

Supporting Information

for *Part. Part. Sys. Charact.*, DOI: 10.1002/ppsc. 201200047

Tunable Visible Emission of Luminescent Hybrid Nanoparticles Incorporating Two Complementary Luminophores: ZnO Nanocrystals and [Mo₆Br₁₄]²⁻ Nanosized Cluster Units

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1. Description and properties of the $[\text{Mo}_6\text{Br}_{14}]^{2-}$ cluster units

The $[\text{Mo}_6\text{Br}_{14}]^{2-}$ cluster unit is represented on **Figure S1**. It consists in an octahedral hexanuclear Mo_6 cluster (in blue on Figure S1). The cluster is bonded to 8 inner Br ligands (Br^i , $i = \text{inner}$), which are face capping the Mo_6 octahedron (in red on Figure S1), and 6 apical Br ligands (Br^a , $a = \text{apical}$), which are in terminal position of the Mo_6 octahedron (in green on Figure S1). In solid state the $[\text{Mo}_6\text{Br}_{14}]^{2-}$ cluster units co-crystallize with Cs^+ counter cation to form the $\text{Cs}_2[\text{Mo}_6\text{Br}_{14}]$ cluster compound. The size of one cluster unit is approximately 1 nm according to the lattice parameter of the $\text{Cs}_2[\text{Mo}_6\text{Br}_{14}]$ cluster compound.

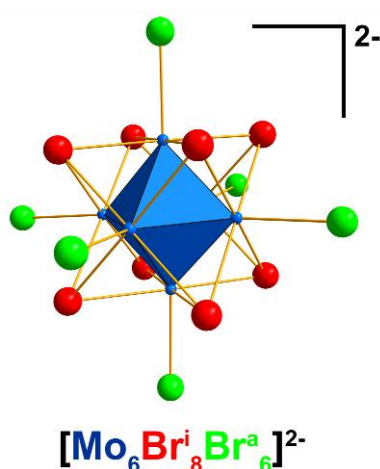


Figure S1. Schematic representation of the $[\text{Mo}_6\text{Br}_{14}]^{2-}$ cluster unit.

The $[\text{Mo}_6\text{Br}_{14}]^{2-}$ cluster units are nanosized luminescent entities that emit in the red and near infrared regions (600 to 900 nm) under UV or visible excitation. The emission and excitation spectra of the $\text{Cs}_2[\text{Mo}_6\text{Br}_{14}]$ cluster compound are reported on **Figure S2**. These spectra were recorded on solid state using a Horiba Jobin Yvon FluoroLog spectrophotometer. Maverick *et al.* reported a luminescence lifetime of 130 μs with a quantum yield of 23 % for these cluster units in acetonitrile solution at room temperature.^[1]

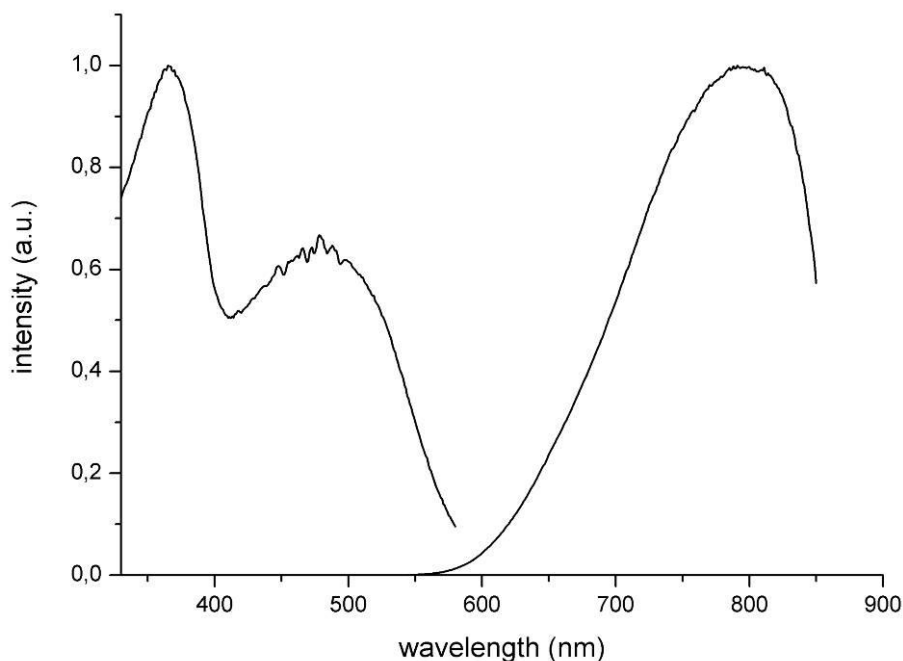


Figure S2. Emission and excitation spectra of the $\text{Cs}_2[\text{Mo}_6\text{Br}_{14}]$ cluster compound. The emission spectrum was recorded for an excitation wavelength of 450 nm and the excitation spectrum was recorded by detecting the emission at 700 nm. The spectra are corrected regarding the sensibility of the detector (photomultiplier) and normalized regarding their maximum.

