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Synthesis, electrochemical and photophysical properties of covalently linked porphyrin-polyoxometalates

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Two covalently linked porphyrin-polyoxometalate hybrids have been prepared: an Anderson-type hexamolybdate $[N(C_4H_9)_4]_3[MnMo_6O_{18}{(OCH_2)_3CNHCO(ZnTPP)}_2]$ with two pendant zinc(II)-tetraphenylporphyrins, and a Dawson-type vanadotungstate $[N(C_4H_9)_4]_5H[P_2V_3W_{15}O_{59} {(OCH_2)_3CNHCO(ZnTPP)}]$ with one porphyrin. Electrochemical studies show independent redox processes for the organic and inorganic parts at usual potentials. Photophysical studies reveal an electron transfer from the excited porphyrin to the Dawson polyoxometalate, but not to the Anderson polyoxometalate. Time resolved absorption spectroscopy allows the identification of the electron transfer pathways and the determination of the time constants.

15 Introduction

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Polyoxometalates (POMs) are attractive molecular clusters not only because of their rich structural chemistry,¹ but also due to their rich electronic and optical properties.² In particular, they are known for their ability to reversibly accept electrons without 20 significant structural changes.1 Porphyrins are also very appealing and have photophysical properties that are widely used in photoactive systems.³ Indeed, with appropriate metal ions, they have been shown to act as electron donors in a variety of supramolecular systems.⁴ Thus the combination of porphyrins 25 with POMs is expected to yield promising organic-inorganic hybrids^{5, 6} capable of forming charge-separated states by photoinduced electron transfer.⁷ Assemblies linking POMs and porphyrins have been prepared as bulk materials⁸ or as thin films,⁹ and used as catalysts¹⁰ or for electrocatalytic reductions.¹¹ 30 However, systems with stronger links and better control of the stoichiometry and the relative orientation of the components

stoichiometry and the relative orientation of the components would be of interest for some applications such as photocatalysis¹² or Non-Linear-Optic materials.¹³

We prepared a series of coordination complexes between ³⁵ POMs bearing pendant pyridyl groups and metalloporphyrins.¹⁴ Electronic communication between the polyoxometalate and the porphyrin was established, but our study showed that a stronger association between the two components of the complexes was desirable. Covalent attachment of organic ligands to the POMs ⁴⁰ appears as the way of choice.⁵ Harriman, Odobel and coll. have reported their seminal work on single porphyrins and porphyrin assemblies connected to monolacunary α_2 -[P₂W₁₇O₆₁]¹⁰⁻¹⁵

Fukuzumi et al. presented recently the intramolecular photoinduced electron transfer between a tin(IV) porphyrin and $_{45}$ directly coordinated $\left[PW_{12}O_{40}\right]^{3-16}$

We present here the preparation and characterization of

porphyrin-POM hybrids connected via a tris-alkoxo linker. Anderson-type POM { $MnMo_6O_{24}$ } and Dawson-type POM [$P_2V_3W_{15}O_{62}$]⁹⁻ were investigated to study the influence of the ⁵⁰ POM on the electrochemical and photophysical properties of zinc(II)-tetraphenylporphyrin.

Results and Discussion

Synthesis

Porphyrin ZnTPP-Tris (1, Scheme 1) was synthesized in three 55 steps with an overall 8.8% yield, which is satisfactory for porphyrin derivatives. Detailed procedures are in the ESI. 5-(4carboxyphenyl)-10,15,20-triphenylporphyrin was prepared by the Lindsey synthesis,¹⁷ and then metallated with zinc(II) acetate. Amidation with tris-hydroxymethylmethane¹⁸ introduced the 60 necessary triol function. Functionalized Anderson-type POM $[N(C_4H_9)_4]_3[MnMo_6O_{18}{(OCH_2)_3CNHCO(ZnTPP)}_2]$ (2) was prepared by the reaction of $[N(C_4H_9)_4]_4[\alpha-Mo_8O_{26}]$ with Mn(OAc)₃ and ZnTPP-Tris 1 in N,N-dimethylacetamide (DMA) for 60 h at 80-90°C, in adaptation of our published procedure.¹⁹ 65 In this synthesis, the functionalized POM is formed in a selfassembly type reaction from molybdate, Mn^{III} ion and triol. Because trivanadium substituted Dawson-type heteropolyanions are known to be catalytically active,^{20, 21} we synthesized also $[N(C_4H_9)_4]_5H[P_2V_3W_{15}O_{59}{(OCH_2)_3CNHCO(ZnTPP)}]$ **3** by 70 reacting 1 with $[N(C_4H_9)_4]_5H_4 [P_2V_3W_{15}O_{62}]$ in DMA for 7 days at 80-90°C, in adaptation of a procedure of Hill.^{20, 21} Here, the POM structure is preformed and then grafted with the triol. Both POMs were obtained in good yields (80%). They were isolated as solids by precipitation with ether from the reaction mixtures and 75 thoroughly washed to obtain satisfactory chemical analysis and clean NMR spectra. For the photophysical studies reported below, the microcrystalline powders were redissolved in

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acetonitrile and precipitated in ethyl acetate (repeated five times). The mother liquor was very slightly coloured purple.



