Journal of
Materials Chemistry C

PAPER

Cite this: *J. Mater. Chem. C*, 2014, **2**, 1539

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

Pei-Yang Gu,[a] Junkuo Gao,[b] Qichun Zhang,[b] Gaoyan Liu,[a] Feng Zhou,[a] Qing-Feng Xu*[a] and Jian-Mei Lu*[a]

Received 13th October 2013
Accepted 19th November 2013

DOI: 10.1039/c3tc32025a

www.rsc.org/MaterialsC

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 the pH value increased from 1.70 to 13.29, respectively. It is worth noting that the fluorescence quantum yields of ImPhTz did not reduce with the increase in pH values. Thus, multicolor photoluminescence has been achieved based on a single organic chromophore. Comparatively, ImPhOz was less sensitive to environmental stimulus due to a lower degree of conjugation. The emission wavelength of ImPhOz is red-shifted 82 nm and 69 nm when the excitation wavelengths and pH values increased, respectively. Moreover, the maximum two photon absorption cross-section value of ImPhTz (190 GM) is also higher than ImPhOz (27 GM). In other words, the optical properties of molecules equipped with thiadiazole may be more sensitive to the environment than those equipped with oxadiazole.

1 Introduction

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

It is our interest to investigate the optical properties of multifunctional phenanthroline compounds: two phenanthroline derivatives containing imidazole and thiadiazole/oxadiazole (Chart 1). Although ImPhOz has been reported to be an active element in organic light-emitting diodes (OLEDs),[21] the optical properties of ImPhOz tuned by excitation wavelengths or pH values have not been determined. On the other hand, Jansson *et al.* employed density functional theory to investigate a series of thiadiazole-based molecules as electron transport materials and found that 2,5-diphenyl-1,3,4-thiadiazole displayed stabilized LUMO levels and its structure was the one closest to linearity when compared to the triazole and oxadiazole analogues.[22] We are interested in

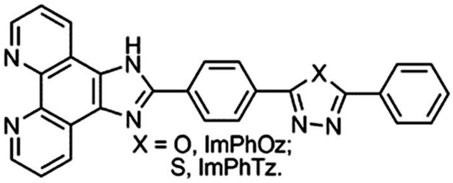


Chart 1 Chemical structures of ImPhOz and ImPhTz.

---

[a] College of Chemistry, Chemical Engineering and Materials Science, Collaborative Innovation Center of Suzhou Nano Science and Technology, Soochow University, Suzhou 215123, China. E-mail: lujm@suda.edu.cn; xuqingfeng@suda.edu.cn; Fax: +86 512 65880367; Tel: +86 512 65880368

[b] School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore

† Electronic supplementary information (ESI) available: Details of the synthesis and characterization of ImPhOz and 2-(4-(bromomethyl)phenyl)-5-phenyl-1,3,4-thiadiazole. See DOI: 10.1039/c3tc32025a

the possibility of combining the advantages of imidazole and thiadiazole into one molecule to achieve multifunctional performance, which might have 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.

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 the solvent and tetramethylsilane (TMS) as the internal standard, ^1H NMR and ^{13}C NMR spectra were measured on an 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 produced at room temperature using an Edinburgh-920 fluorescence spectra photometer. The ground-state geometry of the two compounds was 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 the two compounds under acidic and neutral conditions were determined using quinine bisulfate (Φ_F = 0.546 in 0.1 mol L^{-1} H_2SO_4) as the standard, whereas under basic conditions fluorescein (Φ_F = 0.79 in 0.1 mol L^{-1} NaOH) was used as the 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 a 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 efficiency after two-photon excitation was the same as those after one-photon excitation. The TPA cross sections were obtained by calibration against fluorescein with a 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 a concentration of about 1.0×10^{-4} mol L^{-1}. The error in TPEF measurements is about 15%. To ensure that the measured signals were solely 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:

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

where δ is the TPA cross section, C and n are the concentration and refractive index of the sample solution respectively, 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 for ImPhOz. The detailed characterizations are provided in the ESI.†

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. The mixture was then cooled to room temperature and stirred for another 1.5 h. The precipitate was filtered off and washed three times with $CHCl_3$. The crude intermediate was then mixed with 75% glacial acetic acid (75 mL) and refluxed for 3 h. The reaction mixture was subsequently filtered off and washed with 75% glacial acetic acid 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).

