Supporting Information

Time-Gated Luminescence Bioimaging with new Luminescent Nanocolloids based on $[Mo_6I_8(C_2F_5COO)_6]^{2-}$ Metal Atom Clusters

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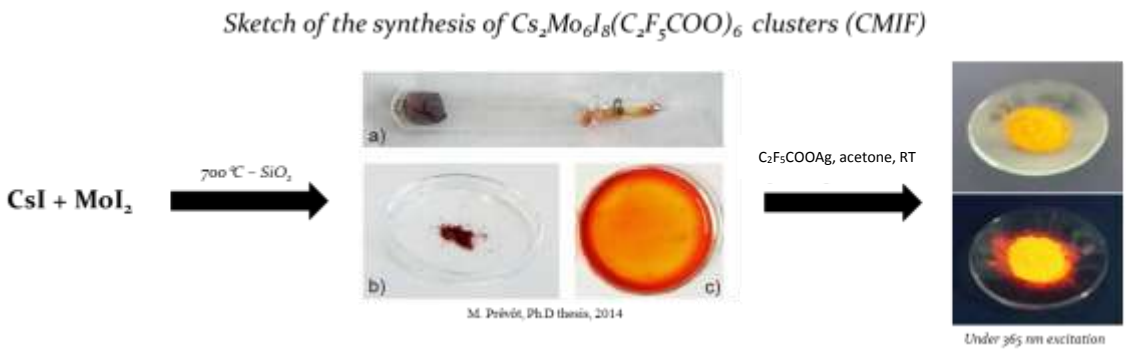
Experimental

Preparation of $Cs_2Mo_6I_8(C_2F_5COO)_6$ Metal Clusters

The $Cs_2Mo_6I_8(C_2F_5COO)_6$ cluster compound was prepared from $Cs_2Mo_6I_{14}$ and $AgOCOC_2F_5$

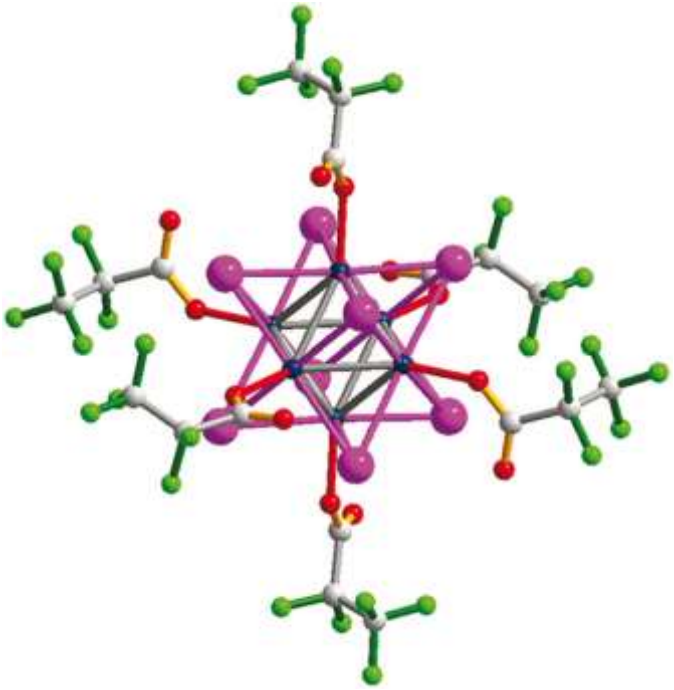
(See sketch below)



$Cs_2Mo_6I_{14}$: First, MoI_2 starting compound was synthesized by heating a stoichiometric mixture of Mo (Plansee 99.8 %) and I_2 (Alfa Aesar 99.8 %) at 700 °C for 4 days in a silica tube (noted SiO_2 in the sketch) sealed under vacuum. Afterwards, $Cs_2Mo_6I_{14}$ was prepared using CsI (Alfa Aesar 99.9 %) and MoI_2. The mixture (0.5 g) was ground, formed as a pellet and placed into silica tube (o.d. 9 mm, i.d. 7 mm, length 70 mm). Once sealed under vacuum, the tube was heated for three days at 700 °C. The X-ray powder pattern of the final product did not evidence the presence of any impurity. Red thin plate-shaped crystals of $Cs_2Mo_6I_{14}$ were obtained after a 100 °C/day cooling rate of temperature.

$Cs_2Mo_6I_8(C_2F_5COO)_6$: To a solution of $Cs_2Mo_6I_{14}$ (1.5 g, 0.52 mmol) in 20 mL of acetone, was added a solution of silver pentafluoropropionate (0.935 g, 3.42 mmol) in 10 mL of acetone under argon and in the dark. The mixture was stirred for 48 h in the dark and then was filtered through a Celite® pad. The red solution was then evaporated to yield a red-orange powder. Yield = 97%. ^{19}F-NMR (acetone-d_6): δ (ppm) = −83 (3F), −120 (2F). EDAX: Cs 2, Mo 8, I 11, F 77, no Ag.

