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Note

A pyrenyl-appended triazole-based ribose as a fluorescent sensor for Hg^{2+} ion

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ABSTRACT

For the efficient detection of toxic trace metal ions, two pyrenyl-appended triazole-based D-ribose fluorescent chemosensors **6** and **7** were prepared and their fluoroionophoric properties toward transition metal ions were investigated. Chemosensors **6** and **7** exhibit highly selective recognition toward Hg^{2+} ion among a series of tested metal ions in CH_2Cl_2/MeOH solution. The association constants of **6** and **7** are calculated to be $1.73 \times 10^5\ M^{-1}$ and $4.44 \times 10^5\ M^{-1}$, respectively. Both **6** and **7** formed complexes with the Hg^{2+} ion at a 1:1 ligand-to-metal ratio with a detection limit of 10–15 μM Hg^{2+}. Computational analysis demonstrated that the Hg^{2+} ion occupied the coordination center of **6** with N^2 and N^3 atoms in two triazole groups, thus separating and distorting the two parallel pyrenes away from each other.

The design and synthesis of new chemosensors for the efficient detection of trace metal ions are among the most important research topics in environmental chemistry and biology.[1] In particular, mercury ion is a significant environmental pollutant that accumulates in plants, soil, and water. In the marine environment, mercury ion is converted by bacteria into methylmercury, a highly potent neurotoxin. Methylmercury is passed up the food chain and bioaccumulates in humans.[2–4] Accordingly, it is imperative to develop analytical methods for the sensitive and selective detection of trace amounts of mercury ion.[5,6]

Carbohydrate-based chemosensors are chiral entities with hydroxyl groups and oxygen atoms that form quite suitable cation binding sites. Thus, in the design of chemosensors, the incorporation of sugar molecules is a good strategy for capturing cations.[7–9] Currently, there are very few sugar-based fluorescent chemosensors for selective detection of mercury ion described in the literature.[10] A good chemosensor must also possess a selective and sensitive signaling mechanism. Recently, pyrene has emerged as one of the most effective functional groups for fluorescence signaling.[11–15] In this study, we combined these two entities in a novel chemosensor by connection with triazole groups for metal ion screening studies because the triazole groups are lately recognized as potential metal ion binding site.[15,16] The designed ribose-based pyrenyl-appended chemosensors **6** and **7** exhibit high selectivity and sensitivity for Hg^{2+} ion compared to other transition and heavy metal ions.

The synthesis of fluorescent sensors is outlined in Scheme 1. The 5-*O*-Ms-*C*-riboside **1** can be easily prepared from ribose in five steps.[17] The ester groups of **1** were hydrolyzed with NaOH to produce the corresponding acid **2** in 70% yield. We used Steglich esterification to couple compound **2** with two different lengths of polyethylene glycol in the presence of DMAP and DCC to obtain **3** or **4** in 68% and 63% yields, respectively. Under microwave conditions, **3** or **4** was treated with 1-(propagyloxymethyl)pyrene **5** and PPh_3·CuBr as the catalyst in toluene at reflux to obtain compound **6** or **7** in 63% and 57% yields, respectively.

We first studied the optical properties of both **6** and **7** in CH_2Cl_2/MeOH solution. On excitation at 343 nm, the maximum absorption wavelength of the pyrene in **6** and **7** displayed a strong excimer emission at 478 nm and a weak monomer emission at 395 nm (Fig. 1a and b), respectively. The relative ratio of excimer to monomer ($I_{excimer}/I_{monomer}$) bands for **6** and **7** is about 5–5.5 indicating that **6** and **7** have similar conformational rigidity. The chemosensing behavior of **6** (10 μM) and **7** (15 μM) was investigated by comparing their fluorescence intensities before and after addition of 10 equiv of the following 11 metal ions (as perchlorate salts): Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Hg^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+}. The results indicated that the monomer and excimer emissions of **6** were strongly quenched only in the presence of the Hg^{2+} ion (Fig. 1a). This selective quenching by the Hg^{2+} ion was also observed for compound **7** (Fig. 1b). The quenching efficiency ($I - I_0/I_0 \times 100\%$) for **6** and **7** observed at 478 nm was nearly 100% (Fig. 2); in contrast, the other metal ions caused comparatively small changes in fluorescence intensity.

In addition, Cd^{2+} is an important cation because, like Hg^{2+} it is also toxic. Therefore, we also performed the selectivity study on Cd^{2+}. The results showed almost no effect on the fluorescence changes of **6** and **7** upon addition of Cd^{2+} (Fig. S14). Moreover, we tested whether the addition of excess metal ions would change the UV–vis spectra of both **6** and **7**. We found that the spectra of

