Supporting Information

High Nuclearity Polyoxometalates and Colloidal TiO_2 Assemblies as Efficient Multielectron Photocatalysts under Visible or Sun Light Irradiation

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Experimental

Reagents and Materials

$H_3PW_{12}O_{40}$•$nH_2O$was purchased from Aldrich while **1**, **2** and **3** were prepared according to literature methods.[1-3] Orange II sodium salt was obtained from Aldrich with purity greater than 85%.

Hydrochloric acid, perchloric acid for analysis were from Acros.

Extra pure argon was used for deaeration of solutions.

Poly(vinyl alcohol) (PVA), 99+% hydrolyzed, typical average MW 85000-124000, was from Aldrich.

Titanium tetraisopropoxide $Ti(OCH(CH_3)_2)_4$, 98+% and 2-propanol, 99.5+% were from Aldrich.

The UV-vis absorption spectra were recorded on a Perkin Elmer Lambda 19 spectrophotometer. Irradiations were performed with a 500 W ozone-free Xe arc lamp (Oriel Research) equipped with a cold water circulating filter (Oriel Research) and a 320 nm or 400 nm cut-off filter (Oriel Research). Irradiations were carried out in a 1.00 optical path quartz cuvette with 1 mL solution. Sun light experiments were performed at Orsay (France) during 2009 and 2010 summers.

The effect of POM concentration on the decoloration process of **AO7** was studied between 5.10^{-5} M and 5.10^{-4} M. As expected, the kinetic of the reaction increases proportionally with the POM concentration and finally reaches a plateau.

Electrochemistry: materials, apparatus and procedures. For electrochemical experiments, the source, mounting and polishing of the glassy carbon (GC) electrodes (Le Carbone Lorraine, France) have been described previously.[4] The electrochemical set-up was an EG &

G 273 A driven by a PC with the M270 software. Potentials are measured against a saturated calomel reference electrode (SCE). The counter electrode was a platinum gauze of large surface area. Pure water from a RiOs 8 unit followed by a Millipore-Q Academic purification set was used throughout. The solutions were dearated thoroughly for at least 30 minutes with pure argon and kept under a positive pressure of this gas during the experiments. Controlled potential coulometry experiments were carried out with a large surface area carbon plate.

Preparation of TiO_2

Colloidal TiO_2 was prepared by the method described by Yoon et *al.*[5] Titanium(IV) tetraisopropoxide (0.25 mL) was added in 4.75 mL of 2-propanol. A 2 mL sample of this solution was slowly injected into 20 mL of acidified water (pH 1.5, adjusted with HCI). A transparent solution of colloidal TiO_2 particles is thus obtained with a TiO_2 content of 2.36 mg/mL.

Preparation of POM/2-Propanol catalysts

In a typical experiment, 1 mL of aqueous solution containing 0.5 M of 2-propanol and 5.10^{-5} M of POM catalyst was prepared. The pH of solutions was adjusted to 1 with HCl.

Preparation of POM/TiO_2/PVA catalysts

In a typical experiment, 1 mL of aqueous solution containing 2 mg/mL of PVA, 0.38 mM of TiO_2 and 5.10^{-5} M of POM catalyst was prepared. The pH of solutions was adjusted to 1 with HCl solution.

The solutions were poured in a spectrophotometer cell (1.00 cm optical path length), and deaerated if necessary.

UV-visible spectra

Figure S1 shows the UV-visible absorption spectra of the non-reduced POMs**.** A pH 1 medium was used because of the hydrolytic instability of **PW_{12}** at pH >1.2; the other three POMs are, at least, stable up to pH 7. All POMs exhibit strong absorption in the range 200 to 400 nm but that of the smallest POM, i.e. **PW_{12}** is the less intense (figure S1A). The threshold of the spectra is also a function of the POM size.[6] Apart from some exceptions, the smaller the size of the POM, the smaller is the threshold wavelength. In the explored domain, all the spectra are characterized by a peak located between 240 and 270 nm followed by a broad peak around 350 for **1** and **2** (Figure S1A). These absorption bands are due to the oxygen-to-tungsten charge transfer transition.[7] In the visible light region, the spectra of the complexes **1**, **2** and **3** present additional bands attributed respectively to the cobalt and nickel centers (Figure S1B). The main absorption spectra characteristics of the non-reduced POMs are given in Table S1. Depending on the POM, the absorption spectra characteristics vary more or less with the pH.

Table S1: Characteristics of UV-visible NIR spectra of the POMs in aqueous solution 0.1 M HCl pH 1.

