]_2\text{O}]$ (1a-CP salt): IR (KBr): $\nu = 3126$ (w), 3060 (w), 2918 (s), 2850 (s), 1737 (w), 1632 (m), 1506 (w), 1485 (m), 1462 (m), 1373 (w), 1208 (m), 1173 (m), 1094 (m), 948 (s), 875 (br s), 819 (s), 734 (s), 682 (s), 645 (w), 549 (w), 525 cm^{-1} (m); anal. calcd. for $\text{C}_{218}\text{H}_{176}\text{N}_6\text{O}_{41}\text{Si}_3\text{W}_{10}$: C 47.97, H 3.25, N 1.54; found: C 48.93, H 3.41, N 1.86.

$(\text{CP})_4[\gamma\text{-SiW}_{10}\text{O}_{36}[\text{N-methyl-2-(10-silyldecyl)-3,4-fulleropyrrolidine}]_2\text{O}]$ (1b-CP salt): IR (KBr): $\nu = 3126$ (w), 3059 (w), 2921 (s), 2850 (s), 1631 (m), 1485 (m), 1461 (m), 1373 (w), 1171 (w), 1093 (m), 1045 (w), 1003 (w), 948 (s), 884 (br s), 819 (s), 731 (br s), 682 (m), 643 (w), 555 (w), 525 cm^{-1} (m); anal. calcd. for $\text{C}_{230}\text{H}_{204}\text{N}_6\text{O}_{37}\text{Si}_3\text{W}_{10}$: C 49.62, H 3.69, N 1.51; found: C 49.12, H 4.10, N 1.59.

$(n\text{-Bu}_4\text{N})_3\text{H}[\gamma\text{-SiW}_{10}\text{O}_{36}[\text{NH}_2(\text{CH}_2)_3\text{Si}_2\text{O}]]$ (1c): ^1H NMR ($\text{DMSO}-d_6$): $\delta = 0.51$ (t, 4H), 0.93 (t, 36H), 1.30 (m, 24H), 1.57 (m, 28H), 2.82 (m, 4H), 3.17 (m, 24H), 7.60 (m, 4H); ^{183}W NMR (DMSO): $\delta = -108.5$ (4W), -132.5 (2W), -143.7 (4W); ^{29}Si NMR ($\text{DMSO}-d_6$): $\delta = -63.6$ (2Si), -88.8 (1Si); IR (KBr): $\nu = 2961$ (s), 2934 (s), 2872 (s), 1624 (w), 1482 (s), 1467 (m), 1380 (m), 1101 (m), 1041 (m), 1001 (m), 962 (s), 901 (br s), 837 (s), 819 (s), 775 (br s), 547 cm^{-1} (m); anal. calcd. for $\text{C}_{54}\text{H}_{124}\text{N}_3\text{O}_{37}\text{Si}_3\text{W}_{10}$: C 19.31, H 3.72, N 2.09; found: C 19.16, H 3.68, N 1.85.

$(n\text{-Bu}_4\text{N})_3\text{H}[\gamma\text{-SiW}_{10}\text{O}_{36}[\text{PhCH}_2\text{CH}_2\text{Si}_2\text{O}]]$ (1d): ^1H NMR ($\text{DMSO}-d_6$): $\delta = 0.76$ (m, 4H), 0.93 (t, 36H), 1.30 (m, 24H), 1.56 (m, 24H), 2.63 (m, 4H), 3.16 (m, 24H), 7.16 (m, 10H); ^{183}W NMR (DMSO): $\delta = -107.8$ (4W), -134.8 (2W), -141.3 (4W); ^{29}Si NMR ($\text{DMSO}-d_6$): $\delta = -63.8$ (2Si), -88.6 (1Si); IR (KBr): $\nu = 2961$ (s), 2934 (m), 2872 (m), 1629 (w), 1482 (s), 1379 (m), 1100 (m), 1042 (m), 1003 (m), 963 (s), 930 (s), 901 (s), 883 (s), 818 (s), 736 (s br), 546 (m), 510 cm^{-1} (m); anal. calcd. for $\text{C}_{64}\text{H}_{127}\text{N}_3\text{O}_{37}\text{Si}_3\text{W}_{10}$: C 22.26, H 3.71, N 1.22; found: C 21.02, H 3.38, N 1.31.

$(\text{Ph}_4\text{P})_2\text{H}_2[\gamma\text{-SiW}_{10}\text{O}_{36}[\text{n-PrSi}_2\text{O}]]$ (1e): ^1H NMR ($\text{DMSO}-d_6$): $\delta = 0.41$ (t, 4H), 0.90 (m, 6H), 1.33 (m, 4H), 7.78 (m, 40H); ^{183}W NMR (DMSO): $\delta = -106.6$ (4W), -136.7 (2W), -142.2 (4W); ^{29}Si NMR ($\text{DMSO}-d_6$): $\delta = -62.7$ (2Si), -88.8 (1Si); IR (KBr): $\nu = 3059$ (w), 2952 (w), 2866 (w), 1623 (m), 1584 (m), 1482 (m), 1404 (m), 1437 (s), 1336 (w), 1316 (w), 1189 (w), 1164 (w), 1107 (s), 1044 (m), 997 (m), 963 (s), 900

(br s), 818 (s), 743 (s), 720 (s), 686 (s), 525 cm^{-1} (s); anal. calcd. for $\text{C}_{34}\text{H}_{56}\text{O}_{37}\text{P}_2\text{Si}_3\text{W}_{10}$: C 19.76, H 1.72; found: C 21.39, H 1.66.

