Sensors and Actuators B 242 (2017) 632–636

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

A fluorescent probe for organotin bromides based on the halogen replacement reaction of lead(II) halide anionic clusters

Yufen Niu, Xiaoyu Chen, Yuan Zhu, Shunhua Li*

Department of Chemistry and the MOE Key Laboratory of Spectrochemical Analysis & Instrumentation, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, 361005, China

ARTICLE INFO

Article history:
Received 16 June 2016
Received in revised form 25 October 2016
Accepted 19 November 2016
Available online 21 November 2016

Keywords:
Organotins
Fluorescent chemosensors
Cluster compounds
Bromide

ABSTRACT

Design of fluorescent chemosensors for convenient detection of organotin species is an important but challenging task. Herein, a highly selective fluorescent sensing system for organotin bromides (OTBs) has been developed based on $Pb_nCl_{3n}{}^{n-}$ clusters. This type of clusters can be easily formed by inexpensive off-the-shelf reagents. Addition of OTBs rapidly induces a transformation from $Pb_nCl_{3n}{}^{n-}$ to $Pb_nBr_{3n}{}^{n-}$ clusters via halogen replacement reaction. Both of the chloride and bromide clusters are found to be fluorescent with unusually large Stokes' shifts and have been characterized by single crystal X-ray diffraction. A remarkable fluorescence change is observed with high selectivity toward OTBs over organotin fluorides, organotin chlorides, ionic bromides, or other covalent organobromines. Taking advantage of the fluorescence response, quantitative detection of OTBs at the micromolar concentration level in aprotic solvents can be established.

1. Introduction

Organotin compounds (OTs) have been attracting great analytical interest due to their wide distribution and strongly toxic effect on marine organisms [1–4]. The determination of organotin levels in environmental samples relies heavily on chromatography and is a complex process involving several analytical steps [5–8]. Optical chemosensors for OTs are highly desirable in terms of the merit of rapid, straightforward and inexpensive detection. OTs are generally represented by the formula R_nSnX_{4-n}, where Sn is the tin atom, R is an alkyl or aryl group, X is a halide, hydroxide, −OR', or −SR', and n ranges from 1 to 4. Currently, considerable analytical attention has been drawn to the R groups. However, the evolution and diversity of X groups is also an important topic associated with the degradation, metabolism, and delayed toxicity of OTs [9–12]. For detection of organotin halides, chromatography was generally combined with mass spectrometry which was employed as an identification tool [13–15], and thus led to a costly and time-consuming analytical process. Seeking convenient detection, we have synthesized the first fluorescent probes for hydroxylated organotins [16] and organotin halides [17]. Herein reported is the first fluorescent sensing system for organotin bromides (OTBs), which can be easily formed by inexpensive off-the-shelf reagents.

Our OTB sensing system is based on lead(II) halide clusters. As previously reported [18,19], luminescent lead(II) bromide clusters can be directly formed by inorganic lead(II) salts and tetraalkylammonium bromide in aprotic solvents at room temperature. In this research, we found that luminescent lead(II) chloride clusters could be formed in a similar way. The unique photoluminescence properties and high halogen replacement reactivity of these polyanionic lead(II) halide clusters enlighten us to investigate them as a new optical sensing platform for biologically or environmentally important halogen-containing species.

2. Materials and methods

2.1. Reagents and apparatus

The solvent (acetonitrile) were distilled from calcium hydride under a nitrogen atmosphere prior to use. Tetraalkylammonium chlorides or bromides, 1,2-dibromoethylene, 1,3-dibromopropane, and all the investigated organotin compounds were purchased from Sigma-Aldrich Co., Ltd. They were used without any further purification. All other reagents were of analytical grade or better and used without further purification. The solutions of lead(II) halide clusters were prepared by directly mixing inorganic lead(II) salts and tetrabutylammonium halides in acetonitrile.

Absorption and fluorescence spectra were recorded on a Hitachi U-3900 ultraviolet–visible spectrophotometer and a Hitachi F-7400

---

* Corresponding author.
E-mail address: lishua@xmu.edu.cn (S. Li).

http://dx.doi.org/10.1016/j.snb.2016.11.095
0925-4005/© 2016 Elsevier B.V. All rights reserved.

