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An unprecedented $\{\text{Ni}_{14}\text{SiW}_9\}$ hybrid polyoxometalate with high photocatalytic hydrogen evolution activity

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A unique polyoxometalate complex made of a tetradecanuclear nickel bisphosphonate cluster capping a $\{\text{SiW}_9\}$ unit has been characterized. This stable compound exhibits a high hydrogen evolution reaction photocatalytic activity under visible light irradiation via a reductive quenching mechanism.

The photocatalytic activity of polyoxometalates (POMs) has been widely studied mainly due to their exceptional ability to perform photoinduced multi-electron reactions. Over the past decade, their relevance to both photooxidation (water oxidation, oxidation of organic pollutants,...) and photoreduction (reduction of metal cations, protons,...) reactions has been evidenced and studied with a growing interest.¹ In the subfield of the hydrogen evolution reaction (HER), the activity of POMs assisted by co-catalysts (in particular platinum-based co-catalysts) has been well investigated.² Nevertheless, very few systems incorporating only POMs and a photosensitizer (PS) have been found to be efficient for the reduction of protons. Noticeably, Izzet *et al.* reported in 2013 an elegant HER-active POM hybrid compound whereby two iridium complexes, playing the role of visible-light PS, are covalently linked to a Dawson $[\text{P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ unit, with a Turn-Over number (TON) of 41 after 7 days in homogeneous conditions.³ Another covalently linked iridium/POM system, where an Anderson platform is decorated by two iridium complexes, was reported by the group of Streb, with a TON of

80 after one week.⁴ In the meantime, the group of Hill evidenced that the TBA salt of $[(\text{PW}_9\text{O}_{34})_2\text{Ni}_4(\text{H}_2\text{O})_2]^{10-}$ (TBA = tetrabutylammonium) tetranuclear Ni^{II} complex (noted **TBA- $\text{P}_2\text{W}_{18}\text{Ni}_4$**) produces H_2 with a TON of 6500 after one week in presence of $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})]^+$ as PS (noted [Ir], with ppy = 2-phenylpyridine and dtbbpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine) and triethanolamine (TEOA) as sacrificial electron donor.⁵ The catalytic activity of such fully inorganic multinuclear Ni^{II} polyoxotungstates has been recently confirmed,⁶ while it has been showed that simple monosubstituted Ni^{II} Keggin POMs can also present an HER activity with $[\text{Ru}(\text{bpy})_3]^{2+}$ (bpy = bipyridin) as PS.⁷ It thus appears that, even if some POMs incorporating other 3d centers (Fe^{III} , Cu^{II})⁸ or lanthanide cations⁹ have been scarcely reported as HER complexes, Ni^{II} polyoxotungstates are particularly attractive HER photocatalysts.

These last years, some of us have shown that bisphosphonate (BP) ligands can structure solution-stable Ni^{II} polyoxotungstates, as exemplified by the characterization of the $[\{(\text{B-PW}_9\text{O}_{34})\text{Ni}_3(\text{OH})(\text{H}_2\text{O})_2(\text{Ale})\}_2\text{Ni}]^{14-}$ (noted **$\text{P}_2\text{W}_{18}\text{Ni}_7\text{Ale}_2$** , with Ale = alendronate = $[\text{O}_3\text{PC}(\text{C}_3\text{H}_6\text{NH}_3)(\text{O})\text{PO}_3]^{4-}$) sandwich-type complex where two $\{\text{PW}_9\}$ units encapsulate a heptanuclear $\{\text{Ni}_7(\text{Ale})_2\}$ core.¹⁰ Such species were shown to be highly stable in the 7-10 pH range, and derivatives with various organic groups or coordination complexes were further reported.^{10,11} Herein, we show up the richness of this BP POM chemistry, reporting on a novel complex where a $\{\text{Ni}_{14}\}$ fragment structured by Ale ligands caps a $\{\text{SiW}_9\}$ trivacant POM. To the best of our knowledge, such arrangement is unique in POM chemistry, this compound constituting by far the polyoxotungstate with the highest 3d metal/tungsten atomic ratio reported to date. The HER activity of this functionalizable, high-nuclearity 3d system has been investigated in detail, highlighting the benefit of accumulating 3d centers on the photocatalytic properties.

