PCCP

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/pccp

Journal Name

RSCPublishing

COMMUNICATION

Cite this: DOI: 10.1039/x0xx00000x

Copper clusters as novel fluorescence probes for lead ions detection and their photocatalytic elimination

N. Vilar-Vidal,[a,b] J. Rivas[a,b] and M.A. López-Quintela[a]

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

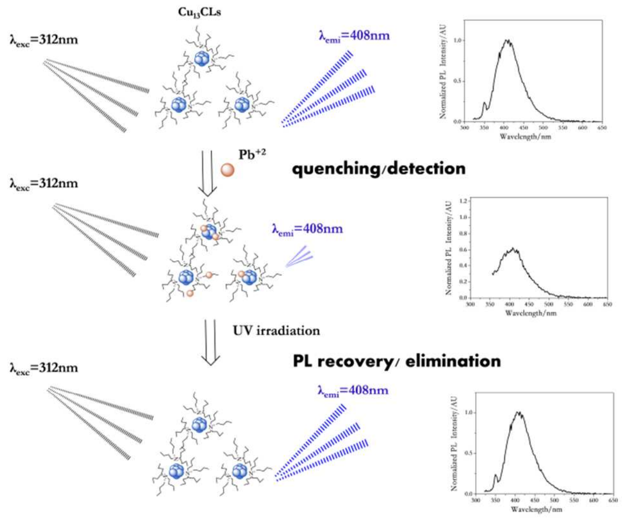
A new homogeneous assay for a fast, selective and sensitive detection and elimination of lead ions has been developed using copper clusters as novel fluorescence probes in aqueous solutions. At the same time, their elimination is achieved using the efficient photocatalytic activity of such clusters. Both effects are explained in terms of an efficient electron transfer due to the cluster´s LUMO overlapping with the ion redox potential. The mechanism, which allows explaining previous 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 atoms have attracted much attention in recent years.[1] The strong quantum confinement of electrons in the ultrasmall size regime provide to them molecule-like properties, such as discrete electronic states, size-dependent fluorescence, high photobleaching threshold and excellent photostability make them promising candidates in the fields of molecular imaging[2] and sensing applications.[3] Besides they can overcome the bigger problems of the traditional organic dyes -such their relatively low photostability-[4] or the toxicity and photoblinking showed by the quantum dots.[5] Besides, compared to common semiconductor quantum dots, metal clusters seem to have fewer toxicity concerns. Up to now, copper clusters (CuCLs) have attracted less attention than their counterparts (gold and silver). However, due to their low cost and unique optical and catalytic properties some studies have been recently reported about the synthesis and properties of CuCLs.[6]

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, food industry and clinical diagnosis.[7] The detection of toxic metals (like Hg^{+2}, Pb^{+2}, etc.) in solution is a possible analytical application of metal clusters.[8] Among them, the detection of lead ion, Pb^{+2}, commonly used in the automobile, paint and plastic industries, is receiving increasing attention due to its toxic (bone-seeking element and damage to kidney and nervous system) and bio-accumulative properties in the human body. Classical detection methods like atomic absorption spectrometry, fluorescence or mass spectrometry, have their limits, such as 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^{+2} 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[9] (LOD= 100nM-0.5nM) or gold nanorods[10] (LOD= 0.1nM), mass spectrometry (LOD=0.5nM) assays with AuNPs,[11] fluorimetric detection by using AuNPs onto graphene surfaces[12] (LOD= 10nM), dsDNA-templated CuNPs as fluorescence probes[13] (LOD= 5nM) or fluorescence quenching based on gold[14] (LOD=2nM) or copper clusters.[15]

We demonstrate here a new strategy (see Scheme 1) for the selective detection of Pb^{+2} 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[16] (details can be seen in the supporting information-SI- Figures S1, S2 and S3). Medium sized Cu_{13} clusters were chosen in first place for the main study. These CuCLs show emission at 408nm (3.04eV) by being excited at 312 nm (3.97 eV) as it can be seen on Figure 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), the conduction and valence band energy values for such clusters (according to previous results[16]) are summarized in Table S1. As it was previously reported,[16] large photoluminescence stability and no photobleaching during continuous irradiation after, at least, 20 min (Figure S4) are characteristics for these clusters.



