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ARTICLE TYPE

Tuning optical properties of phenanthroline derivatives through varying excitation wavelength and pH values

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Organic emissive materials equipped with tuneable optical properties have gained serious attention. Herein, two phenanthroline derivatives (ImPhTz and ImPhOz) have been prepared to possess an imidazole-thiadiazole/oxadiazole core and their tuneable emission behaviors have been investigated. As a result, ImPhTz is described with emission wavelengths spanning the visible region (λ_{em} = 481 – 611 nm) with different excitation wavelengths. The absorption (359 nm) and emission (478 nm) wavelengths of ImPhTz were red-shifted 52 nm and 93 nm when pH value increased from 1.70 to 13.29, respectively. It is worth noting that fluorescence quantum yields of ImPhTz did not reduce with the increase pH values. Thus, multicolor photoluminescence has been realized based on a single organic chromophore. In comparison, ImPhOz was less sensitive to environment stimulus because of lower degree of conjugation. Emission wavelength of ImPhOz is red-shifted 82 nm and 69 nm when the excitation wavelengths and pH values increased, respectively. Moreover, the maxima two photon absorption cross-section values of ImPhTz (190 GM) is also higher than ImPhOz (27 GM). In a word, the optical property of molecules equipped with thiadiazole may be more sensitive to environment than that of those equipped with oxadiazole.

1 Introduction

The discovery and development of novel organic emissive materials with dual and multiple photoresponses to exotic stimulus such as pH, temperature, light, or mechanical interaction has a lot of interests in both foundational researches and technical applications.[1-10] Although Kasha's rule has already predicted that fluorescence of organic emissive compounds should be independent on the excitation wavelength, several exceptional cases for polar molecules have been reported.[11-17] For example, benzobis(imidazolium) salts displayed red-shifted emission wavelengths and exhibited large multiphoton fluorescence action cross sections when the excitation wavelength increase.[12] In addition, the unsubstituted N-atom in imidazole is sensitive to pH and could induce pH-dependent fluorescence.[18-20] Although imidazole derivatives displayed many attractive optical properties, there are less reports to systematically study on excitation-wavelength or pH dependent optical properties based on this type of materials.

It is our interest to investigate the optical properties of multifuncional phenanthroline compounds: two phenanthroline derivatives containing imidazole and thiadiazole/oxadiazole (Chart 1). Although ImPhOz has been reported as an active element in organic light-emitting diodes (OLEDs),[21] the optical properties of ImPhOz tuned by excitation-wavelength or pH values are uncultured. On the other hand, Jansson et al. employed density functional theory to investigate a series of thiadiazole-based molecules as electron transportation materials and found that 2,5-diphenyl-1,3,4-thiadiazole displayed the stabilized LUMO levels and the 2,5-diphenyl-1,3,4-thiadiazole structure was the one closest to linearity compared to the triazole and oxadiazole analogues.[22] We are interested in the possibility to combine the advantages from imidazole and thiadiazole into one molecule to achieve multifunctional performances, which might have a broad applications in a lot of detection fields.

Herein, two phenanthroline derivatives containing imidazole and thiadiazole/oxadiazole have been successfully synthesized and their tuneable emission behaviors have been investigated. Our results show that both compounds exhibit three modes of pH sensitivity in the range of pH 1-14 due to the protonated, neutral, and deprotonated forms of imidazole with different emission wavelengths. Moreover, ImPhTz is described with emission wavelengths spanning the visible region (λ_{em} = 481 – 611 nm) with different excitation wavelengths.

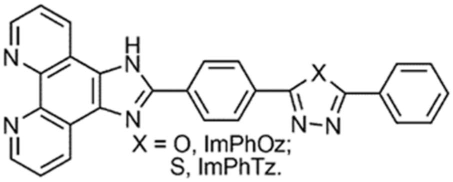


Chart 1 Chemical structures of ImPhOz and ImPhTz.

2 Experimental

2.1 Materials

Benzoylhydrazine, p-toluoyl chloride, 1,10-phenanthroline-5,6-dione, and lawesson's reagent were purchased from Tokyo chemical industry (TCI) company. Other chemicals and solvents were purchased from Sinopharm Chemical Reagent Co, Ltd.

