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Complexes $\{\text{Pt(bzq)(μ-C7H4NS2-κN,S)}_2\}$ and $\{\text{Pt(bzq)(μ-C7H4NOS-κN,S)}_2\}$ are two new selective colorimetric and turn-off phosphorescent chemosensors of Hg$^{2+}$ in DMSO-H$_2$O solution.

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ABSTRACT

The platinum(II) half-lantern dinuclear complexes \([\{\text{Pt(bzq)}(\mu-C_7H_4NS_2-\kappa N,S)\}_2]\textsuperscript{A}\) and \([\{\text{Pt(bzq)}(\mu-C_7H_4NOS-\kappa N,S)\}_2]\textsuperscript{B}\) [bzq = benzo[h]quinolinate, \(C_7H_4NS_2 = 2\)-mercaptobenzothiazolate, \(C_7H_4NOS = 2\)-mercaptobenzoxazolate] in solution of DMSO-H\textsubscript{2}O undergo dramatic color change from yellowish-orange to purple and turn-off phosphorescence in the presence of small amount of Hg\textsuperscript{2+}, being discernible by the naked-eye and by spectroscopic methods. Other metal ions as Ag\textsuperscript{+}, Li\textsuperscript{+}, Na\textsuperscript{+}, K\textsuperscript{+}, Ca\textsuperscript{2+}, Mg\textsuperscript{2+}, Ba\textsuperscript{2+}, Pb\textsuperscript{2+}, Cd\textsuperscript{2+}, Zn\textsuperscript{2+} and Tl\textsuperscript{+} were tested and, even in a big excess, showed no interference in the selective detection of Hg\textsuperscript{2+} in water. Job’s plot analysis indicated a 1:1 stoichiometry in the complexation mode of Hg\textsuperscript{2+} by A/B. The phosphorescence quenching attributed to the formation of \([A/B: \text{Hg}^{2+}]\) complexes showed binding constants of \(K = 1.13 \times 10^5 \text{ M}^{-1}\) (A) and \(K = 1.99 \times 10^4 \text{ M}^{-1}\) (B). The limit of detection has been also evaluated. In addition, dried paper test strips impregnated in DMSO solutions of A and B can detect concentration of Hg\textsuperscript{2+} in water as low as \(1 \times 10^{-5} \text{ M}\) for B and \(5 \times 10^{-5} \text{ M}\) for A, making these complexes good candidates to be used as real-
time detectors of Hg$^{2+}$. The nature of the interactions of the Pt$_2$ half-lantern complex A with the Hg$^{2+}$ cation, has been investigated by theoretical calculations.

**Keywords:** Mercury(II) ion; Sensor; Detection; Cyclometalated; Half-Lantern; Platinum(II).

**INTRODUCTION**

Mercury is one of the most harmful and toxic heavy metal present in the environment. Inorganic mercury, Hg(0) and Hg(II), is released into the environment through natural or industrial sources. The well-known bioaccumulation of the mercury provides routes to enter into the food chain and cause serious health affections\(^1\)\(^2\) which justify the importance of monitoring mercury levels in the environment. Conventional analytical methods to detect mercury in water require complicated, multistep sample preparation, expensive instrumentation and long measuring time. That is why the achievement of easily manipulable tools for selective detection of mercury would be a great advantage in this field.

An important number of chemosensors of Hg(II) have been reported\(^1\)\(^3\) that combine easy use, high sensitivity and selectivity, quick response and low detection limits. Among them, small-molecule-based “turn-on” or “turn-off” fluorescent as well as colorimetric sensors for optical detection, operating in organic, aqueous or aqueous/organic solution.\(^4\)\(^5\) Nowadays the use of phosphorescent heavy-metal complexes as chemosensors are attracting much attention because of their advantageous photophysical properties including sensitivity of emission properties to changes in the local environment, high quantum yields, long emission lifetimes and significant Stokes shifts making easy the separation between excitation and emission wavelength. Moreover, the luminescence properties of the heavy-metal complexes can be fine-tuned...
by modification of ligand structure or metal center. Some of these complexes have been described as chemosensors for oxygen, volatile organic compounds (VOCs), metal cations or anions. Some phosphorescent heavy-metal complexes have been successfully developed as Hg(II) detectors, as some Ir(III) complexes that exhibit very low detection limits (3.5 x 10^-6 M – 6.7 x 10^-8 M). The sensing properties are based in reactions promoted by mercury ions or in the interaction between the complex and mercury ions through sulfur-containing ligands, which promote colorimetric and/or luminescence changes.