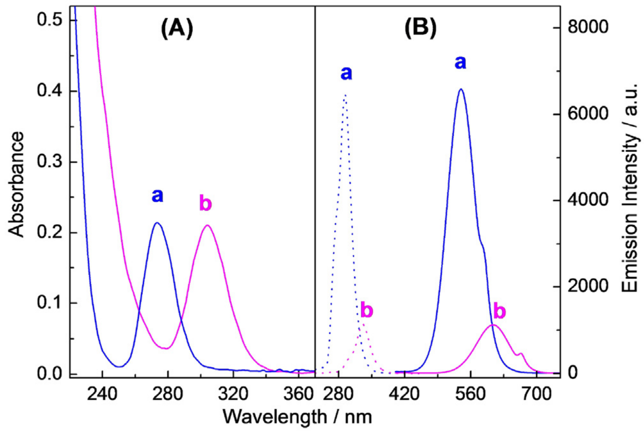

Fig. 1. Absorption (A, [Pb] = 40 μM) and photoluminescence (B, [Pb] = 1.6 mM) spectra of the lead(II) halides clusters in acetonitrile. The cluster ensembles were formed by lead(II) nitrate and tetrabutylammonium halides (a, chloride; b, bromide) with an n_N/n_{Pb} of 5:1. The emission spectra of $Pb_nCl_{3n}{}^{n-}$ and $Pb_nBr_{3n}{}^{n-}$ clusters were recorded upon excitation at 295 nm and 330 nm, respectively. The shoulder peaks at 590 nm (for $Pb_nCl_{3n}{}^{n-}$ clusters) and 660 nm (for $Pb_nBr_{3n}{}^{n-}$ clusters) in emission spectra were assigned to scattering signals.

fluorophotometer, respectively. Dynamic light scattering (DLS) data were collected from a Malvern Zetasizer Nano-zsMPT-2 particle size and zeta potential analyzer. The emission decay times were acquired with a HORIBA Jobin Yvon FluoroMax-4 TCSPC time-resolved fluorophotometer, which was equipped with an F-3018 integrating sphere accessory and further employed to measure the absolute fluorescence quantum yields by the integrating sphere approach.

2.2. X-ray crystallography

The crystal of $Pb_nCl_{3n}{}^{n-}$ cluster suitable for X-ray diffraction was grown from a solution of benzyltriethylammonium chloride (24 mM) and lead(II) chloride (1.6 mM) in anhydrous acetonitrile. The crystal of $Pb_nBr_{3n}{}^{n-}$ cluster was grown in a similar procedure using benzyltriethylammonium bromide as the bromine source. Upon UV irradiation, the chloride and bromide cluster displayed intense green and orange luminescence, respectively (Supplementary Fig. S2). Single-crystal X-ray diffraction data were collected on an Oxford Gemini S Ultra CCD Area Detector using graphite-monochromated Mo Ka radiation (λ = 0.71073 Å). All of the data were corrected for absorption effects using the multi-scan technique (Table 1). The structure was solved by direct methods, expanded by difference Fourier syntheses and refined by full matrix least-squares on F^2 using Bruker SHELXTL (Version 6.10) program package. The X-ray crystal structures have been deposited in the Cambridge Crystallographic Data Centre (CCDC) under the deposition numbers CCDC-900867 ($Pb_nBr_{3n}{}^{n-}$ clusters) and CCDC-900868 ($Pb_nCl_{3n}{}^{n-}$ clusters). The data can be obtained free of charge from the CCDC (www.ccdc.cam.ac.uk/data_request/cif).

3. Results and discussion

3.1. Photoluminescence properties and structures of the lead(II) halide clusters

The absorption and photoluminescence spectra of the clusters formed by lead(II) nitrate and tetrabutylammonium halides in acetonitrile were shown in Fig. 1. Strong luminescence with a large Stokes' shift was also observed from the chloride clusters, despite of an obvious blue shift compared with the emission signal of the bromide clusters. Under the investigated conditions, the average quantum yields of the chloride and bromide clusters are 6.9% and 4.3% respectively, and the emission lifetimes of the chloride and bromide clusters are 40 ns and 20 ns respectively (Supplementary Fig. S3). It is noteworthy that the optimum excitation wavelengths of these clusters display obvious red shifts compared with their absorption maximums probably because of the occurrence of excited-state reactions.