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

In order to test the ability of CuCLs as fluorescence probes we carry out experiments with different ions, investigating the selectivity of these CuCLs to different metal cations (Al^{+3}, Zn^{+2}, Ni^{+2}, Fe^{+3}, Pb^{+2}, K^{+} and Cu^{+2}) ([ion] = 20μM, evaluation time=14s). The fluorescence intensity of the CuCLs remains almost constant in the presence of all metal ions except for the Pb^{+2} ions, which agrees with previous results obtained by Goswami et al. [15] using CuCLs of similar sizes. Thus, from these observations it is clear that these CuCLs are very selective for sensing Pb^{+2} ions in water (Fig. 1B-Fig. S5-S7). It has to be noticed that these quenching effects occurred immediately once the quencher was added to the CuCLs solution. Such 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 Cu_{13} clusters at 408 nm upon addition of increasing concentrations of Pb^{+2}. The fluorescence quenching data were analysed by using the Stern–Volmer equation.[17] The fitted linear data could be expressed as $I_0/I=1.14 + 0.0094\ [Pb^{+2}]$ (R^2=0.9176) (Fig. 1D). The limit of detection (LOD) for Pb^{+2} was 4.9 μM (Fig. S8).

Based on the remarkable photocatalytic activities displayed by CuCLs,[18] recently reported by us, we tried if, after sensing, one could photocatalytically eliminate the detected Pb^{+2} ions. For this purpose an aqueous solution of Cu_{13} CLs in presence of Pb^{+2} ions was continuously irradiated under UV light (254nm) –see experimental details in the SI-. As it can be seen in Figure 2A the initial intensity emission of the Cu_{13}CLs (quenched in the presence of Pb^{+2} ions) was completely recovered after 21 h irradiation.

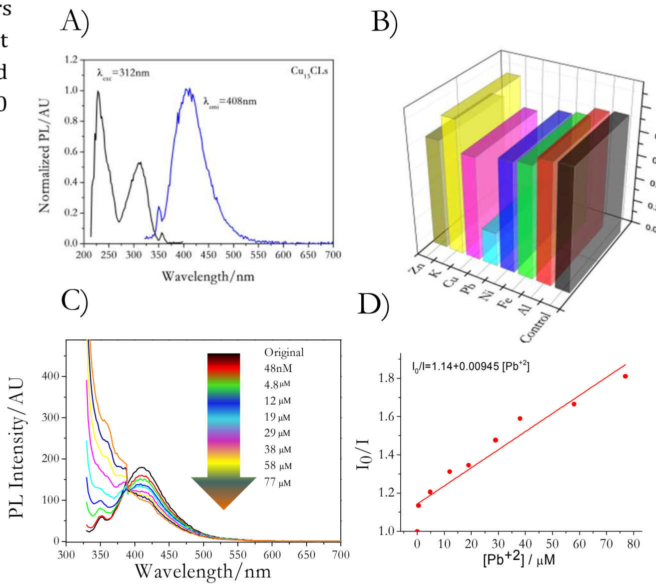


Fig.1 A) Normalized Fluorescence intensity of the Cu_{13} clusters, excitation at 312nm emission at 408nm. B) Selectivity of the Cu_{13} clusters towards the different ions in water: fluorescence intensity ratios (I/I_0) emitting at 408nm for the Cu_{13} CLs in presence of different ions. C) Sensitivity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

