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PAPER

Imidazole-bearing tetraphenylethylene: fluorescent probe for metal ions based on AIE feature†

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With an aggregation-induced emission feature, a suspension of imidazole-bearing tetraphenylethylene in a tetrahydrofuran–water mixture with a high water fraction is highly emissive, and can be completely quenched by Fe^{3+} ions due to the coordination between imidazole moieties and the Fe^{3+} ion.

The development of artificial fluorescent receptors for the sensing and recognition of environmentally and biologically important ionic species, especially transition-metal ions, is currently of great interest, because their fluorescence-based sensing and recognition are highly sensitive, convenient, cost-effective, and easy to scale-up to a high-throughput screening format. The toxicity of certain metal ions has been a constant cause of environmental concern. Thirteen transition-metal ions, such as chromium, manganese, cobalt, copper, zinc, molybdenum, silver, mercury, cadmium, lead, iron, and nickel, are listed as "priority pollutants" by the Environmental Protection Agency.[1]

Recently, molecules with aggregation-induced emission (AIE) characteristics have been developed and have drawn much attention due to their enhanced emission in aggregate form or solid-state.[2] The AIE effect can significantly improve the fluorescence quantum yields of the molecules by up to three orders of magnitude, enhancing the photoluminescence intensity from faint luminophores into strong emitters.[3] Tetraphenylethylene (TPE), as one of most studied AIE luminophors, has already been demonstrated to show practical applications in OLEDs,[4] chemosensors,[5] and bioprobes,[6] owing to their facile preparation and easy functionalization.

Iron(III) is an important trace element for biological systems, which plays an essential role in oxygen uptake of heme, oxygen metabolism, and a cofactor in many enzymatic reactions. But the concentration of iron(III) must be moderate in mammals, both its insufficiency and excess can lead to a variety of diseases such as anemia, hepatic cirrhosis, and hereditary hemochromatosis.[7] Therefore, much attention has been drawn to the design of probes for the detection of iron ion based on conjugated polymers or organic dyes.[8] However, the detection sensitivity is strongly dependent on the organic solvent content in the detecting solution system. Most of them work well in a pure organic solvent medium or an aqueous solution containing at least 50% organic co-solvent. Furthermore, aggregation-caused fluorescence quenching of traditional dyes often takes place when dispersed in aqueous media or interacted with biomacromolecules, resulting in a drastically negative effect on efficiencies and sensitivities of biosensors or bioprobes.[9] These limitations, including organic co-solvent dependence and aggregation-caused quenching, to some extent, lower the sensitivity and restrict the application of sensors in biological systems and environmental determinations.

Imidazole has been widely employed in coordination chemistry and supramolecular chemistry, and is a good ligand for transition-metal ions.[10] In this work, an imidazole-bearing tetraphenylethylene derivative, **Im-TPE**, was prepared as a fluorescent probe for an iron ion assay based on the aggregation-induced emission effect.

The synthetic route to **Im-TPE** is shown in Scheme 1. Dihydroxy-tetraphenylethylene (**2**) was prepared from methoxybenzophenone through two steps that were a McMurry and demethylated reaction, respectively, according to a reported method.[6a] After being treated with 1,2-dibromoethane under basic conditions, dihydroxy-tetraphenylethylene was converted to TPE-based bromide (**3**), which was reacted with imidazole to afford the desired product **Im-TPE** efficiently.

Im-TPE is soluble in common organic solvents such as acetonitrile, chloroform, and tetrahydrofuran (THF), but insoluble in water. In dilute THF solution, **Im-TPE**, as expected, shows almost no luminescence. However, its suspension in a THF–water mixture with a high water fraction is highly emissive. As shown in Fig. 1, from the molecular solution in THF to the aggregate suspension in a THF–water mixture (1 : 99, v/v), the photoluminescence emission of **Im-TPE** at 471 nm significantly increases. Furthermore, **Im-TPE** shows a

