New metal-coordination-inhibited charge transfer emission for terfluorenes: highly sensitive and selective detection for Hg^{2+} with ratiometric "turn-on" fluorescence response†

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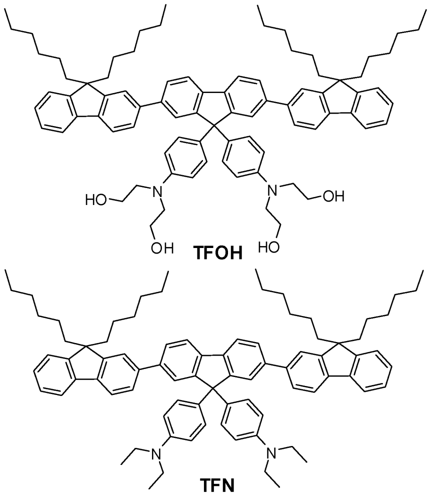
Two terfluorenes TFOH and TFN exhibit high sensitivity and selectivity for the detection of Hg^{2+} with ratiometric fluorescence response. The sensory mechanism is attributed to a new metal-coordination-inhibited spiroconjugation-like charge transfer emission.

The significance of monitoring environmental contamination is arousing more and more attention nowadays. Mercury, as a poisonous heavy metal, could easily accumulate in organisms, and cause irreversible damage to the central nervous and endocrine systems.[1] Highly sensitive and selective Hg^{2+} sensors are in high demand for mercury pollution monitoring.[2] Most of the reported fluorescent chemosensors for Hg^{2+} are turn-off detection because of the intrinsic property of Hg^{2+} to quench fluorophore emission.[3] Designing fluorescent chemosensors for Hg^{2+} with turn-on response is a considerable challenge. In addition, ratiometric fluorescence is an alternative approach for the detection of Hg^{2+} which can offer advantages in eliminating the background interferences, and consequently be of significance in biological contexts. Although only a few examples of ratiometric Hg^{2+} detectors have been reported, this method is gaining attention in the heavy-metal sensing community.[4] As far as the receptor unit of a Hg^{2+} fluorescent chemosensor is concerned, a couple of heteroatoms (N, O, S, *et al.*) are usually involved in order to afford high association constants. To date the detection of Hg^{2+} ions with a single heteroatom has rarely been reported due to the poor binding ability and the lack of selectivity.[5]

Over the past few years, polyfluorenes as both chemosensors and biosensors have been widely explored.[6] Nevertheless, oligofluorenes have rarely been applied in the detection area, despite their unique electronic and photonic properties.[6a,7] We have recently reported a series of novel terfluorenes exhibiting dual fluorescence emissions, which can be assigned to a π–π* transition from the fluorene chain and a new intramolecular through-space charge transfer emission (spiroconjugation-like charge transfer) from the pendent aminophenyl group to the fluorene chain. Furthermore, the dual emissions of terfluorene derivatives could be facilely tuned by the electronic nature of pendent aminophenyl groups.[8] This may provide a good model to develop ratiometric fluorescent chemosensors.[9] To this end, we chose the typical terfluorene TFOH with 4-(bis(2-hydroxyethyl)amino)phenyl pendent group to exploit its application as a fluorescent chemosensor for metal ions. To study the binding position between the terfluorene derivatives and metal ions, we also designed and synthesized a new terfluorene derivative, namely TFN, with two 4-(diethylamino)-phenyl side groups (Scheme 1). Their fluorescence responses toward different metal ions are investigated. It turns out that both terfluorenes are able to work as ratiometric fluorescent chemosensors for Hg^{2+} exclusively, irrespective of the structure of receptor units.

The synthesis of TFOH has been described elsewhere,[10] and that of TFN is presented in the ESI. TFN exhibits similar photophysical behaviors to TFOH, with green emission in THF solution and significant bathochromic shift with the increase of solvent polarity (see Fig. S1 in ESI).

We initially investigated their fluorescence emission changes toward different metal ions. The metal ion detection procedures were carried out in THF–MeOH mixtures, with TFOH/TFN at a concentration of 5 μM in THF, and all metal ions dissolved in MeOH at a concentration of 5 mM. Both terfluorenes show distinct low energy emission around 500 nm, and quite weak high energy emission around 410 nm. Of the metal ions investigated, both terfluorenes show unexpected high selectivity toward Hg^{2+}. Intuitively, their emission colors change significantly from green to bright blue upon addition of Hg^{2+}, while the other metal ions have almost negligible effect on the fluorescence change, except that Cu^{2+} only



Scheme 1 Chemical structures of TFOH and TFN.

