Electronic Supplementary Information

$Pb_4Br_{11}^{3-}$ Cluster as a Fluorescent "Ruler" for Micro Water Content in Aprotic Organic Solvents

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1. Reagents

Acetonitrile used for the spectroscopic measurements was purchased from Aldrich Chemical Co. as 'anhydrous' grade (water content <0.001%). THF was distilled over sodium/benzophenone under a dry nitrogen atmosphere immediately prior to use. Acetone and DMSO were distilled over CaH_2 under a nitrogen atmosphere and stored over molecular sieves (4 Å) for at least 12 h. All other reagents including the undydrated lead(II) salts and tetraalkylammonium bromides were of analytical grade or better and used without further purification.

A typical preparation of luminescent crystals of the $Pb_4Br_{11}^{3-}$ cluster ensemble was described as follows. Tetrabutylammonium bromide (129 mg, 0.4 mmol) with lead(II) nitrate (13 mg, 0.04 mmol) were dissolved in 25 mL acetonitrile. After addition of tetraethylammonium bromide (84 mg, 0.4 mmol), the mixture was shaked to give a clear colorless solution. This solution was kept quiescent over night and the crystals of $Pb_4Br_{11}^{3-}$ cluster appeared as colorless needles. The volume of the solvent was reduced by volatilization in air. The crystals were collected and air dried for fluorescent photomicrograph studies. XPS spectrum of the $Pb_4Br_{11}^{3-}$ crystal was not available in the attempt due to its meltability at high temperature.

Lead (II) in polar organic solvents with bromide in excess generates the highly luminescent lead-halide cluster $Pb_4Br_{11}^{3-}$. Although the cluster ensemble was not strictly characterized due to its peculiar existence condition, absorption and fluorescence measurements performed in acetonitrile were in accord with what had been previously observed (Ref. 10-12) .

2. Water dependences of the fluorescence spectra of $Pb_4Br_{11}^{3-}$ in acetonitrile

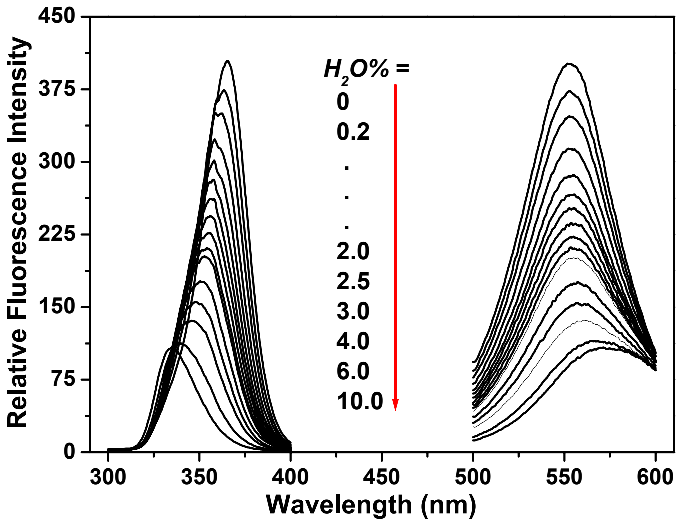

Fig. 1 Water dependences of the fluorescence spectra of $Pb_4Br_{11}^{3-}$ cluster ensemble (4.0×10^{-4} mol L) formed by lead(II) nitrate and tetrabutylammonium bromide with a n_{Br}/n_{Pb} ratio of 20 in acetonitrile at room temperature.