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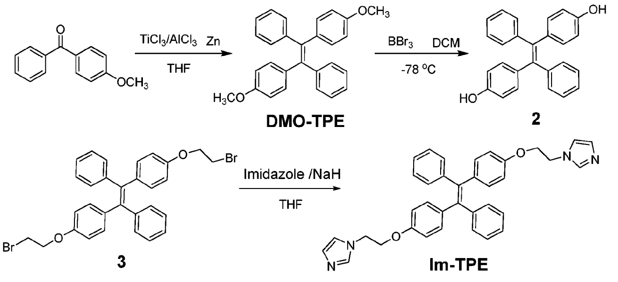
† Electronic supplementary information (ESI) available: Details of related fluorescence spectra and Hill plot of **Im-TPE**, mass spectrum, ^{1}H NMR, and ^{13}C NMR spectra of **Im-TPE** and TPE derivative **3**. See DOI: 10.1039/c1nj20122k



Scheme 1 Synthetic route to **Im-TPE**.

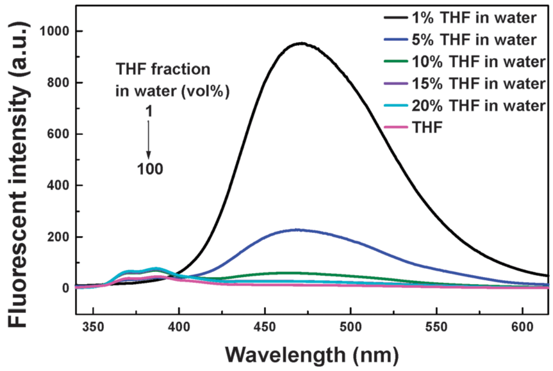


Fig. 1 Fluorescent spectra of **Im-TPE** (20 μM) in a THF–water mixture (excitation wavelength was 320 nm).

strong blue emission in solid-state. These data clearly indicate that **Im-TPE** exhibits a significant feature of aggregation-induced emission.

Fig. 2a shows the fluorescent spectra of **Im-TPE** in the presence of various metal ions (Ag^+, Cd^{2+}, Co^{2+}, Cu^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+}, Fe^{2+}, and Fe^{3+}) at the same concentration. The concentration of **Im-TPE** in a THF–water mixture with 99% water fraction was fixed at 20 μM, and the final concentration of metal ions was fixed at 50 μM. It can be seen that Cu^{2+}, Fe^{2+}, and Fe^{3+} lead to an efficient fluorescence quenching of **Im-TPE**. Especially, when treated with Fe^{3+}, nearly complete fluorescence quenching of **Im-TPE** was observed. The other metal ions such as Zn^{2+}, Cd^{2+}, Mn^{2+}, Ni^{2+}, and Co^{2+} cause a slight fluorescence quenching of **Im-TPE**. As a control study, dimethoxy-tetraphenylethylene (**DMO-TPE**) was also exposed to the same amount of Fe^{3+} under the same condition, and its fluorescence spectrum in the solution shows almost no change (see supporting information, Fig. S1†). Therefore, the corresponding changes of **Im-TPE** fluorescence spectra in the presence of different metal ions can be ascribed to the existence of imidazole groups. The distinct responsive behaviors of **Im-TPE** to various metal ions reveal the different coordination ability of transition-metal ions with imidazole receptors. It should be noted that the fluorescence intensity of **Im-TPE** has been enhanced *ca.* 10% by the Ag^+ ion compared with the intensity of the blank system. Such fluorescence enhancement observed for **Im-TPE** in the presence of Ag^+ is attributed to the coordination of imidazole moieties of **Im-TPE** with Ag^+ ions leading to formation of coordination complexes that may further aggregate due to the low solubility. A similar result was also reported for Ag^+-induced aggregation of adenine-functionalized TPE.[5] The photograph given in Fig. 2b clearly displays the emissive nature of **Im-TPE** affected by various metal ions in a THF–water mixture with a 99% water fraction under UV light illumination (365 nm).