2.2 General information

Using $CDCl_3$, CF_3COOD (TFA) or DMSO-d_6 as solvent and tetramethylsilane (TMS) as the internal standard, ^1H NMR and ^{13}C NMR spectra were measured on INOVA 300 or 400 MHz NMR spectrometer at ambient temperature. UV-vis absorption spectra were determined on a Shimadzu RF540 spectrophotometer. The emission and excitation spectra were carried out at room temperature through Edinburgh-920 fluorescence spectra photometer. The ground-state geometry of two compounds were optimized *via* the hybrid density functional theory (B3LYP) with the 6-31G* basis set using the Gaussian 03 program package.[23-25] The fluorescent quantum yields (QYs) of two compounds under acidic and neutral conditions were determined using quinine bisulfate ($\Phi_F = 0.546$ in 0.1 mol L^{-1} H_2SO_4) as standard, where under basic conditions fluorescein ($\Phi_F = 0.79$ in 0.1 mol L^{-1} NaOH) was used as standard.

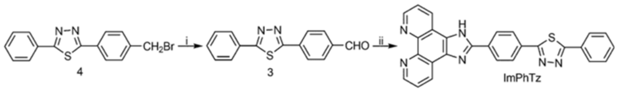
The two-photon excitation fluorescence (TPEF) measurements were performed using an Avesta femtosecond Ti: sapphire oscillator as the excitation source. The output laser pulses have a tuneable centre wavelength from 750 to 870 nm with pulse duration of 80 fs and a repetition rate of 85 MHz.[26] Two-photon absorption (TPA) cross sections were determined by the TPEF method and it is assumed that the quantum efficiencies after two-photon excitation were the same as those after one-photon excitation. The TPA cross sections were obtained by calibration against fluorescein with known $\Phi\delta$ value in aqueous NaOH solution (pH = 11) at concentrations of 1.0×10^{-4} mol L^{-1}. The samples were dissolved in solvents at the concentration of about 1.0×10^{-4} mol L^{-1}. The error of TPEF measurement is about 15 %. To ensure that the measured signals were sole due to TPA, the dependence of TPEF on the incident intensity was verified in each case to be quadratic. Then, the TPA cross section δ values were calculated on the basis of the following expression:

$$\delta_s = \delta_r \frac{C_r}{C_s}\frac{n_r}{n_s}\frac{F_s}{F_r}\frac{\Phi_r}{\Phi_s} \qquad (1)$$

where δ is TPA cross section, C and n are the concentration and refractive index of the sample solution, and F is the integrated area under the TPEF spectrum.

2.3 Synthesis

4-(5-phenyl-1,3,4-thiadiazol-2-yl)benzaldehyde was synthesized according to our previous report.[27] The synthesis of ImPhTz (Scheme 1) was similar to the reported method to prepare ImPhOz. The detailed characterizations were provided in supporting information.



Scheme 1 Synthesis of ImPhTz: (i) hexamethylenetetramine, $CHCl_3$, reflux; CH_3COOH, reflux, 40%; (ii) 1,10-phenanthroline-5,6-dione, CH_3COOH, CH_3COONH_4, reflux, 35%.

4-(5-phenyl-1,3,4-thiadiazol-2-yl)benzaldehyde (3)

2-(4-(bromomethyl)phenyl)-5-phenyl-1,3,4-thiadiazole 4 (3.3 g, 10 mmol) and hexamethylenetetramine (1.4 g, 10 mmol) were dissolved in dry $CHCl_3$ (75 mL) and heated to reflux for 2-3 h. Then, the mixture was cooled to room temperature and stirred for another 1.5 h. The precipitate was filtered off and was washed three times with $CHCl_3$. Then, the crude intermediate was mixed with 75 % glacial acetic acid (75 mL) and refluxed for 3 h. Then, the reaction mixture was filtered off and washed with 75% glacial acetic acid for three times to give 1.32 g, 4 mmol (yield, 40%) white solid.

^1H NMR (400 MHz, $CDCl_3$) δ 10.10 (s, 1H), 8.20 (d, J = 8.2 Hz, 2H), 8.03 (t, J = 6.7 Hz, 4H), 7.53 (d, J = 1.5 Hz, 3H).

^{13}C NMR (400 MHz, $CDCl_3$) δ 191.31, 169.22, 166.63, 137.78, 135.31, 131.54, 130.41, 129.82, 129.32, 128.45, 128.07.

