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RESEARCH ARTICLE

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Fluorogenic Zn(II) and Chromogenic Fe(II) Sensors Based on Terpyridine-Substituted Tetraphenylethenes with Aggregation-Induced Emission Characteristics

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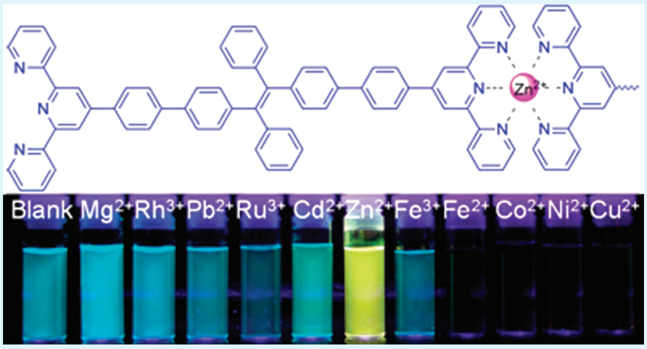
Supporting Information

ABSTRACT: Terpyridine-containing tetraphenylethenes (TPEs) are synthesized and their optical and metal sensing properties are investigated. They are practically nonluminescent in the solution state but become highly emissive as nanoparticle suspensions in poor solvents or thin films in the solid state, demonstrating a novel phenomenon of aggregation-induced emission (AIE). The emission of the nanoaggregates of TPEs is pH-sensitive: it is decreased and eventually quenched upon protonation of their terpyridine units because of their AIE nature. The TPEs can work as "turn-off" fluorescent chemosensors for metal ions and display different fluorescence responses to various metal ions. A characteristic red shift in the emission spectra is observed in the presence of Zn^{2+}, which facilitates the discrimination of Zn^{2+} from other metal ions. Because of the metal-to-ligand-charge-transfer process, terpyridine-substituted TPEs display an obvious magenta color upon selectively binding with Fe^{2+}, allowing a rapid identification of Fe^{2+} in the aqueous media by naked eyes.



KEYWORDS: Zn(II) sensor, Fe(II) sensor, aggregation-induced emission, terpyridine, fluorescence detection

INTRODUCTION

Zinc is an essential trace element necessary for plants, animals, and microorganisms.[1] It is the second most abundant transition metal in the human body after iron. Zinc is one of the most important cations in catalytic centers and structural cofactors of many enzymes and metalloproteins.[2] It is an essential factor in many biological processes such as the metabolism of DNA and RNA, signal transduction, and gene expression, as well as the pathological processes in many diseases including Alzheimer's disease, epilepsy, and ischemic stroke.[3,4] In blood plasma, zinc is bound to and transported by albumin and transferrin. Since transferrin also transports iron, excessive amount of zinc will result in insufficient absorption of iron.[5] Although most zinc ions are tightly bound to enzymes and proteins, the physiological roles of free zinc pools in certain tissues await to be explored.[6] Unlike other biological transition metal ions such as Fe^{2+} and Cu^{2+}, Zn^{2+} is spectroscopically and magnetically silent because of its d^{10} electron configuration. As a result, sensitive and noninvasive fluorescence-based techniques stand out as a method of choice for zinc analysis and imaging.[3,7]

Conventional organic luminophors enjoy high fluorescence in the dilute solutions but suffer from the notorious effect of aggregation-caused quenching in the condensed phase.[8] When dispersed in aqueous media or fabricated into solid film, the fluorescence of conventional luminophors is often weakened or even quenched, which greatly limits their real-world applications. Our group has recently observed an exactly opposite effect: nonemissive molecules in the solution state are induced to emit by aggregate formation. We thus coined "aggregation-induced emission" (AIE) for this novel phenomenon.[9] Restriction of intramolecular torsional/rotational motions is identified as a main cause for the AIE effect. Tetraphenylethene (TPE) is an archetypal AIE luminogens.[10] Through proper molecular engineering endeavor, TPEs are not only excellent emitters for the fabrication of efficient light-emitting diodes but also sensitive probes for the detection and visualization of biomolecules.[11−13] To endow TPE

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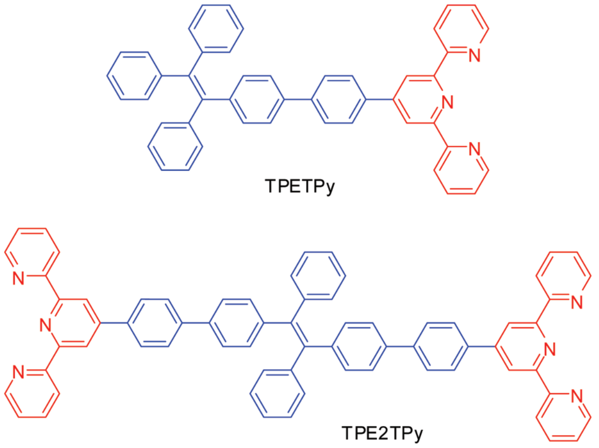
with metal chelating ability, in this study, we have functionalized the TPE core with terpyridine moiety, because of its strong and directed metal coordination capacity,[14] and investigated their photophysical properties and potential applications as metal ion sensors.

