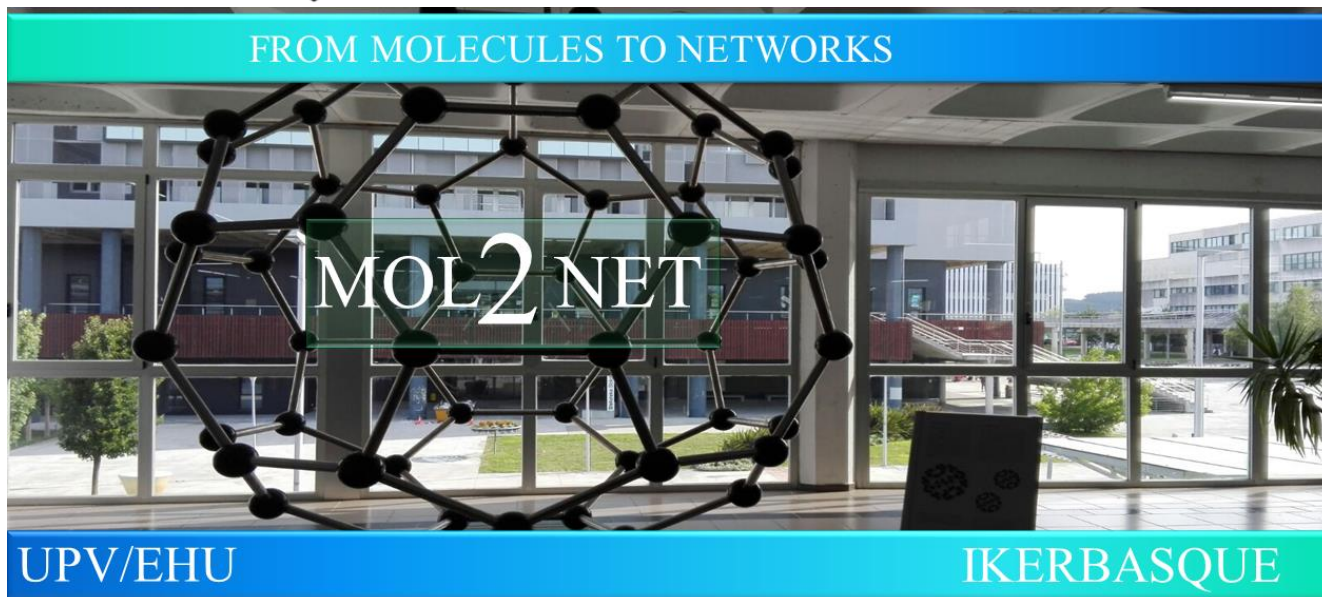




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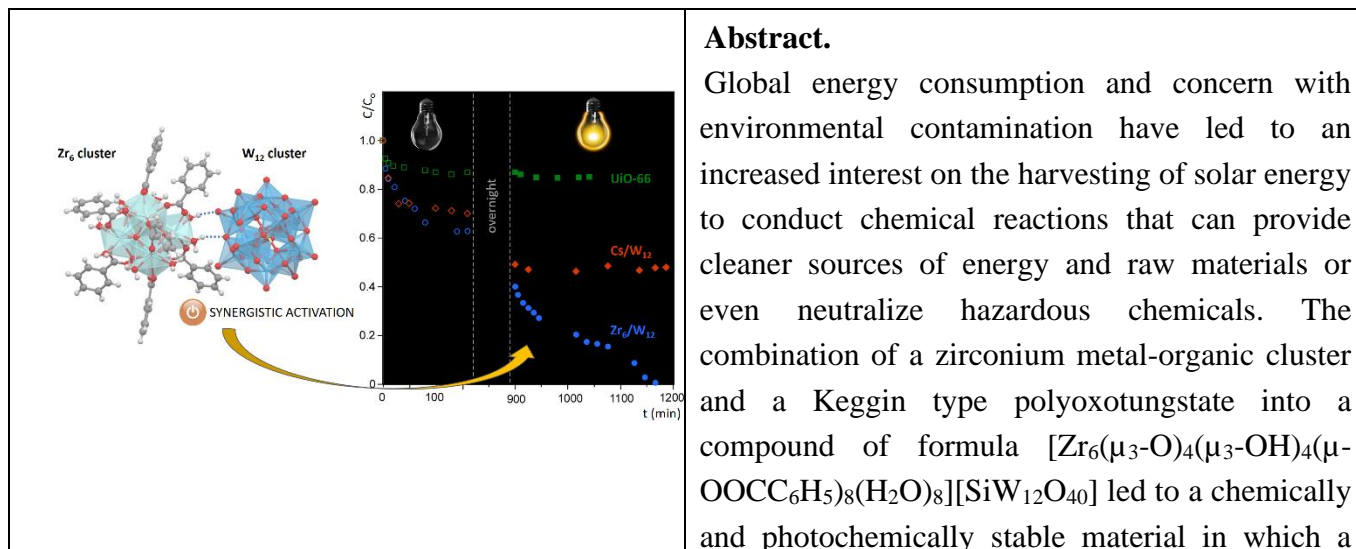


