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The electrochemical properties of several polyoxometalate-porphyrin films are related to the geometry of the linkers installed on the organo-POM monomers.

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ARTICLE TYPE

Synthesis and Characterization of Conjugated Polyoxometalate-Porphyrin Copolymers Obtained from a Dawson-Type Polyoxophosphovanadotungstate

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Hybrid polyoxometalate-porphyrin copolymeric films were obtained by the electro-oxidation of zinc octaethylporphyrin (ZnOEP) in the presence of a Dawson type polyoxometalate bearing two pyridyl ¹⁰ groups (POM(py)₂). The synthesis of a series of POM(py)₂ consisting of [P₂W₁₅V₃O₆₂]⁹⁻ functionalized

with diol-amide or triol moieties, as well as the characterization of the copolymers are presented.

Introduction

Polyoxometalates (POMs) are a structurally diverse family of anionic metal oxide molecular analogues with applications in ¹⁵ analytics, medicine, catalysis and photocatalysis, electronics and material science.¹ One of the most interesting features of POMs is their rich photoredox chemistry.² Typically, upon light irradiation electrons are promoted from an oxygen-centered 2*p* orbital to an empty metallic *d*-orbital, generating a highly reactive charge-

- 20 separated state. The photoexcited POM has an increased oxidizing power, and organic substrates can be oxidized while the POM is converted into its reduced form. The later can subsequently be re-oxidized with molecular oxygen or by reducing a second substrate.
- ²⁵ Interestingly, owing to their robustness and large number of metallic centers, POMs can undergo reversible and multi-electron photoredox processes without decomposition. However, in most of the cases, the O \rightarrow M Ligand-to-Metal Charge Transfer (LMCT) absorption band lies in the UV region (λ = 200-400nm)
- ³⁰ which strongly limits the use of POMs in solar visible light conversion materials.

In order to overcome this problem, POMs can be linked to visible light sensitive molecules *via* covalent, coordination or non-covalent bonding.

³⁵ The non-covalent approach is based on Van der Waals or Coulombic interactions and does not need POM prefuncionalization. Since POMs are anionic clusters, they can form electrostatic complexes with cationic chromophores such as Ru or Re polypyridyl complexes^{3–5}, organics dyes^{6–8}, or porphyrins and ⁴⁰ phthalocyanines.^{9–11}

POM-porphyrin coordination complexes were also reported.^{12–15} However, stronger POM-chromophore bonds are required to avoid dissociation and ensure better electronic communication.

The third approach is based on covalent linkage between the

⁴⁵ POM and the visible light photosensitizer. The recent progress in organo-polyoxometalate chemistry ensures that virtually any organic function can be added to POM structures, whose design can be synthetically controlled.^{16,17}



⁵⁰ Scheme 1 a) Schematic representation of the two step synthesis of POMporphyrin copolymer using molecular building blocks. b) Representation of ZnOEP, TBA₅H₄[P₂V₃W₁₅O₆₂] and the tris- (tvb3,3) or diol-amide (dvb3,3, dvb3,4 and dvb4,4) ligands.

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The use of a spacer adds versatility. Hence, functional molecular devices with varied POM/chromophore ratios, spatial geometry, etc. can be obtained.

- Several covalent donor-acceptor dyads based on POMs were ⁵ prepared using ferrocenyl^{18,19}, pyrene and perylene^{20–22}, Ru and Ir complexes^{21,23}, and porphyrins.^{24–27}
- The introduction of POM-chromophore hybrids in polymeric and surface supported materials is the next step toward functional devices with catalytic, optic or photovoltaic properties.²⁸
- ¹⁰ The alternate deposition of anionic POMs and cationic sensitizers such as metal complexes^{29,30}, organic dyes^{31,32} and porphyrins^{33,34} on surfaces using the layer-by-layer (LbL) technique generates thin-films with controlled thickness. Some of us recently reported the first POM cationic porphyrin-based photovoltaic multilayered
- ¹⁵ film obtained by LbL showing photocurrent production under visible-light irradiation.³⁴

Peng reported the synthesis of a Fe(terpyridine)₂-Lindqvist molybdate coordination polymer³⁵ as well as hybrid (co)polymers with conjugated photoactive backbones and the POM inserted in the main-chain^{36,37} or as a side-chain pendant.^{38,39} A photovoltaic device constructed from the POM main-chain containing polymer showed a power conversion of 0.15%.³⁷ More recently, we reported the formation of a mixed POM-porphyrin copolymer

film with an Anderson type POM $_{25}$ [MnMo₆O₁₈{(OCH₂)₃CNHCO(4-C₅H₄N)}₂]³⁻ and ZnOEP via an original electropolymerization/deposition process. The photoactive film was used as heterogeneous photocatalyst for the reduction of Ag⁺ under visible light.⁴⁰

However, none of the polymers examined thus far were based on ³⁰ POMs with reversible redox behavior, and conjugated spacers. In the present paper, we introduce such covalently bonded conjugated POM-porphyrin copolymers using our $[P_2W_{15}V_3O_{62}]^{9-}$ diolamide-grafting method⁴¹ toward devising more efficient photoactive films. We report herein the bottom-up ³⁵ synthesis and characterization of films obtained from bispyridinesubstituted molecular organo-polyoxometallic bricks with different geometries, and examine the influence of the monomer structure on the architecture of the polymers as a prerequisite to understand their photocatalytic properties.

