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Direct Integration of Red-NIR Emissive Ceramic-like $A_nM_6X_iX_a^6$ Metal Cluster Salts in Organic Copolymers Using Supramolecular Interactions.

Malo Robin,^{[a], [b]} Noée Dumait,^[a] Maria Amela-Cortes,^[a] Claire Roiland,^[a] Maxime Harnois,^[b] Emmanuel Jacques,^[b] Hervé Folliot,^[c] and Yann Molard*^[a]

Abstract: Hybrid nanomaterials made of inorganic nanocomponents dispersed in an organic host raise an increasing interest as low-cost solution-processable functional materials. However, preventing phase segregation while allowing a high inorganic doping content remains a major challenge, and usual methods require a functionalization step prior integration. Herein, we report a new approach to design such nanocomposite in which ceramic-like metallic nanocluster compounds are embedded at 10 wt % in organic copolymers, without any functionalization. Dispersion homogeneity and stability are ensured by weak interactions occurring between the copolymer lateral chains and the nanocluster compound. Hybrids could be ink-jet printed and casted on a blue LED. This proof-of-concept device emits in the Red-NIR area and generates singlet oxygen, $O_2(^1\Delta_g)$, of particular interest for lightings, display, sensors or photodynamic based therapy applications.

Integrating inorganic nanocomponents in polymer matrices has become a pre-requisite to design easy to shape 3D functional nanomaterials dedicated to optoelectronic applications.^[1] Indeed, technologies like dip- or spin-coating, drop casting or printing can be used to deposit them, lowering the devices production costs compared to technics involving high temperatures (400-1400°C) and/or high vacuum such as Chemical Vapor Deposition or Plasma induced Chemical Vapor Deposition. However, a key challenge remains for nanocomposite large-scale and cost-effective production, meanwhile allowing high inorganic doping content: controlling the inorganic components dispersion within the organic host. This step is mandatory to prevent the nanocomponents self-aggregation responsible of the nanoscopic dimension benefits loss, light scattering and premature ageing. To

do so, the interactions between the organic and inorganic phases have to be carefully considered.^[2] Thus, several strategies have been developed, beside the simple blending technic that generally leads to phase segregation with ageing. An obvious approach is to modify the inorganic nanoobjects, *via* covalent grafting, with organic moieties able, either to act as compatibilizers with the organic host,^[3] or to react with the host during a copolymerization.^[4] A second strategy relies on designing hybrid building blocks in which tailor-made organic polymerizable ligands are interacting electrostatically with the inorganic component. It was used by *e.g.* L. Wu and co-workers^[5] to integrate polyoxometalate polyanions in polyacrylate matrices. These integration approaches, although very efficient, imply to finely engineer the chemical nature of the organic ligands *via* multi-step organic synthesis and often lead to nanoobjects surface state modifications. Here, we describe a general method allowing the homogeneous integration of non-functionalized inorganic ionic nanocomponents in organic polymers. To illustrate our strategy, we base our demonstration on rare earth-free, lead-free and cadmium-free M_6 transition metal nanocluster compounds and a poly(methylmethacrylate) (PMMA) copolymer derivative.

Considered as intermediates between transition metal complexes and nanoparticles,^[6] octahedral metal cluster compounds of general formula $A_nM_6X_iL^a_6$ (A: alkali cation; M: Mo, W, Re; Xⁱ: inner ligand; L^a: apical ligand; **Figure 1**) are obtained as ternary salt ceramic-like powders by high temperature synthesis and emit very efficiently in the red NIR area when excited in the UV-blue region. Several groups including our, used the previously described ways to integrate these phosphorescent emitters in hybrid materials.^[7] In all cases, a modification of the inorganic salt was necessary to maximize the interactions between components either by a covalent grafting on the clusters apical positions^[8] or by exchanging its alkali cations with functional organic ones.^[9] Such functionalization can have a strong impact on the native cluster emission properties, rendering the ones of resulting hybrids difficult to anticipate.^[10] In this work, a metallic nanocluster compound is integrated without any chemical modifications in the host matrix, and keeps intact its intrinsic properties.

