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## Photoisomerisation and light-induced morphological switching of a polyoxometalate-azobenzene hybrid

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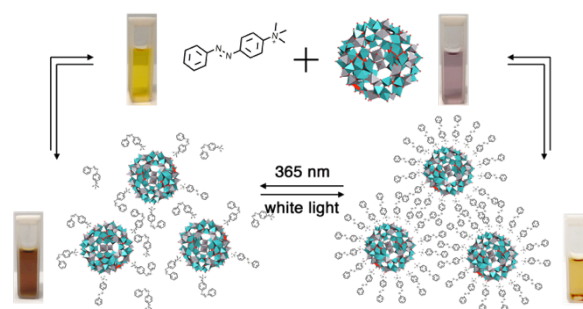
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**Functionalization of a spherical Keplerate-type polyoxometalate {Mo<sub>72</sub>V<sub>30</sub>} with a cationic azobenzene surfactant has been achieved through ionic self-assembly. The photoisomerisation reaction of this complex, which emerges in a light-triggered aggregation-disaggregation process, has been followed by <sup>1</sup>H NMR spectroscopy, dynamic light scattering, absorption spectroscopy and scanning electron microscopy analyses.**

Stimuli-responsive materials, particularly those involving photosensitive assemblies, are of great interest due to their tuneable physicochemical properties.<sup>1-2</sup> Such complex assemblies have found application, for example, in switchable catalysis,<sup>3</sup> drug delivery,<sup>4</sup> and generation of fluorescence nanopores.<sup>5</sup> Such “smart” materials have been mostly assembled via covalent chemistry by using multi-step synthetic approaches.<sup>6</sup> An alternative yet less developed approach utilizes electrostatic interactions, where oppositely charged ionic species undergo self-assembly into well-defined supramolecular architectures.<sup>7</sup> Polyoxometalates (POMs)<sup>8</sup> are a versatile family of discrete nanometer-sized polyanionic clusters with two main constituents, i.e. transition metal ions in their highest oxidation state and terminal oxygen atoms. While the former are typically Mo<sup>+6</sup>, V<sup>+5</sup>, W<sup>+6</sup> or Nb<sup>+5</sup>, and give specific features of the clusters, such as redox or catalytic properties, the latter function as bridging species for metal ions or ligands, and determine the overall charge of POM.<sup>9</sup> Due to their high negative charge, ability of forming salts, high molecular weight, and good solubility in polar solvents, POMs possess interesting catalytic, photochemical and magnetic properties.<sup>10</sup> This makes them promising candidates as molecular platforms for the construction of advanced

materials and high-tech devices<sup>11</sup> and thus to their emergence as scientific mainstream in many research groups.<sup>12-13</sup> Such groups have demonstrated considerable creativity and skill in the design, construction and application of these nanometer-scale polyanionic clusters in the supramolecular chemistry field, especially insofar as it concerns assembly driven by electrostatic interactions.<sup>9,14</sup>

Azobenzene is a well-known photochromic molecule that undergoes reversible photochemical isomerization between a planar *trans*-isomer and a bulky *cis*-form. When attached to (supra)molecular building blocks, azobenzene can confer them a photo-responsive nature.<sup>15</sup> Several self-assembled structures based on azobenzene dyes have been developed in the last decade, including those relying on covalent gold-sulfur interactions where azobenzenes were chemisorbed on Au nanoparticles, or immobilized on flat Au surfaces.<sup>16-18</sup> Azobenzenes have also been covalently grafted on Anderson-type POM clusters, and the morphology changes upon UV light irradiation were studied.<sup>19</sup> Significantly, [P<sub>4</sub>W<sub>30</sub>] clusters have been decorated *via* electrostatic interactions with quaternary ammonium salts containing azobenzene moieties, and well-organised photo-responsive complexes were obtained.<sup>3, 20-22</sup>



**Fig. 1** Schematic representation of a formation of {Mo<sub>72</sub>V<sub>30</sub>}-Azo complex and a cartoon of the inter-{Mo<sub>72</sub>V<sub>30</sub>}-Azo interactions in the two isomerization states.