2-(4-(1*H*-imidazo[4,5-*f*][1,10]phenanthrolin-2-yl)phenyl)-5-phenyl-1,3,4-thiadiazole (2)

A mixture of 4-(5-phenyl-1,3,4-thiadiazol-2-yl)benzaldehyde **3** (2.66 g, 10 mmol), 1,10-phenanthroline-5,6-dione (2.1 g, 10 mmol), ammonium acetate (15.4 g, 200 mmol) and glacial acetic acid (100 mL) was added to the flask and refluxed for 4 h, and then cooled to room temperature. The precipitate was collected, washed completely with H_2O for three times, and dried in vacuum. The yellow powder (1.60 g, 3.5 mmol, yield, 35%) was obtained.

^1H NMR (400 MHz, CF_3COOD) δ: 9.49 (s, 2H), 9.24 (s, 2H), 8.43 (s, 2H), 8.31 (d, J = 21.9 Hz, 4H), 7.95 (s, 2H), 7.75 (s, 1H), 7.60 (s, 2H).

^{13}C NMR (400 MHz, CF_3COOD) δ: 175.68, 166.69, 148.21, 146.56, 135.96, 135.39, 130.10, 129.40, 128.53, 128.35, 127.61, 126.19, 124.80, 124.49, 120.44, 118.63.

HRMS-ESI (m/z): $[M+H]^+$ Calcd for $C_{27}H_{17}N_6S$, 457.1230, found, 457.1230.

3 Results and discussion

3.1 One-photon optical properties

The absorption and emission spectra of ImPhTz and ImPhOz were recorded in DMF solution. As shown in Figure 1, the absorption spectrum of ImPhTz exhibits two prominent bands at 285 nm and 369 nm, which can be ascribed to the different π-conjugated moieties of the molecule. ImPhTz emits strong blue fluorescence with maxima peak at 479 nm (λ_{ex} = 370 nm), while the absorption spectrum of ImPhOz exhibits two prominent bands at 284 nm and 356 nm and emission wavelength is 442 nm (λ_{ex} = 360 nm). Changing oxygen to sulfur atom could shift the absorption and emission band to red region because of the different donor (D) - acceptor (A) interaction and degree of conjugation in two compounds. Generally, the more electronegative oxygen atom is expected to increase the D-A interaction and thus exhibits the lower band gap. However, experimental evidence shows the opposite trend due to the lower ionization potential of the heavier chalcogen atoms.[28-30] Furthermore, the conjugated degree of thiadiazole system is higher than the oxadiazole system according to literatures.[22, 31]

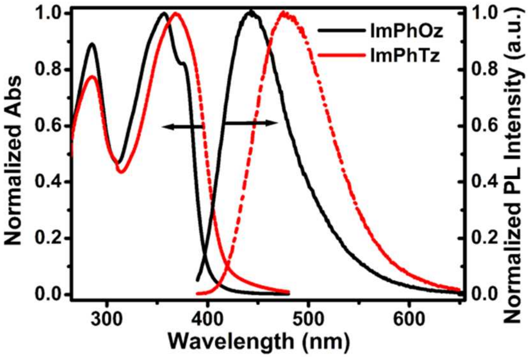


Figure 1 Normalized absorption and emission spectra of ImPhTz and ImPhOz in DMF solution. (λ_{ex} = 370 nm for ImPhTz and 360 nm for ImPhOz)

Table 1 Photophysical properties of ImPhTz and ImPhOz in DMF.

Samples	λ_{abs} [a]	λ_{em} [b]	λ_{em} [c]	ε [d]	φ [e]	δ_{max} [f]
ImPhTz	285, 369	$479^{g}/611^{h}$	$456^{i}/524^{j}$	3.79×10^{-4}	0.56	190
ImPhOz	284, 356	$442^{k}/524^{l}$	$444^{m}/456^{n}$	3.12×10^{-4}	0.53	27

a, b and c is one-photon absorption, one-photon and two-photon fluorescence maxima peak (nm), respectively. d is molar absorption coefficient, mol^{-1} L cm^{-1}. e is fluorescence quantum yield. f is the maximum two-photon cross section (GM). g-n is different excitation wavelength (370, 450, 770, 860, 360, 430, 765 and 860 nm, respectively)

3.2 Red-Edge Effect

A red-edge effect (REE) refers to the shifting of emission wavelength to longer wavelengths in response to increase the excitation wavelength. Multiple polar organic fluorophores including imidazole derivatives have been found to exhibit REEs, and these phenomena have been found a lot of applications. As shown in Figure 2, the emission wavelength of ImPhTz was red-shifted from 479 nm to 611 nm when the excitation wavelength was increased from 390 nm to 450 nm. In comparison to ImPhTz, ImPhOz is less sensitive to the change of excitation wavelength. The red-shifted wavelength (132 nm) in ImPhTz is higher than that of ImPhOz (82 nm). Upon increasing the excitation wavelength for ImPhOz, the PL intensity of the short-wavelength band at 442 nm decreased while the PL intensity of the long-wavelength band at 524 nm increases. The mechanism of the REEs in imidazole derivatives is not entirely understood. Its origins might involve different ground-state orientations of the associated species. In our systems, the different degree of conjugation in two compounds might response to the red-shifted emission when the excitation wavelength changed.