40 Results and Discussion

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Our strategy for the synthesis of the films relies on the electrocopolymerization of porphyrins with several bis-pyridine-capped phosphovanadotungstate $[P_2W_{15}V_3O_{62}]^{9-}$ (Scheme 1). The organo-POM monomer was designed around 1,3,5-trisubstituted ⁴⁵ benzene rings, which serve as conjugated turntables. Two of the substituents were connected to the pyridines (two needed for polymerization), while the last one was connected to the POM. We used one porphyrin (Zinc octaethyl porphyrin, ZnOEP), and selected four organic connectors. Three of them relied on the

- ⁵⁰ diolamide coupling⁴¹ to establish full conjugation in the polymer between the organic backbone and the pendant POM framework through the incorporated carbonyl function. They differed by the relative positions of the two nitrogen atoms of the pyridines (3,3; 3,4; 4,4), while the fourth was a triol-capping ligand,⁴² chosen to a essente a protect of the achieved to the POM
- 55 assess the exact role of the conjugation to the POM.

Preparation of the organic ligands

The preparation of the diolamine/triol bis-pyridine ligands started with 1,3,5-tribromobenzene (1, Scheme 2), which was ⁶⁰ carbonylated to 3,5-dibromobenzaldehyde (2) *via* its monolithiated anion.⁴³ The aldehyde was olefinated to ester **3** *via* a Wittig reaction.⁴⁴ **3** was a key intermediate to the four ligands of this study, which were obtained via double Pd-catalyzed Sonogashira cross-couplings. **3** was doubly coupled to 3-⁶⁵ ethynylpyridine in the presence of tetrakis(triphenylphosphine) palladium, CuI and triethylamine,⁴⁵ quantitatively leading to **evb3,3**.



Scheme 2 Synthesis of the ligands dvb3,3, dvb3,4, dvb4,4 and tvb3,3

4-ethynylpyridine However, the same reaction from hydrochloride only gave the mono-coupled product in poor yield. We changed the solvent system to DMF/Et₃N (2:1) and it was 75 then possible to isolate the bis ethynylpyridine derivative (evb4.4, 55%) together with some remaining mono-coupled evb4,Br (26%), which were separated by column chromatography. Interestingly, the isolation of the latter allowed us to prepare the dissymmetric cinnamic ester evb3,4 via a Sonogashira coupling 80 with 3-ethynylpyridine (65%). The diol and triol functions were then installed via amide formation from 2-amino-2-ethyl-1,3propanediol and 2-amino-2-(hydroxymethyl)-1,3-propanediol, as reported previously.^{41,42} The former delivered ligands **dvb3,3** (for

<u>*d*</u>iolamide <u>v</u>inyl <u>*b*</u>enzoate ethynyl <u>3</u>-pyridine, ethynyl <u>3</u>-pyridine), **dvb3,4** and **dvb4,4** in 80%, 75% and 60% yields respectively. The latter gave **tvb3,3** (for <u>*t*</u>riolamide <u>v</u>inyl <u>*b*</u>enzoate ethynyl <u>3</u>pyridine, ethynyl <u>3</u>-pyridine) in 60% yield.

Preparation of the organo-POM monomers

TBA₅H₄[P₂V₃W₁₅O₆₂] was reacted with the diol-amide ligands **dvb3,3**, **dvb3,4** and **dvb4,4** in DMAc at 80°C under microwave irradiation (Scheme 3, right).⁴¹ The desired organic-inorganic ¹⁰ POM hybrids **POM-dvb3,3**, **POM-dvb3,4** and **POM-dvb4,4** were isolated in 72%, 46% and 70% yield respectively after several purifications by selective precipitation with ethanol or ether from an acetonitrile solution. Triol **tvb3,3** was converted to **POM-tvb3,3** upon heating it at 90°C in the presence of ¹⁵ TBA₅H₄[P₂V₃W₁₅O₆₂] for 2 weeks (50% yield).⁴² The four organo-POM monomers were fully characterized by ¹H, ¹³C and ³¹P NMR, MS, IR, UV-Vis spectroscopy, elemental analysis and electrochemistry.



