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Graphical Abstract

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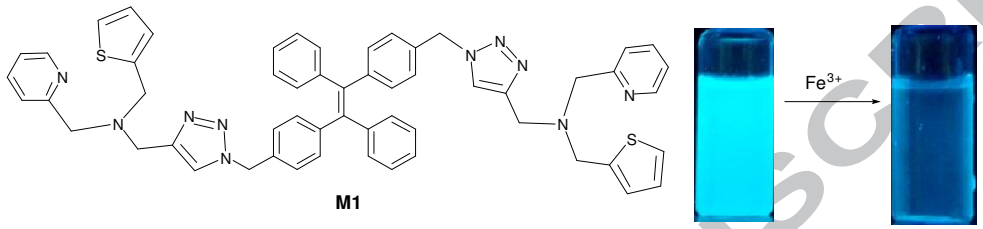

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A new Fe^{3+} fluorescent chemosensor based on aggregation-induced emission

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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 towards 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.

1. 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 duet 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.[2,3,4] 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.

2. 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.

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%.

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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 were 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).

The fluorescence spectra of compound **M1** upon titration with Fe^{3+} ion was recorded in the next experiment for the investigation of the AIE quenching behavior of Fe^{3+} ion in details. As shown in Figure 3, The fluorescence of compound **M1** (10 μM) in THF/H_2O (1:2, v:v) at 408 nm 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 detecting 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** towards 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 any effect on the fluorescence quenching of compound **M1** (Supplementary data Fig. S7).

Similar to other reported TPE-based fluorescent probes, the AIE quench response of probe **M1** toward Fe^{3+} is the result of the intermolecular coordination of probe **M1** with Fe^{3+} by its two chelators bearing pyridine and thiophene units, which have been proven to show strong affinity to Fe^{3+}.[10g-h,10k,10m,11b] The coordination will release the restriction for the intramolecular rotations of compound **M1** under aggregation state to display a remarkable fluorescence quenching. In order to quantify the stoichiometry of the complex of **M1** and Fe^{3+}, a Job's plot analysis was carried out, by keeping the sum of the initial concentration of Fe^{3+} ion and **1** at 20 μM, and changing the molar ratio of Fe^{3+} ion from 0.1 to 0.9. The fluorescence of **M1** in the absence (F_0) or presence (F_i) of Fe^{3+} ion was determined respectively. A plot of ΔF (F_0-F_i) versus the molar fraction of Fe^{3+} ion is provided in Figure 6. It shows that the ΔF value goes through a maximum at a molar fraction of about 0.67, exhibiting a 2:1 stoichiometry of the Fe^{3+} to **M1** in the complex. The equilibrium constant K was calculated to be 7.05×10^{15}, suggesting a good binding affinity of the probe **M1** to Fe^{3+} (Supplementary data Fig. S14).

To further elucidate the recognizing mechanism of compound **M1** for Fe^{3+} based on the structure of the **M1**-2Fe^{3+} complex, the ^{1}H NMR titration experiment was performed by the addition of $FeCl_3$ solution (in D_2O and from 0 to 0.4, 0.8, 1.6, and 2.0 mM respectively) to the solution of **M1** (0. 1 mM in THF-d_8). As shown in Figure 7, the signal of the H_a proton was gradually upfield shifted from 8.43 ppm to 8.20 ppm with increasing the amounts of Fe^{3+} (from 0 to 0.8 equiv). When the amounts of Fe^{3+} increased from 0.8 equiv to 2.0 equiv, the signal of the H_a proton were slightly downfield shifted from 8.20 ppm to 8.27 ppm. Similarly, the signal of the H_g proton was upfield shifted from 5.44 ppm to 5.34 ppm followed by downfield shifted from 5.34 ppm to 5.50 ppm. On the contrast, the signals of the H_c, H_d, and H_e protons were gradually downfield shifted with increasing the amounts of Fe^{3+} from 0 to 2.0 equiv. Meanwhile, the signals of the H_b and H_f protons were downfield shifted initially, and were then upfield shifted with the increasing the amounts of Fe^{3+}. All the signal variations of the protons suggested that the chemical circumstances of them have been changed due to the coordination between **M1** and Fe^{3+}. The facts of the changes of the signals illustrate that the N-atom on pyridine unit and the S-atom on thiophene unit bond to the metal ion. The chemical shift of proton in triazole unit in our previous reported AIE-based Ag^+ chemosensor exhibits downshift when the Ag^+ ion concentration was not more than 1 equiv, and the chemical shift of proton in triazole unit exhibits upshift when the Ag^+ ion concentration was more than 1 equiv.[12] In contrast, the chemical shift of proton in triazole unit in this Fe^{3+} chemosensor **M1** exhibits downshift followed by slight upshift. Based on these results, the coordination type of probe **M1** with Fe^{3+} was proposed in Scheme 2. Furthermore, the above AIE recognizing mechanism was confirmed employing EDTA as a much stronger chelating agent. As shown in Figure 8, the fluorescent intensity of **M1**-Fe^{3+} system can be recovered to the original value of **M1** in a THF/H_2O (v:v) mixture when treated with EDTA. This indicates that the fluorescence quenching of **M1** induced by the chelating Fe^{3+} is due to the formation of coordination complexes between **M1** and Fe^{3+} ions. Excess EDTA can snatch the Fe^{3+} ions from the chelators of **M1** and interrupt the interaction between the Fe^{3+} ions and the chelators of **M1** to form new more stable complexes with a much higher stability. Due to the much stronger complex binding between EDTA and Fe^{3+} ions, the **M1**-Fe^{3+} complex is destroyed, and the fluorescence of **M1** switches on in the aggregated form.