Scheme 1: Synthesis of porphyrin-POM hybrids 2 and 3.

⁵ For compound **2** grafting of the organic ligand onto the paramagnetic POM is evidenced in ¹H NMR by a broad singlet at $\delta = 64$ ppm for the CH₂O groups linked to the POM, as well as a strong line broadening for the porphyrin signals (see ESI) in accordance with analogous structures.^{19,22} The ratio of integration ¹⁰ ligand / TBA cations is consistent with the grafting of two porphyrins per POM unit. For compound **3**, ¹H, and ³¹P NMR spectra are consistent with earlier work ^{20, 21,23} and indicate the substitution of the three μ_2 -oxo ligands of the V₃ cap in the parent polyoxometalate by the three μ_2 -alkoxy groups of the triol **1**. In ¹⁵ addition, ⁵¹V and ¹⁸³W NMR spectra (see ESI, Figures S6 and S7)

show respectively one ($\delta = -538.3 \text{ ppm}$) and three peaks ($\delta = -121.5, -150.1, -163.3 \text{ ppm}$), which is characteristic of a local C_{3v} symmetry.²⁴ By comparison with literature data,²⁵ the two narrow ¹⁸³W NMR signals at -121.5 and -163.3 ppm can be ²⁰ assigned to the W₃ cap and the adjacent W₆ belt. The third signal at -150.1 ppm is broadened as expected for the W₆ belt linked to the quadrupolar V atoms.

The IR spectra of **2** and **3** (see ESI) are also in agreement with the proposed structures. They display the strong metal-oxo ²⁵ vibrational bands between 700 and 1000 cm⁻¹ for the inorganic framework, and the bands for the organic ligand. Finally, the electrospray mass spectra (see ESI) display the molecular anions associated to varying numbers of TBA⁺ and H⁺ cations. All signals of significant intensity are assigned, and all charge states ³⁰ that fall within the spectral window are observed.

Electrochemistry

Electrochemical data of compounds 1-3, Anderson-type POM $[MnMo_6O_{18}\{(OCH_2)_3CNHCO(4-C_5H_4N)\}_2]^{3-}$ (4),¹⁴ and Dawson-type POM $[P_2V_3W_{15}O_{62}]^{9-}$ (5)²⁰ in organic solution (acetonitrile ³⁵ or DMF) are gathered in Table 1 and typical cyclic voltammograms (CV) are presented in Figure 1. All redox potentials E, evaluated from cyclic voltammetry as $(E^a_p + E^c_p)/2$, are reported in V versus the standard saturated calomel electrode (SCE). The electrochemical behavior of metalloporphyrins ⁴⁰ involving nonelectroactive metals is well documented.^{26,...,30} In the potential range of +1.5 to -2.5 V vs. Fc⁺/Fc, the oxidation and the reduction of the π ring proceed both via two reversible one-electron steps, generating radical cations and dications or radical anions and dianions, respectively.

⁴⁵ Early electrochemical studies of the octaethylporphyrin (OEP) and tetraphenylporphyrin (TPP) complexes – including their Zn^{II} complexes – utilized in large part cyclic voltammetry to measure half-wave potentials of each redox reaction. They demonstrated that most of the porphyrins exhibited a constant potential ⁵⁰ difference between the first and second macrocycle-centered oxidation, and between the first and second macrocycle-centered reduction.²⁸ These porphyrins have also a similar HOMO-LUMO gap of 2.25 ± 0.15 V, which corresponds to $\Delta E = \Delta |E_{Red1}-E_{OXI}|$.³¹ This constant gap ΔE was then used as diagnostic criteria to ⁵⁵ distinguish macrocycle-centered reactions from metal-centered ones.