2. ZnO colloids

2.1. Size and morphology of the ZnO nanocrystals

The size and morphology of the ZnO nanocrystals were determined by transmission electron microscopy (TEM), X-ray diffraction (XRD) and dynamic light scattering (DLS). For the XRD analysis, some ZnO nanocrystals were dried after precipitation with heptane during the purification procedure instead of being dispersed in ethanol. The XRD diffractogram recorded for the obtained ZnO powder is reported on **Figure S3**. The size of the nanocrystals has been determined by the refinement of the microstructure using the pattern matching method with the software FullProf. The calculation has been done considering the space group $P6_3mc$ and the cell parameters of the wurtzite phase. The residual of the refinement is low indicating that it is the right crystalline structure. The Scherrer formula applied to this refinement indicates an apparent size (ϵ_β) of 4.2 nm. The real size of the nanocrystals is deducted from ϵ_β , by multiplying it with a shape factor. In our case, we considered the

nanocrystals as spheres, meaning a shape factor of $4/3$, what gives an average diameter of 5.6 nm.

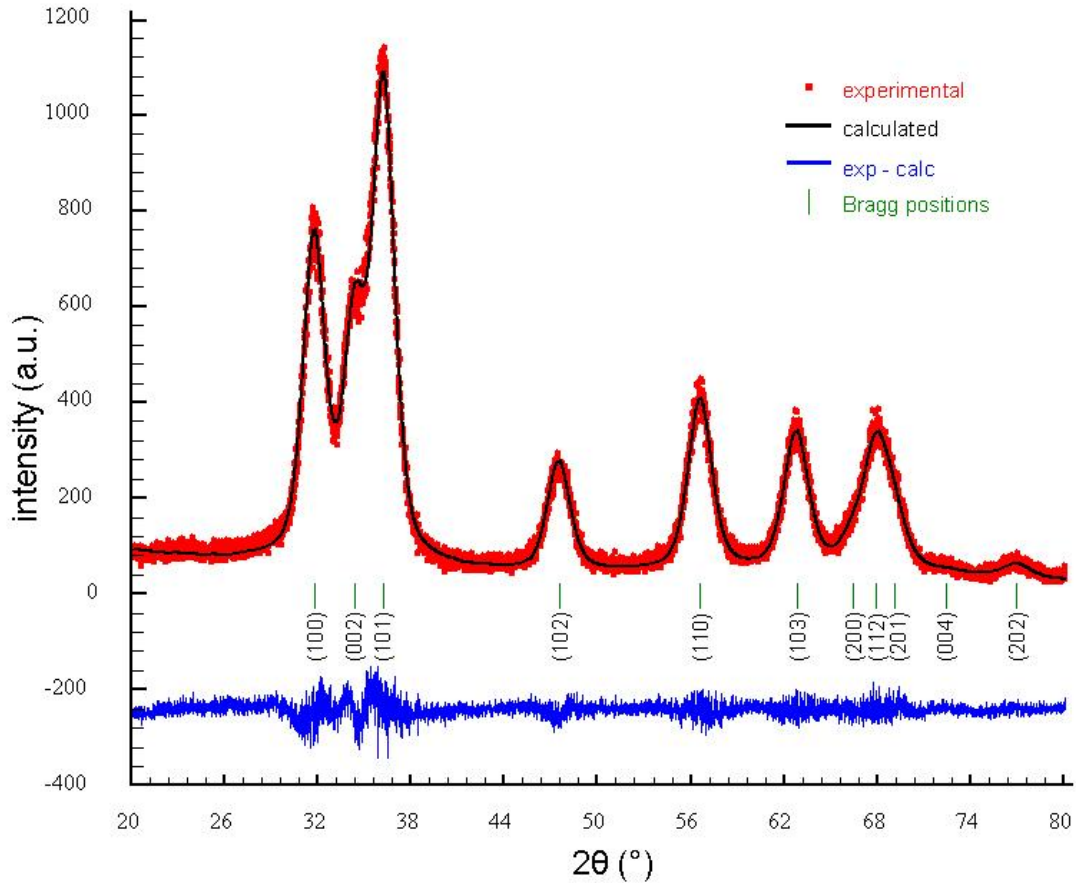


Figure S3. XRD diffractogram of a powder of nanocrystalline ZnO with the result of the refinement of the microstructure and the position of the Bragg peaks (indexation in space group $P6_3mc$).