Terpyridine-containing TPEs, i.e., TPETPy and TPE2TPy, are designed and synthesized (Chart 1). Being insoluble in the aqueous media, the terpyridine-containing TPEs form nanoaggregates and emit strong greenish blue light, thanks to the AIE characteristics of the TPE core. The emission can be gradually decreased and eventually quenched upon protonation. When exposed to different metal ions, the fluorescence of these nanoaggregates is quenched/enhanced and/or spectral-shifted. Among a variety of these ions, only can Zn^{2+} alter the emission color to yellow effectively, demonstrating their promising application as zinc sensors. Owing to metal-to-ligand-charge-transfer, terpyridine-containing TPEs experience color change selectively in the presence of Fe^{2+}, which allows the discrimination of Fe^{2+} from other metal ions by naked eyes.

RESULTS AND DISCUSSION

Dye Synthesis. Terpyridine-containing TPEs 1-[4′-(4′-2,2′:6′,2″-terpyridyl)-biphenyl-4-yl]-1,2,2-triphenylethene (TPETPy) and 1,2-bis[4′-(4′-2,2′:6′,2″-terpyridyl)-biphenyl-4-yl]-1,2-diphenylethene (TPE2TPy) were prepared according to the synthetic routes shown in Scheme S1 in Supporting Information. 4′-(4-Bromophenyl)-2,2′:6′,2″-terpyridine was synthesized under a benign reaction condition using poly(ethylene glycol) as medium.[15] Suzuki coupling of 4′-(4-bromophenyl)-2,2′:6′,2″-terpyridine with 4-(1,2,2-triphenylvinyl)phenylboronic acid and 4,4′-(1,2-diphenylethene-1,2-diyl) bis(1,4-phenylene)diboronic acid generated TPETPy and TPE2TPy, respectively. The reaction intermediates and final products were fully characterized by spectroscopic methods from which satisfactory analysis data were obtained. Both TPETPy and TPE2TPy are soluble in acetonitrile, THF, and dimethylsulfoxide, slightly soluble in ethanol and methanol, and completely insoluble in water.

Chart 1. Chemical Structures of Terpyridine-Based TPE Derivatives



Aggregation-Induced Emission. TPETPy and TPE2TPy are practically nonluminescent when molecularly dissolved in good solvents. Addition of poor solvents into their solutions drastically boosts their light emissions. A dilute THF solution of TPETPy, for example, emits faintly at ~400 nm when photoexcited at 350 nm (Figure 1A). In THF/water mixture with 99 vol% of water, the resultant mixture shows an intense fluorescence spectrum with a peak at 484 nm under the same measurement condition.

As water is a poor solvent of TPETPy, its molecules must aggregate in the aqueous mixtures with high water fractions.[9] The mixture is transparent and homogeneous, suggesting that the dye aggregates suspended in the mixture are nanosized. Particle size analysis by dynamic light scattering (DLS) reveals the existence of particles with average size of ca. 100 nm in the solvent mixtures with 99% water (see Figure S1 in Supporting Information), confirming that the TPE molecules have indeed aggregated into nanoparticles in the mixed solvent. TPETPy is therefore induced to emit light by aggregate formation; in other words, it is AIE active. In the dilute THF solution, the phenyl rings of the TPE core can rotate freely against the central olefinic double bond, which nonradiatively deactivates the excited species and renders the dye nonemissive. The intramolecular motions are restricted in the nanoaggregates in the THF/water mixture with high water fraction, which block the nonradiative decay channels and make dye molecules highly luminescent.

To have a quantitative picture, we estimated the quantum yield (Φ_F) values of TPEs in THF and THF/water mixtures, using quinine sulfate as standard. The Φ_F value of TPETPy in pure

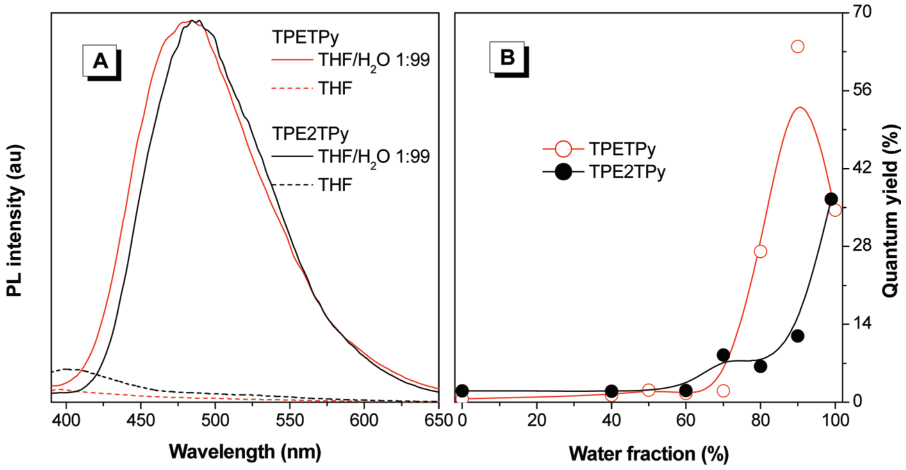


Figure 1. (A) Emission spectra of solutions of TPETPy and TPE2TPy in THF and THF/water mixture (1:99 v/v). (B) Dependence of quantum yields on solvent compositions of the THF/water mixtures. [TPE] = 1.0 μM; λ_{ex} = 350 nm.