Scheme 3 Synthesis of POM-tvb3,3, POM-dvb3,3, POM-dvb3,4 and POM-dvb4,4

Characterizations of the organo-POM monomers

25 IR characterization

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The IR spectra of the hybrid monomers showed peaks at 1087 (\mathcal{V}_{P-O}), 950 ($\mathcal{V}_{W=O}$), 900 (\mathcal{V}_{W-Oc-W}), 815 (\mathcal{V}_{W-Oe-W}) cm⁻¹, which are characteristic of the Dawson phosphovanadotungstate.^{46,47} The signals corresponding to the organic part were found at the ³⁰ expected wavenumbers, albeit weak due to the relatively low content in the hybrids.

Mass spectroscopy

Fig. 1 presents an ESI-MS spectrum obtained for the **POM**-³⁵ **dvb3**,**3** hybrid. The main peak corresponds to the 5– ion stripped of all cations. Peaks assignable to the clusters associated to one TBA, one H⁺ or two TBA cations were also observed. Also, some reduced forms of the hybrid most likely produced during the ionization process were detected (minor peaks). The other POM ⁴⁰ monomers behaved similarly (see SI).



Fig. 1 Obtained ESI MS data for POM-dvb3,3 solution in CH₃CN (50 μM)

NMR characterization

⁴⁵ The ³¹P NMR of all hybrids reveals only two signals around -7 and -13 ppm. This confirms the presence of the two chemically inequivalent phosphate templates of the Dawson structure, and proves that the hybrid is free of unfunctionalized [P₂W₁₅V₃O₆₂]⁹⁻, or any P-containing degradation product. The ¹H NMR spectra ⁵⁰ present the signals from the grafted organic bipyridine ligands (around 7 ppm), the diols (or triol) and the TBA counterions.



Fig. 2 a) ³¹P NMR spectrum of POM-dvb3,3 in CD₃CN. b) ¹H NMR spectra 55 of dvb3,3 in CDCI₃ and POM-dvb3,3 in CD₃CN, zoom of the aromatic region.

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The chemical shift differences between the functionalized and the free organic part ($\Delta\delta$, in ppm) are reported in Table 1. The full comparison of the chemical shifts of the free ligand and those of the grafted ones (Fig.2b for POM-dvb3,3) gave strong evidence

- 5 of the covalent grafting of the organic part. In particular, the signal for the CH₂OH is strongly deshielded (about 1.8 ppm) upon attachment to the vanadate cap. This is likely caused by the strong electron withdrawing effect of the POM. Interestingly, the presence of the POM impacts all the signals of the organic part in
- 10 the diol-amide chemistry but only small chemical shift changes were observed in the case of triol functionalized hybrids $(\Delta \delta_{\text{max}} = 0.07 \text{ ppm}, \text{ except for CH}_2\text{OV})$. We believe this is a further indication that the carbonyl incorporation into the POM structure induces a good electronic communication between the 15 inorganic and the organic parts (effect over more than ten C-C
- bonds), while in the case of triol functionalization, the electronic effects of the POM are limited to the first C-C bond.

Table 1. ¹H NMR chemical shift difference ($\Delta\delta$ in ppm) between the 20 POM(py)2 hybrid and the free ligand.

		POM- dvb3,3	POM- dvb3,4		POM- dvb4,4	POM- tvb3,3
CH ₂ OV		1.81	1.94		1.72	2.02
Ethylenic	$H_{Et}1)$	1.22	1.21		0.83	-0.02
	$H_{Et}(2)$	0.63	0.54		0.41	0.04
Aromatic	$H_{Ar}(1)$	0.71	0.92 / 0.67		0.67	0.07
	$H_{Ar}(2)$	0.19	0.20		0.11	0.04
			Зру	4py		
Pyridine	H^2	0.06	0.12	0.23	0.24	0.04
	H^3	-	-	0.18	0.14	-
	H^4	0.06	0.10	-	-	0.07
	H^{5}	0.24	0.23	0.18	0.14	0.07
	H^{6}	0.33	0.31	0.23	0.24	0.07

UV-Visible charaterization

The UV spectra of the hybrids are the sum of the oxygen-to-metal 25 charge transfer (LMCT) bands and the organic ligand absorbance around 280 nm (Fig. 3). The combined bands extend into the visible, which explains the yellow color of the POM(py)₂ hybrids.