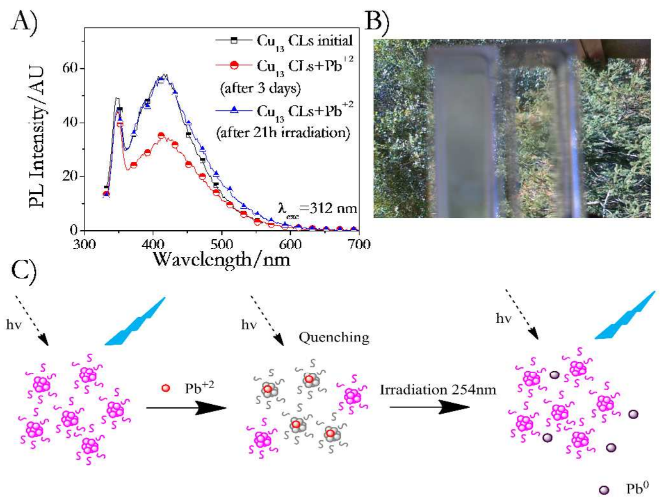
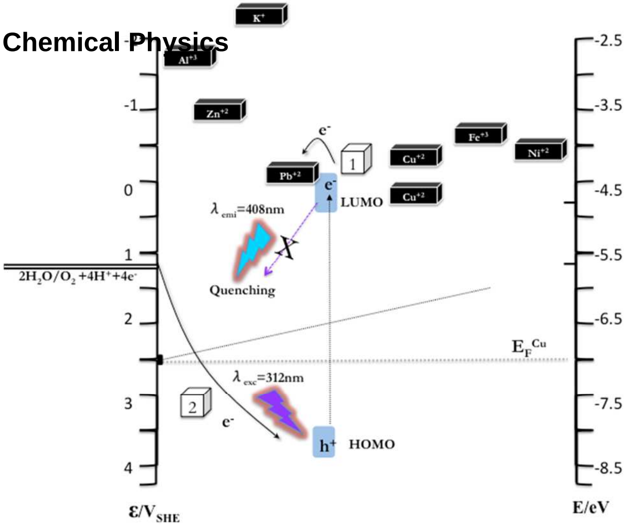


Fig.2 A) Fluorescence intensity recovering after the irradiation of the sample with 254nm UV lamp in presence of CuCLs. B) Photograph of the quartz cuvettes where the reaction was carried out: left sample, right reference. C) Schematic diagram of the possible mechanism.

Visually, it can be seen the formation of a greyish-white precipitate onto the walls of the cuvette corresponding to a colloidal dispersion of Pb(0) (Figure 2B, left), which is not observed for the reference sample (irradiation in absence of CuCLs). This precipitate can be ascribed to the formation of Pb(0) originated by the ion redox reduction through an e^- *transfer process* due to the proximity of the Pb^{+2}/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 extremely oxidant power, as it is schematically shown in Scheme 2.

The proposed mechanism for the quenching/elimination of Pb^{+2} ions, through the *cluster's LUMO energy overlapping with the ion redox potential* differs from the mechanisms until now proposed for the cluster-PL sensors for metal ions. Some authors explained the PL quenching by a cluster *aggregation* though a coordination effect due to the stronger affinity between some ions (for ex. Cu^{+2}, Hg^{+2}) and the –COOH groups of the protecting ligands on the surfaces of the clusters.[19]



Scheme 2. Schematic energy diagram explaining the Pb^{+2} detection by using fluorescent Cu_{13} CLs.

According to such explanation, the carboxylic groups are hard donor ligands, which preferentially bind with hard acid metals or with another d^{10} centers by a highly metallophilic bonding, e.g. Hg^{2+} and Au^+, quenching the cluster fluorescence as in the case of Au-BSA interactions.[20] Another proposed explanation is that the PL quenching could be due to the paramagnetic properties of some metal ions (i.e. Cu^{+2}) via electron or energy transfer.[21] Some authors ascribe also the selective metal ion response of metal clusters through a photo-induced electron transfer process[22] 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 carries being reduced from its n^{+x} state to n^{+x-1}, which would disrupt the radiative recombination of the holes and the excited electrons causing the quenching of the metal clusters. But, even being this last mechanism the 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) induce also PL quenching?* (c) *how can be explained the PL recovery after irradiation as it was 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 the Table S2. Energy diagrams for the detected ions with the schematic representation of the HOMO/LUMO band gap for each cluster have been also displayed in Figures S9-S12. For this purpose the Cluster's E_{gap} was approximated using the $E_{emission}$ like the E_{gap} , being -5.5eV the E_{Fermi} for the Au and Ag clusters, and -7eV for Cu clusters (in this last case, a dependence of the Fermi evergy with the cluster size has been considered: E_F (eV) = - E_F (M_{bulk}) +$CN^{-1/3}$, as it was previously reported[16b]). As it can be observed, most of the given examples can easily be explained by the electron transfer overlapping mechanism, despite of the very rough band gap approximation, which does not take into account effects, like the ligands 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 (Cu_7CLs-emission at 340nm (3.65eV) - and Cu_{20}CLs –emission at 466nm (2.66 eV) -) (Figure S1). The same series of ions were used for such experiments under similar experimental conditions (details SI). It can be observed that small Cu_7CLs do not shown any selectivity, being the PL quenched by almost every cation, and observing only a higher decrease for Al^{+3}>Fe^{+3}>K^+ (Figures S13A, S14). On the other hand, larger Cu_{20} CLs show almost no perceptible quenching effects (Figures S12B, S13B and S15). These results showing different quenching effects depending on the cluster sizes further support the proposed *overlapping mechanism* schematically displayed in Figure S16.

