Dalton Transactions

Cite this: *Dalton Trans.*, 2012, **41**, 13292

www.rsc.org/dalton

PAPER

A ruthenium(II) complex with environment-responsive dual emission and its application in the detection of cysteine/homocysteine†

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Received 1st June 2012, Accepted 10th July 2012
DOI: 10.1039/c2dt31180a

A ruthenium polypyridine complex $[Ru(phen)_2(IPBA)](PF_6)_2$ (complex **1**) (IPBA = 4-(1*H*-imidazo[4,5-*f*]-[1,9]phenanthroline-2-yl)benzaldehyde), which displays environment-responsive dual emissive properties, was designed and synthesized. In aprotic solvent, such as DMSO, DMF or CH_3CN, the complex emits strong cyan light. When in protic solvent, it emits orange light. Similarly, the response of the complex to homocysteine and cysteine (Hcy/Cys) also shows obvious solvent dependence. TDDFT calculations reveal that the protonation of imidazole nitrogen in protic solution is responsible for the luminescent red shift. Hence, the complex could be used to detect Hcy/Cys in aprotic solvent, as well as in protic solvent.

Introduction

The use of phosphorescent heavy-metal complexes as chemosensors and bioimaging probes has recently attracted considerable interest,[1] because of advantageous photophysical properties such as high luminescence efficiency, tunable excitation and emission wavelength over the whole visible range, significant Stokes shifts, and relatively long lifetimes. As one of the best families of phosphorescent dyes, ruthenium complexes, particularly ruthenium polypyridine complexes, have attracted widespread interest due to their abundant optical-property-based MLCT. They have been studied in many fields, such as chemical sensors,[2–10] chemistry analysis,[11–13] catalyzation,[14] electroluminescent devices,[15–20] DNA structure probes,[21–26] and so on. Many ruthenium complexes with different properties have already been synthesized and utilized. Most reported ruthenium complexes emit red light attributed to ^{3}MLCT at room temperature.[2–7,11,18–23] Their emissive states are insensitive to their ligands and local environment.

Until now, the development of ruthenium complexes that display environment-responsive dual emissive properties under ambient conditions has not been reported. It has, however, been reported that iridium(III) complexes with environment-responsive dual emissive properties could be used as luminescent biosensors.[27] Establishing the relationship between the structure and properties of ruthenium complexes is still one of the crucial problems for the chemical scientist. As reported here, a ruthenium polypyridine complex $[Ru(phen)_2(IPBA)](PF_6)_2$ (**1**) (IPBA = 4-(1*H*-imidazo[4,5-*f*][1,9]phenanthroline-2-yl)benzaldehyde), having environment-responsive dual emissive properties, has been designed and synthesized.

The thiol-containing amino acids homocysteine (Hcy) and cysteine (Cys) are essential biological molecules and play a crucial multidimensional role in maintaining biological redox homeostasis. An abnormal level of Hcy in plasma is an indicator of various disorders, including cardiovascular and Alzheimer's disease, osteoporosis, *etc*.[28] Cys deficiency has been linked to slowed growth in children, liver damage, muscle and fat loss, skin lesions, and weakness.[29] Great effort has gone into the detection of Hcy and Cys, including by high performance liquid chromatography,[30–33] capillary electrophoresis,[34] electrochemical detection,[35–37] and optical detection.[38] Due to the simple, easy operation and high sensitivity, fluorescence technologies have been applied for the specific detection of Hcy and Cys over the past decade. Sensing approaches include indicator displacement assays (IDA),[39–41] cyclization with aldehyde,[42–47] thiolysis of sulfonate ester[48] sulfonamide,[49] cleavage of selenium–nitrogen bonds by thiols,[50] cleavage of disulfide by thiols[51,52] and others.[53] However, most of these approaches are limited to fluorescent detection based on organic dyes as probes. Ruthenium complexes as Hcy/Cys sensors are still limited. Recently, Yuan reported a ruthenium complex as a turn-on luminescent probe for Cys/Hcy.[54] Herein, we report a novel dual-responsive Cys/Hcy sensor based on the cyclization with aldehyde of a ruthenium complex $[Ru(phen)_2(IPBA)](PF_6)_2$ (**1**) (IPBA = 4-(1*H*-imidazo[4,5-*f*][1,9]phenanthroline-2-yl)benzaldehyde) (Scheme 1). As expected, the complex might preferentially react with Hcy/Cys over other amino acids, as confirmed by luminescence spectra, absorption spectra, ^{1}H NMR spectra and ESI.