Our strategy relies on weak supramolecular interactions occurring between oxygen atoms contained in polyethylenoxide (PEO) chains and the alkali ions of the inorganic salt. In fact, it is well known since the pioneering work of the 1987 Nobel Prize of Chemistry C. J. Pedersen that, when ethylene oxide fragments

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are organized in cyclic oligomers, they form crown ether macrocycles able to form stable complexes with alkali ions.^[11] We recently demonstrated that these macrocycles could be used to design nanocluster containing liquid crystals.^[12] Herein, we expect that using linear PEO chains instead of macrocycles would generate weak interactions, yet strong enough to maintain homogeneity and stability within the hybrid material. A similar approach was used by T. Mori *et al.* in Japan to develop Cs molecular sensors after the Fukushima Daiichi nuclear disaster.^[13]

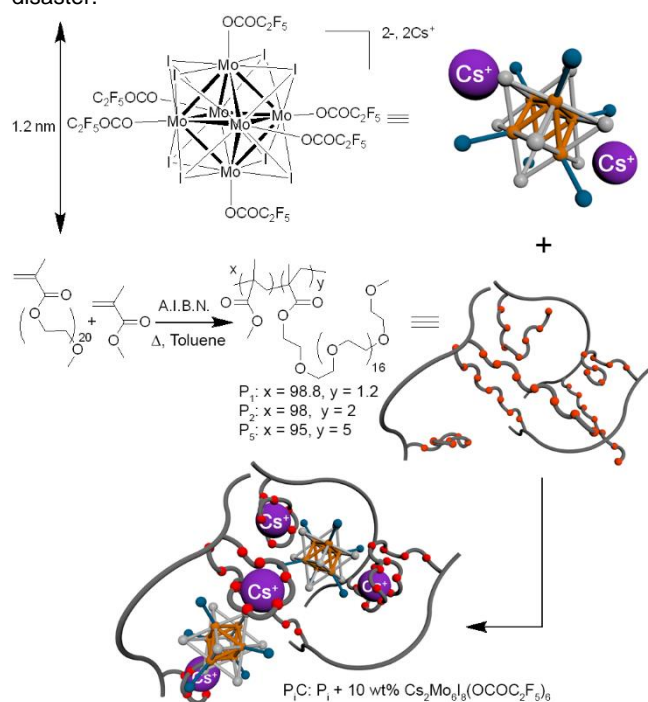


Figure 1. Schematic representation of the nanocluster ternary salt and its integration in the PMMA-PEOMA copolymer.

At first sight, we suspected that, by controlling the amount of PEO chains in the copolymers, we would tailor the inorganic-organic interactions and, as a result, control the homogeneity of our hybrid material. Hence, several poly(methylmethacrylate-polyethylexidemethacrylate) (PMMA-PEOMA) copolymers containing 1.2, 2 or 5 mol% of PEOMA (respectively referenced as P1, P2 and P5) were synthesized in solution by radical polymerization using azobisisobutyronitrile (AIBN) as radical initiator (see ESI for experimental details). Copolymers were characterized by ¹H NMR, differential scanning calorimetry (DSC) and FTIR spectroscopy (ESI, **Figures S1-S7**). $\text{Cs}_2\text{Mo}_6\text{I}_8(\text{OCOC}_2\text{F}_5)_6$ nanocluster salt based on the $[\text{Mo}_6\text{I}_8(\text{OCOC}_2\text{F}_5)_6]^{2-}$ dianionic cluster unit was chosen for its excellent ability to emit compared to fully halogenated salts.^[14] Hybrids PiC samples (with $i=1, 2$ or 5) containing 10 wt% of inorganic emitter were easily obtained by blending solutions of both components in an adequate ratio, followed by solvent evaporation and drying (other doping concentration will be reported in due course). The interactions between the copolymer and the nanocluster could not be evidenced by IR spectroscopy

as no shift of the absorption bands related to the inorganic moieties or the ethylenoxide chains is observed.

Magic Angle Spinning (MAS) solid state ¹³³Cs NMR experiments are, among all available technics, the best illustrative ones to observe the interactions between the alkali cations and the polymer PEO lateral chains. Indeed, ¹³³Cs NMR spectra (see ESI **Figure S8**) contain two signals located at -4.97 ppm and -106.52 ppm either when they are recorded for $\text{Cs}_2\text{Mo}_6\text{I}_8(\text{OCOC}_2\text{F}_5)_6$ in its crystalline form (Cs^+ location is shared between two crystallographic positions)^[9b] or when it is embedded in pure PMMA. This indicates that the inorganic salt crystallizes within the polymer matrix and therefore that the mixture is segregating. In PiC ($i = 1-5$) sample ¹³³Cs spectra, only one signal, located at -30.69 ppm, -36.56 ppm, and -37.92 ppm, for P₁C, P₂C and P₅C respectively, are observed. The presence of only one signal reveals that Cs cations are equivalent when the cluster salt is interacting with the PEO lateral chains and that no crystallization occurs. The signal shift to higher field with the increase of PEO content characterizes the increase of the Cs⁺ electronic density due to its interactions with the oxygen free electronic doublets contained in the PEO chains. It shows as expected, that these interactions become stronger with an increase of PEO content. These interactions are responsible of the hybrid homogeneity and physical stability. Increasing the PEOMA/MMA ratio has a strong plastisizing effect on the resulting pure copolymer. Indeed, DSC measurements show that the glass transition temperature decreases from 118°C for pure PMMA to 36°C for copolymer containing 5 mol% of PEOMA (see **Table 1**).

