

## Electronic Supporting Information (ESI)

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

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## 1. General

All chemicals and solvents were purchased from commercial sources (mainly Sigma-Aldrich) and used without further purification.

NMR Spectra were recorded on Bruker Fourier 300 MHz spectrometer (5 mm 1H/13C probe). NMR solvents were purchased from Euriso-Top or Deutero GmbH, and used as received. All irradiations were performed directly in the Quartz NMR tubes (Deutero GmbH, Qtz500-5-7). Spectra were referenced at solvents residual peaks ( $^1\text{H}$ : DMF *d*-7: quintet 2.92 ppm;  $^{13}\text{C}$ : DMSO *d*-6: 39.52 ppm).

*Trans/cis* isomers ratios were obtained from the integrations of *N*-methyl groups  $^1\text{H}$  signals, and (at higher *cis* isomer concentrations) cross checked with the integrations of the signals from aromatic protons.

The UV-Vis absorption spectra were recorded using Jasco V-650 UV-Vis spectrophotometer, in quartz Suprasil® 1cm optical path length cuvettes (Hellma). The irradiation lamp was a UV lamp with  $\lambda_{\text{max}} = 365$  nm (Herolab 6M/L). For visible light irradiation a halogen lamp (Schott kl200) was used.

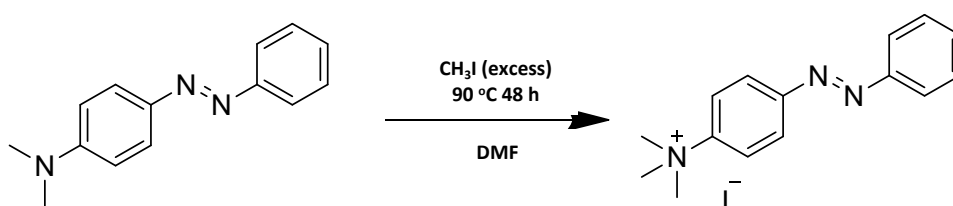
Dynamic light scattering measurements were performed using a Malvern Zetasizer Nano S instrument, equipped with a 630 nm He-Ne laser, with the detector collecting the backscattering signal (173° geometry). Prior to DLS analysis, dispersions were filtrated through PTFE syringe filters with 0.2  $\mu\text{m}$  pore diameter. Filtration was performed in order to prevent the eventual presence of larger particles (*e.g.* dust) from hiding the scattering due by the smallest present in the dispersion (according to Rayleigh theory,  $I \propto d^6$  where *I* equals the intensity of light scattered and *d* the diameter of the particle).

Thermogravimetric (TG) analysis was performed on a Mettler Toledo STAR System TGA/DSC 2 instrument with a heating rate of 10  $^\circ\text{C min}^{-1}$  under flowing air.

## 2. NMR Sample preparation details

Given mass of **Azo**, and  $\{\text{Mo}_{72}\text{V}_{30}\}$ -**Azo** adduct were placed in NMR tubes, and the tubes were backfilled with argon. In dark room, 500  $\mu\text{l}$  of dimethylformamide *d*-7 was added via syringe, and the sample was carefully shaken until full dissolution was obtained. After the blank spectra were recorded. Samples were irradiated directly in the NMR tubes, by placing them 2 cm below 4 W 365 nm UV-lamp. After irradiation, the tube was put imminently into the NMR magnet, and the spectra were taken. To obtain repetitive line shapes, and intervals in irradiation/record times, autoshim protocol (Bruker gradshim 1d2h) were used.

## 3. Azo synthesis



Into the Schlenk tube *trans*-*N,N*-dimethyl-4-(phenyldiazenyl)aniline (225 mg, 1.00 mmol), methyl iodide (1 ml, excess), and DMF (4 ml) were added. The mixture obtained were stirred and heated at 90 °C for 48 h. After, the excess of methyl iodide were evaporated, the residue solution was added dropwise into 50 ml of diethyl ether in the ultrasonic bath. 334 mg (Yield=91%) of *trans*-*N,N,N*-trimethyl-4-(phenylazo)benzenammonium iodide were obtained as a yellowish brown powder.

$^1\text{H NMR}$  (300 MHz, DMF *d*-7)  $\delta$  8.43 (d,  $J = 9.3$  Hz, 2H), 8.17 (d,  $J = 9.3$  Hz, 2H), 8.06 – 7.95 (m, 2H), 7.75 – 7.63 (m, 3H), 3.99 (s, 9H).  $^{13}\text{C NMR}$  (75 MHz, DMSO)  $\delta$  151.97, 151.73, 148.67, 132.44, 129.64, 123.59, 122.90, 122.17, 56.52. ESI MS Calc: 240.1495; Found[M] $^+$  : 240.1511.

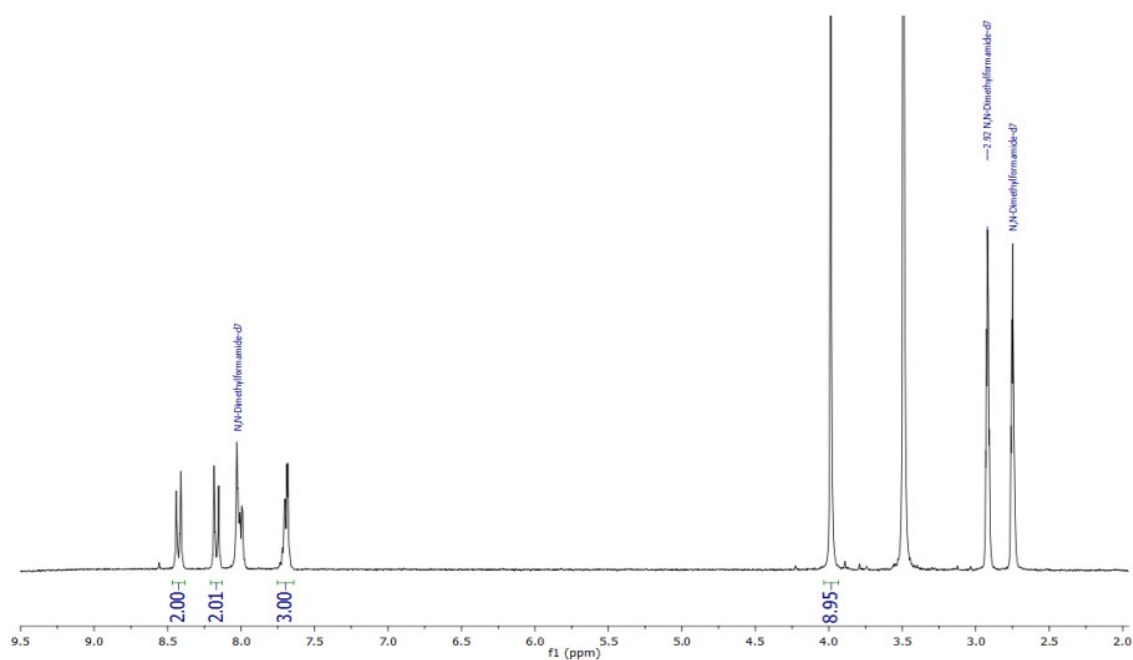


Figure S1.  $^1\text{H NMR}$  (300 MHz, DMF *d*-7) spectrum of Azo.