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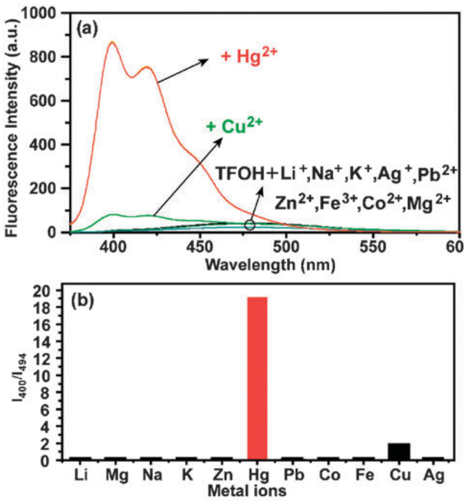

Fig. 1 (a) Fluorescence responses of TFOH (5 μM in THF) toward different metal ions (5 mM in MeOH, each metal ion was of 50 equiv of TFOH). (b) Fluorescence intensity ratio of 400 nm *versus* 494 nm upon addition of 25 equiv different metal ions.

causes a small enhancement of the blue emission (Fig. 1 for TFOH and Fig. S3 for TFN).

Fluorescence titration experiments of the two terfluorenes toward Hg^{2+} are shown in Fig. 2. For both TFOH and TFN, the intensities of green emission bands gradually decrease, while those of the blue emission bands strikingly increase as the concentration of Hg^{2+} ions grows. A comparison of the I_{400}/I_{494} ratio before and after the addition of Hg^{2+} gives an approximate 205 fold ratiometric fluorescence change for TFOH and 294 fold for TFN. According to a non-linear fitting equation,[11] the binding constants are determined to be 3.3×10^4 M^{-1} for TFOH–Hg^{2+}, and 4.3×10^5 M^{-1} for TFN–Hg^{2+}. It is noteworthy that the simple receptor unit, especially only N atoms for TFN, exhibits high sensitivity and selectivity toward Hg^{2+}.

We also tested the interference of other metal ions toward Hg^{2+} detection (Fig. S4 in ESI). The intensities of blue emission only slightly increase when the examined metal ions (Fe^{3+}, Co^{2+}, Zn^{2+}, Ag^{+}, K^{+}, Pb^{2+}, Cu^{2+}, Mg^{2+}, and Li^{+}) are added, however a prominent increase of the blue emission is observed when Hg^{2+} is added to the above solution. The result indicates that the two terfluorenes are able to detect Hg^{2+} with the coexistence of other usual transition metal ions.

The recognition process of Hg^{2+} is reversible, as the subsequent addition of an excess of EDTA aqueous solution can fully recover the original green emission of TFOH (Fig. 3). The same is true for TFN (Fig. S5 in ESI).

In view of the chemical structure of TFOH and TFN, as well as their exceptional emission behaviours, we may deduce that the coordination of Hg^{2+} with the *N*,*N′*-di(2-hydroxyethyl)amino or *N*,*N′*-diethylamino groups weakens the electron-donating ability of nitrogen atoms, thus the spiroconjugation-like charge transfer process leading to green emission can be suppressed. To further understand the complexation modes, we investigated the ^1H NMR spectra of TFOH and TFN in the absence and presence of Hg^{2+} (Fig. 4). After addition of Hg^{2+} into TFOH in $CDCl_3:CD_3CN$ (v : v/1 : 3) mixture, the resonances of the eight aromatic protons at 7.13 and 6.61 ppm assigned to the pendent phenyl exhibit significant downfield shifts, where they are merged with the protons of fluorene. Evidently, the coordination of nitrogen with Hg^{2+} lowers the electron density of the benzene rings, which causes a deshielding effect. In addition, the resonances of the protons between 3.6 and 3.4 ppm assigned to two methene on the *N*,*N′*-di(2-hydroxyethyl)amino groups become broadened. Similar changes of ^1H NMR are also observed for TFN before and after the addition of Hg^{2+} (Fig. 4), indicating that a sole nitrogen atom on the pendent groups can also bind Hg^{2+} ions.

