



Photovoltaic properties of supramolecular assemblies obtained by incorporation of Preyler's type polyoxometalate in a polycationic copolymer of porphyrin

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ABSTRACT

Poly-zinc-octaethylporphyrin/P₅W₃₀ films have been obtained through incorporation of Preyler-type polyoxometalate ions, namely [NaP₅W₃₀O₁₁₀]¹⁴⁻ (**P₅W₃₀**) into zinc octaethylporphyrin/viologen-based polymers (**poly-ZnOEP**) films. The latter has been achieved through a metathesis reaction involving exchange of the initial counter ions (PF₆⁻) of the positively charged **poly-ZnOEP** by **P₅W₃₀**. The investigated polymers involve **ZnOEP** units covalently linked either through a dicationic mono-viologen or through a tetracationic bis-viologen spacer. These copolymers have been characterized by UV/Vis absorption spectroscopy, X-ray photoelectron spectroscopy, electrochemistry, AFM and by electrochemical impedance spectroscopy. Formation of the polymers through electropolymerization of viologen and porphyrin building blocks has also been monitored by EQCM. QCM measurements have been carried out to study the exchange of PF₆⁻ by [NaP₅W₃₀O₁₁₀]¹⁴⁻. Finally, the photovoltaic performances of these polymers have been assessed by photocurrent transient measurements carried out under visible illumination.

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1. Introduction

Polyoxometalates (POMs) are a structurally diverse family of anionic metal-oxygen cluster anions constituted of metal elements in their highest oxidation states finding applications in analytical chemistry, medicine, homogeneous and heterogeneous catalysis, electronics and materials science [1]. Owing to their robustness and large number of metallic centers, POMs can undergo multi-electron photoredox reversible processes without structural alteration [2]. It is furthermore possible to use various type of structure (Lindqvist, Keggin, Dawson, Sandwich types...) and to change the heteroatoms

(V^V, Nb^V, Mo^{VI}, W^{VI}, ...) involved in their structure so as to adjust their oxidation and/or reduction potentials. Preyler-type POMs, K_{12.5}Na_{1.5}[NaP₅W₃₀O₁₁₀], have already been incorporated in photochromic [3] and thermochromic [4] composite films showing good reversibility in the coloration/decoloration process.

The great thermal stability and processability of POM-containing polymers make them perfectly suited to the development of functional photovoltaic devices. Peng et al. have reported the first example of polymer featuring conjugated photoactive organic moieties [5] associated to hexamolybdate type polyoxometalates (POM) inserted into the main-chain or as side-chain pendant groups [6,7]. These hybrid polymers have been shown to exhibit intense visible absorption whose fluorescence is quenched by the POM clusters. Such polymers have been used as key components within single-layer photovoltaic devices (indium tin oxide

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(ITO)/polymer/Ca configuration) featuring a power conversion efficiency (PCE) of 0.15% [7b]. More recently, Peng et al. have reported much higher PCEs, reaching 0.31% [7b], with a different type of hybrid copolymer exhibiting different loadings of hexamolybdate-based POMs covalently embedded in the main chain together with imide-functionalized naphthodithiophene or 3,3'-didodecyloxy bithiophene units. The photovoltaic performance of this two hybrid materials are already very encouraging, even if further improvements are still obviously needed for applications. Several other covalently-linked POM–polymer hybrids have been described but their photovoltaic properties have not been reported [8]. The low photovoltaic efficiency reported in the articles mentioned above may, in part, be explained by the fact that POMs are usually excited under UV irradiations ($O \rightarrow M$ ligand-to-metal charge-transfer absorption band). This means that only a small fraction of the incoming light can be converted into electrical energy, which severely limits the applications of such materials in photovoltaics and may explain the small power conversion efficiency (PCE) reported by Peng et al. [8].

To address this issue, POMs can be associated *via* covalent, coordination or non-covalent bonding to porphyrin-based chromophores known to absorb visible light [9–11]. The association of electron-accepting POMs with efficient light absorbing molecules is moreover expected to improve the charge separation efficiency and to decrease the recombination rate, the POMs acting as redox mediators for electrons transferred from the porphyrins to the ITO current collector through the covalent viologen spacers. The introduction of POM–porphyrin hybrids into polymeric and surface supported materials is thus a very promising approach toward functional devices with efficient photocatalytic or photovoltaic properties.

In line with this strategy, we have previously reported a straightforward and efficient electropolymerization procedure leading to mixed porphyrin–POM copolymer films, involving either Anderson, Dawson or Linqvist [12] type of POMs, with remarkable photocatalytic properties under visible light illumination.