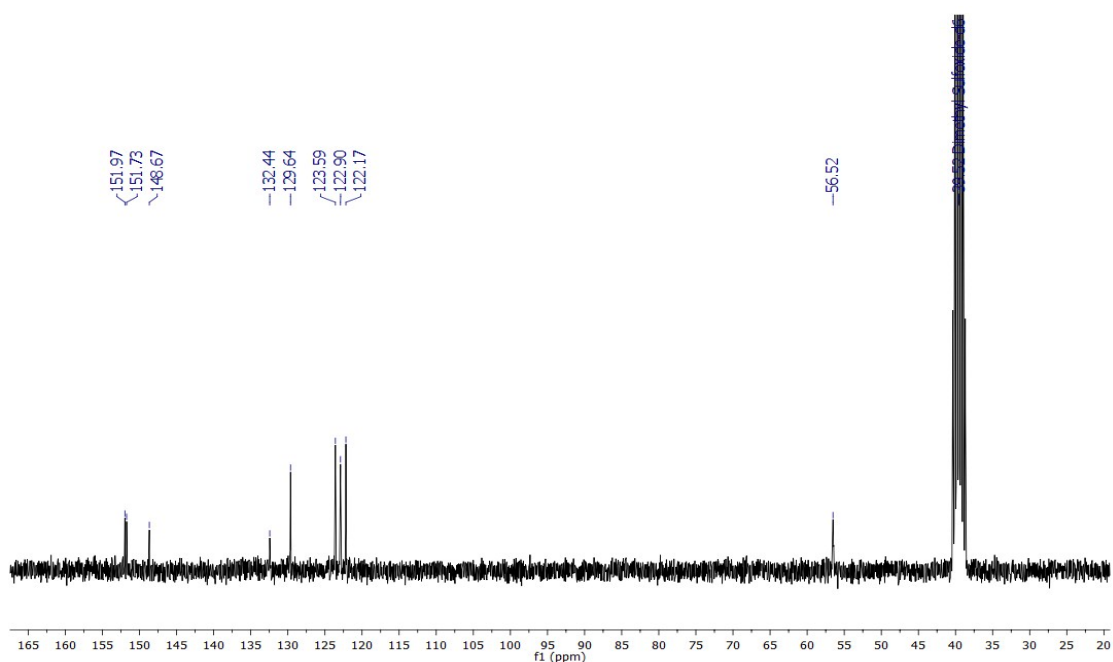


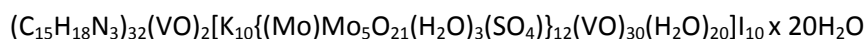
Figure S2.  $^{13}\text{C}$  NMR (75 MHz, DMSO *d*-6) spectrum of **Azo**.

#### 4. $\{\text{Mo}_{72}\text{V}_{30}\}$ -**Azo** synthesis

$\{\text{Mo}_{72}\text{V}_{30}\}$  was synthesised according to the procedure previously reported by Müller and co-workers.<sup>1</sup> 100 mg of precursor  $\text{Na}_8\text{K}_{14}(\text{VO})_2[\text{K}_{10}\{(\text{Mo})\text{Mo}_5\text{O}_{21}(\text{H}_2\text{O})_3(\text{SO}_4)\}_{12}(\text{VO})_{30}(\text{H}_2\text{O})_{20}\} \cdot \approx 150\text{H}_2\text{O}$   $\{\text{Mo}_{72}\text{V}_{30}\}$  were dissolved in water (10 ml) to give dark violet solution. To this solution was added an excess of *trans*-N,N,N-trimethyl-4-(phenylazo)benzenammonium iodide (**Azo**) (200 mg) solubilised in chloroform (10 ml) under vigorous stirring during 3 hours at room temperature. After decantation and addition of absolute ethanol (about 40 ml) the precipitation of the target compound as a dark powder which was isolated by filtration, washed with ethanol and dried in air. (m=178 mg, yield 89%).

The charge density of POM macroions often cannot be easily tuned to desired values from synthesis.  $\{\text{Mo}_{72}\text{V}_{30}\}$  is a type of spherical "Keplerate" with 26 inherent charges. Each  $\{\text{Mo}_{72}\text{V}_{30}\}$  can partially deprotonate the water ligands (~5 of each cluster) and theoretically carries (in very diluted solution) ~31 charge on average, with the counterions including  $\text{K}^+$ ,  $\text{VO}^{2+}$  and also with surfactants.<sup>2</sup> Following this line of thought we proposed formula of  $\{\text{Mo}_{72}\text{V}_{30}\}$ -**Azo** using iodide anions as counterions. We obtained a stoichiometric ratio of **Azo** :  $\{\text{Mo}_{72}\text{V}_{30}\} = 32 : 1$ .

Expected formula of  $\{\text{Mo}_{72}\text{V}_{30}\}$ -**Azo** :



Elemental analysis:

Calculated: C 23,02 H 2,97 N 5,37

Found: C 23,02 H 2,82 N 4,99

Organic elemental analysis (C,H,N) was done by following standard procedure using Thermo Scientific FLASH 2000 HT/IRMS Analyzers.