THF solution is merely 0.49% (Figure 1B), which remains almost unchanged in mixed solvents with less than 60 vol % of water. Afterward, it starts to increase swiftly. At a water fraction of 90 vol%, the Φ_F value rises to 63.9%, which is 130-fold higher than that in pure THF. The trajectory of the Φ_F change suggests that the molecularly dissolved dye molecules starts to aggregate at a water fraction of ~60 vol% and the population of the aggregates increases with a further increase in the water fraction. Similar phenomenon is observed in TPE2TPy. The Φ_F value of pure THF solution of TPE2TPy is 2.07%, which is higher than that of TPETPy. This can be explained by the AIE mechanism. In TPE2TPy, one more phenyl ring of the TPE core is substituted by the bulky terpyridine unit, which further imposes barrier for intramolecular rotation and hence makes TPE2TPy more emissive in the solution state. The AIE effect has enabled the TPEs to emit efficiently in the solid state: the fluorescence (FL) efficiencies of the thin films ($\Phi_{F,film}$) of TPETPy and TPE2TPy determined by a calibrated integrating sphere are 74.7 and 98.7%, respectively.

The fluorescence properties of TPETPy and TPE2TPy are summarized in Table 1. Apart from the enhancement in quantum efficiency, the emission maximum (λ_{em}) of the nanoaggregates is largely red-shifted as compared to their solution state. In THF solution, the phenyl rings on the TPE molecules undergo active intramolecular torsional/rotational motions against the central double bond. The TPE molecules may adopt very twisted conformations and emit at shorter wavelength. In the aggregate state, the intramolecular torsional/rotational motions are greatly suppressed. The TPE molecules assume less twisted, most stable conformations, resulting in red-shifted emission. The shift in the absorption maximum also supports this hypothesis.

On the other hand, thin films of the TPE molecules emit at shorter wavelength than their aggregates in solution. The degree of aggregation as well as the packing mode may be the decisive factor. In the solid thin film, the poly(methyl methacrylate) (PMMA) matrix serves as a solid "solvent" to disperse the TPE molecules. The emission comes from sole TPE molecules with their intramolecular motions restricted in the solid matrix. The TPE derivatives may take relatively twisted but rigid geometries in such congested circumstance and thus emit more intensely at shorter wavelength. In THF/water mixture with high water fraction, the molecules may abruptly agglomerate into amorphous aggregates with solvent trapped inside. Inside these "loose" particles, the TPE molecules may still undergo partial intramolecular motions, which make them less emissive than the one in solid film. Without the solid constraint, the TPE molecules in the amorphous phase may assume a more planar conformation and thus show luminescence at longer wavelength.

pH-Driven Emission. Terpyridine has acidic and basic functionalities. It is envisioned that the luminescence of terpyridine-containing TPEs will be affected by the pH of the surroundings.[16] In neutral and basic aqueous solution (pH > 7), molecules of TPETPy and TPE2TPy aggregate and emit (see Figure S2 in the Supporting Information). The emission, however, is weakened in low pH medium. At low pH, the pyridine units can be protonated and transformed to pyridium salts, which may make the TPE molecules soluble in water. Because of the AIE nature, the genuine dissolution of the TPEs at the molecular level in the acidic medium turns off their emission.[17]

To verify our hypothesis, the FL behaviors of the TPEs upon protonation are investigated. Different amounts of trifluoroacetic acid (TFA) are added to the TPE solutions in THF/water mixtures. As shown in Figure 2A, the aqueous solution of TPETPy emits an intense greenish-blue light at 485 nm. Addition of 1 mM of TFA into the solution decreases the emission by ~30%. Further addition of TFA gradually weakens and eventually quenches the emission. Upon addition of TFA, the terpyridine units of TPETPy are ionized, which makes the dye molecules more or less soluble in water and hence quench the light emission. With the increase in TFA concentration, more TPETPy molecules are protonated and weaker emission is observed (Figure 2B). On the contrary, the emission of the THF solution of TPETPy is enhanced upon addition of TFA (see Figure S3 in the Supporting Information). THF is good solvent for TPETPy and thus it is weakly fluorescent according to the AIE mechanism. In the presence of TFA, TPETPy is protonated and becomes less soluble in THF. Under such circumstance, the TPETPy molecules start to aggregate and thus fluoresce. Same phenomenon is observed in TPE2TPy (Figure 2C, D).

Table 1. Absorption and Emission Characteristics of TPE Derivatives in Solution (Soln)[a] and Aggregate (Aggr)[b] States

	λ_{ab} (nm)[c]		λ_{em} (nm)[d]		
	Soln	Aggr	Soln (Φ_F)	Aggr (Φ_F)	Film (Φ_F)[e]
TPETPy	317	322	400 (0.49)	484 (34.5)	466 (74.7)
TPE2TPy	320	326	402 (2.07)	490 (36.5)	475 (98.7)

[a] In THF solution (1 μM). [b] In THF/water (1:99 v/v) mixture (1 μM). [c] Absorption maximum. [d] Emission maximum with quantum yield (%) given in the parentheses; excitation wavelength: 350 nm. [e] Solid-state quantum yield determined by a calibrated integrating sphere.