The potential application of azobenzene-based materials requires full control over the isomerisation between the two isomers. To date, little attention has been paid to the study of

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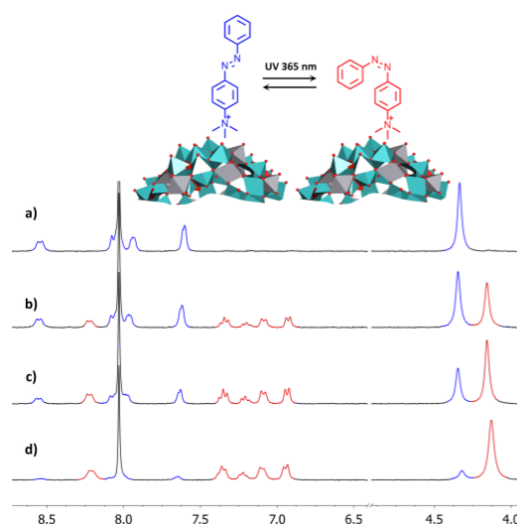
morphological changes of hybrid materials composed by POMs and azobenzene-derived photochromic units, the focus of most published work being upon the catalytic properties of the systems obtained. Among various types of POMs, polyoxomolybdates, which include the wheel-shaped molybdenum blue anions and spherical keplerates, are of particular interest because of their ion-trapping properties.<sup>23</sup> Yet, no examples of stimuli-responsive architectures based on a spherical Keplerate-type POMs encapsulated *via* weak noncovalent interactions have been reported, in particular where they involve formation of well-organized superstructures influenced by intermolecular  $\pi$ - $\pi$  stacking.

Here, we report on a new generation of self-assembled structures, held together by electrostatic and  $\pi$ - $\pi$  stacking interactions that combine the unique optical and electronic properties of POMs with the light-responsive nature of azobenzene-based photochromic moieties. The cationic anchoring group was placed directly on the azobenzene (Azo) core, and detailed comparison of the photoisomerisation of the free Azo dye and the POM-Azo hybrid material is discussed. Moreover, the morphological changes resulting from the photoisomerisation of the hybrid material were investigated and imaged by scanning electron microscopy (SEM).

The  $\{\text{Mo}_{72}\text{V}_{30}\}$ -Azo hybrid was obtained reacting *trans*-N,N,N-trimethyl-4-(phenylazo)benzenammonium iodide with a Keplerate-type polyoxomolybdate  $\{\text{Mo}_{72}\text{V}_{30}\}$ , in an ionic self-assembly process (Fig. 1).  $\{\text{Mo}_{72}\text{V}_{30}\}$  was synthesised according to the procedure previously reported by Müller and co-workers.<sup>24</sup> Preparation of the azobenzene derivative and the  $\{\text{Mo}_{72}\text{V}_{30}\}$ -Azo complex are described in the ESI†. Unlike the  $\{\text{Mo}_{72}\text{V}_{30}\}$  cluster that is soluble in water, the obtained  $\{\text{Mo}_{72}\text{V}_{30}\}$ -Azo complex was insoluble in water but readily dissolved in DMF. The solubility change indicates successful complexation of Azo and  $\{\text{Mo}_{72}\text{V}_{30}\}$ , and the obtained complex has an average chemical formula of  $(\text{Azo})_{32}(\text{VO})_2[\text{K}_{10}\{(\text{Mo})\text{Mo}_5\text{O}_{21}(\text{H}_2\text{O})_3(\text{SO}_4)_{12}(\text{VO})_{30}(\text{H}_2\text{O})_{20}\}]_{10} \times 20\text{H}_2\text{O}$  as determined by elemental analysis.<sup>25</sup>