## 5. NMR analysis

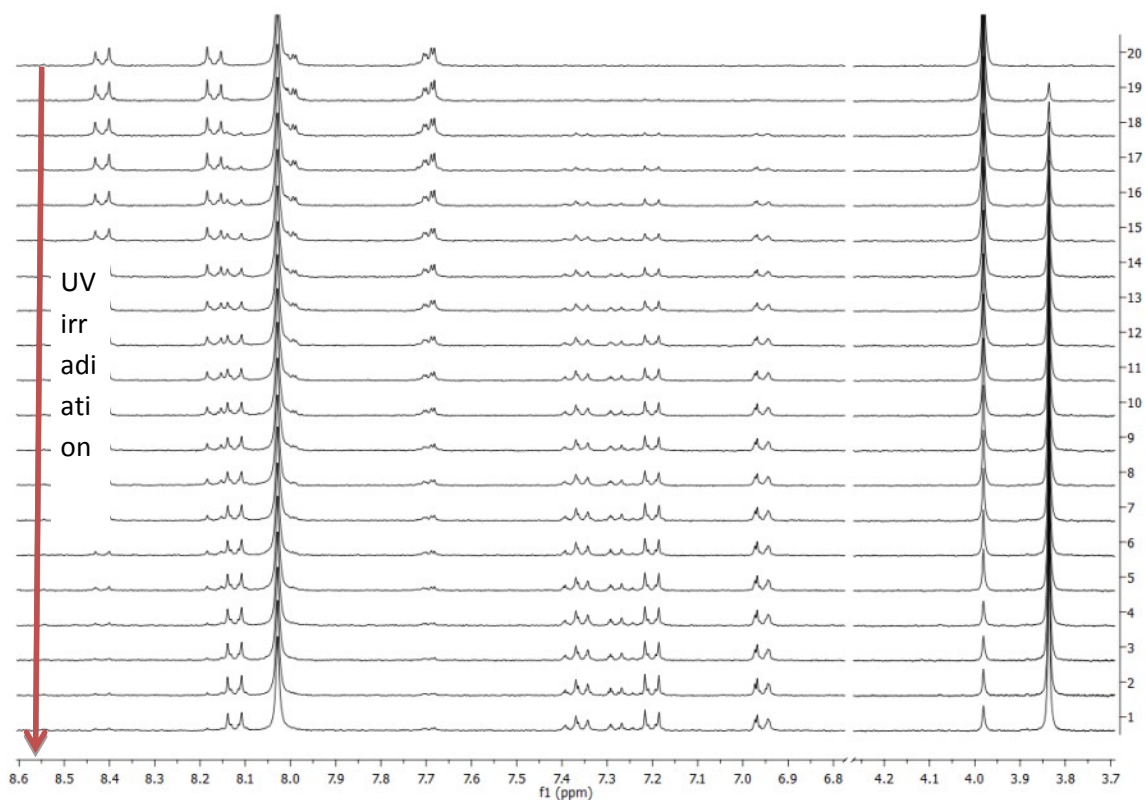


Figure S3.  $^1\text{H}$  NMR (300 MHz, DMF  $d_7$ ) UV (365 nm) irradiation stacked spectra of Azo (0.5 mg/ml).