POMs	λ_1 /nm (ε /M^{-1} cm^{-1})	λ_2 /nm (ε /M^{-1} cm^{-1})	λ_3 /nm (ε /M^{-1} cm^{-1})	λ_4 /nm (ε /M^{-1} cm^{-1})
1	253 (70900)	346 (6215)	449 (36)	497 (49)
2	243 (64550)	333 (5987)	450 (45)	497 (63)
3	241 (70475)	409 (113)	698 (29)	780 (39)
PW_{12}	261 (49280)	-	-	-

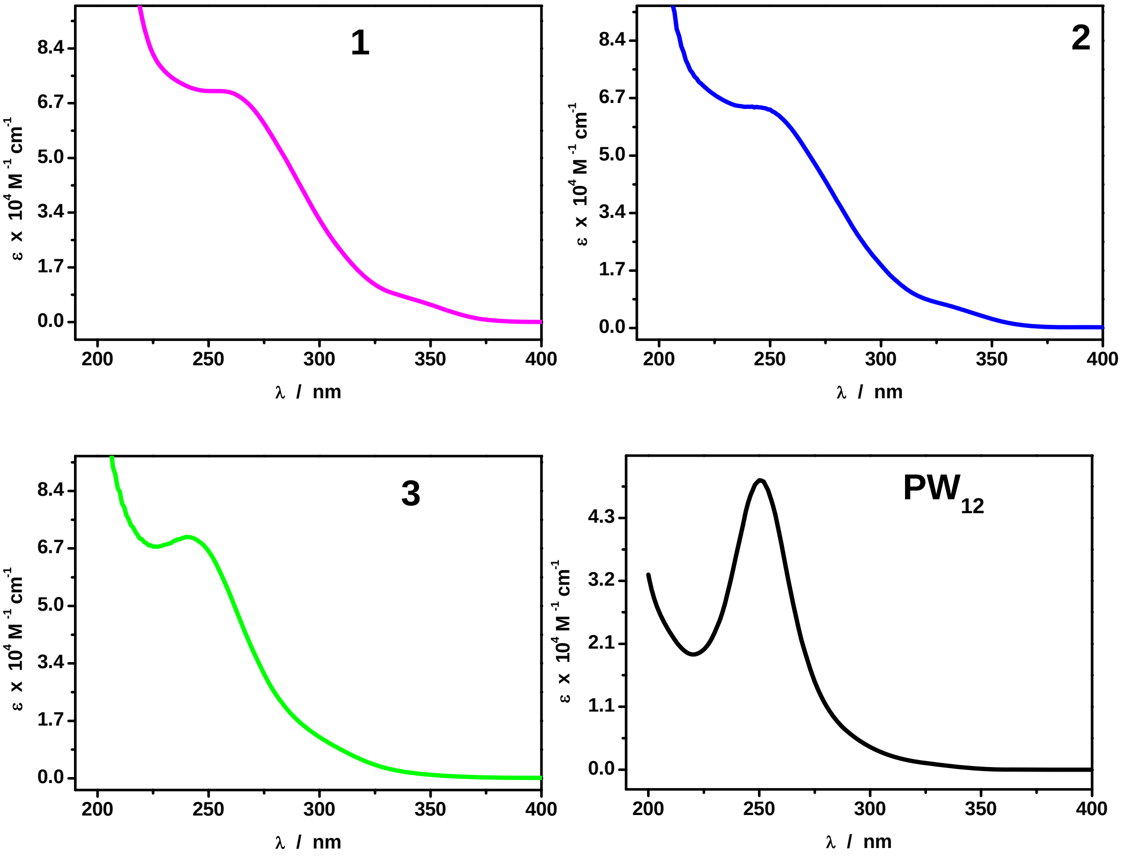

Figure S1A: UV-near-vis absorption spectra of the POMs in aqueous solution (pH 1, HCl).