Fluorogenic Zn(II) Sensing. As terpyridine is a well-known metal chelating unit, we thus utilized the TPETPy and TPE2TPy as chemosensors for metal ions. We carried out the sensory experiments using TPE nanoaggregates in THF/water mixture (1:99 v/v) because of their high FL efficiency as well as their amplification ability, as compared to the isolated TPE molecules.[18] Meanwhile, a variety of metal salts can dissolve well in aqueous media.

Figure 3A shows the fluorescence response of the nanoaggregates of TPETPy to various metal ions. As terpyridine does not coordinate with alkali metal cations, Na^+ and K^+ thus exert no effect on the fluorescence of TPETPy (data not shown). The spectral pattern keeps unchanged in the presence of Mg^{2+} and Ag^{2+} ions but the fluorescence becomes weaker. When exposed to Cd^{2+} and Zn^{2+}, the FL spectra show a significant bathochromic shift. Cu^{2+} and group VIIIA metal ions (Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Ru^{3+}, Rh^{3+}, etc.) efficiently quench the emission of TPETPy. The emission spectra of TPE2TPy upon exposure to different cations are shown in Figure 3C. In the presence of Mg^{2+} the emission of the nanoaggregates of TPE2TPy is enhanced, instead of quenched, by 10%. Its fluorescence is weakened upon exposure to Fe^{3+}, Ru^{3+}, Rh^{3+}, and Pb^{2+}, and completely quenched by Fe^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+}. Similar to TPETPy, the emission spectra shift to the redder region when Cd^{2+} and Zn^{2+} ions are added.

The change in the FL intensity and the emission maximum (λ_{max}) of TPEs with various metal ions are summarized in Figure 3B and D. The λ_{max} values of both TPETPy and TPE2TPy are red-shifted by ca. 50 to 540 nm in the presence of Zn^{2+}. However, Cd^{2+} ions only exert 10 nm bathochromic shift under the same experimental conditions. Generally, it is difficult for most fluorophores to discriminate Cd^{2+} and Zn^{2+}

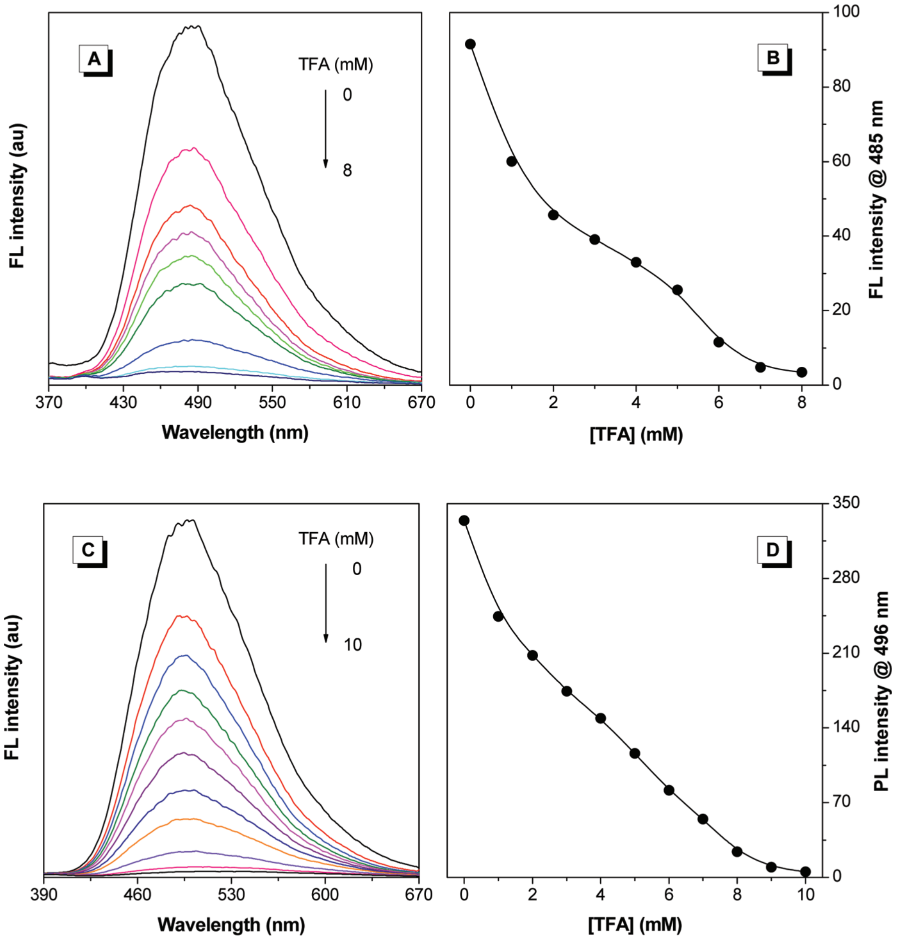


Figure 2. Emission spectra of (A) TPETPy and (C) TPE2TPy in THF/water mixtures (1:99 v/v) with different amounts of trifluoroacetic acid (TFA). Change in FL intensity of (B) TPETPy and (D) TPE2TPy with TFA concentration. [TPE] = 1.0 μM; λ_{ex} = 350 nm.

because they are in the same group of the Periodic Table and exhibit similar properties.[19] The fluorophores we present here show green emission in the presence of Cd^{2+} but yellow emission when reacted with Zn^{2+}, thus allowing the differentiation between the two cations (Figure 4). Because TPETPy and TPE2TPy exhibit similar behaviors and TPE2TPy shows higher quantum efficiency in the aggregate state, we will focus our investigation on the metal sensing property of TPE2TPy in the following discussion.