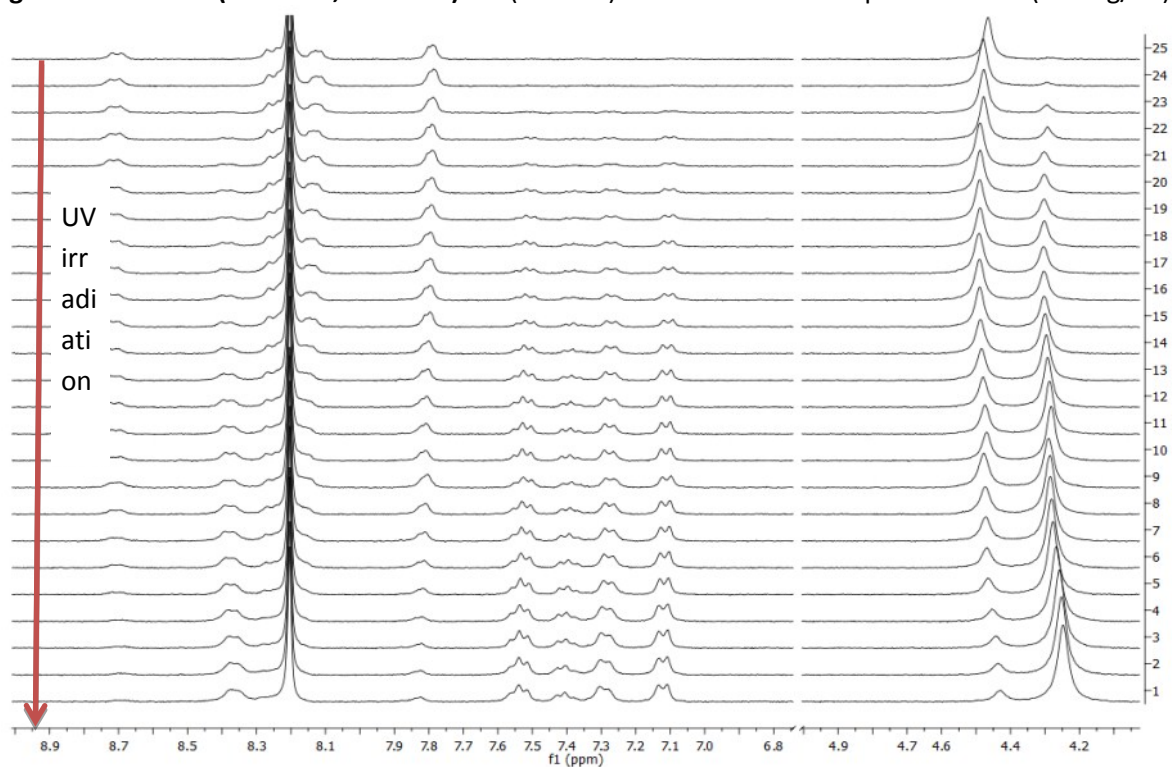
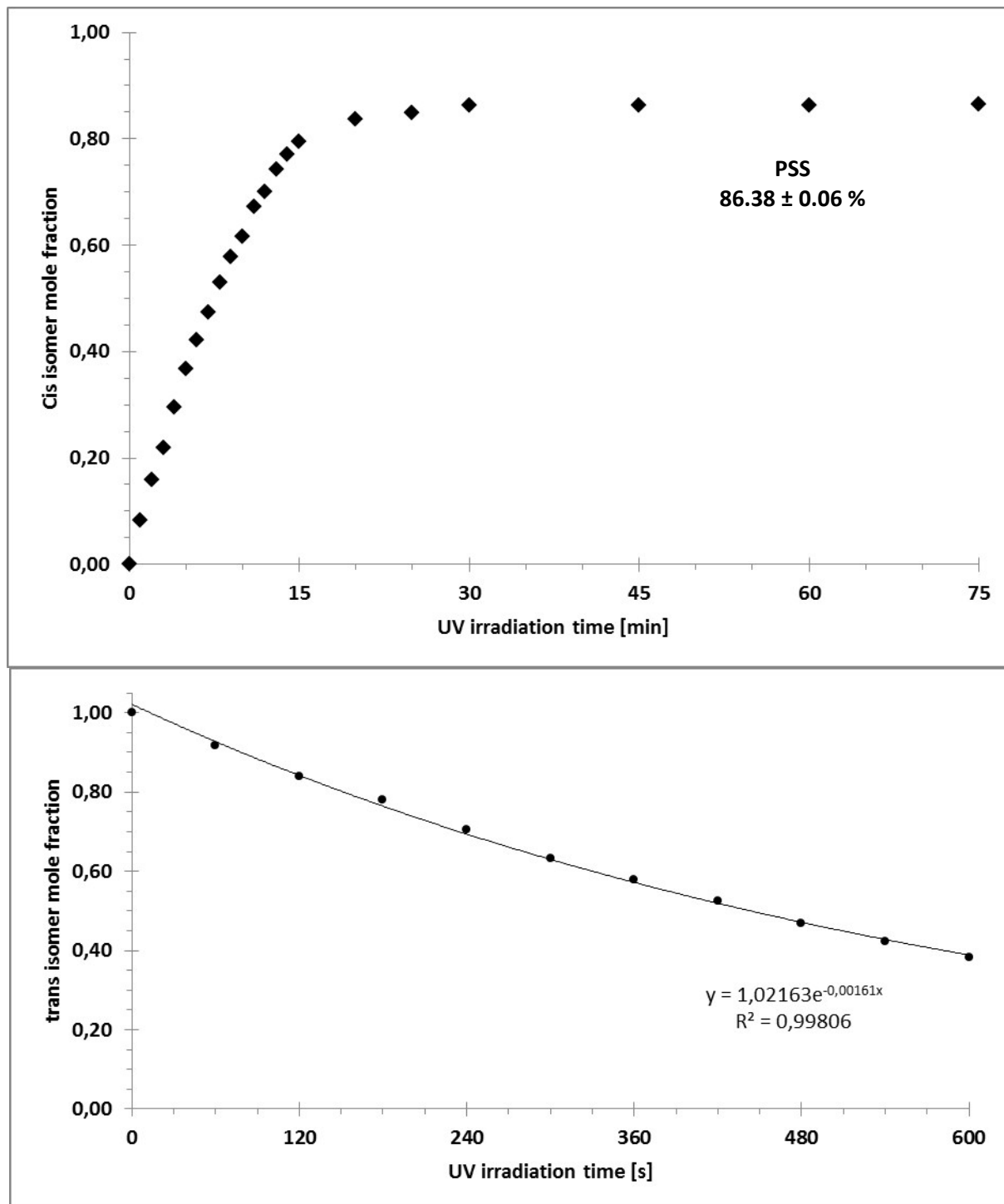
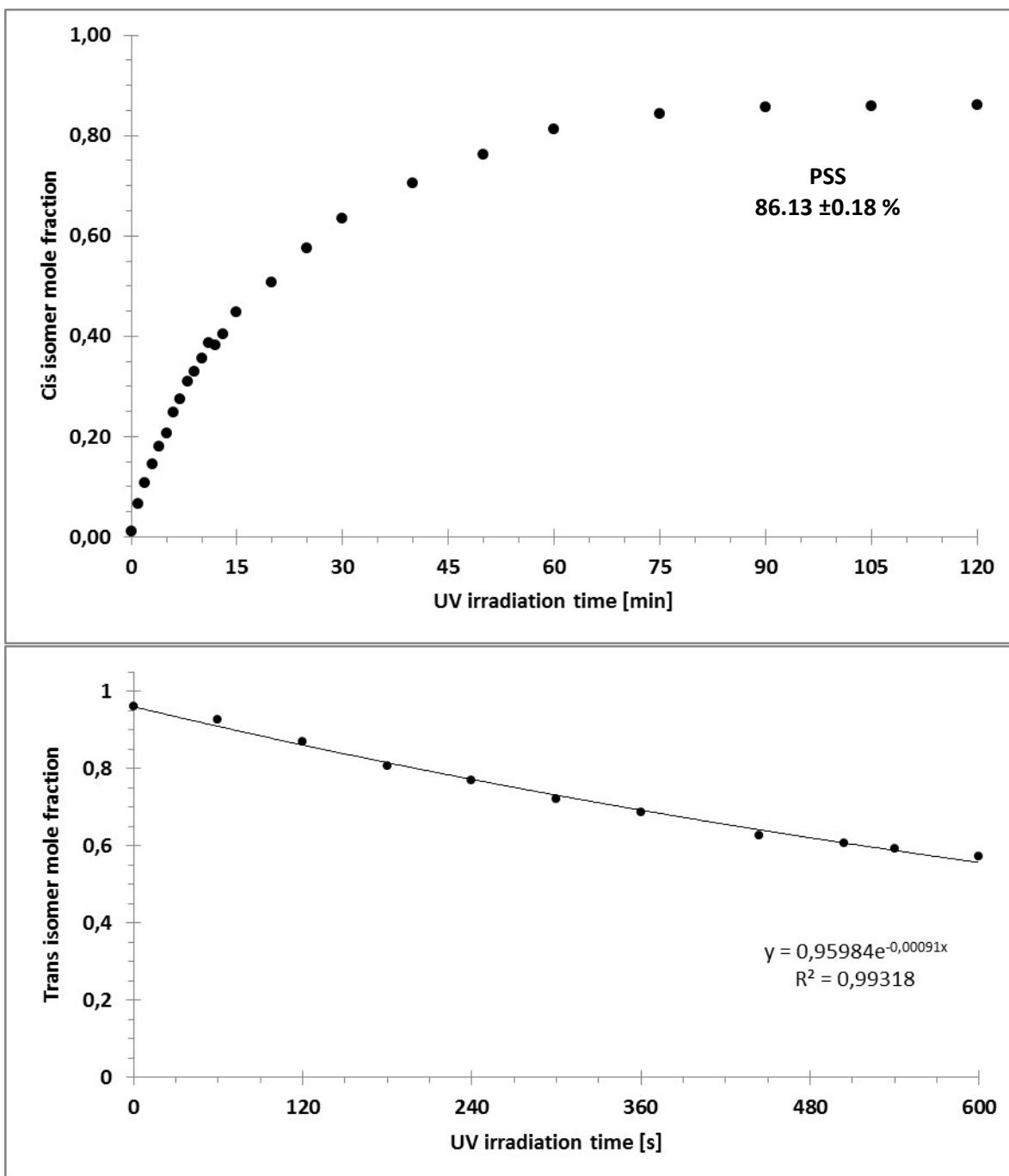


Figure S4.  $^1\text{H}$  NMR (300 MHz, DMF  $d_7$ ) UV (365 nm) irradiation stacked spectra of POM-Azo (4 mg/ml).

