



Application of polyoxometalate-ionic liquids (POM-ILs) in dye-sensitized solar cells (DSSCs)



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ABSTRACT

Polyoxometalates (POMs) as anionic metal oxides are promising candidates for application in dye-sensitized solar cells (DSSCs) due to their peculiar properties including a reversible and multi-electron redox behavior. In this work, four polyoxometalate as ionic liquids (POM-ILs) based on the combination between phosphomolybdate anion ($\text{PMo}_{12}\text{O}_{40}^{3-}$) and organic cations such as $[\text{BMIM}]^+$, $[\text{BPy}]^+$, $[\text{HDPy}]^+$ and $[\text{P}_{6,6,6,14}]^+$ were prepared and characterized. A detailed chemical structural elucidation by elemental analysis, ATR-FTIR, ^1H and ^{31}P NMR spectroscopies have been performed. These POM-ILs were tested as photosensitizers by adsorption to the photoanode (TiO_2 film) for different times (15 min to 17 h). The DSSCs performance can be highly improved comparing the commercially available compound and POM-ILs. The electrodeposition process is an excellent alternative to adsorption in order to improve the overall efficiencies. In general, $[\text{BPy}]_3[\text{PMo}_{12}\text{O}_{40}]$ and $[\text{P}_{6,6,6,14}]_3[\text{PMo}_{12}\text{O}_{40}]$ are the most promissory compounds for DSSC approaches.

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1. Introduction

Polyoxometalates (POMs) are anionic metal oxides based on early transition metals, in a high oxidation state, that exhibit unique physical and chemical properties, such as high thermal stability, reversible and multi-electron redox and catalytic properties, strong electron acceptability and photosensitivity [1–4]. These properties can be finely tuned by changing the metal ions, the heteroatoms and appropriate counter ions [1]. For all these reasons, they are promising candidates to be applied in the different components of Dye-sensitized solar cells (DSSCs) and this field has been explored in the last decade [2–4]. Dye-sensitized solar cells developed by Grätzel and O'Regan are photovoltaic devices that use a transparent film of titanium dioxide coated with a dye to sensitize the film for light harvesting [5,6]. These devices belong to the third generation of solar cells that have attracted much attention due to their relatively low-cost processes of fabrication, large flexibility in shape, color, transparency and compatibility with flexible substrates. They are typically formed by four components: a photosensitive dye, a semiconductor anode (usually TiO_2), an electrolyte with a redox couple (for example I^-/I_3^-) and a counter electrode (normally a conductor noble metal, such as Pt) (Fig. 1)

[2]. The dye is responsible for light absorption and injection of the excited electrons into the conduction band (CB) of the semiconductor. The oxidized dye is regenerated by the electrons transferred by the redox mediator. The redox mediator is in turn regenerated at the counter electrode.

POMs on the other hand have been shown to play many roles in DSSCs: as photoanodes, photosensitizers or co-sensitizers, electrolyte and counter electrode [4].

Parayil et al. [7] incorporated for the first time heteropolytungstic acid into TiO_2 nanodiscs as photoanode and observed a further enhancement of the energy conversion efficiency of 23% and 9% using ruthenium or porphyrin dyes, respectively. Since then several works have been reported, ZnO [8,9] and TiO_2 [10–13] modified photoanodes containing POMs have shown an improvement of the photovoltaic performance, which was interpreted as being related to reduced electron recombination, increased electron lifetime and in some cases also to enhanced light harvesting. They have also been reported as photosensitizers [14,15] or co-sensitizers [15–17] in n-type DSSCs and in p-type DSSCs as pure inorganic dyes [18,19] or co-sensitizers [19,20]. When they are used as photosensitizers the efficiencies of the solar cells are in the range of 0.029–0.2% [14,15] in n-type DSSCs, and values of 0.0016 to 0.038% for p-type cells [18,19]. While used as co-sensitizers, the overall power conversion efficiency is enhanced through increasing spectral absorption, accelerating electron transport and restraining charge recombination [15,17] or through