The emission spectra of TPE2TPy upon titration with Zn^{2+} are shown in Figure S4A in the Supporting Information. In aqueous solution, the hydrophobic TPE2TPy molecules form nanoaggregates, which emit strongly at 490 nm. Addition of Zn^{2+} ions into the solution gradually red-shifts the spectrum and decreases the emission. Change of the FL intensity versus Zn^{2+} concentration is shown in Figure S4B in the Supporting Information, which facilitates the quantitative analysis of Zn^{2+} in aqueous media. TPE2TPy is nonemissive in THF. Addition of Zn^{2+}, [e.g., $Zn(ClO_4)_2$] into the THF solution, however, turns on the emission and generates a pronounced emission peak at ca. 550 nm (see Figure S5 in the Supporting Information). The selectivity of the TPEs to Zn^{2+} is preserved in organic solvents, as shown in Figure S6 in the Supporting Information. Because of the AIE property, the TPEs are non fluorescent in organic solvent. Upon coordination with Zn^{2+}, the conjugation may be greatly extended, which enhances and red-shifts the emission in THF.

To determine the binding stoichiometry for TPE2TPy and Zn^{2+}, the continuous variation method of analysis is employed. The concentrations of TPE2TPy and Zn^{2+} are varied, while the sum of the two concentrations is kept constant at 10.0 μM. As can be seen from Figure 5A, with an increase in the Zn^{2+} concentration, the emission intensity decreases accompanied with a spectral shift to the longer wavelength region. The change in the λ_{max} with the concentration ratio of TPE2TPy to Zn^{2+} is shown in Figure 5B. At equal molar concentration, the λ_{max} value is the largest and equal to 540 nm. Further increment of the Zn^{2+} concentration causes no more shift in the peak position. The corresponding binding ratio is thus given as 1:1 for TPE2TPy to Zn^{2+}, which is consistent with the binding mode of terpyridine to Zn^{2+} reported in the literature.[14]

Figure 6A shows the possible Zn^{2+}-TPE2TPy complex according to the 1:1 binding ratio, in which two terpyridine units from adjacent TPE2TPy molecules coordinate with a zinc ion to form oligomeric or polymeric complex. Similar binding mode of TPE2TPy to Zn^{2+} is deduced in THF solution, indicating the aggregation of the dye molecules would not affect the coordination of the substituted ligands with Zn^{2+} (see Figure S7 in the Supporting Information).

The selective binding ability of TPE2TPy for Zn^{2+} over other metal ions is investigated by measuring the FL of TPE2TPy with Zn^{2+} ions in the presence of other competitive cations. As shown in Figure S8 in the Supporting Information, the characteristic