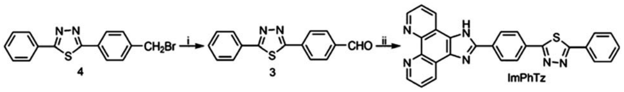
^{13}C NMR (400 MHz, $CDCl_3$) δ: 191.31, 169.22, 166.63, 137.78, 135.31, 131.54, 130.41, 129.82, 129.32, 128.45, 128.07.

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 three times, and dried under vacuum. A 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 (Table 1).



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%.

Table 1 Photophysical properties of ImPhTz and ImPhOz in DMF[a]

Samples	$\lambda_{abs}{}^{a}$	$\lambda_{em}{}^{b}$	$\lambda_{em}{}^{c}$	ε^{d}	φ^{e}	$\delta_{max}{}^{f}$
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] (a–c) are one-photon absorption, one-photon and two-photon fluorescence maxima peaks (nm), respectively; (d) is the molar absorption coefficient, $\mathrm{mol^{-1}\ L\ cm^{-1}}$; (e) is the fluorescence quantum yield; (f) is the maximum two-photon cross section (GM) and (g–n) are the different excitation wavelengths (370, 450, 770, 860, 360, 430, 765 and 860 nm, respectively).

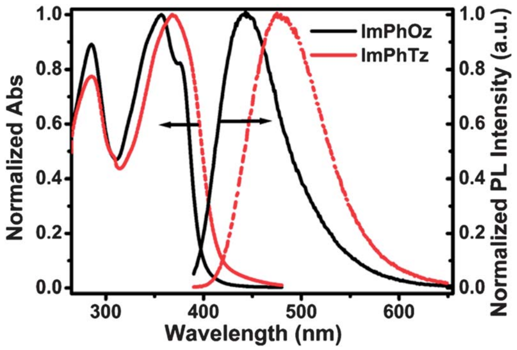


Fig. 1 Normalized absorption and emission spectra of ImPhTz and ImPhOz in DMF solution (λ_{ex} = 370 nm for ImPhTz and 360 nm for ImPhOz).

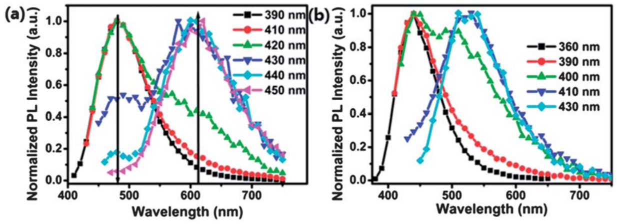


Fig. 2 Emission spectra of (a) ImPhTz and (b) ImPhOz in DMF solution with increasing excitation wavelength.

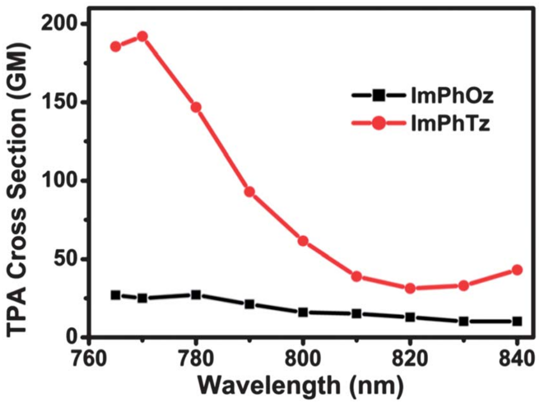


Fig. 3 TPA spectra of ImPhTz and ImPhOz in DMF solution.

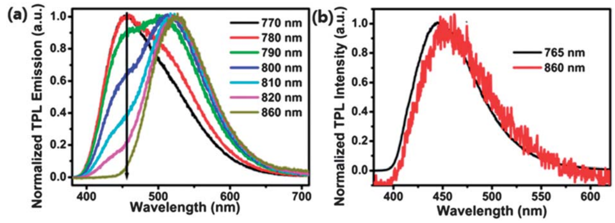


Fig. 4 TPF spectra of (a) ImPhTz and (b) ImPhOz with increasing excitation wavelength.