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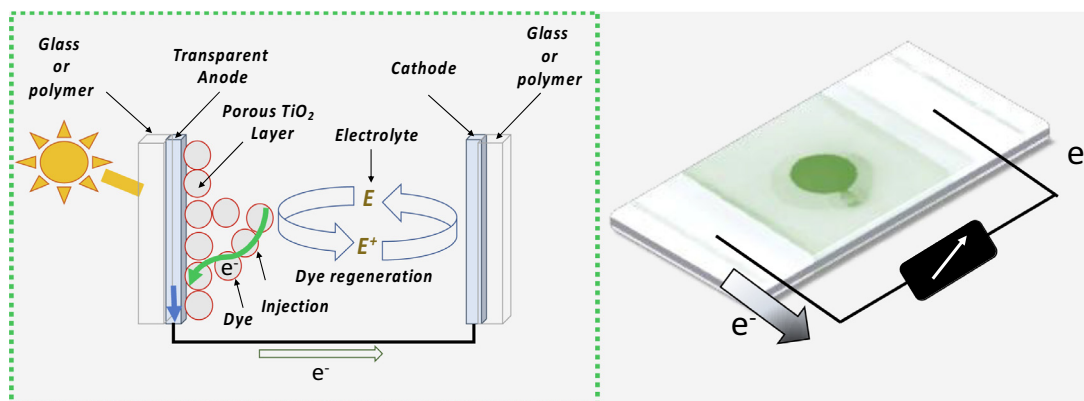


Fig. 1. Schematic representation of Dye-Sensitized Solar Cell (DSSC).

synergistic effect of POMs and dyes [16]. When used as counter electrodes, a conversion efficiency comparable to that of Pt electrodes can be achieved when assembled on single-walled carbon nanotubes [21] and quantum dot-sensitized solar cells (QDSSCs). [22] They have also been used as electrolytes [23,24] and a recent study reported an increase in V_{OC} (up to a 5 fold) when compared to the traditional I^-/I_3^- redox couple in a p-type DSSC [25].

In this work, we applied several polyoxometalate based ionic liquids (POMs-ILs) in DSSCs as photosensitizers. These compounds were prepared from the combination of phosphomolybdate anion ($PMo_{12}O_{40}^{3-}$) and 1-butyl-3-methylimidazolium (BMIM), 1-butylpyridinium (BPy), hexadecylpyridinium (HDPy) and trihexyltetradecylphosphonium ($P_{6,6,6,14}$) as organic cations.

2. Results and discussion

2.1. Synthesis of POM-ILs

The POM-ILs $[BMIM]_3[PMo_{12}O_{40}]$, $[BPy]_3[PMo_{12}O_{40}]$ and $[P_{6,6,6,14}]_3[PMo_{12}O_{40}]$ (Fig. 2) were prepared from an acid-base reaction using $H_3PMo_{12}O_{40}$ and the hydroxide forms of 1-butyl-3-methylimidazolium, 1-butylpyridinium and trihexyltetradecylphosphonium, respectively. The hydroxide forms were previously prepared from the corresponding chlorides ionic liquids by exchange of the chloride to the hydroxide using an ion exchange resin Amberlist (in the OH form) (Fig. 2). $[BMIM]_3[PMo_{12}O_{40}]$ and $[BPy]_3[PMo_{12}O_{40}]$ were available from previous studies and their syntheses and characterization described elsewhere [26]. $[HDPy]_3[PMo_{12}O_{40}]$ was prepared following the method described in literature [27,28]. These compounds were characterized by elemental analyses, ATR-FTIR, 1H and ^{31}P NMR spectroscopies confirming the expected structure as well as the presence of the phosphomolybdate anion (see details in ESI) which is in accordance with the literature [26,29,30].

2.2. DSSCs photovoltaic performance

One important measure to validate the possible application of dyes for DSSCs applications is by the determination of the energy band gaps, the HOMO and LUMO energies of the dye- TiO_2 complex. In here we considered electron injection into the TiO_2 conduction band (-4.24 eV), when evaluating electron injection ability. A schematic representation of the energy levels of the POMs-ILs versus the TiO_2 conduction band (-4.24 eV) and the calculated redox potential of the redox couple I^-/I_3^- (-4.72 eV) is represented in scheme 1. All the studied POMs and POMs-ILs should be able to inject electrons into the TiO_2 CB, given that for every case the difference between the LUMO and the potential of the TiO_2 is ~ 1 eV.