Cyclic Voltammetry and Differential Pulse Voltammetry

30 The cyclic voltammograms and differential pulse voltammograms of POM-tvb3,3, POM-dvb4,4, POM-dvb3,4, POM-dvb3,3 and the parent POM [P₂V₃W₁₅O₆₂]⁹⁻ show three monoelectronic successive reductions, corresponding to the reversible reduction of the three V^V between +0.1 V and -0.9 V vs. SCE. It is the first

 $_{35}$ time that separate waves for the reduction of the three V^V are observed. Indeed, only two reversible redox processes concerning

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 V^V were reported by Hill⁴² for $[P_2V_3W_{15}O_{62}]^{9-}$ and triol-capped [CH₃C(CH₂O)₃P₂V₃W₁₅O₅₉]⁶⁻. Similarly, we have observed that porphyrin/triol-capped $[P_2V_3^VW_{15}O_{59}\{(OCH_2)_3C$ in the $_{40}$ NHC(=O)(ZnTPP)}],²⁷ the first reduction process of the trivanadium cap involves one electron, while the second process involves the two other V^V atoms together.

In the present study, $[P_2V_3^VW_{15}O_{62}]^{9-}$ shows two successive processes. However, its differential pulse reduction 45 voltammogram presents a tiny splitting of the second process, suggesting that two close monoelectronic waves are present (bottom of Fig 4). In the case of POM-tvb3,3, POM-dvb4,4, POM-dvb3,4 and POM-dvb3,3, the splitting of the second process is well observed. The reduction potential of the 50 trivanadate cap depends mostly of the type of grafting (compare curves in Figure 4 with tvb and dvb grafting), as one would expect for such structures (Table 2).



Fig. 3 UV-vis absorption spectra of POM (black doted curve), dvb3,3 55 (light doted purple curve) and POM-dvb3,3 (plain purple curve) in CH₃CN solution (c = 6.25 10^{-6} M). POM = $[P_2V_3W_{15}O_{62}]^{9-}$.

Finally, the difference between the oxidative and the reductive peak potentials ($\Delta E_{\rm p}$) increases after each reduction of the V^V For example, ΔE_p for the first, second and third reductions of V^V 60 measured for POM-tvb3,3 are 104, 220, and 325 mV respectively (Table 2). This indicates that the electron transfer becomes increasingly slow, in agreement with the localization of the added electrons in the vanadium cap, where consequently the electron density would increase. The approach of the molecule 65 with the side of the partially reduced trivadanadate cap to exchange further electrons at the negatively polarized electrode thus becomes increasingly difficult because of the important electrostatic repulsion.



Fig. 4 a) Cyclic voltammograms **of POM-tvb3,3**, **POM-dvb4,4**, **POM-dvb3,4**, **POM-dvb3,3**, and POM (TBA₅H₄[P₂V₃W₁₅O₆₂]) at c=5.10⁻⁴ molL⁻¹ and v=10 mVs⁻¹. b) Differential pulse voltammograms at 25 mVs⁻¹ in 1,2-C₂H₄Cl₂/CH₃CN (7/3), containing 0.1 molL⁻¹ NBu₄PF₆. Working electrode: glassy carbon. *Adsorption peak.

5 Synthesis and characterization of the Poly-ZnOEP-POM Copolymers

Copolymer Synthesis

We have shown that exhaustive electro-oxidation of zinc β octaethylporphyrin (ZnOEP) in the presence of an excess of ¹⁰ nucleophile at a potential of the first oxidation allows the formation of the mono-substituted zinc *meso*-Nu⁺- β octaethylporphyrin (ZnOEP(Nu)⁺) in good yield.^{48–50} This reactivity of oxidized porphyrins has been advantageously used to develop an easy and original method of electropolymerization of ¹⁵ porphyrins when a difunctional nucleophile such as 4,4'-

- ¹⁵ porphythis when a undertophat indeteophile such as 4,4 bipyridine was used.^{51,52} When the iterative scans were performed at a sufficiently high potential in the anodic part (*i.e.* allowing the formation of the porphyrin dication), the formation of a conducting polymer with viologen spacers between porphyrins ²⁰ coating the working electrode was observed. Indeed, while the
- ²⁰ coating the working electrode was observed. Indeed, while the formation of radical cations was sufficient to perform monosubstitutions on porphyrins, the electropolymerization process required the formation of the dications, undoubtedly due to kinetic problems (the dications react faster with nucleophiles than
- ²⁵ the radical cations). Hence an $E_1(E_{2i}C_{Nmeso}E_{2i+1}C_B)_{i=1\rightarrow n}E_{2(n+1)}$ mechanism can be proposed to explain the electropolymerization process where C_{Nmeso} corresponds to the nucleophilic attack at the meso position of the porphyrin which form an isoporphyrin.^{52,53} The isoporphyrin is then oxidized (electrochemical step E_{2i+1}) and

 $_{30}$ the proton present initially on the meso-carbon is released

(chemical step C_B). For a degree of polymerization n, the corresponding global reaction can be written as:

 $(n+1)ZnOEP + (n+1)Py-R-Py \rightarrow$

³⁵ ZnOEP-(Py^+ -R- Py^+ -ZnOEP)_n-Py-R-Py + (2n+1)H⁺ + (4n+2)e⁻ (R = spacer) The reactions generated H^+ ions. According to previous work, scanning between -1.30 or -1.50 V and +1.80 V reduced these ⁴⁰ protons to H₂, and they were accumulated in solution when the scan was limited from 0.00 V to +1.80 V. Even in the second case, they did not perturb the coating of the electrodes. The demetalation of the metalloporphyrins was controlled by UVvisible spectroscopy and did not occur.

- ⁴⁵ Thus, it is possible to easily modulate the nature of the bridging spacers between the porphyrin macrocycles. Indeed, instead of using 4,4'-bipyridine, this process of electropolymerization can be extended to molecules with various spacers between two pyridyl groups. The spacers can be selected for their specific ⁵⁰ chemical or structural properties: rigid or not; long or short; electron conducting or not; with conjugated π -bonds (alkene, alkyne or aromatic chains) or successive σ -bonds (alkyl chains), etc., allowing one to modulate the communication between porphyrin macrocycles within the polymeric chains.
- $_{\rm 55}$ We applied this concept to POMs and prepared POM-porphyrin copolymer films with the Anderson type POM $[{\rm MnMo_6O_{18}}\{({\rm OCH_2})_3{\rm CNHCO}(4{\rm -}{\rm C_5H_4N})\}_2]^{3-}$ and ZnOEP, 40 which presented good photocatalytic 54,55 and photovoltaic 34 properties.
- ⁶⁰ In the present work, all electropolymerizations have been carried out under the same experimental conditions by iterative scans in 0.1 mol L⁻¹ solutions of tetrabutylammonium hexafluorophosphate in 1,2-C₂H₄Cl₂/CH₃CN (7:3) containing ZnOEP (0.25 mmol L⁻¹) and POM(py)₂ (0.25 mmol 65 L⁻¹) under an argon atmosphere.
 - Figure 5 illustrates the evolution of the CVs during the electropolymerization of ZnOEP with **POM-dvb4,4**. Cyclic scanning was applied at potentials between -1.45 and 1.90 V vs. SCE or between -0.05 and +1.90 V vs. SCE. During the first scan

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in reduction, only signals assigned to the reduction of the **POM-dvb4,4** were detected between -0.05 and -1.45 V vs. SCE.

- In the second scan, one additional irreversible reduction peak ⁵ appeared between -0.75 to -0.95 V vs. SCE (peak a, Fig. 5), which corresponds to the reduction of the pyridinium units of the dipyridinium-POM spacers of the generated copolymer **poly-POM-dvb4,4-ZnOEP** (ZnOEP-Py⁺-POM-Py⁺)_n] (Scheme 3).^{51,52,56-61} The height of this peak grew with repetitive scans at ¹⁰ the beginning of the deposition and then reached a plateau. The irreversibility of the signal indicated that the generated pyridyl radicals are not stable and react further⁶²⁻⁶⁴ as already observed in the case of copolymer with Anderson type POM.⁴⁰
- Similar behaviors were observed for the synthesis of copolymers ¹⁵ poly-POM-dvb3,4-ZnOEP, poly-POM-dvb4,4-ZnOEP and poly-POM-tvb3,3-ZnOEP except that the reduction of the POM V^V/V^{IV} couple) became more difficult to observe. Analogous electrochemical behavior was observed in the coordination complexes between [MnMo₆O₁₈{(OCH₂)₃CNHCO(4-C₅H₄N)}₂]³⁻
- ²⁰ and [Ru(CO)TPP] (TPP = tetraphenylporphyrin) or ZnTPP where it was noticed that the Mn^{III}/Mn^{II} redox process was remarkably slowed down with the quasi-complete disappearance of the electrochemical signal, even at the glassy carbon electrode.¹³

²⁵ Table 2 Electrochemical data for POM-tvb3,3, POM-dvb3,4 and POM-dvb4,4 and copolymers poly-POM-tvb3,3-ZnOEP, poly-POM-dvb3,3-ZnOEP, poly-POM-dvb3,4-ZnOEP and poly-POM-dvb4,4-ZnOEP.^a