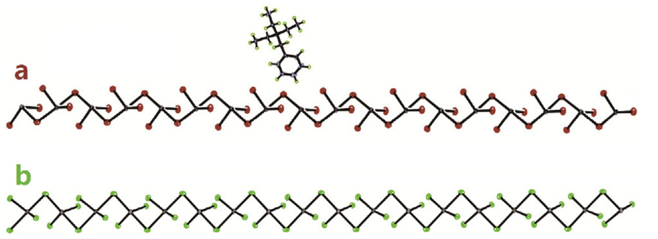

Fig. 2. Structures of the polyanionic skeletons of the investigated lead(II) halide clusters (a, $Pb_nBr_{3n}{}^{n-}$; b, $Pb_nCl_{3n}{}^{n-}$) (ellipsoids at the 50% probability level). The tetraalkylammonium stabilizing layers are omitted for clarity except for the retention of one counter cation (benzyltriethylammonium) in (a). Selected bond lengths [Å] and angles [°]: Pb – Br1 2.988(2), Pb – Br2 2.7939(19), Pb – Br3 2.8314(19), Pb – Br1′ 3.0312(19); Br1 – Pb – Br2 93.39(6), Br1 – Pb – Br3 87.83(5), Br2 – Pb – Br3 93.35(6), Br1 – Pb – Br1′ 178.05(5), Br2 – Pb – Br1′ 85.38(5), Br3 – Pb – Br1′ 93.75(6), Pb – Br1 – Pb′ 83.82(5); Pb – Cl1 2.886(3), Pb – Cl2 2.681(3), Pb – Cl3 2.658(2), Pb – Cl1′ 2.871(3); Cl1 – Pb – Cl2 85.64(8), Cl1 – Pb – Cl3 94.85(7), Cl1 – Pb – Cl1′ 178.73(5), Cl2 – Pb – Cl3 94.06(8), Cl2 – Pb – Cl1′ 95.63(8), Cl3 – Pb – Cl1′ 85.23(7), Pb – Cl1 – Pb′ 86.38(7).

For an in-depth study on the structures of these luminophores, high-quality single crystals of both the bromide and chloride clusters were prepared using benzyltriethyl-ammonium as a relatively rigid ammonium source. X-ray diffraction experiments revealed that the cluster skeleton, which was capped by a tetraalkylammonium stabilizing layer, was a $Pb_nX_{3n}{}^{n-}$ polyanion consisting of many $PbX_3{}^-$ repeating units (Fig. 2). This is the first time that the structures of this type of lead(II) halide clusters have been clarified.

3.2. Spectral responses of $Pb_nCl_{3n}{}^{n-}$ clusters to OTBs

The described high structural similarity between $Pb_nCl_{3n}{}^{n-}$ and $Pb_nBr_{3n}{}^{n-}$ clusters enlightened us to investigate the halogen replacement reactivity of these unique inorganic fluorophores. The $Pb_nCl_{3n}{}^{n-}$ clusters formed by lead(II) nitrate and tetrabutylammonium chloride in acetonitrile were tested, although alteration of the lead(II) salt or tetrabutylammonium source results in similar fluorescence behaviors (Supplementary Fig. S4). As shown in Fig. 3, the solution of $Pb_nCl_{3n}{}^{n-}$ clusters displays rapid and remarkable spectral changes in the presence of OTBs. The absorption band shifts from 274 nm to 305 nm while the emission signal shifts from 540 nm to 608 nm, indicating the transformation of the clusters from $Pb_nCl_{3n}{}^{n-}$ to $Pb_nBr_{3n}{}^{n-}$. Addition of other organobromine species or organotin chlorides induced no obvious spectral change except that a luminescent intermediate (λ_{abs} = 284 nm; λ_{em} = 566 nm) was formed in the presence of excess tetraalkylammonium bromide. This luminescent intermediate is assigned to a polyanionic product from the partial halogen replacement reaction of $Pb_nCl_{3n}{}^{n-}$ because of the co-existence of tetraalkylammonium chloride and bromide, which was presumed to bear $PbCl_2Br^-$ and/or $PbClBr_2{}^-$ luminecscent units.

Unlike ionic tetraalkylammonium bromide, organotin bromide induces the transformation from $Pb_nCl_{3n}{}^{n-}$ to $Pb_nBr_{3n}{}^{n-}$ efficiently. This is interpreted by the covalent nature [20,21] and the resulting high halogen replacement reactivity [22] of organotin halides. Since there is an additional benefit that many disturbances from other HCSs can be excluded by the tetraalkylammonium stabilizing layer, highly selective fluorescent sensing of OTBs by $Pb_nCl_{3n}{}^{n-}$ clusters can be established.

Table 1
Crystal data and structure refinement for the lead(II) halide clusters.