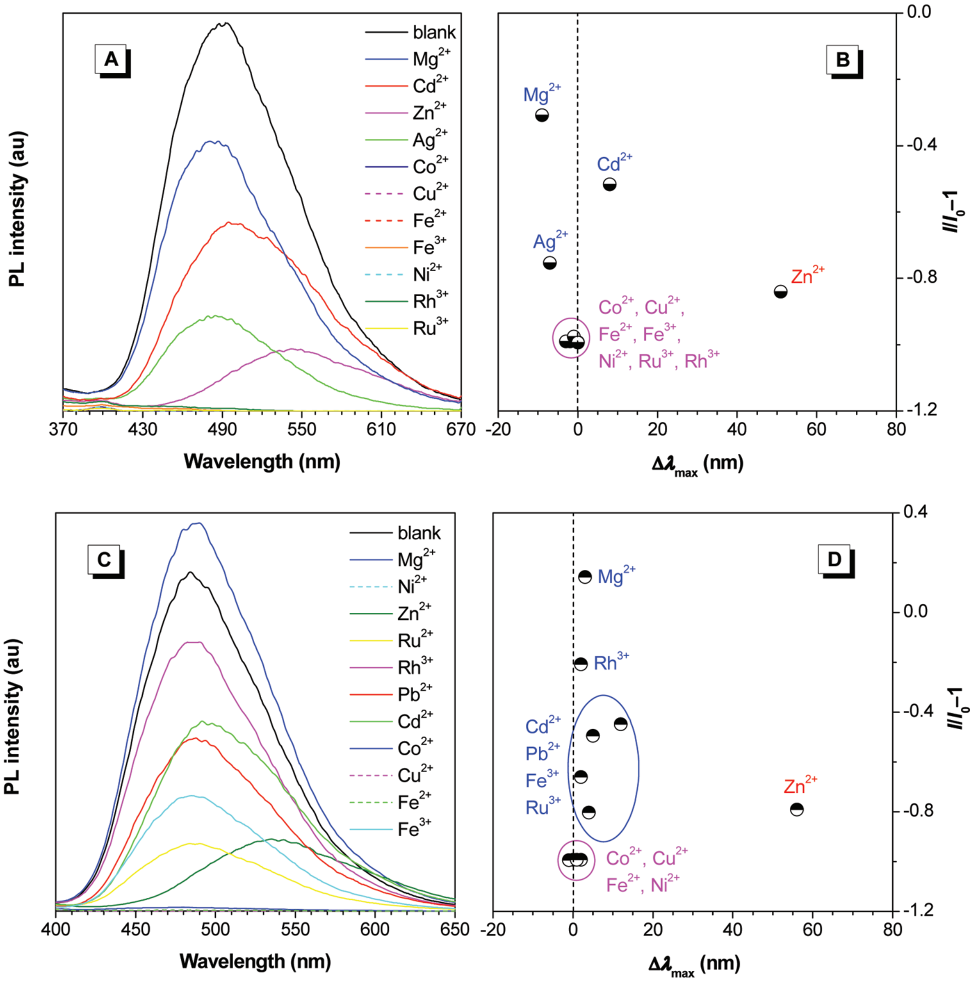


Figure 3. Emission spectra of (A) TPETPy and (C) TPE2TPy in the presence of various cations in THF/water mixtures (1:99 v/v). FL response of nanoaggregates of (B) TPETPy and (D) TPE2TPy to cations. The *x*-axis and *y*-axis corresponds to the shift in the emission maximum (λ_{max}) and the enhancement of FL intensity as referred to the FL spectra without metal ions.

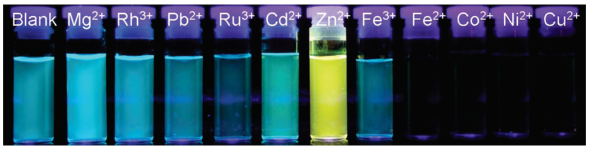


Figure 4. Photograph of the aqueous solutions of TPE2TPy/cation mixtures taken under UV illumination.

emission of the TPE2TPy/Zn^{2+} complex is still observed at ca. 540 nm when Cd^{2+}, Rh^{3+}, Pb^{2+}, and Mg^{2+} are added, albeit in a lower intensity, implying that these metal ions interfere little with the affinity of TPE2TPy to Zn^{2+}. In the presence of Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, or Cu^{2+}, the emission, however, is quenched. The bathochromic shift of TPE2TPy upon interaction with Zn^{2+} may be ascribed to intramolecular charge transfer (ICT) effect. Terpyridine is slightly electron-withdrawing as compared to the TPE core. The electron-withdrawing character of terpyridine is intensified upon complexation with Zn^{2+}, which promotes the occurrence of the ICT process from TPE core to the terpyridine−Zn^{2+} moiety. The push−pull effect is strengthened and thus shifts the emission to the longer wavelengths. Because of the electron-withdrawing nature of the terpyridine ligand, the energy level of the lowest unoccupied molecular orbital will decrease more significantly than the highest occupied molecular orbital upon complexation with metal, thus leading to the red shift of the spectrum (Figure 6C). Another possibility is that the conjugation plane is enlarged when terpyridine−Zn^{2+} complex forms, which narrows the band gap and red-shifts the emission. As shown in Figure S9 in the Supporting Information, a new shoulder peak is at 370 nm in absorption; spectra appears upon complexation with Zn^{2+}.

The AIE characteristics of the TPEs prompt us to apply the materials in the solid state. To test the feasibility, PMMA films doped with TPETPy and TPE2TPy were fabricated to produce highly fluorescent plastic materials for metal sensing. Exposure of the films to a solution of Zn^{2+} ions caused the change of emission color from blue to green or yellow (Figure 7). The blue emission of the thin films can be recovered by treatment with a zinc competitor, such as 2,2′-dipicolylamine. Owing to the AIE feature, the sensing of Zn^{2+} ions by terpyridine-substituted TPEs is applicable in different solid substrate, such as filter paper and thin layer chromatography (TLC) plate (see Figure S10 in the Supporting Information).

Chromogenic Fe(II) Sensing. The nanoaggregates of TPE2TPy are capable of distinguishing Fe^{2+} from Fe^{3+}. The