## Merging the chemistry of metal-organic and polyoxometalate clusters into an enhanced photocatalytic material

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	<p>synergistic effect between the metal-organic cluster and the polyoxometalate allows to markedly overpass the permanent porosity of the referential compounds, the hybrid material surpasses their methylene blue adsorption capacity (Zr6/W12-NP: 73 <math>\mu\text{g}/\text{mg}</math>; Cs/W12: 63 <math>\mu\text{g}/\text{mg}</math>; UiO-66: 16 <math>\mu\text{g}/\text{mg}</math>). Interestingly, the photochemical activity was also compromised to a the quantitative photodegradation of the dye in 4 h (<math>k = 7.7 \cdot 10^{-3} \text{ min}^{-1}</math>), while the referential compounds did not exhibit any substantial activity toward the photooxidation of methylene blue.</p>
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## Introduction

In this regard, during the last few years, zirconium based metal-organic frameworks (MOFs) have been intensively explored as heterogeneous photocatalysts due to both the *ad-hoc* setting of the surface chemistry and the proficient chemical stability provided by Zr–O bonds.<sup>1,2,3</sup> Some successful examples include the photocatalytic removal of pollutants,<sup>4</sup> production of hydrogen,<sup>5</sup> photoreduction of CO<sub>2</sub>,<sup>6</sup> and selective transformation of organics into valuable chemicals.<sup>7</sup> The metal clusters and organic ligands building up this type of MOFs can be regarded as isolated quantum dots and light-harvesting antenna, respectively.<sup>8</sup> Accordingly, discrete zirconium clusters can also behave as efficient heterogeneous photocatalyst if they are embedded into an insoluble matrix.

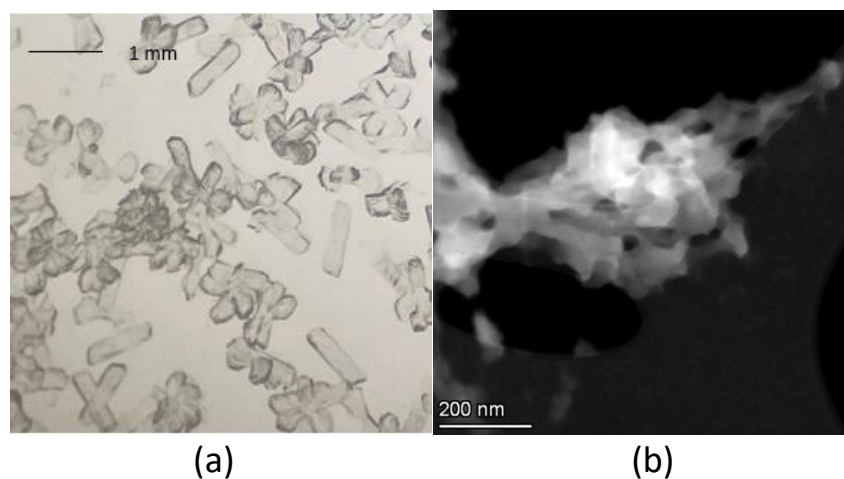
Upon controlled reaction conditions Zr(IV) tends to yield hexanuclear clusters of formula [Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>]<sup>12+</sup> in which the charge can be modulated by the anchoring of a variable number (*n*) of carboxylic ligands: [Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(OOCR)<sub>*n*</sub>]<sup>12-*n*</sup>.<sup>9</sup> When this kind of discrete complexes are crystalized using simple counterions (such as chloride, sulphate...) they lead to compounds of frail stability, soluble in common solvents and therefore, unsuitable as heterogeneous catalyst. Nonetheless, the adequate selection of the counterion can emend such drawbacks. In this sense, polyoxometalates (POMs) constitute a fine solution since their size is comparable to that of zirconium clusters and their anionic charge is relatively high, so the combination of both type of entities can yield highly insoluble and stable ionic molecular compounds.

