Electronic Supporting Information

Photoactive hexanuclear molybdenum nanoclusters embedded in molecular organogels

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Experimental Section

Materials and methods. Steady-state emission of the samples was recorded with a Varian Cary-Eclipse spectrofluorometer. For measurements of gel samples hot solutions were introduced into quartz cells before cooling at room temperature. After the gel formation, the emission was recorded setting the excitation at 400 nm (aerated solutions). Photoluminescence quantum yields (PLQY) were measured with a Hamamatsu C9920-02 integrating sphere. Confocal laser scanning microscopy (CLSM) was performed on an inverted confocal microscope Leica TCS SP8. Images were obtained with an HCX PL APO CS 63x/0.40 OIL objective. Excitation of samples was done with an argon laser (488 nm) and images were acquired with a PMT detector. The gels were observed directly on sterilized Ibidi m-Slide 8 Well Glass Bottom: # 1.5H (170 mm 5 mm) Schott glass. Transmission electron microscopy (TEM) measurements were performed with a JEOL JEM 1010 (100 kV) apparatus at the University of Valencia. Scanning Transmission Electron Microscopy (STEM) and Energy Dispersive X-ray Spectroscopy (EDS) measurements were performed with a JEOL JEM 2100F (200 kV) apparatus at the Polytechnic University of Valencia.

Preparation of gels. Gel without cluster: organogelator **2** (10 mg) was placed in a vial and then 2 mL of DCM were added (same procedure for toluene gels). The mixture was heated till dissolution and afterwards it was left to cool to room temperature (10 min.). The formation of the gel was checked by turning the vial upside down (no flow of the fluid was observed). Gel with cluster: organogelator **2** (10 mg) was placed in a vial and then 1 mL of DCM and 1 mL of a stock solution of cluster **1** in DCM (0.12 mg/mL) were added. The mixture was heated till dissolution and afterwards it was left to cool to room temperature (10 min.). Final concentration of **1** is 0.06 mg/mL for the steady state emission measurements and for the photochemical reactions. For TEM, STEM, EDS, PLQY and CLSM a higher concentration of stock of **1** was used in such a way that the final concentration of cluster was 0.5 mg/mL. **Photochemical reactions.** Photochemical reactions were performed inside quartz cells containing the gel formed as described above but a solution of DMA 0.1 mM in DCM was used instead of pure DCM.

Irradiations were carried out using two LED lamps (11 W each, Lexman, ca. 400–700 nm emission output; the irradiance of this setup was measured with a Delta Ohm HD 2302.0 photoradiometer resulting an average fluence rate of 15.6 mW/cm²) placed 1 cm away from the quartz cell (same procedure for toluene gels). The evolution of the photoreactions was monitored over time by means of UV-vis absorption spectrophotometry (decrease of absorbance at 376 nm (DMA) or at 330 nm (DHN)). The initial points of the kinetic traces were fitted to a pseudo-first order model (In C/C₀ = - k_{obs} ·t, where C is the concentration of DMA or DHN at a certain time t and C₀ is the initial concentration of DMA or DHN).

Synthesis of 1. See details in the literature.¹

Synthesis of 2. See details in the literature.²

¹ Mikhailov, M. A.; Brylev, K. A.; Abramov, P. A.; Sakuda, E.; Akagi, S.; Ito, A.; Kitamura, N.; Sokolov, M. N., *Inorg. Chem.* **2016**, *55*, 8437-8445.

² Torres-Martínez, A.; Angulo-Pachón, C. A.; Galindo, F., Miravet, J. F., *Soft Matter* **2019** DOI: 10.1039/C9SM00252A



Figure S1. UV-vis absorption measurements of the light scattering produced by the dichloromethane gels at 800 nm, in order to obtain the melting temperatures (Tg). Conditions: [1] = 14.6 mM (5 mg/mL), [2] = 0.03 mM (0.06 mg/mL).



Figure S2. Chromatic coordinates of materials made with **2** doped with **1**: gel (left) and xerogel (right). Conditions for dichloromethane gel: [2] = 14.6 mM (5 mg/mL), [1] = 0.25 mM (0.5 mg/mL). Xerogel material was prepared allowing gel to evaporate.



Figure S3. Pictures of xerogel (from dichloromthane gel) made with **2** and **1** (see conditions in Figure S4). Picture *a* is under visible light, and pictures *b* and *c* are under 365 nm excitation.



Figure S4. Additional TEM pictures.



Figure S5. Additional STEM pictures.





Figure S6. EDS analysis (part 1 of 2).





Figure S7. EDS analysis (part 2 of 2).

500nm