	Oxidation		VV/VIV	Reductio	n nv+	πring
	<i>n</i> -ring		• / •		py '	n-mg
POM-tvb3,3		-0.11 ^b (104)	-0.48 ^b (220)	-0.85 ^b (325)		
POM-dvb3,3		0.06 ^b (87)	-0.26 ^b (117)	-0.43 ^b (166)		
POM-dvb3,4		0.06 ^b (84)	-0.29 ^b (139)	-0.43 ^{b,} *		
POM-dvb4,4		0.06 ^b (113)	-0.31 ^b (222)	-0.41 ^{b,} *		
ZnOEP	0.94 / 0.68					-1.60 ^b
poly-POM- tvb3,3-ZnOEP)				-1.02 ^{irr,c}	-1.70 ^c
poly-POM- dvb3,3-ZnOEF	þ	e	e	e	-1.02 ^{irr,c}	-1.32 ^{irr,c}
poly-POM- dvb3,4-ZnOEF	þ	e	e	e	-0.87 ^{irr,c}	-1.47 ^{irr,c}
poly-POM- dvb4,4-ZnOEF	0	e	e	e	-0.79 ^{irr,c}	-1.54 ^{irr,c}

^{*a*} All potentials in V versus SCE were obtained from cyclic voltammetry ³⁰ in 1,2-C₂H₄Cl₂/CH₃CN (7:3) containing 0.1 mol L⁻¹ (NBu₄)PF₆. Scan rate = 0.1 V s⁻¹. ^b Working electrode: glassy carbon electrode. ^c ITO, S = 1 cm² after 25 scans. The given half-wave potentials in the case of the reversible couple are equal to $E_{1/2} = (Epa - Epc)/2$. Under bracket: (ΔEp, peak splitting in mV). ^e not observed. ΔEp is the difference potential between ³⁵ the oxidative and the reductive peak potentials. * Measured from DPV.







Fig. 5 Cyclic voltammograms for the electropolymerization of ZnOEP (0.25 mM) with POM-dvb4,4 (0.25 mM) in $1,2-C_2H_4Cl_2/CH_3CN$ (7:3) TBAPF₆ 0.1mol L⁻¹. Working electrode: ITO. S = 1 cm². Scan rate: 0.1 V s⁻¹. s (←) Start of the scan. Cyclic scanning (0.1 V s⁻¹) was applied at potentials between -0.05 and +1.90 V versus SCE (top) and between -1.45 and 1.90 V versus SCE (bottom).

This significant electron-transfer rate constant attenuation is believed to be the consequence of long-distance electron transfer ¹⁰ from the working electrode to the electroactive site of the molecule⁶⁵ because of the hindered approach of the POM to the electrode in the presence of coordinated porphyrin. A similar explanation can also be proposed in the present work where the coordination complex between ZnOEP and POM(py)₂ can also be ¹⁵ formed.

Cyclic Voltammetry of the copolymeric films

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- ²⁰ The electrochemical behavior of these films has been studied by cyclic voltammetry (Figure 6a). Typically, two irreversible reduction peaks appeared, that correspond to the pyridium reductions and the first reduction of the ZnOEP macrocycle respectively (Table 2).
- ²⁵ The pyridinium reductions were observed at -1.02 V, -0.87 V and -0.79 V vs. SCE for poly-POM-dvb3,3-ZnOEP, poly-POM-dvb3,4-ZnOEP and poly-POM-dvb4,4-ZnOEP respectively, showing the strong influence of the isomer on the reduction potential of the pyridinium spacers. It can tentatively be
- ³⁰ explained in terms of π -conjugation (see SI Fig S4). For **poly-POM-dvb4,4-ZnOEP**, the delocalization of the pyridyl radical is larger than for **poly-POM-dvb3,4-ZnOEP** because of the

conjugation with the central benzene group, leading to a stabilisation of the reduced intermediate. In **poly-POM-dvb3,3- ZnOEP**, no stabilisation can occurs since the delocalization of the radical is only possible within the pyridyl ring. The more

stable reduced form was obtained at less negative potentials. On the contrary, the porphyrin reductions were measured at -1.32 V, -1.47 V and -1.57 V vs. SCE for **poly-POM-dvb3,3-**

⁴⁰ ZnOEP, poly-POM-dvb3,4-ZnOEP and poly-POM-dvb4,4-ZnOEP respectively. These results show that when the delocalization of the radical of the reduced pyridinium is only possible onto the pyridyl ring, the localization of the radical is more on the nitrogen atom. It renders the reduction of the ⁴⁵ porphyrin easier because of the possibility of delocalization onto the macrocycle when the porphyrin is reduced. In the case of poly-POM-dvb4,4-ZnOEP, the reduction potential of the porphyrin is nearly the same as the potential measured for ZnOEP alone. Since the reduced pyridinium radical is delocalized on the ⁵⁰ entire dvb4,4 ligand, delocalization of the reduced porphyrin radical is limited to the macrocyle. Thus, it explains a reduction potential of the ZnOEP subunit close to the potential measured for the starting ZnOEP.