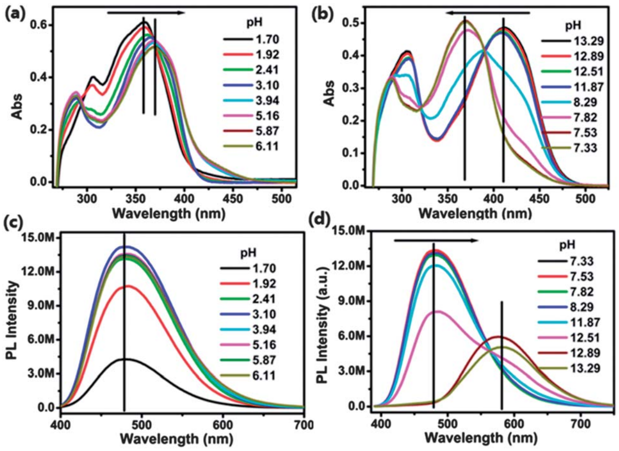


Fig. 5 Absorption (a and b) and emission (c and d) spectra of ImPhTz under acidic (a and c) and basic (b and d) conditions in DMF–water (v/v = 9 : 1) with an excitation wavelength of 370 nm.

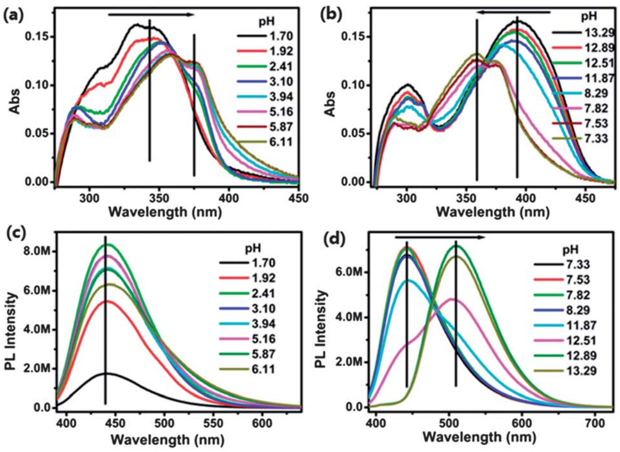
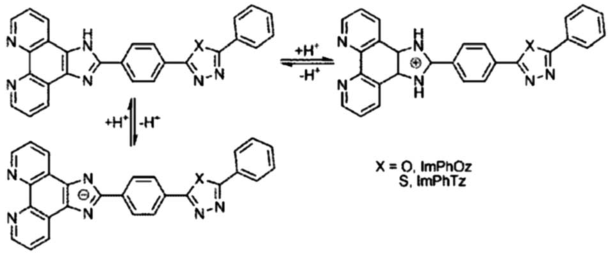


Fig. 6 Absorption (a and b) and emission (c and d) spectra of ImPhOz under acidic (a and c) and basic (b and d) conditions in DMF–water (v/v = 9 : 1) with an excitation wavelength of 360 nm.

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 Fig. 1, the absorption spectrum of ImPhTz exhibits two prominent bands at 285 nm and



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

Table 2 Photophysical properties of ImPhTz and ImPhOz in different pH DMF–H_2O solutions

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] UV-vis absorption (nm). [b] Photon fluorescence maxima peak (nm). [c] Stoke shifted (nm). [d] Fluorescence quantum yield (Fig. 6).

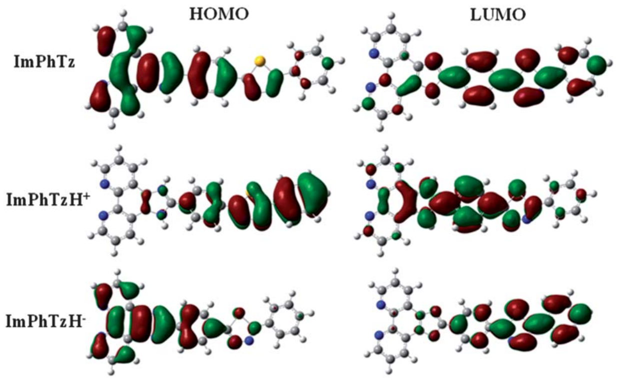


Fig. 7 DFT molecular simulation results: HOMO and LUMO of ImPhTz under acidic, neutral, and basic conditions.