The presence of sharp and well-separated singlets derived from the *trans/cis* N-methyl group protons of the Azo in  $^1\text{H}$  NMR spectra enabled the determination of the relative amounts of both isomers in the sample. Such analysis was used to follow the *trans*-to-*cis* photoisomerisation kinetics of Azo and  $\{\text{Mo}_{72}\text{V}_{30}\}$ -Azo hybrid upon UV (8 W, 365 nm, 0.34 mW cm<sup>-2</sup>, Herolab GmbH) irradiation in the solution (DMF d-7) state. The  $^1\text{H}$  NMR spectrum of Azo showed that initially only the *trans* form was present, as revealed by the four aromatic signals in the 8.45–7.65 ppm range, and a sharp N-methyl singlet at 3.98 ppm (Fig. S1 in ESI†). The sample was then exposed to UV light before recording the  $^1\text{H}$  NMR spectrum. This procedure was repeated until a photostationary state (PSS) has been reached (see ESI† for details). During UV irradiation, proton signals typical of the *trans* isomer were progressively replaced by five upfield signals at 8.15–6.95 ppm, and a singlet at 3.84 ppm as a consequence of transformation into the *cis* state (Fig. S3). The isomerization into the *cis* isomer reduces the intramolecular distance between aromatic rings,

and slows the rotation around C-N bonds, leading to their mutual shielding, and better separation of the proton signals. Similar irradiation results were obtained for  $\{\text{Mo}_{72}\text{V}_{30}\}$ -Azo complex (Fig. 2), however in this case all signals were slightly broadened and de-shielded. An explanation of this phenomenon should be sought in combined effect of (i) averaging of the resonance frequencies of the Azo moieties in the obtained aggregate,<sup>26</sup> (ii) reduced diffusion rate of the complex in comparison with the unbounded Azo molecules,<sup>27-28</sup> and (iii) magnetic properties of the polyoxometalate.<sup>29</sup>

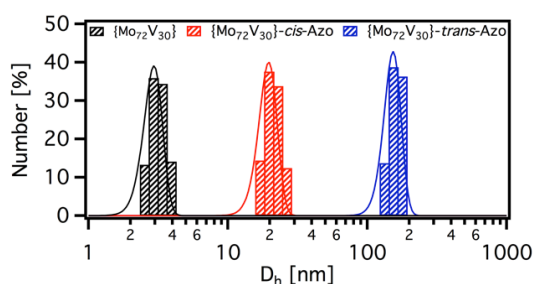


**Fig. 2** Top: Schematic representation of the photoisomerisation reaction. Bottom:  $^1\text{H}$  NMR spectra (300 MHz, DMF d-7) of  $\{\text{Mo}_{72}\text{V}_{30}\}$ -Azo obtained during UV irradiation. a)  $\{\text{Mo}_{72}\text{V}_{30}\}$ -*trans*-Azo before irradiation. b) after 15 min of irradiation at 365 nm (44% *cis*). c) after 30 min of irradiation (63% *cis*). d) Photostationary state reached after 75 min of irradiation. (86% *cis*).

Nevertheless, N-methyl group singlets were observed at 4.31 and 4.12 ppm for the *trans* and *cis* forms, respectively, allowing their precise integration for kinetic studies (sections S5, S6 in ESI†). A significant difference between the NMR spectra of Azo and  $\{\text{Mo}_{72}\text{V}_{30}\}$ -Azo as a function of the irradiation time concerns the actual chemical shift values for the signals attributed to the two isomers. As already noted, the two isomers of the Azo cation are readily distinguished and in the case of the free dye, the chemical shifts of both forms are entirely independent of the photoisomerisation degree, indicating a negligible effect of any association process with this species. On the other hand,  $\{\text{Mo}_{72}\text{V}_{30}\}$ -Azo chemical shifts of the N-methyl singlets vary during the approach to the PSS, this variation being consistently to higher field for the *cis* isomer but involving an initial downfield shift followed by an upfield return for the *trans* isomer (Fig. S7). These continuous changes in chemical shifts suggest, that the ion-ion interaction energy between the negatively charged POM and the cationic surfactant molecules fluctuate during photoisomerisation of the POM-Azo complex as a result of partial photo-reduction of vanadium cores.<sup>30</sup> This leads to an increase in the total negative charge of the polyoxometalate core and simultaneously the energy of the electrostatic attraction with the positively charged moieties. These spectroscopic effects

may also be related to the partial dissociation of the surfactant molecules during isomerisation, since this reaction reduces the total charge of the surfactant layer, at the same time increasing the energy of the interactions between POM and the cations remaining on the surface.