Although all the POMs compounds possess a HOMO energy level below the potential of I^-/I_3^- , thus being able to be reduced by the electrolyte, for POMs-ILs $Na_3PMo_{12}O_{40}$, $Bpy_3PMo_{12}O_{40}$ and $BMIM_3PMo_{12}O_{40}$ this difference is quite small (**0.07, 0.05 and 0.09 eV, respectively**). This fact can result in inefficient regeneration of the compounds by the electrolyte, affecting the performance of the cell. In the case of dyes $H_3PMo_{12}O_{40}$, and $(P_{66614})_3PMo_{12}O_{40}$, this difference is higher than 0.1 eV, rendering these compounds easier to regenerate by the electrolyte as can be seen for the $(P_{66614})_3PMo_{12}O_{40}$ [31].

2.3. POMs-ILs as photosensitizers

The commercially available phosphomolybdic acid $H_3PMo_{12}O_{40}$ and the POMs-ILs $[BMIM]_3[PMo_{12}O_{40}]$ and $[P_{6,6,6,14}]_3[PMo_{12}O_{40}]$ (Fig. 1) were tested as photosensitizers by adsorption to the photoanode (TiO_2 film) for 17 h. Two control experiments were done, one with the reference dye (N719) and the other with TiO_2 with no dye adsorbed. The DSSCs performance results are shown in Table 1 and as can be observed both POMs-ILs and $H_3PMo_{12}O_{40}$ show worse efficiency than the TiO_2 without dye. This is due to a decreased response both in the J_{SC} and the V_{OC} produced by the cells. The low results obtained were expected since the POMs-ILs solutions showed light/ to no colour, and the consequent photoanodes showed no evident colour as well. Since dye sensitization plays a crucial role in the photocurrent produced by the cell, using compounds with no absorption in the visible range of the spectrum presents a limitation to the efficiencies obtained.

An interesting result, however, is the fact that a high improvement from the commercially available compound to the POMs-ILs is verified (around 37 times higher of overall efficiency) both in terms of J_{SC} , as well as V_{OC} results. Since these low results could be an effect of aggregation of the compounds, shorter times of adsorption (2 h and 15 min) were used and in this case the two commercially available compounds $H_3PMo_{12}O_{40}$ and $Na_3PMo_{12}O_{40}$ and all the POMs-ILs prepared were tested (Table 1).

The energy conversion efficiency was enhanced as the time of adsorption decreases, for example for $[BMIM]_3[PMo_{12}O_{40}]$ it increases around 4.5 times (from 17 h to 15 min) and for $[P_{6,6,6,14}]_3[PMo_{12}O_{40}]$ it increases around 3.5 times, nevertheless the values are smaller than those obtained for the control experiment with TiO_2 without dye (Reference as mentioned in Table 1 and Fig. 3).

Since POMs present different redox potentials, they can work as 'electron traps' thus reducing the energy conversion in the cell, regardless of the inexistence of color. An attempt was made to deposit the POM-ILs in their reduced form *via* electrodeposition onto the surface of the TiO_2 film. Electrodeposition was used to

