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# Tunable Visible Emission of Luminescent Hybrid Nanoparticles Incorporating Two Complementary Luminophores: ZnO Nanocrystals and [Mo<sub>6</sub>Br<sub>14</sub>]<sup>2-</sup> Nanosized Cluster Units

Tangi Aubert, Nicolas Nerambourg, Noriko Saito, Hajime Haneda, Naoki Ohashi, Michel Mortier, Stéphane Cordier, Fabien Grasset

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## Tunable Visible Emission of Luminescent Hybrid Nanoparticles Incorporating Two Complementary Luminophores: ZnO Nanocrystals and [Mo<sub>6</sub>Br<sub>14</sub>]<sup>2-</sup> Nanosized Cluster Units



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Abstract:	We report the stabilization in presence of water of colloidal solutions associating ZnO nanocrystals and [Mo <sub>6</sub> Br <sub>14</sub> ] <sup>2-</sup> cluster units using polyvinylpyrrolidone (PVP). The resulting ZnO-Cs <sub>2</sub> [Mo <sub>6</sub> Br <sub>14</sub> ] <sup>2-</sup> @PVP solutions were stable even in the presence of water and could be used for the preparation of transparent and luminescent polymer thin films and ZnO-Cs <sub>2</sub> [Mo <sub>6</sub> Br <sub>14</sub> ] <sup>2-</sup> @SiO <sub>2</sub> silica nanoparticles. This article presents the first syntheses of luminescent functional thin films or silica nanoparticles based on [Mo <sub>6</sub> X <sub>14</sub> ] <sup>2-</sup> @ZnO hybrid. The nanomaterials have been fully characterized by the means of FE-SEM, STEM, X-ray diffraction techniques, dynamic light scattering, UV-Vis absorption and emission spectroscopies. Luminescence experiments have shown that the intrinsic photophysical properties of the cluster anion or ZnO nanocrystal are not affected by their inclusion in PVP or silica matrix, even after several month of aging in water solution. Therefore, we have shown that we could prepare versatile luminescent nanomaterials with broad scale signal in the visible part.

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**Tunable Visible Emission of Luminescent Hybrid Nanoparticles Incorporating Two Complementary Luminophores: ZnO Nanocrystals and  $[\text{Mo}_6\text{Br}_{14}]^{2-}$  Nanosized Cluster Units**

*Tangi Aubert<sup>&§\*</sup>, Nicolas Nerambourg<sup>&</sup>, Noriko Saito<sup>§</sup>, Hajime Haneda<sup>§</sup>, Naoki Ohashi<sup>§</sup>, Michel Mortier<sup>£</sup>, Stéphane Cordier<sup>&\*</sup>, and Fabien Grasset<sup>&\*</sup>*

[&] Dr. T. Aubert, Dr. N. Nerambourg, Dr. S. Cordier, Dr. F. Grasset  
Université de Rennes 1, UMR Institut des Sciences Chimiques de Rennes UR1-CNRS 6226,  
Equipe Chimie du Solide et Matériaux, 263 av. du Général Leclerc, 35042 Rennes, France

[§] Dr. N. Saito, Prof. H. Haneda, Dr. N. Ohashi

National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-044, Japan

[£] Dr. Michel Mortier

Ecole Nationale Supérieure de Chimie de Paris, ENSCP, 11 rue Pierre et Marie Curie, 75005  
Paris, France

[§] Present address: Ghent University, Department of Inorganic and Physical Chemistry,  
Physics and Chemistry of Nanostructures group, Krijgslaan 281-S3, 9000 Gent, Belgium

\* E-mail: tangi.aubert@ugent.be, fabien.grasset@univ-rennes1.fr, stephane.cordier@univ-rennes1.fr