Porphyrin-based redox processes

Porphyrin 1 presents the usual two one-electron reduction and two one-electron oxidation steps (Figure 1). For compounds 2 60 and 3, similar signals are detected without a significant change of the redox potentials (peaks labeled \blacktriangle in Figure 1, Table 1). They are therefore assigned to the porphyrin ligands on the POMs. The potential difference between the first and second porphyrin reduction is 0.41 V in 2 and 0.30 V in 3. The corresponding 65 values for porphyrin oxidation in 2 and 3 is 0.31 V. These values are close to those typically observed for ring reductions and oxidations of metalloporphyrins,²⁸ and compare well to those in 1 (0.35 V and 0.31 V for reduction and oxidation, respectively). The new irreversible wave for 3 observed at 0.81 V vs. Fc^+/Fc 70 (E_{0x3} , Table 1 and Figure 1) may be attributed to the oxidation of an isoporphyrin,^{32, 33} which implies a nucleophilic attack of the porphyrin dication ZnTPP²⁺ subunit. This agrees well with the known redox behaviour of porphyrins in the presence of nucleophiles³⁴ and in particular with the well documented reports 75 of Hinman.³² We propose that the nucleophile is trace amount of water present in the solution. The presence of reduction peak \triangle on the CV curves of 3 (Figure 1) could be explained by reduction of such an isoporphyrin. Similar reductions steps characterized the redox chemistry of isoporphyrins.³⁵ The oxidation peak \triangle ⁸⁰ around -1.0 V only occurs after scanning beyond -2.5 V (compare with the dotted CV in Figure 1). We attribute it to a chemical reaction (protonation) of the dianion porphyrin which becomes a strong base.

The experimental ΔE values (HOMO-LUMO gap) of **1**, **2** and ⁸⁵ **3** are in the range of 2.05 to 2.10 V, very close to the calculated values of 2.25 ± 0.15 V, obtained by Zerner and Gouterman for ZnTPP.³¹ Published on 22 November 2012 on http://pubs.rsc.org | doi:10.1039/C2DT31415K

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Table 1: Electrochemical data for compounds 1, 2, 3, 4 and 5^[a]

Compounds	Reduction					Oxidation			
	V ^V /V ^{IV}	Mn ^{III} /Mn ^{II}	Ring		M ^{VI} /M ^V (W or Mo)	Mn ^{III/IV}	Ring		
			E _{red1}	E _{red2}			E _{ox1}	E _{ox2}	E _{ox3}
1			-1.78	-2.13			0.29	0.60	
2		$E_{pc} = -1.64$ $E_{pa} = -0.71$	-1.76	-2.17	-2.34	0.39	0.29	0.60	
3	-0.50^{b}		-1.76 ^b	-2.06 ^b	-2.24		0.34 ^b	0.65 ^{b,c}	0.81 ^{b,c}
4	-1.40	-1.03 ^b			-2.36	0.44 ^b			
5 ²⁰	-0.31								
	-0.60								

[a]: Data obtained from cyclic voltammetry (scan rate 100 mV/s) on glassy carbon electrode. Analyte concentration: 0.5 mM, with 0.1 M TBAPF₆ as electrolyte and DMF as a solvent unless otherwise noted. E_i , approximated by $(E_p^a + E_p^c)/2$, are given in V vs. Fc⁺/Fc. [b]: in CH₃CN, [c]: irreversible.

The electrochemical oxidations and reductions have also been monitored by spectroelectrochemistry (see below) and these results confirm these assignments.



⁵ Figure 1. Cyclic voltammograms of compounds 1 and 2 in DMF and of 3 in CH₃CN, using 0.1 M TBAPF₆ as electrolyte. v = 100 mV·s⁻¹. (▲) first two oxidation and reduction peaks of 1. (△) peaks resulting from chemical reactions after generation of the dianion or dication porphyrin (see text). (▼) peaks attributed to the reduction or oxidation of 2. (●) ¹⁰ reduction peaks related to 3. c = 0.5 mmol·L⁻¹.

POM-based redox processes

The CV present furthermore the typical redox processes for the POM frameworks. Considering the oxidation of the Anderson ¹⁵ POM **2**, only the wave for Mn^{III}/Mn^{IV} is well resolved at +0.39 V vs. Fc⁺/Fc (\checkmark). Controlled-potential coulometry at +0.47 V, after this and the next anodic process (because the waves are too close to be discriminated), results in the exchange of 4.1 electrons per compound **2**. The normal pulse voltammogram, the linear ²⁰ sweep voltammogram and the differential pulse voltammogram

presented in Figure S17 (ESI), indicate that only three electrons

are exchanged after these first two oxidations. This apparent contradiction may be explained by a subsequent chemical reaction in the case of electrolysis. At the electrode occurs the ²⁵ first oxidation of the two metalloporphyrins as well the oxidation of Mn^{III} to Mn^{IV}. This in turn might react with itself by disproportionation to form 0.5 equiv. of manganese (V) and 0.5 equiv. of the starting manganese (III) species. This species would then be oxidized again at the electrode to manganese (IV). In the ³⁰ end, such disproportionation would result in the overall transfer of 2 electrons during bulk electrolysis and the formation of a manganese (V) species.¹⁴

