A pyridinyl-functionalized tetraphenylethylene (Py-TPE) was synthesized and it demonstrated colorimetric and ratiometric fluorescent responses to trivalent metal cations (M3+, M = Cr, Fe, Al) over a variety of monovalent and divalent metal cations.

Exploring fluorescent chemosensors for trivalent metal cations (M3+) is an important research subject. On the one hand, fluorescent techniques offer the feasibility of fast, facile and highly sensitive detection of target analytes. On the other hand, M3+ ions have their own biological significance and environmental importance. For example, Cr3+ is a necessary trace element in human nutrition. Overdose of Cr3+ negatively affects cellular structure and function and causes disturbance in glucose levels and lipid metabolism, while a deficiency of Cr3+ in humans can cause diabetes and cardiovascular disease. Meanwhile, industrial runoff of Cr3+ may lead to detrimental pollution. As the third most abundant metal in the Earth’s crust, Al3+ is also one of the common species of metal cations. It is common sense that increasing free Al3+ due to acidic rain and human activities in the environment and surface water is detrimental to growing plants. And in recent years, it has been recognized that excessive intake of Al3+ leads to a wide range of diseases, such as Alzheimer’s disease and osteoporosis. As to Fe3+, its vital roles in a variety of cell functions have been summarized in tutorial reviews.

There have been research efforts to develop luminescence turn-on and/or ratiometric sensors based on available fluorogens such as rhodamine, fluorescein, BODIPY, and cyclometalated Ir(n) complex ([Ir(dfppy)2phen]). The sensing mechanism depends on the fluorogen’s structure and the situation in which the fluorogen is used. For instance, Lu et al. reported a highly selective and sensitive fluorescent turn-on chemosensor for Al3+ based on a photoinduced electron transfer (PET) approach. Li and colleagues demonstrated that a dyad containing a rhodamine and a naphthalimide moiety could be used as a Cr3+-selective fluorescent probe for monitoring Cr3+ in living cells with a ratiometric fluorescent method. The working mechanism is ascribed to fluorescence resonance energy transfer (FRET) from 1,8-naphthalimide to rhodamine. Dong and colleagues recently reported a fluorescent turn-on chemosensor for the selective detection of Al3+ based on an aggregation-induced emission (AIE) mechanism. AIE drives at a unique fluorescent behavior of some fluorogens that emit very weakly in dilute solution but become highly emissive when their molecules form aggregates or they are frozen in solid matrices.

The complexity of carboxylic groups on the pentaphenylpyrrole moiety and Al3+ results in molecular aggregation. More recently, Barba-Bon et al. described a highly efficient fluorescent probe for trivalent cations. The fluorescence (FL) turn-on was realized via the formation of 1 : 1 or 2 : 1 ligand–metal complexes.

Herein, we demonstrate a different method for the fluorescent sensing of M3+ ions (M = Cr, Fe and Al) by using a pyridinyl-functionalized tetraphenylethene (TPE) fluorogen. The chemical structure of the target compound (Py-TPE) and its synthetic route are displayed in Scheme 1, the experimental details are described in the ESL. The resultant was characterized by 1H-NMR, 13C-NMR, high-resolution mass spectrometry, elemental analysis and satisfactory results were obtained (ESI† and Fig. S1, S2 and S3). Our original intention of acquiring Py-TPE was to make use of the AIE properties of the TPE and the complexation ability of the pyridine moieties, because TPE is a representative AIE-active fluorogen and widely used as a converter to turn classical
The detection of $\text{Zn}^{2+}$ in Py-TPE ethanol solution. This result is out of our expectation. Because we have reckoned that $\text{Zn}^{2+}$ has a strong affinity to the pyridinyl group and the derived complex has low solubility and readily precipitates in the solution, then the aggregates give rise to strong FL. To check whether the unexpected result is observed by chance or is a general phenomenon, we tried different metal cations in three categories. (i) Metal cations in the same period as $\text{Zn}^{2+}$ in the periodic table of elements, including $\text{Cr}^{3+}$, $\text{Mn}^{2+}$, $\text{Fe}^{2+}/\text{Fe}^{3+}$, $\text{Co}^{2+}$, $\text{Ni}^{2+}$, and $\text{Cu}^{2+}$. (ii) Some hazardous heavy metal ions such as $\text{Pb}^{2+}$, $\text{Hg}^{2+}$ and $\text{Ag}^{+}$. (iii) A few metal cations in the IA, IIA and IIIA groups such as $\text{Na}^{+}$, $\text{K}^{+}$, $\text{Ca}^{2+}$, $\text{Mg}^{2+}$, and $\text{Al}^{3+}$. The results are displayed in Fig. 1. Surveying these data, two characteristics can be found. The first is that all of the trivalent cations showed positive fluorescent responses to the fluorescent probe, as quantitatively and visually showed in Fig. 1. Surveying these data, two characteristics can be found. The first is that all of the trivalent cations showed positive fluorescent responses to the fluorescent probe, as quantitatively and visually revealed by Fig. 1A and B, respectively. The second is that the emission colour changes from blue of Py-TPE to red when enough $\text{M}^{3+}$ aqueous solution is added into the Py-TPE ethanol solution (Fig. 1C). In all of the tested $\text{M}^{-}$ and $\text{M}^{2+}$ ions, only $\text{Hg}^{2+}$ shows a positive fluorescent response to Py-TPE. As revealed by the spectra and image in Fig. S5 (ESI†), orange fluorescence (peak at 597 nm) can be observed. Though $\text{Hg}^{2+}$ can also induce a change in emission feature, it is easy to recognize $\text{Hg}^{2+}$ from $\text{M}^{3+}$ ions by the difference in emission colour (orange for $\text{Hg}^{2+}$ and red for $\text{M}^{3+}$ ions).

