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Highly selective ratiometric fluorescent recognition of histidine by tetraphenylethene-terpyridine-Zn(II) complexes

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Abstract: The TPE-monoTpy and TPE-diTpy compounds (TPE = tetraphenylethene. Tpy = 2,2':6',2"-terpyridine) were prepared which showed significant red shifts in fluorescence upon coordination to $Zn(NO_3)_2$ in THF:HEPES (1:4) solutions. These in situ prepared Zn(II) complexes have achieved highly selective ratiometric fluorescent recognition of histidine even in the presence of other natural amino acids and metal cations. This fluorescent recognition of histidine is visually observable with distinctive color changes under UV irradiation. The mechanism for the interaction of the Zn(II) complexes with histidine was studied by UV-Vis absorption, NMR and MS.

1. Introduction

Histidine is an indispensable amino acid for humans and other mammals. It is not only essential for human growth but also acts as a neurotransmitter in the central nervous system of mammals.[1] Abnormal level of histidine in biological system could indicate a variety of diseases. Therefore, detection of histidine in biological fluids has become an important goal and a number of methods have been developed for this purpose.[2–4] Among these methods, using molecular fluorescent sensors has attracted extensive attention due to the high sensitivity of fluorescence, the easy availability of instruments and the potential for remote observation.[4]

Terpyridine (Tpy) is a tridentate chelating ligand capable of binding a variety of metal cations[5] and this binding ability has been utilized in sensing.[6] We have studied the use of the Tpy metal complexes in the fluorescent recognition of histidine. In our previous work, we have found that the classical $TpyCuCl_2$ complex **1** exhibited greatly enhanced fluorescence when treated with histidine or cysteine (Figure 1).[7a,b] It was shown that coordination of Cu(II) with Tpy quenched its fluorescence which can be turned on upon interaction with histidine or cysteine. We further designed a crown ether-Tpy compound **2** and found that its *in situ* generated Zn(II) complex can distinguish histidine from cysteine as well as other amino acids by showing significant fluorescence enhancement with histidine only.[7c] In addition, this fluorescent sensor can also differentiate histidine from other imidazole derivatives. This high selectivity is attributed to the cooperative interaction of both the crown ether and the Tpy sites.

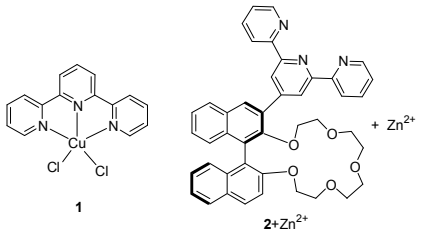

Figure 1. Tpy-based fluorescent sensors **1** and **2**+Zn^{2+} for histidine.

When the complexes **1** and **2**+Zn^{2+} were used to recognize histidine, the fluorescent enhancements were observed at $\lambda \leq$ 400 nm. It would be desirable that if the fluorescent response could be observed at longer wavelengths in the visible region under aqueous conditions. In order to shift the fluorescent response to the longer wavelength, we propose to incorporate the Tpy ligand with fluorophores of longer wavelength emission.

Since 2001, Tang and many research groups have conducted extensive studies on the aggregation-induced emission of organic materials.[8] For example, the propeller-shaped molecules such as tetraphenylethene (TPE) exhibit greatly enhanced emission in the visible region when water is added to its THF solution.[9] That is, addition of water promotes the aggregation of the TPE molecules, leading to the fluorescent enhancement. In order to utilize the unique fluorescent properties of the TPE molecules under aqueous conditions for the Tpy-based fluorescent recognition, we have synthesized the TPE-Tpy conjugates **3** and **4** and explored their fluorescent response toward metal cations and amino acids (Figure 2). We have demonstrated that the Zn^{2+} complexes of these compounds are highly selective ratiometric fluorescent sensors toward histidine. The fluorescent responses are visually observable with distinctive color changes. Herein these results are reported.

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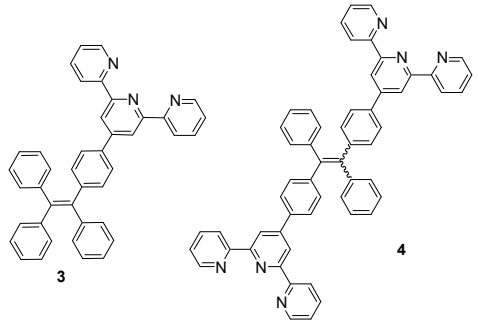
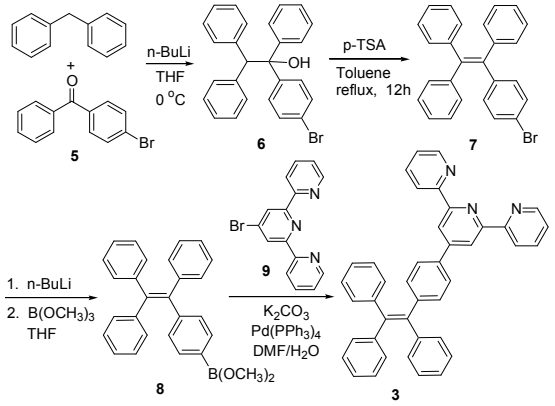


Figure 2. TPE-monoTpy and TPE-diTpy compounds.

2. Results and Discussion

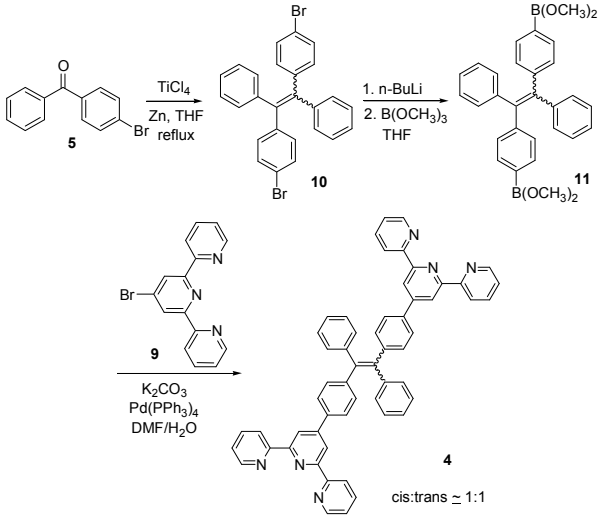
*2.1. Synthesis of the TPE-monoTpy and –diTpy compounds **3**[10] and **4**.*

The synthesis of the TPE-monoTpy compound **3** is shown in Scheme 1. Deprotonation of diphenylmethane with *n*-BuLi followed by addition of the diaryl ketone **5** gave the alcohol **6**.[11] Dehydration of **6** in the presence of *p*-toluensulfonic acid (p-TSA) in refluxing toluene gave the brominated TPE compound **7**.[11] This compound was then converted to the boronic ester **8** by reaction with *n*-BuLi and then $B(OCH_3)_3$.[12] The Suzuki coupling of **8** with 4-bromoTpy **9** gave the desired TPE-monoTpy compound **3**.



Scheme 1. Synthesis of the TPE-monoTpy compound **3**.