Results and discussion

Photophysical properties of 1

The absorption spectrum (Fig. 1) of **1** shows intense high-energy absorption bands at approximately 270–300 nm, assigned to

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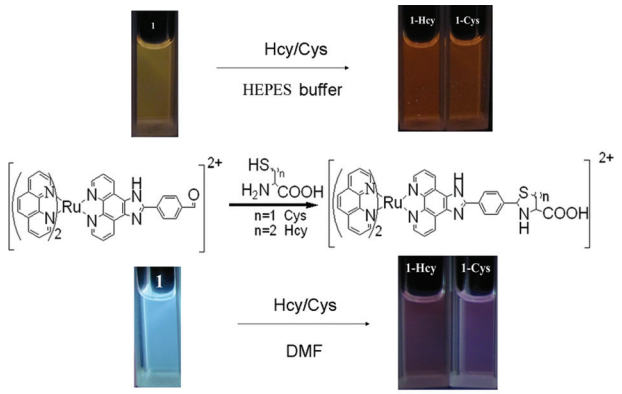
†Electronic supplementary information (ESI) available: Absorption and emission spectra and ESI mass spectra. See DOI: 10.1039/c2dt31180a



Scheme 1

Scheme 1 The proposed response mechanism of complex **1** with Hcy/Cys and the photoluminescence in different solvents.

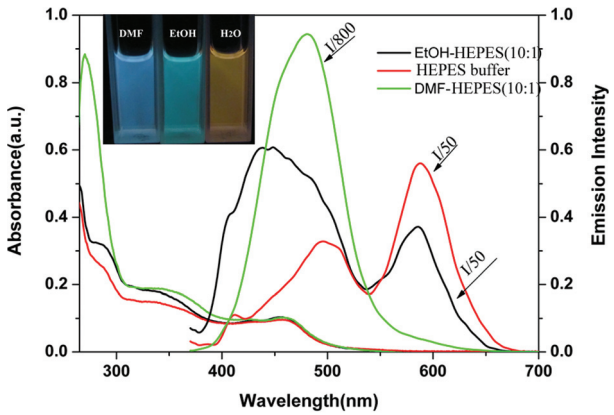


Figure 1

Fig. 1 The absorption and emission spectra of **1** in different solvents. For comparison, the intensities in DMF were divided by 800, while the intensities in EtOH and HEPES buffer were divided by 50.

intraligand π–π* transition, medium absorption bands at 300–370 nm, assigned to intraligand n–π* (CHO on IPBA), and weak absorption bands at 400–470 nm, assigned to spin-allowed metal-to-ligand charge-transfer (MLCT) transitions with reference to previous photophysical studies on related ruthenium(III) diimine systems[55–57] and the control complex $[Ru(phen)_2(PMIP)](PF_6)_2$ (**2**) (PMIP = 2-(4-methylphenyl)imidazo[4,5-*f*]-1,10-phenanthroline)[58] (Fig. S1, ESI†). In protic solvent, the bands assigned to intraligand n–π* at 300–370 nm show a blue-shift and hypochromicity. It is possible that hydrogen bonds form between the aldehyde group and protic solvent.[59] In contrast, the bands derived from the MLCT transition are more stable, and are not affected by solvents.

Upon irradiation, **1** exhibited intense luminescence in fluid solutions (Fig. 1 and Fig. S2, ESI†). The photophysical data are listed in Table 1. Interestingly, it shows dual emission peaks with a high-energy (HE) structured band at about 440–500 nm and a low-energy (LE) band at approximately 600 nm. Similarly, room temperature luminescence of **1** also depends on the type of solvent used (Fig. S2, ESI†). In aprotic solvents, such as DMF, DMSO or CH_3CN, the emission intensity of the HE band is much higher than that of the LE band, with strong light in the cyan range (Φ = 0.038 in DMF), while in protic solvents, such as EtOH, the HE band becomes much weaker, and the LE band is much higher (Φ = 0.023 in EtOH). In aqueous buffer, the emission intensity of the HE band is comparable to that of the LE band (Φ = 0.003 in H_2O), with an orange emission light. With increasing solvent polarity, the HE band shifts to red from 440 nm in EtOH to 495 nm in the HEPES buffer. Interestingly, an analogue complex **2** does not display dual emission in aqueous solution (Fig. S3, ESI†). The only broad band of this complex (at around 550–650 nm) is assigned to a charge-transfer (CT) state of mixed ^{3}MLCT and ligand-to-ligand charge-transfer (^{3}LLCT) character. The effect of the solvent hydrophilicity on the luminescent spectrum indicates hydrogen bonding between solute and solvent formed because hydrogen bonding presumably enhances intersystem crossing.[60] On the basis of the spectral profiles, emission wavelengths, and lifetimes of the two bands of **1** (Table 1), we have tentatively assigned (1) the HE band to a singlet intraligand IL (π–π*) excited state,[59] and (2) the LE feature to an excited state with high ^{3}MLCT/^{3}LLCT character. The luminescence properties indicate that the aprotic solvent is unfavorable for intersystem crossing (ISC) and prohibits the phosphorescence of the complex.