After the purification process, some ZnO nanocrystals were dispersed in ethanol. They were analyzed by TEM using a JEOL JEM-1400 operating at 120 kV. The images on **Figure S4** show nanocrystals with an average size of 5.6 ± 0.7 nm. Most of the nanocrystals appear faceted, highlighting their nanocrystalline character, and moreover some clearly exhibit a triangular shape (in 2 dimensional view) indicating a growth along the hexagonal structural plan. In addition, they often appear as aggregated two by two by interaction between two faces of the triangles.

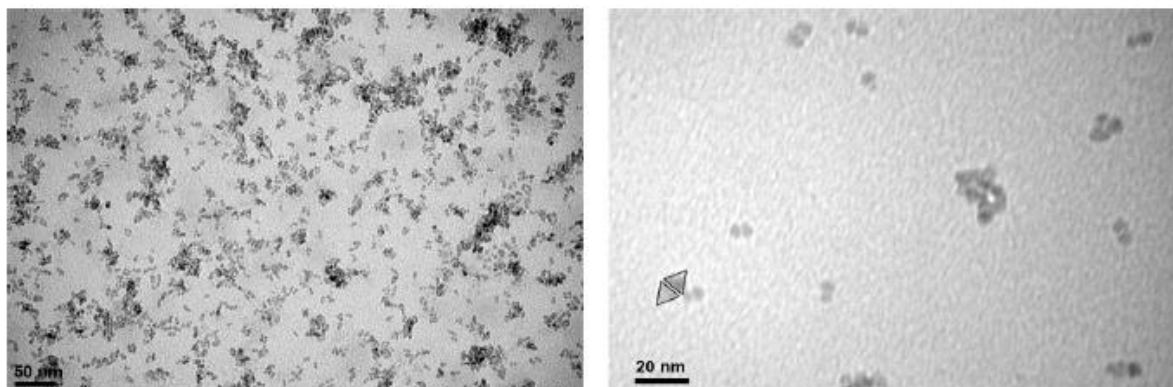


Figure S4. TEM images of ZnO nanocrystals. The triangles on the right image illustrate the shape and aggregation state of the nanocrystals.

The aggregation state of the ZnO nanocrystals has been highlighted with DLS measurements. After purification, the ZnO colloid shows an average hydrodynamic diameter of 15 nm (**Figure S5**). This size is higher than what was found with XRD and TEM analyses and results from the aggregation of two or more nanocrystals.

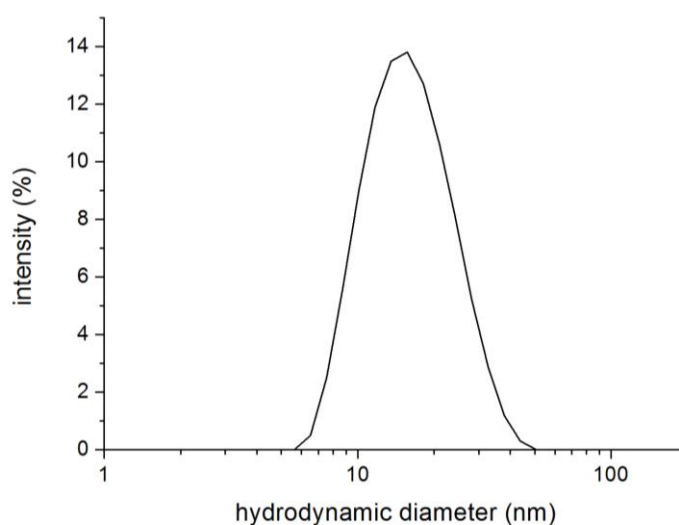


Figure S5. Hydrodynamic diameter and size distribution of a ZnO colloid analyzed by DLS.

2.2. Luminescence properties

The emission spectrum of the ZnO colloid has been recorded in ethanolic solution using a Horiba Jobin Yvon FluoroLog spectrophotometer and is reported on **Figure S6**. The emission spectrum is a combination of two spectra, one recorded for an excitation wavelength of 280 nm and the other one for an excitation wavelength of 380 nm. The emission spectrum on

Figure S6 illustrates the UV excitonic emission at 370 nm and the visible trap emission on the ZnO nanocrystals which with this spectrometer is centered around 575 nm.