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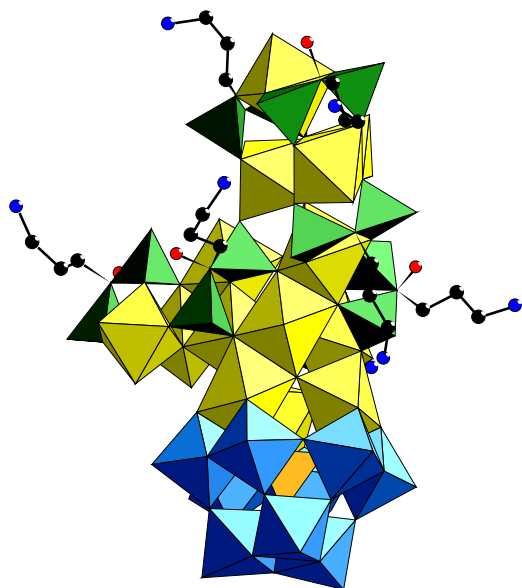


Fig. 1. Polyhedral and ball-and-stick representation of $\text{SiW}_9\text{Ni}_{14}\text{Ale}_7$; blue octahedra: WO_6 , yellow octahedra: NiO_6 , green tetrahedra: PO_3C , orange tetrahedron: SiO_4 , black spheres: C, blue spheres: N, red spheres: O. The hydrogen atoms have been omitted for clarity.

$\text{Na}_{12}[(\alpha\text{-A-SiW}_9\text{O}_{34})\text{Ni}_{14}(\text{AleH})_5(\text{Ale})_2(\text{H}_2\text{O})_{11}(\text{OH})_7] \cdot 75\text{H}_2\text{O}$ (**Na-SiW₉Ni₁₄Ale₇**) was synthesized in water by heating at 80 °C a solution of nickel chloride, alendronic acid and $[\alpha\text{-A-SiW}_9\text{O}_{34}]^{10-}$ (SiW_9) at a pH adjusted to 9.1 with sodium carbonate. The trivalent POM was used in excess, since attempts with the SiW_9 :Ni 1:14 stoichiometric ratio have only afforded powders that we did not succeed to characterize. After cooling the mixture at room temperature, a crystalline yellow powder slowly precipitated. Single-crystals of **Na-SiW₉Ni₁₄Ale₇** were obtained by recrystallization in water. The single-crystal X-Ray diffraction experiments (see Table S1, ESI[†], for crystallographic data) showed that **SiW₉Ni₁₄Ale₇** consists in a $\{\alpha\text{-A-SiW}_9\}$ unit capped by a tetradecanuclear Ni^{II} cluster which is structured by seven Ale ligands (Fig. 1). In addition, seven μ_3 -hydroxo ligands (Bond Valence Sum calculations = 0.94–1.13) ensure the cohesion of the $\{\text{Ni}_{14}\}$ cluster. The paramagnetic centers complete their coordination spheres with a total of eleven terminal water molecules. Elemental analysis together with EDS measurements confirmed the composition of **Na-SiW₉Ni₁₄Ale₇** (see ESI[†] for details). Magnetic measurements are also in agreement with the determined structure. The $\chi_{\text{M}}T$ product vs. T curve related to a crystalline sample of **Na-SiW₉Ni₁₄Ale₇** is represented in Fig. S1, ESI[†]. First, a plateau is observed between 300 and 100 K, with a $\chi_{\text{M}}T$ value of 17.6 $\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ corresponding to $g = 2.24$ considering fourteen $S = 1$ Ni^{II} non-interacting magnetic centers. The g value is in perfect agreement with that found for the **P₂W₁₈Ni₇Ale₂** compound previously reported,¹⁰ confirming the Ni:W ratio in **Na-SiW₉Ni₁₄Ale₇**. Below 100 K, the $\chi_{\text{M}}T$ product continuously decreases to 2 K ($\chi_{\text{M}}T = 2.5 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$), indicating that in addition to magnetic anisotropy characterizing such $S = 1$ Ni^{II}