Table 1. Physical and photophysical parameters of hybrids and cluster precursor (A and B). Glass transition temperature (T_g), calculated absolute quantum yield values under air and N₂ atmosphere (Φ), emission maximum position, full width at half height of emission signal, and calculated phosphorescence lifetime decay (contribution in parenthesis) for doped copolymers.

Sample	T _g ^[a]	Φ		λ _{max}	fwhm	τ [μs]	
	[°C]	Air	N ₂	[nm]	[cm ⁻¹]	Air	N ₂
P ₁ C	77 (95.5)	16	50	674	2329	30 (0.53) 80 (0.47)	30 (0.20) 200 (0.80)
P ₂ C	66 (64)	16	51	676	2342	30 (0.59) 90 (0.41)	30 (0.24) 190 (0.76)
P ₅ C	42.5 (36)	8	50	679	2367	20 (0.05) 70 (0.95)	50 (0.10) 210 (0.90)
A	-	35	-	660	2292	5 (0.28) 50 (0.72)	-
B	-	1	49 ^[b]	668	2294	2	269 ^[b]

[a] values in parenthesis are given for non doped copolymer; [b] calculated value for a deaerated solution. A : $\text{Cs}_2\text{Mo}_6\text{I}_8(\text{OCOC}_2\text{F}_5)_6$ in crystalline powder; B : $\text{Cs}_2\text{Mo}_6\text{I}_8(\text{OCOC}_2\text{F}_5)_6$ in solution.

This behavior is related to the lateral PEO chains that increase the distance between polymer main chains. Introducing 10 wt% of nanoclusters in the organic matrix affects also the T_g value. While a plastisizing effect is observed for polymers with low PEOMA/MMA ratio, an increase of the glass transition is observed

for P₅C showing that, in this particular case, nanocluster-polymer interactions lead to a stiffness of the organic scaffold.

Absorption measurements realized in acetonitrile solution for all samples show that pure copolymers have a very low absorption after 320 nm (see ESI, **Figures S9-11**). Thus, doped copolymers absorption spectra contain mainly the cluster absorption bands between 350 and 450 nm. **Figures 2a and 2b** present the excitation maps recorded in this wavelength range for a deaerated acetone solution of Cs₂Mo₆I₈(OCOC₂F₅)₆ and P₁C respectively. Similar results are obtained when hybrids are deposited on quartz substrate (see ESI **Figure S12**) for pictures of deposited films. The optimal excitation wavelength to observe the strong red-NIR emission of the ternary salt does not depend on the host matrix and is located at 400 nm. As depicted in **Figure 2c**, introducing the cluster in the copolymer does not change the general shape of its emission band as the full width at half height (FWHM) is nearly not modified (variation of less than 2%). However, a slight red shift of the emission maximum, increasing with the PEO polymer content is observed (**Table 1**). The ability of hybrids to emit light was characterized further with absolute quantum yield (AQY) measurements. A perfectly reversible enhancement of the AQY from 16 % up to 51% (table 1 and inset Figure 2c) for P₁C was observed when passing from an air to a N₂ atmosphere in the integrating sphere. The same trend, even more pronounced, was observed when measurements were realized on a deaerated or

aerated acetone solution of Cs₂Mo₆I₈(OCOC₂F₅)₆ with a variation from 49% to 1% respectively. Such change in the emission efficiency is due to the quenching of the nanocluster excited state by triplet oxygen and is known to generate the emissive O₂ (¹Δ_g) (*vide infra*).^[15] This phenomenon being a physical one, it does not imply any degradation of the emitter and is perfectly reversible. Oxygen strongly influences also the cluster phosphorescence emission decay. Indeed, a 269 μs phosphorescence lifetime decay could be determined for a deaerated acetone solution of Cs₂Mo₆I₈(OCOC₂F₅)₆, value consistent with previously reported one for Mo₆ based nanocluster compounds.^[16] This decay dropped down to 2 μs for the same solution, but aerated (see ESI, **Figures S13-S15**). In the solid state or once Cs₂Mo₆I₈(OCOC₂F₅)₆ is embedded in the P_i matrix, the emission decay profile could be fitted with a long and a short components as we previously observed when the same inorganic anion was integrated *via* ionic assembling in a polyurethane matrix.^[17] Blowing N₂ on P_iC samples during the measurements induces an increase of the longer component from 80 μs to around 200 μs that correlates well with the behavior of phosphorescent dyes dynamically quenched by molecular oxygen.^[18] Hence, The integration method developed in this work does not affect the abilities of nanoclusters to strongly emit which pushes us forward to investigate the process ability of these new hybrids.