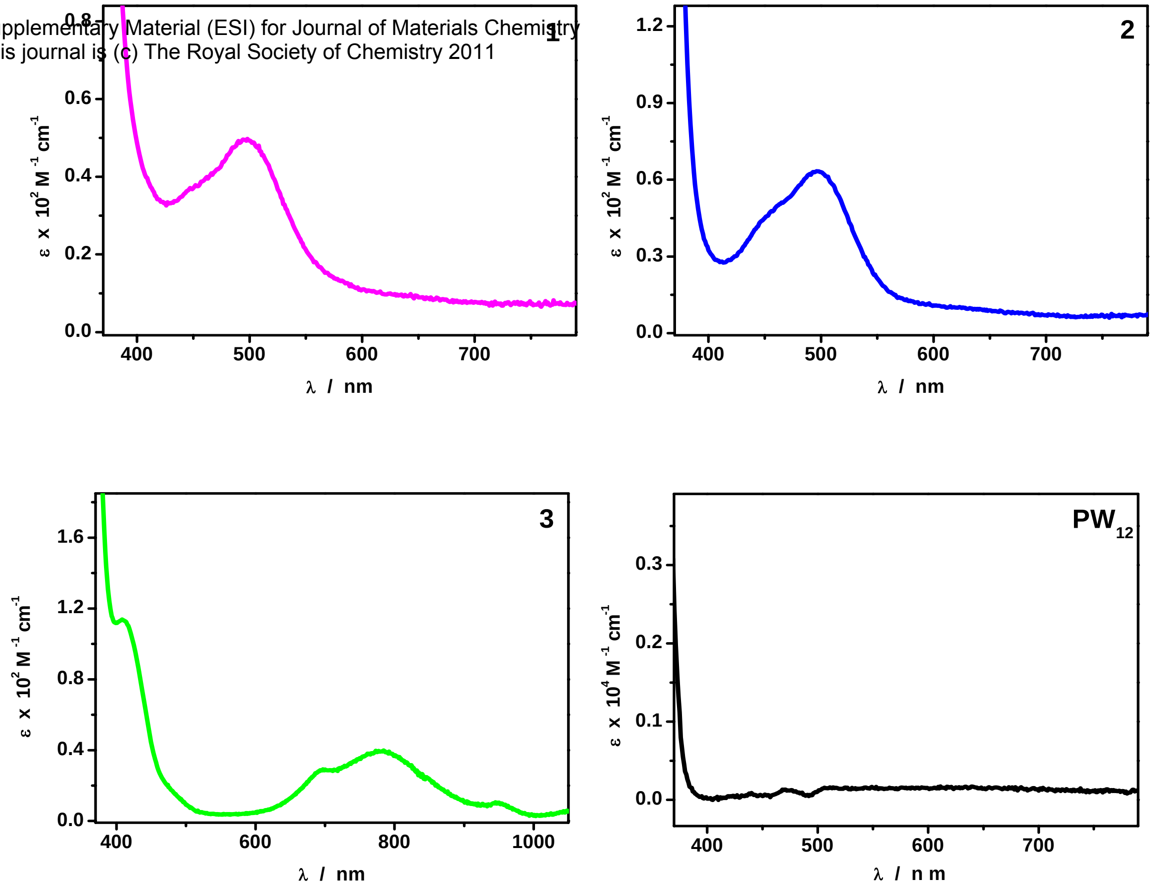

Figure S1B: Visible-NIR region of absorption spectra of POM in aqueous solution (pH 1, HCl).