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Luminescent silica nanoparticles have numerous applications in the fields of biotechnologies<sup>[1,2]</sup> or photonics.<sup>[3,4]</sup> They are usually achieved through the encapsulation in a silica matrix of a luminophore such as organic dyes,<sup>[5-8]</sup> semi-conductor quantum dots,<sup>[9-13]</sup> organometallic complexes<sup>[14-17]</sup> or rare-earth-doped nanocrystals.<sup>[18-20]</sup> Most of these materials are limited to single narrow emission properties. However, the increasing complexity of the applications of nanomaterials in the fields of photonic or light emitting devices requires materials with always more sophisticated emission properties. In particular, the achievement of materials with tunable and broad emission properties is of major interest for the field of photonics and for the manipulation of light over a large spectral range. In this frame, Zhou *et al.* reported materials with tunable and broad emission properties by stabilizing multivalent bismuth nanocrystals in a porous silica matrix.<sup>[21]</sup> With their approach, they realized

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macrosized glass chips exhibiting blue-green, orange, red or white emission depending on the excitation wavelength.

We present here the synthesis and characterization of materials based on silica nanoparticles incorporating two kinds of luminophores namely ZnO nanocrystals and  $[\text{Mo}_6\text{Br}_{14}]^{2-}$  cluster units. Interestingly, ZnO nanocrystals and nanosized  $[\text{Mo}_6\text{Br}^i\text{Br}^a_6]^{2-}$  units are two luminophores which exhibit complementary emission properties. ZnO is a semiconductor material with a large energy gap between the conduction and valence bands (3.37 eV). Regardless to their bulk or nanosized forms, ZnO materials show an excitonic UV emission under UV irradiation related to the energy band gap of the electronic structure. In addition to the latter emission, ZnO nanocrystals often show a supplementary large emission band (from 500 to 700 nm) generally centered between 550 and 600 nm. This visible emission known as trap emission, originates from defects located at the surface of the ZnO nanocrystals and more precisely from oxygen vacancies.<sup>[22, 23]</sup> On the other hand, under UV or visible excitation,  $[\text{Mo}_6\text{Br}_{14}]^{2-}$  cluster units exhibit a broad emission window from 550 to 900 nm centred around 780 nm.<sup>[24]</sup>  $[\text{Mo}_6\text{X}^i_8\text{X}^a_6]^{2-}$  nanosized cluster units are built up from an octahedral  $\text{Mo}_6$  cluster bonded to eight inner face-capping ligands ( $\text{X}^i$ ,  $i = \text{inner}$ ) and to six bromine apical ligands ( $\text{X}^a$ ,  $a = \text{apical}$ ) located in terminal positions.  $[\text{Mo}_6\text{X}^i_8\text{X}^a_6]^{2-}$  ( $\text{X} = \text{Cl}, \text{Br}$  and  $\text{I}$ ) are associated with inorganic or organic cations in many compounds of general formula  $\text{A}_2[\text{Mo}_6\text{X}^i_8\text{X}^a_6]$  ( $\text{A} = \text{alkali cation, quaternary ammonium, H}_3\text{O}^+ \dots$ ) prepared either by solid state chemistry or by combined use of solid state and solution chemistries.  $\text{A}_2[\text{Mo}_6\text{X}^i_8\text{X}^a_6]$  series afford thus useful  $[\text{Mo}_6\text{X}^i_8\text{X}^a_6]^{2-}$  building blocks with specific physico-chemical properties that can be involved in the preparation of molecular assemblies and nanomaterials (e.g.: dendrimers, liquid crystal and polymer nanocomposites, functional surfaces).<sup>[25-34]</sup>