In the chemistry of platinum, Sun and coworkers developed a terpyridine Pt(II) complex with a dithiaazacrown moiety as a good sensitive and selective colorimetric mercury sensor with detection limit on the order of micromolar concentration. Cho, Kim et al., reported a colorimetric and turn-on fluorescence sensor based on cyclometalated CNN-Pt(II)-rhodamine derivative useful as Hg^{2+} sensor with very low detection limit (4.9 x 10^{-7} M).

In the course of our research on phosphorescent platinum (II) cyclometalated complexes, we reported the half-lantern dinuclear complexes [{Pt(bzq)(µ-C_7H_4NS_2κN,S)}_2](A) and [{Pt(bzq)(µ-C_7H_4NOSκN,S)}_2](B) [bzq = benzo[h]quinolinate, C_7H_4NS_2 = 2-mercaptobenzothiazolate, C_7H_4NOS = 2-mercaptobenzoxazolate] which show yellowish-orange color in solution and intense red phosphorescence arising from ^1,3MMLCT transitions. These good properties prompted us to study their photophysical response to different metal ions with the aim of finding new sensors for highly toxic heavy metal. As result of this study, herein we report that complexes A and B have good sensitivity and selective colorimetric and turn-off luminescence response towards Hg^{2+} in the presence of various competitive metal ions. The dramatic color change from yellowish-orange to purple and the loss of phosphorescence of A and B in DMSO / H_2O
solution or even in paper test strips allow these compounds to be used as chemosensors for naked-eye detection of Hg$^{2+}$. The complexation process of Hg$^{2+}$ by A and B and its reversibility have been also studied. As far as we know, A and B are the first examples of phosphorescent Pt(II) complexes as selective Hg$^{2+}$ naked-eye and spectroscopic chemosensors.

**RESULTS AND DISCUSSION**

The dinuclear half-lantern complexes $\{[\text{Pt(bzq)(μ-C}_7\text{H}_4\text{NS}_2\text{-κN,S})]_2\}$ and $\{[\text{Pt(bzq)(μ-C}_7\text{H}_4\text{NOS-κN,S})]_2\}$ are orange solids which give yellowish-orange solutions in DMSO with the lowest absorption band centered at about 480 nm. These complexes present an intense red $^3$MMLCT emission at room temperature in DMSO-H$_2$O ($\lambda_{\text{max}} \sim 665$ nm) upon UV light excitation ($\lambda_{\text{exc}} = 365$ nm). Our target was to test changes in the color, absorption and emission spectra of their solutions upon interaction with several metal ions as basis for naked-eye visible detection.

**Selective visual detection of Hg(II).** A solution ($2 \times 10^{-4}$ M) of A in DMSO shows a yellowish-orange color in DMSO / H$_2$O (5mL:0.5 mL) that changed to purple in the presence of Hg$^{2+}$ (molar ratio 1:5) but remain insensitive to the presence of Ca$^{2+}$ (molar ratio 1:5), Ag$^+$, Li$^+$, Na$^+$, K$^+$, Mg$^{2+}$, Ba$^{2+}$, Pb$^{2+}$, Cd$^{2+}$, Zn$^{2+}$ and Tl$^+$ (molar ratio 1:50) (Figure 1a). In addition, competitive metal-ion selectivity experiments were carried out which resulted in the no interference of the tested cations with Hg$^{2+}$. Analogous results were obtained with solutions of compound B (Figure S1). In the other hand, the presence of Hg$^{2+}$ ions causes the turn-off luminescence of A in solution of DMSO / H$_2$O under UV light ($\lambda_{\text{exc}} = 365$ nm) while no or negligible changes in the emission intensity are observed in the presence of any of the tested metal ions (Figure 1b).
Aiming to evaluate the suitability of A and B to be used as naked-eye colorimetric sensor of Hg\(^{2+}\) we examined the sensitivity of diluted solutions (2 x 10\(^{-5}\) M) of them in DMSO to detect low concentrations of Hg\(^{2+}\) in water. As can be seen in Figures 2 and S2, for A and B respectively, in both cases it was possible to distinguish loss of luminescence at initial concentrations of Hg\(^{2+}\) in water on the order of micromolar (A).

