Octahedral Molybdenum Cluster-Based Single Crystals as Fabry–Pérot Microresonators

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Supporting Information Placeholder

ABSTRACT: Single crystals built-up from octahedral Mo_6 cluster units, with appropriate geometry and size, constitute Fabry-Pérot type optical microcavities with well-defined resonances. Such resonances appear in the VIS-NIR range when performing optical transmittance (OT) or photoluminescence (PL) measurements. They strongly depend on the crystal thickness and on the optical constants of the material, specifically the real and the imaginary parts of the refractive index. In this work, the accurate measurement of the crystal thickness is used for the determination of the optical constants by means of a fitting process, and the preferred orientation of the crystals was determined by X-ray diffraction. **KEYWORDS:** cluster; molybdenum; single crystal; optical cavities; resonance modes

In the last decades, octahedral molybdenum clusters have attracted increasing attention from the scientific community due to their intrinsic photophysical and redox properties. These clusters are found in complexes with general formula $[Mo_6X^i_8L^a_6]^n$ ($-2 \leq n \leq 4$), where X^i are inner halide ligands and L^a correspond to organic or inorganic apical (or terminal) ligands. These clusters have outstanding optical properties such as absorption of light in the UV-visible range, bright emission in the red/near IR region with high quantum yields and PL lifetimes up to several hundreds of microseconds.[1–4] It is also well-known that these clusters act as efficient photosensitizers in processes related to the generation of singlet oxygen. These properties make these inorganic compounds particularly attractive in design of functional hybrid nanomaterials with potential applications in nanoarchitectonics,[5,6] optoelectronics,[7–20] lighting,[21] hydrogen storage,[22] biomedicine,[4,23–32] and catalysis.[33–44] Surprisingly, only scarce studies about the optical and electronic properties of octahedral molybdenum cluster-based materials at the single crystal level and at the micrometer scale are reported, and those are limited to $Cs_2[Mo_6X^i_8X^a_6]$ (X = Cl, Br, I) compounds.[45–51]

Getting single crystals at the micrometer and nanometer scales is advantageous for device manufacturing in the development of high-efficiency solar cells, photonic and optoelectronic devices, sensors and photocatalysts. The difficulties of growing bigger crystals are avoided and a low defect density and interferences from the grain boundaries are expected. One area of great interest for applications in optics and sensing is the use of single crystal materials as Fabry-Pérot microresonators. Fabry–Pérot cavities are fundamental and ubiquitous optical elements frequently used in many important devices, such as lasers or narrowband wavelength filters in spectrometers.[52–57] In this sense, it is crucial to study deeply the intrinsic optical properties of molybdenum cluster-based materials at the single crystal level. While the molybdenum cluster composition determines the refractive index, the shape of crystals provides the type of attainable optical modes. Both, a high refractive index and a geometry with parallel facets are expected to favor the appearance of Fabry-Pérot resonances. As far as we know, the refractive index of octahedral-based cluster materials was only reported twice: first, for immobilized $[Mo_6I^i_8]^{4+}$ cluster cores onto *p*- and *n*-doped Si(111) surfaces through complexation by a pyridine-terminated organic monolayer previously covalently bound to hydrogen-terminated Si(111).[58] In that study, an increase of the real part of the refractive index (*n*) of the pyridine-terminated Si(111) monolayer was observed after the molybdenum cluster immobilization (from 1.67 ± 0.03 to 1.79 ± 0.02, respectively). The Brewster angle technique was also used to determine the real part of the refractive index at 650 nm of a polydimethylsiloxane (PDMS) doped with 2 wt% of $[Mo_6I_8(OCOC_2F_5)_6]^{2-}$ cluster anion and 0.5 wt% of a blue green emissive organic luminophore.[9] In this case, the increase of n from 1.42 up to 1.48 upon doping allows waveguiding propagation under perpendicular or longitudinal excitation of the emitted white light in a silica microfiber containing the doped polymer.