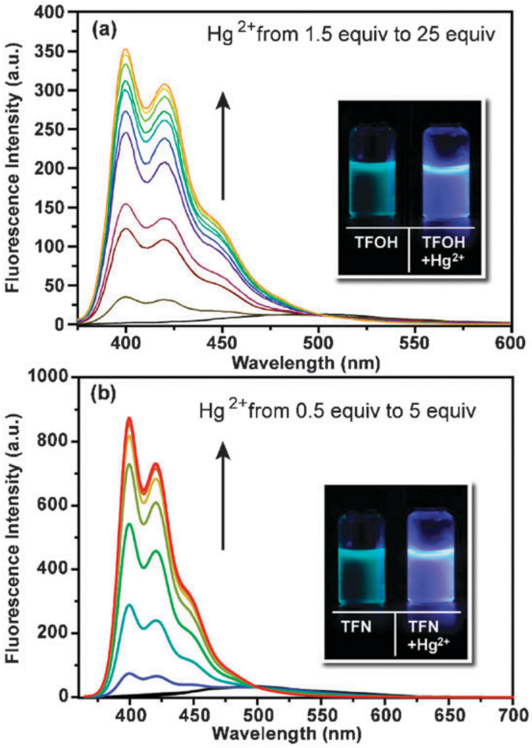

Fig. 2 Fluorescence spectra of TFOH and TFN (5 μM in THF) in the presence of Hg^{2+}. λ_{ex} = 350 nm. Inset shows the visual fluorescence change of TFOH after the addition of 25 equiv Hg^{2+}.

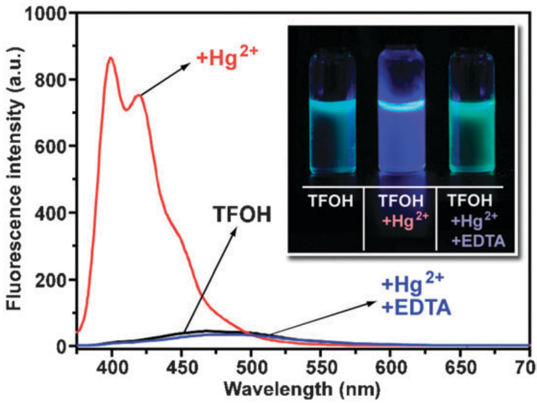

Fig. 3 Fluorescence reversibility of TFOH (5 μM in THF) on detection of Hg^{2+} (5 mM in MeOH). Inset shows the visual fluorescence change of TFOH after the addition of Hg^{2+}, and sequential addition of EDTA aqueous solution, respectively. The photos were taken under a handheld UV (365 nm) lamp as soon as the substances were added.

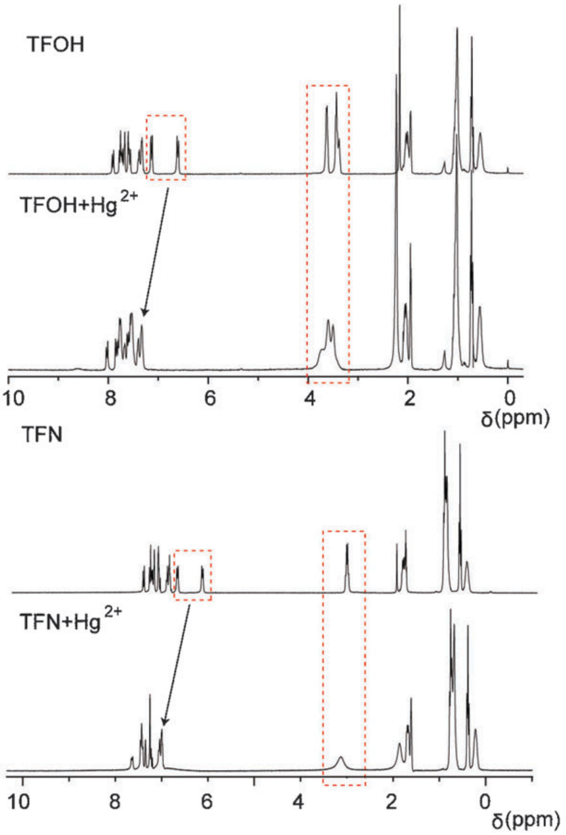

Fig. 4 ^{1}H NMR spectra of TFOH and TFN (5 mM in $CDCl_3$: CD_3CN (v : v/1 : 3) mixture) before and after the addition of Hg^{2+}, respectively.

In conclusion, we have successfully utilized the specific spiroconjugation-like charge transfer to design new ratiometric fluorescent chemosensors for Hg^{2+} with high sensitivity and selectivity. The monitoring event could facilely be observed under UV light irradiation, as the emission color changes intuitively from weak green to bright blue. We note that the detection of Hg^{2+} ions is realized by only a single nitrogen atom as receptor unit. Most previous fluorescence sensing mechanisms for metal ions include photoinduced electron transfer (PET), intramolecular charge transfer (ICT), fluorescence resonance energy transfer (FRET), and the heavy atom quenching effect. In this work, the metal-coordination-inhibited spiroconjugation-like charge transfer emission presents a new methodology for designing fluorescence sensors. On the other hand, the sensory mechanism also further verifies our assignment for the dual fluorescence emissions of the terfluorene derivatives.[8] Further study on modification of trifluorenes in order to detect metal ions in aqueous systems and biological contexts is under way.

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