	$PhCH_2NEt_3{\cdot}PbBr_3$	$PhCH_2NEt_3{\cdot}PbCl_3$
formula	$C_{13}H_{22}Br_3NPb$	$C_{13}H_{22}Cl_3NPb$
Mr	639.24	505.86
temperature [K]	173(2)	173(2)
crystal system	orthorhombic	orthorhombic
space group	$P2_12_12_1$	$P2_12_12_1$
a [Å]	8.0412(16)	7.8788(17)
b [Å]	13.164(3)	15.900(3)
c [Å]	16.407(3)	12.877(3)
a [°]	90.00	90.00
b [°]	90.00	90.00
g [°]	90.00	90.00
V [Å^3]	1736.7(6)	1613.1(6)
Z	4	4
r_{calcd} [g m^{-3}]	2.445	2.083
μ [mm^{-1}]	16.602	10.940
F(000)	1176.0	960.0
crystal size [mm^3]	0.20 × 0.10 × 0.10	0.30 × 0.20 × 0.20
θ range [°]	6.18–49.98	4.08–49.98
index ranges	$-9 \le h \le 9$, $-15 \le k \le 15$, $-19 \le l \le 19$	$-9 \le h \le 9$, $-12 \le k \le 18$, $-15 \le l \le 15$
reflns collected	12862	7452
independent reflns	3064 [R(int) = 0.1257]	2809 [R(int) = 0.0964]
data/restraints/parameters	3064/12/163	2809/0/163
GOF on F^2	1.024	0.731
R_1/wR_2 [$I \ge 2\sigma(I)$]	0.0549/0.1297	0.0525/0.1353
R_1/wR_2 (all data)	0.0695/0.1350	0.0562/0.1394
largest peak/hole [e Å^{-3}]	2.71/−1.63	2.79/−2.10
flack parameter	0.01(3)	0.037(18)

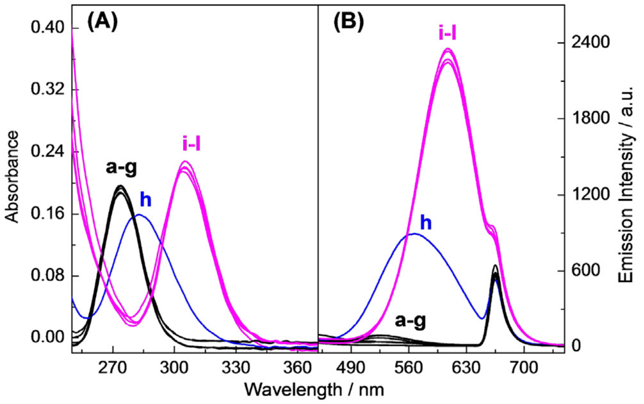

Fig. 3. Absorption (A) and photoluminescence (B) spectra of $Pb_nCl_{3n}{}^{n-}$ clusters in the presence of different halogen-containing species (HCSs). a, blank; b, Me_2SnCl_2; c, Bu_2SnCl_2; d, Bu_3SnCl; e, $BuSn(OH)_2Cl$; f, 1,2-dibromoethylene; g, 1,3-dibromopropane; h, Bu_4NBr; i, Me_2SnBr_2; j, Me_3SnBr; k, Bu_3SnBr; l, Et_3SnBr. The emission spectra were recorded upon excitation at 330 nm. Concentrations: A, [Pb] = 40 μM, [HCS] = 1.6 mM; B, [Pb] = 0.30 mM, [HCS] = 12 mM. The cluster ensembles were formed by lead(II) nitrate and tetrabutylammonium chlorides with an n_N/n_{Pb} of 5:1.

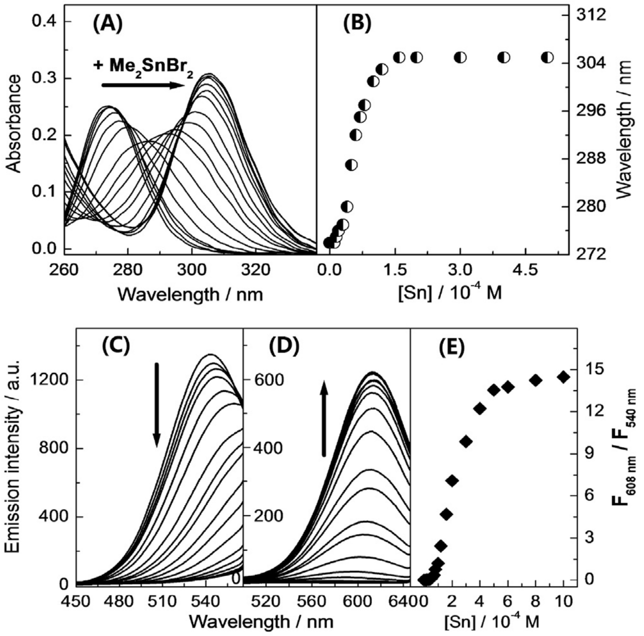

Fig. 4. Effect of Me_2SnBr_2 concentration on the absorption (A&B) and fluorescence (C, D & E) spectral behaviors of $Pb_nCl_{3n}{}^{n-}$ clusters ([Pb] = 50 μM) formed by lead(II) nitrate and tetrabutylammonium chloride with an n_N/n_{Pb} of 5:1 in acetonitrile. B shows a dependence of the maximum wavelength of the characteristic absorption band on the amount of Me_2SnBr_2 according to A. The excitation wavelengths for the emission spectra in C and D were 295 nm and 330 nm, respectively. It should be noted that the red shift of the $Pb_nCl_{3n}{}^{n-}$-dominated emission in (C) is a false appearance caused by the influence of the scattering signal at 590 nm.