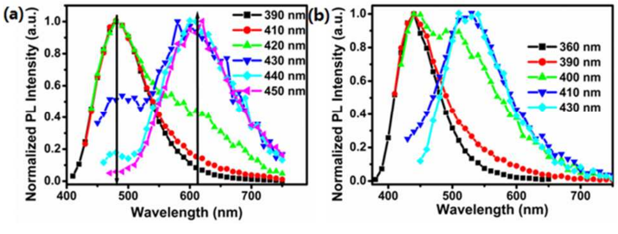


Figure 2 Emission spectra of (a) ImPhTz and (b) ImPhOz in DMF solution with increasing the excitation wavelength.

33 Two-photon optical properties

Two-photon absorption spectra of ImPhTz and ImPhOz were measured using TPEF method, in which excitation wavelength was adjusted from 760 to 840 nm. The two-photon cross sections of two compounds with the same concentration in DMF at different excitation wavelength were shown in Figure 3. The maximum two photon absorption cross-section values of ImPhTz and ImPhOz are 190 GM and 27 GM, respectively. The difference between two compounds might come from the different D-A interaction. In addition, the degree of conjugation of ImPhTz is higher than ImPhOz, which could be also responsible for the large cross-section.

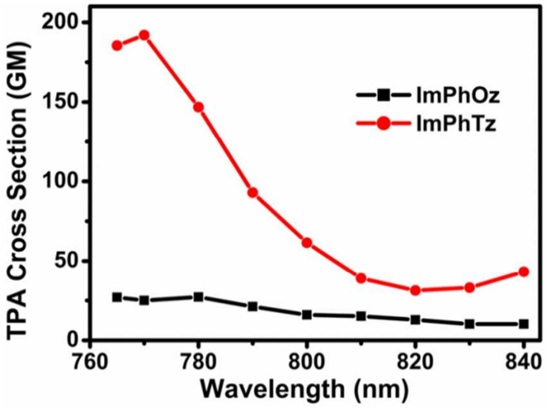


Figure 3 TPA spectra of ImPhTz and ImPhOz in DMF solution.

Normalized two-photon emission (TPL) spectra of two compounds were shown in Figure 4. Upon increasing the excitation wavelength, TPL wavelengths were red-shifted only 10 nm for ImPhOZ but 68 nm for ImPhTz. There might be two reasons to explain this: first, due to the limitation of our detecting equipment, we cannot measure the two-photon emission spectra with longer excitation wavelength because the emission peaks may be red-shifted to the wavelength more than 860 nm and, second, the emission could occur from the different state of one-photon and two-photon excitation.

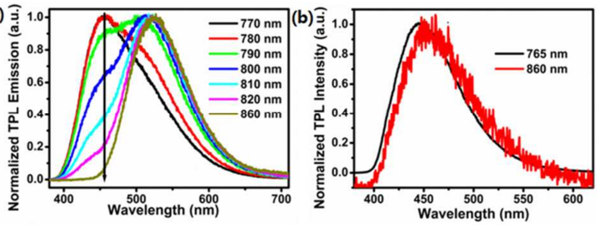


Figure 4 TPF spectra of (a) ImPhTz and (b) ImPhOz with increasing the excited wavelength.

3.4 pH-dependent optical properties

For the analysis of pH-dependent properties, the absorption and emission spectra of two compounds were recorded in DMF/water (9:1, by volume) with pH values change from 1.0 to 14.0. For compound ImPhTz, at lower pH value, the absorption wavelength changed from 359 nm (pH = 1.70) to 369 nm (pH = 3.94) with an isosbestic point at 369 nm. The absorption wavelength didn't show any change when pH value was between 3.94 and 7.82. However, when the solution became more basic, the absorption wavelength continued to be red-shifted from 369 nm at pH = 7.82 to 411 nm at pH = 13.29. These phenomena suggested the existence of three states, which could be assigned as the protonated, neutral, deprotonated forms of imidazole (Scheme 2).