The next step was to prepare test strips by immersion of filter paper into a solution of A/B in DMSO (2 x 10\(^{-4}\) M) and drying in the oven. Then they were immersed into water and aqueous solutions of Hg\(^{2+}\) ions with different concentrations. The dry test strips show discernible change of color from light-orange to purple and loss of luminescence (Figure 3 and S3) when the concentration of Hg\(^{2+}\) in the aqueous solution was as low as 1 x 10\(^{-5}\) M for B and 5 x 10\(^{-5}\) M for A. All these observations indicated that A and B could be used as potential chemosensors for naked-eye detection of Hg\(^{2+}\) at low concentrations in water, even in the presence of various competitive metal ions, by using a very simple procedure.

**Spectroscopic detection of Hg\(^{2+}\).** The electronic absorption spectrum of A and B in DMSO / H\(_2\)O (5mL, 2 x 10\(^{-4}\) M)/ H\(_2\)O (0.5 mL) are analogous to those obtained in other solvents, as reported previously.\(^{16-17}\) The most significant feature is in each case the presence of a weak low energy band (\(\lambda_{\text{max}} = 486\) nm, \(\varepsilon = 2967.03\) M\(^{-1}\) cm\(^{-1}\) A, 480 nm, \(\varepsilon = 2967.03\) M\(^{-1}\) cm\(^{-1}\) B) assigned to metal-metal-to-ligand charge transfer (\(^1\)MMLCT) [\(d\sigma^*\)(Pt-Pt) \(\rightarrow \pi^*\)(bzq)]. The presence of a great excess of various metal cations [Ca\(^{2+}\) (molar ratio 1:5), Ag\(^+\), Li\(^+\), Na\(^+\), K\(^+\), Mg\(^{2+}\), Br\(^-\), Pb\(^{2+}\), Cd\(^{2+}\), Zn\(^{2+}\) and Tl\(^+\) (molar ratio 1:50)] does not produce any change in the original absorption spectra while the presence of Hg\(^{2+}\) (molar ratio 1:5) does (Figures 4 for A and S4 for B). As can be seen in Figure 4, the vis-UV spectrum of the mixture (A + Hg\(^{2+}\), 1:5 molar ratio) shows at \(\lambda > 450\) nm
two bands instead of one with increased intensities ($\varepsilon = 17032.96 \, \text{M}^{-1} \, \text{cm}^{-1}$, $\lambda_{\text{max}} = 467 \, \text{nm}$; $\varepsilon = 11153.85 \, \text{M}^{-1} \, \text{cm}^{-1}$, $\lambda_{\text{max}} = 554 \, \text{nm}$), the lower energy band being the responsible for the color purple of the mixture. Similar results were obtained for complex B (see Figure S4). In this case, the original absorption of B at 480 nm disappears while two new more intense bands appear at 460 nm ($\varepsilon = 14230.77 \, \text{M}^{-1} \, \text{cm}^{-1}$) and 557 nm ($\varepsilon = 11538.46 \, \text{M}^{-1} \, \text{cm}^{-1}$). The lack of interference of the other tested metal ions in the detection of Hg$^{2+}$ by A / B using vis-UV spectroscopy can be observed in Figures 5 (A) and S5 (B).

Aiming to clarify the kind of interaction between Hg$^{2+}$ and complexes A and B, quantitative titrations of solutions of them in DMSO (3 mL, $10^{-4} \, \text{M}$) were performed by addition of increasing amounts of Hg(ClO$_4$)$_2$·3H$_2$O (Figures 6 and S6). Job’s plot analysis revealed a 1:1 [A / B : Hg$^{2+}$] stoichiometry (see insets of Figures 6 and S6).

