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Lead as Its Own Luminescent Sensor

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Lead (II) in polar organic solvents such as acetone, acetonitrile, and propylenecarbonate with excess bromide generates the highly luminescent lead–halide cluster $Pb_4Br_{11}^{3-}$. This in situ sensor does not rely on a host–guest relationship and, thus, is intrinsically selective and sensitive, allowing for the detection of lead at nanomolar concentrations. The cluster's emission maximum and relaxation kinetics are temperature dependent and indicate a close spacing of intralead and intracluster electronic energy levels.

There has been considerable interest recently in developing luminescent sensors for various ions and molecules, particularly heavy metals such as Pb^{2+}. Previous sensor molecules use a host−guest strategy where a molecular assembly is constructed which couples a luminescent fragment with a receptor fragment that has a particular selectivity for Pb^{2+} over other species. Herein, we report an alternative approach that uses the emission from Pb^{2+} itself as the sensor. The cluster $Pb_4Br_{11}^{3-}$ is highly emissive and may be used as a sensor for lead that is sensitive and, in principle, absolutely specific because it does not rely on a competitive host−guest relationship. This cluster is prepared in situ by the addition of bromide to polar organic solvents containing Pb^{2+}. Because the lead is acting as its own sensor, the chances for a false positive luminescent response due to nonspecific interactions between the luminescent sensor and its environment is diminished, if not eliminated.

Supramolecular[1] host−guest Pb^{2+} sensor systems typically rely on the specific association with Pb^{2+} to perturb the sensor's emission properties by altering its geometry[2] or its electronic microenvironment[3] upon coordination or macromolecular assembly. Many believe that the lead itself is not emissive,[3] and that the presence of a heavy atom such as Pb^{2+} results in quenching of the sensor's basal luminescence. Our results show that $Pb_4Br_{11}^{3-}$ does not quench an emissive molecule like $Ru(bpy)_3^{2+}$, and that $Ru(bpy)_3^{2+}$ does not quench the emission from $Pb_4Br_{11}^{3-}$, even though the ruthenium emissive state is lower in energy by about 1500 cm^{-1}.

The emission behavior of a Pb^{2+} solution depends considerably on the conditions of the solution under investigation. For example, a saturated solution of $PbBr_2$ in air-equilibrated acetonitrile at room temperature has an emission maximum at 610 nm with a quantum yield of 0.0053.[5] Upon addition of excess bromide, the weak red emission shifts to 560 nm, and its quantum yield increases by more than 10× to 0.055 (Figure 1). Similarly, a solution of $Pb(CF_3SO_3)_2$ in acetonitrile, which is only slightly luminescent, becomes highly emissive upon addition of an excess of bromide. Irrespective of the starting point, for example, lead carbonate, or lead acetate, addition of an excess of bromide in an aprotic polar organic solvent results in the formation of the same highly luminescent lead complex.[6] The resulting $Pb_4Br_{11}^{3-}$ complex formed in situ enables detection of Pb^{2+} at nanomolar concentrations (Figure 2).[7] Ions such as Cl^-, I^-, Ca^{2+}, Ag^+, or Hg^{2+} do not interfere with this emission.[8]

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[2] Perkovic, M. W. *Inorg. Chem.* **2000**, *39*, 4962.

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[4] Emission intensities were normalized to illustrate the spectral differences. A direct comparison of emission intensities is not meaningful because the nature of the emitting species changes upon addition of Br^-.

[5] Quantum yields were determined by comparing the integrated intensity of the samples to that of an absorbance-matched standard, $Ru(bpy)_3^{2+}$, $\phi = 0.062$. Dupray, L. M.; Meyer, T. J. *Inorg. Chem.* **1996**, *35*, 6299.

[6] Solvents studied include acetone, acetonitrile, butyronitrile, propylene carbonate, and DMF. All data presented here were obtained with 0.1 M $(Bu)_4NBr$. Protic solvents such as water and alcohols do not work, presumably because they prevent cluster formation.