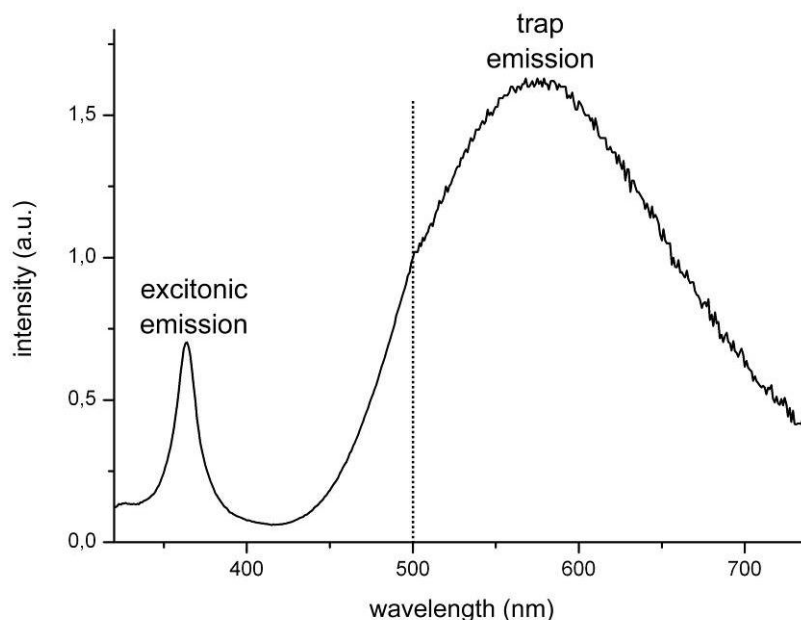


Figure S6. Emission spectrum of a ZnO colloid in ethanol. The spectrum is a reconstitution of two spectra obtained for an excitation wavelength 280 nm and 380 nm (separation at the dotted line).

3. Optical properties of the $[\text{ZnO-Cs}_2[\text{Mo}_6\text{Br}_{14}]\text{@PVP}]_{\text{films}}$

In addition to the $[\text{ZnO-Cs}_2[\text{Mo}_6\text{Br}_{14}]\text{@PVP}]_{\text{film}}$, pure $[\text{PVP}]_{\text{film}}$, $[\text{Cs}_2[\text{Mo}_6\text{Br}_{14}]\text{@PVP}]_{\text{film}}$ and $[\text{ZnO@PVP}]_{\text{film}}$ were also prepared with in each case the same concentration of the corresponding luminophores as for $[\text{ZnO-Cs}_2[\text{Mo}_6\text{Br}_{14}]\text{@PVP}]_{\text{film}}$. The optical properties of these films are presented here.

3.1. UV-visible absorption

The UV-visible absorption spectra were recorded using a Shimadzu SolidSpec 3700 spectrophotometer. The spectra of the films, as well as the spectra of the substrate (soda lime glass), are presented on **Figure S7**. It appears that the absorption spectrum of the $[\text{ZnO-Cs}_2[\text{Mo}_6\text{Br}_{14}]\text{@PVP}]_{\text{film}}$ shows the characteristic spectral signature of the cluster compound and of the ZnO nanocrystals.

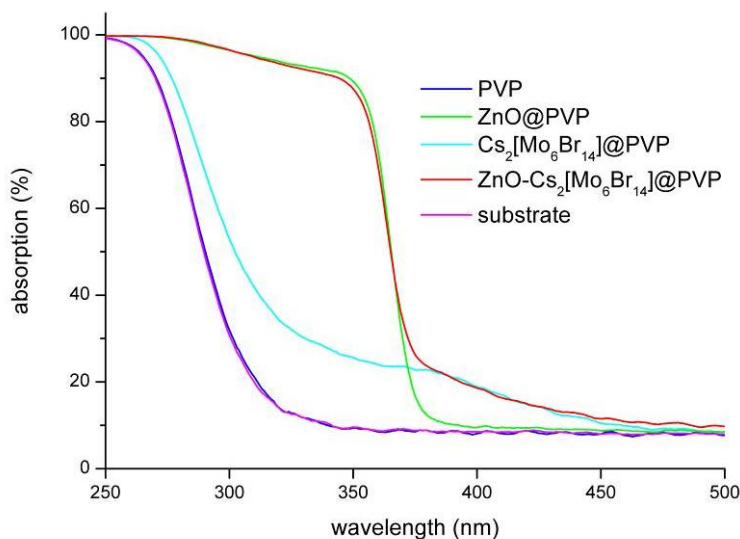


Figure S7. UV-visible absorption spectra of [PVP]_{film}, [Cs₂[Mo₆Br₁₄]]@PVP_{film}, [ZnO@PVP]_{film}, [ZnO-Cs₂[Mo₆Br₁₄]]@PVP_{film} and of the substrate (soda lime glass).