Moreover, the cathodic redox process Mn^{III}/Mn^{II} is very slow with the reduction peak at -1.64 V and the corresponding ³⁵ reoxidation peak at -0.71 V (▼) (see also ESI, Figure S14). For the structurally close Anderson POM $[MnMo_6O_{18}{(OCH_2)_3CNHCO(4-C_5H_4N)}_2]$ 4 ¹⁴ functionalized by two pyridines instead of porphyrins, both redox couples Mn^{III}/Mn^{IV} and Mn^{III}/Mn^{II} showed rapid, reversible electron 40 exchange (Table 1), but the couple Mn^{III}/Mn^{II} was also remarkably slowed down upon formation of a complex with [Ru(CO)TPP].¹⁴ Thus, this process is most sensitive to the ligands grafted onto the POM. The first reduction associated to the Mo^{VI}/Mo^V couple is measured at -2.34 V ($\mathbf{\nabla}$) close to the ⁴⁵ potential observed for **4**.¹⁴ A linear dependence of cathodic peak currents of Mn^{III}/Mn^{II} on the square root of the scan rates ($v^{1/2}$) (Figure S15, ESI) indicates that this process is diffusioncontrolled. Thus this wave is clearly not due to adsorption onto the electrode but corresponds to the reversible exchange of the 50 electron which is slow in this case.

Exhaustive bulk electrolysis of **2** is also carried out in the reduction part. Controlled-potential coulometry at -1.70 V yielded 0.9 electron exchanged, which demonstrates that the first reduction process involves only one electron. Electrolysis at ⁵⁵ -1.88 V shows the transfer of 3.0 electrons. The two additional electrons of the second wave correspond to the first reduction of both ZnTPP macrocycles. The normal pulse voltammogram, the linear sweep voltammogram and the differential pulse voltammogram presented in Figure S17 (ESI) agree with this

observation. They show the sequence: a one electron wave $(Mn^{III/II}$ couple of the POM subunit) followed by two twoelectron waves (first and second reductions of both porphyrins) and a one-electron wave (Mo^{IV/V} couple of the POM subunit).

- ⁵ Thin-layer visible spectroscopy during the reduction of Anderson POM 2 further confirms these assignments (see Figure S18, ESI). At -1.70 V no change of the spectrum is observed. Only upon reduction at -1.98 V, the intensity decrease of the Soret and Q bands and the increase of two new bands at ca 460 nm and 715
- ¹⁰ nm are observed. These changes are typical for the generation of porphyrin π -anion radicals.³⁶ The reduced complex reverts quantitatively to the initial compound **2** on the reverse potential scan at -0.48 V. The change of the POM band (UV domain) has not been examined because the used Pyrex cell cuts the ¹⁵ wavelength bellow 280 nm.³⁷
- In the case of Dawson POM **3**, the reduction processes at -0.50 V and -1.48 V (\bullet) correspond to the quasi-reversible reduction of the V^V, the first reduction W^{VI}/W^V being observed at -2.24 V. Such quasi-reversible redox processes concerning V^V were ²⁰ already reported by Hill²⁰ for $[P_2V_3W_{15}O_{62}]^{9-}$ and $[CH_3C(CH_2O)_3P_2V_3W_{15}O_{59}]^{6-}$, even if the potentials are somewhat shifted. These compounds have a high tendency to
- stick to the electrode. Exhaustive bulk electrolysis of Dawson POM **3** at -0.68 V yields ²⁵ 1.0 electron transferred. Running the electrolysis of this compound at -1.63 V yields 2.9 electrons. This demonstrates that the first reduction process involves one electron while at the potential of the second process, all the V^V atoms seem to be reduced to V^{IV}. Electrolysis at the intermediate potential -1.18 V ³⁰ yields 2.0 electrons transferred, suggesting that one process of reduction of V^V to V^{IV} is masked but probably exists. Indeed, in some scans, one ill-defined and broad additional wave can be observed, which makes in total three processes for the three vanadium reductions.

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 $_{35}$ Electrolysis at -1.88 V shows the exchange of 4.1 electrons per POM **3** in agreement with the reduction of the tri-vanadium (V) cap and the first reduction of the ZnTPP macrocycle.

Furthermore, the electrochemical reduction of compound 3 has also been monitored by spectroelectrochemistry (Figure S19).