3. Conclusion

In conclusion, a new tetraphenylethylene (TPE)-based chemosensor **M1** bearing triazole, pyridine and thiophene motifs was designed and prepared successfully. Compound **M1** demonstrates a highly sensitive and selective sensing behavior for Fe^{3+} in THF/H_2O solution based on the AIE quenching mechanism. The experiment results including the lower detection limit (0.7 μM) indicate that compound **M1** can be promoted for a lot of practical applications in chemical, environmental and biological systems.

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Supplementary data

Supplementary material associated with this article can be found, in the online version, at doi:

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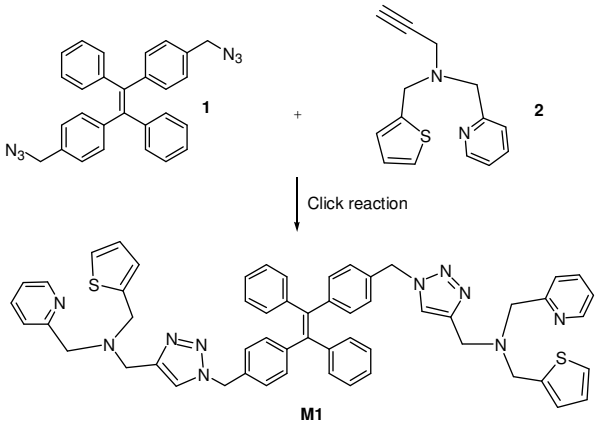


Scheme 1. Synthesis of Sensor **M1**

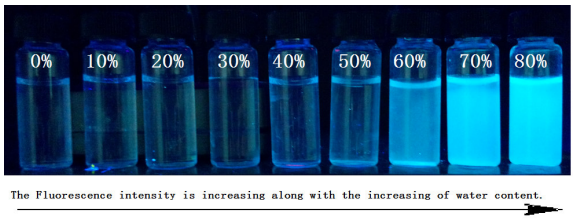


Figure 1. The aggregation-induced emission (AIE) effect (365 nm UV lamp) of **M1** in different ratios of THF and H_2O (THF/H_2O, v/v)

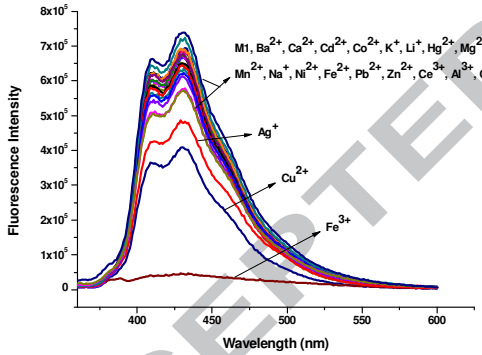


Figure 2. The Fluorescence spectra of compound **M1** (10 μM) in THF/ H_2O (1:2, v/v) upon addition of different metal ions (40 μM, 4 equiv). All metal ions were added separately (λ_{em} = 431 nm, λ_{ex} = 342 nm).