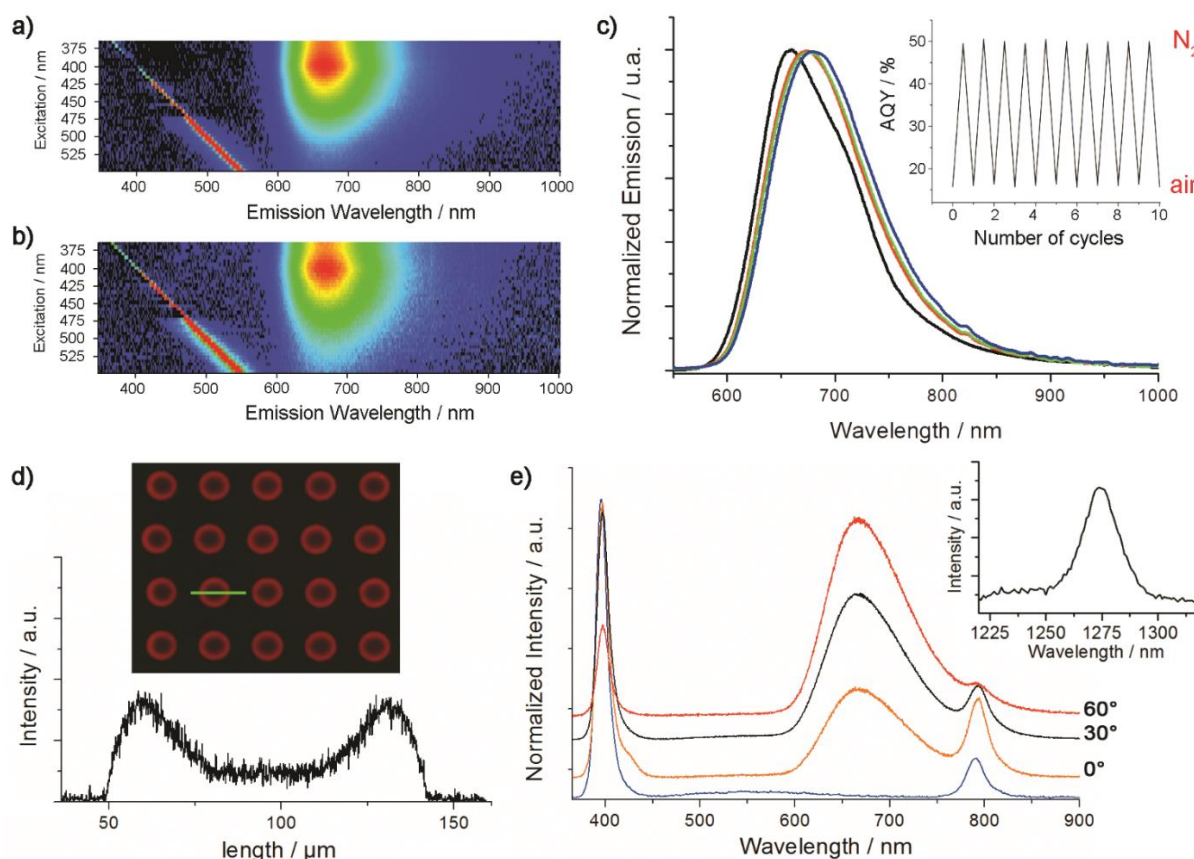


Figure 2. a) Excitation map of Cs₂Mo₆I₈(OCOC₂F₅)₆ in deaerated acetone solution; b) excitation map of P₁C (the blue and red colors correspond to a weak and strong intensity respectively); c) emission spectra ($\lambda_{exc} = 370$ nm) of crystalline Cs₂Mo₆I₈(OCOC₂F₅)₆ (black), P₁C (red), P₂C (green) and P₅C (blue), inset: AQY variation of P₁C depending on its atmosphere content; d) inkJet printed P₁C patterns under UV light excitation and corresponding colorimetric profiles for drops matrix; e) emission spectra recorded for 395 nm commercial blue-led (in blue) and P₁C covered blue LED recorded at various angle, inset: NIR corrected emission spectrum generated with the covered blue led.