- ⁴⁰ Study at -1.58 V (after the second reduction wave of vanadium observed) shows a decrease of the band at ca 320 nm that is POM-based. This is accompanied by small variations of porphyrin based Soret and Q bands. Thus, at this applied potential, the POM is reduced which affects slightly the ZnTPP.
- ⁴⁵ However, upon reduction at -1.83 V, a decrease in the intensity of the Soret and Q bands accompanied by an increase of two new bands at ca 460 nm and 715 nm, typical for the generation of porphyrin π -anion radicals,³⁶ are observed. The reduced complex reverts quantitatively to the initial compound **3** on the reverse ⁵⁰ potential scan at -0.38 V.
- Spectroelectrochemical studies have also been performed for the oxidations of POMs 2 and 3. For instance, thin-layer visible spectroscopy obtained during the oxidation of Anderson POM 2 indicates that electrolysis at +0.42 V produces the porphyrin π -
- ⁵⁵ cation radicals with the expected weakening of the Soret band accompanied by the increase of new bands, one at ca 450 nm and a broad band near 720-900 nm region (see Figure 18, ESI).³⁷ The spectral changes of **3** upon oxidation are similar to that of **2**.
- In conclusion, spectroscopic and electrochemical data are 60 consistent with our assignments of the redox processes in Table

Photophysical properties

The steady-state absorption and fluorescence spectra recorded for the ZnTPP-Tris porphyrin **1** in DMF are identical to those obtained for ZnTPP in the same solvent,^{38, 43} showing that the tris

- substituent on one phenyl group has little influence on the electronic transitions of the macrocycle. The electronic absorption spectrum exhibits the expected Soret band at 426 nm and the Q bands at 559 and 600 nm, associated to the $S_0 \rightarrow S_2$ 70 and $S_0 \rightarrow S_1$ electronic transitions, respectively. The fluorescence
- emission presents two bands at 610 and 665 nm.
- The UV-vis absorption spectra (see ESI, Figure S8) of both hybrid compounds **2** and **3** in DMF correspond to the superpositions of the spectra of the precursors (compound **1** and
- ⁷⁵ POM). Neither the position nor the intensity of the porphyrin absorption bands are significantly influenced by the POM, and no additional band is observed. This indicates the lack of strong electronic interaction between the polyoxometalate and the porphyrin in the ground state.
- ⁸⁰ The fluorescence emission spectra of ZnTPP-Tris and the two hybrids in DMF are shown in Figure 2. The emission of Anderson 2 is identical to that of ZnTPP-tris, with the presence of two bands peaking at 610 and 665 nm respectively. Whereas no quenching is observed for 2, the fluorescence is strongly ⁸⁵ quenched for 3. The emission intensity for Dawson 3 is reduced by about 97% with respect to that of compound 1 (Figure 2). This fluorescence quenching attests to a coupling between the excited porphyrin and the POM cluster in hybrid 3. It is to note that, although the fluorescence is always quenched for 3 compared to a 1 the relative intensity and the president of the amigien hands.
- 90 1, the relative intensity and the position of the emission bands depend on the excitation wavelength and that a band around 720 nm is also detected. While the excitation spectrum recorded at 610 nm is identical to the absorption spectrum of hybrid 3, the excitation spectrum recorded at 720 nm presents the characteristic
- $_{95}$ features (Soret and four Q bands) of free-base porphyrins (see ESI, Figure S9). These results reveal the presence of small traces of free base porphyrin H₂TPP-Tris produced during the synthesis of hybrid **3** and not entirely removed by purification.





Fluorescence quenching in compound **3** could occur either from ¹⁰⁵ energy or electron transfer process within the hybrid complex. In order to make the difference, it is useful to estimate the redox Published on 22 November 2012 on http://pubs.rsc.org | doi:10.1039/C2DT31415K

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potentials of the excited porphyrin. Given the electrochemical data, the oxidation potential of the excited porphyrin, E_{ox}^* , can be approximated using the formula:

$E_{ox}^* = E_{ox1} - E_{tr} (1)$

- s where E_{ox1} is the first oxidation potential of the macrocycle and E_{tr} corresponds to the energy of the electronic transition. The obtained values are $E_{ox1}*=-1.73$ V and $E_{ox2}*=-2.57$ V vs. Fc⁺/Fc, for the porphyrin in the S₁ or S₂ excited singlet state, respectively. Those values are well below the first reduction ¹⁰ potential of POM ($E_{red}(V^V/V^{IV}) = -0.50$ V vs. Fc⁺/Fc) leading to
- ¹⁰ potential of POM ($E_{red}(V'/V'') = -0.50$ V vs. Fc /Fc) leading to negative ΔG° for the electron transfer reactions from S₁ and S₂ ($\Delta G_1^{\circ} = -1.13$ and $\Delta G_2^{\circ} = -1.97$ eV, respectively). So, the quenching in compound **3** is mainly attributed to electron transfers from the excited states of the porphyrin to the POM.
- ¹⁵ In the case of compound 2, the fluorescence results give no evidence of an electron transfer within the complex. From electrochemical data, the electron transfer from the excited porphyrin to the Anderson POM is thermodynamically feasible, although less favourable. But, as the Mn^{III}/Mn^{II} reduction appears ²⁰ strongly slowed down in the hybrid, the electron transfer could be
- avoided for kinetic reasons.

