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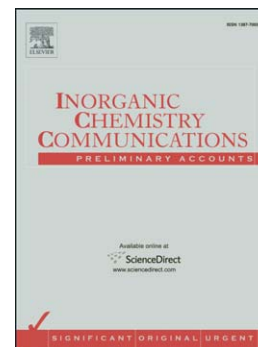
A highly selective turn-on sensor for Hg^{2+} based on a phosphorescent iridium (III) complex

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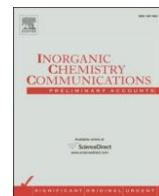
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Short Communication

A highly selective turn-on sensor for Hg^{2+} based on a phosphorescent iridium (III) complexQunbo Mei^{a,*}, Yujie Shi^a, Chen Chen^a, Qingfang Hua^a, Bihai Tong^{b,*}^a Key Laboratory for Organic Electronics and Information Displays & Institute of Advanced Materials (IAM), Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Nanjing University of Posts & Telecommunications, 9 Wenyuan Road, Nanjing 210023, China;^b College of Metallurgy and Resources, Anhui University of Technology, Ma'anshan, Anhui 243002, P. R. China.

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abstract

A highly selective phosphorescent chemosensor for Hg^{2+} based on the iridium (III) complex $\text{Ir}(\text{DTBT})_2(\text{acac})$ ($\text{DTBT} = 2-(5-(1,2\text{-dihydroacenaphthylen-5-yl})\text{thiophen-2-yl})\text{benzothiazole}$, $\text{acac} = \text{acetylacetonate}$) was synthesized and characterized. $\text{Ir}(\text{DTBT})_2(\text{acac})$ exhibited relatively weak fluorescence at about 700 nm. $\text{Ir}(\text{DTBT})_2(\text{acac})$ displayed a dramatic color change from near-infrared to yellow-green with the addition of Hg^{2+} . More significantly, the chemosensor performed “turn-on” phosphorescent responses toward Hg^{2+} .

Mercury is currently used in a wide range of products, such as industrial chemicals, electrical or electronic devices, dental amalgam, energy-efficient fluorescent light bulbs and batteries, which is one of the most dangerous and ubiquitous pollutants [1-3]. Among various heavy and soft cations, Hg^{2+} is one of the most toxic heavy metal ions. Once mercury ions enter the environment, bacteria can convert the inorganic Hg^{2+} into methylmercury or dimethylmercury. Some research implicated that mercury pollution can cause some serious irreversible neurological damage [4]. Thus, the development of methods for the Hg^{2+} determination is significant for environment and human health. Several techniques for the determination of Hg^{2+} have been devised by utilizing electrochemical, chromogenic, and fluorogenic properties as output signals over the past few years [5-7]. Heavy metal complexes, which have more advantages with long excited state lifetime, high photoluminescence efficiency and excellent color tuning, have been received more and more attention in OLEDs and chemosensors [8-11]. Phosphorescent iridium (III) complex is also widely used to detect Hg^{2+} for its excellent properties [12-14]. In our previous work [15], we have synthesized iridium (III) complex $\text{Ir}(\text{TBT})_2(\text{acac})$ ($\text{TBT} = \text{thiophen-2-yl-benzothiazole}$) which can be used as a phosphorescent chemosensor with high sensitivity and selectivity for detecting of Hg^{2+} . This chemosensor was easily prepared and found to be possible to detect the Hg^{2+} with dramatic color change of the solution. Nevertheless, this chemosensor performed the “turn-off” response to Hg^{2+} . We also introduced a weak electron-drawing group acenaphthene into TBT unit to synthesize DTBT which can be used as Hg^{2+} probe simultaneously [16]. Upon addition of Hg^{2+} into dichloromethane (DCM) solution of DTBT, the solution was changed from colorless to yellow. Most of all, DTBT shown a “turn-on” response to Hg^{2+} . Therefore, we hope to

synthesize a phosphorescent iridium (III) complex chemosensor employing DTBT as cyclometalated ligand which can exhibited “turn-on” phosphorescent response toward Hg^{2+} . In this work, we report a novel iridium (III) complex $\text{Ir}(\text{DTBT})_2(\text{acac})$, which can also serve as a “naked-eye” detector for Hg^{2+} , but with “turn-on” response to Hg^{2+} . Furthermore, complex $\text{Ir}(\text{DTBT})_2(\text{acac})$ displayed a near-infrared emission, which can be also used in biological detection.

The synthesis method of $\text{Ir}(\text{DTBT})_2(\text{acac})$ was according to literature [17-19]. As shown in Scheme 1, $\text{Ir}(\text{DTBT})_2(\text{acac})$ was acquired successfully in 58.96% yield. The structure of $\text{Ir}(\text{DTBT})_2(\text{acac})$ was confirmed by ^1H NMR, ^{13}C NMR, and MALDI-TOF. The detail descriptions of these characterizations for $\text{Ir}(\text{DTBT})_2(\text{acac})$ are available in supporting information.

Iridium (III) complex $\text{Ir}(\text{DTBT})_2(\text{acac})$ was further identified using single crystal X-ray analysis to establish their exact solid state structure. As shown in Fig. 1, the complex has distorted octahedral coordination geometry around iridium atom with two cyclometalated ligands DTBT and one ancillary ligand acetylacetonate. The DTBT with the nitrogen atoms N1 and N2 residing at the *trans* locations, and the Ir–N distances lie between 2.0636 and 2.0741 Å. The cyclometalated carbon atoms C9 and C32 are mutually *cis* on the iridium and show marginally shorter distances 1.9830 and 1.9950 Å. It implied that there is a stronger *trans* influence of the phenyl group. The bond lengths between Ir center and the O1, O2 of ancillary ligand are ranging from 2.1187 to 2.1419 Å, which are longer than that between the Ir center and the cyclometalated ligands. The detail single crystal data of $\text{Ir}(\text{DTBT})_2(\text{acac})$ are showed in Tables S1 and S2.

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