We have previously reported the synthesis of $(H_3O)_2[Mo_6Br^i_8(OH)^a_6]\cdot 10H_2O$ (**MC**) single crystals by hydrolysis of the $(TBA)_2[Mo_6Br^i_8F^a_6]$ (TBA = tetrabutylammonium) precursor.[42] The chemical composition was confirmed by XPS and EDX-SEM analyses. The Raman spectrum showed the characteristic band shifts of the Mo_6 cluster based unit. The structure of **MC** was determined by single crystal X-ray diffraction. It crystallizes in the *R*-3*m* space group (N°166) with the following unit cell parameters: a = 15.2455(8) Å, c = 11.1440(8). Schematically, the structure can be depicted as the stacking of $[Mo_6Br^i_8(OH)^a_6]^{2-}$ cluster units according to a A-B-C-A mode. Water molecules are ordered and located within the voids generated by the cluster units stacking. It is worth noting that a strong hydrogen-bond network develops between the clusters and the water molecules.[15] The latter is magnified by the presence of protons that counter balance the charge of the cluster unit. They are statistically shared by apical hydroxyl groups between adjacent clusters leading to protonic conductivity. This crystalline material remains, till nowadays, as the highest ac-

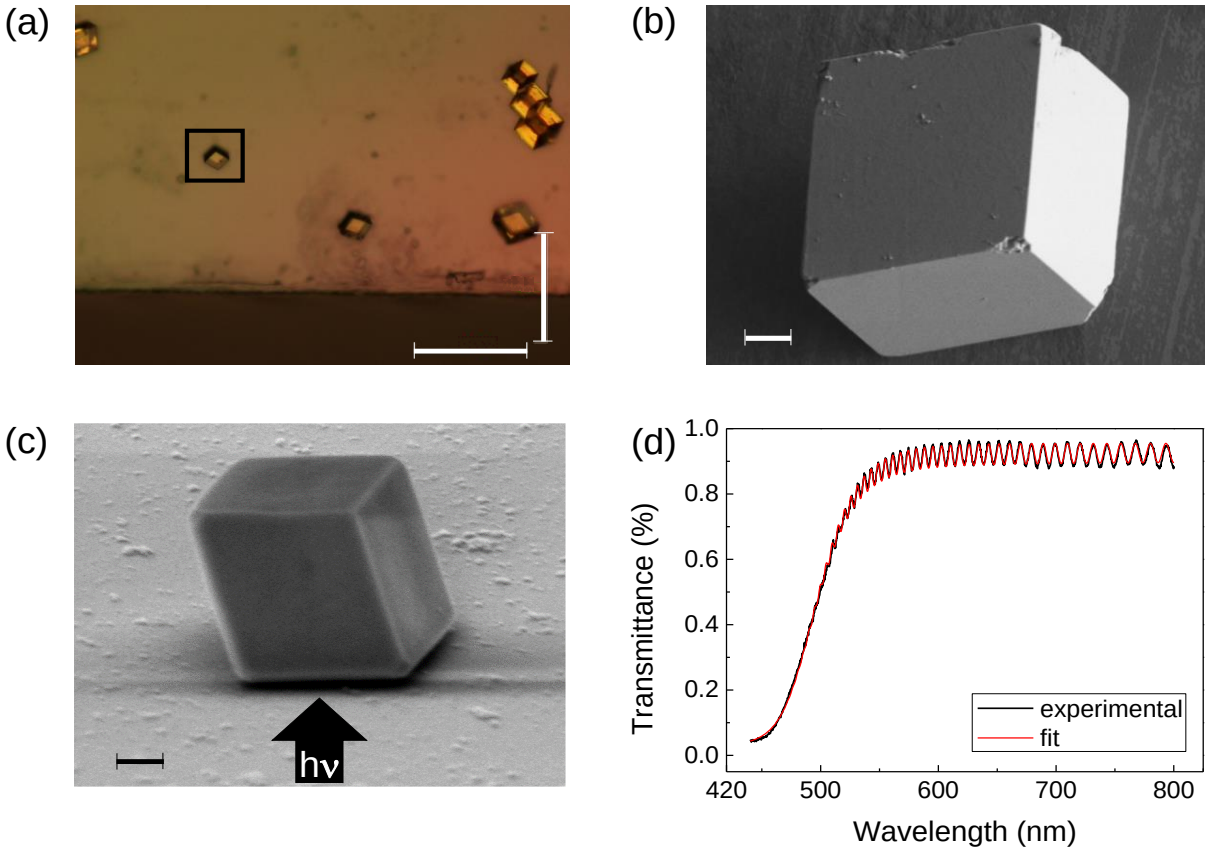

Figure 1. Optical microscopy of several crystals of **MC** deposited on a glass substrate (a), FESEM images of the top view (b) and cross-sectional view (c) of two crystals, and experimental and fitted OT spectra (d) of the selected crystal in (a) measured in the direction indicated by the arrow in (c). Scale bars in a): 100 μm; in b) and c): 1 μm.

tive catalyst in the light-driven water reduction to molecular hydrogen among the Mo_6-cluster based materials tested, achieving productions up to 4298 μmol gr^{-1} catalyst of H_2 after 5 hours of illumination.[42] The optical studies of these cluster single crystals are limited to PL, showing the characteristic cluster emission in the red region of the spectrum.