Interestingly, under acidic conditions, the emission wavelength of ImPhTz didn't show any change (λ_{ex} = 370 nm). However, under basic conditions, when the emission wavelength (λ_{ex} = 370 nm) increased from 479 nm (pH = 7.33) to 581 nm (pH = 13.29). It is worthy to note that QYs of ImPhTz did not reduce with the increase pH value (Table 2). These results could be explained as following: in an acidic environment, imidazole group was protonated, which was more electron-withdrawing than that under neutral conditions, while under basic condition, deprotonated imidazole group could serve as electron donors. This conclusion was further confirmed by density functional theory (DFT) calculation.

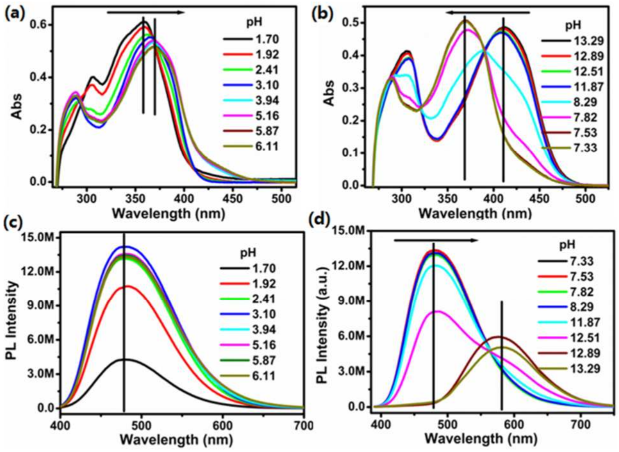
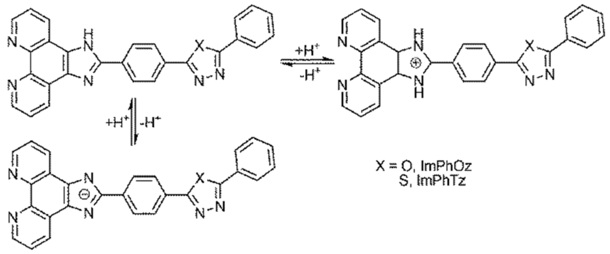


Figure 5 Absorption (a, b) and emission (c, d) spectra of ImPhTz under acidic (a, c) and basic (b, d) conditions in DMF/water (v: v = 9: 1) with the excitation wavelength 370 nm.



Scheme 2. Proposed mechanism of two compounds under acidic, neutral, and basic conditions.

The phenomena of ImPhOz were similar to ImPhTz. However, the absorption wavelength was red-shifted 50 nm from 343 nm (pH = 1.70) to 356 nm (pH = 3.94-7.82) to 393 nm (pH = 13.29) and emission wavelength was red-shifted 69 nm from 440 nm (pH = 1.70) to 509 nm (pH = 13.29). In a word, ImPhTz was more sensitive to environment stimulus due to thiadiazole.

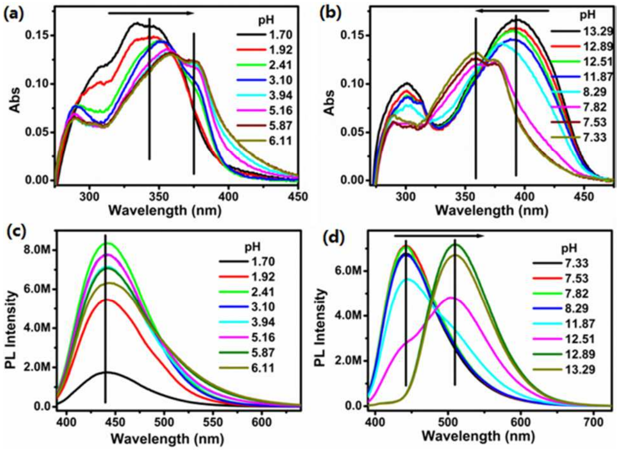


Figure 6 Absorption (a, b) and emission (c, d) spectra of ImPhOz under acidic (a, c) and basic (b, d) conditions in DMF/water (v: v = 9: 1) with the excitation wavelength 360 nm.