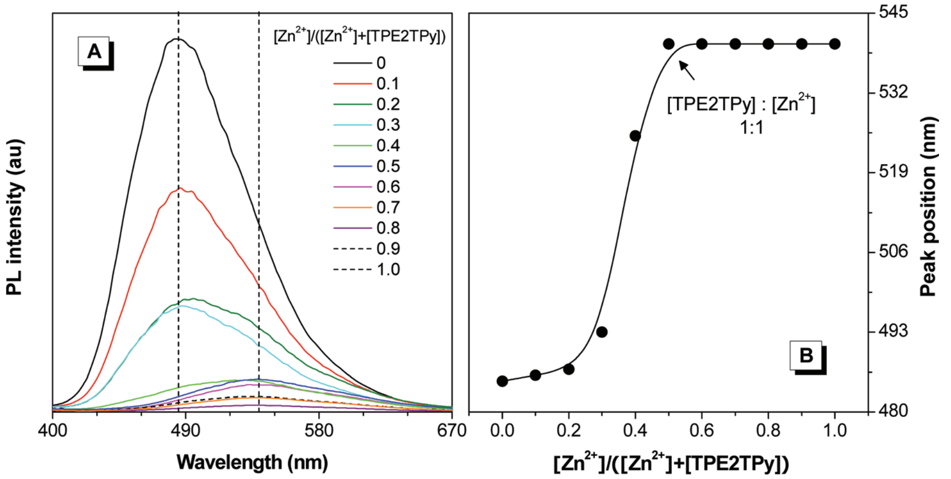


Figure 5. Determination of the stoichiometry in the binding process of TPE2TPy to Zn^{2+}. (A) Emission spectra of TPE2TPy/Zn^{2+} complex formed by using different concentration ratios of TPE2TPy to Zn^{2+} in THF/water mixture (1:99 v/v). (B) Dependence of the emission peak position vs the concentration ratio of Zn^{2+} to the total concentrations of TPE2TPy and Zn^{2+} (10 μM). λ_{ex} = 350 nm.

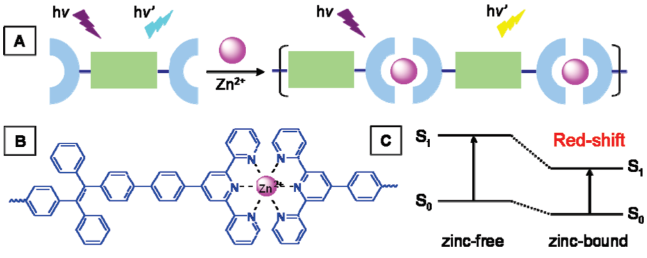


Figure 6. (A) Possible stoichiometry of zinc-TPE2TPy complex. (B) Structure of zinc-bound TPE2TPy. (C) Proposed mechanism for the spectral red-shift of TPE2TPy upon binding to Zn^{2+}.

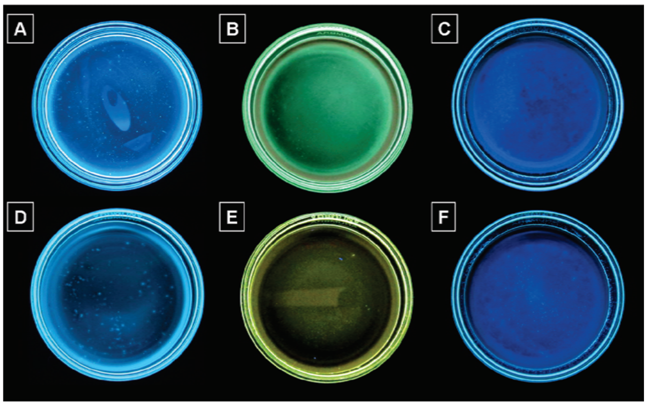


Figure 7. Fluorescence images of PMMA matrices blended with (A−C) TPETPy and (D−F) TPE2TPy (A, D) before and (B, E) after exposure to $Zn(ClO_4)_2$. (C, F) The films in B and E exposed to 2,2′-dipicolylamine.

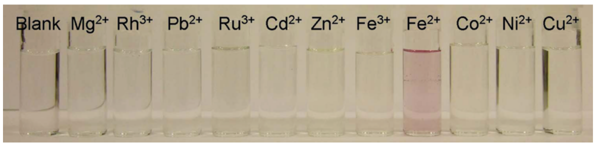


Figure 8. Photograph of the aqueous solutions of TPE2TPy/cation mixtures taken under daylight.

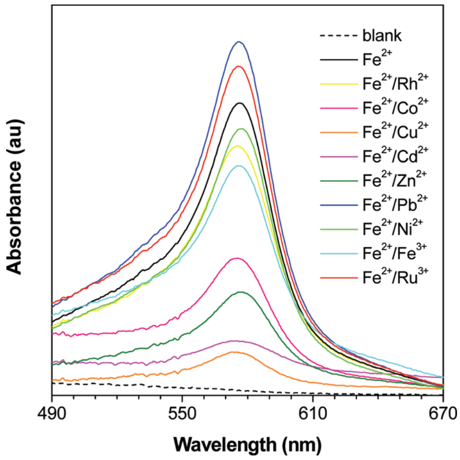


Figure 9. UV spectra of TPE2TPy/Fe^{2+} complex in THF/H_2O mixtures (1:99 v/v) containing different metal ions. [TPE2TPy] = 5 μM; [metal ion] = 10 μM; [Fe^{2+}] = 10 μM.

fluorescence of TPE2TPy decreases slightly by Fe^{3+} but quenches by Fe^{2+} at the same concentration (cf. Figure 4). Meanwhile, the color of the solution changes from pale yellow to light magenta in the presence of Fe^{2+} but remains unchanged when admixed with Fe^{3+} (Figure 8). The selective response of TPE2TPy toward Fe^{2+} and Fe^{3+} are shown in Figure S11 in the Supporting Information. An absorption peak at 576 nm stands out in the presence of Fe^{2+}, which is responsible for the solution color change. Terpyridine-containing chemosensors are reported to respond to both Fe^{2+} and Fe^{3+}.[20] The color change, however, is observed only in TPE2TPy upon exposure to Fe^{2+} but not Fe^{3+}, making TPE2TPy useful for the differentiation of iron species in different oxidative states.