The first characteristic suggests that fluorescent response relates to the ionic valence rather than to the kind of cation. Some $\text{M}^{3+}$ ions that have higher capacity for coordinating with the pyridine moiety (i.e. $\text{Zn}^{2+}$, $\text{Co}^{2+}$, and $\text{Cu}^{2+}$) are regardless to the existence of Py-TPE and show no FL change. While the $\text{M}^{3+}$ ions demonstrate evident fluorescent responses though it is well-known that pyridine is not a proper ligand to $\text{Cr}^{3+}$, $\text{Fe}^{3+}$ or $\text{Al}^{3+}$. The second characteristic implies that the red emission may come from new fluorescent species other than Py-TPE aggregates, otherwise blue emission should be observed (see Fig. S4, ESI†). The fact that Py-TPE has not formed aggregates is also confirmed by the photographs of the mixtures taken in daylight, which show no precipitates in the solutions.

To gain a better understanding of the impact of $\text{M}^{3+}$ on the fluorescent behaviour of Py-TPE, $\text{Cr}^{3+}$ was used as a representative (named as $\text{Cr}^{3+}$@Py-TPE system) and the FL changes of Py-TPE with different concentrations of $\text{Cr}^{3+}$ ([Cr$^{3+}$]) were monitored (Fig. 2). Without $\text{Cr}^{3+}$, Py-TPE itself emits weak blue FL in ethanol solution with a maximum at 488 nm. When $\text{Cr}^{3+}$ is introduced into the solution, the blue emission band is decreased. Meanwhile, a new red emission band with a peak at 630 nm grows as [Cr$^{3+}$] increases. This red band begins to be visually observed at a [Cr$^{3+}$] of 6 μM and becomes dominant when [Cr$^{3+}$] is higher than 20 μM. These results indicate that Py-TPE has a higher $\text{Cr}^{3+}$ cation sensitivity (as low as 6 μM) over the reported $\text{Cr}^{3+}$ fluorescent probes based on chelating, PET and FRET mechanisms. The plot of $I_{488}/I_{630}$ vs. [Cr$^{3+}$] and the FL images of the mixtures shown in Fig. 2B and the inset provide visual and clear information of the colorimetric fluorescent detection of $\text{Cr}^{3+}$ using Py-TPE as a fluorescent probe. Similar results were monitored in the cases of $\text{Fe}^{3+}$ and $\text{Al}^{3+}$ (Fig. S6 and S7, ESI†). It is noticeable that there is an isosbestic point at 535 nm in Fig. 2A and similar points are also observed for the systems of $\text{Fe}^{3+}$@Py-TPE and $\text{Al}^{3+}$@Py-TPE (Fig. S6 and S7, ESI†). The existence of an isosbestic point further verifies that the red emission originates from distinct species from Py-TPE. The red-emission species cannot be complexes of $\text{M}^{3+}$($\text{Py}$-TPE)$_x$, on the one hand, $\text{Cr}^{3+}$($\text{Py}$-TPE)$_x$, $\text{Fe}^{3+}$($\text{Py}$-TPE)$_x$, and $\text{Al}^{3+}$($\text{Py}$-TPE)$_x$ should give different FL features due to the different electronic structures of the central cations. On the other hand, $\text{M}^{3+}$($\text{Py}$-TPE)$_x$ would precipitate, because the coordination of the pyridine moiety with $\text{M}^{3+}$ bestows the complex with a
The hydrophobic aromatic shell that makes the molecule hardly soluble in water–ethanol mixtures. However, the experimental results show that Cr\(^{3+}\)@Py-TPE, Fe\(^{3+}\)@Py-TPE and Al\(^{3+}\)@Py-TPE exhibit identical fluorescent behaviour and no precipitates have been observed for the three systems (Fig. 2B, Fig. S6 and S7, ESI†). Furthermore, the absorption spectra of Cr\(^{3+}\)@Py-TPE, Fe\(^{3+}\)@Py-TPE and Al\(^{3+}\)@Py-TPE systems all show evidently red-shifted absorption bands as compared to Py-TPE (Fig. S8 to S11, ESI†). These results indicate that the addition of M\(^{3+}\) to Py-TPE ethanol solution must have triggered the formation of new species in the mixture.

