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A new Fe^{3+} fluorescent chemosensor based on aggregation-induced emission

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ABSTRACT

A new tetraphenylethylene (TPE)-based sensor **M1** bearing double 2-methylpyridyl-2-methylthiophenylamino units linked with triazole moieties was reported. Both UV–vis and fluorescence spectroscopic studies demonstrated that **M1** was highly sensitive and selective toward Fe^{3+} over other metal ions in THF/H_2O solution based on the aggregation-induced emission quenching mechanism. The lowest detection limit of **M1** for Fe^{3+} is 0.7 μM. The detailed fluorescent titration study suggested that the binding stoichiometry of the **M1**–Fe^{3+} complex was 1:2, and the structure between **M1** and the Fe^{3+} complex was confirmed by the ^1H NMR titration.

Introduction

Over recent decades, the fluorescence-based detection of heavy and transition metal ions based on the has received increasing attention due to the importance of metal ions in the chemistry, biology, and environment due to its advantages of simplicity, high sensitivity, and selectivity.[1] Among the heavy and transition metal ions, Fe^{3+}, as a physiologically important metal ion, plays a catalytic role in chemical and biological processes such as oxygen metabolism and electron transfer, and both its deficiency and excess in the human body can induce a variety of diseases.[2–4] Up to now, only a few fluorescence probes for Fe^{3+} have been achieved.[5]

In 2001, Tang and co-workers first reported aggregation-induced emission (AIE)-active molecules.[6] AIE-active molecules display no emission in solution, but an intense emission when aggregated or in the solid state because of suppression of nonradiative deactivation associated with restriction of intramolecular rotations.[7,8] Based on the aggregation state-dependent fluorescence, many AIE-active molecules, such as tetraphenylethene (TPE) derivatives, can be used as an alternative sensing element through the introduction of functional groups into AIE molecules which favor new development of chemosensors for detecting metal cations, biomolecules, organic vapors, chiral molecules, and explosives.[9] Up to now, various fluorescent probes for Fe^{3+} have been achieved,[10] but the AIE-based fluorescent probes were very rare.[11] Herein, we report the design and synthesis of a new fluorescent chemosensor for the highly selective detection of Fe^{3+} using AIE-active tetraphenylethene (TPE) bearing pyridine and thiophene substituents based on click chemistry.

Recently, our group found that a new TPE derivative based on the click linkage of TPE core with multiple-pyridine substituents exhibited good AIE property of the highly selective response to Ag^+.[12] In addition, on the basis of the strong affinity between metal ions and sulfur, some fluorescent probes bearing thiophene groups have been designed and synthesized for the sufficient detection of the metal ions.[11b,13] The TPE core and thiophene units were introduced into the probe structure. With these in mind, we designed and synthesized a new fluorescence chemosensor **M1**. Compound **M1** is composed of two moieties, one is an AIE fluorophore, for which TPE platform is selected as the AIE signal transducer. The other moiety is the Fe^{3+}-response switch, for which 2-methylpyridyl-2-methylthiophenylamino unit is chosen as the modulator.

Results and discussion

The synthetic pathway of compound **M1** is outlined in Scheme 1. The target compound **M1** was synthesized from the substrates **1** and **2** through click reaction efficiently (Scheme 1).[12,14] The chemical structure of compound **M1** was characterized by spectroscopic and elemental analysis data.

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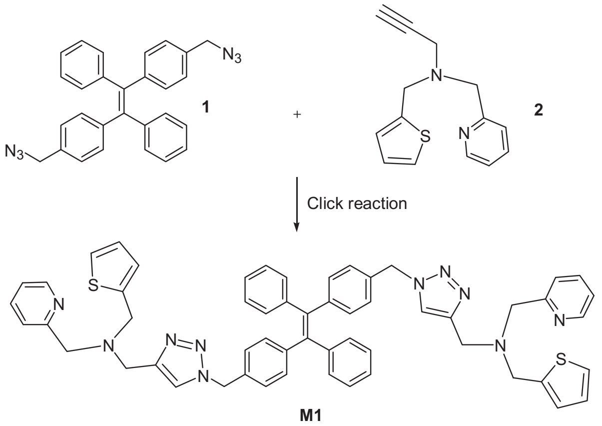

Scheme 1. Synthesis of Sensor **M1**.

Compound **M1** is soluble in common organic solvents such as acetonitrile, chloroform, ethyl ethanoate, and tetrahydrofuran (THF), but insoluble in water. We first investigated the AIE behavior of compound **M1** in aqueous THF with different THF/water ratios. As shown in Figure 1, when the water fraction in dilute THF solution is increased from 0% to 50%, compound **M1** shows almost no fluorescence as expected. However, its suspension in a THF–water mixture with a high water fraction is highly emissive when the water fraction is increased over 60%. Based on above AIE behavior of compound **M1**, the UV–vis and fluorescence experiments were carried out in THF/H_2O (1:2, v:v) aqueous solution. As shown in Figure S2 (Supplementary data), the UV–visible absorption titration of the Fe^{3+} ion was carried out using a solution of 10 μM of compound **M1** in THF/H_2O (1:2, v:v), which exhibited two absorption bands at 316 nm and 238 nm. The absorption spectral increasing of compound **M1** upon the addition of Fe^{3+} was observed. Meanwhile, compound **M1** shows two fluorescent emission peaks at 408 nm and 432 nm. Upon addition of 4 equiv of different metal ions respectively, the significant fluorescence decrease was detected only after the addition of Fe^{3+} which disturbed the aggregation of compound **M1** in THF/H_2O (1:2, v:v) solution through the coordination of Fe^{3+} ion with pyridine and thiophene units to free the intramolecular rotations of compound **M1**. The other two metal ions, Ag^+ and Cu^{2+}, cause a slight fluorescence quenching of compound **M1** (Fig. 2).