Scheme 2 gives the synthesis of the TPE-diTpy compound **4**. The McMurry coupling of the diarylketone **5** in the presence of $TiCl_4$ and Zn gave the dibrominated TPE compound **10**.[13]



Scheme 2. Synthesis of the TPE-diTpy compound **4**.

This compound was found to be a 1:1 mixture of the *cis* and *trans* isomers.[14] Treatment of **10** with *n*-BuLi followed by addition of $B(OCH_3)_3$ produced the TPE-diboronic ester **11**,[13] which was then couple with the 4-bromoTpy **9** in the presence of a palladium catalyst to give the desired compound **4** as a 1:1 mixture of the *cis* and *trans* isomers.

*2.2. Study of the interaction of the TPE-diTpy compound **4** with metal ions and amino acids*

2.2.1. Fluorescence Study

The TPE-diTpy compound **4** (1.0×10^{-5} M) showed very weak emission in pure THF. When we increased the water fraction of the solvent from 0–70%, very little change in the fluorescence was observed (Figure 3). As we further increased the water fraction, the fluorescence of compound **4** showed a sharp increase (near 100 fold) and reached maximum in THF/H_2O = 1:4. Then the fluorescence showed some decrease when the water fraction was more than 80%. The fluorescent responses of **4** in the THF/water mixed solvents suggest that compound **4** is AIE active.

Compound **4** (1.0×10^{-5} M in $THF:H_2O$ = 1: 4) showed strong green emission at λ = 495 nm. We studied its interaction with various metal ions, including Zn^{2+}, Cd^{2+}, Cr^{3+}, Al^{3+}, Fe^{3+}, Ag^{+}, Mg^{2+}, Li^{+}, Ni^{2+}, Co^{2+}, Cu^{2+}, Cu^{2+}, K^{+}, Mn^{2+} and Ca^{2+} and different fluorescent responses were observed (Figure 4). Addition of 5 equiv of Cu^{2+}, Ni^{2+} or Co^{2+} completely quenched its fluorescence. Treatment of **4** with 5 equiv of Fe^{2+}, Mn^{2+}, Fe^{3+}, Zn^{2+} and Ag^{+} significantly quenched its fluorescence with $I/I_0 < 0.1$ for Fe^{2+}, Mn^{2+}, Fe^{3+} and Zn^{2+}, and $I/I_0 = 0.25$ for Ag^{+}. Other metal ions such as Cr^{3+}, Cd^{2+}, Ca^{2+}, Na^{+}, Hg^{+} and Pb^{2+} caused much smaller fluorescence changes to **4**. Notably, addition of 5 equiv of Zn^{2+} to **4** caused red shift of the maximum emission from 495 nm to 560 nm with significantly decreased fluorescence intensity. The plot of the fluorescence intensity ratio I_{560}/I_{495} of various metals clearly demonstrates the high selectivity for Zn^{2+} (Figure 4c). This ratio for Zn^{2+} is 4.0 while those for all the other metals are lower than 0.8. Thus, the TPE-diTpy compound **4** shows highly ratiometric selective fluorescent

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response toward Zn^{2+}. In addition, Figure 8c also demonstrates that with the use of **4**, Zn^{2+} can be successfully differentiated from Cd^{2+}, a common interference for the recognition of Zn^{2+}. Treatment of **4** with Zn^{2+} led to a visually observable color change from green to yellow under a UV lamp.

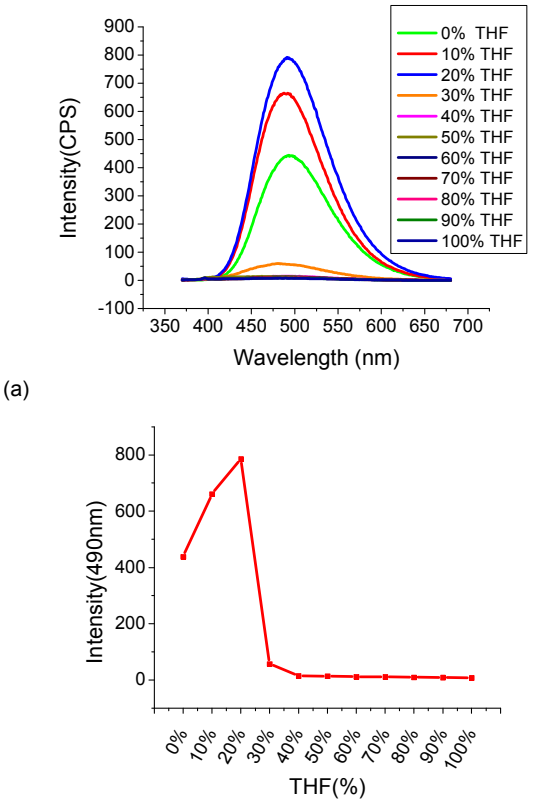
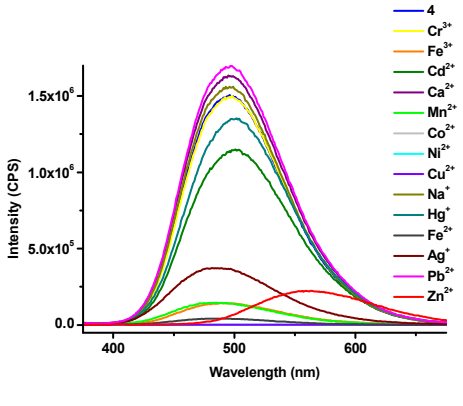


Figure 3. (a) Fluorescent spectra of **4** (1.0×10^{-5} M) in THF/H_2O mixed solvents. (b) The fluorescent intensity of **4** at 495 nm versus the THF fraction. (λ_{exc}= 355 nm, slits: 2 nm/2 nm)



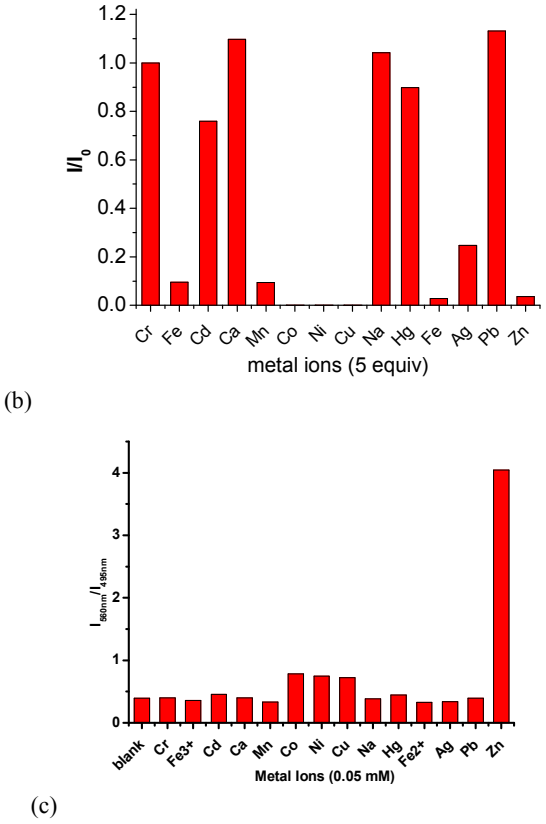
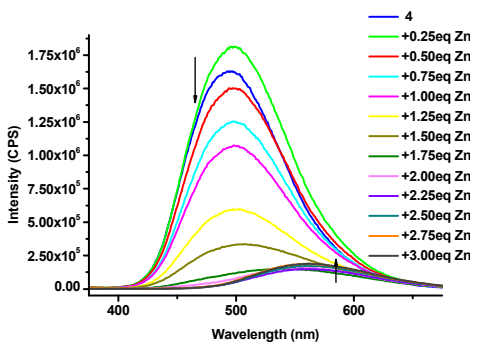