3.3. The OTB-responsive mechanism of $Pb_nCl_{3n}{}^{n-}$ clusters

The spectral evolutions of $Pb_nCl_{3n}{}^{n-}$ clusters in the presence of increasing amount of OTBs were shown in Fig. 4. A gradual absorption shift from 274 nm to 305 nm without isosbestic points was observed (Fig. 4,A and B), indicating that an array of $Pb_nX_{3n}{}^{n-}$ clusters with different number of the $PbX_3{}^-$ repeating units, instead of a simple transformation from $PbCl_3{}^-$ to $PbBr_3{}^-$, were involved in this titration process. Surprisingly, only the luminescence signals of $Pb_nCl_{3n}{}^{n-}$ and $Pb_nBr_{3n}{}^{n-}$ clusters had been observed from the Me_2SnBr_2-titrated solutions (Fig. 4,C and D), while no intermediate luminophores similar to the Bu_4NBr-titrated product appeared in this process, thus indicating a difference in halogen replacement reactions induced by OTBs and tetraalkylammonium bromide. In addition, only the crystals of $Pb_nBr_{3n}{}^{n-}$ and $Pb_nCl_{3n}{}^{n-}$ clusters had been obtained in the partially OTB-treated solutions, as revealed by X-ray diffraction study. DLS study (Fig. 5) revealed that the particles sizes of the investigated clusters were at the level of 10^{-7} m. The sizes were reduced in titration with Me_2SnBr_2 and then increased to a level comparable to that of the plain $Pb_nBr_{3n}{}^{n-}$ clusters after addition with excess Me_2SnBr_2. It is regarded as the cause of these observations that the lead(II) chloride polyanions

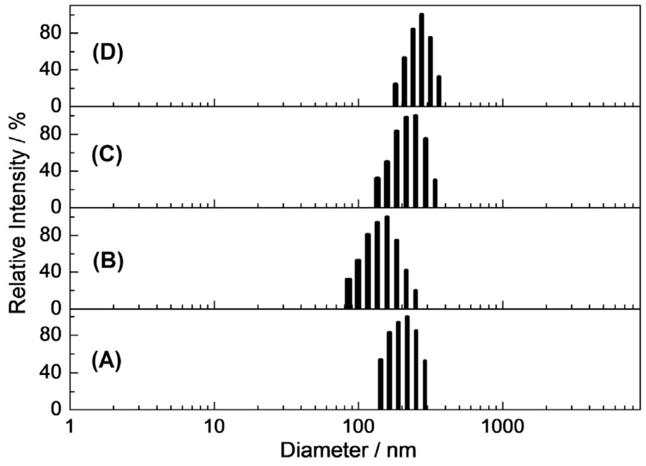

Fig. 5. Sizes of the particles in the solutions of $Pb_nCl_{3n}{}^{n-}$ clusters with different amount of Me_2SnBr_2 (A, blank; B, [Sn] = 3.0 [Pb]; C, [Sn] = 10 [Pb]) and $Pb_nBr_{3n}{}^{n-}$ clusters (D) in acetonitrile. The cluster ensembles were formed by lead(II) nitrate and tetrabutylammonium halides ([Pb] = 40 μM; n_N/n_{Pb} = 5:1).

participating in the halogen replacement reaction are broken down to form $Pb_nBr_{3n}{}^{n-}$ polyanions with increasing chain lengths and $Pb_nCl_{3n}{}^{n-}$ residues with decreasing chain lengths upon titration with OTBs.

Accompanying the absorption change, a reduction of the emission at 540 nm and a synchronous enhancement of the emission at 608 nm were observed upon addition of Me_2SnBr_2 (Fig. 4,C and D). Unlike the absorption response, the new emission band displayed no obvious shift during the titration. It is a supposition that the $Pb_nX_{3n}{}^{n-}$ polyanionic backbones were broken in the excited states and the emissions were generated by the resulting $PbX_3{}^-$ units, thus also explaining the usually large Stokes' shifts of these luminophores.