ions, overall weak antiferromagnetic interactions are predominant. Considering both the high nuclearity and the C_2 symmetry of the $\{\text{Ni}_{14}\}$ core, no attempt to fit the data with a Heisenberg Hamiltonian was performed. The IR spectrum of **Na-SiW₉Ni₁₄Ale₇** (Fig. S2, ESI[†]) presents the typical vibrational bands of the SiW_9 fragment (990 – 670 cm^{-1}) and of the P-O groups of the Ale ligands (1050 cm^{-1}). The IR spectrum of a powder obtained by dissolution in water of **Na-SiW₉Ni₁₄Ale₇** followed by the addition of NaCl is strictly similar to that of **Na-SiW₉Ni₁₄Ale₇** (Fig. S2, ESI[†]), strongly suggesting that the title complex is stable in aqueous solution. Note that the IR spectrum of **Na-SiW₉Ni₁₄Ale₇** is highly characteristic. The $I_{\text{W-O}}/I_{\text{P-O}}$ ratio (where $I_{\text{W-O}}$ and $I_{\text{P-O}}$ stands for the intensity of the W-O and P-O vibrations, respectively) is indeed much higher for **SiW₉Ni₁₄Ale₇** than for the other Ale/3d metal/polyoxotungstates previously reported, in agreement with a Ale:W₉ (X = Si, P) ratio of 7:1 in **SiW₉Ni₁₄Ale₇**, at variance with the 1:1 ratio reported for the earlier published compounds.^{10–12} In addition, UV-Vis spectroscopy in aqueous solution revealed no significant variation over a period of 12h of the Ni^{II} d-d transition bands characterizing **SiW₉Ni₁₄Ale₇** (Fig. S3, ESI[†]). In order to obtain a derivative of **SiW₉Ni₁₄Ale₇** soluble in organic solvent, metathesis of the sodium counteranions with bis(triphenylphosphoranylidene)ammonium (P_2N) cations has been performed, affording the $(\text{P}_2\text{NC}_3\text{H}_3\text{O})_8\text{Na}_4[(\alpha\text{-A-SiW}_9\text{O}_{34})\text{Ni}^{\text{II}}_{14}(\text{AleOH})_5(\text{AleO})_2(\text{H}_2\text{O})_{11}(\text{OH})_7] \cdot 60\text{H}_2\text{O}$ (**P₂N-SiW₉Ni₁₄Ale₇**) complex. The IR spectrum of the organo-soluble **P₂N-SiW₉Ni₁₄Ale₇** clearly shows the bands characteristic of both the **SiW₉Ni₁₄Ale₇** POM and the P_2N counteranions (Fig. S4, ESI[†]). Its composition was further confirmed by elemental analysis and EDS measurements (see ESI[†] for details). The HER catalytic activity of **P₂N-SiW₉Ni₁₄Ale₇** was investigated in acetonitrile under visible light irradiation using [Ir] as PS, TEOA as a proton donor and 1-benzyl-1,4-dihydroxycotinamide (BNAH) as the sacrificial electron donor. Various concentrations of the catalyst were investigated, from 5 to 60 μM . H_2 formation was monitored by gas chromatography. As shown in Fig. 2, upon irradiation, H_2 was formed immediately and its production increased with time up to a plateau, reached at various reaction times depending on the catalyst concentration: the larger the concentration, the later the plateau.

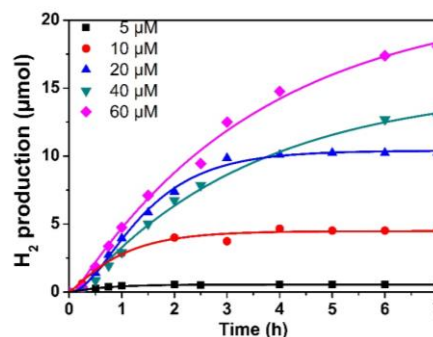


Fig. 2. Photocatalytic HER at different concentrations of **P₂N-SiW₉Ni₁₄Ale₇**. Conditions: Xenon arc lamp (280 W, 415 < λ < 800 nm), [Ir] (0.2 mM), TEOA (0.25M), BNAH (0.1 M), 2mL of CH_3CN deaerated with N_2 .