Figure 4. Responses of **4** (1.0×10^{-5} M in THF:H2O = 1: 4) toward various metal ions (5.0 eq): (a) fluorescent spectra, (b) fluorescent intensity ratio I_{495}/I_0, (c) fluorescent intensity ratio I_{560}/I_{495}. (λ_{exc}= 355 nm, slits: 2 nm/2 nm)

Fluorescent titration of **4** (1.0×10^{-5} M in THF:HEPES = 1: 4) with $Zn(NO_3)_2.6H_2O$ was studied.[15] As shown in Figure 5a, the fluorescent intensity of **4** gradually decreased with addition of Zn^{2+}. When more than 1.5 equiv of Zn^{2+} was added, the emission maximum was observed to undergo red shift. When more than 2 equiv of Zn^{2+} was added, no significant fluorescent change was observed and the emission maximum was at 560 nm. Figure 5b plots the fluorescent intensity ratio I_{560}/I_{495} versus the stoichiometry of the Zn^{2+} added. When more than 2 equiv of Zn^{2+} was added, the I_{560}/I_{495} ratio stabilized at around 3.7.



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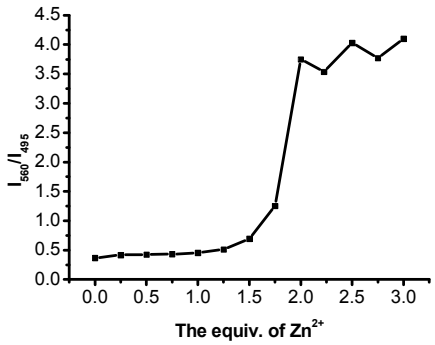
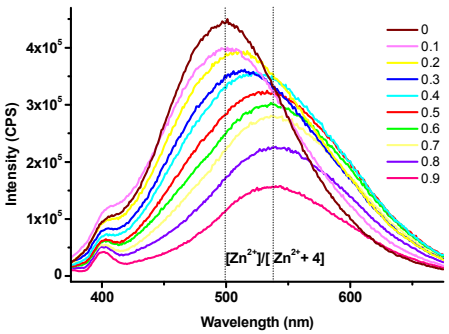


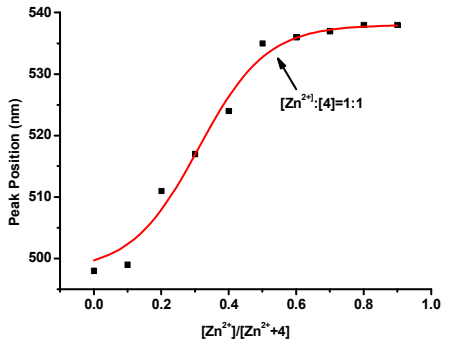
(b)

Figure 5. (a) Fluorescence titration of **4** (1.0×10^{-5} M in THF: HEPES = 1: 4) with $Zn(NO_3)_2.6H_2O$. (b) Fluorescence intensity ratio I_{560}/I_{495} for the fluorescence titration. (λexc= 355 nm, slits: 2 nm/2 nm)

In order to determine the stoichiometry for the complexation of **4** with Zn^{2+}, we studied the fluorescent response while maintaining a constant total molar concentration of **4** + Zn^{2+} and varying their mole fractions. The maximum emission wavelength was employed to make the job plot (Figure 6). When the Zn^{2+} fraction increased from 0.1 to 0.5, the fluorescence emission maximum underwent red shift to 538 nm. Further increase of the Zn^{2+} concentration caused no more shift in the peak position. The corresponding binding ratio is thus given as 1:1 for **4** to Zn^{2+}.



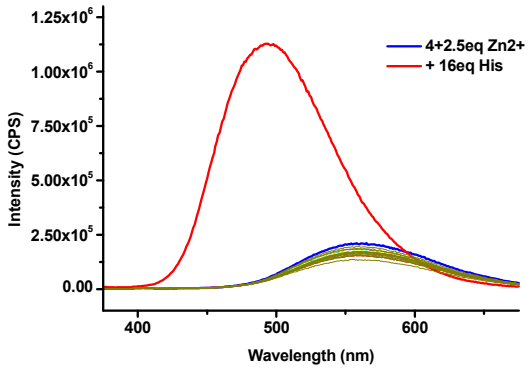
(a)



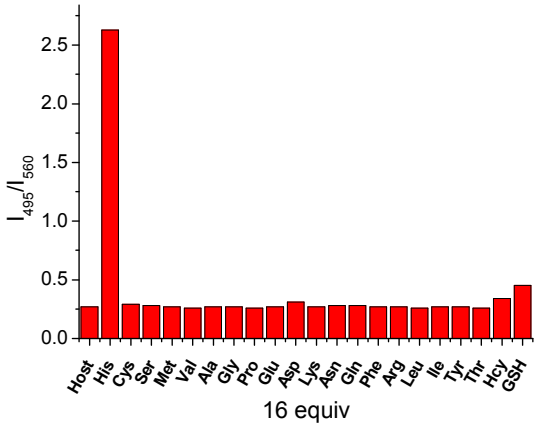
(b)

Figure 6. (a) Fluorescence spectra of job plot (total concentration: 1.0×10^{-5} M). (b) Job plot of **4** with Zn^{2+}. (λexc = 355 nm, slits: 5 nm/5 nm, THF:HEPES = 1:1)

We then studied the fluorescent response of the *in situ* prepared complex **4**+Zn^{2+} (2.5 equiv) toward amino acids and biological amino thiols. In the mixed solvents of THF and water (1:4), **4** has poor solubility and emits very strong fluorescence, but its Zn^{2+} complex can be completely dissolved and emits weaker and red-shifted fluorescence. We thus used THF:HEPES (1:4) as the solvent for the amino acid study while maintaining the pH at 7.4. The fluorescent responses of the **4**+Zn^{2+} (2.5 equiv) complex in the presence of 16 equiv of various amino acids and biological amino thiols including Hcy and GSH were examined (Figure 7a). Of all the tested amino acids and amino thiols, none of them caused significant fluorescent change except histidine which greatly enhanced the fluorescence and shifted the emission from λ = 560 nm back to λ = 495 nm. The fluorescent intensity ratio I_{495}/I_{560} of the **4**+Zn^{2+} complex in the presence of 16 equiv of histidine is 2.6 and that for all the other amino acids and amino thiols is around 0.3 (Figure 7b). As shown in Figure 8, the highly selective fluorescent response of the **4**+Zn^{2+} complex toward histidine can also be detected visually under UV irradiation (365 nm). That is, only the addition of histidine turned the solution to emit blue-greenish light while the addition of all other amino acids caused no change in the original yellow emission.