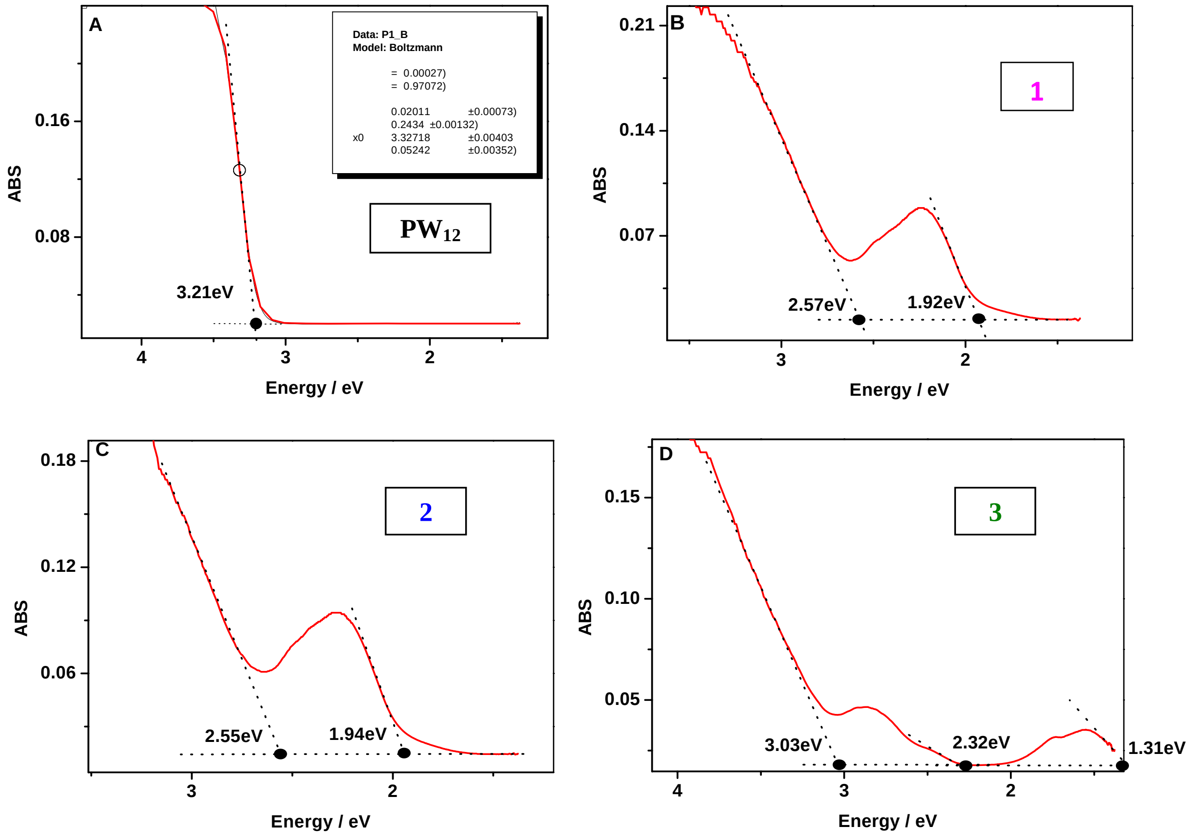

Figure S2: UV-vis- NIR diffuse reflectance spectra (DRS) of the POMs.

Table S2: absorption edge wavelengths (λ) of POMs and corresponding energies (E). The values are restricted to the LMCT transition O^{2-} to W^{6+}.

POM	Solution λ/nm	Solid λ/nm	Solution E/eV	Solid E/eV
1	469	482	2.64	2.57
2	464	486	2.67	2.55
3	395	409	3.14	3.03
PW_{12}	363	386	3.42	3.21

Electrochemistry

We have already published the electrochemical properties of the three compounds[1-3] and those of PW_{12} are well-known. However, to our knowledge, the spectroscopic properties of electro-reduced **1**, **2** and **3** have not been reported. In the media used here, their W^{VI} centers are the only ones to be electro-reducible through pH dependent multi-electron processes.[1-3] The cyclic voltammograms (CVs) for **1** and **2** present two reversible two-electron W-reduction processes followed by multi-electronic waves which will not be further considered here. The CV characteristics of **1** and **2** are similar; their two-electron W-reduction waves are roughly located respectively at -0.160 V and -0.300 V. The W centers of **3** are more difficult to reduce. Indeed the first reduction wave of **3** is located at -0.570 V. In the following, the study is restricted to this wave which features a six-electron reversible process.[3] The CV of **PW_{12}** shows two one-electron and a two reversible W-reduction located respectively at -0.068V, -0.344V and -0.704V.