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In a previous work we showed that the association of ZnO nanocrystals and Mo<sub>6</sub>-based cluster units lead to colloidal materials with unique tunable emission properties.<sup>[35]</sup> Depending on the excitation wavelength, the resulting cluster@ZnO hybrid nanoparticles showed either the visible emission of ZnO or the emission of the clusters, or even a combination of both of them, resulting in a broad emission covering almost all the visible range of light. Besides visible emission upon irradiation, clusters are known to generate singlet oxygen<sup>[36]</sup> whilst single ZnO nanocrystals can generate second order NLO.<sup>[37]</sup> Indeed, the targeted hybrid cluster@ZnO nanoparticles should afford promising multifunctional materials with potential applications in nanobiotechnology, in photodynamic therapy (PDT) or nonlinear optical (NLO) bioimaging. Before applications, the stabilisation and dispersion of cluster@ZnO nanoparticles in stable organic or inorganic matrix constitutes a mandatory step. A straightforward strategy to obtain a homogeneous and stable material is the embedding of the cluster@ZnO nanoparticles in silica matrix. This technique is well known for providing nanomaterials with enhanced colloidal and physico-chemical stability as well as biocompatibility.<sup>[38]</sup> The encapsulation of cluster units based on Mo<sub>6</sub> and Re<sub>6</sub> clusters in silica nanoparticles has already been demonstrated in the past few years.<sup>[39-41]</sup> The cluster embedding in silica matrix efficiently decreases quenching phenomena that alter the cluster luminescence properties in solution.<sup>[40]</sup> The latter usually results from the presence of dissolved oxygen.<sup>[36]</sup> If the Mo<sub>6</sub> cluster solution chemistry is compatible with silica formation reactions, this is not true for the solution chemistry of ZnO nanocrystals. This feature makes the encapsulation of ZnO nanocrystals in a silica matrix much trickier than that of [Mo<sub>6</sub>Br<sub>14</sub>]<sup>2-</sup> cluster units. Indeed, ZnO nanocrystals hardly stand the presence of water, an essential reactant for the sol-gel chemistry of silica, which provokes their aggregation. In addition, the traditional processes for the synthesis of spherical and monodisperse silica particles such as the Stöber process usually requires high pH values.<sup>[42]</sup> This is in contradiction with the

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stability of ZnO nanocrystals that dissolve for pH value higher than 9. It explains why the references dealing with the preparation of ZnO@SiO<sub>2</sub> nanoparticles are scarce. Tang *et al.*<sup>[43]</sup> reported the preparation of such nanoparticles through a modified Stöber process, resulting in materials whose emission properties depend on the precipitation pH value of the ZnO nanocrystals. On the other hand, Wang *et al.*<sup>[44]</sup> reported the preparation of ZnO@SiO<sub>2</sub> through a water-in-oil microemulsion process, but they did not study the luminescence properties of their materials. The stabilization of ZnO nanocrystals in aqueous solutions has been reported through their functionalization with polymers,<sup>[45, 46]</sup> organic ligands<sup>[47]</sup> or even organosilanes.<sup>[48, 49]</sup>

We report here the stabilization in presence of water of colloidal solutions associating ZnO nanocrystals and [Mo<sub>6</sub>Br<sub>14</sub>]<sup>2-</sup> cluster units using polyvinylpyrrolidone (PVP; M<sub>w</sub> = 40000 g mol<sup>-1</sup>) as stabiliser, which is a widely used capping agent.<sup>[50]</sup> The resulting ZnO-Cs<sub>2</sub>[Mo<sub>6</sub>Br<sub>14</sub>]@PVP colloidal solutions were stable even in the presence of water and could be therefore used for the preparation of transparent and luminescent polymer thin films and ZnO-Cs<sub>2</sub>[Mo<sub>6</sub>Br<sub>14</sub>]@SiO<sub>2</sub> silica nanoparticles. The thin films were prepared by dip-coating in the ZnO-Cs<sub>2</sub>[Mo<sub>6</sub>Br<sub>14</sub>]@PVP solutions and were characterized by field-emission scanning electron microscopy (FE-SEM) and luminescence spectrometry. ZnO-Cs<sub>2</sub>[Mo<sub>6</sub>Br<sub>14</sub>]@SiO<sub>2</sub> silica nanoparticles were obtained by the concomitant encapsulation of the two luminophores ZnO nanocrystals and [Mo<sub>6</sub>Br<sub>14</sub>]<sup>2-</sup> cluster units in silica nanoparticles through a modified Stöber process thanks to the use of ZnO-Cs<sub>2</sub>[Mo<sub>6</sub>Br<sub>14</sub>]@PVP as precursor. Resulting ZnO-Cs<sub>2</sub>[Mo<sub>6</sub>Br<sub>14</sub>]@SiO<sub>2</sub> nanoparticles were characterized by scanning transmission electron microscope (STEM), luminescence spectroscopy and X-ray diffraction (XRD). Both the films and the nanoparticles exhibited tunable luminescence properties as their emission spectra depended on the excitation wavelength. In addition, it is worth noting that the luminescence

