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## Copper clusters as novel fluorescent probes for the detection and photocatalytic elimination of lead ions†

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**A new homogeneous assay for a fast, selective and sensitive detection and elimination of lead ions has been developed using copper clusters as novel fluorescent probes in aqueous solutions. At the same time, their elimination is achieved using the efficient photocatalytic activity of such clusters. Both effects are explained in terms of an efficient electron transfer due to the LUMO energy of the cluster overlapping with the ion redox potential. The mechanism, which allows the explanation of previously reported results for different types of metal clusters, is further confirmed using smaller and larger Cu clusters displaying non-selective and non-quenching luminescence in the presence of different cations.**

Metal clusters (NCs), in general, consisting of several to tens of atoms have attracted much attention in recent years.<sup>1</sup> The strong quantum confinement of electrons in the ultrasmall size regime provides them with molecule-like properties, such as discrete electronic states, size-dependent fluorescence, high photobleaching threshold and excellent photostability, which makes them promising candidates in the fields of molecular imaging<sup>2</sup> and sensing applications.<sup>3</sup> Besides they can overcome the bigger problems of the traditional organic dyes – such as their relatively low photostability<sup>4</sup> – or the toxicity and photoblinking shown by the quantum dots.<sup>5</sup> Besides, compared to common semiconductor quantum dots, metal clusters seem to have fewer toxicity concerns. Until now, copper clusters (CuCLs) have attracted less attention compared to their counterparts (gold and silver). However, due to their low cost and unique optical and catalytic properties some studies have recently been reported on the synthesis and properties of CuCLs.<sup>6</sup>

Heavy metal pollution is a global problem that is a growing threat to the environment and humanity. Detection and quantification

of metal ions is important for environmental monitoring, in the food industry and in clinical diagnosis.<sup>7</sup> The detection of toxic metals (like Hg<sup>+2</sup>, Pb<sup>+2</sup>, *etc.*) in solution is a possible analytical application of metal clusters.<sup>8</sup> Among the metals, the detection of lead ions, Pb<sup>+2</sup>, commonly used in the automobile, paint and plastic industries, is receiving increasing attention due to its toxic (bone-seeking element and damage to the kidneys and nervous system) and bio-accumulative properties in the human body. Classical detection methods like atomic absorption spectrometry, and fluorescence or mass spectrometry have their limitations, including high cost, robust sample handling, *etc.* Therefore, it is very important to develop a simple, highly sensitive and selective method for the detection of Pb<sup>+2</sup> in aqueous media, and what is also very important, a simple method for their elimination from the contaminated aqueous media. Recently, several nano-based approaches were reported for the detection of very small amounts of lead ions: colorimetric assays based on gold nanoparticles<sup>9</sup> (LOD = 100 nM to 0.5 nM) or gold nanorods<sup>10</sup> (LOD = 0.1 nM), mass spectrometry (LOD = 0.5 nM) assays with AuNPs,<sup>11</sup> fluorimetric detection by using AuNPs on graphene surfaces<sup>12</sup> (LOD = 10 nM), dsDNA-templated CuNPs as fluorescent probes<sup>13</sup> (LOD = 5 nM) or fluorescence quenching based on gold<sup>14</sup> (LOD = 2 nM) or copper clusters.<sup>15</sup>

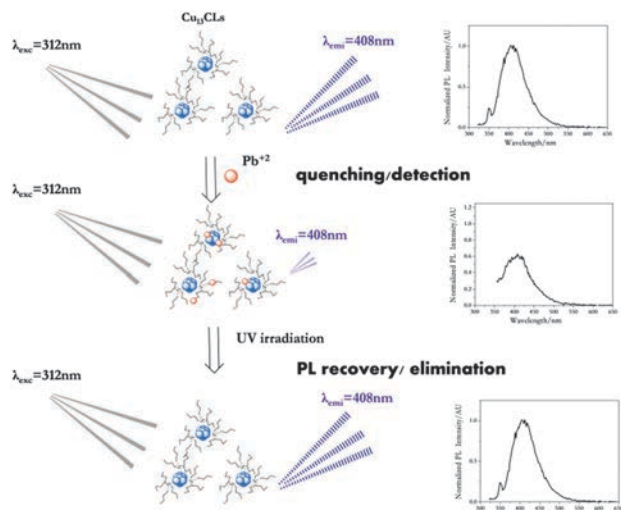
We demonstrate here a new strategy (see Scheme 1) for the selective detection of Pb<sup>+2</sup> using copper clusters (CuCLs) as fluorescent (PL) probes and also, at the same time, their elimination using continuous UV irradiation due to their photocatalytic activity.