## Results and Discussion

Single crystal X-ray diffraction data allowed to elucidate the crystal structure of **Zr<sub>6</sub>/W<sub>12</sub>-MC**.<sup>‡</sup> As expected the Zr atoms of the [Zr<sub>6</sub>( $\mu_3$ -O)<sub>4</sub>( $\mu_3$ -OH)<sub>4</sub>( $\mu$ -OOC<sub>6</sub>H<sub>5</sub>)<sub>8</sub>(H<sub>2</sub>O)<sub>8</sub>]<sup>4+</sup> entity exhibit an octahedral disposition, in such way that oxide and hydroxide anions are alternately placed in the triangular faces (Fig. 1). All the oxide and hydroxide anions can be crystallographically distinguished on the basis of the coordination bond distances and the deviations from the plane defined by the three Zr atoms they bind. Hydroxide anions establish longer coordination bonds (2.21–2.26 Å) than oxides (2.06–2.08 Å), due to the weaker bond strength of the former. This fact also implies a greater deviation from the mean plane hydroxide (1.090–1.101 Å) than for the oxide (0.410–0.415 Å). Each benzoato ligand links two Zr atoms by  $\mu$ - $\kappa\text{O}:\kappa\text{O}'$  coordination mode, filling four upper and four lower axial edges of the

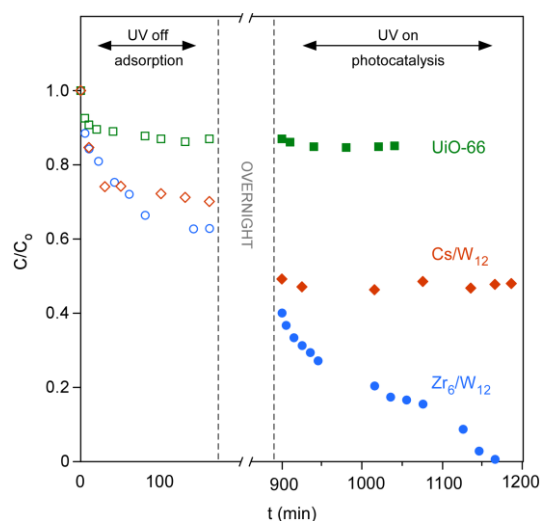
octahedron. The remaining 4 equatorial edges of the octahedron are completed by eight coordination water molecules (two per Zr-atom). As a result, all the metal atoms of the cationic cluster exhibit  $ZrO_8$  type coordination sphere with square antiprismatic geometry.

The  $[SiW_{12}O_{40}]^{4-}$  anion ( $W_{12}$ ) displays the well-known  $\alpha$ -Keggin type structure, which is constituted by four  $\{W_3O_{13}\}$  trimers formed each by three edge-sharing  $WO_6$  octahedra. These trimers are linked to each other and to the central  $\{SiO_4\}$  tetrahedron through corner-sharing in ideal  $T_d$  symmetry. However, as it usually happens, they are disordered over two positions related by a centre of inversion sited on the central Si atom for one of the crystallographically independent heteropolyoxometalate clusters (Si2) and close to it in the second one (Si1).



**Fig. 1** (a) Optic micrograph of  $Zr_6/W_{12}$ -MC and (b) TEM image of  $Zr_6/W_{12}$ -NP.

Fig. 2 compares the adsorption and photooxidation capacity of methylene blue for each selected solid. Despite the permanent porosity of the referential compounds (Fig. S7), the hybrid material surpasses their methylene blue adsorption capacity ( $Zr_6/W_{12}$ -NP:  $73 \mu\text{g}/\text{mg}$ ;  $Cs/W_{12}$ :  $63 \mu\text{g}/\text{mg}$ ;  $UiO-66$ :  $16 \mu\text{g}/\text{mg}$ ), which can probably be ascribed to both its ionic nature and small particle size. Interestingly, the illumination with a neodymium daylight lamp (100 W) promoted the quantitative photodegradation of the dye in 4 h ( $k = 7.7 \cdot 10^{-3} \text{ min}^{-1}$ ), while the referential compounds did not exhibit any substantial activity. Such result is a clear evidence of a synergistic effect between both types of ionic building blocks that comprise our hybrid material. It deserves to note that  $Zr_6/W_{12}$ -NP remained stable after the experiment.



**Fig. 3** Capture and photo-oxidation of methylene blue by **Zr<sub>6</sub>/W<sub>12</sub>-NP** compared to that displayed by **UiO-66** and **Cs/W<sub>12</sub>**.

### Conclusions

It can be concluded that this work demonstrates how the combination of a zirconium metal-organic cluster and a polyoxotungstate into a single ionic molecular material yields a chemically and photochemically stable porous material. Furthermore, the HOMO/LUMO energy distribution provides a Z-scheme mechanism with spatially separated reduction and oxidation units, which could prolong the lifetime of photogenerated  $e^-/h^+$  and explains the synergetic boosting of the catalytic performance provided by the coexistence of the metal-organic and polyoxometalate clusters. All in all, this work opens the opportunity to design novel heterogeneous photocatalysts based on the hybridization of metal-organic clusters and polyoxometalates, given that the stability of the material and the potential to get an enhanced performance can be achieved by the rational selection of the ionic building blocks.

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