3.2. Luminescence properties

The luminescence properties of the [PVP]_{film}, [Cs₂[Mo₆Br₁₄]]@PVP_{film}, [ZnO@PVP]_{film} and [ZnO-Cs₂[Mo₆Br₁₄]]@PVP_{film} were investigated using an Accent RPM 2000 spectrophotometer. The emission spectra of the films obtained for an excitation wavelength of 325 nm are presented on **Figure S8**. On this figure, one can notice that both contribution of the ZnO and cluster are present in the emission of the [ZnO-Cs₂[Mo₆Br₁₄]]@PVP_{film}.

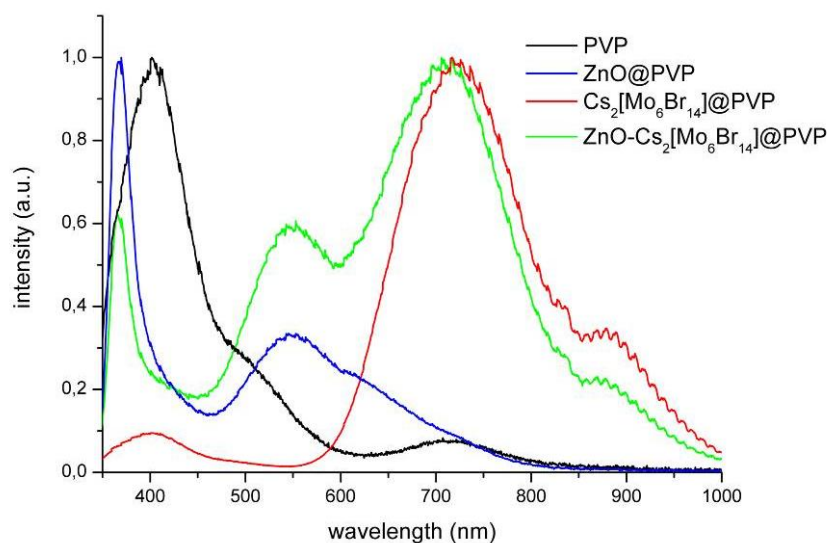


Figure S8. Emission spectra of [PVP]_{film}, [Cs₂[Mo₆Br₁₄]]@PVP_{film}, [ZnO@PVP]_{film} and [ZnO-Cs₂[Mo₆Br₁₄]]@PVP_{film} for an excitation wavelength of 325 nm. The films were stored in room conditions. The spectra are normalized to their respective maximum.

4. ZnO-Cs₂[Mo₆Br₁₄]₂@SiO₂ nanoparticles

4.1. XRD analyses

After synthesis and purification, the ZnO-Cs₂[Mo₆Br₁₄]₂@SiO₂ nanoparticles were analyzed by XRD in order to verify that the ZnO did not dissolve during the process. The XRD diffractogram on **Figure S9** shows the typical diffraction peaks of the ZnO nanocrystals. This allows us to state that what is visible inside the silica nanoparticles by STEM are indeed ZnO nanocrystals.

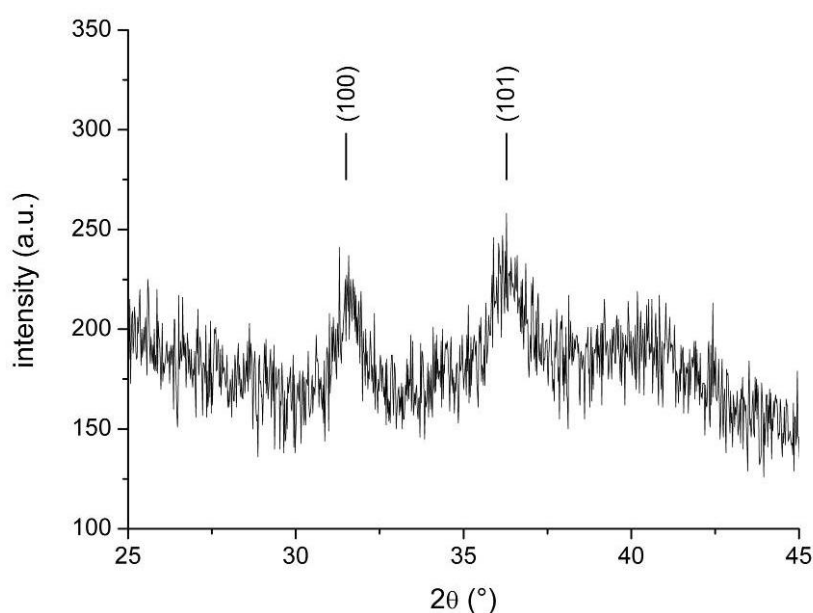


Figure S9. XRD diffractogram of a powder of ZnO-Cs₂[Mo₆Br₁₄]₂@SiO₂ nanoparticles. The position of the main diffraction peaks of nanocrystalline ZnO are indicated (see Figure S3).