Aqueous soluble fluorescent CuCLs were synthesized following a previous protocol<sup>16</sup> (details can be seen in the ESI† – Fig. S1–S3). Medium sized Cu<sub>13</sub> clusters were chosen in the first place for the main study. These CuCLs show emission at 408 nm (3.04 eV) by being excited at 312 nm (3.97 eV) as can be seen in Fig. 1A. The cluster size (by using Jellium approximation,  $E_g = AN^{-1/3}$ , where  $A = E_F$  (7 eV) = Fermi energy of the bulk material and  $N$  is the number of atoms per cluster), conduction and valence band energy values for such clusters (according to previous results<sup>16</sup>) are summarized in Table S1 (ESI†). As was previously reported,<sup>16</sup>

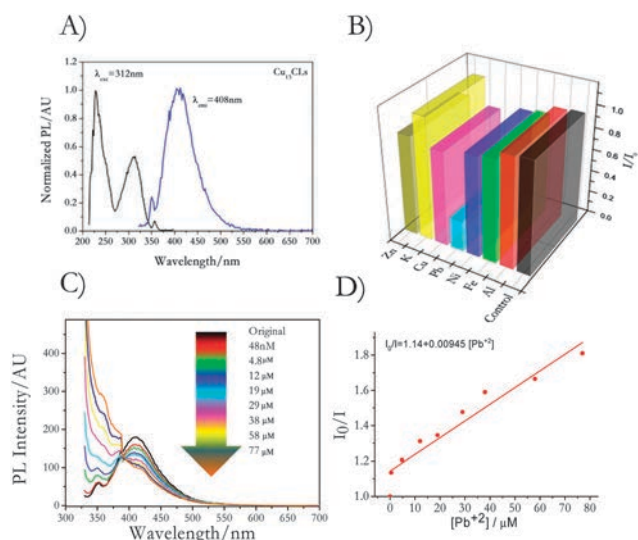
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**Scheme 1** Schematic representation showing the protocol for the detection and elimination of  $\text{Pb}^{2+}$  using the fluorescent and photocatalytic properties of CuCLs.



**Fig. 1** (A) Normalized fluorescence intensity of the  $\text{Cu}_{13}$  clusters, excitation at 312 nm emission at 408 nm. (B) Selectivity of the  $\text{Cu}_{13}$  clusters towards the different ions in water: fluorescence intensity ratios ( $I/I_0$ ) emitting at 408 nm for the  $\text{Cu}_{13}\text{CLs}$  in presence of different ions. (C) Sensitivity of  $\text{Cu}_{13}\text{CLs}$  fluorescence emission spectra to different  $\text{Pb}^{2+}$  concentrations increasing from 48 nM to 77  $\mu\text{M}$  in aqueous solution by exciting at 312 nm. (D) Linear fitting of the relative fluorescence intensity of CuCLs ( $I_0/I$ ) vs.  $[\text{Pb}^{2+}]$ .

large photoluminescence stability and no photobleaching during continuous irradiation after, at least, 20 min (Fig. S4, ESI†) are characteristic of these clusters.

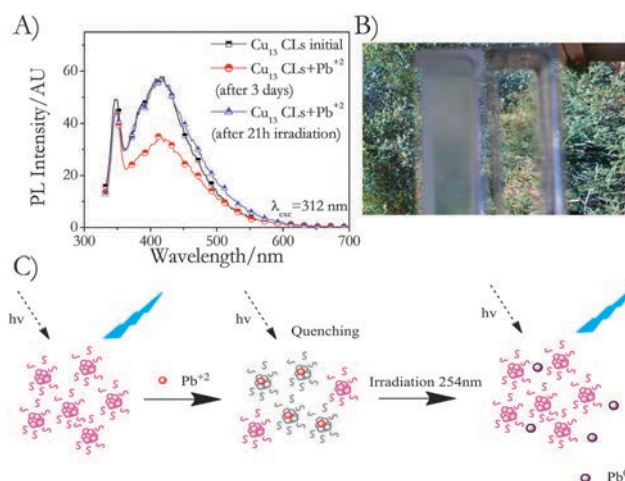
In order to test the ability of CuCLs as fluorescent probes we carry out experiments using different ions, investigating the selectivity of these CuCLs to different metal cations ( $\text{Al}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Pb}^{2+}$ ,  $\text{K}^+$  and  $\text{Cu}^{2+}$ ) ( $[\text{ion}] = 20\text{ }\mu\text{M}$ , evaluation time = 14 s). The fluorescence intensity of the CuCLs remains almost constant in the presence of all metal ions except the  $\text{Pb}^{2+}$  ions, which agrees with previous results obtained by Goswami *et al.*<sup>15</sup>