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properties of ZnO-Cs<sub>2</sub>[Mo<sub>6</sub>Br<sub>14</sub>]*@*SiO<sub>2</sub> nanoparticles are stable in water solution even after 3 months of ageing.

The Cs<sub>2</sub>[Mo<sub>6</sub>Br<sub>14</sub>] cluster compound was synthesized by solid state chemistry at high temperature, according to an already published procedure.<sup>[51]</sup>

The ZnO colloid was synthesized by a sol-gel route as described in the experimental section and adapted from a previously reported procedure.<sup>[52, 53]</sup> The obtained ZnO colloidal solution consisted of 5 nm sized nanocrystals (see Supporting Information for dynamic light scattering measurements and transmission electron microscopy images). The ZnO concentration of the colloidal solution after purification was 0.5 M, as determined by inductively coupled plasma optical emission spectrometry (ICP-OES) measurements.

The colloidal solution of clusters and ZnO nanocrystals was prepared by dissolving 70 mg of Cs<sub>2</sub>[Mo<sub>6</sub>Br<sub>14</sub>] in a mixture of 5 ml of ethanol and 1 ml of distilled water. Then, 2 g of PVP (M<sub>w</sub> = 40000 g mol<sup>-1</sup>) were dissolved in the resulting cluster sol. Finally, 5 ml of the ZnO colloidal solution in ethanol were added to the mixture. Thus, in this procedure, the ZnO nanocrystals could be stabilized in the presence of water after prior synthesis and purification of the ZnO colloids and further addition in a PVP solution. Indeed, if introduced during the synthesis of ZnO, the PVP could decrease the surface defects of the nanocrystals resulting in the loss of the visible emission.<sup>[54]</sup>

From the stabilised colloidal solution, denoted ZnO-Cs<sub>2</sub>[Mo<sub>6</sub>Br<sub>14</sub>]*@*PVP, films were deposited on soda lime glass slides by dip-coating. The above mentioned ZnO-Cs<sub>2</sub>[Mo<sub>6</sub>Br<sub>14</sub>]*@*PVP solution was placed in a Teflon® container and the substrate was introduced in the solution. After one minute of immersion, the substrate was pulled up at 200 mm min<sup>-1</sup>. After deposition, the films were dried at room temperature. According to the quantities of precursors introduced in the synthesis, the composition of the films after complete evaporation of the solvent was 88.0 wt% of PVP, 8.9 wt% of ZnO and 3.1 wt% of

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$\text{Cs}_2[\text{Mo}_6\text{Br}_{14}]$ . These films are denoted as  $[\text{ZnO}-\text{Cs}_2[\text{Mo}_6\text{Br}_{14}]]@\text{PVP}$ <sub>film</sub>. The homogeneity and the thickness of the  $[\text{ZnO}-\text{Cs}_2[\text{Mo}_6\text{Br}_{14}]]@\text{PVP}$ <sub>film</sub> have been determined by FE-SEM. The cross section of the material was observed after breaking the slide in the direction of the pulling up axe (i.e. longitudinal section). The FE-SEM image on **Figure 1** illustrates a perfectly homogeneous film with an average thickness of 3  $\mu\text{m}$ . Additional experiments showed that the thickness of the film could easily be controlled by varying the pulling speed or the viscosity (i.e. concentration of PVP) of the solution, up to 7  $\mu\text{m}$  thick films. These films are transparent in the visible range and luminescent under UV excitation (365 nm, 4 watt lamp) (Figure 1). For an excitation wavelength of 325 nm, the emission properties of the  $[\text{ZnO}-\text{Cs}_2[\text{Mo}_6\text{Br}_{14}]]@\text{PVP}$ <sub>film</sub> produced a large emission band covering almost all the visible range (see Supporting Information **Figure S8**).