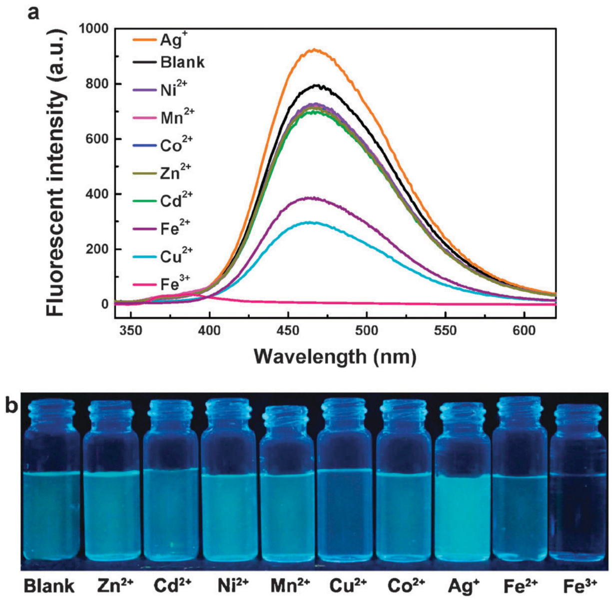


Fig. 2 (a) Fluorescent spectra of **Im-TPE** (20 μM) in the presence of various metal ions (50 μM) in THF–water (1 : 99, v/v); (b) the photograph displays the emissive nature of **Im-TPE** affected by various metal ions under UV light illumination (365 nm).

The competition experiment was also carried out by adding Fe^{3+} to the aqueous solutions of **Im-TPE** in the presence of another metal ion, shown in Fig. 3. The results indicate that the sensing of Fe^{3+} by **Im-TPE** is hardly affected by these commonly coexistent ions, which shows the fluorescence response of **Im-TPE** is selective towards Fe^{3+} rather than other

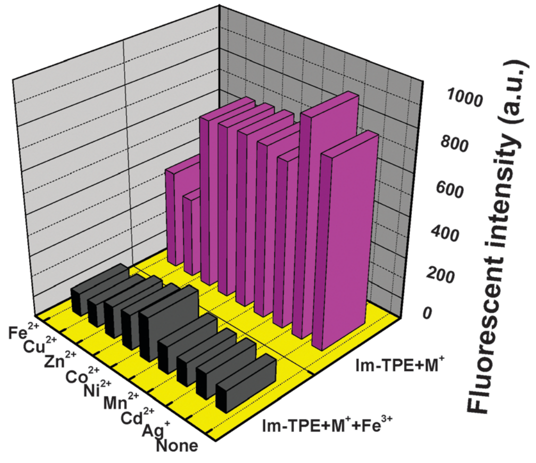


Fig. 3 Fluorescent response of **Im-TPE** (20 μM) with various other metal ions. Violet bars represent the addition of various metal ions (50 μM) to **Im-TPE** solution (20 μM), black bars represent subsequent addition of Fe^{3+} (50 μM) to the former solution. For all measurements, the excitation wavelength was set at 320 nm and the emission was monitored at 471 nm.

transition-metal ions investigated. In addition, the anions such as Cl^-, CH_3COO^-, NO_3^-, and SO_4^{2-} show a slight effect on the emission of **Im-TPE** (see supporting information, Fig. S2†), which can exclude disturbance from anions. In light of the data aforementioned, it can be confirmed that **Im-TPE** is a useful fluorogenic sensing material for selective detection of Fe^{3+} in the presence of other ions.

To study the quenching behavior of Fe^{3+} ion in details, we investigated the decrease in fluorescence intensity upon successive addition of aliquots of aqueous solution of Fe^{3+} ion to the diluted **Im-TPE** solution in a THF–water mixture with 99% water fraction. As shown in Fig. 4a, quenching of photoluminescence is observed at a very low level of Fe^{3+}, and the fluorescent intensity decreases rapidly upon the increase in the concentration of Fe^{3+}. At the very beginning, the Fe^{3+} ions of only 5 μM, which is only 25% of the **Im-TPE** concentration, cause the fluorescence emission of **Im-TPE** to quench to 70% of its original emission intensity. When the concentration of Fe^{3+} increases up to 30 μM, almost no luminescence is observed. The emission quenching is observed at a concentration of Fe^{3+} as low as 1.0 μM, which is not the lowest detecting concentration compared to the reported literature.[8] However, it is a promising example of the selective detection of Fe^{3+} with efficiently prepared **Im-TPE** in aqueous solution based on the AIE characteristics. As shown by the inset in Fig. 4a, the nonlinear curve of the Stern–Volmer plot indicates that the mechanism of the quenching process involves complexation rather than collisional deactivation in this case.[11]