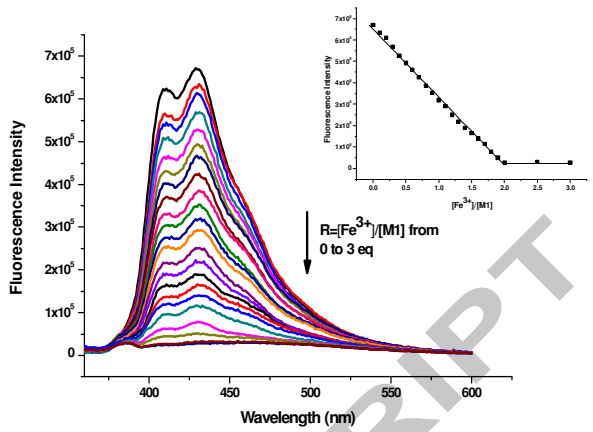


Figure 3. Fluorescence intensity of compound **M1** (10 μM) in THF/H_2O (1:2, v/v) in the presence of Fe^{3+} (0 to 30 μM, 0 to 3 equiv). Inset: plot of fluorescence intensity of compound **M1** towards the concentration of Fe^{3+} (λ_{em} = 431 nm, λ_{ex} = 342 nm).

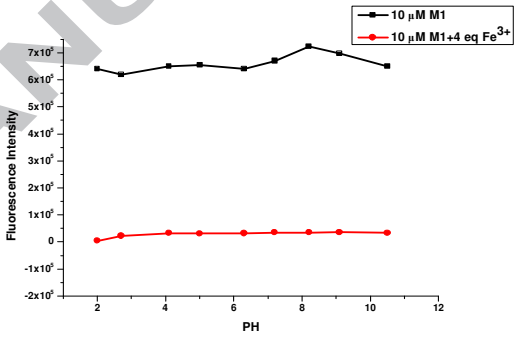


Figure 4. Fluorescence intensity (at 431 nm) of free **M1** (10 μM) and in the presence of 4 equiv Fe^{3+} in KOH/HNO_3 water solution with different pH conditions (λ_{em} = 431 nm, λ_{ex} = 342 nm).

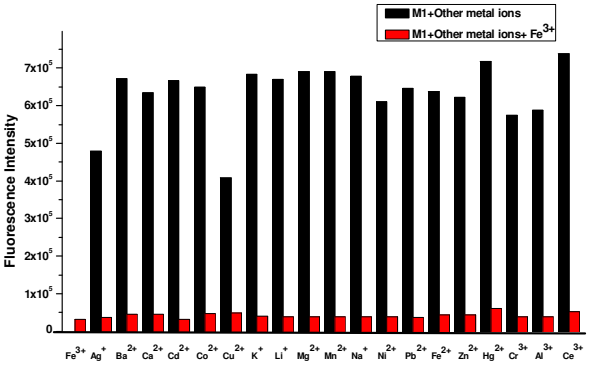


Figure 5. Fluorescence responses of **M1** (10 μM) upon addition of various metal ions (100 μM, 10 equiv) in the absence and presence of Fe^{3+} (40 μM, 4 equiv) in THF/H_2O (1:2, v/v) media. (Black bars: compound **M1** with other metals, red bars: compound **M1** with other metals and Fe^{3+} (λ_{em} = 431 nm, λ_{ex} = 342 nm).

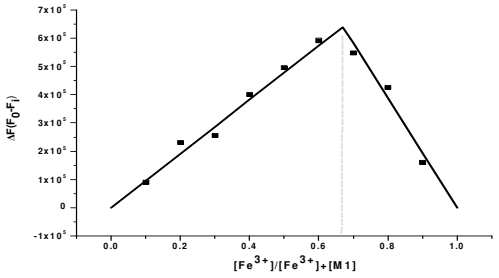
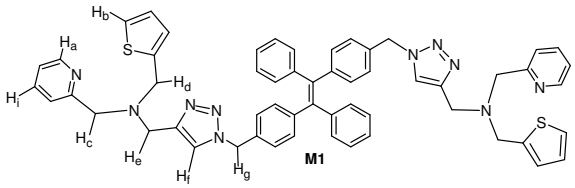


Figure 6. Job plot of compound **M1** with Fe^{3+} ([**M1**] + [Fe^{3+}] = 20 μM) in THF/H_2O (1:2, v/v). The ordinate △F = F_0-F_i represents the change of the Fluorescence intensity, while the abscissa represents the ratio of [Fe^{3+}] in [Fe^{3+}]+[**M1**] which represents the total concentration. (λ_{ex} = 342 nm, λ_{em} = 431 nm)