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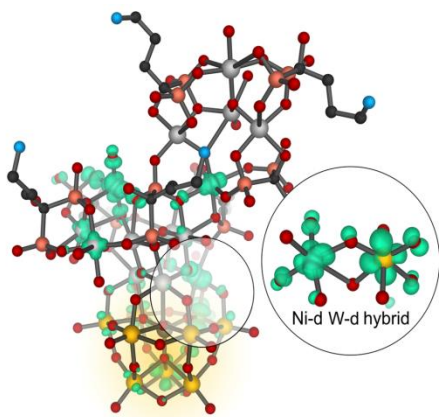


Fig. 3. One illustrative frontier unoccupied orbital of **SiW₉Ni₁₄Ale₇**, composed of hybrid W-d and Ni-d orbitals. Electron density, shown in green, is drawn at $0.01 \text{ e}^-/\text{\AA}^3$. Atoms depicted: W (yellow), Ni (grey), Si (grey), C (black), O (red), N (blue), P (orange).

This is even better seen in Fig. S5 which translates the data of Fig. 2 in TON values as a function of time. We have established that this plateau is the result of the inactivation of the PS and not of the POM. Indeed, immediately after addition of a fresh solution of the [Ir] complex (final [Ir] concentration $200 \mu\text{M}$) in the reaction medium after reaching the plateau, hydrogen production resumed with a rate similar to the initial one (Fig. S6, ESI[†]). As a further indication of the stability of the catalyst, the IR spectrum of the POM precipitated with $[\text{Ru}(\text{bpy})_3]^{2+}$ from a postcatalytic solution after 4h of illumination presents, together with the bands of the counter-cation, the characteristic signatures of **SiW₉Ni₁₄Ale₇** (Fig. S7, ESI[†]). Based on the data of Fig. 2, the highest amount of H_2 ($18 \mu\text{mol}$ after 7h) was obtained with the most stable system ($60 \mu\text{M}$ POM). However the highest initial TOF (Turn-Over Frequency) values were obtained with $10\text{--}20 \mu\text{M}$ POM concentrations ($2.7 \times 10^{-2} \text{ s}^{-1}$) and the highest TON value was 256 for a concentration of $20 \mu\text{M}$ (Fig. S5, ESI[†]) after 4h reaction. Compared in the same conditions, **TBA-P₂W₁₈Ni₄** exhibited a TON of 41 after 4h and an initial TOF of $9.8 \times 10^{-3} \text{ s}^{-1}$ (Fig. S8, ESI[†]).

To assess the contribution of each component to the photo-system, several control experiments were conducted. No hydrogen production could be detected in the absence of catalyst or in the dark, and a negligible amount of hydrogen was measured when BNAH was removed or replaced with water (Fig. S9, ESI[†]). In addition, experiments using 14 equivalent of a Ni^{II} salt rather than the POM catalyst showed no catalytic activity (Fig. S9, ESI[†]). Furthermore, the addition of 150 mg of mercury in the reaction medium did not influence the production of hydrogen, showing that the active species is neither cationic nickel in solution nor Ni^0 nanoparticles, as also confirmed by DLS measurements.

Preliminary quantum chemical simulations were performed to elucidate the nature of the band edges in **SiW₉Ni₁₄Ale₇** (computational details are provided in the ESI[†]). Owing to the low molecular symmetry of the polyoxometalate catalyst, there are numerous unoccupied frontier orbitals composed of hybrid W-d and Ni-d metal-centered orbitals. We present one of the LUMOs by projecting the electronic density corresponding to

the Kohn-Sham orbital equal to half the number of electrons + 1, *i.e.* the first unoccupied molecular orbital, Fig. 3. Other LUMOs feature similar metal-d orbitals in various combinations. This unoccupied metal-d band is in good agreement with other transition metal-containing tungsten-based POMs¹³ suggesting that here both W- and Ni- centers may participate to HER.