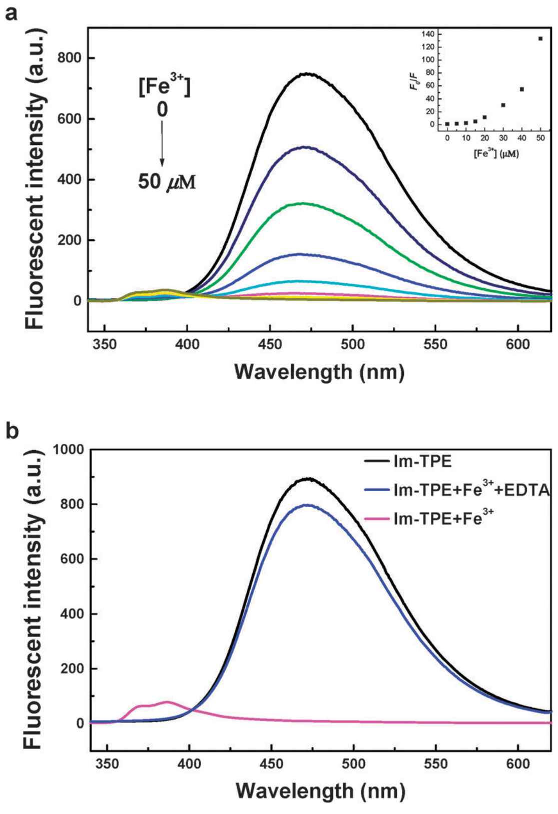


Fig. 4 (a) Fluorescence spectra and Stern–Volmer plot (inset) of **Im-TPE** (20 μM) in the absence and presence of Fe^{3+} ions at different concentrations in a THF–water mixture (1 : 99, v/v); (b) fluorescence spectra of **Im-TPE** (20 μM), **Im-TPE**–Fe^{3+} mixture, and **Im-TPE**–Fe^{3+} mixture (Fe^{3+}, 50 μM) with addition of EDTA (70 μM) in a THF–water mixture (1 : 99, v/v) at room temperature.

The possible quenching mechanism is proposed through experimental phenomenon. At first, no luminescence is observed when **Im-TPE** is dissolved in THF solution. Thanks to the AIE characteristics, strong emission is detected as **Im-TPE** is dispersed in a THF–water mixture with 99% water fraction owing to aggregate formation. The efficient fluorescence quenching is caused by successive addition of aliquots of Fe^{3+} ions to the diluted **Im-TPE** suspension in a THF–water mixture. Imidazole moiety is an excellent acceptor to Fe^{3+} and the suspension converted gradually into more water-soluble **Im-TPE**–Fe^{3+} complex. Fig. S4 displays the turbid **Im-TPE** suspension in a THF–water mixture with 99% water fraction, which turns clear when treated with Fe^{3+}.† Therefore, the aggregated **Im-TPE** is gradually disassembled, and the corresponding fluorescence intensity reduces significantly. We observed that the molar ratio of Fe^{3+} ions to the **Im-TPE** is about 1.0 when the fluorescence intensity approaches the minimum (see supporting information, Fig. S5†), where the aggregate is completely broken.[12]