4.2. Color coordinates

The color coordinates of the emission of the ZnO-Cs₂[Mo₆Br₁₄]₂@SiO₂ nanoparticles depending on the excitation wavelength have been determined from the emission spectra (Figure 3 in the article). They have been calculated following the convention of the “Commission International de l’Eclairage” (CIE) of 1931 and using the software MATLAB with the toolbox OptProp.^[2] These CIE_{xy} coordinates are reported together with their location in the chromaticity diagram in **Figure S10**. It appears that, in spite of the very broad emission of the nanoparticles for an excitation wavelength of 365 nm, combining ZnO nanocrystals and Cs₂[Mo₆Br₁₄]₂ is not sufficient to produce white light. A blue component would be necessary for this goal. This could be achieved by adding smaller ZnO nanocrystals that would have a

blue shifted trap emission.^[3] Another possibility would be to use these ZnO-Cs₂[Mo₆Br₁₄]₂@SiO₂ nanoparticles as remote phosphors combined with a blue LED.

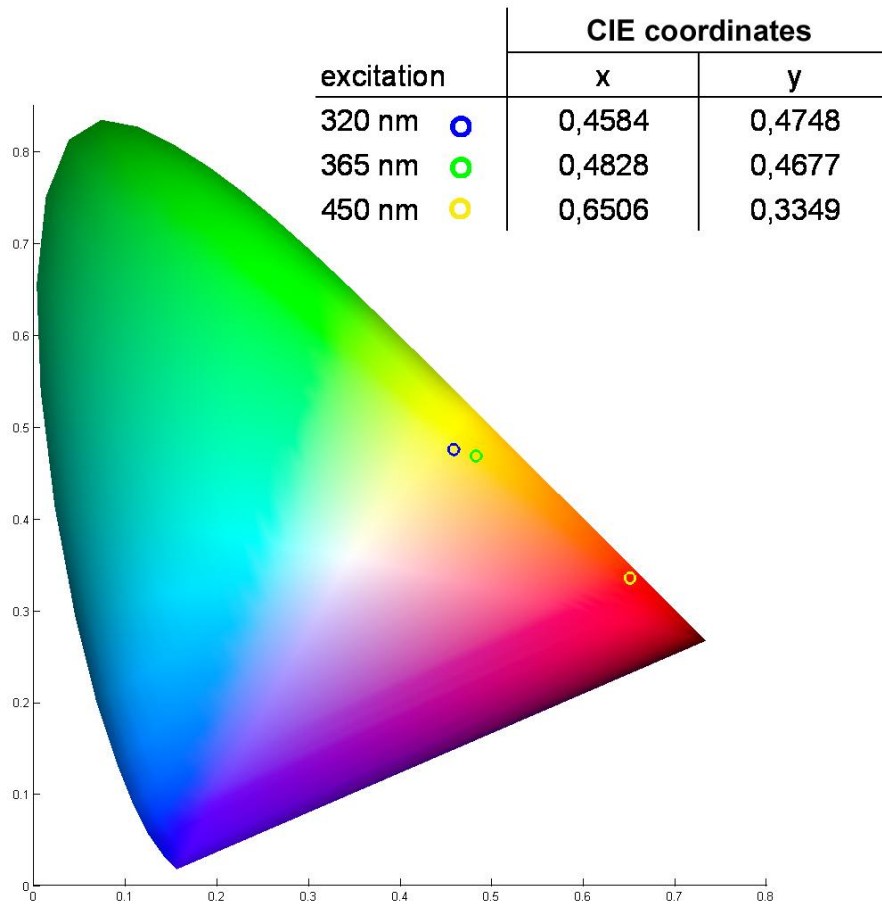


Figure S10. Color coordinates of the emission of ZnO-Cs₂[Mo₆Br₁₄]₂@SiO₂ nanoparticles depending on the excitation wavelength and their position in the CIE chromaticity diagram.

4.3. Time-resolved photoluminescence analyses

For each excitation wavelength ($\lambda_{\text{exc}} = 380$ and 450 nm), the obtained emission spectrum of the ZnO-Cs₂[Mo₆Br₁₄]₂@SiO₂ nanoparticles was deconvoluted in order to distinguish the contribution of each luminophores in the overall emission (**Figure S11 and S12**). For each observation wavelength ($\lambda_{\text{obs}} = 550$ and 725 nm) the signal was collected over a 10 nm wide spectral window centered at λ_{obs} in order to have a sufficient intensity. The photoluminescence decay curves are reported in **Figure S13 and S14**.