[7] The detection limit was determined by serial dilution of a standard solution keeping the $[Br^-]$ constant at 0.1 M with $(Bu)_4NBr$. Spectra were recorded using a PTI Quantum Master fluorimeter exciting at 333 nm, or by exciting the sample with the 355 nm harmonic of an Nd:YAG laser and recording the spectrum using a Princeton Instruments CCD interfaced to an Acton 1/3m spectrograph.

[8] These heavy metal salts have a reasonable solubility in 0.1 M $(Bu)_4NBr$/acetonitrile. For example, 20 mg of AgBr readily dissolves in 1 mL of solution.

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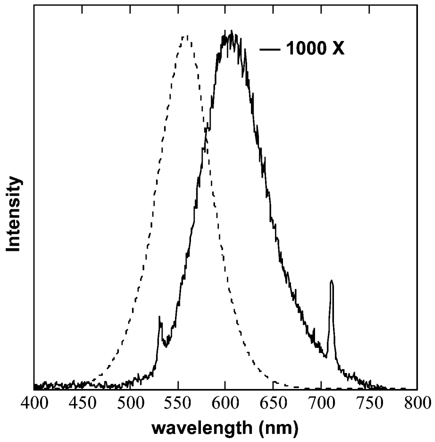

Figure 1. Intensity normalized[4] luminescence spectra of $PbBr_2$ at room temperature in CH_3CN before (- -) and after (····) addition of excess $(Bu)_4NBr$. The spikes at 532 and 710 nm correspond to laser scatter.

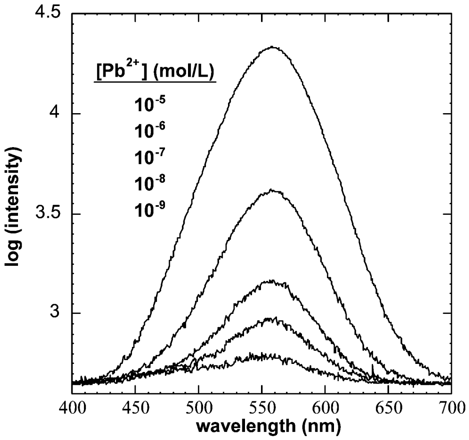

Figure 2. Luminescence from $Pb(CF_3SO_3)_2$ in 0.1 M $(Bu)_4NBr$ in CH_3-CN. Excitation at 355 nm. Similar results are obtained when a broad-band UV lamp is used as the excitation source.[9]

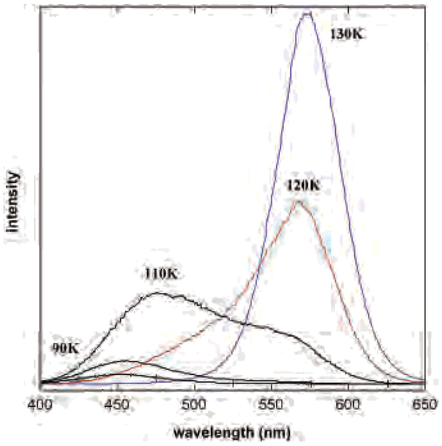

Figure 3. Variable temperature steady state luminescence spectra of $Pb_4Br_{11}^{3-}$ in butyronitrile.

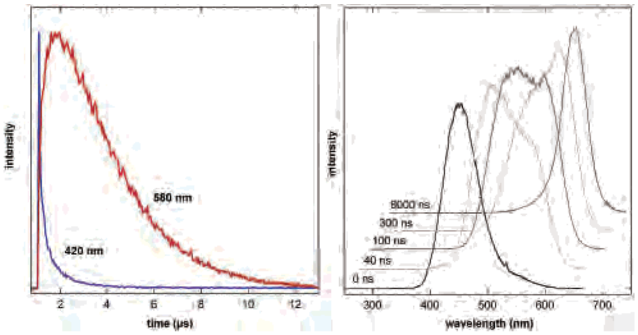

Figure 4. Decay kinetics (left) and intensity normalized time-resolved emission spectra (right) recorded at various time delays of $Pb_4Br_{11}^{3-}$ in butyronitrile at 120 K.