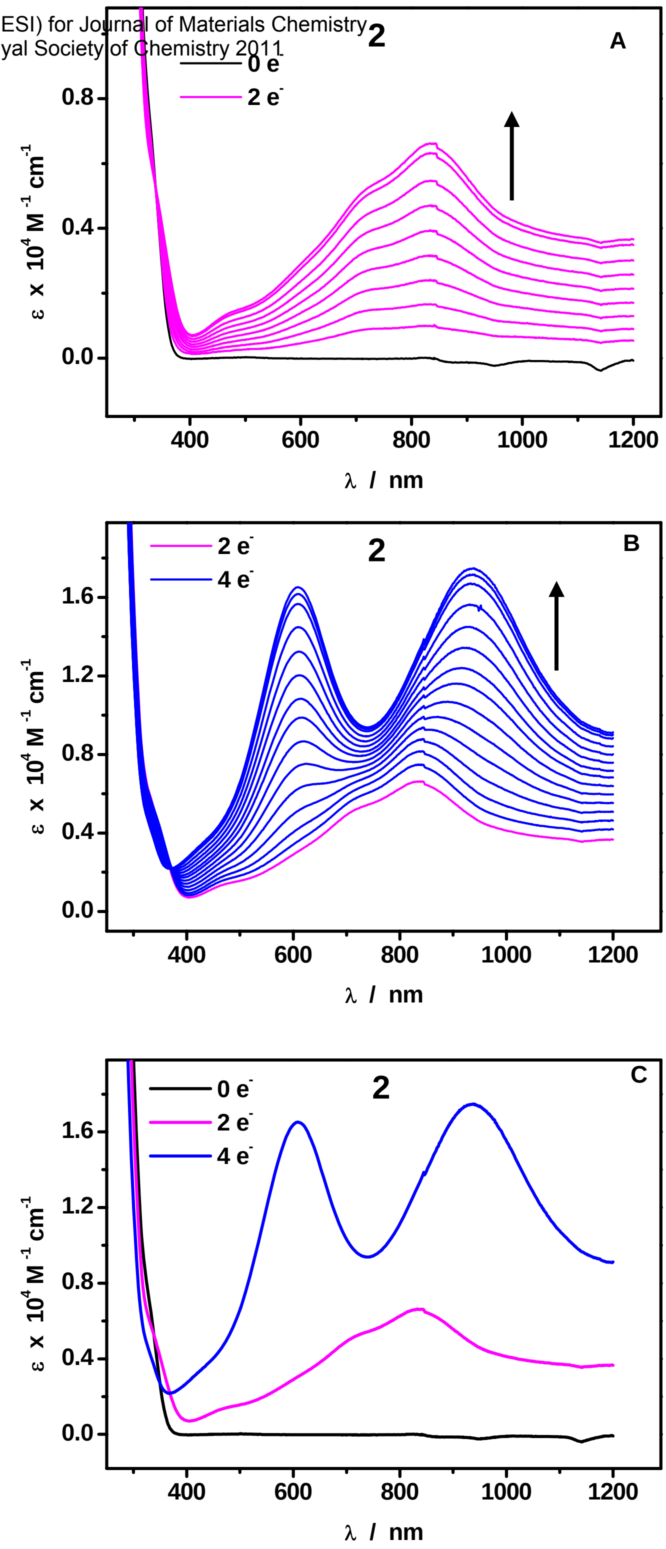

Figure S3: Spectroelectrochemical reduction of 5.10^{-5} M of **2** in a deaerated aqueous solution (pH 1, HCl) as monitored by the UV-visible spectra (A) The reduction potential was set to the first wave and the coulometry gradually performed to completion of the two-electron reduced species (B) After completion of step A, the reduction potential was set to the second wave and the electrolysis gradually continued to completion of the four-electron reduced species (C) Summary showing in superposition the final UV-visible spectra of the two- and four –electron reduced species of **2**. The spectrum of oxidized **2** is added for comparison.

*Photoreduction pathways of **1** upon irradiation of its mixture with Me_2CHOH*

For clarity, the known preassociation of POMs with 2-propanol will be omitted. In addition, it is hypothesised, as usual[7,8], that the POM photoreduction remains sequential, even though only two- and four-electrons processes are directly observed in the present experimental conditions. Detailed mechanistic study of the photoreduction and/or of the electrochemical reduction of the POM implying ECE (Electrochemical-Chemical-Electrochemical) and disproportionation-type steps and the protonation states of the reduced species is beyond the scope of the present work.

$\mathrm{POM} + h\nu \rightarrow \mathrm{POM^*}$

$\mathrm{POM^* + Me_2CHOH \rightarrow POM(e^-) + Me_2COH + H^+}$

$\mathrm{POM^* + H_2O \rightarrow POM(e^-) + OH + H^+}$

$\mathrm{OH + Me_2CHOH \rightarrow Me_2COH + H_2O}$

$\mathrm{POM(e^-) + POM(e^-) \rightarrow POM(2e^-) + POM}$

$\mathrm{POM + Me_2COH \rightarrow POM(e^-) + Me_2CO + H^+}$

$\mathrm{OH + Me_2COH \rightarrow Me_2CO + H_2O}$

$\mathrm{POM(e^-) + Me_2COH \rightarrow POM(2e^-) + Me_2CO + H^+}$

It has been checked that Me_2COH with a redox potential of – 1.7 V vs NHE at pH = 5 can drive this last process.[9] The possible absorption of visible light by POM(e^-) and the evolution of the corresponding excited state toward POM($2e^-$) should also be considered.

An analogous set of reactions can be written for the generation of the 4-electron reduced POM.

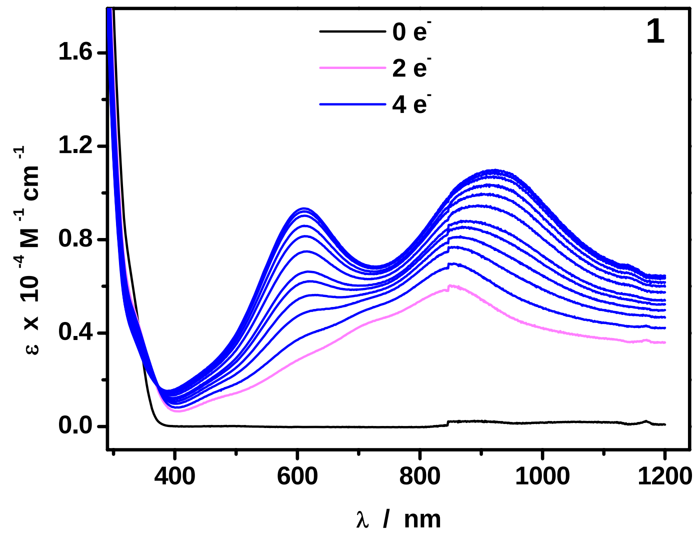

Figure S4: UV-vis spectra of photoreduced **1** upon irradiation of deaerated aqueous solutions containing 2-propanol 0.5 M, [**1**] 0.05mM (pH 1), for various irradiation times (0, 5, 10, 15, 20, 25, 30, 40, 50, 60, 70, 80 min). λ > 400 nm.