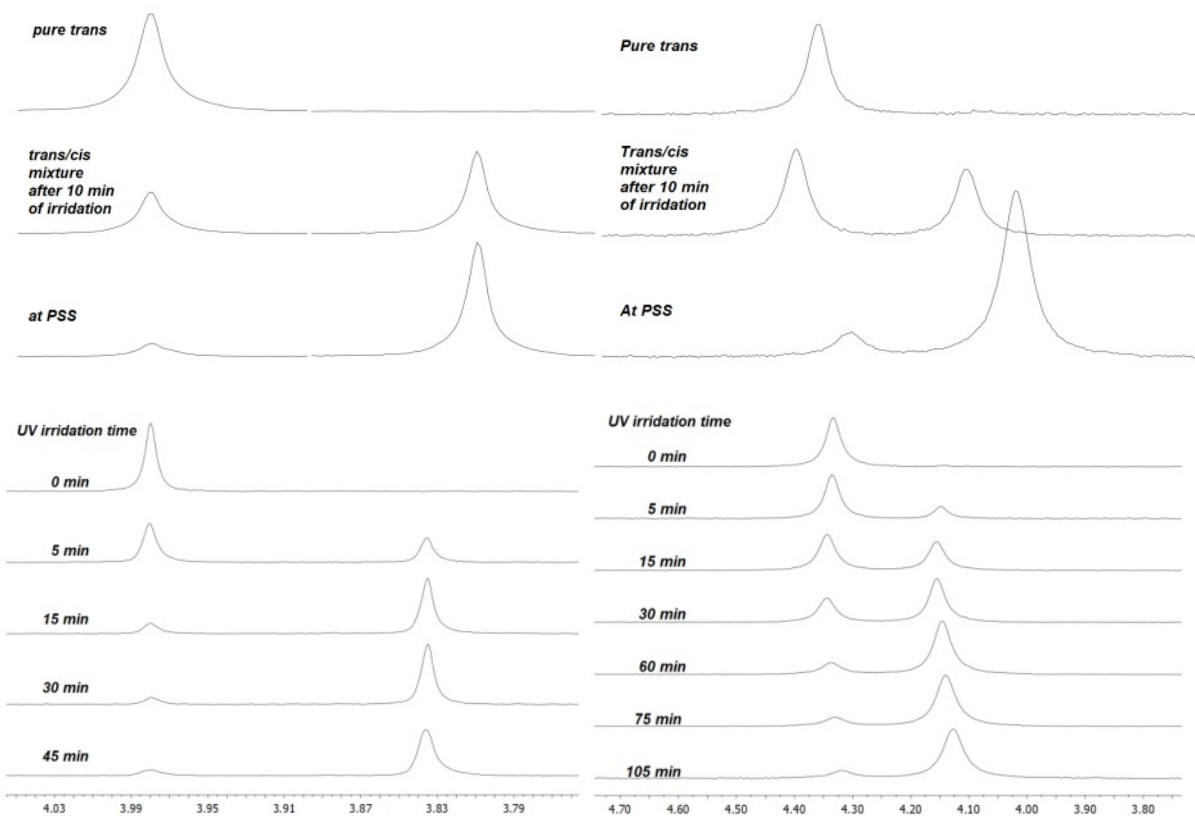
*Trans* isomer concentrations obtained during irradiation (first 10 min. of irradiation, were fitted to an exponential decay, consistent with first order kinetics. *Trans*-to-*cis* conversion for free **Azo** was found to be ca. two times faster than the same conversion conducted on the POM surface ( $k_{\text{Azo}} = 1.61 \times 10^{-3} \text{ s}^{-1}$  and  $k_{\{\text{Mo}_{72}\text{V}_{30}\}\text{-Azo}} = 0.91 \times 10^{-3} \text{ s}^{-1}$ ). Nonetheless, both photostationary states, i.e. **Azo** and POM-**Azo** hybrid are both composed of 86% of *cis* isomer (Fig. S5, S6).



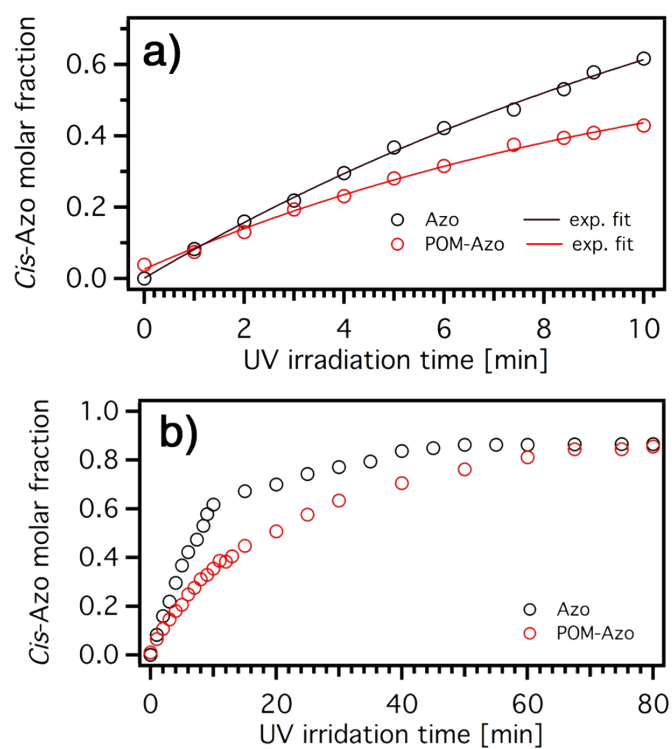
**Figure S5.** Azo photoisomerisation kinetics plots **Top:** long time kinetics with PSS value. **Bottom:** Short time kinetics with  $k$  value obtained from exponential regression line.



**Figure S6.** {Mo<sub>72</sub>V<sub>30</sub>}-Azo photoisomerisation kinetics plots. **Top:** long time kinetics with PSS value. **Bottom:** Short time kinetics with *k* value obtained from exponential regression lines.