General Procedure for the Synthesis of Hybrid Salts 2–4

$(n\text{-Bu}_4\text{N})_4[\text{W}_{10}\text{O}_{32}]$ or $(n\text{-Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{19}]$ (30 to 50 μmol) was dissolved in CH_3CN (10 mL) followed by addition of the cationic sensitizer (1.2 equivs.) dissolved in water (10 mL). The precipitate was separated by centrifugation and washed with CH_3CN -water mixture and with water until colorless (10 $\times$ 5 mL). The product was dried under high vacuum at room temperature with yields in the range 50–75%.

Ru(bpy)₃[Mo₆O₁₉] (2): IR (KBr): ν = 3074 (w), 1602 (w), 1462 (w), 1444 (m), 1425, (w), 952 (s), 791 (s), 753 (s), 726 cm^{-1} (m); ^1H NMR ($\text{DMSO}-d_6$): δ = 8.84 (d, 6H), 8.16 (td, 6H), 7.73 (d, 6H), 7.52 (td, 6H); UV (DMSO): λ = 294.4 (ϵ = $79 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$), 455.2 nm (ϵ = $55 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$); anal. calcd. for $\text{C}_{30}\text{H}_{24}\text{N}_6\text{O}_{19}\text{Mo}_6\text{Ru}$: C 24.86, H 1.67, N 5.80; found: C 25.58, H 1.55, N 5.90.

[Ru(bpy)₃]₂[W₁₀O₃₂] (3): IR (KBr): ν = 3074 (w), 1629 (br m), 1601 (w), 1462 (w), 1444 (m), 1425, (w), 995 (w), 958 (s), 897 (s), 806 (s), 794 (s), 761 (s), 730 (w), 583 cm^{-1} (br w); ^1H NMR ($\text{DMSO}-d_6$): δ = 8.84 (d, 12H), 8.17 (td, 12H), 7.73 (d, 12H), 7.52 (td, 12H); UV (DMSO): λ = 290.4 (ϵ = $117 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$), 455.2 nm (ϵ = $22 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$); anal. calcd. for $\text{C}_{60}\text{H}_{48}\text{N}_{12}\text{O}_{32}\text{Ru}_2\text{W}_{10}$: C 20.65, H 1.39, N 4.81; found: C 20.52, H 1.22, N 4.66.

(MB)₄[W₁₀O₃₂] (4): IR (KBr): ν = 1598 (s), 1529 (w), 1489 (m), 1439 (m), 1391 (s), 1334 (s), 1249 (m), 1221 (w), 1175 (m), 1140 (m), 1038 (w), 956 (s), 887 (s), 794 (s), 667 cm^{-1} (w); UV (DMSO): λ = 296.8 (ϵ = $178 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$); 322.4 (ϵ = $51 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$); 624.0 (ϵ = $159 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$), 670.4 nm (ϵ = $372 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$); anal. calcd. for $\text{C}_{64}\text{H}_{72}\text{N}_{12}\text{O}_{32}\text{S}_4\text{W}_{10}$: C 22.04, H 2.08, N 4.82, S 3.68; found: C 21.39, H 1.91, N 4.49, S 3.73.

Photooxidation Procedure

Photocatalytic experiments were carried out employing a standard spectrophotometric quartz cell hosted in a thermostatted holder (8.5 cm distance from the focusing lens), to collect all the focused radiation. The reaction solution (H_2O , 2.5 mL, 20 mM carbonate buffer, pH = 10.5) containing phenol (4 mM, 1×10^{-2} mmol) and the catalyst (loading in the range $9\text{--}37 \times 10^{-5}$ mmol, according to the molecular composition, so to provide 14.8×10^{-2} mM concentration of the sensitizer core) was sonicated and placed in the cell, under magnetic stirring, oxygen atmosphere and irradiated at $\lambda > 375$ nm. The reactions were monitored over time at 266 nm by quantitative HPLC analysis and with the photodiode array detector scanning from 250 to 350 nm [eluent: $\text{CH}_3\text{OH}:\text{H}_2\text{O}$ (1% HAc) = 35:65, flow rate 0.8 mL/min, *p*-nitrophenol as chromatographic standard]. The photoproducts and starting materials were identified by comparison of their retention times and absorption spectra with those of authentic samples: 1,4-benzoquinone 5.8 min, 1,2-dihydroxybenzene 7.6 min, phenol 13.5 min, *p*-nitrophenol 21.1 min. At the end of irradiation, the catalyst was recovered from the reaction mixture, thoroughly washed with water and dried. Initial rates were calculated by linear regres-

sion fitting of the kinetic data relative to phenol disappearance at < 20% conversion. Replicate experiments allowed us to estimate a 15–20% error for R_0 , while for phenol conversion and TON the errors were in the range 10–15%. COD determinations were carried on 0.2 mL of reaction mixture, filtered or treated with Cs_2SO_4 to precipitate the homogeneous polyoxometalate, diluted to 2 mL and reacted with the Idrimeter kit at 148 °C for 2 h. After the complete oxidation of all oxidizable compounds by Cr^{VI} , the absorbance of the mixtures, proportional to the concentration of Cr^{III} , was determined at 445 nm by UV-Vis analysis and correlated to the experimental COD (ppm O_2) with a calibration curve; estimated errors for this measure were around 10%. COD for homogeneous solutions were not determined because of the interference of the sensitizer itself (12–20% of the oxidizable material in solution). Methionine solutions were prepared by dissolving the substrate (15 mM, 3×10^{-2} mmol) in D_2O (2 mL, pD 5.5) and in the presence of the photocatalyst (1.5×10^{-4} mmol). Product analysis was carried out as described previously.^[6] Homogeneous photooxidations with sodium decatungstate were carried out by dissolving the catalyst (1.5 mM, 3.8×10^{-3} mmol) in aqueous solution (pH 2, H_2SO_4), containing phenol 4 mM. Irradiation was performed with a 345 nm cut-off optical filter.

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