To gain a better understanding of the photophysical properties of compounds 2 and 3, time-resolved emission and both nanosecond and femtosecond transient absorption studies were undertaken.

- 25 The experimental results detailed below yield ultimately the schematic diagram for electron transfer in Figure 6.
- The fluorescence decay profiles recorded at 610 nm for the three compounds are depicted in Figure 3. The emission signal of ZnTPP-Tris follows a monoexponential decay with a lifetime of ³⁰ 1.9 ns, in agreement with data reported for related porphyrins in
- ³⁰ ^{1.9} ns, in agreement with data reported for related porphytins in DMF.³⁸⁻, The emission profile of compound **2** is identical to that of the non-complexed porphyrin indicating the absence of fast processes from the lowest singlet excited state in compound **2**. In contrast, the signal of compound **3** is satisfactorily fitted by a ³⁵ four-exponential decay with time constants: $\tau_{f1} = 60$ ps (76%),
- $\tau_{f2} = 255 \text{ ps} (22\%), \tau_{f3} = 1.9 \text{ ns} (2\%), \tau_{f4} \approx 8.4 \text{ ns} (0.03\%).$ It is to note that the relative contributions to the decay depend on factors such as the fluorescence quantum yield of the species and excitation and detection conditions. It is therefore not possible to
- ⁴⁰ relate them to relative amounts of different species. The slowest and fourth component with a very small contribution is attributed to the presence of slight traces of free-base porphyrin. The obtained lifetime is also in agreement with reported values.^{38,39} Steady-state fluorescence and time-resolved measurements
- ⁴⁵ performed on **3** before and after additional purification (see ESI, Figure S10) indicate that we could reduce the presence of this very small impurity, but not remove it entirely. The third component has the lifetime of the free precursor porphyrin **1** (also not detected by NMR spectroscopy) while the first two
- ⁵⁰ components show that fast intramolecular quenching processes take place. These first two lifetimes are related to either different species or distinct conformers of compound **3**. As there are traces of non-complexed free-base porphyrin H₂TPP-Tris, one can argue that traces of a Dawson-H₂TPP-Tris complex might be produced
- ⁵⁵ during the synthesis. However, such tiny amounts should not have any significant contribution. It rather seems highly probable that there exist distinct conformations that differ according to their ability to undergo quenching (electron transfer) due to the

structural flexibility in compound **3**. Indeed, distinct conformers ⁶⁰ with different quenching efficiency have already been reported for Dawson-type POM covalently linked to porphyrin residues.¹⁵



Figure 3: Fluorescence decay profiles of compounds 1 (black), 2 (blue) and 3 (red) in DMF recorded at 610 nm (excitation wavelength 420 nm).

- 65 Nanosecond transient differential absorption spectra of the three compounds in deoxygenated DMF solution were recorded after excitation with 3 ns laser pulses at 532 nm (see ESI Figure S11). Porphyrin 1 shows the formation of a long-lived triplet state (τ_T = 1.1 ms), consistent with literature data for meso-tetraphenyl-⁷⁰ porphyrin derivatives.^{39, 40, 41} The T₁ triplet state is formed for the hybrids too, but the lifetime and yield depend on the POM. For the Anderson hybrid 2, the triplet lifetime is considerably shortened ($\tau_T = 7.5 \mu s$) while the initial differential absorbance is roughly 90% of that determined for ZnTPP-Tris. For the Dawson 75 compound **3**, the triplet lifetime is slightly reduced ($\tau_{\rm T} = 0.60$ ms) but the initial differential absorbance corresponds to only 2% of the value obtained for ZnTPP-Tris in the same conditions (same absorbance at the excitation wavelength, same laser pulse energy). These results have to be regarded together with the 80 fluorescence data. For compound 2, in the absence of fluorescence quenching, the triplet state originates from the hybrid and its decay is accelerated because of heavy and paramagnetic atom effects. For compound 3 with high fluorescence quenching, we assume that the triplet signals, as 85 well as the remaining steady-state fluorescence and the $\tau_{f3} = 1.9$ ns fluorescence lifetime, are due to the presence of traces of non-complexed porphyrin.
- Femtosecond transient absorption spectroscopy brings information about fast photoinduced transformation. The excited ⁹⁰ state properties of ZnTPP-Tris are found similar to those reported for ZnTPP.^{41,42} The picosecond differential spectrum of **1** in DMF solution is characterised by a strong absorption band peaking at 456 nm between the Soret-band and Q-band bleachings and a broad absorption band over 570-700 nm (see ESI Figure S12). 95 These spectral features correspond to the S₁ excited state of the porphyrin. The transient absorption kinetics reveal that the absorption band around 460 nm and the stimulated emission around 660 nm appear with a time constant of 1.3 ps due to $S_2 \rightarrow$ S1 internal conversion after 395 nm excitation in the Soret band 100 (see ESI Figure S12). This time constant is in agreement with previous values reported for the S₂ state depopulation of ZnTPP