3.4. Fluorescent sensing of OTBs in acetonitrile

Based on the fluorescence response, quantitation of OTBs can be carried out by measuring the ratio of the emission intensity at 608 nm to that at 540 nm (Fig. 4E). The luminescence of $PbX_{3n}{}^{n-}$ clusters is susceptible to the micro-environmental factors such as micro water content in the solvent. However, the high similarity of both the structure and luminescence properties between the $PbCl_{3n}{}^{n-}$and $PbBr_{3n}{}^{n-}$ clusters contributes to a reliable emission ratio response for organotin quantitation. It should also be noted that the sensitivity of the OTB-induced optical responses shows a dependence on the molar ratio of tetraalkylammonium chloride to lead(II) (n_N/n_{Pb}) (Fig. 6). High n_N/n_{Pb} means that the $Pb_nCl_{3n}{}^{n-}$ fluorophores are surrounded by heavy tetraalkylammonium stabilizing layers. A lower n_N/n_{Pb} results in a higher sensitivity because of the easier access of OTBs to the $Pb_nCl_{3n}{}^{n-}$ fluorophores. When the lead(II) concentration is at the level of 10^{-5} M with a n_N/n_{Pb} of 5, fluorescent detection of OTBs can be well established at a concentration level of 10^{-5}–10^{-4} M.

A variety of OTBs (R_nSnBr_{4-n}, n = 1, 2, 3) with different R groups have been tested as the sensing targets. Both the absorption and fluorescence responses were determined by the bromination degree of organotins and immune to the variation of R. As exemplified in Fig. 7, the spectral responses to varied mixtures of Me_2SnBr_2 and Bu_3SnBr with different molar ratios but a fixed amount of Sn-Br groups remain almost unchanged. The easily-prepared solution of $Pb_nCl_{3n}{}^{n-}$ clusters can therefore be used as an efficient tool for evaluation of the total bromination degree of organotins.

The OTB sensing performance of $Pb_nCl_{3n}{}^{n-}$ clusters was further evaluated in the presence of high concentration of other organotin and organobromine species (Fig. 8). Generally, the optical response to the OTB target species was not affected by equivalent amount of organotin fluorides, organotin chlorides, ionic bromides, or other covalent organobromines. However, the coexistence of excess organotin chlorides weakened the fluorescence response induced by low concentration of OTBs, because the Cl → Br halogen replacement was reduced by additional resource of chlorides. It should be particularly mentioned that the coexistence of organotin iodides (OTIs) led to a different response. Both the emissions from $Pb_nCl_{3n}{}^{n-}$ and $Pb_nBr_{3n}{}^{n-}$ clusters were quenched. This is attributed to the formation of lead(II) iodide clusters (λ_{abs} = 368 nm, Supplementary Fig. S6) which are non-luminescent probably because of the heavy-atom effect, since the halogen replacement reactivity of OTIs is higher than that of OTBs. Known as some artificially synthesized catalysts, OTIs were generally not included in the organotin list in previous analytical practices yet can herein be distinguished out of the list by the described absorption and fluorescence responses.

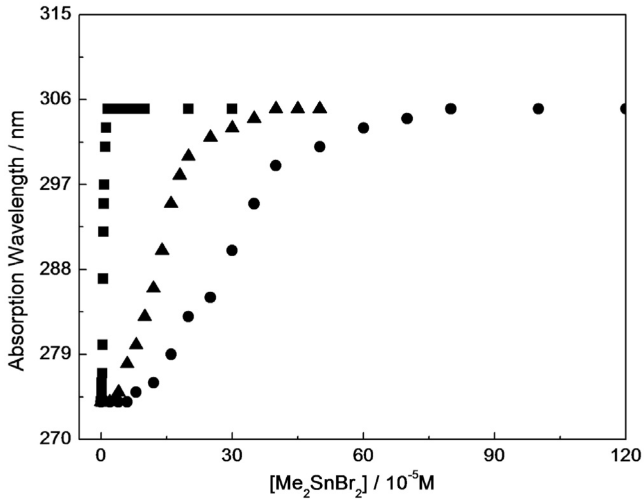

Fig. 6. Effect of Me_2SnBr_2 concentration on the absorption spectra of $Pb_nCl_{3n}{}^{n-}$ clusters ([Pb] = 40 μM) formed by lead(II) nitrate and tetrabutylammonium chloride with different n_N/n_{Pb} ratios (■, 5:1; ▲, 10:1; ●, 20:1) in acetonitrile.