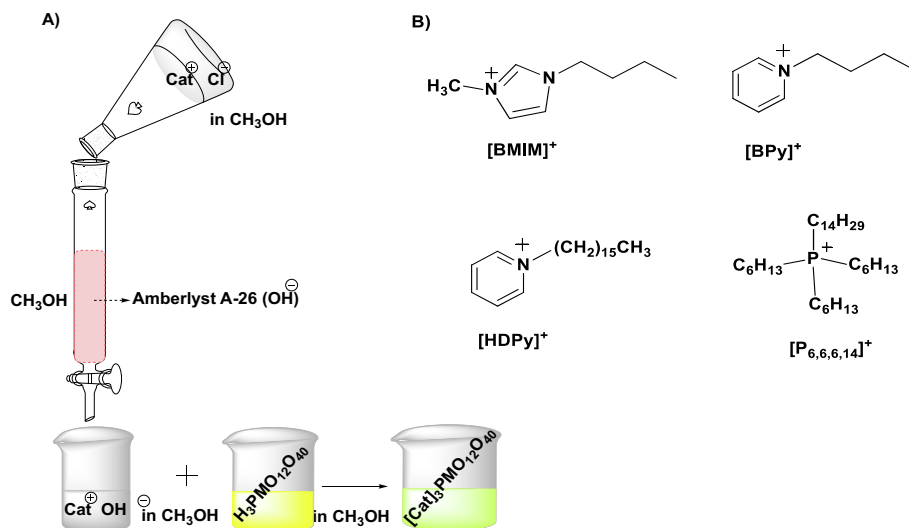
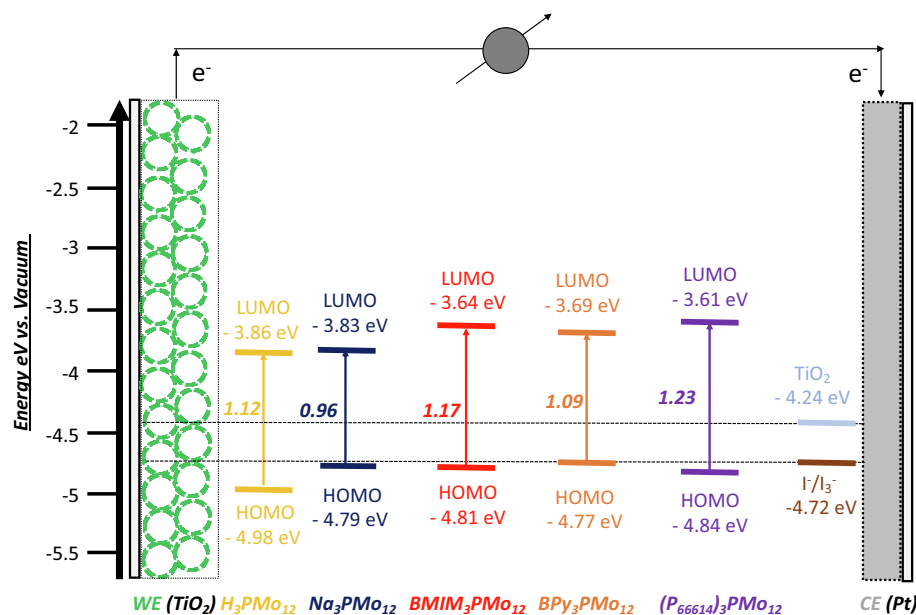


Fig. 2. A) Schematic representation of the method used for the preparation of [BMIM]₃[PMO₁₂O₄₀], [BPy]₃[PMO₁₂O₄₀] and [P_{6,6,6,14}]₃[PMO₁₂O₄₀]. B) Structures of the cations used in the preparation of POM-ILs.



Scheme 1. Schematic representation of the energy level diagram (HOMO_{dye@TiO₂} and LUMO_{dye@TiO₂}) of the POMs dyes adsorbed onto the TiO₂ film vs. the FTO and I⁻/I₃⁻ redox potentials.

Table 1

ADSORPTION times: Photovoltaic performance of the best performing DSSCs based on POMs-ILs as dye-sensitizers, deposited by 17, 2 h and 15 min of adsorption, under 100 mW cm⁻² simulated AM 1.5 illumination. Reference: represents no addition of dye, meaning an anode with only the TiO₂ film.

| ADSORPTION time | Dye | V _{oc} (mV) | J _{sc} (mA/cm ²) | V _{max} (mV) | J _{max} (mA/cm ²) | FF | η (%) |
|-----------------|-----------------------|----------------------|---------------------------------------|-----------------------|----------------------------------------|------|--------|
| - | Reference | 367 | 0.37 | 280 | 0.29 | 0.60 | 0.0830 |
| 17 h | H ₃ | 17 | 0.05 | 10 | 0.03 | 0.26 | 0.0002 |
| | BMIM | 142 | 0.12 | 95 | 0.08 | 0.46 | 0.0080 |
| | P _{6,6,6,14} | 185 | 0.15 | 130 | 0.10 | 0.49 | 0.0130 |
| | H ₃ | 30 | 0.07 | 15 | 0.04 | 0.27 | 0.0005 |
| 2 h | Na ₃ | 51 | 0.04 | 27 | 0.02 | 0.29 | 0.0060 |
| | BMIM ₃ | 168 | 0.12 | 115 | 0.09 | 0.5 | 0.0100 |
| | BPy ₃ | 157 | 0.12 | 104 | 0.08 | 0.45 | 0.0080 |
| | DPy ₃ | 185 | 0.14 | 131 | 0.10 | 0.51 | 0.0130 |
| | P _{6,6,6,14} | 221 | 0.21 | 162 | 0.16 | 0.57 | 0.0260 |
| | H ₃ | 24 | 0.03 | 12 | 0.02 | 0.26 | 0.0002 |
| 15 min | BMIM | 271 | 0.23 | 202 | 0.18 | 0.56 | 0.0360 |
| | BPy | 240 | 0.19 | 171 | 0.13 | 0.51 | 0.0230 |
| | P _{6,6,6,14} | 276 | 0.28 | 212 | 0.21 | 0.60 | 0.0460 |