Conclusions

Fluorescent medium copper (Cu_{13}) clusters have demonstrated to be very selective for the detection of Pb^{+2} ions by PL quenching. The CuCLs photoluminescence can be recovered under UV light irradiation due to the photocatalytic ion reduction by the CuCLs. Using clusters of different sizes (Cu_7CLs and Cu_{20} CLs) it was also observed that the smallest CuCLs show no selectivity and that, on the contrary, the largest ones are not sensitive to the ions. Such results can be explained by an overlapping mechanism here proposed, which also explains most of the sensing properties of different metal cluster nanoprobes clusters reported until now. The sensitivity and fast response of the medium size Cu_{13} CLs, together with their photocatalytic activities, make them as efficient *off-on recyclable nanosensors and nano-cleaners*.

Acknowledgements

This work was supported by the funding of different organizations : European Commission through FEDER program (0681_InveNNta_1_E);MCI, Spain (MAT2010-20442; MAT2011-28673-C02-01); MINECO, Spain (MAT2012-36754-C02-01); Xunta de Galicia, Spain (GRC2013-044, FEDER Funds); and Obra Social Fundación La Caixa (OSLC-2012-007).

Notes and references

[a] Nanomag Laboratory, Research Technological Institute. University of Santiago de Compostela, E-15782, Santiago de Compostela, Spain. E-mail: noelia.vilar@usc.es, malopez.quintela@usc.es
[b] INL-International Iberian Nanotechnology Laboratory, 4715-310, Braga, Portugal.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