(a)



(b)

Figure 7. Responses of **4**+Zn^{2+} (2.5 equiv) (1.0×10^{-5} M in THF:HEPES = 1: 4) toward 16 equiv of various amino acids: (a) fluorescence spectra, (b) fluorescence intensity ratio I_{495}/I_{560}. (λ_{exc} = 355 nm, slits: 2 nm/2 nm)

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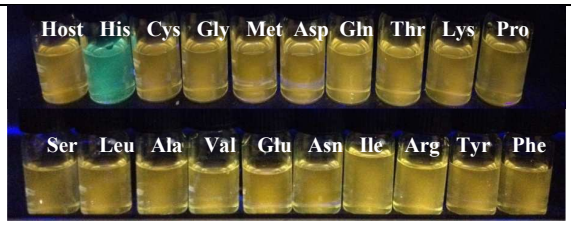
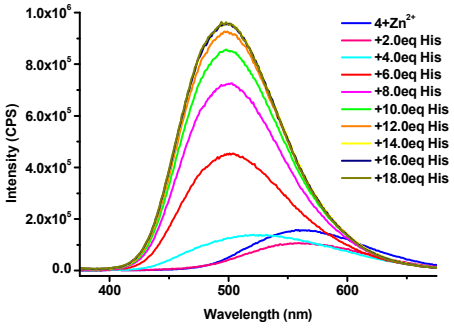


Figure 8. Photos of **4**+Zn^{2+} (2.5 equiv) (1.0×10^{-5} M in THF:HEPES= 1: 4) in the presence of various amino acids (20 equiv) under UV irradiation (365 nm).

We then conducted a fluorescent titration of the **4**+Zn^{2+} (2.5 equiv) complex (1.0×10^{-5} M in THF:HEPES = 1: 4) with histidine at 2 equiv increments. As shown in Figure 9a, the emission of this Zn^{2+} complex at 560 nm was first slightly quenched with 2 equiv histidine. With an additional 2 equiv histidine, the maximum emission underwent significant blue shift. Large fluorescent enhancement was observed with further increased amount of histidine while the emission maximum was shifted to 495 nm. With the addition of more than 16 equiv of histidine, no more change in fluorescence was observed. Formation of white precipitate was observed with the clear solution gradually turning into a white slurry. Under UV irradiation, it was clearly observed that the yellow solution gradually turned blue greenish. We plotted the fluorescent intensity ratio I_{495}/I_{560} versus the equiv of histidine in Figure 9b. This ratio shows a sharp increase from 0.3 to 2.2 in the range of 2–8 equiv of histidine, which demonstrates a ratiometric fluorescent response of the **4**+Zn^{2+} complex toward histidine.



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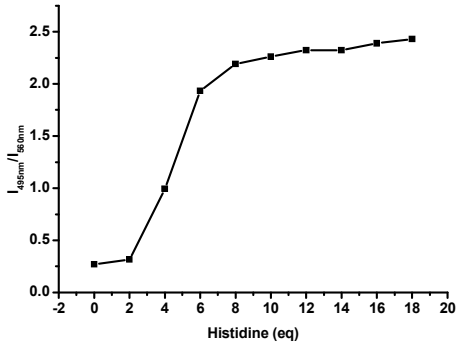

(b)

Figure 9. (a) Fluorescence titration of complex **4**+Zn^{2+} (2.5 equiv) (1.0×10^{-5} M in THF: HEPES = 1: 4) with histidine. (b) Fluorescence intensity ratio I_{495}/I_{560} for the fluorescence titration. (λ_{exc} = 355 nm, slits: 2 nm/2 nm)

We tested the fluorescence recovery of the **4**+Zn^{2+} complex in the presence of the mixtures of histidine with other species in biological systems including the common metal ions Mg^{2+}, Fe^{3+}, K^{+}, Ca^{2+} and Na^{+}, the natural amino acids and amino thiols. The results are summarized in Figure 10 and Table 1. All the tested metal ions (20 equiv) except Fe^{3+} had little effect on the fluorescent recognition of histidine by the Zn^{2+} complex. Addition of 20 equiv of Fe^{3+} partially quenched the fluorescence and the emission wavelength remained. The interference caused by Fe^{3+} might be attributed to its strong coordination to Tpy. All the other natural amino acids and amino thiols, including the commonly interfering amino acids such as serine and arginine, had little effect on the fluorescent recognition of histidine by the **4**+Zn^{2+} complex.

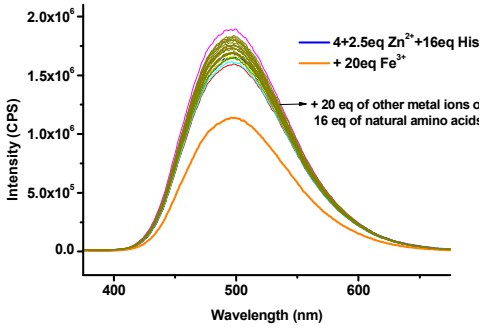

Figure 10. Fluorescence spectra of the **4**+Zn^{2+} (2.5 equiv) complex solution (1.0×10^{-5} M in THF: HEPES = 1: 4) in the presence of 16 equiv of histidine and 20 equiv of various metal ions (Mg^{2+}, Fe^{3+}, K^{+}, Ca^{2+} and Na^{+}) or 16 equiv of the natural amino acids. (λ_{exc} = 355 nm, slits: 2 nm/2 nm)

Table 1. Fluorescence recovery of **4**+Zn^{2+} (2.5 equiv) (1.0×10^{-5} M in THF: HEPES = 1: 4) in the presence of the mixtures of 16 equiv of histidine with metal ions or other natural amino acids. (λ_{exc} = 355 nm, slits: 2 nm/2 nm)

Added species	Conc. (μM)	Recovery (%)	Added species	Conc. (μM)	Recovery (%)
Asp	160	110	Val	160	110
Lys	160	115	Arg	160	107
Gly	160	101	Cys	160	109
Ile	160	111	Met	160	103
Asn	160	108	Ala	160	102
Gln	160	109	Hcy	160	109
Tyr	160	109	GSH	160	116
Phe	160	102	$MgCl_2$	200	105
Thr	160	104	$FeCl_3$	200	69
Pro	160	102	KCl	200	105
Leu	160	106	$CaCl_2$	200	102

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Glu	160	100	NaCl	200	102
Ser	160	106.47			

2.2.2. UV–Vis study

The UV–Vis spectrum of **4** (1.0×10^{-5} M in THF: HEPES= 1: 4) showed a sharp peak at 218 nm, broad peaks at 255 nm and 295 nm, and a shoulder at 366 nm. Upon addition of 2.5 equiv of Zn^{2+} the broad peaks at 255 nm and 295 nm disappeared and a new peak at 283 nm showed up (Figure 11). When the **4**+Zn^{2+} (2.5 equiv) complex (1.0×10^{-5} M in THF:HEPES = 1: 4) was titrated with histidine, this new peak at 283 nm gradually decreased and the characteristic absorption of **4** at 255 nm appeared (Figure 12). This suggests the displacement of the coordinated Zn^{2+} from the **4**+Zn^{2+} complex by the amino acid.