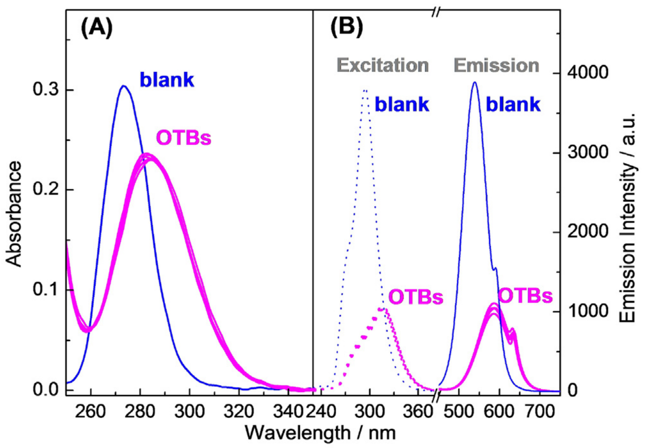

Fig. 7. Absorption (A, [Pb] = 60 μM) and fluorescence (B, [Pb] = 0.32 mM) spectra of $Pb_nCl_{3n}{}^{n-}$ clusters in the presence of the mixtures ([Br] = 80 μM) of Me_2SnBr_2 and Bu_3SnBr with different molar ratios including 3.0 : 0, 2.5 : 1.0, 2.0 : 2.0, 1.5 : 3.0, 1.0 : 4.0, 0.5 : 5.0, and 0 : 6.0. The cluster ensembles were formed by lead(II) nitrate and tetrabutylammonium chlorides with an n_N/n_{Pb} of 5:1.

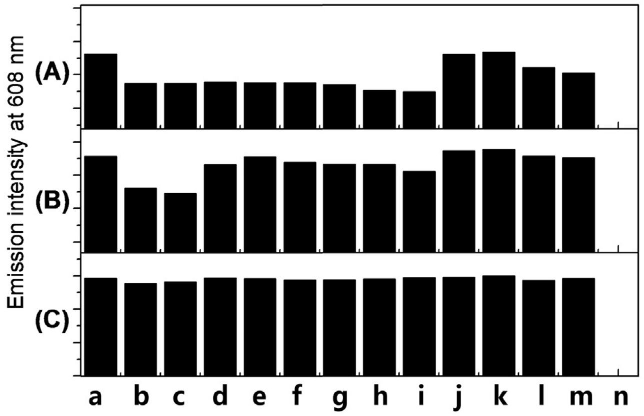

Fig. 8. The influence of coexisting species on the Me_2SnBr_2 sensing response of $Pb_nCl_{3n}{}^{n-}$ clusters ([Pb] = 40 μM) in acetonitrile upon excitation at 330 nm. Coexisting species: a, blank; b, Me_2SnCl_2; c, Bu_2SnCl_2; d, 1,3-dibromopropane; e, Bu_4Sn; f, Bu_3SnCl; g, bromobenzene; h, 1,2-dibromoethylene; i, Bu_3SnAc; j, Bu_4NBr; k, $MePh_3PBr$; l, $Bu(OH)_2SnCl$; m, Bu_3SnF; n, Bu_3SnI. The concentration of Me_2SnBr_2 is 20 μM (A), 50 μM (B), and 250 μM (C), respectively. All the coexisting species are at a same concentration of 250 μM.

4. Conclusions

In summary, we have developed a convenient fluorescent sensing system for OTBs based on $Pb_nCl_{3n}{}^{n-}$ clusters. The sensory solutions of $Pb_nCl_{3n}{}^{n-}$ clusters can be easily prepared by mixing inorganic lead(II) salts and tetraalkylammonium chloride directly in aprotic solvents. Upon interaction with OTBs, $Pb_nCl_{3n}{}^{n-}$ clusters undergo a halogen replacement process to form $Pb_nBr_{3n}{}^{n-}$ clusters with a remarkable spectral change. Taking advantage of the resulting fluorescent response with unusually large Stokes' shifts, quantitative detection of OTBs can be carried out at the micromolar concentration level. Our study provides a convenient and efficient tool for the analysis of OTBs when coupled with necessary extraction and enrichment processes.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (21475111, 21521004 and 21175113), the Program for Changjiang Scholars and Innovative Research Team in University (IRT13036), and the Fundamental Research Funds for the Central Universities (20720150141).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.snb.2016.11.095.