1) a) L. Shang, S.J. Dong, G.U. Nienhaus, *Nano Today* 2011, **6**, 401. b) Y. Lu, W. Chen Chem. Soc. Rev., 2012, **41**, 3594. c) R. Jin *Nanoscale*, 2010, **2**, 343.
2) a) J. Zhang, Y. Fu, C. V. Conroy, Z. Tang, G. Li, R. Y. Zhao and G. Wang, *J. Phys. Chem. C* , 2012, **116** , 26561. b) Y. Bao, H-C. Yeh, C. Zhong, S. A. Ivanov, J. K. Sharma, M. L. Neidig, D. M. Vu, A. P. Shreve, R. B Dyer, J. H. Werner, J. S. Martinez *J. Phys. Chem. C* 2010, **114**, 15879. c) J. Yu, S. A. Patel, R. M. Dickson *Angew. Chem. Int. Ed.* 2007, **46**, 2028. d) N. Makarava, A. Parfenov, I. V. Baskakov, *Biophys J.*, 2005, **89**, 572.
3) a) B. Adhikari, A. Banerjee *Chem. Mater.* 2010, **22**, 4364. b) J. Xie, Y. Zheng, J.Y. Ying *Chem. Commun.* 2010, **46,** 961. c) C. C. Huang, Z. Yang, K.-H. Lee, H.T. Chang *Angew. Chem.* 2007, **119,** 6948. d) M. Zhang, B.-C. Ye *Analyst* 2011, **136,** 5139. e) C. V. Durgadas, C.P. Sharma, K. Sreenivasan *Analyst* 2011, **136,** 933. f) H. Liu, X. Zhang, X. Wu, L. Jiang, C. Burda, J.J. Zhu *Chem. Commun*. 2011, **47,** 4237.
4) J. Zhang, Y. Fu, C. V. Conroy, Z. Tang, G. Li, R. Y. Zhao, G. Wang, *J. Phys. Chem. C,* 2014, dx.doi.org/10.1021/jp306036y.
5) A. M. Smith, S. Nie, *Nat. Biotechnol.* 2009, **27**, 732.
6) a) C. Vázquez-Vázquez, M. Bañobre-López, A. Mitra, M.A. López-Quintela, J. Rivas, *Langmuir* 2009, **25,** 8208. b) N. Vilar-Vidal, M.C. Blanco, M.A. López-Quintela, J. Rivas, C. Serra, *J. Phys. Chem. C* 2010, **114,** 15924. c) H. Kawasaki, Y. Kosaka, Y. Myoujin, T. Narushima, T. Yonezawa, R. Arakawa, *Chem. Commun*. 2011, **47,** 7740. d) W. Wei, Y. Lu, W. Chen, S. Chen, *J. Am. Chem. Soc.* 2011, **133,** 2060.
7) P. Chen, C. He, *J. Am. Chem. Soc.* 2004, **126**, 728.
8) a) B. Adhikari, A. Banerjee *Chem. Mater.* 2010, **22**, 4364. b) Z. Yuan, M. Peng, Y. He, E. S. Yeung *Chem. Commun*. 2011, **47,** 11981.
9) a) F. Chai, C. Wang, T. Wang, L. Li, Z. Su, *ACS Applied Materials and Interfaces*, 2010, **2**, 1466. b) N. Ding, Q. Cao, H. Zhao, Y. Yang, L. Zeng, Y. He, K. Xiang, G. Wang *Sensors* 2010, **10**, 11144. c) Y. Y. Chen, H. T. Chang, Y. C. Shiang, Y. L. Hung, C. K. Chiang, C. C. Huang, *Anal. Chem*. 2009, 81, 9433.
10) H. Cai, D. Lin, J. Wang, P.Yang, J. Cai *Sensors and Actuators B: Chemical*, 2014, **196**, 252.
11) Y. C. Liu, C. K. Chiang, H. T. Chang, Y. F. Lee, C. C. Huang, *Adv. Funct. Mater*. 2011, **21**, 4448.
12) X. Fu, T. Lou, Z. Chen, M. Lin, W. Feng, L. Chen *ACS Appl. Mater. Interfaces* 2012, **4**, 1080.
13) J. Chen, J. Liu, Z. Fang, L. Zeng *Chem. Commun*., 2012, **48**, 1057.
14) Z. Yuan, M. Peng, Y. He, E.S. Yeung *Chem. Commun.* 2011, **47**, 11981.
15) N. Goswami, A. Giri, M.S. Bootharaju, P. L. Xabier, T. Pradeep, S.K. Pal *Anal. Chem.* 2011, **83**, 9676.
16) a) N. Vilar-Vidal, M. C. Blanco, M. A. López-Quintela, J. Rivas, C. Serra, *J. Phys. Chem. C,* 2010, **114**, 15924. b) N.Vilar-Vidal, J. Rivas, M. A. López-Quintela *ACS Catal.* 2012, **2**, 1693.
17) J. R. Lakowicz, Principles of Fluorescence Spectroscopy, Kluwer Academic/Plenum Press, New York, 1999.
18) N. Vilar-Vidal, J. Rivas, M. A. López-Quintela, *Small,* 2014, doi: 10.1002/smll.201400679.
19) a) B. Adhikari and A. Banerjee, Chem. Mater., 2010, **22**, 4364. b) J. Liu, X. Ren, X. Meng, Z. Fang, F. Tang *Nanoscale*, 2013, **5,** 10022. c) L. Shang, S. Dong *J. Mater. Chem.,* 2008, **18**, 4636. d) J.-M. Liu, L.-p. Lin, X.-X. Wang, S.-Q. Lin, W.-L. Cai, L.-H. Zhang, Z.-Y. Zheng, *Analyst* 2012, **137**, 2637.
20) J. Xie, Y. Zheng, J. Y. Ying, *Chem. Commun.* 2010, **46**, 961.
21) A. W. Varnes, R. B. Dodson and E. L. Wehry, *J. Am. Chem. Soc.*, 1972, **94**, 946.
22) a) Henglein, A. *Chem. Mater.* 1998, **10**, 444. c) D. Hu, Z. Sheng, P. Gong, P. Zhang, L. Cai *Analyst* 2010, **135**, 1411.