**Figure S7.** Comparison of the <sup>1</sup>H NMR shifts (N-methyl groups) during UV irradiation. **Left: Azo**  
**Right: {Mo<sub>72</sub>V<sub>30</sub>}-Azo.**

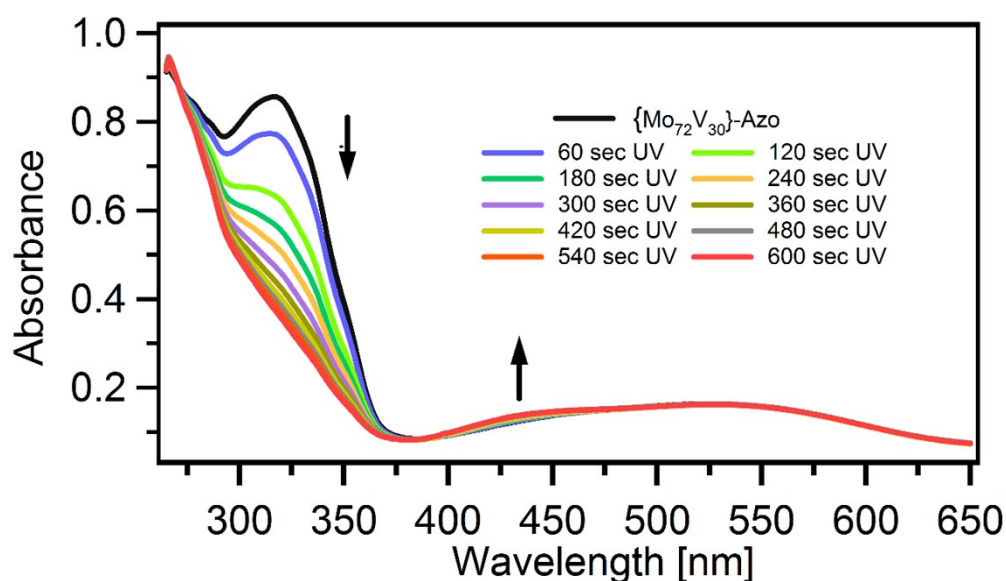


**Figure S8.** a) Short-time <sup>1</sup>H NMR photoisomerization kinetic plots obtained for **Azo** and {Mo<sub>72</sub>V<sub>30</sub>}-**Azo**; b) long-time photoisomerization kinetic plots showing the PSS.

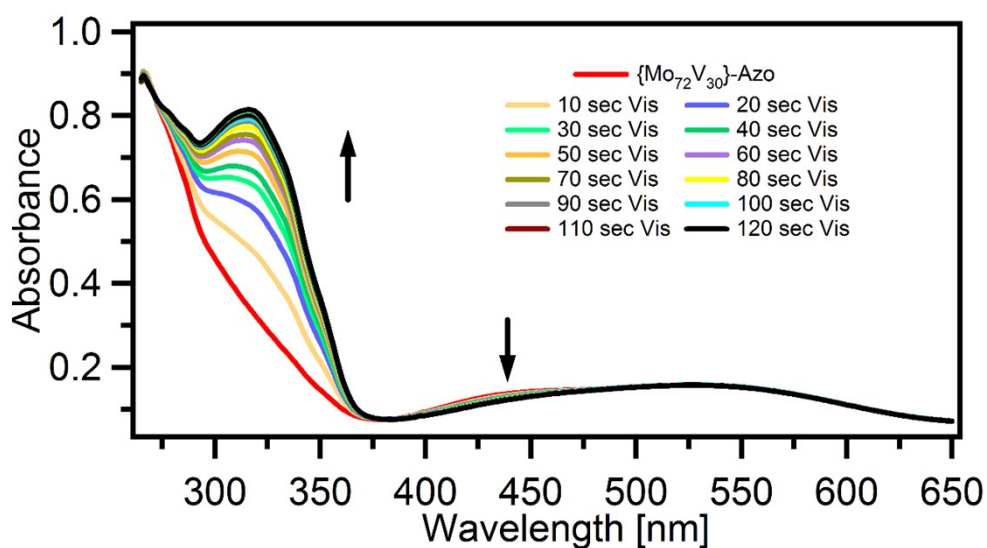


## 6. UV-Vis analysis

Further assessment of the photoisomerisation reaction was based on spectrophotometric measurements involving lower concentrations than those used for NMR spectroscopy and thus being less affected by aggregation between the nanoparticles. Similar estimations of the rate constants were obtained, nonetheless. Previous studies<sup>3</sup> on the isomerization of azobenzene dyes in the presence of light showed that the reaction follows first-order kinetics. Spectra were taken during UV (Fig. S9) and white light (Fig. S10) irradiation of the **Azo** and {Mo<sub>72</sub>V<sub>30</sub>}-**Azo** solutions in DMF. As in the NMR measurements, *trans*-to-*cis* conversion for free **Azo** was found to be ca. twice as fast as the conversion of **Azo** molecules in the {Mo<sub>72</sub>V<sub>30</sub>}-**Azo** complex, where the individual *k* values were:  $k_{1\text{Azo}} = 7.6 \times 10^{-3} \text{ s}^{-1}$  and  $k_{1\text{POM-Azo}} = 4.4 \times 10^{-3} \text{ s}^{-1}$ .

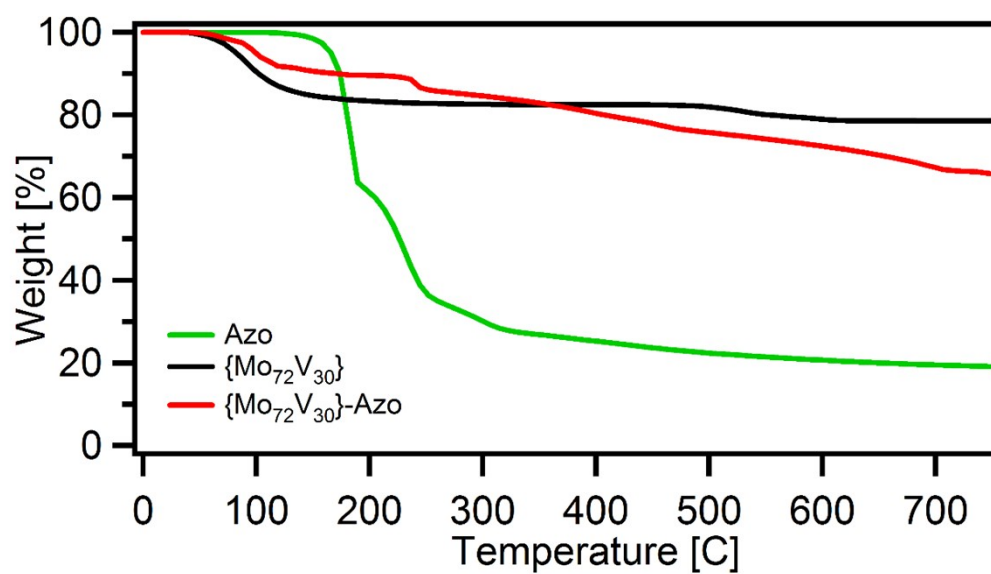


**Figure S9.** UV-Vis spectra of the {Mo<sub>72</sub>V<sub>30</sub>}-**Azo** *trans*-to-*cis* conversion upon UV irradiation: black line, before irradiation with UV light at 365 nm.