A similar electropolymerization procedure was also implemented with dipyrindyl ligands but without polyoxometalate, to provide access to a series of cationic porphyrin- and viologen-based copolymers. In this case, the associated POM–porphyrin films could be prepared by exchanging the PF_6^- counter ions with Keggin type polyanion $[SiW_{12}O_{40}]^{4-}$. This doping process was found to induce drastic modifications of the morphology as evidenced by AFM measurements [13]. Such porphyrin–POM electrostatic assemblies could potentially be involved in photoinduced electron transfers from the porphyrin antenna (donor of electron) to the viologen spacers and to the POM (acceptors of electron). These materials are thus promising for the development of photoelectric devices where the type of POMs can be modulated easily. In a previous report, [14] only the fabrication of the electrostatic supramolecular structure was described, and the photocurrent generation as well as the photocatalytic behavior, under irradiation was not studied.

In the present paper, we have further exploited this strategy to incorporate a Preyssler-type POM ($[NaP_5W_{30}O_{110}]^{14-}$; P_5W_{30}) into two kinds of electropolymerized **poly-ZnOEP** films, involving either simple rigid viologen ($-py^+-py^-$) or more flexible bis-viologen, ($-py^+-py^+-(CH_2)_3-py^+-py^+$) spacers introduced between the zinc- β -octaethylporphyrin (**ZnOEP**) units.

The Preyssler-type POM ($[NaP_5W_{30}O_{110}]^{14-}$; P_5W_{30}) has been selected in order to prevent its diffusion inside the film during the metathesis reaction involving exchange of the PF_6^- counter-anions due to *i*) its large size, and *ii*) the 14 negative charges carried by the Preyssler-type POM which will promote coulombic interactions with the positively charged viologen spacers.

XPS analyses and UV–visible absorption measurements have

been carried out before and after incorporation of P_5W_{30} . It was expected that this species could potentially behave in the polymer as an electron relay between the excited **ZnOEP** (donor) and the viologen (or bis-viologen) acceptors. We have systematically investigated the photocurrent generation with **poly-ZnOEP** and of **poly-ZnOEP/ P_5W_{30}** under visible-light illumination in the presence of I_3^-/I^- used as redox mediator in acetonitrile as well as in aqueous medium.

2. Experimental

2.1. Materials

All solvents were of reagent grade quality and used without further purification. The zinc- β -octaethylporphyrin (**ZnOEP**) and ligand 4,4'-bipyridine (4,4'-bpy) was purchased from Sigma–Aldrich and used without further purification. The 1,1'-(1,3-propanediyl)bis-4,4'-bipyridinium hexafluorophosphate salt ($bpy^+-CH_2-CH_2-CH_2-bpy^+ \cdot 2PF_6^-$) was synthesized according to procedures described in literature [14]. Preyssler-type polyoxometalate P_5W_{30} , namely $K_{12.5}Na_{1.5}[NaP_5W_{30}O_{110}] \cdot 15H_2O$, were prepared as previously reported [15].

2.2. Electrochemistry and photoelectrochemistry

Voltammetric and electrochemical impedance measurements have been performed with a standard three-electrode system using a PARSTAT 2273 potentiostat. Glassy carbon or single-side coated indium-tin-oxide (ITO, SOLEMS, 25–35 Ω /sq) electrodes, with a surface of about 1 cm² has been used as working electrode. A platinum wire has been used as auxiliary electrode. The reference electrode was a saturated calomel electrode (SCE). It was electrically connected to the solution by a junction bridge filled with the electrolyte. Photoelectrochemical responses for films were obtained by on-off light illumination of a 300 W Xe arc lamp (with $\lambda > 385$ nm long pass filter) in acetonitrile containing 5 mmol L⁻¹ of I_2 and 0.5 mol L⁻¹ of NaI with two-electrode system. In solution I_2 reacts with I^- to give I_3^- . I_3^- and I^- anions act as reversible redox mediator and also as electrolyte in order to improve the conductivity and thus increase the current magnitude.

2.3. UV–visible spectroscopic measurements

UV–vis absorption spectra of the copolymers deposited on ITO or in DMF solution have been recorded on an Agilent 8453 spectrophotometer.

2.4. X-ray photoelectron spectroscopy (XPS)

XPS experiments were carried out on a RBD upgraded PHI-5000C ESCA system (Perkin-Elmer) with MgKR radiation ($h = 1253.6$ eV) or Al KR radiation ($h = 1486.6$ eV). In general, the X-ray anode was run at 250 W and the high voltage was kept at 14.0 kV with a detection angle at 54°. The pass energy was fixed at 23.5, 46.95, or 93.90 eV to ensure sufficient resolution and sensitivity. The base pressure of the analyzer chamber was about 5×10^{-8} Pa. The sample was directly pressed to a self-supported disk (10 \times 10 mm) and mounted on a sample holder then transferred into the analyzer chamber. The whole spectra (0–1100 eV) and the narrow spectra of all the elements with higher resolution were both recorded by using RBD 147 interface (RBD Enterprises, U.S.A.) through the Auger Scan 3.21 software. Binding energies were calibrated by using the containment carbon (C1s = 284.6 eV). The data analysis was implemented by using the RBD Auger Scan 3.21 software provided by RBD Enterprises or XPS Peak4.1 provided

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