Herein, we controlled the growth and isolated single crystals of **MC** with different crystal sizes. It is shown herein the possibility to use these crystals as optical cavities for potential applications in photonic technologies. This molybdenum cluster-based material was studied with an home-made optical system, and the crystals emission and transmittance spectra were analyzed in order to extract the optical constants of the material.[59]

The preparation of single crystals with composition **MC** was optimized by cautious control of the crystallization conditions to obtain the targeted size.[42] Single crystals of **MC** were obtained with regular shapes, parallel faces and with low density of defects with a yield around 90%. The remaining material was associated to some agglomerates and irregular particles. Small sized (less than 30 μm) crystals were selected and their morphology was studied. **Figure 1**a and **S1** (see Supporting Information) show the optical microscopy images of several crystals supported on a glass substrate. The top view and cross section field-emission scanning electron microscopy (FESEM) images for the collected single crystals (**Figure 1**b and c, respectively) reveal a rhombohedral crystal habit with average crystal faces with angles of 107.4 and 71.9° for crystals with sizes between *ca.* 15 and 5 μm. At this degree of magnification, some defects and small-attached particles were detected from the chosen specimen.

Aiming to study the orientation of the deposited single crystals, the X-ray pattern of few single crystals dispersed onto a Si(911) substrate was recorded. Five diffraction peaks are identified in the diffractogram (**Figure S2**, Supporting Information) and correspond to the family of planes in the {-111} direction, with an interplanar distance between peaks of 8.516 Å, in the basis of the symmetry of the single crystals. This unique disposition of the {-111} facets confirms a preferential orientation of the single crystals, resting on their flat surfaces upon deposition onto a surface. The X-ray patterns acquired after optical studies remained unaltered (**Figure 2**) which confirms the single crystals stability under light irradiation with standard measurement conditions.

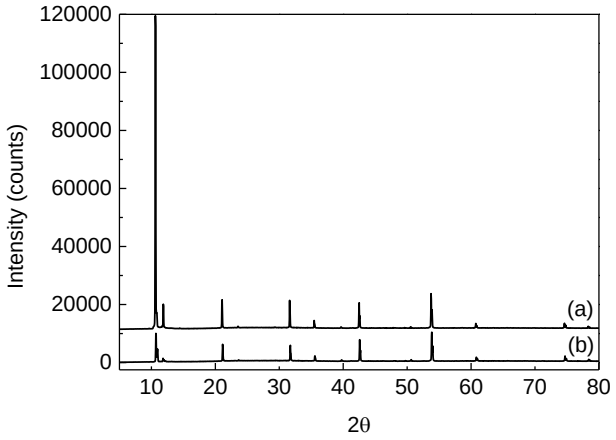

Figure 2. X ray patterns of a set of single crystals of **MC** before (a) and after optical studies (b).