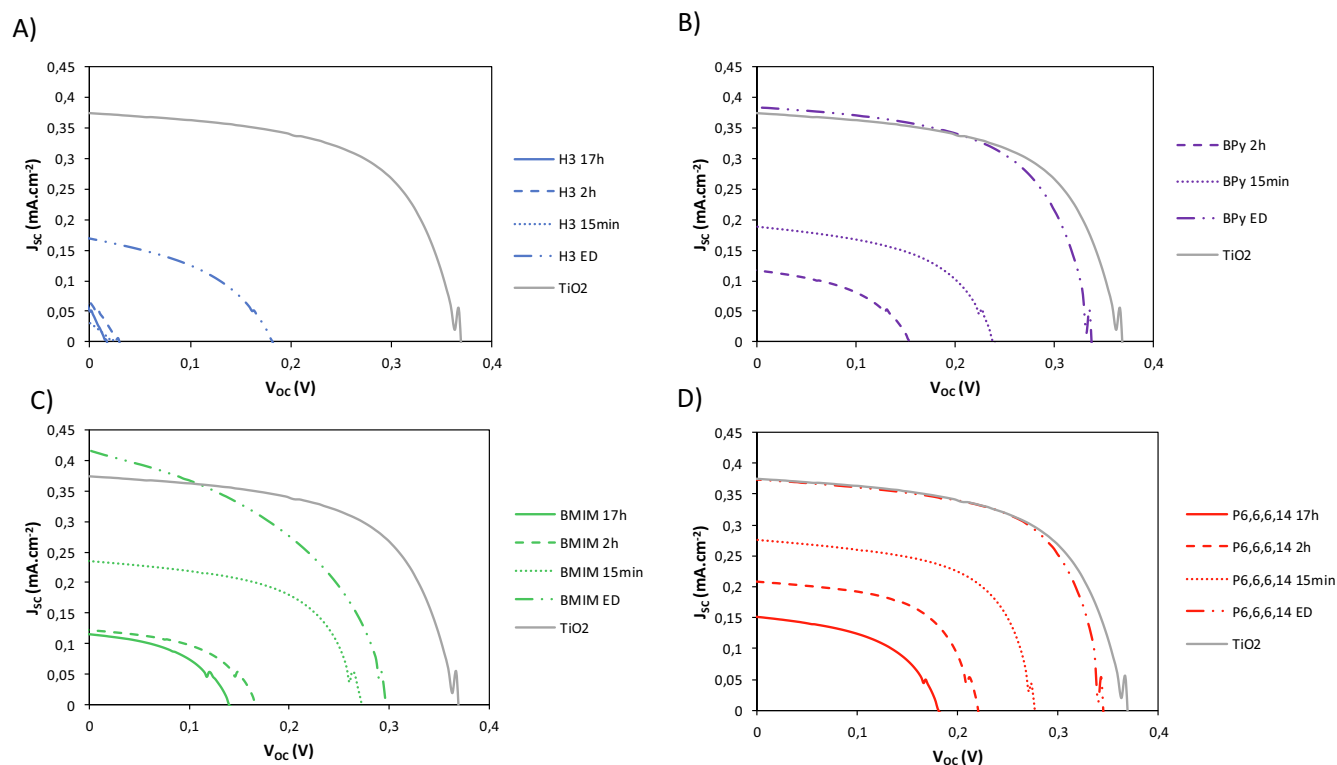


Fig. 3. J–V curves of DSSCs based on POMs-ILs with different deposition times, under $100 \text{ mW}\cdot\text{cm}^{-2}$ simulated AM 1.5 illumination: A) $\text{H}_3\text{PMo}_{12}\text{O}_{40}$, B) $[\text{Bpy}]_3[\text{PMo}_{12}\text{O}_{40}]$, C) $[\text{BMIM}]_3[\text{PMo}_{12}\text{O}_{40}]$ and D) $[\text{P}_{6,6,6,14}]_3[\text{PMo}_{12}\text{O}_{40}]$.

coat the TiO_2 films with the POM-ILs as dyes instead of adsorption and the results of the DSSCs performance are shown in Table 2.