When a solution of $Ru(bpy)_3^{2+}$, which is well-known to participate in energy and electron transfer processes with many electronically excited molecules, is mixed with $PbBr_2$ and 0.1 M Br^-, the emission properties of the lead cluster remains unchanged both in terms of the spectral distribution and kinetic behavior. Similarly, the emission properties of the ruthenium complex remain unaltered indicating that the ability of lead to act as a quencher under these conditions is not significant.

Absorption measurements performed in acetonitrile or butyronitrile are in accord with what was previously observed by Jones and Aikens.[10] Their detailed spectrophotometric equilibrium study confirms that the species generated in situ is $Pb_4Br_{11}^{3-}$. The absorption maximum is 333 nm, and the extinction coefficient is 3250 M^{-1} cm^{-1}.[11] This extinction coefficient is larger than one expects for an intralead $^1S_0-{}^1P_1$ transition and suggests that the absorption is the result of a charge transfer transition. However, we observe no change in the absorption or emission spectrum upon steady state photolysis with a 75 W Xe arc lamp filtered at 333 nm band-pass for 12 h, indicating that the cluster is photochemically stable. This is in contrast to $PbBr_3^-$ and $PbBr_4^{2-}$ which can undergo a photochemical reductive elimination upon irradiation.[12]

The lead cluster has a temperature dependent emission spectrum with components that become apparent below 130 K and that dominate at temperatures below 100 K (Figure 3). The component at 560 nm, which is the only observable feature in the spectrum above ca. 130 K, has a room temperature excited state lifetime in air-equilibrated acetonitrile of 24 ns.[13] Deaeration had no measurable effect on the relaxation kinetics. At low temperature, the kinetics of this spectral feature becomes more complicated, exhibiting a 172 ns rise time followed by a 3.3 μs decay (Figure 4). The blue component at 475 nm, which becomes apparent below 130 K, has a lifetime of 384 ns. The lifetime does not change appreciably between 130 and 77 K. The kinetic behavior is echoed in the time-resolved emission spectra that show the blue component at short times after excitation which evolves into the yellow-green component within a microsecond.

For simple s^2d^{10} systems of the type PbX_2 (where X = chloride and bromide),[14,15] the emission is attributable to an sp excited state.[16,17] In a cluster, charge transfer states and

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(9) A plot of the integrated emission intensity vs $[Pb^{2+}]$ is linear between 10^{-9} and 10^{-4} M Pb^{2+}. At $[Pb^{2+}] > 10^{-4}$ M, the samples are no longer optically dilute resulting in substantial beam attenuation.

(10) Jones, A. R.; Aikens, D. A. *Polyhedron* **1982**, *1*, 169.

(11) We measured 13000 M^{-1} cm^{-1} per equivalent of $PbBr_2$.

(12) Oldenburg, K.; Vogler, A. *Z. Naturforsch.* **1993**, *48b*, 1519.

(13) See ref 2 for details of the photophysical experimental protocol.

states delocalized over the bromide-bridged lead ions become important.[17] Because no photochemistry is observed in fluid solution, it is reasonable to assign the 560 nm emission to a delocalized cluster state. The fast relaxation kinetics of the 450 nm component of the low-temperature spectrum suggests an intralead sp origin for this transition.

Using a heavy metal as an in situ luminescent sensor for itself is a significant departure from the host−guest approach often employed in this field. The approach is potentially interference-free, insofar as a false positive resulting from nonspecific binding luminescence is minimized. Because the emission is essentially binary in its response, on−off rather than manifested by small changes in a large luminescent signal, it is also potentially highly sensitive. Factors may conspire to preclude cluster formation; however, we have not yet observed any problem as the result of the presence of simple cations and anions. We expect that this approach may be applicable to a variety of heavy metal ions that share the same closed s and d shell electronic configurations.

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