in DMF.43-45

The transient absorption spectra obtained for compound **3** in DMF solution after excitation with 100 fs laser pulses at 395 nm are shown in Figure 4. The spectrum at 1 ps with an absorption ⁵ band maximum located at 445 nm differs from the spectrum recorded for ZnTPP-Tris with a maximum at 456 nm. For the first 3 ps, a band around 442 nm rises, then drops revealing a band around 460 nm. Subsequently, the band at 460 nm also decreases and after 500 ps a spectrum with an absorption band maximum at 10 447 nm is observed. This spectrum differs notably from those

obtained for the S_1 or T_1 excited states of ZnTPP-Tris revealing the formation of a new long-lived state. The lifetime of this state is too long to be determined within the time window of our set-up (700 ps).



Figure 4: Transient absorption spectra obtained for compound **3** in DMF solution after excitation with 100 fs laser pulse at 395 nm.

The transient absorption kinetics analysis shows that all the signals can be fitted by a constant associated with the final long-²⁰ lived state and a three-exponential function with the same time constants, $\tau_1 = 830 \pm 90$ fs, $\tau_2 = 9.0 \pm 1.3$ ps and $\tau_3 = 93.5 \pm 3.5$ ps (Figure 5). The absorption signal at 442 nm rises with the time constant $\tau_1 = 830$ fs and then decay according to a bi-exponential law with time constants $\tau_2 = 9$ ps and $\tau_3 = 93.5$ ps. The kinetics ²⁵ profiles obtained at 460 and 520 nm are fitted by a bi-exponential rise ($\tau_1 = 830$ fs and $\tau_2 = 9$ ps) and a slow exponential decay ($\tau_3 = 93.5$ ps). The bleaching signal at 560 nm and the signal at 650 nm correspond to three-exponential decays.



Figure 5: Transient absorption kinetics obtained for compound 3 in DMF solution after excitation with 100 fs laser pulse at 395 nm. Solid lines are three-exponential fits.

³⁵ The formation of the S₁ state by internal conversion (IC) from the S₂ state is characterized by the appearance of both intense absorption at 460 nm and stimulated emission around 660 nm. These signals grow with a time constant of 830 fs, faster than for the free porphyrin **1**. Moreover, a new band at 442 nm appears ⁴⁰ with the same time constant. That suggests the presence of an additionnal deactivation pathway for the S₂ state in the complex. We assign this deactivation channel to an electron transfer from the excited porphyrin to the linked POM inducing the formation of a charge transfer (CT) state which absorbs mainly around 440 ⁴⁵ nm. From the measured lifetimes ($\tau_1 = 830$ fs for compound **3** and $\tau_{IC} = 1.3$ ps for ZnTPP-Tris), the electron transfer rate, $k_{ET}^{S_2}$ is evaluated according to equation 2:

$$k_{ET}^{S_2} = \frac{1}{\tau_1} - \frac{1}{\tau_{IC}}$$
(2)

The $k_{ET}^{S_2}$ value is found to be $4.3 \times 10^{11} \text{ s}^{-1}$, of the same order of ⁵⁰ magnitude as the reported values for rate constants of electron transfer from S₂ in covalently linked ZnTPP-acceptor molecules.^{42,44}

The S_1 state of the porphyrin in the complex, observed mainly at 460 nm follows a 93.5 ps decay, much faster than that measured ⁵⁵ for the free porphyrin. That shows the existence of a new

deactivation process from the S_1 state. We consider that, as for S_2 ,

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the new deactivation pathway from S_1 is an electron transfer process leading to a long-lived CT state. It is to note that the time constant of 93.5 ps determined by transient absorption does not match the fast lifetimes obtained by time-resolved fluorescence