Compounds A and B exhibit intense phosphorescence in DMSO solution ($\lambda_{\text{max}} \sim 665 \, \text{nm}$) at 298 K that turn-off in the presence of Hg$^{2+}$ ions (see insets of Figures 7 A, S7 B). The addition of Hg$^{2+}$ to a solution of A/B in DMSO-H$_2$O induced a decrease in the emission intensity of 25 %/ 27 % if the molar ratio Hg$^{2+}$: A/ B was 0.5:1 or 75 % / 56 % for a molar ratio 1:1. The limit of detection defined here as the concentration equivalent to a signal of blank plus three times the standard deviation of the blank was calculated to be $7.27 \times 10^{-5} \, \text{M}$ (A), $2.63 \times 10^{-5} \, \text{M}$ (B).

Emission lifetimes of A (DMSO $10^{-4}$M) in absence and in presence of increasing amounts of Hg$^{2+}$ (H$_2$O, $3 \times 10^{-3} \, \text{M}$; HEPES, 20 mM, pH=7.0) were quite similar (see Table S1) and do not depend on the concentration of Hg$^{2+}$. Because of that, the phosphorescence quenching could be attributed to the formation of non-emissive A/B: Hg$^{2+}$ complexes (equation 1) following a static quenching process. Then, the binding
constant of the complexes, coincident with the $K_{SV}$, could be calculated from the Stern-Volmer plots (Figure S8) with $K$ values of $1.13 \times 10^5 \text{M}^{-1}$ (A) and $1.99 \times 10^4 \text{M}^{-1}$ (B).

$$
\text{A/B} + \text{Hg}^{2+} \rightleftharpoons K \text{A/B:Hg}^{2+} \quad \text{(eq.1)}
$$

Moreover, the reversibility of the Hg$^{2+}$ binding to complex A/B was confirmed by using KI (Scheme 1; Figures 7 A, S7 B). Addition of KI (1:2 molar ratio Hg$^{2+}$: I$^-$) to a purple solution of A/B: Hg(ClO$_4$)$_2$·3H$_2$O (1:1 molar ratio) turned the solution orange and luminescent again ($\lambda_{\text{max}} \sim 665 \text{nm}$). This was repeated consecutively for several times, although with the inevitable dilution of samples, showing that the luminescence of compound A/B was recovered and only decreases significantly in intensity after the sixth cycle. The easy regeneration of complex A/B points to think that its interaction with Hg$^{2+}$ does not cause dramatic transformation nor decomposition of the Pt$_2$(II,II) complex. Instead of that a simple complexation in the electron donor-acceptor sense seems to be more likely as it will be explained further on. To ascertain the applicability of A/B as Hg$^{2+}$ selective phosphorescent chemosensors we carried out competitive experiments and followed them by luminescence (Figures 8 A, S9 B). In these experiments water solutions of tested metal ions were added to a solution of A/B in DMSO (50:1 C$^{n+}$: A / B molar ratio) and then a solution of Hg$^{2+}$ was added to them (5:1 Hg$^{2+}$: A / B molar ratio). As can be seen in Figure 8 no discernible change in the phosphorescence intensity of A was found by addition of other tested cations except for Ag$^+$, which enhances the emission intensity to ca. 234 %. The emission of all of these mixtures (C$^{n+}$: A) was completely quenched by the subsequent addition of Hg$^{2+}$ even in the case of Ag$^+$. Experiments carried out with complex B (Figure S9) showed a similar behavior but in this case, with exception of Ag$^+$ that enhances the emission intensity of B (ca. 162 %), the rest of the tested metal ions induced a lessening of it. For this reason
although the emission of all of these mixtures ($C^{n+}$: $B$) was completely quenched by the subsequent addition of Hg$^{2+}$, the phosphorescent sensing properties of $A$ for selective detection of Hg$^{2+}$ seem better than those of $B$.

**Proposed mechanism for sensing’s response.** As it has been described above, from all the tested metal ions only Ag$^+$ enhances the emission intensity of $A$/$B$ while Hg$^{2+}$ turns-off it completely, even if Ag$^+$ is present in the mixture. Because of that we asked about the kind of interaction between $A$/$B$ and Ag$^+$ or Hg$^{2+}$. Concerning Ag$^+$, single crystals of $B$:2Ag$^+$ were obtained from the corresponding solution. They showed no good quality for X-ray purposes (Figure S10) but they allowed us to establish undoubtedly the connectivity of the atoms and to confirm the existence of Pt$\rightarrow$Ag bonds. Consistently with the weakness of this interaction, addition of KI to solutions containing $A$/$B$ and Ag$^+$ (1:1 molar ratio Ag$^+$: I$^-$; Scheme 1) produce the precipitation of AgI and the regeneration of the starting Pt$_2$ complexes, $A$/$B$.