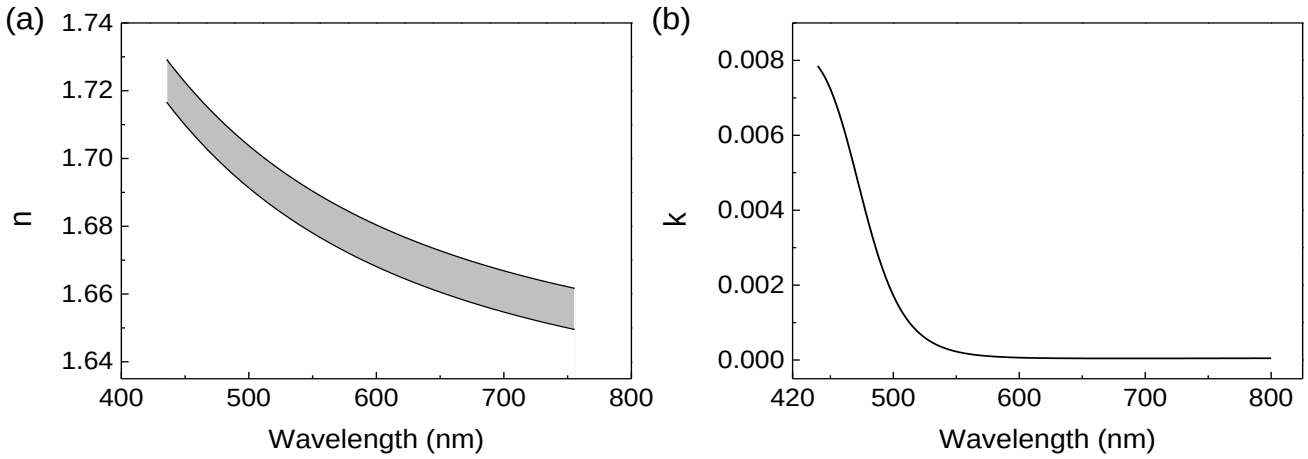

Figure 3. Fitted real (a) and imaginary (b) parts of the refractive index for the crystal selected in Figure 1(a).

The thermogravimetric/differential thermal analysis (TG/DTA) registered for the crystalline samples of **MC** also probe their thermal stability under operational conditions. The TG/DTA curves (**Figure S3**, Supporting Information) obtained under dry atmosphere show that the crystals remain stable up to 63 °C. This thermal stability confirms their potential applications as optical microcavities. At higher temperatures (63-81 °C), the sample displays a weight loss of 14% that we associate to water molecules, and this could be responsible of a structural reorganization of the crystals.

Flat and clean facets are convenient for observing optical resonances. A clear resonance phenomenon was observed in most of the crystals analyzed, in spite of the fact that some of them had defects and, eventually, other smaller attached particles. **Figure 1**d shows the OT spectrum measured in the direction perpendicular to the supporting substrate of the single crystal selected in **Figure 1**a. The spectrum consists of two different regions. One region at shorter wavelengths (from 425 to *ca.* 550 nm) is characterized by an abrupt transition from vanishing to high transmittance. The strong absorption of the material observed in the diffuse reflectance spectrum in this wavelength range (**Figure S3**, Supporting Information) prevents the optical resonance phenomenon to occur. The second region, displayed in the range from *ca.* 550 nm to longer wavelengths, shows a low absorption and clear interference fringes, which indicate that the crystal behaves as an optical microcavity. Such fringes depend basically on two parameters: refractive index and crystal thickness.[60] Thus, for a given refractive index dispersion, the thinner is the crystal, the more separated are the fringes.[61] Such parameters can be deduced by fitting the transmittance spectrum to an appropriate model (see Supporting Information). However, it is convenient to determine the crystal thickness by other means firstly in order to avoid spurious solutions. **Figure 1**d illustrates the fitted spectrum to a reported model[59] for a crystal thickness, determined by optical profilometry of (13650 ± 50) nm. **Figure 3**a and b show the respective fitted real (*n*) and imaginary (*k*) parts of the refractive index. The real part of the refractive index is comparable to those reported for other molybdenum materials, such as molybdenum oxide films, that usually appear in the range of 1.7–2.3.[62–66] The error in the measurement of the thickness yields, in the case of *n*, a confidence interval indicated by the grey area (**Figure 3a**). Regarding *k*, the fitted values should be considered cautiously because OT measurements include most probably optical scattering, which cannot be distinguished from optical absorption, and it was not considered in the fitting model. As another example, **Figure S4** (see Supporting Information) shows the OT