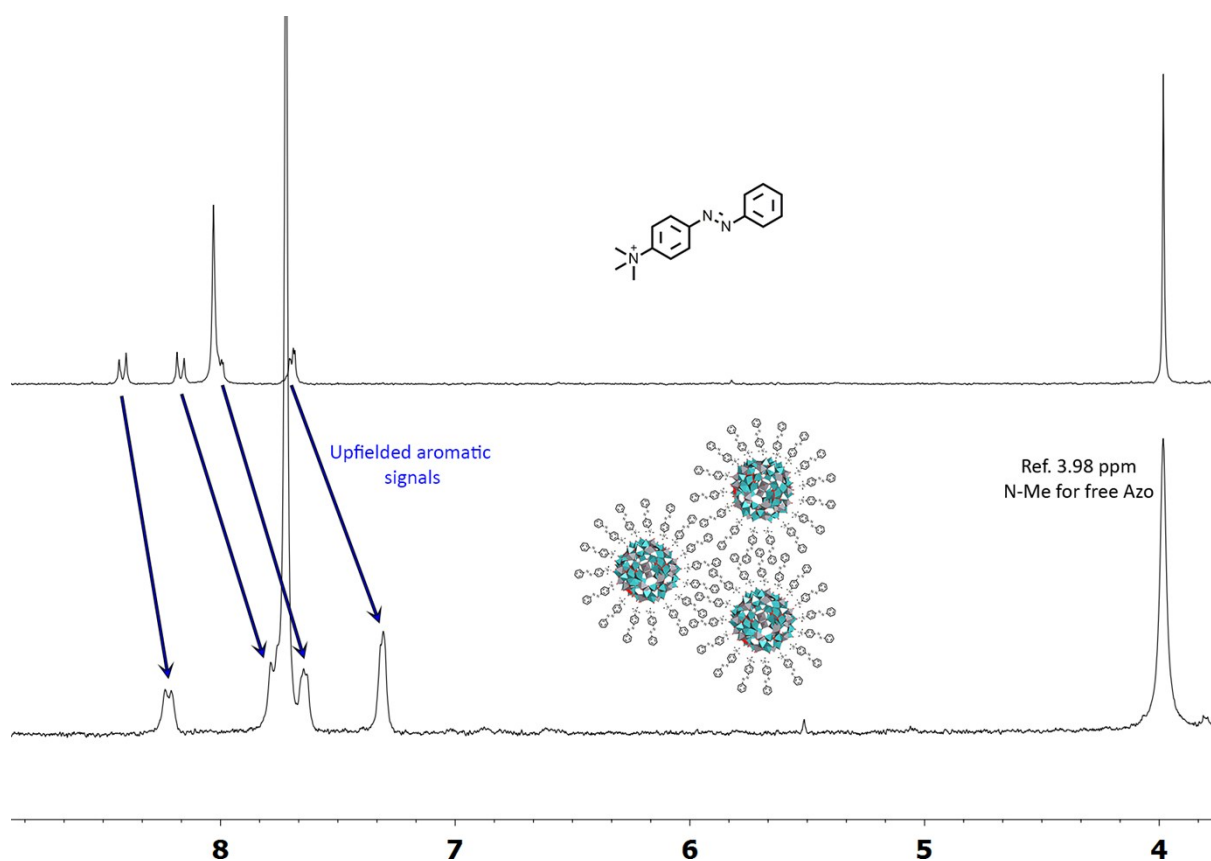
**Figure S10.** UV-Vis spectra of the {Mo<sub>72</sub>V<sub>30</sub>}-**Azo** *cis*-to-*trans* conversion upon visible light irradiation.

## 7. TGA analysis



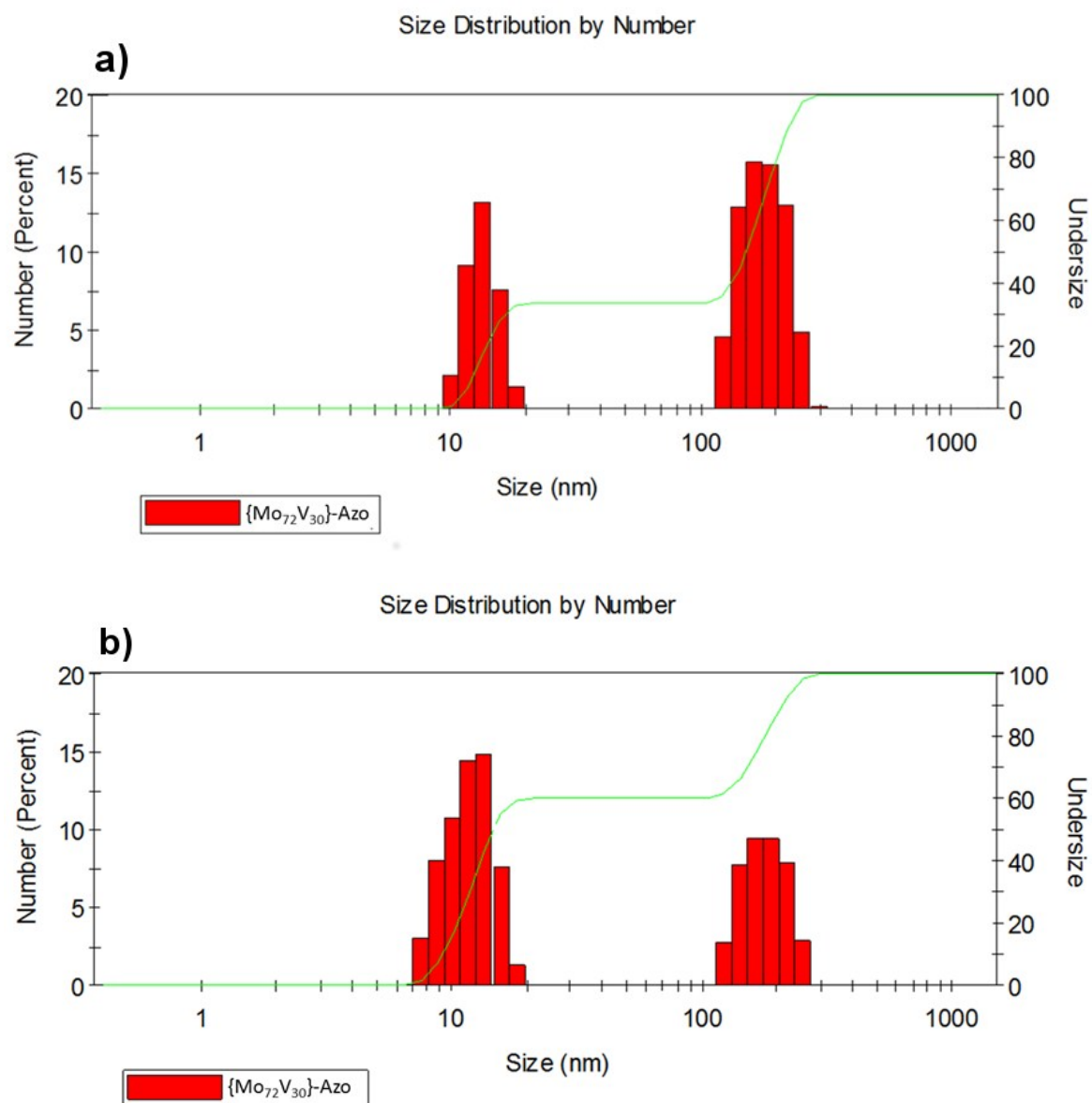
**Figure S11.** TGA analysis of {Mo<sub>72</sub>V<sub>30</sub>}-Azo, {Mo<sub>72</sub>V<sub>30</sub>} and Azo (blanks), heating rate 10 °C/min.