The same kind of interaction should be expected for the adducts $A$/$B$: Hg$^{2+}$ considering the easy regeneration of complexes $A$ and $B$ by addition of KI to solutions containing $A$/$B$: Hg$^{2+}$(1:2 molar ratio Hg$^{2+}$: I, Scheme 1). Moreover, metallophilic bonding in which a d$^8$ square-planar complex acts as a Lewis base through the filled d$_z^2$ orbital for a Lewis-acidic metal to give complexes containing M $\rightarrow$ M’ donor-acceptor bond has been hugely documented,\textsuperscript{18} including some examples in which M’ = Hg, as Au(I) $\rightarrow$Hg(II),\textsuperscript{19} Pt(II) $\rightarrow$Hg(II)\textsuperscript{20} or Pd(II) $\rightarrow$Hg(II) bonds.\textsuperscript{21} In half-lantern Pt$_2$(II,II) or Pd$_2$(II,II) complexes, the filled $\sigma^*$ orbital, resulting from the interaction of d$_z^2$ ones is higher in energy than the original, which should lead to an increase of the basicity of the molecule and to stronger donor-acceptor bonds.\textsuperscript{21} A few examples of complexes involving half-lantern Pt$_2$(II,II) or Pd$_2$(II,II) fragments as Lewis base through the filled
σ* orbital have been reported: cis-\([\{\text{Pt}(\text{NH}_3)_2(1\text{-MeC}^-)_2\}_2\text{Ag}\}]((\text{NO}_3)_3\cdot\text{H}_2\text{O},\)\(^{22}\)
\([\{\text{Pd}(\text{ppy})(\mu\text{-acetate})\}_2\text{Hg}(\text{C}_6\text{F}_5)_2\}] (\text{ppy} = 2\text{-phenylpyridine-κC,N}),^{21}\) or \([\{\text{Pd}(\text{bzq})(\text{OAc-κO,O'})\}_2(\text{TCE})]\) (TCE = tetracyanoethylene ).\(^{23}\) This donor-acceptor interaction leads to species with shorter intermetallic distance and higher metal-metal bond order,\(^{21,23}\) and in consequence, with the HOMO raised in energy with respect to that of the starting complex.

Complexes A and B are Pt\(_2\) half-lantern species with the HOMO being mainly a σ* orbital oriented outward along the M-M axis,\(^{16-17}\) and could act as Lewis bases for a Lewis-acid as Ag\(^+\), Hg\(^{2+}\) or others. The existence of Pt\(_2\) → Hg donor-acceptor interaction in the adducts is expected to increase the Pt-Pt metal-metal bond order, raise the energy of the HOMO and lessen the energy of the MMLCT absorption band with respect to the Pt\(_2\) starting complex (λ \approx 480 nm). Therefore it could justify the presence of a lower energy absorption band (λ \approx 554 nm) red-shifted with respect to that in the starting Pt\(_2\) complex. However, the interaction of Hg\(^{2+}\) at other sites of the molecules, such as the S atoms of the bridging ligands, is also quite likely and also could justify the easy regeneration of complex A/ B upon addition of KI to solutions containing A/B: Hg\(^{2+}\) (1:2 molar ratio Hg\(^{2+}\): I\(^-\), Scheme 1).