369 nm, which can be ascribed to the different π-conjugated moieties of the molecule. ImPhTz emits strong blue fluorescence with a maximum 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 its emission wavelength is 442 nm (λ_{ex} = 360 nm). Changing oxygen to a sulfur atom could shift the absorption and emission band to the red region because of the different donor (D)–acceptor (A) interactions and the degree of conjugation in the two compounds. Generally, the more electronegative oxygen atom is expected to increase the D–A interaction and thus exhibit a 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 the thiadiazole system is higher than the oxadiazole system according to previous literature.[22,31]

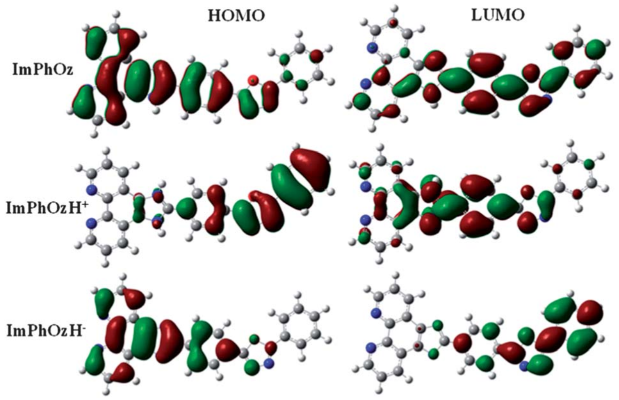


Fig. 8 DFT molecular simulation results: HOMO and LUMO of ImPhOz under acidic, neutral, and basic conditions.

3.2 Red-edge effect

A red-edge effect (REE) refers to the shifting of emission wavelength to longer wavelengths in response to an increase in the excitation wavelength. Multiple polar organic fluorophores including imidazole derivatives have been found to exhibit REEs, and this phenomenon has found a lot of applications. As shown in Fig. 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 in 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 increased. 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 difference in degree of conjugation in the two compounds might respond to the red-shifted emission when the excitation wavelength changes.

3.3 Two-photon optical properties

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

The normalized two-photon emission (TPL) spectra of the two compounds are shown in Fig. 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 limitations in our detecting equipment, we cannot measure two-photon emission spectra with longer excitation wavelengths because the emission peaks may be red-shifted to a wavelength more than 860 nm and, second, the emission may occur due to the different state of the one-photon and two-photon excitation (Fig. 5).

3.4 pH-dependent optical properties

For the analysis of pH-dependent properties, the absorption and emission spectra of the two compounds were recorded in DMF–water (9 : 1, by volume) with pH values changing from 1.0 to 14.0. For compound ImPhTz, at lower pH values, 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 the 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 suggest the existence of three states, which can be assigned as the protonated, neutral and deprotonated forms of imidazole (Scheme 2).

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

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 the emission wavelength was red-shifted 69 nm from 440 nm (pH = 1.70) to 509 nm (pH = 13.29). In other words, ImPhTz was more sensitive to environmental stimuli due to thiadiazole.

3.5 Calculation

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

4 Conclusions

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

Acknowledgements

The authors graciously thank Prof. Qing-Hua Xu (National University of Singapore) for such beneficial discussions and Dr Tingting Zhao (National University of Singapore) for the two-photon excitation fluorescence (TPEF) measurements. The authors graciously thank the Chinese Natural Science Foundation (21071105, 21371128 and 21336005), Chinese-Singapore Joint Project (2012DFG41900) and the Specialized Research Fund for the Doctoral Program of Higher Education of China (grant no. 20113201130003).

Notes and references

1 Q. Li, Y. He, J. Chang, L. Wang, H. Chen, Y. W. Tan, H. Wang and Z. Shao, *J. Am. Chem. Soc.*, 2013, **135**, 14924.

2 Q. Zhang, D. H. Qu, X. Ma and H. Tian, *Chem. Commun.*, 2013, **49**, 9800.

3 J. Olejniczak, J. Sankaranarayanan, M. L. Viger and A. Almutairi, *ACS Macro Lett.*, 2013, **2**, 683.

4 G. Zhang, S. E. Kooi, J. N. Demas and C. L. Fraser, *Adv. Mater.*, 2008, **20**, 2099.

5 Y. Sagara and T. Kato, *Angew. Chem., Int. Ed.*, 2011, **50**, 9128.

6 D. A. Davis, A. Hamilton, J. Yang, L. D. Cremar, D. Van Gough, S. L. Potisek, M. T. Ong, P. V. Braun, T. J. Martinez, S. R. White, J. S. Moore and N. R. Sottos, *Nature*, 2009, **459**, 68.