## 8. π-π stacking confirmation

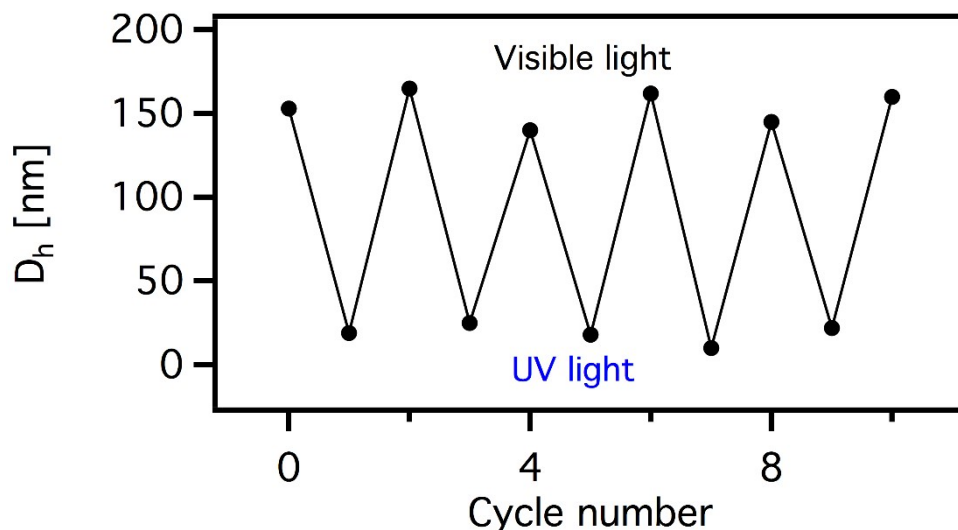


**Figure S12.** Top: <sup>1</sup>H NMR (300 MHz DMF d-7) spectrum of free Azo. Bottom: <sup>1</sup>H NMR (300 MHz DMF d-7) spectrum of {Mo<sub>72</sub>V<sub>30</sub>}-Azo. Upfielded aromatic signals typical for π- stacking systems.

## 9. Dynamic light scattering measurements



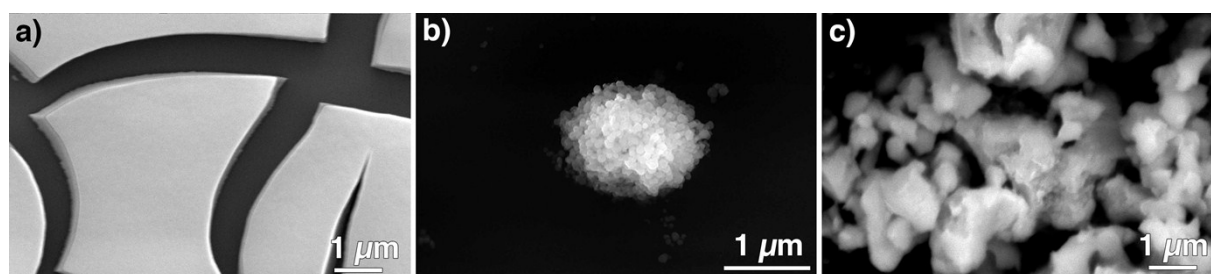
**Figure S13.** Dynamic light scattering (DLS) diagrams of  $\{Mo_{72}V_{30}\}$ -*trans*-Azo after a) 3 min b) 6 min irradiation with UV light.



**Figure S14.** Plot of the hydrodynamic diameter ( $D_h$ ) of  $\{\text{Mo}_{72}\text{V}_{30}\}$ -**Azo** upon ten cycles of alternate irradiations with UV and visible light.

## 11. Scanning Electron Microscopy analyses

The SEM characterization discussed in the Main Text has been carried out by analysing samples prepared by deposition of non-filtered dispersions on native silicon oxide. As discussed in the DLS section, the DLS analysis has been carried out on the filtered solutions, therefore we have performed additional studies, where the filtered dispersions have been used for sample preparation and the results are shown in Figure S15:



**Fig. S15** Scanning electron microscopy (SEM) images of dry films prepared by drop-casting filtrated (filters with 0.2  $\mu\text{m}$  pore diameter) solutions 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, 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.

We have observed that the morphology of  $\{\text{Mo}_{72}\text{V}_{30}\}$  films is identical for the films prepared from non-filtered and filtered solutions. In the case of  $\{\text{Mo}_{72}\text{V}_{30}\}$ -*trans*-**Azo** hybrid structures, the observed structures obtained from filtered solutions slightly differ from those prepared from non-filtered ones, 1  $\mu\text{m}$  aggregates composed of ca. 100 nm particles are observed, which is in a good accordance with DLS results. Films of  $\{\text{Mo}_{72}\text{V}_{30}\}$ -*cis*-**Azo** obtained upon UV-light irradiation (365 nm) of the  $\{\text{Mo}_{72}\text{V}_{30}\}$  -

*trans-Azo* filtrated solution prior to drop-casting revealed the formation of different type of aggregated structures.

## 12. References

1. A. Müller, A. M. Todea, J. van Slageren, M. Dressel, H. Bogge, M. Schmidtman, M. Luban, L. Engelhardt and M. Rusu, *Angew. Chem. Int. Ed.*, 2005, **44**, 3857-3861.
2. B. Doughty, P. C. Yin and Y. Z. Ma, *Langmuir*, 2016, **32**, 8116-8122.
3. A. Airinei, N. Fifere, M. Homocianu, C. Gaina, V. Gaina and B. C. Simionescu, *Int. J. Mol. Sci.*, 2011, **12**, 6176-6193.