The  $\text{ZnO}-\text{Cs}_2[\text{Mo}_6\text{Br}_{14}]]@\text{SiO}_2$  nanoparticles were synthesized through a modified Stöber process, using TMAOH as the base instead of the classical ammonia solution. In a synthesis, 1 ml of the above mentioned  $\text{ZnO}-\text{Cs}_2[\text{Mo}_6\text{Br}_{14}]]@\text{PVP}$  solution was diluted in 19 ml of ethanol and 1 ml of distilled water. Then, 0.05 ml of TMAOH and 1 ml of TEOS were added to the solution and the reaction was left under stirring for 4 days. Finally the nanoparticles were collected by centrifugation and washed several times with ethanol. In our process, the use of TMAOH instead of ammonia for the base-catalyzed condensation of the silica matrix appeared to be essential. Indeed, all attempts to use ammonia led to a loss of the visible emission of ZnO. However, it was possible to form a thin shell of silica around the ZnO nanocrystals using TMAOH and then add ammonia for further growth of bigger silica nanoparticles. In these conditions, the visible emission of ZnO was preserved after purification and dispersion of the nanoparticles in ethanol, but then the emission always disappeared when drying the nanoparticles. In this latter case the visible emission of ZnO disappeared in about 24 hours after drying the nanoparticles, whereas for ZnO-



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Cs<sub>2</sub>[Mo<sub>6</sub>Br<sub>14</sub>]*@*SiO<sub>2</sub> nanoparticles prepared by using only TMAOH as the base, they remained luminescent even when they were dried or dispersed in water. These observations might be related to the size of the cation balancing the charge of the silica matrix, which are NH<sub>3</sub><sup>+</sup> or (CH<sub>3</sub>)<sub>4</sub>N<sup>+</sup> when using ammonia or TMAOH respectively. Smaller cations will produce silica with higher density, and if the density of the silica matrix at the vicinity of the ZnO nanocrystals is too high it might passivate its surface, resulting in a loss of the trap emission. Moreover, drying the nanoparticles can also provoke an additional densification of the silica matrix, explaining why the loss of the visible emission ZnO only appeared after drying the ZnO-Cs<sub>2</sub>[Mo<sub>6</sub>Br<sub>14</sub>]*@*SiO<sub>2</sub> nanoparticles when using ammonia.

The ZnO-Cs<sub>2</sub>[Mo<sub>6</sub>Br<sub>14</sub>]*@*SiO<sub>2</sub> nanoparticles were observed by STEM. The images on **Figure 2** evidence the presence of ZnO nanocrystals inside the silica matrix. Additional XRD measurements performed on the powder (Supporting Information **Figure S9**) confirmed the presence of crystalline ZnO which was not dissolved during the base-catalyzed encapsulation process. The images in Figure 2 show that the sample consists in vermicular aggregates of ZnO-Cs<sub>2</sub>[Mo<sub>6</sub>Br<sub>14</sub>]*@*SiO<sub>2</sub> nanoparticles. The diameter of the primary nanoparticles is roughly below 30 nm. This aggregation state is explained by the low pH value -lower than 9- used for the synthesis of the silica matrix.

The luminescence properties of the ZnO-Cs<sub>2</sub>[Mo<sub>6</sub>Br<sub>14</sub>]*@*SiO<sub>2</sub> nanoparticles were carefully investigated on solid state. The emission spectra of the nanoparticles depending on the excitation wavelength are reported on **Figure 3**. These spectra highlight the tunable character of the emission of these nanoparticles. For an excitation wavelength of 340 nm, the trap emission of ZnO centered at 575 nm was predominant and masked the emission of the clusters. For an excitation wavelength of 450 nm, the ZnO nanocrystals do not emit anymore and the nanoparticles produced the red emission of the [Mo<sub>6</sub>Br<sub>14</sub>]<sup>2-</sup> cluster units as already observed for Cs<sub>2</sub>[Mo<sub>6</sub>Br<sub>14</sub>]*@*SiO<sub>2</sub> nanoparticles.<sup>[39, 55]</sup> For an excitation wavelength of 365 nm,