In order to get insights into the reaction mechanism, time-resolved fluorescence measurements at 585 nm in CH_3CN solution containing 0.2 mM of [Ir] with increasing concentration of TEOA, BNAH or **P₂N-SiW₉Ni₁₄Ale₇** and irradiated at 430 nm were then performed and analyzed according to the Stern-Volmer equation:

$$\tau_0/\tau = 1 + k_q\tau_0[Q]$$

where τ_0 and τ are the emission lifetimes of [Ir] without and with the quencher Q of concentration [Q], respectively, and k_q is the quenching rate constant. The [Ir] complex indeed displays a broad emission with a maximum at 585 nm (Fig. S10, ESI[†]). From the data shown in Fig. 4 at concentrations used in the photochemical assay (yet lower for BNAH), photoluminescence lifetimes could be obtained (Table 1). Clearly, quenching rate constants in Table S2 deduced from the measurements at various concentrations of Q (Fig. S11) indicated that under the conditions of the photocatalytic assay, the most efficient quenching of the emission was observed with BNAH. It results from this analysis that the reductive quenching of the PS is the dominant path.

The reductive quenching of $[\text{Ir}]^*$ by the sacrificial electron donor is further confirmed by transient absorption measurements. The transient absorption feature centered at 500 nm (Fig. S12, ESI[†]), assigned to the absorption of excited $[\text{Ir}]^*$, decays following a mono-exponential law with a decay time of $520 \pm 20 \text{ ns}$.

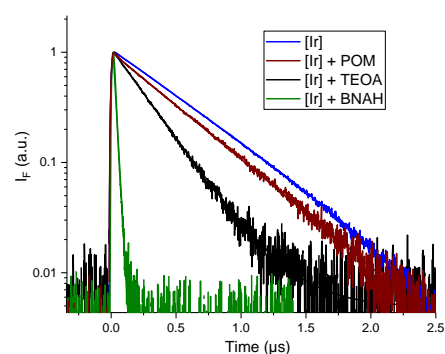


Fig. 4. Normalized time-resolved luminescence decays of [Ir] photosensitizer (0.2 mM), [Ir] with POM ($20 \mu\text{M}$), [Ir] with TEOA (0.25 M) or BNAH (0.01 M) in CH_3CN ($\lambda_{\text{exc}} = 430 \text{ nm}$).

	[Ir]	[Ir] + POM	[Ir] + TEOA	[Ir] + BNAH
Lifetime (ns)	520 ± 20	450 ± 20	260 ± 10	20 ± 10

Table 1. Photoluminescence lifetime of [Ir] photosensitizer ($200 \mu\text{M}$) in the presence of different quenchers: **P₂N-SiW₉Ni₁₄Ale₇**, ($20 \mu\text{M}$), TEOA (0.25 M) or BNAH (0.01 M) in CH_3CN ($\lambda_{\text{exc}} = 430 \text{ nm}$).

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From decay times obtained in the presence of **P₂N-SiW₉Ni₁₄Ale₇**, TEOA or BNAH at the concentrations used in the photochemical assay (Figs. S13, S14 and S15), it appears again that the fastest process is the electron transfer from BNAH to [Ir]^{*}, leading the reduced photosensitizer characterized by an absorption at 535 nm.¹⁴ In short, the present system functions via a reductive quenching of the PS, followed by reduction of the catalyst by the reduced PS. We can note that, under photocatalytic conditions, it has not been possible to evidence via UV-Vis spectroscopy the formation of reduced POM species, suggesting that the reduction of protons by the reduced POM is not the limiting step.

In summary, we reported herein on an unprecedented, stable POM where fourteen Ni^{II} centers cap a single trivacant Keggin unit. The organic/inorganic hybrid nature of this POM opens the way to the elaboration of a full family of derivatives, as already demonstrated for 3d bisphosphonates POMs in which the nitrogen atom of the Ale ligand has been functionalized by various organic or organometallic fragments.^{10,11} While **TBA-P₂W₁₈Ni₄** and **P₂N-SiW₉Ni₁₄Ale₇** incorporate almost the same number of heavy atoms (22 and 23, respectively), a significantly higher HER activity was found for the title complex, suggesting that the accumulation of 3d centers in the POM core enhances the photocatalytic properties of such complex. Time-resolved fluorescence together with transient absorption measurements suggest that during the photocatalytic process, the POM is reduced by the reduced photosensitizer. The immobilization of the reported species in matrices, which could lead to heterogeneous photocatalytic materials, is currently under study.

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Conflicts of interest

There are no conflicts to declare.

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