We next turned our attention to the pyridinyl moiety on Py-TPE which is a typical proton acceptor. Since water–ethanol mixture was used as the detection medium, it is possible to capture protons. Moreover, checking the database of \(K_{sp}\) (the constant of solubility product) of M(OH)\(_n\) (\(n = 1, 2, \) and 3 for M\(^+\), M\(^{2+}\), and M\(^{3+}\) respectively), we found that Fe(OH)\(_3\), Al(OH)\(_3\) and Cr(OH)\(_3\) are the smallest three in all of our tested metal cations.\(^{13}\) Meanwhile, the comparison to Py-TPE (Fig. S8 to S11, ESI†). The results indicate that M\(^{3+}\) is intensively hydrolyzed in water according to the master equation M\(^{3+}\) + \(x\)H\(_2\)O \(\leftrightarrow\) M(OH)\(_x\)M\(^{3+}\) + \(x\)H\(_3\)O\(^+\). Thus the addition of M\(^{3+}\) aqueous solution into Py-TPE ethanol solution is equivalent to protonation of Py-TPE.

Following this concept, we investigated the influence of protons on the FL behavior of Py-TPE. As shown in Fig. 3, on adding trifluoroacetic acid (TFA) into Py-TPE ethanol solution, the FL features gradually change. The red emission peak at 630 nm manifests in the spectra at a TFA concentration ([TFA]) of 4 \(\mu\)M. This red band becomes predominant when [TFA] is equal to and/or higher than 8 \(\mu\)M. The blue emission of Py-TPE (peak at 488 nm) vanishes when [TFA] is equal to or higher than 40 \(\mu\)M. The proton-induced changes in FL intensity and colour are demonstrated by the plot of \(I_{630}/I_{488}\) versus [TFA] and the images in the inset of Fig. 3B. In addition, there exists an isosbestic point at 535 nm in Fig. 3A, which indicates that the blue and red emission bands are ascribed to Py-TPE and protonated Py-TPE species, respectively (inset of Fig. 3B, Fig. S12, ESI†). Theoretical calculations suggest that the protonated Py-TPE, as compared to Py-TPE, has an extended conjugation and a narrowed energy gap (Fig. S13, ESI†). Thus the protonated species can emit red FL. The remarkable homology of the fluorescent behaviour observed for H\(^{+}\)@Py-TPE and M\(^{3+}\)@Py-TPE (M = Cr, Fe, Al) indicates that the colorimetric and ratiometric responses of Py-TPE to M\(^{3+}\) come intrinsically from a proton-binding-induced fluorescence change.

In summary, pyridinyl-functionalized TPE (Py-TPE) has been synthesized and displays weak blue FL in solution. When various mono-, di- and trivalent metal cations were added into the Py-TPE ethanol solution, only Fe\(^{3+}\), Cr\(^{3+}\) and Al\(^{3+}\) can alter the emission feature from weak blue to strong red. By analyzing the similarity between the fluorescent responses of Py-TPE to Fe\(^{3+}\), Cr\(^{3+}\) and Al\(^{3+}\) and comparing the \(K_{sp}\) values of M(OH)\(_n\), for all the measured metal cations, we deduced that the red emission band originates from protonated Py-TPE. This deduction has been validated by both a comparative study of the fluorescent responses of Py-TPE to TFA in different concentrations and theoretical predictions. It is concluded that the differentiated FL response of Py-TPE to M\(^{3+}\) over other tested M\(^{2+}\) and M\(^+\) ions depends on the higher hydrolyzing ability of the M\(^{3+}\), which releases more protons in the water–ethanol mixture. This fluorescent detection of trivalent cations is achieved by a mechanism distinct from literature reported ones. The colorimetric (blue to red) and ratiometric \(I_{630}/I_{488}\) characteristics of this kind of fluorescent probe have their own advantages. In addition, the emission maxima at 630 and 488 nm perfectly match with red and blue laser sources. This colorimetric and ratiometric FL probe may find promising applications as an active element of chemo- and biosensors.

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Notes and references

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13. At 25 °C, for Al(OH)\(_3\), Cr(OH)\(_3\), and Fe(OH)\(_3\), \(K_{sp} = 4.6 \times 10^{-33}\), 1.0 \(\times 10^{-31}\), and 3.0 \(\times 10^{-39}\), respectively.