using CuCLs of similar sizes. Thus, from these observations it is clear that these CuCLs are very selective for sensing  $\text{Pb}^{2+}$  ions in water (Fig. 1B and Fig. S5–S7, ESI†). It should be noticed that these quenching effects occurred as soon as the quencher was added to the CuCL solution. Such a fast response is of particular importance in sensor field applications where individual samples must be analysed in a short period of time. Fig. 1C shows the gradual decrease in the fluorescence of the  $\text{Cu}_{13}$  clusters at 408 nm upon addition of increasing concentrations of  $\text{Pb}^{2+}$ . The fluorescence quenching data were analysed using the Stern–Volmer equation.<sup>17</sup> The fitted linear data could be expressed as  $I_0/I = 1.14 + 0.0094 [\text{Pb}^{2+}]$  ( $R^2 = 0.9176$ ) (Fig. 1D). The limit of detection (LOD) for  $\text{Pb}^{2+}$  was 4.9  $\mu\text{M}$  (Fig. S8, ESI†).

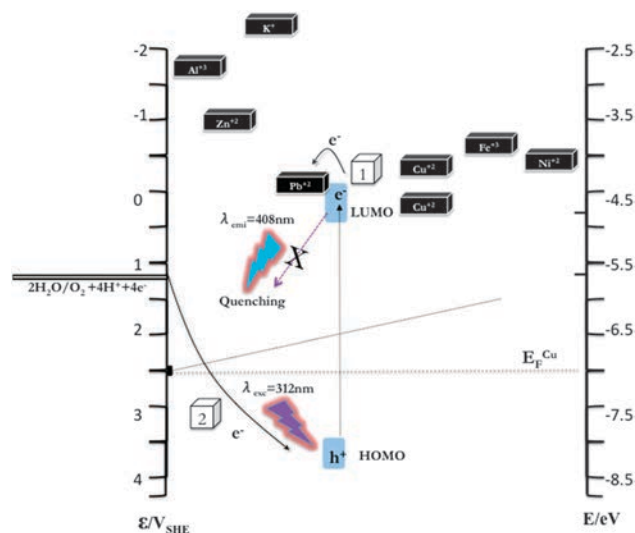
Based on the remarkable photocatalytic activities displayed by CuCLs,<sup>18</sup> recently reported by us, we tried to determine whether, after sensing, one could photocatalytically eliminate the detected  $\text{Pb}^{2+}$  ions. For this purpose an aqueous solution of  $\text{Cu}_{13}\text{CLs}$  in the presence of  $\text{Pb}^{2+}$  ions was continuously irradiated under UV light (254 nm) – see experimental details in the ESI.† As can be seen in Fig. 2A the initial intensity emission of the  $\text{Cu}_{13}\text{CLs}$  (quenched in the presence of  $\text{Pb}^{2+}$  ions) was completely recovered after 21 h irradiation.

Visually, the formation of a greyish-white precipitate onto the walls of the cuvette corresponding to a colloidal dispersion of  $\text{Pb}(0)$  (Fig. 2B, left) can be seen, which is not observed for the reference sample (irradiation in the absence of CuCLs). This precipitate can be ascribed to the formation of  $\text{Pb}(0)$  originated by the ion redox reduction through an  $\text{e}^-$  transfer process due to the proximity of the  $\text{Pb}^{2+}/\text{Pb}$  redox potential to the cluster LUMO energy and the corresponding elimination of the photo-produced holes by the oxidation of water, due to their extreme oxidizing power, as is schematically shown in Scheme 2.

The proposed mechanism for the quenching/elimination of  $\text{Pb}^{2+}$  ions, through the LUMO energy of the cluster overlapping with the ion redox potential differs from the mechanisms proposed



**Fig. 2** (A) Fluorescence intensity recovering after the irradiation of the sample with 254 nm UV lamp in presence of CuCLs. (B) Photograph of the quartz cuvettes where the reaction was carried out: left sample, right reference. (C) Schematic diagram of the possible mechanism.