Aiming to get some insight about the nature of the interaction of A/B with Hg\(^{2+}\) and considering that both complexes show quite similar spectroscopic behaviour upon interaction with Hg\(^{2+}\) in solution, optimization of a series of simulated structures of A:Hg\(^{2+}\) (Figure 9) were carried out at the DFT/M06 level of theory. Interactions of different mercury fragments as \([\text{Hg}(\text{ClO}_4)_4]\), \([\text{Hg}(\text{ClO}_4)(\text{Solv})]\), \([\text{Hg}(\text{ClO}_4)(\text{Solv})_2]\), \([\text{Hg}(\text{Solv})_2]\), and \([\text{Hg}(\text{Solv})_3]\) (Solv = DMSO) with the half-lantern Pt\(_2\) derivative A have been studied and eight different structures have been optimized. Four structures
containing Pt\textsubscript{2}→Hg\textsuperscript{2+} interactions and keeping the original half-lantern structure of precursor A have been modeled (AHg-01-DFT to AHg-04-DFT). Three additional structures arising from the interaction of the mercury center with two sulfur atoms of the NS\textsubscript{2} bridging ligands (AHg-05-DFT to AHg-07-DFT), therefore keeping the half-lantern skeleton untouched and showing no Pt⋯Hg interaction, have been also considered. Finally one more structure has been modeled, resulting from the breakage of the original Pt⋯Pt bond in complex A and leading to the formation of a complex stabilized by Pt⋯Hg⋯Pt interactions (AHg-08-DFT). Time-dependent DFT calculations were subsequently performed in order to calculate the λ of the lowest-energy absorption bands of each optimized structure (see computational details) and then, they were compared with the experimental absorption bands measured for solutions containing A and Hg\textsuperscript{2+} (1:5) (Figure S11). As can be seen, the structures AHg-01-DFT to AHg-04-DFT containing unsupported Pt\textsubscript{2}→Hg\textsuperscript{2+} interactions are the ones that better account for the red shift of the lower-energy absorption bands with respect to that of the starting complex, in line with our previous thoughts.

Although, the existence of other kinds of species in solution could not be completely excluded, the presence of those containing Pt\textsubscript{2}→Hg\textsuperscript{2+} and Pt\textsubscript{2}→Ag\textsuperscript{+} interactions in the solutions containing A/B and Hg\textsuperscript{2+} or Ag\textsuperscript{+} seems quite likely. However, the A/B:2Ag\textsuperscript{+} adducts do not show differences in their absorption spectra in solution with respect to the starting complexes A/B but exhibit a more intense phosphorescence than them. By contrast, formation of A/B:Hg\textsuperscript{2+} adducts, produce additional broad bands in the absorption spectra and the phosphorescence quenching of A/B. This different photophysical behavior showed by the adduct of A/B with Ag\textsuperscript{+} and Hg\textsuperscript{2+} has been observed previously by Nagle et al. when they studied the photophysical behavior of the
lantern complex \( \text{Pt}_2(\text{P}_2\text{O}_3\text{H}_2)_4^{4-} \) (Pt2) in the presence of isoelectronic cations as: \( \text{TI}^+ \), \( \text{Pb}^{2+} \) and \( \text{Sn}^{2+} \). \( \text{TI}^+ \) cations almost do not affect the absorption spectrum of aqueous Pt2 and they interacts with the excited state (*Pt2) at the vacant axial sites to form luminescent exciplexes. However, the divalent cations cause drastic changes on the absorption spectrum of aqueous Pt2 (additional broad bands assigned tentatively to metal-to-metal charge transfer (MMCT) from Pt2 to Pb\(^{2+}\) or Sn\(^{2+}\) were observed) and the phosphorescent quenching of *Pt2.

The complete quenching of the emission of solutions containing A/B and Ag\(^+\) when Hg\(^{2+}\) was added to it (Scheme 1), seems to indicate that the interaction of A/B with Hg\(^{2+}\) is stronger than the Pt\(_2\) \(\rightarrow\) Ag\(^+\) one, which could be related with the relativistic effects, that play a crucial role when the metallophilic interactions involve metal ions from the third row of the transition series.

**CONCLUSIONS**

The organometallic platinum(II) half-lantern complexes A and B in solution of DMSO-H\(_2\)O show yellowish-orange color and an intense red phosphorescence arising from \(^{1,3}\text{MMLCT}\) transitions. These solutions undergo dramatic color change, from yellowish-orange to purple, and turn-off phosphorescence in the presence of small amount of Hg\(^{2+}\). Other metal ions as Ag\(^+\), Li\(^+\), Na\(^+\), K\(^+\), Ca\(^{2+}\), Mg\(^{2+}\), Ba\(^{2+}\), Pb\(^{2+}\), Cd\(^{2+}\), Zn\(^{2+}\) and Ti\(^+\) were tested showing no interference in the selective detection of Hg\(^{2+}\) in water, even if they are in a big excess. Therefore complexes A and B in solution of DMSO are two new selective colorimetric and turn-off phosphorescent chemosensors of Hg\(^{2+}\). The interaction between A/ B and Hg\(^{2+}\) seems to be a simple complexation in the electron donor-acceptor sense with a 1:1 \([\text{A/B}:\text{Hg}^{2+}]\) stoichiometry, since it resulted reversible upon addition of KI. Additionally, A and B are suitable for the naked-eye detection of
Hg$^{2+}$ in water; diluted solutions of them in DMSO can detect the presence of Hg$^{2+}$ in water even if the concentration is as low as $2 \times 10^{-6} \text{ M (A)}$ or $5 \times 10^{-5} \text{ M (B)}$; also, paper test strips impregnated of A and B can detect concentration of Hg$^{2+}$ in water as low as $1 \times 10^{-5} \text{ M for B}$ and $5 \times 10^{-5} \text{ M for A}$, making these complexes good candidates to be used as real-time detectors of Hg$^{2+}$.

