Selective naked-eye sensors for real time detection of mercury ion in water

Mercury (Hg) is one of the most harmful and toxic chemical pollutants, which is released into the environment through natural or industrial sources. This dangerous heavy metal has the ability to enter the food chain and accumulate in organisms causing serious damage to health, and even death in cases of severe mercury poisoning. Conventional analytical methods to detect mercury in water require expensive instrumentation and a long measuring time. Here, we describe easy methods for selective naked-eye detection of mercury (II) in water.

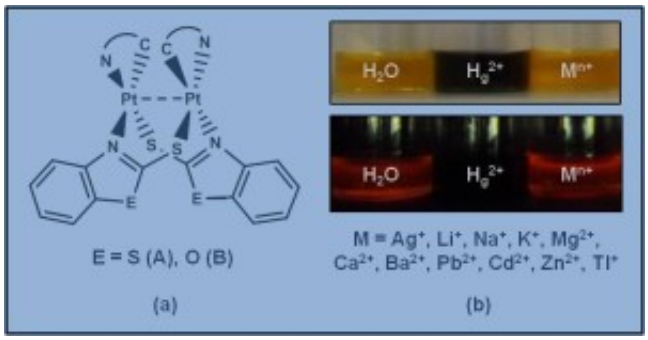

Fig. 1.

The half-lantern dinuclear complexes [{Pt(bzq)(?-$C_7H_4NS_2$-?N,S)}$_2$] (**A**) and [{Pt(bzq)(?-C_7H_4NOS-?N,S)}$_2$] (**B**) [bzq = benzo[h]quinolinate, $C_7H_4NS_2$ = 2-mercaptobenzothiazolate, C_7H_4NOS = 2-mercaptobenzoxazolate] (Fig. 1a) show a yellowish-orange color in solution and intense red phosphorescence upon excitation with ultraviolet light (l= 365 nm). Absorption and emission colors are due to transitions involving excited states (^{1,3}MMLCT) generated by Pt···Pt interaction between two platinum centers located in close proximity.

In these complex molecules the higher filled s* orbital is oriented outward along the Pt-Pt axis and is expected to be able to interact with a Lewis acid such as $Hg^{2+}$and other metal cations (M^{n+}) with resulting changes in their color and emission energies.

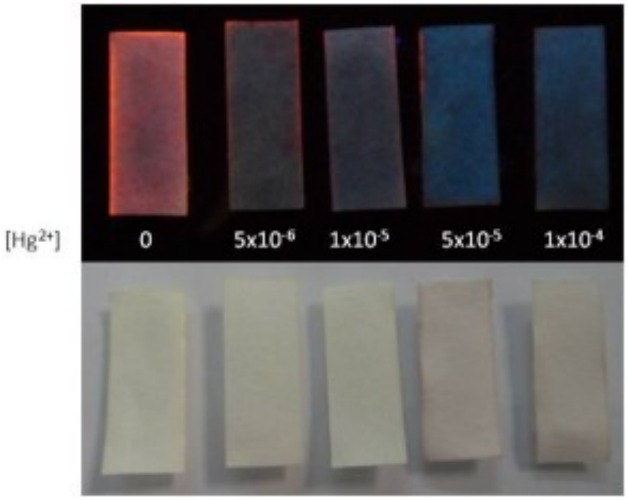

Fig. 2.

Experimentally we observed that **A** and **B** could be used for selective naked-eye detection of Hg^{2+} in water at low concentration. The reason for this is that solutions of **A** and **B** in DMSO (5 ml, 2 x 10^{-4} M) experience a dramatic color change from yellowish-orange to purple (Fig. 1a) and the loss of luminescence (Figure 1b) upon addition of a small volume of a diluted aqueous solution of Hg^{2+} (0,5 mL, 0.01 M). Other ions, such as Ag^{+}, Li^{+}, Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}, Ba^{2+}, Pb^{2+}, Cd^{2+}, $Zn^{2+}$and Tl^{+}, were tested in the same way considering their toxicity or abundance in natural water. Unlike Hg^{2+} none of them caused any changes in the optical properties of **A** and **B** solutions nor interference in the selective detection of Hg^{2+} in water, even when they were present in great excess (up to 50 :1). These diluted solutions of **A**/**B** in DMSO can detect the presence of Hg^{2+} in water even at concentrations as low as 2 × $10^{?6}$ M (**A**) or 5 × $10^{?5}$ M (**B**).

Furthermore, test strips were prepared by immersing filter paper in a solution of **A**/ **B** in DMSO (2 x 10^{-4} M) and drying in an oven. These dry test strips show a discernible change of color from light-orange to purple and loss of luminescence when they are immersed in an aqueous solution containing Hg^{2+} in a concentration as low as 5 × $10^{?5}$ M for **A** and 1 × $10^{?5}$ M for **B** (Fig. 2), making complexes **A** and **B** good candidates for use as real-time Hg^{2+} sensors.

The change of color and the quenching of the intense phosphorescence of diluted solutions of **A**/ **B** in DMSO, caused by the presence of small amounts of Hg^{2+},are easily observed by the naked eye and are also observable spectroscopically. The presence of Hg^{2+}causes the emergence of two absorption bands instead of one in the UV-vis spectra of these solutions at ? > 450 nm ($?_{max}$ = 467 nm, 554 nm **A**; $?_{max}$ = 460 nm, 557 nm, **B**) and the disappearance of phosphorescence (l_{max} ~ 665 nm), with detection limits in the order of 10^{-5} Molar. The metal ions Ag^{+}, Li^{+}, Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}, Ba^{2+}, Pb^{2+}, Cd^{2+}, Zn^{2+} and Tl^{+} showed no interference in the selective detection of Hg^{2+} in water, even when present in great excess.

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