3. Effects of water pH and solution temperature on the water-sensing responses of $Pb_4Br_{11}^{3-}$

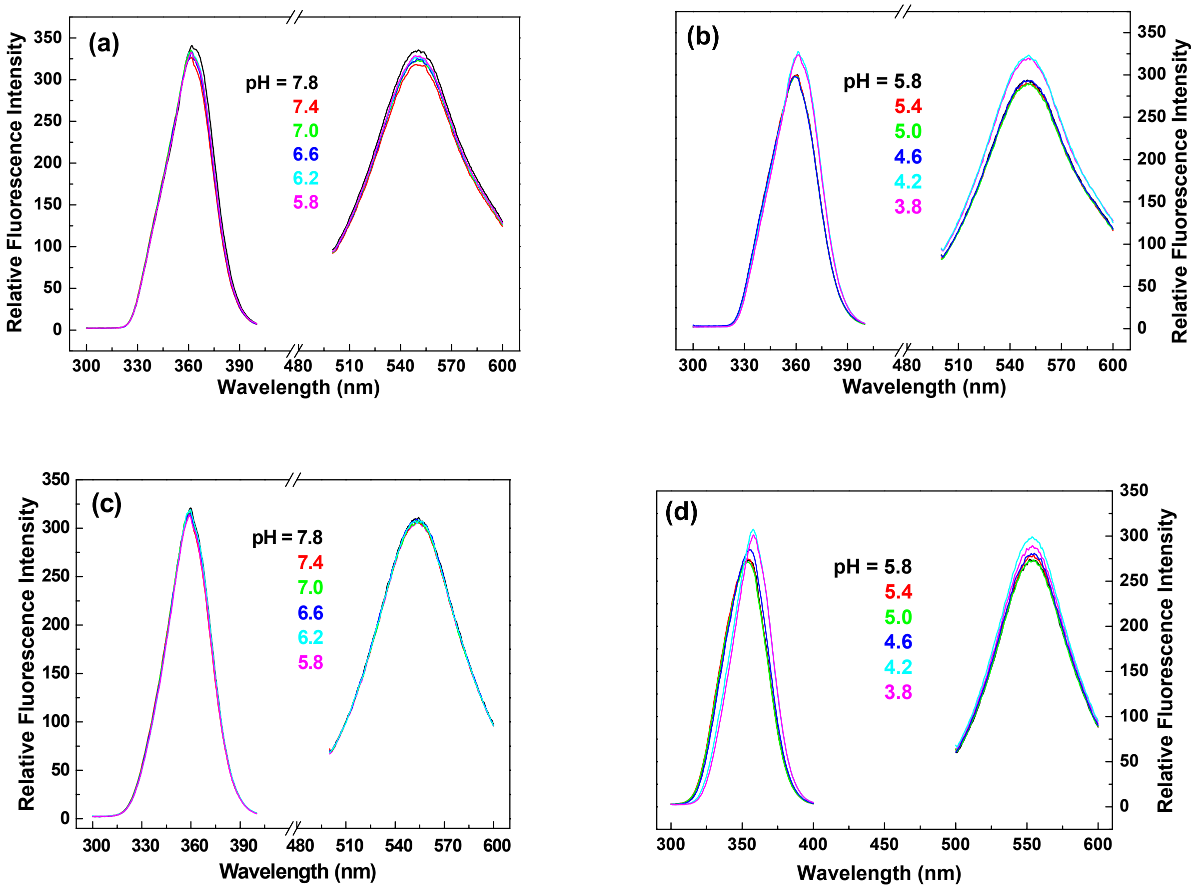

Fig. 2 Effects of water pH on the fluorescence spectra of $Pb_4Br_{11}^{3-}$ cluster ensemble (a-b, 2.0×10^{-4} mol L in acetone; c-d, 3.0×10^{-4} mol L in acetonitrile) formed by lead(II) nitrate and tetrabutylammonium bromide with a n_{Br}/n_{Pb} ratio of 20. Water content: 1.0%, V/V (a, b, c, d); pH of water: buffered by NaH_2PO_4 - Na_2HPO_4 (a, c) and NaAc – HAc (b, d) at 0.20 mol L.

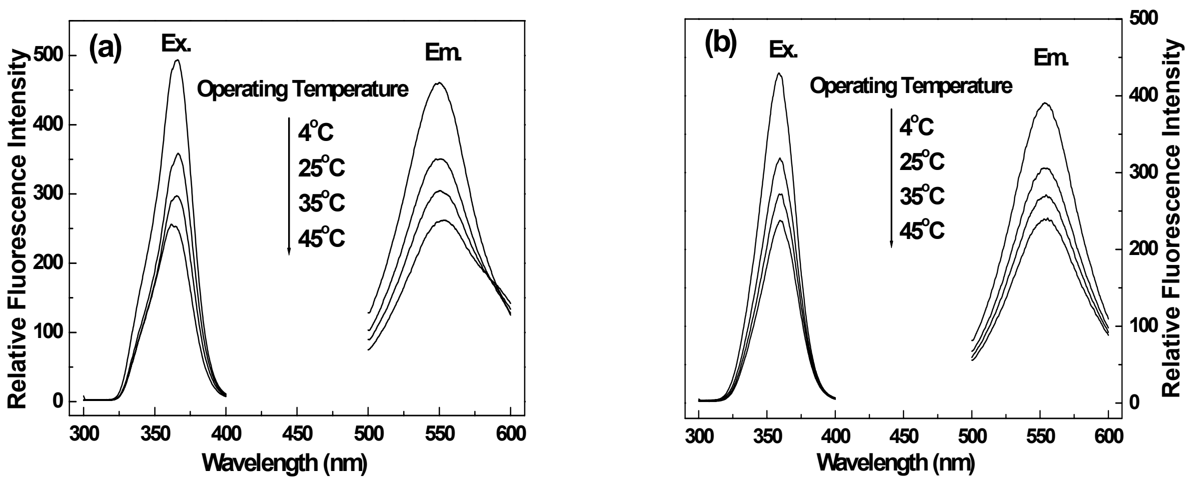

Fig. 3 Effects of solution temperature on the water-sensing responses of $Pb_4Br_{11}^{3-}$ cluster ensemble (a, 2.0×10^{-4} mol L in acetone; b, 3.0×10^{-4} mol L in acetonitrile) formed by lead(II) nitrate and tetrabutylammonium bromide with a n_{Br}/n_{Pb} ratio of 20. Water content: 1.0%, V/V (a, b).