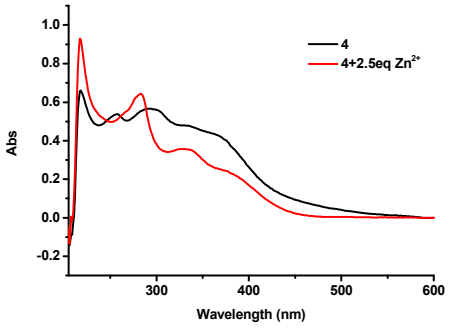

Figure 11. UV–Vis spectra of **4** (1.0×10^{-5} M in THF:HEPES = 1:4) in the absence and presence of 2.5 equiv. of Zn^{2+}.

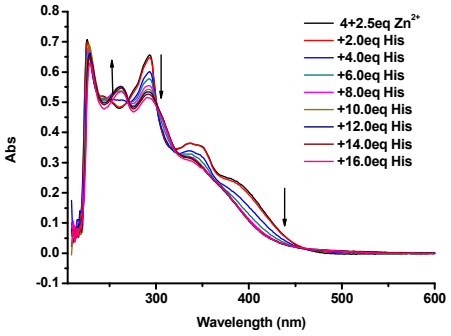

Figure 12. UV–Vis titration of **4**+Zn^{2+} (2.5 equiv) (1.0×10^{-5} M in THF: HEPES = 1: 4) with histidine.

2.2.3. NMR and MS study

In order to gain further understanding on the interaction of the **4**+Zn^{2+} complex with histidine, we conducted ^{1}H NMR and mass spectroscopic analyses. Figure 13 shows the ^{1}H NMR spectra when **4** (3 mM) was treated with 2.5 equiv. of $Zn(OAc)_2$ in THF-d_8:D_2O (4:1) solution. Broadened peaks and changes in the chemical shifts were observed, indicating coordination of Zn^{2+} as well as possible formation of multiple complexes. When histidine was added to this system, characteristic singlet peak at δ 9.39 and two doublet peaks at δ 7.91 and 7.85 of **4** gradually reappeared, indicating the release of **4** from its Zn^{2+} complex.

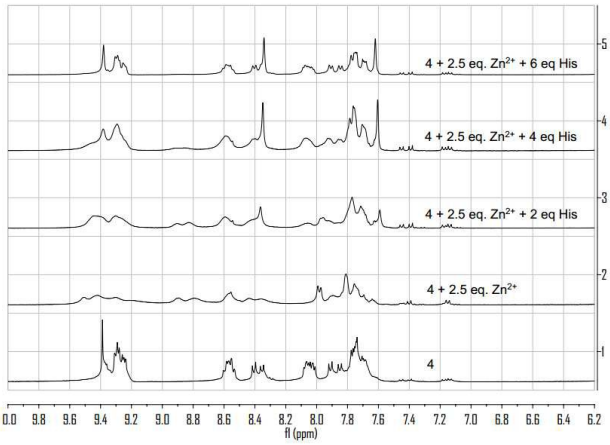

Figure 13. ^{1}H NMR spectra of **4** with the addition of $Zn(NO_3)_2$ (2.5 equiv) and histidine in THF-d_8:D_2O (4:1).

In the mass spectrum obtained for the **4**+Zn^{2+} (1.5 equiv.) complex in CH_3CN:H_2O (4:1), a base peak at m/z = 827.28 is assigned to the 2:1 complex (**12**+2H)$^{2+}$. A peak at 1716.58 can be assigned to that of (**12**+Zn)$^+$, a 2:2 complex. A peak at m/z = 1891.65 can be assigned to the 2:3 complex (**13**-2H)$^+$. A peak at 1335.45 can be assigned to a 3:4 complex of (**34**+4Zn+2OH)$^{2+}$ (calc: 2670.65/2). A peak at 920.24 is assigned to the 1:1 complex **14**. A peak at m/z = 1095.35 is proposed for that of the 1:2 complex (**15**-H)$^+$. With the addition of histidine, the relative intensity of the peak at m/z = 795.32 (**4**+H^+) gradually increased. A new peak at m/z = 1012.32 assigned to the ternary complex **16** (**4**+Zn^{2+}+His) was also observed with increasing intensity.

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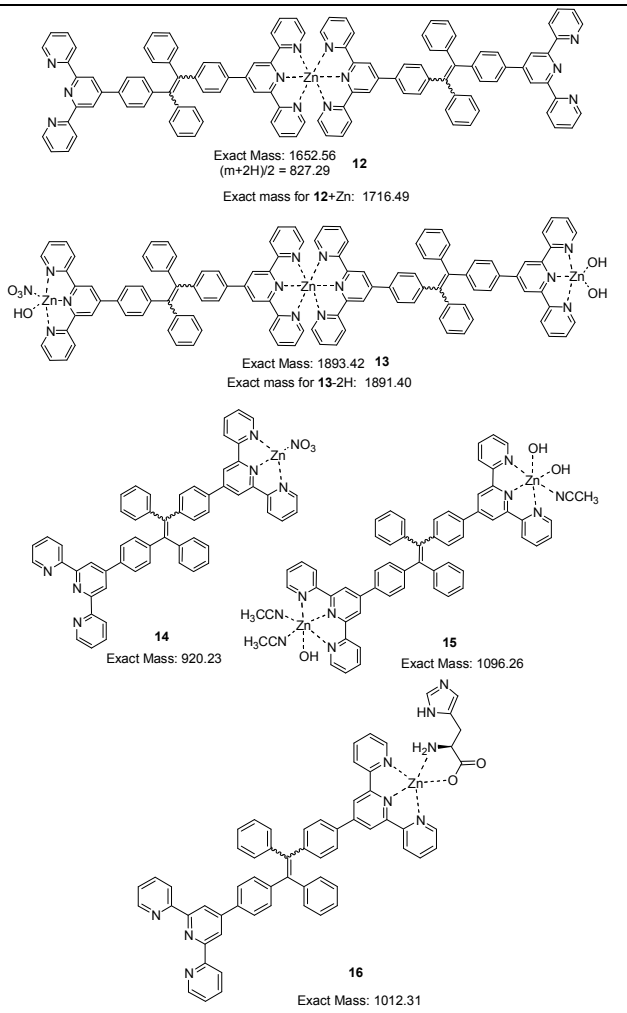

Figure 14. Proposed structures of the Zn^{2+} complexes of **4** before and after the addition of histidine.

The observations of the mass, ^1H NMR and UV spectroscopic analyses substantiate the hypothesis that addition of histidine to the **4**+Zn^{2+} complex initially coordinate to the Zn^{2+} center to form the ternary complex **16** which upon further reaction with histidine displaces the Zn^{2+} ion off the TPE-diTpy ligand **4**. The observed formation of white slurry can be attributed to the formation of **4** which has poor solubility in the reaction media without Zn^{2+} coordination and exhibits the aggregation induced emission.