Fig. 6 Top: Cyclic voltammograms of poly-POM-dvb3,3-ZnOEP, poly-POM-dvb3,4-ZnOEP and poly-POM-dvb4,4-ZnOEP films (25 iterative scans between 0 and 1.90 V versus SCE) on ITO 1,2-C₂H₄Cl₂/CH₃CN(7:3)
 ⁶⁰ (NBu₄)PF₆ 0.1mol L⁻¹ at 100 mVs⁻¹. Bottom: Cyclic voltammograms of 1 mM of K₃Fe(CN)₆, in 0.5 M Na₂SO₄ of modified ITO electrode with poly-POM-dvb3,3-ZnOEP film (full violin line) and of noncoated ITO electrode (dotted black line). v=100 mV s⁻¹.

The redox behavior of **poly-POM-tvb3,3-ZnOEP** is close to that of **poly-POM-dvb3,3-ZnOEP**, suggesting that conjugation to the POM is not crucial.

Permeability to Anionic Probes of the Films

The permeability of these films toward electrochemically active probe molecules has also been studied. For bare ITO electrode ¹⁰ (unmodified), the redox probe Fe(CN)₆³⁻ showed a quasi-reversible cyclic voltammetry (peak-to-peak separation 219 mV, Fig. 6b dotted-line), indicating that the probe diffuses freely to the ITO electrode surface and undergoes electron-transfer at the electrode. In contrast, in the presence of **poly-POM-dvb3,3**-¹⁵ **ZnOEP** film, the peak current decreased a lot and reached zero. Similar behaviour were observed for **poly-POM-dvb3,4**-**ZnOEP**, and **poly-POM-dvb4,4-ZnOEP**, but also for **poly-POM-tvb3,3-ZnOEP** films, suggesting that all these films were impermeable to Fe(CN)₆³⁻.



Fig. 7 Normalized UV-vis spectra of the modified ITO electrodes with poly-POM-dvb3,3-ZnOEP obtained after 25 iterative scans between 0 25 and 1.90 V versus SCE (dotted pink line), and of poly-POM-dvb3,3-ZnOEP (purple line) and of ZnOEP (black line) in DMF solution.

UV-Visible Characterization of the copolymeric films

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- All the UV-visible spectra recorded on ITO electrodes coated with the copolymers presented identical characteristics. A typical UV-visible spectrum is represented in Figure 7. The large Soret absorption band was red shifted compared to the ZnOEP
- ³⁵ monomer. This evolution can be understood by the excitoncoupling theory concerning intra- or intermolecular excitonic interactions between the ZnOEP subunits.^{48,66–68} Similar spectral effects in dimeric or trimeric porphyrins have been reported and analyzed as dependent on the interporphyrin angles, the direction
- ⁴⁰ of the transition dipole moments in the monomer subunits, and also the distances between the porphyrins.^{69–71}

The films were then removed from the ITO electrodes by dissolution in DMF. The profile of the UV-vis absorption bands

of the solutions became sharper in comparison to those recorded ⁴⁵ on the solid films, but remained larger than for ZnOEP. This evolution suggests that for the most part intramolecular interactions remained when the copolymers were in solution.

50 X-ray Photoelectron Spectra (XPS)

This type of characterization has been employed to determine the elemental composition of the films. While XPS is not an accurate quantitative measurement of the individual atoms, it helps to ⁵⁵ determine the elements present and their oxidation states within the film. For example, the XPS measurement for **POM-dvb3,3-ZnOEP** (Fig. 8) confirms the presence of F, C, N, O, P, V and W for the copolymer onto ITO electrode.



Fig. 8 XPS spectra of the modified ITO electrodes with **POM-dvb3,3-ZnOEP** obtained after 25 iterative scans between 0 and 1.90 V versus SCE. a) Global XPS spectra, b) C1s, c) O1s , d) N1s, e) P 2p3, f) W 4f7, g) V 2p3.

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The film exhibited peaks corresponding to P2p (133.2 eV), O1s (530.6 eV), V2p (V2p_{1/2} = 522.0 eV and V2p_{3/2} = 516.2 eV) and W4f levels (W4f_{5/2} = 37.2 and W4f_{7/2} = 35.4 eV) coming from the phosphorous, oxygen and tungsten atoms in the POM, while the

s C1s and N1s signals (at 284.6, 402.2 and 686.6 eV, respectively) result from the porphyrin ligand and the TBA counterions.

F1s signals (686.6 eV) can also be observed since PF_6^- anions can be trapped in the copolymer structure to balance pyridium charge. Thus, both POM phosphates and PF_6^- contribute to the P2p peak. The signal of the Zn element is not detectable.