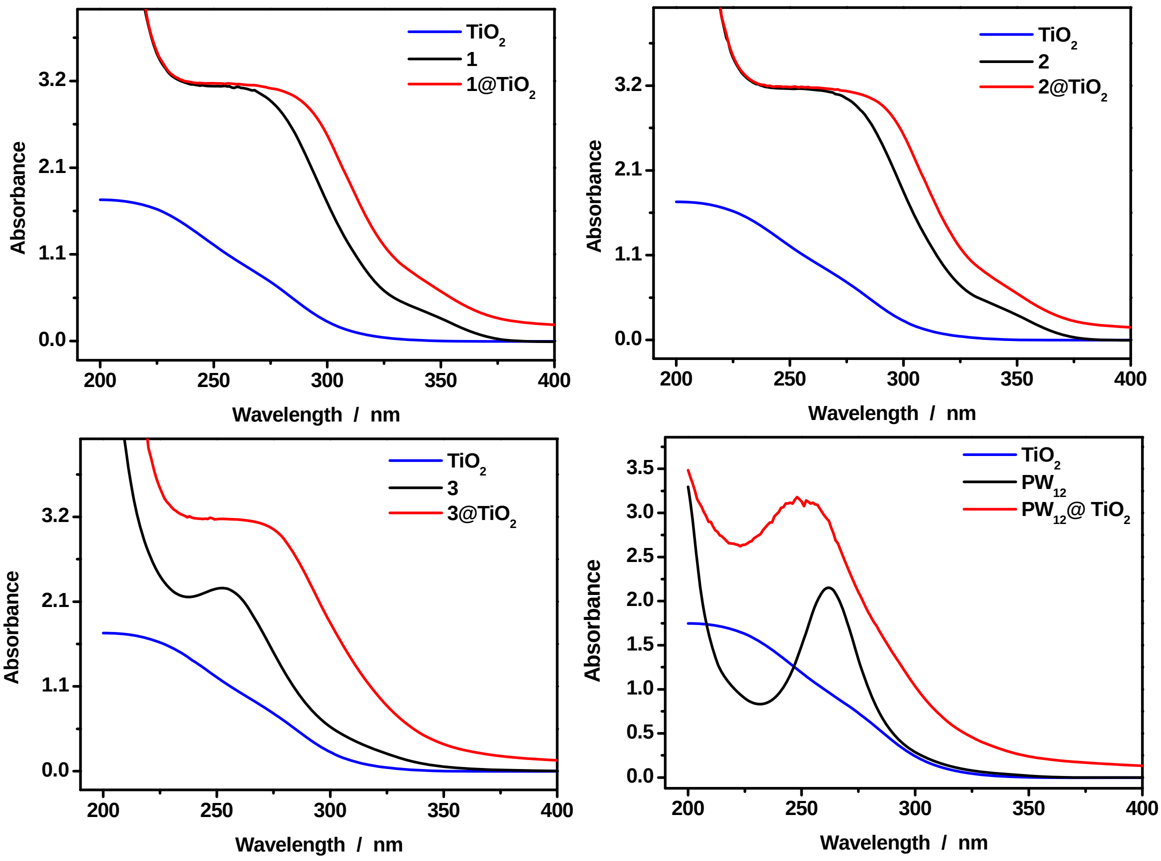

Figure S5: Comparison of UV absorption spectra of 0.05 mM POM in the absence and presence of TiO_2 (pH 1). The spectrum of 0.384 mM TiO_2 is added for comparison. 1.000 cm optical path quartz cuvettes were used.