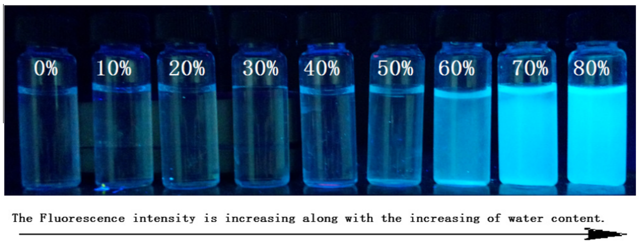

Figure 1. The aggregation-induced emission (AIE) effect (365 nm UV lamp) of **M1** in different ratios of THF and H_2O (THF/H_2O, v/v).

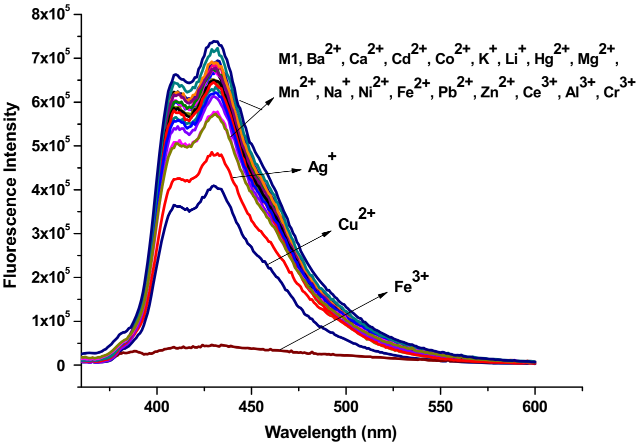

Figure 2. The fluorescence spectra of compound **M1** (10 μM) in THF/ H_2O (1:2, v/v) upon addition of different metal ions (40 μM, 4 equiv). All metal ions were added separately (λ_{em} = 431 nm, λ_{ex} = 342 nm).

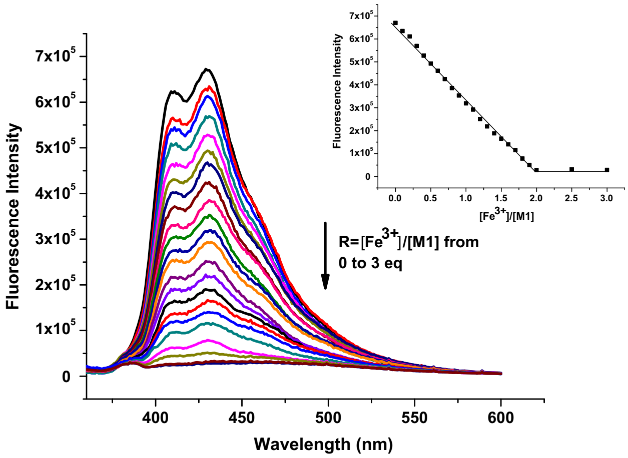

Figure 3. Fluorescence intensity of compound **M1** (10 μM) in THF/H_2O (1:2, v/v) in the presence of Fe^{3+} (0 to 30 μM, 0–3 equiv). Inset: plot of fluorescence intensity of compound **M1** toward the concentration of Fe^{3+} (λ_{em} = 431 nm, λ_{ex} = 342 nm).

The fluorescence spectra of compound **M1** upon titration with Fe^{3+} ion were recorded in the next experiment for the investigation of the AIE quenching behavior of Fe^{3+} ion in detail. As shown in Figure 3, the fluorescence of compound **M1** (10 μM) in THF/H_2O (1:2, v:v) at 408 and 432 nm was dramatically decreased with the virtually unchanged emission shift upon addition of Fe^{3+}. The changes of the emission intensities became constant and 95% of the quenched fluorescence of **M1** was observed eventually when the amount of Fe^{3+} added reached 2.0 equiv (20 μM), and there was a good linear relationship in this range (R^2 = 0.997). Moreover, the detection limit was measured to be 0.7 μM (Supplementary data Fig. S6).

For practical applicability, the effect of the pH on the fluorescence of **M1** was investigated in THF/H_2O (1:2, v:v). As shown in Figure 4, no change of the fluorescence emission of **M1** was observed between pH 2 and 11, suggesting that the compound **M1** is stable over a wide pH range. In addition, no obvious change of the fluorescence emission of **M1** upon the addition of 4 equiv of Fe^{3+} was observed in the same pH range, which shows that the compound **M1** is the potential fluorescent sensor for the detection of Fe^{3+}.

Then, a competition experiment was carried out by adding Fe^{3+} to the THF/H_2O (1:2, v:v) solution of **M1** in the presence of other metal ions, and the results are shown in Figure 5. The fluorescence response to the addition of these commonly coexistent ions (Ag^+, Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, K^+, Li^+, Na^+, Mg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Fe^{2+}, Zn^{2+}, and Hg^{2+}) was hardly affected by the presence of Fe^{3+} suggesting the exclusive sensitivity of **M1** toward Fe^{3+} rather than other transition-metal ions investigated. On the other hand, the higher selectivity of **M1** for Fe^{3+} over Fe^{2+} shows that this probe has metal and redox specificity. In addition, the anions such as Cl^-, Br^-, F^-, NO_3^-, ClO_4^- and SO_4^{2-} show almost no effect on the fluorescence quenching of compound **M1** (Supplementary data Fig. S7).