Table 2 Photophysical properties of ImPhTz and ImPhOz in different pH DMF/H_2O solution

Samples	λ_{abs}^{a}	λ_{em}^{b}	$\Delta\lambda^{c}$	φ^{d}
ImPhTz	369	479	110	0.56
ImPhTzH+	359	478	119	0.55
ImPhTzH-	411	581	170	0.58
ImPhOz	356	442	86	0.53
ImPhOzH+	343	440	97	0.52
ImPhOzH-	393	509	116	0.57

a is Uv/vis absorption (nm), b is photon fluorescence maxima peak (nm), c is stoke shifted (nm), d is fluorescence quantum yield.

3.5 Calculation

The ground-state geometries of two compounds were optimized *via* the density functional theory (B3LYP) with 6-31G* basis set using the Gaussian 03 program package. The energies of HOMO and LUMO orbitals of two compounds under acidic, neutral, and basic conditions are shown in Figure 7/8. The electron density distributions of two compounds change very little between the HOMO and LUMO under neutral condition. The HOMOs are localized mainly on the imidazole and phenanthroline while the LUMOs are mainly centred on 1,3,4-oxadiazole and 1,3,4-thiadiazole, respectively. In an acidic environment, imidazole group was protonated, thus it was more electron-withdrawing than that under neutral conditions. Thus, the electron density distributions of two compounds on LUMO orbits are mainly concentrated on imidazole. However, under basic condition, deprotonated imidazole group served as electron donors, the electron density distributions of two compounds on HOMO orbits are mainly concentrated on imidazole.

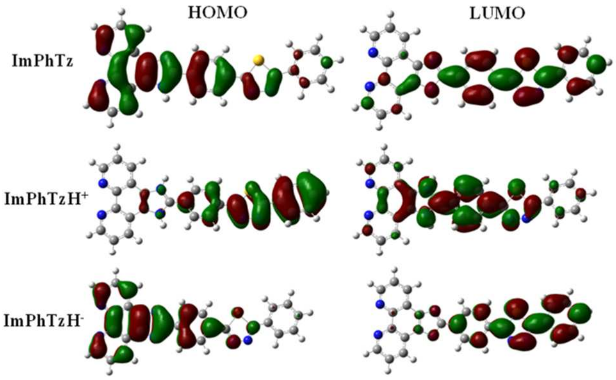


Figure 7 DFT molecular simulation results: HOMO and LUMO of ImPhTz under acidic, neutral, and basic conditions.

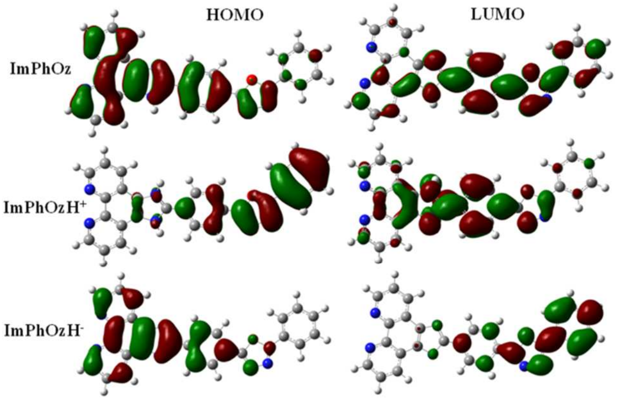


Figure 8 DFT molecular simulation results: HOMO and LUMO of ImPhOz under acidic, neutral, and basic conditions.

4 Conclusions

In this work, two multifunctional 1,10-phenanthroline derivatives have been successfully synthesized and characterized. Emission wavelength of both ImPhOz and ImPhTz was red-shifted when the excitation wavelength was changed. Upon increasing the excitation wavelength, TPL wavelength were red-shifted only 12 nm for ImPhOz but 68 nm for ImPhTz. Absorption and emission wavelength for both compounds were also red-shifted when pH values changed from 1.70 to 13.29. In comparison, ImPhTz was more sensitive to environment stimulus. The absorption and emission wavelength were also red-shifted 52 nm and 93 nm when pH value changed from 1.70 to 13.29, respectively. The maxima TPA cross-section value of ImPhTz (190 GM) was also higher than that of ImPhOz (27 GM). In a word, the fluorescence of molecules equipped with thiadiazole group may be more sensitive to environment than that of those equipped with oxadiazole group.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [details of synthesis and characterizations of ImPhOz and 2-(4-(bromomethyl)phenyl)-5-phenyl-1,3,4-thiadiazole]. See DOI: 10.1039/b000000x/

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