*2.3. Study of the interaction of the TPE-monoTpy compound **3** with metal ions and amino acids*

The TPE-monoTpy compound **3** (1.0×10^{-5} M in THF: HEPES = 1: 4) shows strong blue-green emission at λ = 485 nm, 10 nm shorter than that of **4** due to the less conjugation. We also studied its interaction with various metal ions (Figure 15). Similar to **4**, addition of 3 equiv of Cu^{2+}, Ni^{2+}, Co^{2+} completely quenched its fluorescence. Partial fluorescent quenching was observed for the addition of 3 equiv of Cd^{2+} (I_{485}/I_0 = 0.32), Cr^{3+} (I_{485}/I_0 = 0.51), Al^{3+} (I_{485}/I_0 = 0.89), Fe^{3+} (I_{485}/I_0 = 0.32), Ag^+ (I_{485}/I_0 = 0.79), Mn^{2+} (I_{485}/I_0 = 0.68) and Ca^{2+} (I_{485}/I_0 = 0.79). Addition of Mg^{2+} caused no change to the fluorescence of **3** and Li^+ slightly increased its fluorescence. It is notable that addition of 3 equiv. of Zn^{2+} caused red shift of the emission maximum from 485 nm to 530 nm with significantly decreased fluorescence intensity. Figure 15c plots the fluorescence intensity ratio I_{530}/I_{485} of **3** upon addition of various metal ions. This ratio for Zn^{2+} is as high as 1.7 while that for all the other metals is in the range of 0.5 to 0.7. As shown in Figure 16, under UV irradiation (365 nm), addition of 3 equiv Zn^{2+} to **3** changed the solution from the blue-green emission to a weak yellow emission that was visually observable.

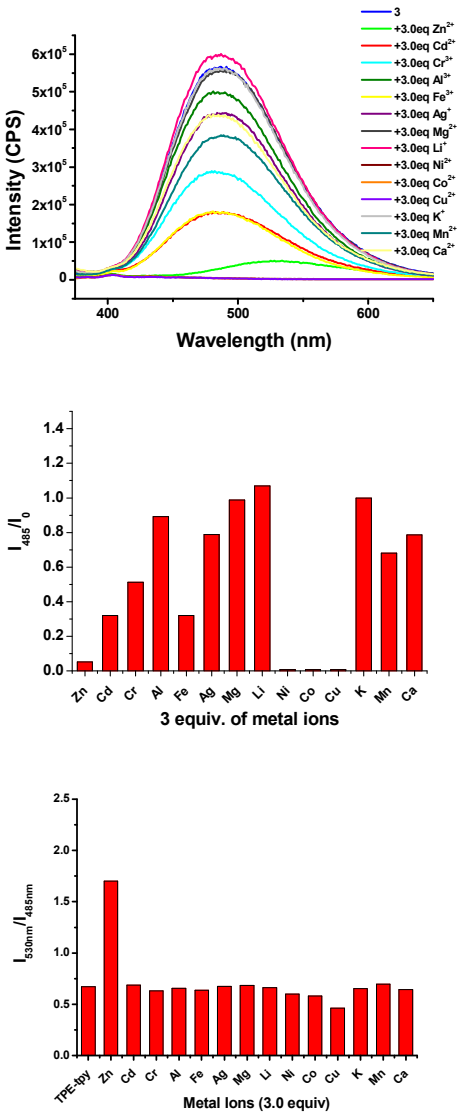

Figure 15. (a) Fluorescent spectra of **3** (1.0×10^{-5} M in THF:HEPES = 1:4) in the presence of various metal ions (3.0 equiv). (b) The fluorescent intensity ratio I_{485}/I_0 of compound **3** (1.0×10^{-5} M in THF:HEPES = 1:4) in the presence of various metal ions (3.0 equiv). (c) The fluorescent intensity ratio I_{530}/I_{485} of compound **3** (1.0×10^{-5} M in THF:HEPES = 1:4) in the presence of various metal ions (3.0 equiv). (λ_{exc} = 354 nm, slits: 3 nm/3 nm)

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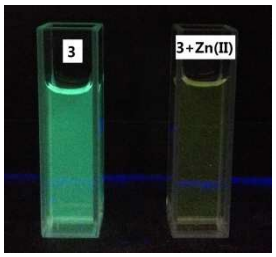
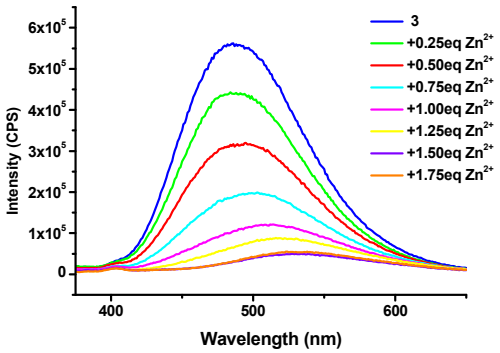
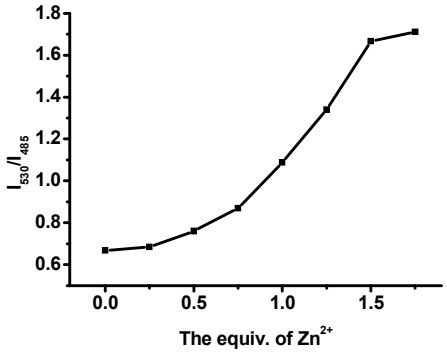


Figure 16. Fluorescence of compound **3** (1.0×10^{-5} M in THF:HEPES = 1:4) in the absence or presence of 3 equiv of Zn^{2+} under UV irradiation (365 nm).

We then titrated **3** (1.0×10^{-5} M in THF: HEPES = 1: 4) with Zn^{2+} in 0.25 equiv increment and monitored its fluorescence after each addition.[15] As shown in Figure 17a, the fluorescence of **3** decreased with addition of Zn^{2+}. When 1.5 equiv of Zn^{2+} was added, the fluorescence stabilized with the emission maximum shifted to 530 nm. Figure 17b plots the fluorescence intensity ratio I_{530}/I_{485} of compound **3** versus the concentration of Zn^{2+}. This ratio first increased and then reached a plateau after 1.5 equiv of Zn^{2+}.



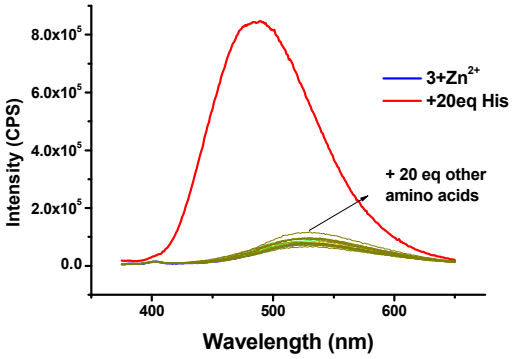
(a)



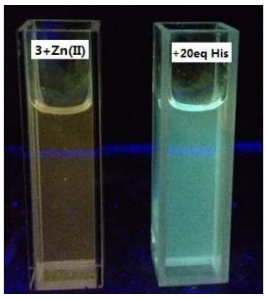
(b)

Figure 17. (a) Fluorescence titration of compound **3** (1.0×10^{-5} M in THF:HEPES = 1:4) with Zn^{2+}. (b) Fluorescence intensity ratio I_{530}/I_{485} for the fluorescence titration. (λ_{exc}= 354 nm, slits: 3 nm/3 nm)

We then studied the fluorescent response of the **3**+Zn^{2+} (1.5 equiv) complex (1.0×10^{-5} M in THF:HEPES = 1:4, prepared in situ) with 20 equiv of various natural amino acids. As shown in Figure 18a, this Zn(II) complex exhibited very high selectivity for the fluorescent recognition of histidine. Histidine greatly enhanced the fluorescence of the complex and shifted the emission maximum from 530 nm back to 485 nm while all the other amino acids caused little effect on the fluorescence of the **3**+Zn^{2+} complex. Figure 18b shows the color change of the **3**+Zn^{2+} complex under UV irradiation upon treatment with histidine. Thus, the **3**+Zn^{2+} complex can also be used for the fluorescent recognition of histidine, similar to that observed for the **4**+Zn^{2+} complex.