Given that the cation-anion interactions result in a formation of a spherical complex with an aromatic sheath formed by the **Azo** molecules, the resulting complexes may aggregate *via*  $\pi$ - $\pi$  stacking interactions, leading to obtain huge *non*-covalent supramolecules. These interactions were indeed observed on both NMR spectra of  $\{\text{Mo}_{72}\text{V}_{30}\}$ -**Azo** (Fig. S12), as well as in other systems with *trans*-azobenzene dyes deposited on nanoparticles.<sup>18</sup>



**Fig. 3** Dynamic light scattering (DLS) diagrams of  $\{\text{Mo}_{72}\text{V}_{30}\}$  (in  $\text{H}_2\text{O}$ ),  $\{\text{Mo}_{72}\text{V}_{30}\}$ -*trans*-**Azo** and  $\{\text{Mo}_{72}\text{V}_{30}\}$ -*cis*-**Azo** (both in DMF).

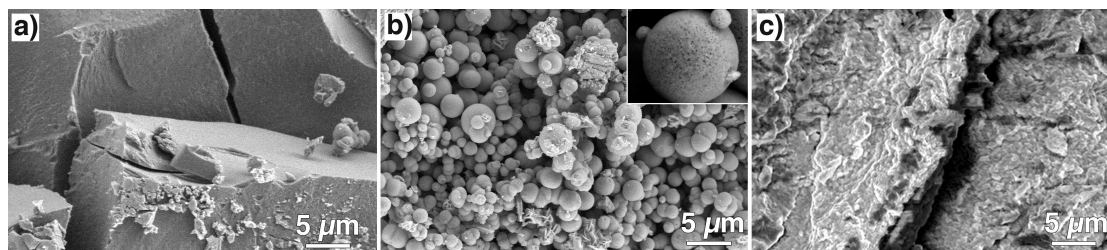
Dynamic light scattering (DLS) results revealed that  $\{\text{Mo}_{72}\text{V}_{30}\}$ -*trans*-**Azo** in DMF is in the assembled state with a hydrodynamic diameter ( $D_h$ ) of ca. 153 nm (Fig. 3). We infer that such self-assembly behaviour of  $\{\text{Mo}_{72}\text{V}_{30}\}$ -**Azo** clusters is primarily governed by  $\pi$ - $\pi$  stacking among *trans*-**Azo** molecules, which acts as a linker between  $\{\text{Mo}_{72}\text{V}_{30}\}$ -**Azo**. Interestingly, upon UV irradiation, the self-assemblies disappear gradually (see Fig. S13 in ESI<sup>†</sup>), and instead, aggregates with  $D_h$  of 19 nm appear. If one considers the theoretical size of  $\{\text{Mo}_{72}\text{V}_{30}\}$ -*cis*-**Azo** (ca. 4.1 nm) combining the average  $D_h$  of  $\{\text{Mo}_{72}\text{V}_{30}\}$  (2.9 nm, Fig. 3)<sup>31</sup> and the length of two cationic **Azo** molecules (ca. 1.2 nm), it is possible to conclude that  $\{\text{Mo}_{72}\text{V}_{30}\}$ -*cis*-**Azo** assemblies are not monodisperse. Such phenomenon can be explained by the fact that in the PSS ca. 86% of **Azo** molecules exist in the *cis* state (see Fig. S6), therefore remaining *trans*-**Azo** molecules can interact *via*  $\pi$ - $\pi$  stacking with other *trans* species from neighbouring clusters. Upon visible light irradiation  $\{\text{Mo}_{72}\text{V}_{30}\}$ -*trans*-**Azo** assemblies

emerge again with a size close to 150 nm (see Fig. S14). Such  $D_h$  changes indicate the assembly and disassembly of  $\{\text{Mo}_{72}\text{V}_{30}\}$ -**Azo** in solution, controlled by irradiation at alternating wavelength.