The reduction in fluorescent intensity is used to obtain the constant in a Hill plot through $\log[(I - I_{\min})/(I_{\max} - I_{\min})]$ *versus* $\log[Fe^{3+}]$ of the emission data and yield a $\log K_a$ of 12.67 (see supporting information, Fig. S3†).[13] The result indicates that after being attached to the TPE, the imidazole moieties might efficiently chelate iron ions to form a more water-soluble nonfluorescent complex from the highly emissive **Im-TPE** aggregate form. Thus, the strong luminescence of TPE is quenched. As for a d^5 ion such as Fe^{3+}, the five electrons may present as two orbitals occupied by two pairs of electrons and one orbital having single occupancy. So it could form an inner-orbital complex for Fe^{3+}, which is more stable than the other imidazole–metal complexes.[14] Therefore, when treated with Fe^{3+}, nearly complete fluorescence quenching of **Im-TPE** is observed in aqueous solution, due to the disassembly of the aggregate suspension to the more water-soluble **Im-TPE**–Fe^{3+} complex. So **Im-TPE** can be utilized as a selective chemosensor to iron ion at low concentration.

In order to confirm the above mechanism, an additional experiment was conducted employing EDTA as a much stronger chelating agent. Fig. 4b shows that the fluorescent intensity of **Im-TPE**–Fe^{3+} system can be recovered to the original value of **Im-TPE** in a THF–water mixture when treated with EDTA. This indicates that the fluorescence quenching of **Im-TPE** induced by the chelating iron ion is due to the formation of coordination complexes between **Im-TPE** and iron ions. Excess EDTA can snatch the Fe^{3+} ions from the imidazole moieties and interrupt the interaction between the Fe^{3+} ions and the imidazole moieties to form new more stable complexes with a much higher stability constant ($\log K_a = 25.1$). Due to the much stronger complex binding between EDTA and Fe^{3+} ions, the more water-soluble **Im-TPE**–Fe^{3+} complex is destroyed, and the fluorescence of **Im-TPE** switches on in the aggregate form. The absorbance spectrum also confirms that the new chelated complex was formed by **Im-TPE** and Fe^{3+} ions. The broad and flat absorbance peaks of **Im-TPE** at 325 and 253 nm indicate

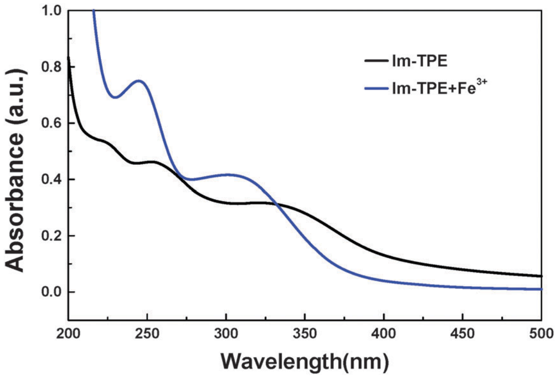


Fig. 5 Absorbance spectra of **Im-TPE** (20 μM) in the absence and presence of Fe^{3+} in a THF–water (1 : 99, v/v) mixture.

the aggregate state in the aqueous solution. After adding Fe^{3+} into **Im-TPE** suspension, the absorbance peaks get sharper and narrower, and are blue-shifted to 304 and 245 nm, respectively (Fig. 5). It can be inferred that the aggregated **Im-TPE** is disassembled due to formation of the more water-soluble **Im-TPE**–Fe^{3+} complex, which is also an evidence for the proposed quenching mechanism.

In summary, imidazole-bearing tetraphenylethylene, **Im-TPE**, is efficiently prepared and is highly emissive in a THF–water mixture with a high water fraction (99%) due to the aggregation-induced emission feature of tetraphenylethylene moieties. When exposed to Fe^{3+} ions (50 μM), nearly complete quenching of the **Im-TPE** fluorescence is observed. Further treatment of **Im-TPE**–Fe^{3+} mixture with EDTA can make the fluorescence emission of resulting solution recover almost to the original value, which proves that the fluorescence quenching of **Im-TPE** induced by the formation of more water-soluble coordinated complexes between **Im-TPE** and Fe^{3+} ions. As a fluorescent probe for iron ion assay in 99% water solution, owing to its sensitivity and selectivity, **Im-TPE** will have potential applications in biosensing and environmental analysis.