**EXPERIMENTAL SECTION**

**General procedures and materials.** UV-Vis absorption spectra were recorded on a Thermo Electron Corporation evolution 600 spectrophotometer or on a Varian Cary 50 spectrophotometer. Steady-state photoluminescence spectra were recorded on a Jobin-Yvon Horiba Fluorolog FL-3-11 Tau 3 spectrofluorimeter using band pathways of 3 nm for both excitation and emission.

The starting materials $\text{[\{Pt(bzq)(\mu-C_7H_4NS_2-\kappa N,S)\}_2\]}(\text{A})^{16}$ and $\text{[\{Pt(bzq)(\mu-C_7H_4NOS-\kappa N,S)\}_2\]}(\text{B})^{17}$ were prepared as described elsewhere. Nitrate salts: Pb(NO$_3$)$_2$, Ca(NO$_3$)$_2$, Ba(NO$_3$)$_2$, Tl(NO$_3$)$_3$, Ag(NO$_3$)$_2$, Na(NO$_3$); perchlorate salts: Mg(ClO$_4$)$_2$, Cd(ClO$_4$)$_2$·$\text{H}_2\text{O}$, Zn(ClO$_4$)$_2$·$6\text{H}_2\text{O}$, Li(ClO$_4$)·$3\text{H}_2\text{O}$, Hg(ClO$_4$)$_2$·$3\text{H}_2\text{O}$ and hexafluorophosphate salts: K(PF$_6$) were used as purchased from different suppliers.

**Safety note:** perchlorate salts of metal ions are potentially explosive. Only small amounts of material should be used and handled with great caution.

**UV-Vis and Luminescence Studies.** Stock solution of A / B for electronic and emission studies was prepared in DMSO. Stock solutions of different metal cations (0.01 M for Hg$^{2+}$, Ca$^{2+}$ and 0.1 M for Ag$^+$, Li$^+$, Na$^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$, Ba$^{2+}$, Pb$^{2+}$, Cd$^{2+}$, Zn$^{2+}$ and Tl$^+$) were prepared by solving the corresponding salt in distilled water. In titration experiments, 3 mL of A or B solution (DMSO, $10^{-4} \text{ M}$) was placed in a quartz
cuvette (path length, 1 cm) and the buffer solution of Hg$^{2+}$ (H$_2$O, 3 x 10$^{-3}$ M; HEPES, 20 mM, pH=7.0) was added gradually with the help of a micropipet.

**Computational Details.** Quantum mechanical calculations were performed with the Gaussian09 package at the DFT/M06 level of theory. SDD basis set and its corresponding effective core potentials were used to describe the Platinum and Mercury atoms. Carbon, Nitrogen, Hydrogen, Sulfur, Oxygen and Chlorine atoms were described with a 6-31G(d) basis set. All the discussed structures were optimized in the gas phase, with no symmetry restrictions. The computed minima were subsequently characterized by analytically computing the Hessian matrix. TD-DFT calculations were performed on the optimized structures and in dichloromethane as solvent by using the polarizable continuum model (PCM) approach implemented in the Gaussian 09 software.