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the nanoparticles produced a large emission band covering almost all the visible range as found earlier for  $((n\text{-C}_4\text{H}_9)_4\text{N})_2\text{Mo}_6\text{Br}_{14}@ZnO$  colloidal solutions and nanopowders. The color coordinates of these emission spectra have calculated and are represented in a chromaticity diagram in supporting information (**Figure S10**). Owing to the silica matrix, the  $ZnO\text{-Cs}_2[\text{Mo}_6\text{Br}_{14}]@SiO_2$  nanoparticles are more stable than  $((n\text{-C}_4\text{H}_9)_4\text{N})_2[\text{Mo}_6\text{Br}_{14}]@ZnO$  colloids. Indeed,  $((n\text{-C}_4\text{H}_9)_4\text{N})_2[\text{Mo}_6\text{Br}_{14}]@ZnO$  nanoparticles are stable only in organic media and the luminescence of the cluster units is quenched by oxygen. A major finding of the present work is that the luminescence of the  $ZnO\text{-Cs}_2[\text{Mo}_6\text{Br}_{14}]@SiO_2$  nanoparticles is preserved when dispersed in water, even after several months of aging. This is illustrated in Figure 3 which shows photography under a UV lamp of an aqueous solution of dispersed  $ZnO\text{-Cs}_2[\text{Mo}_6\text{Br}_{14}]@SiO_2$  nanoparticles after three months of storage. The relatively equal contributions of the ZnO and of the clusters in the emission of the nanoparticles for an excitation of 365 nm result from an appropriate ratio between these two luminophores, which in this case was about 70 ( $ZnO/Cs_2[\text{Mo}_6\text{Br}_{14}]$  molar ratio). The excitation wavelength at which a broad emission is obtained can therefore be tuned by varying the respective proportions of ZnO and clusters.

In order to study the luminescence properties of the  $[\text{Mo}_6\text{Br}_{14}]^{2-}$  cluster units and the ZnO nanocrystals within the silica matrix, time-resolved photoluminescence experiments were carried out at room temperature on  $ZnO\text{-Cs}_2[\text{Mo}_6\text{Br}_{14}]@SiO_2$  powders. Lifetime measurements on  $Cs_2[\text{Mo}_6\text{Br}_{14}]@SiO_2$  nanoparticles were previously reported.<sup>[39]</sup> The results are summarized in **Table 1**. For each experiment, excepted for  $Cs_2[\text{Mo}_6\text{Br}_{14}]@SiO_2$ , three lifetimes were obtained.

For each excitation wavelength ( $\lambda_{exc} = 380$  and 450 nm), the photoluminescence spectra of the  $ZnO\text{-Cs}_2[\text{Mo}_6\text{Br}_{14}]@SiO_2$  nanoparticles were deconvoluted in order to distinguish the respective contribution of the two different luminophores. Indeed, for  $\lambda_{exc} = 380$  nm both ZnO

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nanocrystals and  $[\text{Mo}_6\text{Br}_{14}]^{2-}$  cluster units contribute to the emission at 550 nm (supporting information **Figure S11**). Thus, for  $\lambda_{\text{exc}} = 380$  nm and  $\lambda_{\text{obs}} = 550$  nm, we expected to find a long lifetime related to the cluster units and a short lifetime related to the ZnO nanocrystals. The longest lifetime obtained in these conditions (26.67  $\mu\text{s}$ ) with a relatively weak amplitude is consequently attributed to the emission of the  $[\text{Mo}_6\text{Br}_{14}]^{2-}$  cluster units. Regarding the lifetime of 2.83  $\mu\text{s}$ , this value is in good agreement with that previously reported for the ZnO visible emission signal.<sup>[23]</sup> Then, the shortest lifetime value (0.95  $\mu\text{s}$ ) which corresponds to the largest contribution might be attributed to energy transfers between ZnO nanocrystals and the silica matrix or between ZnO nanocrystals and the cluster units.