Following a procedure, we developed for a freshly doped epoxy based ink, P₁C was inkjet printed on glass substrates.^[19] **Figure 2d** shows printed drops (see ESI **Figure S16**, for printed film studies) under UV light excitation ($\lambda_{exc} = 370$ nm).

Regarding morphological aspects, the patterns clearly shows the usual coffee stain effect responsible for the ring shape.^[20] Emission light intensity profiles highlight this phenomenon and show that material amount varies along the drop. Thickness profile measured by mechanical profilometry shows a similar shape (see ESI, **Figure S16**). Thus, high AQY combined with high doping level with no phase segregation and printing-abilities make this hybrid copolymer an excellent candidate for optical applications. To demonstrate such potentialities, P₁C was casted on top of a commercial 395 nm UV-blue LED. The emission spectra were recorded for the LED with and without copolymer coating and with different viewing angles (**Figure 2e**). The native UV-Blue LED emission spectrum possesses an intense band centered at 395 nm and its second diffraction order at 790 nm. Once coated with P₁C, the emission spectra depends significantly on the orientation of the optical fiber used to record the signal compared to the normal of the LED plan. At 0°, the radiative energy transfer from blue to red is only partial because the copolymer layer is not thick enough to absorb all the UV light. As a result, the blue component of the emission is stronger than the red one. When the angle increases, the red emission becomes stronger compared to the blue LED emission. This well-known phenomenon is mainly due i) to the fact that increasing the angle of detection implies that the UV light passes through an increased polymer thickness and thus more clusters are excited, and ii) to the ability of polymers to guide the emitted light which has already been exploited to design active waveguides^[21] or solar cell concentrators^[22] with cluster based materials. Nonetheless, although very simple, this example shows the high potential of this red phosphorescent copolymer as external conversion layer for optical applications. Moreover, we investigated whether it was possible to generate O₂ (¹Δ_g) with our simple device. As shown in the inset of figure 2e, an emission band centered on 1270 nm related to O₂ (¹Δ_g) emission could be detected. Therefore, a simple device made of a UV-LED covered with our copolymer can act as a local O₂ (¹Δ_g) generator, of particular interest for photodynamic therapy like in dermatology for e.g. melanoma treatments,^[23] or for bactericidal photodynamic applications.^[24]

In summary, this work presents the first example of hybrid acrylate in which a metal nanocluster compound, namely Cs₂Mo₆I₈(OCOC₂F₅)₆, is embedded homogeneously at 10 wt % by a simple solution blending. The softness of the integration method, based on weak interactions evidenced by ¹³³Cs NMR, allows the entire properties of the native inorganic salt to be transferred to the hybrid matrix. Compared to pure PMMA, the introduction of lateral PEO chains in the organic matrix insures the hybrid homogeneity and increases its gas permeability leading to highly O₂ sensitive materials. This high sensitivity is highlighted by the detection of O₂ (¹Δ_g) emission when a hybrid thin layer is deposited on a blue LED. Finally, taking into account the wide potentialities offered by inorganic molecular or supermolecular polyanionic species in terms of applicative prospects (energy conversion, catalysis,...) and the ease of integration described herein, the presented strategy offers promising perspectives in the developments of new hybrid copolymers with enhanced functionalities.

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Keywords: Cluster compounds • Energy conversion • Organic-inorganic hybrid composites • Self-assembly • Singlet oxygen

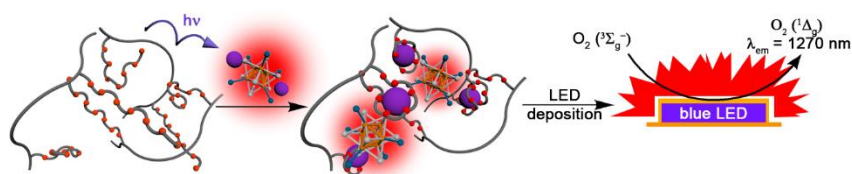
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High content of red-NIR phosphorescent metal clusters are integrated in acrylate copolymers without preliminary functionalization. The hybrid homogeneity is ensured by weak interactions occurring between the cluster salt cations and the lateral chains of the host. The resulting hybrids can be processed by inkjet and, once deposited as a thin film on a blue LED, generates bright red-nir light and singlet oxygen.

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