**Scheme 2** Schematic energy diagram explaining the  $\text{Pb}^{2+}$  detection by using fluorescent  $\text{Cu}_{13}\text{CLs}$ .

until now for the cluster-PL sensors for metal ions. Some authors explained PL quenching by cluster aggregation though a coordination effect due to the stronger affinity between some ions (for example,  $\text{Cu}^{+2}$ ,  $\text{Hg}^{+2}$ ) and the  $-\text{COOH}$  groups of the protecting ligands on the surfaces of the clusters.<sup>19</sup>

According to this explanation, the carboxylic groups are hard donor ligands, which bind preferentially with hard acid metals or with other  $d^{10}$  centers by a highly metallophilic bonding, *e.g.*  $\text{Hg}^{2+}$  and  $\text{Au}^+$ , quenching the cluster fluorescence as in the case of  $\text{Au}$ -BSA interactions.<sup>20</sup> Another proposed explanation is that the PL quenching could be due to the paramagnetic properties of some metal ions (*i.e.*  $\text{Cu}^{+2}$ ) *via* electron or energy transfer.<sup>21</sup> Some authors also ascribe the selective metal ion response of metal clusters through a photo-induced electron transfer process<sup>22</sup> assuming the formation of a complex between the detected ion and the S-group of the thiol protected clusters. In this case the electrons of the clusters would be firstly excited and then the metal ion would intercept one of the charge carriers becoming reduced from the  $n^{+x}$  state to the  $n^{+x-1}$  state, which would disrupt the radiative recombination of the holes and the excited electrons causing the quenching of the metal clusters. But, even though this mechanism is closest to the one we have proposed, there are some questions that could be difficult to explain using such previous explanations:

(a) what is the origin of the selective quenching?; (b) why there are cases where unbound ions (lack of thiol protecting ligands, like in our case) also induce PL quenching? (c) how can the PL recovery be explained after irradiation as reported above?

To confirm the proposed overlapping mechanism we carry out a literature review of the metal clusters used until now as fluorescent nanoprobes. A literature summary about the metal cores, protecting ligands, selectivity, clusters emission wavelength, HOMO/LUMO positions, *etc.* of the clusters involved on the sensing protocol has been summarised in Table S2 (ESI†). Energy diagrams for the detected ions with the schematic representation of the HOMO/LUMO band gap for each cluster

have been also displayed in Fig. S9–S12 (ESI†). For this purpose, the  $E_{\text{gap}}$  of the cluster was approximated using an  $E_{\text{emission}}$  value similar to the  $E_{\text{gap}}$  value, with an  $E_{\text{Fermi}}$  of  $-5.5$  eV for the Au and Ag clusters, and  $-7$  eV for Cu clusters (in this last case, a dependence of the Fermi energy on the cluster size has been considered:  $E_{\text{F}} (\text{eV}) = -E_{\text{F}} (M_{\text{bulk}}) + \text{CN}^{-1/3}$ , as was previously reported<sup>16b</sup>). As can be observed, most of the given examples can easily be explained by the electron transfer overlapping mechanism, despite the very rough band gap approximation, which does not take into account factors, such as the ligand influence, *etc.*

To further confirm that selectivity can also be explained by the proposed mechanism, selectivity experiments were carried out using different copper cluster sizes ( $\text{Cu}_7\text{CLs}$  emission at 340 nm (3.65 eV) and  $\text{Cu}_{20}\text{CLs}$  emission at 466 nm (2.66 eV)) (Fig. S1, ESI†). The same series of ions were used for such experiments under similar experimental conditions (details in the ESI†). It can be observed that small  $\text{Cu}_7\text{CLs}$  do not show any selectivity, the PL being quenched by almost every cation, with only a higher decrease for  $\text{Al}^{+3} > \text{Fe}^{+3} > \text{K}^+$  (Fig. S13A and S14, ESI†). On the other hand, larger  $\text{Cu}_{20}\text{CLs}$  show almost no perceptible quenching effects (Fig. S12B, S13B and S15, ESI†). These results showing different quenching effects depend on the cluster sizes, which further supports the proposed overlapping mechanism schematically displayed in Fig. S16 (ESI†).

## Conclusions

Fluorescent medium copper ( $\text{Cu}_{13}$ ) clusters have been demonstrated to be very selective for the detection of  $\text{Pb}^{+2}$  ions by PL quenching. The  $\text{CuCL}$  photoluminescence can be recovered under UV light irradiation due to the photocatalytic ion reduction by the  $\text{CuCLs}$ . Using clusters of different sizes ( $\text{Cu}_7\text{CLs}$  and  $\text{Cu}_{20}\text{CLs}$ ) it was also observed that the smallest  $\text{CuCLs}$  show no selectivity and that, in contrast, the largest ones are not sensitive to the ions. Such results can be explained by an overlapping mechanism proposed here, which also explains most of the sensing properties of different metal cluster nanoprobes reported to date. The sensitivity and fast response of the medium sized  $\text{Cu}_{13}\text{CLs}$ , together with their photocatalytic activities, makes them efficient off-on recyclable nanosensors and nano-cleaners.

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