References

[1] V.C. Karpiak, C.L. Eyer, Differential gliotoxicity of organotins, Cell Biol. Toxicol. 15 (1999) 261–268.
[2] K.E. Appel, Organotin compounds: toxicokinetic aspects, Drug Metab. Rev. 36 (2004) 763–786.
[3] C. Pellerito, L. Nagy, L. Pellerito, A. Szorcsik, Biological activity studies on organotin (IV) complexes and parent compounds, J. Organomet. Chem. 691 (2006) 1733–1747.
[4] J.B. Graceli, G.C. Sena, P.F.I. Lopes, G.C. Zamprogno, M.B. da Costa, A.F.L. Godoi, D.M. dos Santos, M.R.R. de Marchi, M.A.D. Fernandez, Organotins: a review of their reproductive toxicity biochemistry, and environmental fate, Reproduct. Toxicol. 36 (2013) 40–52.
[5] M. Abalos, J.-M. Bayona, R. Compaño, M. Granados, C. Leal, M.-D. Prat, Analytical procedures for the determination of organotin compounds in sediment and biota: a critical review, J. Chromatogr., A 788 (1997) 1–49.
[6] M. Takeuchi, K. Mizuishi, T. Hobo, Determination of organotin compounds in environmental samples, Anal. Sci. 16 (2000) 349–359.
[7] M. Staniszewska, B. Radke, J. Namie_snik, J. Bolalek, Analytical methods and problems related to the determination of organotin compounds in marine sediments, Int. J. Environ. Anal. Chem. 88 (2008) 747–774.
[8] K. Dubalska, M. Rutkowska, G. Bajger-Nowak, P. Konieczka, J. Namieśnik, Organotin compounds: environmental fate and analytics, Crit. Rev. Anal. Chem. 43 (2013) 35–54.
[9] M. Hoch, Organotin compounds in the environment, Appl. Geochem. 16 (2001) 719–743.
[10] M. Nath, S. Pokharia, R. Yadav, Organotin(IV) complexes of amino acids and peptides, Coord. Chem. Rev. 215 (2001) 99–149.
[11] L. Pellerito, L. Nagy, Organotin(IV) complexes formed with biologically active ligands: equilibrium and structural studies and some biological aspects, Coord. Chem. Rev. 224 (2002) 111–150.
[12] S.K. Dubey, U. Roy, Biodegradation of tributyltins (organotins) by marine bacteria, Appl. Organomet. Chem. 17 (2003) 3–8.
[13] K. Mizuishi, M. Takeuchi, T. Hobo, Trace analysis of tributyltin and triphenyltin compounds in sea water by gas chromatography-negative ion chemical ionization mass spectrometry, J. Chromatogr. A 800 (1998) 267–273.
[14] J.W. Waggoner, L.S. Milstein, M. Belkin, K.L. Sutton, J.A. Caruso, H.B. Fannin, Application of a low power/reduced pressure helium ICP ionization source for mass spectrometric detection of organobromine compounds and derivatized organotincompounds, J. Anal. At. Spectrom. 15 (2000) 13–18.
[15] Z. Mester, R.E. Sturgeon, Detection of volatile organometal chloride species in model atmosphere above seawater and sediment, Environ. Sci. Technol. 36 (2002) 1198–1201.
[16] S.-H. Li, F.-R. Chen, Y.-F. Zhou, J.-N. Wang, H. Zhang, J.-G. Xu, Enhanced fluorescence sensing of hydroxylated organotins by a boronic acid-linked Schiff base, Chem. Commun. (2009) 4179–4181.
[17] Y.-F. Niu, F.-F. Han, Q. Zhang, T.-W. Xie, L. Lu, S.-H. Li, H.-P. Xia, Off/on fluorescent chemosensors for organotin halides based on binuclear ruthenium complexes, Angew. Chem. Int. Ed. 52 (2013) 5599–5603.
[18] S.K. Dutta, M.W. Perkovic, Lead as its own luminescent sensor, Inorg. Chem. 41 (2002) 6938–6940.
[19] S.-H. Li, F.-R. Chen, Y.-F. Zhou, J.-G. Xu, $Pb_4Br_{11}{}^{3-}$cluster as a fluorescent indicator for micro water content in aprotic organic solvents, Analyst 134 (2009) 443–446.
[20] S.R. Wade, G.R. Willey, Co-ordination studies of tris(dimethylamino)phosphine oxide: reactions with the covalent metal halides MCl_3 (M = Ti, V and Cr), MCl_4 (M = Ti, Zr, Hf and Sn) and SnI_4, J. Inorg. Nucl. Chem. 42 (1980) 1133–1135.
[21] N.L. Poon, D.P. Satchell, Kinetics of the covalent metal halide-catalyzed addition of 2,4-dichloroaniline to dimethylketene in diethyl-ether solution, J. Chem. Res., Synop. (1986) 304–305.
[22] J. Vaughan, C.J. Wilkins, Halogen replacement in covalent halides, Nature 167 (1951) 525.

Biographies

Yufen Niu is a master student at Xiamen University, China.

Xiaoyu Chen is a master student at Xiamen University, China.

Yuan Zhu is a master student at Xiamen University, China.

Shunhua Li received his Ph.D. from Xiamen University in 2004. After that, he joined the faculty at Xiamen University as an assistant professor and he is currently an associate professor at the Department of Chemistry. He has been a visiting scholar at the School of Materials Science and Engineering, Georgia Institute of Technology, USA (2013). He is active in the research fields of molecular recognition, optical sensing, luminescent materials and functional self-assemblies.