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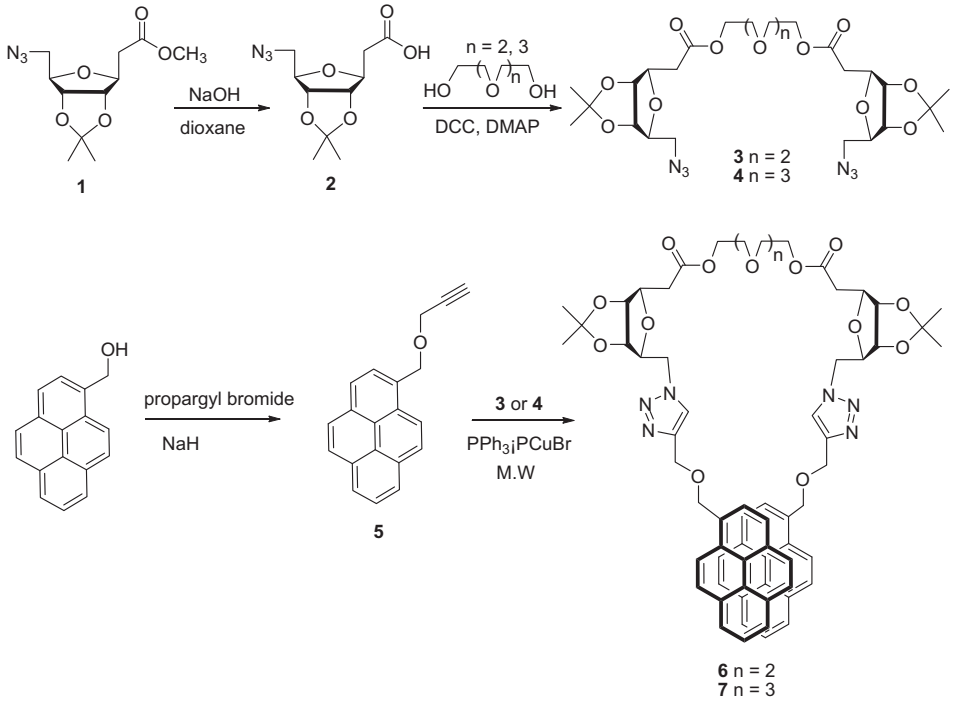

Scheme 1. Synthesis of chemosensors **6** and **7**.

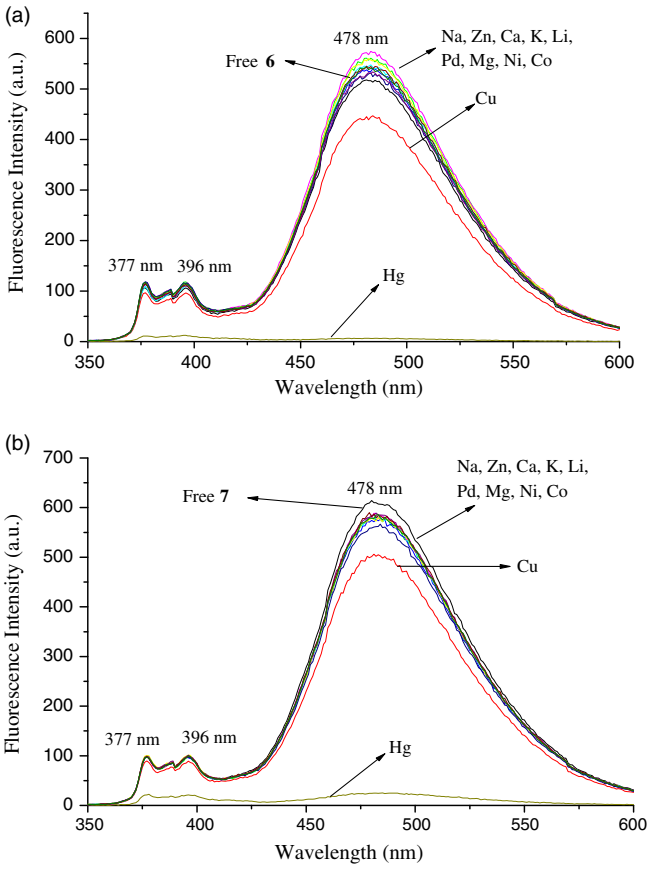

Figure 1. Fluorescence spectra of (a) **6** (10 μM) and (b) **7** (15 μM) in the presence of 10 equiv of various metal ions in CH_2Cl_2/MeOH (80:20, v/v); λ_{ex} = 344 nm.

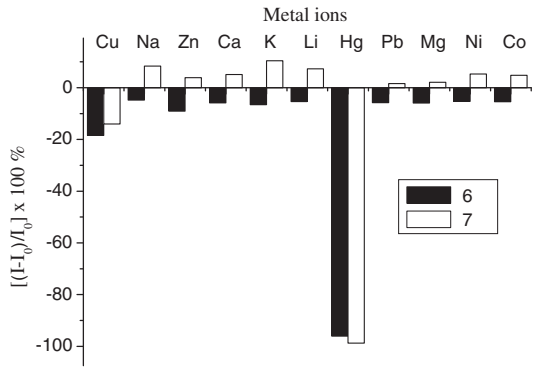

Figure 2. Fluorescence intensity changes ($(I - I_0)/I_0 \times 100\%$) of **6** (10 μM, dark bars) and **7** (15 μM, light bars) in the presence of various metal ions in CH_2Cl_2/MeOH (80:20, v/v); λ_{ex} = 344 nm.

both **6** (Fig. 3a) and **7** (Fig. 3b) were altered only in the presence of the Hg^{2+} ion. The presence of Hg^{2+} ion caused a small red shift that occurred at three λ_{max} absorption wavelengths (312, 328, and 344 nm). These red shifts are attributable to the deformation of electrical environments owing to Hg^{2+} complex formation. Additionally, the chain lengths of the ethylene ethers on **6** and **7** had no influence on the quenching of the excimer and monomer emissions upon the addition of the Hg^{2+} ion.

The declining excimer and monomer emissions that we found in both **6** and **7** were similar to the findings of Kim and coworkers.[13] They showed that once Pb^{2+}, Hg^{2+}, and Cu^{2+}ions were added into a pyrenyl-appended triazole-based calix[4]arene as a fluorescent sensor, a quenched fluorescence in both monomer and excimer emissions was observed. Recently, Chung and coworkers[18] described a bis-triazoles-chained pyrenes fluorescent chemosensor that had dual-mode recognition for Pb^{2+} and Cd^{2+} ions. In comparison, our results showed both **6** and **7** were unimode Hg^{2+}-selective fluorescent sensors. The differences could be attributed to the addition of the ribose-based moiety to the bis-triazoles-chained pyrenes.