For all the compounds the efficiency was improved, and the results obtained for the cells using organic cations [BMIM], [BPy] and $[\text{P}_{6,6,6,14}]$ are close to that obtained for the TiO_2 film with no dye (Fig. 4).

3. Conclusions

Four Polyoxometalate ionic liquids (POM-ILs) based on the combination between phosphomolybdate anion and organic cations such as $[\text{BMIM}]^+$, [BPy], $[\text{HDPy}]^+$ and $[\text{P}_{6,6,6,14}]^+$ were prepared and characterized. The structural elucidation has been checked by elemental analyses, ATR-FT-IR, ^1H and ^{31}P NMR spectroscopies.

All compounds were tested as photosensitizers by adsorption to the photoanode (TiO_2 film) for different times (15 min to 17 h). The DSSCs performance showed a reduced efficiency for the POMs-ILs and $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ comparing to TiO_2 without dye.

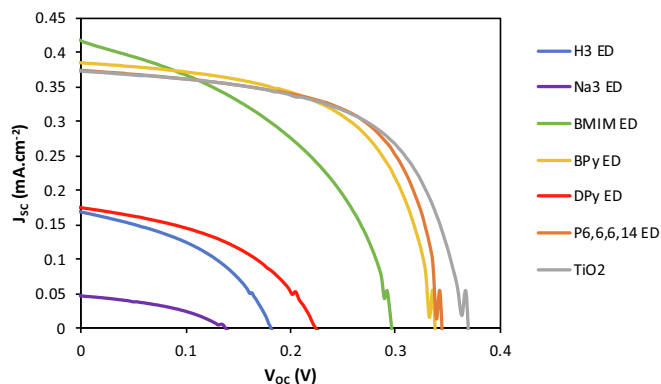


Fig. 4. J–V curves of DSSCs based on POMs-ILs deposited by electrodeposition, under $100 \text{ mW}\cdot\text{cm}^{-2}$ simulated AM 1.5 illumination.

However, a significant improvement at least 37 times higher of overall efficiency is observed comparing the commercially available compound to the POM-ILs.

Table 2
ELECTRODEPOSITION: Photovoltaic performance of the best performing DSSCs based on POMs-ILs as dye-sensitizers, deposited by electrodeposition, under $100 \text{ mW}\cdot\text{cm}^{-2}$ simulated AM 1.5 illumination. Reference: represents no addition of dye, meaning an anode with only the TiO_2 film.

| Dye | V_{oc} (mV) | J_{sc} (mA/cm^2) | V_{max} (mV) | J_{max} (mV/cm^2) | FF | η (%) |
|-----------------------|---------------|--------------------------------------|----------------|---------------------------------------|------|------------|
| H_3 | 182 | 0.17 | 120 | 0.11 | 0.43 | 0.0130 |
| Na_3 | 138 | 0.05 | 87 | 0.03 | 0.39 | 0.0030 |
| BMIM | 295 | 0.42 | 204 | 0.27 | 0.45 | 0.0560 |
| BPy | 337 | 0.38 | 257 | 0.30 | 0.60 | 0.0780 |
| DPy | 225 | 0.18 | 150 | 0.12 | 0.44 | 0.0180 |
| $\text{P}_{6,6,6,14}$ | 344 | 0.37 | 271 | 0.30 | 0.63 | 0.0820 |
| Reference | 367 | 0.37 | 280 | 0.29 | 0.60 | 0.0830 |

The effect of aggregation associated to POM-ILs can be suppressed by the reduction of adsorption times from 17 h to 2 h and 15 min.

Since POMs present different redox potentials, they can work as 'electron traps' thus reducing the energy conversion in the cell, regardless of the inexistence of color. An attempt was made to deposit the POM-ILs in their reduced form *via* electrodeposition onto the surface of the TiO₂ film. In this context, the electrodeposition process as alternative to adsorption in order to coat the TiO₂ films with the POM-ILs as dyes allowed a significant improvement in the DSSC performance.

[BPY]₃[PMO₁₂O₄₀] and [P_{6,6,6,14}]₃[PMO₁₂O₄₀] are the most promissory compounds for DSSC approaches with higher improvements comparing to commercial POMs (H₃PMO₁₂O₄₀ and Na₃PMO₁₂O₄₀).

Conflicts of interest

There are no conflicts of interest related to this paper for the authors.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.mlblux.2019.100033>.

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