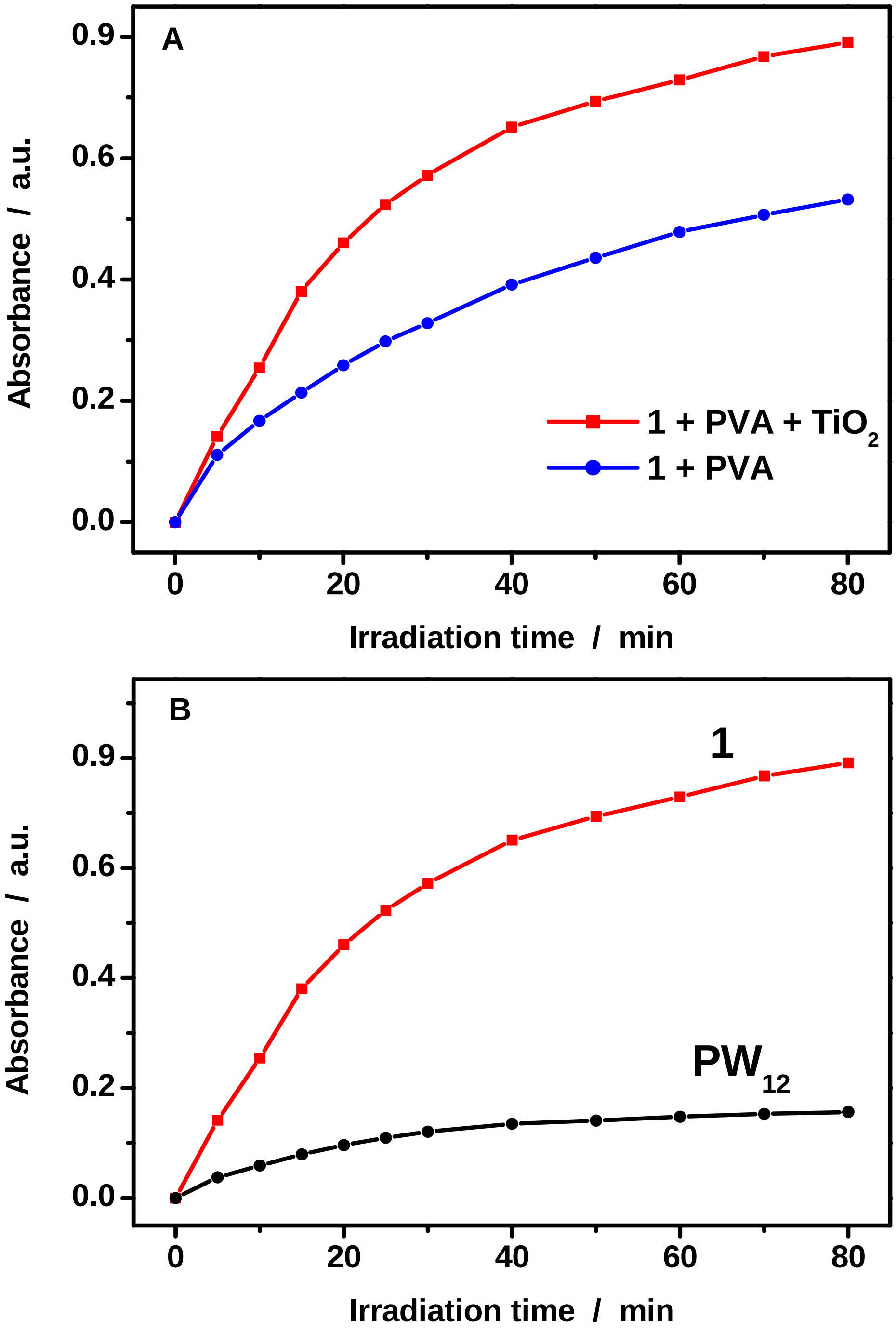

Figure S6: (A) Photoreduction of **1** in PVA aqueous solutions in the absence and in the presence of TiO_2 colloids, as monitored by the absorbance increase at 608 nm as a function of irradiation time (B) Comparison of **1** and **PW_{12}** in PVA aqueous solutions in the presence of TiO_2 colloids, as monitored by the absorbance increase at 608 nm for **1** and 624 nm for **PW_{12}** as a function of irradiation time [POM] 0.05 mM, PVA 2 mg/mL, [TiO_2] 0.38 mM (pH 1). $\lambda >$ 320 nm.