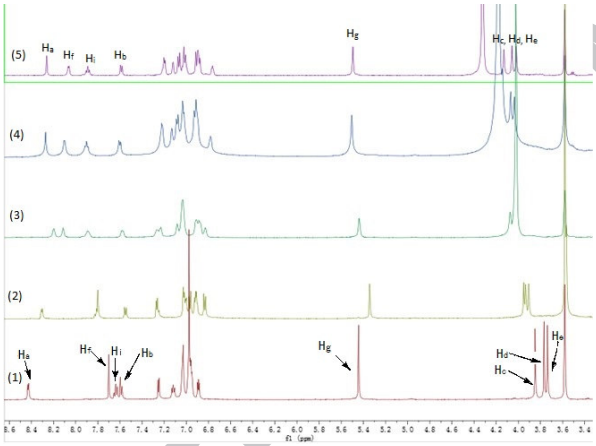
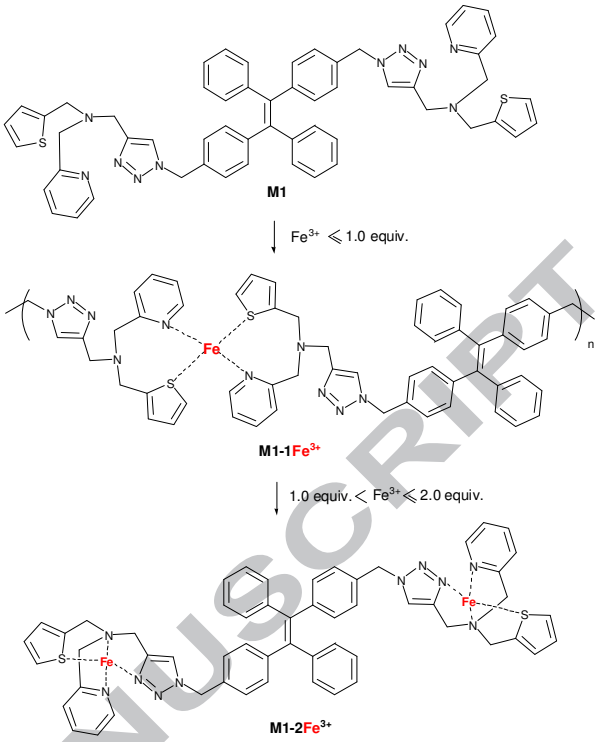


Figure 7. Partial ^{1}H NMR spectra (500 MHz) of compound **M1** (0.1 mM) in THF-d_8 in the presence of increasing amounts of Fe^{3+} (in D_2O): 0, 0.4, 0.8, 1.6, 2.0 equiv [from (1) to (5)].



Scheme 2. Proposed binding mode of **M1** with Fe^{3+}

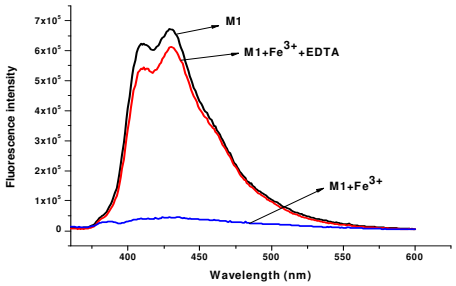
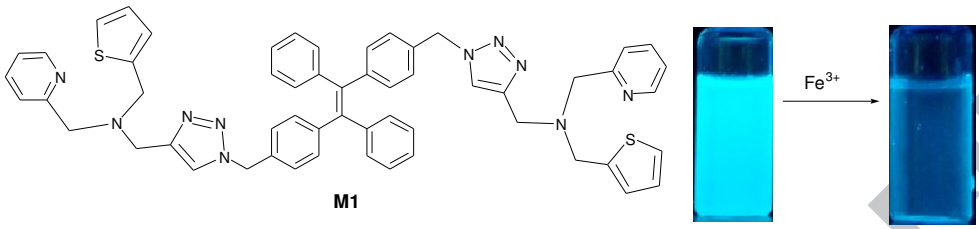


Figure 8. Fluorescence spectra of **M1** (10 μM), **M1**-Fe^{3+} mixture (Fe^{3+}, 40 μM, 4 equiv), and **M1**-Fe^{3+} mixture with addition of EDTA (EDTA, 60 μM, 4 equiv) in THF/H_2O (1:2, v/v) at room temperature. (λ_{ex} = 342 nm, λ_{em} = 431 nm)

Graphical Abstract

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

Jia-Hai Ye, Jian Liu, Zhenghua Wang, Yang Bai, Wenchao Zhang, Weijiang He



M1

Highlights

(1) A new fluorescent chemosensor for Fe^{3+} was developed.

(2) Detection of Fe^{3+} in aqueous solution (THF/H_2O) successfully based on aggregation-induced emission mechanism.

(3) High selectivity and sensitivity with low detection limitation (**0.7 μM**).

(4) The recognizing mechanism was investigated through fluorescence titration and ^1H NMR titration.