(a)



(b)

Figure 18. (a) Fluorescence spectra of **3**+Zn^{2+} (1.5 equiv) (1.0×10^{-5} M in THF: HEPES= 1: 4) in the presence of 20 equiv of various amino acids. (b) **3**+Zn^{2+} (1.5 equiv.) complex solution (1.0×10^{-5} M in THF:HEPES = 1:4) in the absence and presence of 20 equiv of histidine under UV irradiation (365 nm).

Previously, we reported that the Tpy+$CuCl_2$ complex **1** exhibits large fluorescent enhancement in the presence of histidine and cysteine but not with other amino acids and is useful for the fluorescent recognition of the two amino acids.[7a,b] Therefore, we also prepared the **3**+$CuCl_2$ complex and studied its fluorescent response toward amino acids. We found that unlike **1** which is highly selective toward histidine and cysteine, the **3**+$CuCl_2$ complex shows poor selectivity in its fluorescent response since many amino acids can turn on its fluorescence without shift in the emission wavelength (Figure 19). Thus the Cu(II) complex of **3** cannot be used for the fluorescent recognition of histidine. The TPE unit of **3** has greatly altered the fluorescent response of the Tpy-Cu(II) complex in the presence of the amino acids.

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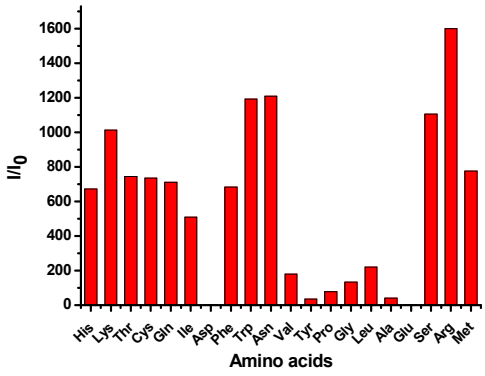

Figure 19. Fluorescence enhancement ratio I/I_0 at 475 nm of **3**+$CuCl_2$ complex (1.0×10^{-5} M in H_2O:THF = 99:1) in the presence of 10 equiv. of various amino acids. (λ_{exc} = 354 nm, slits: 2 nm/2 nm)

3. Conclusions

We have synthesized two TPE-Tpy compounds **3** and **4** which show significant red shift in emission upon coordination to $Zn(NO_3)_2$ in THF:HEPES (1:4) solution. This change is visually observable from blue greenish color to yellow upon UV irradiation. The *in situ* prepared Zn(II) complexes **3**+Zn^{2+} and **4**+Zn^{2+} in THF:HEPES (1:4) have achieved highly selective ratiometric fluorescent recognition of histidine even in the presence of other natural amino acids, amino thiols and metal cations. Comparison of Figure 7a with Figure 18a indicates that the diTpy compound **4** in combination with Zn^{2+} should be a more sensitive fluorescent sensor because of higher fluorescent intensity upon histidine binding than the monoTpy complex **3**+Zn^{2+}. The ratiomertic fluorescent response and the high selectivity of these complexes make them useful for the fluorescent detection of histidine. On the basis of the UV, ^{1}H NMR and mass spectroscopic analyses, it is proposed that the observed highly selective fluorescent response of the **4**+Zn^{2+} complex toward histidine should be due to the coordination of histidine to the Zn^{2+} center of the complex followed by displacement of **4** off to restore its aggregation induced emission.

4. Experimental Section

4.1. General Data:

Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. All the solvents were dried according to the standard methods prior to use. In the optical spectroscopic studies, all the solvents were either HPLC or spectroscopic grade. In the syntheses of compounds **3** and **4**, THF was distilled over sodium and benzophenone under nitrogen atmosphere and stored over 4 Å molecular sieves.

^{1}H and ^{13}C NMR spectra were measured on a Bruker AM400 NMR spectrometer. ^{1}H chemical shifts of NMR spectra were given in ppm relative to internals reference TMS (1H, 0.00 ppm). ESI-MS and HRMS spectral data were recorded on a Finnigan LCQ^{DECA} and a BrukerDaltonics Bio TOF mass spectrometer, respectively. UV-Vis absorption spectra were recorded on a Hitachi U1900 spectrometer. Fluorescence emission spectra were obtained using FluoroMax-4 Spectrofluorophotometer (HORIBA JobinYvon) at 298 K. pH was taken on an ARK PHS-2C pH meter.

*4.2. Synthesis and Characterization of **3**.*

(a) Under nitrogen, to a THF (100 mL) solution of diphenylmethane (2.0 g, 12.0 mmol) was added n-BuLi (6.0 mL, 2.5 M in hexane solution, 15.0 mmol) dropwise. After the mixture was stirred at room temperature for 3 h, a THF (20 mL) solution of **5** (3.1 g, 12.0 mmol) was added dropwise to the reaction mixture. The resulting solution was stirred at room temperature for 8 h, and then quenched with saturated NH_4Cl solution (10 mL). After extraction with CH_2Cl_2 (50 mL × 3), the combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. Filtration followed by evaporation of the solvent and purification of the residue by flash column chromatography on silica gel eluted with petroleum/ethyl acetate (10/1) gave **6** as a white solid. (b) Compound **6** was then dissolved in toluene (50 mL) to which *p*-toluensulfonic acid (3.0 g, 17.4 mmol) was added. The reaction mixture was heated at reflux for 8 h. After cooled down to room temperature, the reaction mixture was extracted with CH_2Cl_2 (3 x 30 mL). The organic layer was collected and concentrated. The crude product was purified by column chromatography on silica gel using hexane as eluent to give product **7** as a white solid (1.1 g). The combined yield of the two steps was 24%. (c) Under nitrogen, **7** (500 mg, 1.2 mmol) was dissolved in THF (50 mL) and the temperature was lowered to -78 ^{o}C. *n*-BuLi (0.58 mL, 2.5 M in hexane, 1.45 mmol) was slowly added to the mixture and after 1 h $B(OCH_3)_3$ (0.2 mL, 1.8 mmol) was added slowly. The reaction mixture was stirred at -78 ^{o}C for 1 h and then the temperature was increased to room temperature. After stirred for 8 h, the reaction was quenched with saturated NH_4Cl solution (5 mL) and extracted with CH_2Cl_2 (3 x 30 mL). The combined organic layer was washed with brine (30 mL) and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified by flash column chromatography on silica gel eluted with petroleum ether/ethyl acetate (5/1) to afford **8** as a white solid (201.1 mg) in 41% yield. (d) Under nitrogen, compound **8** (200 mg, 0.5 mmol) was dissolved in DMF (20 mL) and water (3.6 mL) was added as a cosolvent. Compound **9** (185 mg, 0.6 mmol), K_2CO_3 (1.0 g, 7.2 mmol) and $Pd(PPh_3)_4$ (110 mg, 0.1 mmol) were added to the solution. Then the reaction mixture was heated to 80 ^{o}C and stirred for 8 h. The reaction was extracted with CH_2Cl_2 (3 x 30 mL). The combined organic layer was washed with brine (30 mL) and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified by flash column chromatography on silica gel eluted with petroleum ether/ethyl acetate (3/1) to afford **3** as a light yellow solid (92 mg) in 33% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.09 (d, 2H, J = 4.8 Hz), 8.67-8.65 (m, 4H), 7.87（td，2H，J = 7.8, 1.6 Hz)，7.65 (d, 2H, J = 8.4 Hz), 7.36-7.33 (m, 2H), 7.17-7.04 (m, 17H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.27, 155.82, 150.00, 149.11, 144.75, 143.53, 143.49, 141.57, 140.28, 136.88, 136.24, 131.93, 131.41, 131.35, 131.33, 127.86, 127.75, 127.67, 126.62, 126.58, 126.53,