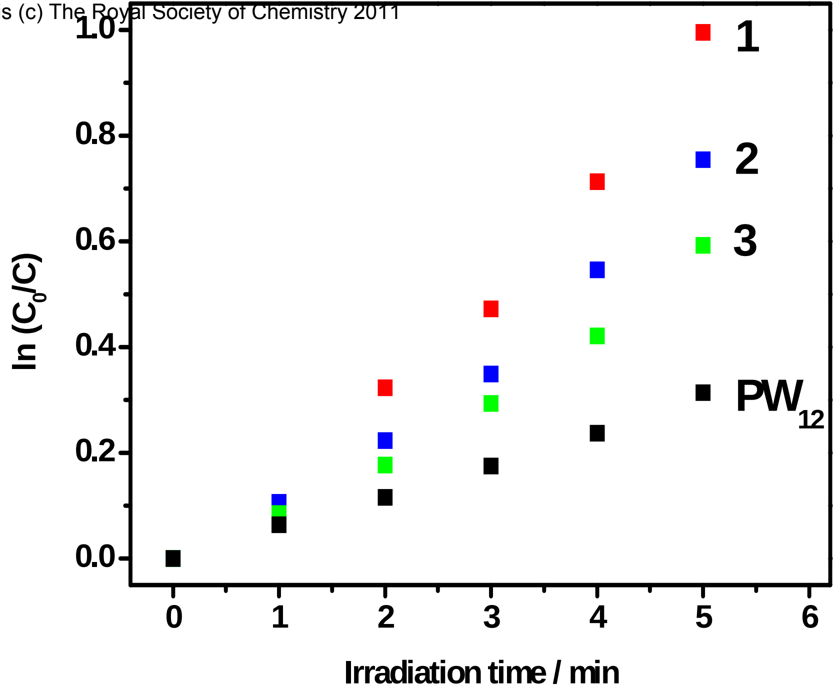

Figure S7: Reductive decomposition: influence of POM photocatalyst, **1**, **2**, **3** and **PW_{12}**, on the rate of **AO7** decoloration upon photolysis of deaerated aqueous solutions containing PVA 2mg/mL, [TiO2] 0.383 mM, [POM] 0.05mM, [**AO7**] 0.05mM (pH1, HCl). First order-linear ln (C_0/C) = f(t). Conditions: $C_0 = 5.10^{-5}$ M. λ > 400 nm.

Table S3: kinetic rate constants of AO7 degradation by visible light irradiation of POM or POM@TiO_2.
[POM] = 5.10^{-5}M, [AO7] = 5.10^{-5}M, 2mg/mL PVA, $3.83.10^{-4}$M TiO_2, HCl pH 1, optical pathway = 1cm, λ > 400nm.

Systems	k (min^{-1})	R*
1	0.060	0.991
1@ TiO_2	0.20	0.998
2 @TiO_2	0.14	0.991
3@TiO_2	0.12	0.991
PW_{12} @TiO_2	0.060	0.998
TiO_2	0.024	0.995

* Correlation coefficient

Photocatalysis

UV and visible light

In 2-propanol, under visible light, the photocatalytic activities of POMs parallel also their photosensitivities. However, the rate constants obtained with **1** and **2** are similar in this medium (~ 0.13min^{-1}). For example, after irradiation for 11min, the conversion of **AO7** reached 99%, 97%, 25% and 6% respectively for **1**, **2**, **PW$_{12}$** and **3**. The **POM@TiO$_2$** composites show much higher photocatalytic activity vis-à-vis the reductive **AO7** decoloration in presence of PVA than pure POMs in 2-propanol, e.g., **1@TiO$_2$** is around 1.6 more efficient than pure **1** for this reaction. This observation is in accordance with the synergic effect of POM and TiO$_2$. In another set of experiments, the decoloration of **AO7** by POMs was carried out in the presence of TiO$_2$ and PVA but under near-UV-visible light (λ>320 nm). Even under these conditions where **PW$_{12}$** has a good photosensitivity, its rate constant is 3.2 and 3.8 less than those of respectively **1** and **2**. It is worth noting that under UV-near-vis light, the rate constant of **2** (1.32 min^{-1}) is around 20% higher than that of **1**. As expected, photodegradation processes are faster under UV-near-vis than upon visible light, e.g., total bleaching of **AO7** by **1@TiO$_2$** and **2@TiO$_2$** is observed in less than 2 min.

Sun light

The decomposition of **AO7** solutions by **1**, **2**, **1@TiO$_2$** or **2@TiO$_2$** was carried out under sun light irradiation in various experimental conditions. In aerated PVA solutions (pH= 1), total bleaching was obtained in less than 4 min with **1@TiO$_2$** or **2@TiO$_2$**. Even though the comparison of this result with those obtained under UV or visible light is qualitative, synergistic effect was also observed upon sun light irradiation, e.g. the relative photoactivities of **POM@TiO$_2$** assemblies are 1.6 to 2 times higher than those obtained respectively with the corresponding pure POMs. In all these media, a series of bleaching processes were successfully carried out, thus establishing the stability of POMs and **POM@TiO$_2$** assemblies . For example, the photocatalytic activity of **1@TiO$_2$** remains unchanged after 20 consecutive bleaching processes. Moreover, after such series of reactions, the solution could be reused several days after. The blank experiments carried out in different conditions showed the following results: i) photodecomposition of **AO7** alone was negligible; ii) in the absence of **AO7** and oxygen, solutions of POMs (in PVA or 2-propanol) or **POM@TiO$_2$** gradually turned blue, ending up with the four-electron reduced POMs. As expected, the presence of oxygen slows down POM photoreduction. In another set of experiments, the photocatalytic activity of **POM@TiO$_2$** towards **AO7** decomposition, under solar light irradiation, was tested in PVA dissolved in aerated pure water (pH~5) because it is known that the efficiency of this reaction is strongly dependent on pH and furthermore, wastewater from industries has generally a large range of pH values. Total bleaching was observed but, as expected, the reaction is slower than in the pH 1 solutions. For example, with **1@POM**, the process is roughly 3 times faster with the more acidic medium.

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