The XPS data confirms that we indeed incorporated the Dawsontype phosphovanadotungstate and the zinc metalloporphyrin into the films, which is in agreement with the UV-vis absorption results. Similar XPS spectra (see SI Fig S7) have been obtained 15 for poly-POM-dvb3,4-ZnOEP and poly-POM-dvb4,4-ZnOEP.



 Fig. 9 a) Picture of the ITO modified electrode with poly-POM-dvb3,3-ZnOEP copolymer obtained after 25 iterative scans between 0 and 1.90 V versus SCE. a) Tapping mode AFM topography of the film on ITO.
 Bottom: Section analysis of the marked white dotted line on the image

Copolymer Morphology (Atomic Force Microscopy)

The coated electrodes were washed with CH₂Cl₂ to remove any ²⁵ trace of the conducting salt present on the film and were examined by scanning atomic force microscopy (AFM). Copolymer **poly-POM-dvb3,3-ZnOEP** appeared in the form of tightly packed coils as already observed in the case of the copolymer with Anderson type polyanion. The morphology did $_{30}$ not depend on whether the coated electrodes were obtained by scanning over the potential range from -1.30 to +1.90 V (Figure 9b) or only from -0.05 to +1.90 V vs. SCE.

The rms surface roughness of the film obtained by 25 iteractive scans from -0.05 to +1.90 V vs SCE was 6.32 nm for 1 μ m² area. ³⁵ The AFM studies showed an increase in the rms surface

roughness with the number of iterative scan.

Similar results have been obtained for poly-POM-dvb3,4-ZnOEP (rms surface roughness: 5.53 nm), poly-POM-dvb4,4-ZnOEP (rms surface roughness: 4.21 nm) and poly-POM-40 tvb3,3-ZnOEP (rms surface roughness: 3.20 nm).

Control of the Thickness of copolymeric films

We have also examined the control of the thickness of the ⁴⁵ deposited polymeric film. For that, two ways of preparation of the polymer coated onto ITO electrode have been followed. In the first experiment, coated electrodes were prepared just by changing the number of iterative scans n during the electropolymerization. Plot of the absorbance at $\lambda = 427$ nm ⁵⁰ (Soret band of the porphyrin) as a function of the number of scans n (Fig. 10a and Fig.10b) shows effectively an increase of the thickness during the first scans and then a constant value. In the second experiment, the thicknesses of the films measured by AFM confirmed this point (Fig 10c and Fig. 10d).

⁵⁵ To measure the thickness, we removed the polymer by scratching the film with a metallic tip, and clearly observed some puffiness induced by the material removal. Analysis of the bottom indicated that we reached the ITO substrate. The thickness was estimated by comparing the height on each side, far from the

60 puffiness. Interestingly, the estimated thickness increased with the scan number with nearly the same trend as the UV-Vis absorbance intensity.

Such behavior fits with the decrease of the film conductivity already observed during the electropolymerization (Figure 5).

⁶⁵ Thus, the deposition which is initially very efficient becomes gradually more difficult and eventually stops. In addition, in the case of **poly-POM-dvb4,4-ZnOEP**, with the same number of iterative scan, the thickness is nearly three times more important. This result can be explained by the better conductivity of the

⁷⁰ films when using the fully conjugated **dvb4,4** ligand.



Fig. 10 a) UV-visible absorption spectra of **poly-POM-dvb4,4-ZnOEP** (onto ITO) with different numbers of iterative scans (between 0 and +1.90 V versus SCE). Only one side is recovered by ITO. b) Plots of the absorbance, measured at λ = 427nm, versus the numbers of iterative scans for **poly-POM-dvb3,3-ZnOEP**, **poly-POM-dvb3,4-ZnOEP**, **poly-POM-dvb4,4-ZnOEP**, and **poly-POM-tvb3,3-ZnOEP**. c) Atomic force micrograph (AFM, surface plot) image of the s modified ITO electrode with **poly-POM-dvb4,4-ZnOEP** obtained after 25 iterative scans. Bottom: section analysis. d) Thickness measured from AFM versus different numbers of iterative scans (between -0.05 and 1.90 V vs. SCE). The red filled black square corresponds to the measurement obtained from c).

Conclusion

- In the present paper we have prepared four films from the anodic ¹⁰ electro-copolymerization of organo-POM bricks with designed geometries and structures, and a porphyrin. The bricks as well as the materials were unambiguously characterized by several analytical techniques.
- The conclusion of the aggregated characterizations show that the ¹⁵ conjugation to the POM may not be a crucial item, at least from an electrochemical point of view, but the geometry of the pyridines on the hybrid monomer is directly related to the performances of the materials.
- Future work will focus on the assessment on the reactivity of the ²⁰ materials under visible light irradiation.

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30 Notes and references

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