- s measurements, but rather their weighted average. That can be explained if the two lifetimes are related to two conformers which undergo electron transfer leading to similar final CT spectra. From the measured lifetime of the S₁ state in the complex $(\tau_{f1} = 60 \text{ ps})$ and in the free porphyrin $(\tau_{SI} = 1.9 \text{ ns})$, the fastest
- ¹⁰ electron transfer rate from S₁ is evaluated to be $k_{ET}^{S_1} = 1.6 \times 10^{10}$ s⁻¹. This value is in line with intramolecular electron transfer rates reported for ZnTPP hybrids or dyads.^{39, 41, 42, 44, 48}
- The final CT state in which an electron has been transferred from the excited singlet state of the zinc porphyrin to the covalently ¹⁵ linked POM is characterized by an absorption less intense and shifted to the blue (447 nm) compared to the absorption of the S₁ state. These spectral features are consistent with the formation of the porphyrin π -radical cation^{49,50} and the reduced Dawson in their ground state. Indeed, the absorption spectra of oxidised ²⁰ ZnTPP porphyrin exhibit a sharp intense Soret band around 410
- nm ($\varepsilon \sim 2 \times 10^5 \text{ mol}^{-1}\text{L cm}^{-1}$) with a shoulder around 450 nm ($\varepsilon \sim 3 \times 10^4 \text{ mol}^{-1}\text{L cm}^{-1}$) and a broad and featureless band over 500-700 nm ($\varepsilon \sim 1 \times 10^4 \text{ mol}^{-1}\text{L cm}^{-1}$).^{51,52} One-electron reduced Dawson polyoxometalates also absorb, but in the UV domain (out ²⁵ of our spectral window) and in the near infra-red region with a low extinction coefficient ($\varepsilon \sim 5000 \text{ mol}^{-1}\text{L cm}^{-1}$).^{53,54} The formed
- CT state disappears due to reverse electron transfer on the nanosecond time scale regenerating the ground-state compound **3**. The band at 442 nm, spectral signature of the photoinduced CT ³⁰ state from S₂, drops with a time constant of 9 ps whereas concomitantly other signals rise or decay. At 30 ps, the measured
- differential absorption spectrum corresponds mainly to a combination of the S_1 state and the final CT state spectra, because the substraction of the 500 ps spectrum from the 30 ps spectrum ³⁵ results in a spectrum similar to that of the S_1 state of the free
- porphyrin (see ESI Figure S13). We assume that the electron transfer from S_2 leads to a vibrationally excited CT state, which converts to the final CT state by vibrational energy relaxation (VR). The measured relaxation time (9 ps) is in accordance with
- ⁴⁰ the time scale of 1-40 ps reported for VR in ZnTPP π-cation radical and porphyrins.^{50,52,55,56} From absorption and fluorescence data, we have no evidence of recombination from unrelaxed CT states to the S₁ state of compound **3**, as recently described for porphyrin-acceptor dyad.⁴⁵ Nevertheless, this pathway cannot be ⁴⁵ completely excluded.

Figure 6 resumes the assumed deactivation processes occuring in hybrid **3**.

Conclusion

In conclusion, covalent porphyrin-POMs have been synthesized ⁵⁰ and characterized. They demonstrate how the fruitful combination of multistep organic and inorganic synthesis yields original functional molecules. Electrochemical studies reveal the separate redox processes on the organic and inorganic parts, and the lack of communication in the ground state. Photophysical

ss studies have shown an influence of the polyoxometalate on the properties of the porphyrin, i. e. communication in the excited state. Indeed, in the case of compound **3**, photoinduced electron

transfers from the excited porphyrin unit to the Dawson POM have been revealed. We will exploit this for the development of 60 porphyrin-POM hybrids with a photocatalytic activity.



Figure 6: Schematic diagram showing the assumed deactivation processes occuring in compound **3**: internal conversion from S₂ to S₁ 65 ($k_{IC} = 7.7 \times 10^{11} \text{ s}^{-1}$), electron transfer from the S₂ state ($k_{ET}^{S_2} = 4.3 \times 10^{11} \text{ s}^{-1}$), electron transfer from the S₁ state ($k_{ET}^{S_1} = 1.6 \times 10^{10} \text{ s}^{-1}$), vibrational relaxation in the charge transfer state ($k_{IR} \approx 1.16 \times 10^{11} \text{ s}^{-1}$) radiative and non radiative desexcitation processes from S₁ to S₀ and intersystem crossing from S₁ to T₁ ($k_S + k_{ISC} = 5.3 \times 10^8 \text{ s}^{-1}$), reverse electron transfer 70 ($k_{RET} < 1 \times 10^9 \text{ s}^{-1}$).

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Table of Contents entry

Two polyoxometalates with the same zincporphyrin photosensitizer are synthesized and ⁵ thoroughly characterized to reveal the possibility of electron transfer.



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Notes and references

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