The UV spectra of TPE2TPy upon titration of Fe^{2+} are shown in Figure S12 in the Supporting Information. The characteristic absorption peak at 576 nm appears even in the presence of low

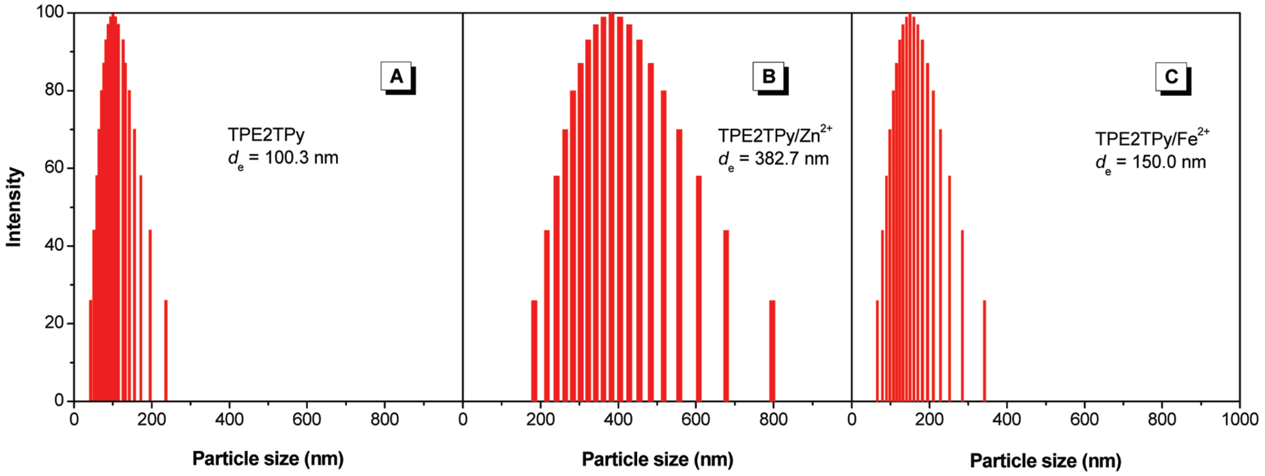


Figure 10. Particle size distributions of (A) TPE2TPy, (B) TPE2TPy with Zn^{2+}, and (C) TPE2TPy with Fe^{2+} in THF/water mixture (1:99 v/v). [TPE2TPy] = 2.5 μM; [metal ion] = 10 μM.

concentration of Fe^{2+}. The absorbance at this wavelength keeps increasing with the increase in Fe^{2+} concentration. The band at 576 nm is corresponding to the metal-to-ligand-charge-transfer.[20a] To determine the selectivity of TPE2TPy toward Fe^{2+}, cross-contamination assays are performed. As shown in Figure 9, although the absorbance varies in the presence of other metal species, the peak at 576 nm can still be discerned with ease, indicating the high selectivity of TPE2TPy toward Fe^{2+}.

The binding ratio of TPE2TPy to Fe^{2+} is estimated by using continuous variation method. Since only TPE2TPy/Fe^{2+} gives the characteristic absorption band at 576 nm, the absorbance at this wavelength can be considered to be proportional to the population of organic—inorganic hybrid (see Figure S13A in the Supporting Information). The Job plot shown in Figure S13B in the Supporting Information indicates that the complex is formed in an approximately 2:3 ratio. To determine whether the nanoaggregates are dissociated or not after coordination with metal ions, particle size analyses by DLS are performed (see Table S1 in the Supporting Information). Interestingly, the changes of the particle size agree well with the results from continuous variation method. With Zn^{2+}, the size of the particles expands from about 100 to 400 nm, implying the formation of oligomeric/polymeric species (cf. Figure 10). The particle size of TPE2TPy nanoaggregates increases slightly when coordination with Fe^{2+} ions, suggesting that the aggregates are not dissociated after coordination with metal ions.

CONCLUSION

In summary, terpyridine-containing TPE derivatives are synthesized and their optical and sensory properties are investigated. Whereas they are practically nonluminescent in the solution state, their nanoaggregates in the aqueous media or films are highly emissive, demonstrating a novel phenomenon of aggregation-induced emission. The emission of the nanoaggregates of these TPEs is pH-driven and is quenched by protonation of their terpyridine units. The TPEs can function as "turn-off" fluorescent chemosensors for metal ions. Addition of Zn^{2+} ions changes the solution color from greenish blue to yellow and shifts the emission spectra by 50 nm, allowing the discrimination of Zn^{2+} ions from other metal cations. The TPEs can also work as highly selective colorimetric sensors for Fe^{2+}, as demonstrated by the obvious color change of their aqueous solutions from colorless to light magenta in the presence of Fe^{2+}. Further exploration of their utility for zinc imaging in live cells is ongoing in our laboratory.

ASSOCIATED CONTENT

S Supporting Information. Experimental details including synthesis and sample preparation, particle size analysis, and PL and UV spectra of TPETPy and TPE2TPy in different pH and in metal sensing. This material is available free of charge via the Internet at http://pubs.acs.org.

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