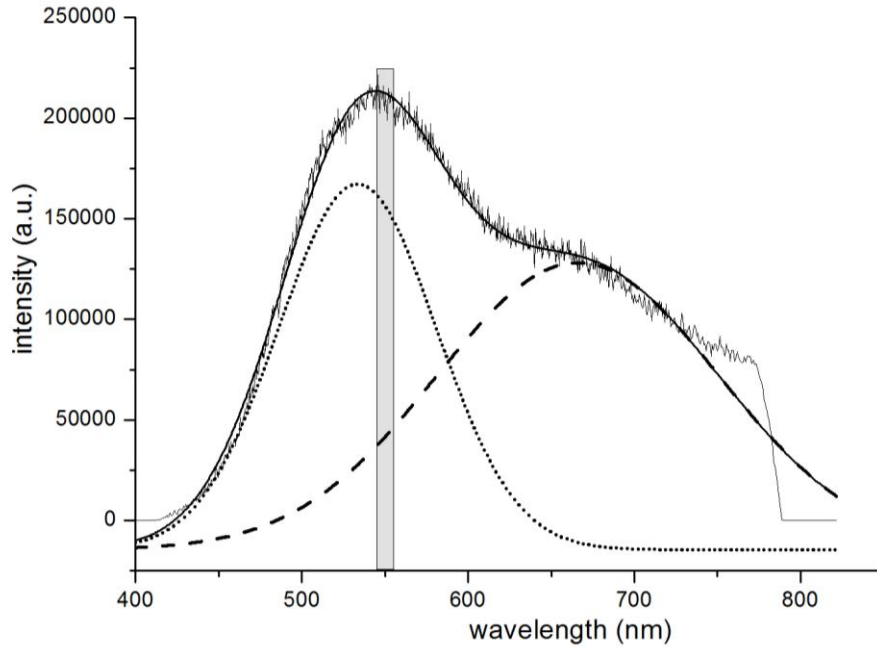


Figure S11. Emission spectrum of ZnO-Cs₂[Mo₆Br₁₄]@SiO₂ nanoparticles ($\lambda_{\text{exc}} = 380$ nm). Dotted and dashed lines: gaussian functions corresponding to the deconvolution of the emission spectrum. The gray rectangle corresponds to the spectral window observed during the photoluminescence decay.

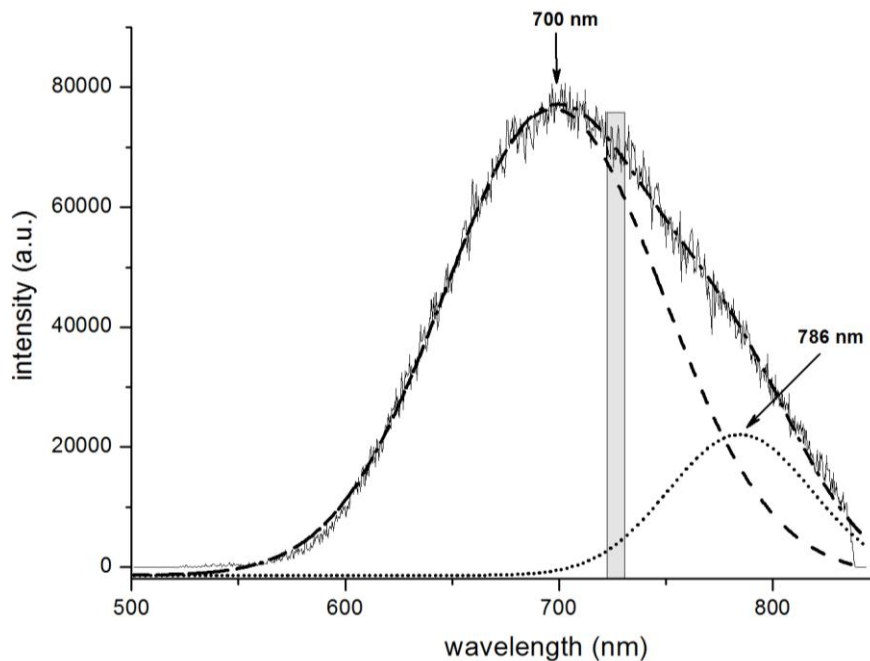


Figure S12. Emission spectrum of ZnO-Cs₂[Mo₆Br₁₄]@SiO₂ nanoparticles ($\lambda_{\text{exc}} = 450$ nm). Dotted and dashed lines: gaussian functions corresponding to the deconvolution of the emission spectrum. The gray rectangle corresponds to the spectral window observed during the photoluminescence decay.