7 Y. Ooyama and Y. Harima, *J. Mater. Chem.*, 2011, **21**, 8372.

8 M. Teng, X. Jia, X. Chen, Z. Ma and Y. Wei, *Chem. Commun.*, 2011, **47**, 6078.

9 G. Zhang, J. Lu and C. L. Fraser, *Inorg. Chem.*, 2010, **49**, 10747.

10 P. Y. Gu, Y. H. Zhang, G. Y. Liu, J. F. Ge, Q. F. Xu, Q. Zhang and J. M. Lu, *Chem.–Asian J.*, 2013, **8**, 2161.

11 Z. Hu and C. J. Margulis, *Acc. Chem. Res.*, 2007, **40**, 1097.

12 X.-J. Zhou, C. Chen, C.-X. Ren, J.-K. Sun and J. Zhang, *J. Mater. Chem. C*, 2013, **1**, 744.

13 X. H. Jin, C. X. Ren, J. K. Sun, X. J. Zhou, L. X. Cai and J. Zhang, *Chem. Commun.*, 2012, **48**, 10422.

14 A. P. Demchenko, *Luminescence*, 2002, **17**, 19.

15 J. Liu, Y. Zhong, J. W. Y. Lam, P. Lu, Y. Hong, Y. Yu, Y. Yue, M. Faisal, H. H. Y. Sung, I. D. Williams, K. S. Wong and B. Z. Tang, *Macromolecules*, 2010, **43**, 4921.

16 M. Józefowicz and J. R. Heldt, *J. Fluoresc.*, 2010, **21**, 239.

17 M. Józefowicz, M. Aleksiejew, J. R. Heldt, A. Bajorek, J. Pączkowski and J. Heldt, *Chem. Phys.*, 2007, **338**, 53.

18 M. Y. Berezin, J. Kao and S. Achilefu, *Chem.–Eur. J.*, 2009, **15**, 3560.

19 J. Dong, K. M. Solntsev, O. Poizat and L. M. Tolbert, *J. Am. Chem. Soc.*, 2007, **129**, 10084.

20 N. Saleh, Y. A. Al-Soud and W. M. Nau, *Spectrochim. Acta, Part A*, 2008, **71**, 818.

21 H. Tang, H. Tang, Z. Zhang, J. Yuan, C. Cong and K. Zhang, *Synth. Met.*, 2009, **159**, 72.

22 E. Jansson, P. C. Jha and H. Agren, *Chem. Phys.*, 2006, **330**, 166.

23 S. Kim, Q. Zheng, G. S. He, D. J. Bharali, H. E. Pudavar, A. Baev and P. N. Prasad, *Adv. Funct. Mater.*, 2006, **16**, 2317.

24 P.-Y. Gu, C.-J. Lu, Z.-J. Hu, N.-J. Li, T.-t. Zhao, Q.-F. Xu, Q.-H. Xu, J.-D. Zhang and J.-M. Lu, *J. Mater. Chem. C*, 2013, **1**, 2599.

25 Y. Zhang, J. Sun, G. Bian, Y. Chen, M. Ouyang, B. Hu and C. Zhang, *Photochem. Photobiol. Sci.*, 2012, **11**, 1414.

26 C. Xu and W. W. Webb, *J. Opt. Soc. Am. B*, 1996, **13**, 481.

27 Y. Tao, Q. Xu, J. Lu and X. Yang, *Dyes Pigm.*, 2010, **84**, 153.

28 G. L. Gibson, T. M. McCormick and D. S. Seferos, *J. Am. Chem. Soc.*, 2012, **134**, 539.

29 J. J. Bryant, B. D. Lindner and U. H. Bunz, *J. Chem. Phys.*, 2013, **78**, 1038.

30 S. Das, P. B. Pati and S. S. Zade, *Macromolecules*, 2012, **45**, 5410.

31 A. Garzon, J. M. Granadino-Roldan, M. Moral, G. Garcia, M. P. Fernandez-Liencres, A. Navarro, T. Pena-Ruiz and M. Fernandez-Gomez, *J. Chem. Phys.*, 2010, **132**, 064901.