For  $\lambda_{\text{exc}} = 450$  nm, only the cluster units contribute to the emission at 725 nm. The deconvolution of the emission spectrum of the  $[\text{Mo}_6\text{Br}_{14}]^{2-}$  cluster units ( $\lambda_{\text{exc}} = 450$  nm) shows two distinct emission bands (see supporting information **Figure S12**) corresponding to different excited states as previously reported in the literature.<sup>[56]</sup> The main band centered at 700 nm is related to the longest (58.14  $\mu\text{s}$ ) and the shortest (1.91  $\mu\text{s}$ ) lifetimes obtained in these conditions. Very similar results were obtained in a previous work concerning the photoluminescence study of  $\text{Cs}_2[\text{Mo}_6\text{Br}_{14}]\text{@SiO}_2$  nanoparticles.<sup>[39]</sup> The longest lifetime of 58.14  $\mu\text{s}$  is thus attributed to the phosphorescence of the  $[\text{Mo}_6\text{Br}_{14}]^{2-}$  cluster units and the shortest one might be attributed to energy transfers between cluster units themselves or between cluster units and the silica matrix. The lifetime value of 14.3  $\mu\text{s}$  also obtained in these conditions ( $\lambda_{\text{exc}} = 450$  nm and  $\lambda_{\text{obs}} = 725$  nm) can be consequently attributed to the second excited state (emission band centered at 786 nm) involved in the photoluminescence electronic transitions. This value was not measured previously<sup>[39]</sup> because this second excited state did not contribute at all in the emission at the observed wavelength ( $\lambda_{\text{obs}} = 670$  nm). The nature of the different electronic states involved in the photoluminescence process will be investigated in a future study.

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In conclusion, we successfully stabilized the ZnO nanocrystals in presence of water using PVP for their further co-encapsulation along with  $[\text{Mo}_6\text{Br}_{14}]^{2-}$  cluster units in silica to form ZnO- $\text{Cs}_2[\text{Mo}_6\text{Br}_{14}]\text{@SiO}_2$  nanoparticles through a modified Stöber process. ZnO- $\text{Cs}_2[\text{Mo}_6\text{Br}_{14}]\text{@SiO}_2$  nanoparticles exhibit tunable emission properties with a broad emission spectrum covering almost all the visible range for an excitation wavelength of 365 nm. Moreover, an important feature is that the luminescence properties are kept intact when the nanoparticles are dispersed in water. Hence, these nanoparticles are suitable for applications in aqueous media such as luminescent markers for bioimaging. Although the morphology of the nanoparticles (sphericity and monodispersity) needs to be improved for their integration in optical devices such as photonic crystals, the materials reported here can already find applications in white light emitting devices, in particular when associated with a blue light-emitting diode.<sup>[57]</sup>

## Experimental Section

*ZnO colloidal solution:* For the synthesis of the ZnO colloidal solution,  $\text{Zn}(\text{Ac})_2 \cdot \text{H}_2\text{O}$  (4.39 g) was suspended in *n*-propanol (40 ml). The mixture was then heated at 125 °C for 5 minutes using a rotary evaporator under ambient atmosphere and resulting in the evaporation of about 9 ml of the solvent. While the solution was still warm (~ 60 °C), TMAOH (9 ml, 25 % in methanol) was added and the mixture was vigorously shaken until a perfectly clear solution was obtained. This ZnO colloidal solution was left under magnetic stirring overnight. In order to remove unreacted species, the nanocrystals were further purified by precipitation with heptane (1:2 volume ratio between ZnO solution and heptane) followed by centrifugation. Finally the collected nanocrystals were dispersed in ethanol (20 ml).

*Characterization techniques:* FE-SEM images were performed with a JEOL JSM 6301F microscope operating at 7 kV. STEM images were performed using a Hitachi SU8000

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microscope operating at 30 kV. Photoluminescence spectra (Figure 3) were recorded using a Horiba Jobin Yvon FluoroLog spectrophotometer using a photomultiplier as detector.