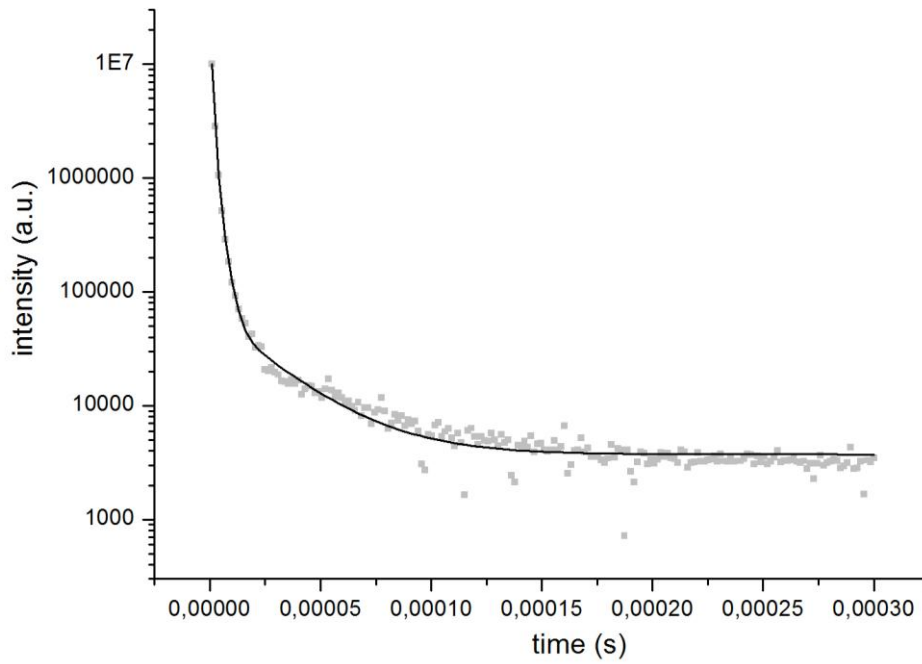


Figure S13. Photoluminescence decay curve of ZnO-Cs₂[Mo₆Br₁₄]@SiO₂ nanoparticles ($\lambda_{\text{exc}} = 380 \text{ nm}$, $\lambda_{\text{obs}} = 550 \pm 5 \text{ nm}$).

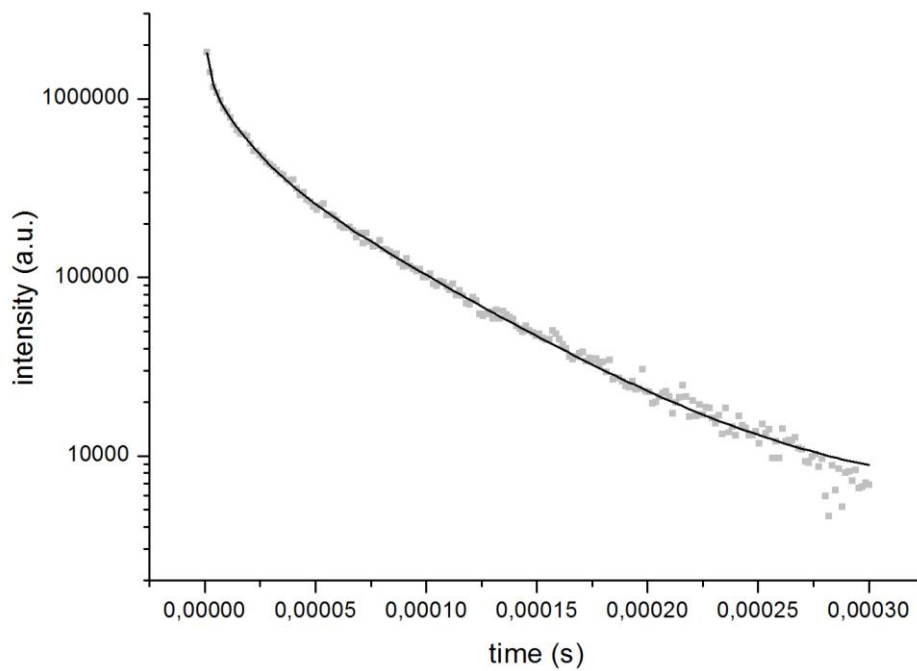


Figure S14. Photoluminescence decay curve of ZnO-Cs₂[Mo₆Br₁₄]@SiO₂ nanoparticles ($\lambda_{\text{exc}} = 450 \text{ nm}$, $\lambda_{\text{obs}} = 725 \pm 5 \text{ nm}$).

5. Additional reference

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