4. Influences of the concentration and n_{Br}/n_{Pb} ratio of $Pb_4Br_{11}^{3-}$ on the water-sensing sensitivity

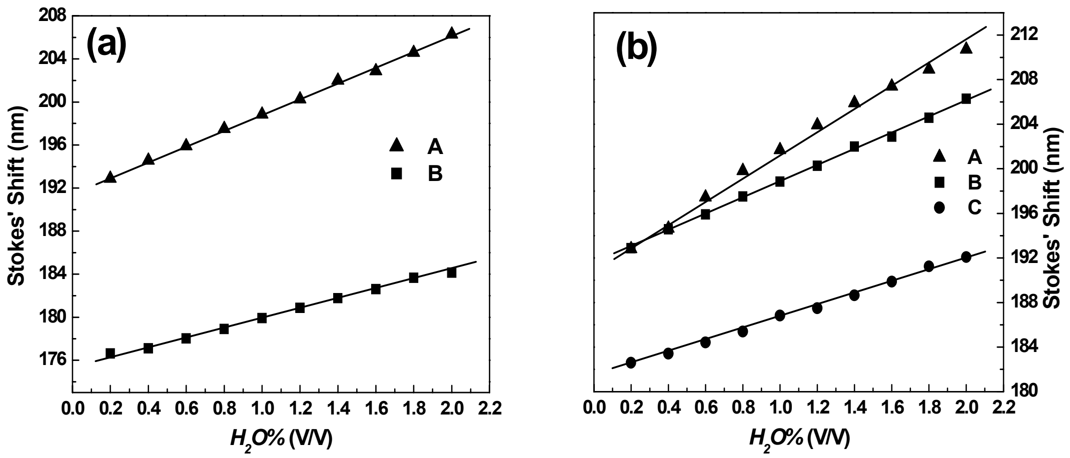

Fig. 4 Influences of the concentration (a) and n_{Br}/n_{Pb} ratio (b) of $Pb_4Br_{11}^{3-}$ clusters on the water-sensing sensitivity. $Pb_4Br_{11}^{3-}$ clusters were formed by lead(II) nitrate and tetrabutylammonium bromide in acetonitrile. (a) Different concentrations of $Pb_4Br_{11}^{3-}$ with a constant n_{Br}/n_{Pb} ratio of 20: A, 3.0×10^{-4} mol L; B, 8.0×10^{-4} mol L. (b) Different n_{Br}/n_{Pb} ratios of $Pb_4Br_{11}^{3-}$ at a constant concentration of 3.0×10^{-4} mol L: A, 15; B, 20; C, 40.

5. Effect of reaction time on the water-sensing responses of $Pb_4Br_{11}^{3-}$

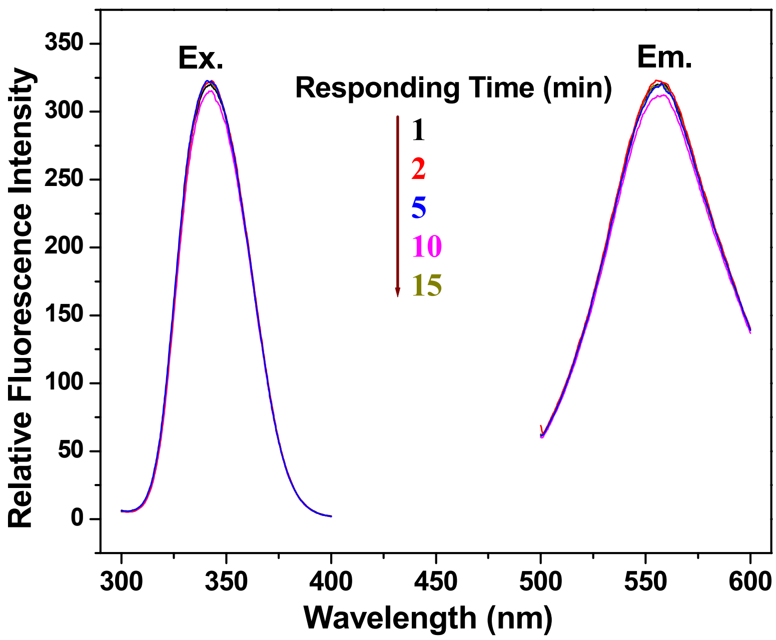

Fig. 5 Effect of reaction time on the water-sensing response of $Pb_4Br_{11}^{3-}$ cluster ensemble (4.0×10^{-4} mol L) formed by lead(II) acetate and tetrabutylammonium bromide with a n_{Br}/n_{Pb} ratio of 20 in acetonitrile at room temperature. Water content: 1.0%, V/V.