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Materials and instrumentations

All chemical reagents were commercially available and used as received unless otherwise stated. Deionized water was purified by a Millipore purification system (Milli-Q water). THF was dried over sodium and distilled under an atmosphere of dry nitrogen.

The ^1H and ^{13}C NMR spectroscopy was performed by a Bruker DMX400 NMR spectrometer using deuterated chloroform as solvent. UV-visible spectra were obtained using a Perkin-Elmer Lamda 950 UV-vis-NIR spectrophotometer and quartz cells with 1 cm path length. The fluorescence spectra were recorded by Perkin-Elmer LS55 luminescence spectrometer in a conventional cell with 1 cm path length. Mass spectrum was obtained using Fennigan LCQ Deca XP MAX liquid chromatography-mass spectrometry (LC-MS).

Experimental section

Synthesis of TPE derivative 3

To a mixture of TPE **2** (2.3 g, 6.3 mmol) and potassium carbonate (7.09 g, 51.3 mmol) in acetone (20 mL) was added 1,2-dibromoethane (4.5 mL, 51.9 mmol). The mixture was refluxed under stirring overnight. The reaction mixture was cooled to room temperature and filtered. After evaporation of the filtrate, the crude product was purified by a silica gel column using petroleum ether and ethyl acetate (30 : 1) as eluent to give compound **3** as a white solid in 68% yield (2.4 g). ^1H NMR (400 MHz, $CDCl_3$): δ 7.12–7.07 (m, 6H), 7.04–6.99 (m, 4H), 6.93 (dd, J = 8.8, 12 Hz, 4H), 6.64 (dd, J = 8.8, 13.2 Hz, 4H), 4.21 (m, 4H), 3.60 (dd, J = 6.3, 13.8 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.6, 144.1, 139.9, 137.2, 131.5, 127.8, 114.0, 67.8, 58.6, 29.3.

Synthesis of Im-TPE

A solution of imidazole (26 mg, 0.382 mmol) in anhydrous THF was added to a stirred suspension of sodium hydride (16 mg, 0.667 mmol) at room temperature. The mixture was stirred for 1 h and then a solution of **3** (90 mg, 0.156 mmol) and tetrabutylammonium iodide (56 mg) in THF was added. The mixture was stirred overnight at room temperature. The reaction mixture was diluted with water (15 mL) and extracted twice by ethyl acetate (50 mL). The combined organic layer was dried with anhydrous sodium sulphate and then concentrated. Silica gel chromatography (petroleum ether–ethyl acetate, 20 : 1) afforded the product as a light yellow solid with 65% yield (16.2 mg). Mp.: 145–147 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.66 (s, 2H), 7.10 (m, 8H), 7.01 (m, 6H), 6.98 (d, J = 8.72 Hz, 4H), 6.58 (d, J = 8.72 Hz, 4H), 4.30 (t, J = 5.12 Hz, 4H), 4.14 (t, J = 5.2 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.4, 144.1, 139.8, 137.6, 137.3, 132.7, 131.4, 129.1, 127.9, 126.5, 119.7, 113.7, 67.1, 46.7. FTIR (KBr) 3035, 2932, 2875, 1607, 1509, 1464, 1244, 817, 759, 699 cm^{-1}. ESI(+)-MS: calcd for $C_{36}H_{32}N_4O_2$: 552.6 [M]; found 553.4 $[M+H]^+$.

Interference experiment of Im-TPE with different metal ions

To a solution of **Im-TPE** in a THF–water mixture with 99% water fraction was added the solution of various metal ions in the same condition. The final concentration of **Im-TPE** was fixed at 20 μM, and the final concentration for the metal ions was fixed at 50 μM. After addition of the metal ion, the sample was allowed to incubate at room temperature for 30 min prior to recording a spectrum. Then, a Fe^{3+} ion solution (50 μM) was added to the previous solution and incubated at room temperature for 30 min to record another spectrum. The excitation wavelength was fixed at 320 nm and the emission was monitored at 471 nm.

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