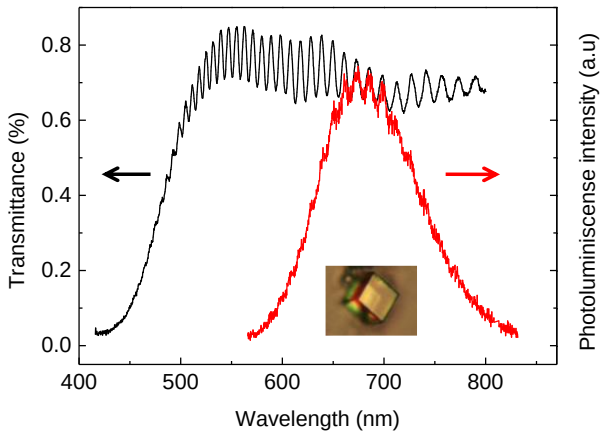

Figure 4. OT (black) and PL (red) spectra of the crystal shown in the inset.

measurement of a crystal of (15800 ± 50) nm in thick and the fit to the same model.[59] **Figure S5**a and b (see Supporting Information) show the corresponding fitted real and imaginary parts respectively of the refractive index (red curves). For comparison, the fitted values for the sample of **Figure 1** are plotted in black in **Figure S5** (Supporting Information). While the values almost coincide in the case of the real part, large discrepancies arise for the imaginary part, especially in the short wavelengths region. This is not surprising and it is attributed to imponderable optical scattering, which depends on the crystal size, the light spot size and its position on the crystal.

Single crystals of **MC** yielded PL when they were excited in the absorption region (**Figure S6**, Supporting Information) and the emission properties have been previously reported (λ_{em} = 670 nm, λ_{exc} = 390 to 430 nm).[42] Such PL can couple to the optical resonance modes of the cavity and produces interference fringes as well. However, because of the envelope curve, they are more difficult to observe than in the case of the OT signal. **Figure 4** shows a crystal (see inset) of (10500 ± 50) nm in thick where both, OT and PL, were measured. It is important to stress that the spectral position of the resonances is the same for both spectra.

In summary, high-quality single crystals of **MC** deposited with a preferred orientation onto a flat surface showed well-defined resonances in the VIS-NIR range when OT or PL measurements were done in a perpendicular direction to the surface. We have proven that selected Mo_6 cluster-based crystals constitute Fabry-

Pérot type optical microcavities with potential applications in photonic devices.

ASSOCIATED CONTENT

Supporting Information

Supporting Information is available free of charge on the ACS Publications website. Experimental details including the preparation of single crystals, the instrumentation and the fitting model used for the optical transmittance and supplementary figures (PDF).

AUTHOR INFORMATION

Notes

The authors declare no competing financial interests.

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Octahedral molybdenum cluster-based single crystals as Fabry-Pérot microresonators

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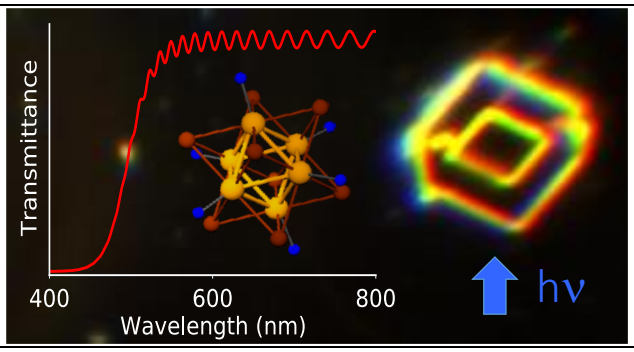

High-quality $(H_3O)_2[Mo_6Br^i_8(OH)^a_6]\cdot 10H_2O$ microcrystals are prepared by controlled growth in solution. Optical transmittance and photoluminescence measurements performed on single crystals demonstrate they behave as photonic micro-resonators in the VIS-NIR range. In addition, their refractive index dispersion is deduced.