Single-crystal X-ray diffraction data of $Cs_2Mo_6(C_2F_5COO)_6$ and $Cs_2Mo_6I_{14}$ were collected at room temperature on a Bruker AXS APEX-II diffractometer or a Nonius KappaCCD X-ray area-detector diffractometer with Mo Kα radiation (λ = 0.71073A) respectively (see references 45 c and d) .

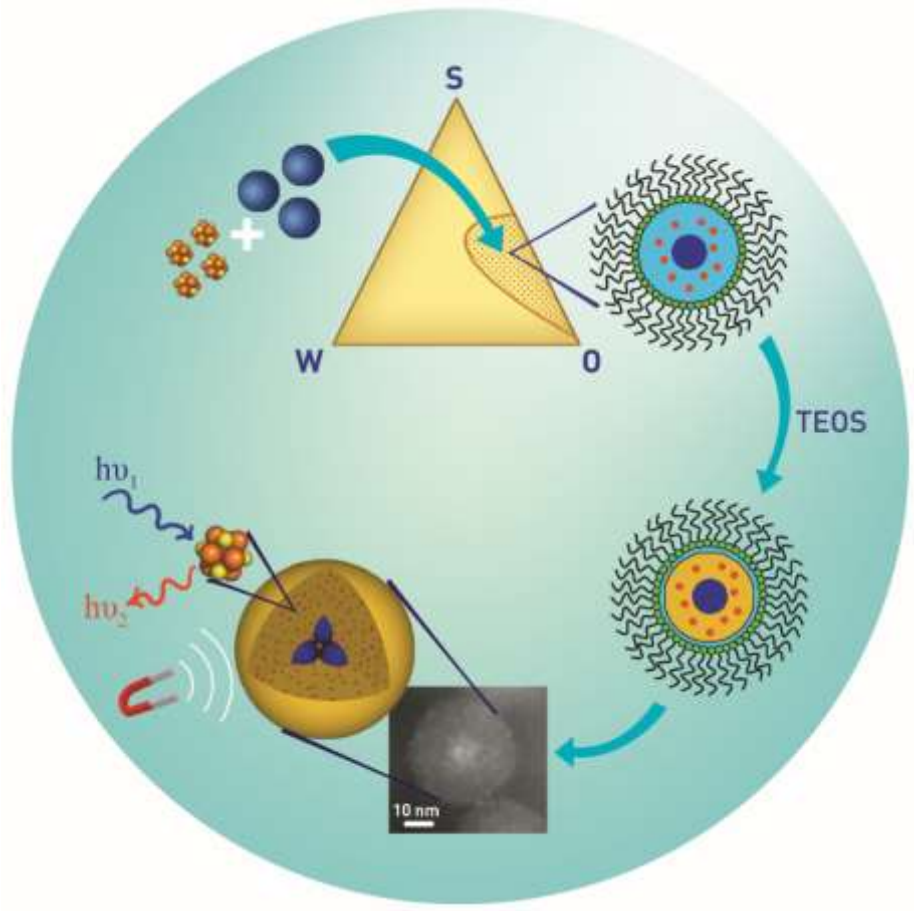


Representation according to single crystal data X-ray diffraction measurements of $Cs_2Mo_6I_8(C_2F_5OCO)_6$. (see reference 45c)

Preparation of $Cs_2Mo_6I_8(C_2F_5COO)_6@SiO_2$ nanocolloids

The functional silica nanoparticles have been prepared using a water-in-oil (W/O) microemulsion process developed by our group since the earlier 2000 (see general sketch below).

The hydrodynamic diameter of all the types of silica nanoparticles was found to be centered around 60 nm from the dynamic light scattering data in aqueous dispersion at pH = 7.



Dynamic Light Scattering (DLS): To determine the mean hydrodynamic diameter, d(H), of the nanocrystals, DLS investigations on sols were performed with a Zetasizer Nano ZS from Malvern Instruments using the new noninvasive backscattering (NIBS) technology and by detecting scattering information at an angle of 173° rather than the conventional 90°. The DLS technique measures the particle diffusion due to Brownian motion and relates it to the particle size. The particle size is classically determined according to the Stokes–Einstein equation.

19F NMR: experiments were realized at 376 MHz on a Bruker Ascend 400 MHz NMR spectrometer.

UV-Vis experiments: They have been conducted using a Cary 5000 UV-Vis-NIR spectrophotometer. Measurements have been realized using Hellma® 101-QS quartz cuvettes (10 mm).