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**Supporting Information Available**

Figures S1 and S2: Photographs of B in DMSO upon addition of aqueous solutions of tested metal ions and aqueous solutions of Hg$^{2+}$ with different concentrations. S3: Photographs of dried test strips of A after immersion in aqueous solution of Hg$^{2+}$ with
different concentrations. S4: Absorption response of B in DMSO after addition of water or aqueous solutions of tested metal ions. S5: Absorption response of B in DMSO (5 mL, 2 x 10^{-4} M) to the presence of several metal ions (0.5 mL, 0.1 M in H_{2}O) with (0.5 mL, 0.01 M in H_{2}O) and without Hg^{2+}. S6: Changes in the UV-Vis absorption spectra of A in DMSO in the titration with Hg^{2+}; titration curve of A with Hg^{2+} and Job’s plot. S7: Reversible Hg^{2+} complexation to B by addition of KI followed by luminescence. Table S1. Emission lifetimes of mixtures A/ Hg^{2+} (DMSO/ H_{2}O). Figure S8: Stern-Volmer plot for the titration of A/ B in DMSO with Hg^{2+}. S9: Luminescence response of B to the presence of tested metal ions before and after addition of Hg^{2+}. Figure S10. Molecular structure of the adduct B: 2Ag^{+}. Figure S11. Comparison of the experimental absorption spectrum of A: Hg^{2+} (1:5) in DMSO/H_{2}O with the ^{1}MMLCT absorption of A and calculated absorption frequencies of the different proposed structures.

REFERENCES


Scheme 1. Proposed mechanism for sensing response of A/B to Hg$^{2+}$ and Ag$^+$.  

Figure 1. a) Photographs of A in DMSO (5 mL, 2 x 10$^{-4}$ M) upon addition of 0.5 mL of water or aqueous solutions of every metal ion (0.01 M for Hg$^{2+}$, Ca$^{2+}$ and 0.1 M, for the rest of the cations); b) Photographs of these solutions when they were irradiated with UV light at $\lambda = 365$ nm.
Figure 2. Lower picture: photographs of A (1 mL, $2 \times 10^{-5}$ M in DMSO) after addition of 3 mL of aqueous solutions of Hg$^{2+}$ with different concentrations. Upper picture: photographs of these solutions irradiated with UV light at $\lambda = 365$ nm.

Figure 3. Lower picture: Photographs of dried test strips of B (DMSO, $2 \times 10^{-4}$ M) after immersion in water or aqueous solutions of Hg$^{2+}$ with different concentrations. Upper picture: photographs of these test strips irradiated with UV light at $\lambda = 365$ nm.
Figure 4. Absorption spectra of A in DMSO (5 mL, $2 \times 10^{-4}$ M) upon addition of 0.5 mL of water or aqueous solutions of every metal ion ($0.01$ M for $\text{Hg}^{2+}$, $\text{Ca}^{2+}$ and $0.1$ M, for the rest of the cations).
Figure 5. Absorption response of A in DMSO (5 mL, $2 \times 10^{-4}$ M) to the presence of several metal ions (0.5 mL, 0.1 M in H$_2$O) with (0.5 mL, 0.01 M in H$_2$O) and without Hg$^{2+}$. 
Figure 6. Changes in the UV-Vis absorption spectra of B in DMSO (3 mL, 10^{-4} M) upon addition of Hg^{2+} (n x10\mu L, 3 x 10^{-3} M; 0-5 B: Hg^{2+} molar ratio) in buffer aqueous solution (HEPES, 20mM, pH=7.0). Inset: a) Titration curve of B with Hg^{2+} b) Job’s plot for determining the stoichiometry of the complex [B-Hg^{2+}] in DMSO / H_{2}O (1:0.1, v/v).
Figure 7. Reversible Hg$^{2+}$ complexation to A by addition of KI followed by luminescence. Inset: orange line, free A (2 x 10$^{-4}$M, DMSO); violet line: A + Hg$^{2+}$ (1:1); grey line: A + Hg$^{2+}$ + KI (1:1:2).
Figure 8. Luminescence response of A (5mL, $2 \times 10^{-4}$M in DMSO) to the presence of tested metal ions (0.5 mL, 0.1 M in H$_2$O) before and after addition of Hg$^{2+}$ (0.5 mL, 0.01 M in H$_2$O). Inset: emission spectra of: A ($\lambda_{exc} = 485$ nm) in DMSO, A+Hg$^{2+}$ and A+Hg$^{2+}$+Ag$^+$. 
Figure 9. Proposed structures for the possible interaction of Hg$^{2+}$ with complex A. Solv = DMSO