*Time-resolved photoluminescence:* Time-resolved photoluminescence measurements were performed with a home-made setup using a CCD camera as detector. The kinetics parameters were determined by fitting the photoluminescence decays with the following equation:  $y = A_1e(-x/\tau_1) + A_2e(-x/\tau_2) + A_3e(-x/\tau_3)$ .

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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For Review Only

## List of figures and table

**Figure 1.** Left: FE-SEM image of the cross section of a  $[\text{ZnO-Cs}_2[\text{Mo}_6\text{Br}_{14}]]@\text{PVP}$  film with an average thickness of 3  $\mu\text{m}$ . Right: emission of a  $[\text{ZnO-Cs}_2[\text{Mo}_6\text{Br}_{14}]]@\text{PVP}$  film under a UV lamp ( $\lambda_{\text{exc}} = 365 \text{ nm}$ ).

**Figure 2.** STEM images of  $\text{ZnO-Cs}_2[\text{Mo}_6\text{Br}_{14}]]@\text{SiO}_2$  nanoparticles.

**Figure 3.** Left: normalized emission spectra of  $\text{ZnO-Cs}_2[\text{Mo}_6\text{Br}_{14}]]@\text{SiO}_2$  nanoparticles depending on the excitation wavelength. Right: emission of  $\text{ZnO-Cs}_2[\text{Mo}_6\text{Br}_{14}]]@\text{SiO}_2$  nanoparticles dispersed in water under UV lamp ( $\lambda_{\text{exc}} = 365 \text{ nm}$ ).

**Table 1.** Photoluminescence lifetimes of  $\text{ZnO-Cs}_2[\text{Mo}_6\text{Br}_{14}]]@\text{SiO}_2$  and  $\text{Cs}_2[\text{Mo}_6\text{Br}_{14}]]@\text{SiO}_2$  nanoparticles under solid state conditions. Experiments on  $\text{Cs}_2[\text{Mo}_6\text{Br}_{14}]]@\text{SiO}_2$  nanoparticles were previously reported by our team.<sup>[39]</sup> Kinetic parameters were obtained by fitting the luminescence decay curves with a three exponential equation (see experimental section).

	$\lambda_{\text{exc}}$ [nm]	$\lambda_{\text{obs}}$ [nm]	$\tau_1$ [ $\mu\text{s}$ ]	$A_1$	$\tau_2$ [ $\mu\text{s}$ ]	$A_2$	$\tau_3$ [ $\mu\text{s}$ ]	$A_3$
$\text{ZnO-Cs}_2[\text{Mo}_6\text{Br}_{14}]]@\text{SiO}_2$	380	550	26.67	0.01	2.83	0.10	0.95	0.89
$\text{ZnO-Cs}_2[\text{Mo}_6\text{Br}_{14}]]@\text{SiO}_2$	450	725	58.14	0.24	14.3	0.32	1.91	0.44
$\text{Cs}_2[\text{Mo}_6\text{Br}_{14}]]@\text{SiO}_2$	340	670	40	0.2	1.9	0.8	–	–

## Table of Contents

**ZnO nanocrystals and Mo<sub>6</sub> clusters are embedded in silica nanoparticles through a modified Stöber process.** The resulting materials offer tunable emission properties with a broad emission covering almost all the visible range for an excitation wavelength of 365 nm. The luminescence properties of the nanoparticles remain stable even when they are dispersed in water.

**Keyword:** metal atom clusters; silica nanoparticles; tunable luminescence; ZnO nanocrystals

T. Aubert\*, N. Nerambourg, N. Saito, H. Haneda, N. Ohashi, M. Mortier, S. Cordier\*, and F. Grasset\*

Tunable Visible Emission of Luminescent Hybrid Nanoparticles Incorporating Two Complementary Luminophores: ZnO Nanocrystals and [Mo<sub>6</sub>Br<sub>14</sub>]<sup>2-</sup> Nanosized Cluster Units