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123.81, 121.34, 118.72. HR-MS (ES+) calculated for $C_{41}H_{29}N_3$ (M+H) 564.2434 and (M+Na) 586.2254, found 564.2430 and 586.2272.

*4.3. Synthesis and Characterization of **4**.*

(a) Under nitrogen, to a THF (100 mL) solution of **5** (5.0 g, 19.0 mmol) were added $TiCl_4$ (2.1 mL, 19.0 mmol) and Zn (3.1 g, 47.7 mmol). The mixture was heated at reflux for 20 h and then filtered. The filtrate was evaporated and purified by column chromatography on silica gel eluted with petroleum ether to afford **10** as a white solid in 95% yield (4.5 g). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.25 (d, J = 8.2 Hz, 4H), 7.21 (d, J = 8.2 Hz, 4H), 7.14 (t, J = 3.2 Hz, 6H), 7.10 (t, J = 3.2 Hz, 6H), 6.97–7.02 (m, 8H), 6.89 (d, J = 8.4 Hz, 4H), 6.87 (d, J = 8.4 Hz, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz) 142.92, 142.82, 142.38, 142.29, 140.27, 132.90, 132.88, 131.22, 131.20, 131.10, 130.90, 128.02, 127.82, 126.95, 126.84, 120.78, 120.65. (b) Under nitrogen, a THF (50 mL) solution of **10** (0.99 g, 2.0 mmol) was dissolved in THF (50 mL) and the temperature was lowered to -78 °C. *n*-BuLi (2.4 mL, 2.5 M in hexane, 6.0 mmol) was slowly added to the mixture. After 1 h, $B(OCH_3)_3$ (1.15 mL, 10.0 mmol) was added slowly. The reaction mixture was stirred at -78 °C for 1 h and then warmed up to room temperature. After stirred for 8 h, the reaction mixture was quenched with saturated NH_4Cl solution (5 mL) and extracted with CH_2Cl_2 (3 x 30 mL). The combined organic layer was washed with brine (30 mL) and dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvent, the residue was purified by flash column chromatography on silica gel eluted with petroleum/ethyl acetate (5/1) to afford **11** as a white solid (0.47 g) in 49% yield. (c) Under nitrogen, compound **11** (500 mg, 1.05 mmol) was dissolved in DMF (20 mL) and water (6 mL). Compound **9** (660 mg, 2.1 mmol), K_2CO_3 (1.6 g, 11.6 mmol) and $Pd(PPh_3)_4$ (150 mg, 0.13 mmol) were added to the solution. After the reaction mixture was heated at 80 °C with stirring for 8 h, it was extracted with CH_2Cl_2 (3 x 30 mL). The combined organic layer was washed with brine (30 mL) and dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvent, the residue was purified by flash column chromatography on silica gel eluted with petroleum/ethyl acetate (5/1) to afford **4** as a light yellow solid in 27% yield (0.215 g). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.72-8.62 (m, 12H), 7.89-7.82 (m, 4H), 7.72-7.66 (m, 4H), 7.35-7.26 (m, 4H), 7.24-7.09 (m,14H). ^{13}C NMR ($CDCl_3$, 100 MHz) 156.31, 156.28, 155.85, 155.83, 149.99, 149.88, 149.13, 149.10, 144.67, 144.60, 143.45, 143.34, 140.94, 140.92, 136.89, 136.80, 136.54, 136.38, 131.98, 131.96, 131.45, 131.44, 127.99, 127.80, 126.91, 126.88, 126.72, 126.67, 123.82, 123.71, 121.35, 121.31, 118.84, 118.75. HR-MS (ES+) calculated for $C_{56}H_{38}N_6$ (M+H) 795.3231 and (M+Na) 817.3050, found 795.3235 and 817.30355.

*4.4. Preparation of Samples of **4**+Zn^{2+} (2.5 equiv) complex（ 1.0 × 10^{-5} M in THF:HEPES = 1:4）*

A portion (0.5 mL) of a stock solution of **4** (1.6 mg/1.0 mL, 2.0 mM in THF) was transferred to a 100 mL volumetric flask, to which was added a solution (100 μL) of $Zn(NO_3)_2$ (c = 74.4 mg/10 mL, 0.025 M in H_2O). Then, 20 mL THF was added and the flask was filled to 100 mL with a HEPES buffer solution.

4.5. Preparation of Samples for Job Plot (total concentration: 1.0 × 10^{-5} M in THF:HEPES = 1:1).

A stock solution of **4** (1.0 mg/1.0 mL, 1.25 mM in THF) and a stock solution of $Zn(NO_3)_2$ (1.5 mg/10.0 mL, 0.50 mM in HEPES) were prepared. These two stock solutions were mixed in 10 mL test tubes according to Table 2. Then 2.5 mL THF and 2.5 mL HEPES were added to the test tubes.

Table 2. Preparation of samples for Job Plot.

Sample No.	4(μL)	$Zn(NO_3)_2.6H_2O$(μL)
1	40	0
2	36	10
3	32	20
4	28	30
5	24	40
6	20	50
7	16	60
8	12	70
9	8	80
10	4	90

4.6. Preparation of samples for mass spectral analyses

A stock solution of **4** (1.6 mg/10.0 mL, 0.20 mM in CH_3CN) was prepared. A portion of this solution (5.0 mL) was transferred to another 10.0 mL volumetric flask to which was added a solution (300 μL) of $Zn(NO_3)_2$ (c = 15.0 mg/10 mL, 5.0 mM in H_2O). Then CH_3CN (3.0 mL) was added and the flask was filled with H_2O. Four potions of this solution (1.0 mL each) were combined with 0, 50, 100 and 150 μL of a histidine solution (c = 16.0 mg/10.0 mL, 10.0 mM in H_2O) respectively. The mass spectra of these solutions were then analyzed.

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Keywords: Histidine• Aggregation Induced Emission • Tetraphenylethene • Zn(II) • Fluorescence • Amino Acid

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