Scanning electron microscopy (SEM) investigation further corroborates the evidences obtained with DLS results. The morphological changes associated to *trans*-to-*cis* isomerization of **Azo** in the  $\{\text{Mo}_{72}\text{V}_{30}\}$ -**Azo** hybrid were monitored in the solid-state by SEM imaging. Initially, a drop of solution containing  $\{\text{Mo}_{72}\text{V}_{30}\}$  was applied to a Si/SiO<sub>2</sub> substrate and dried under atmospheric conditions. The SEM image shown in Fig. 4a displays a featureless film with some cracks formed during the drying process. Conversely, a film prepared by applying a drop of  $\{\text{Mo}_{72}\text{V}_{30}\}$ -*trans*-**Azo** solution showed the formation of spherical objects with a diameter of ca. 1-2  $\mu\text{m}$  (Fig. 4b), larger than those observed with DLS, most likely due to the further assembly and aggregation of  $\{\text{Mo}_{72}\text{V}_{30}\}$ -*trans*-**Azo** during the solvent evaporation.

On the basis of changes in  $D_h$  and in the NMR spectra, some of the *cis* **Azo** cations formed upon irradiation can be detached from the  $\{\text{Mo}_{72}\text{V}_{30}\}$  surface, most likely due to increased steric hindrance. Indeed, the SEM image obtained after UV irradiation of  $\{\text{Mo}_{72}\text{V}_{30}\}$ -*trans*-**Azo** solution (Fig. 4c) differs from that of  $\{\text{Mo}_{72}\text{V}_{30}\}$ -*trans*-**Azo** (Fig. 4b) and  $\{\text{Mo}_{72}\text{V}_{30}\}$  (Fig. 4a) and indicates formation of a hybrid structure in which *cis*-**Azo** molecules are interacting with  $\{\text{Mo}_{72}\text{V}_{30}\}$  and are adsorbed on the  $\{\text{Mo}_{72}\text{V}_{30}\}$  film, which is consistent with the changes seen in the NMR spectra. Additional details on SEM characterization can be found in ESI.

In conclusion, we have demonstrated that Keplerate-type polyoxomolybdate clusters form stable photoswitchable hybrid materials with azobenzene dyes *via* simultaneous operation of electrostatic and  $\pi$ - $\pi$  stacking interactions. By making use of DLS and NMR spectroscopy, we have shown that  $\{\text{Mo}_{72}\text{V}_{30}\}$ -**Azo** may undergo reversible *trans*-to-*cis* light driven conversions. Finally we demonstrated that the light driven transition between the azobenzene isomers has an impact not only on the local geometry of the coating layer on  $\{\text{Mo}_{72}\text{V}_{30}\}$  surface, but also on the hydrodynamic diameter and global morphology of the obtained system.



**Fig. 4** Scanning electron microscopy (SEM) images of dry films prepared by drop-casting on native silicon oxide a)  $\{\text{Mo}_{72}\text{V}_{30}\}$  before functionalization with **Azo** molecules; b)  $\{\text{Mo}_{72}\text{V}_{30}\}$ -*trans*-**Azo** hybrid structure (inset image 1x1  $\mu\text{m}$ ), c)  $\{\text{Mo}_{72}\text{V}_{30}\}$ -*cis*-**Azo** obtained upon UV-light irradiation (365nm) of the  $\{\text{Mo}_{72}\text{V}_{30}\}$ -*trans*-**Azo** solution prior to drop-casting.

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