Table 1 Photophysical properties of **1**, **1**-Cys and **1**-Hcy in different solvents at 298 K

Complex	Solvent	λ_{em}/nm	τ/ns
1	DMF	480	2.2 (χ^2 = 1.017)
	HEPES buffer	495	0.88 (84.46%), 4.88 (15.54%) (χ^2 = 1.062)
		588	352, 575 (χ^2 = 1.135)
1-Cys	DMF	428	1.61, 7.45 (χ^2 = 1.115)
	HEPES buffer	588	438, 754 (χ^2 = 1.12)
1-Hcy	DMF	428	1.70, 9.60 (χ^2 = 1.061)
	HEPES buffer	588	406, 739 (χ^2 = 1.079)

Solvent-dependent luminescent response of 1 to Cys/Hcy. The luminescent response of **1** to Hcy/Cys shows solvent dependence (Fig. 2). In DMF–HEPES buffer (10 : 1, v/v), probe **1** (4.5 μM) shows a very strong fluorescence at 480 nm. However, upon addition of Cys/Hcy, the fluorescence intensity decreases remarkably, and blue-shifts to 428 nm, corresponding to a change in photo color from cyan to purple that can be observed by the naked eye (Fig. 2b and 3). The changes of the emission intensities nearly become constant when the amount of Cys/Hcy added reaches 400 equiv. (Φ = 0.014 for **1**-Hcy, Φ = 0.016 for **1**-Cys). A good exponential decay relationship (Fig. 3, inset) is observed in the conditions. Surprisingly, with the addition of Cys, the color of the solution appears to be a deeper shade of purple than with the addition of Hcy. Comparing the emission properties of **1**-Cys and **1**-Hcy, the emission intensity at 428 nm for **1**-Cys is stronger than that for **1**-Hcy. While in HEPES buffer, **1** emits orange light when excited by a 365 nm UV lamp. With the addition of Cys/Hcy, the band at 500 nm disappears, while the peak at 588 nm elongates somewhat. Simultaneously, the photoluminescence changes to red by "naked eye" (Fig. 2a). The similar luminescence spectra of **1**-Cys/Hcy with that of **2** both in DMF and HEPES buffer indicate the aldehyde moiety of **1** is missing after the interaction of Cys/Hcy (Fig. S1 and S3 in ESI†).

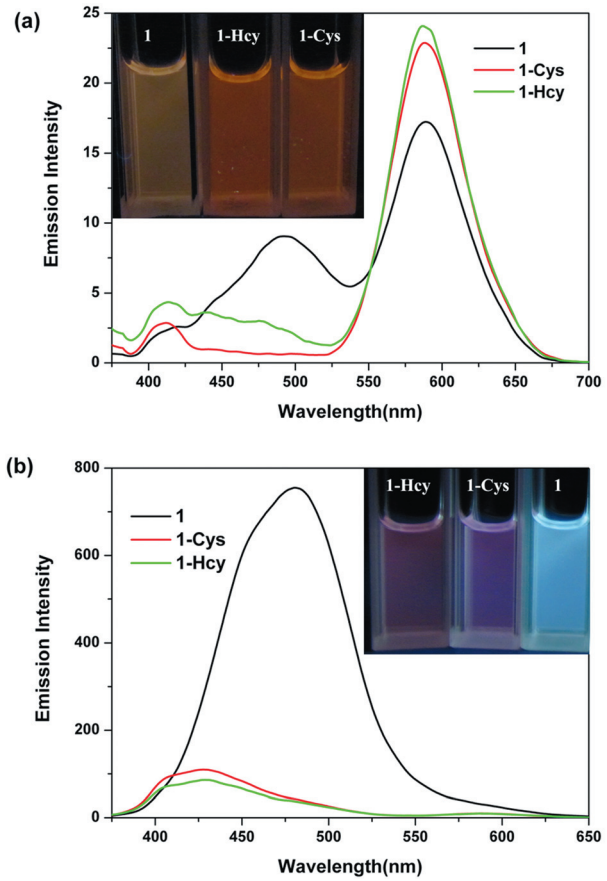


Fig. 2 The luminescence response of **1** to Hcy/Cys in different solvents. (a) HEPES buffer (50 mM, pH 7.0); (b) DMF–HEPES buffer (50 mM, pH 7.0, 10 : 1 v/v).

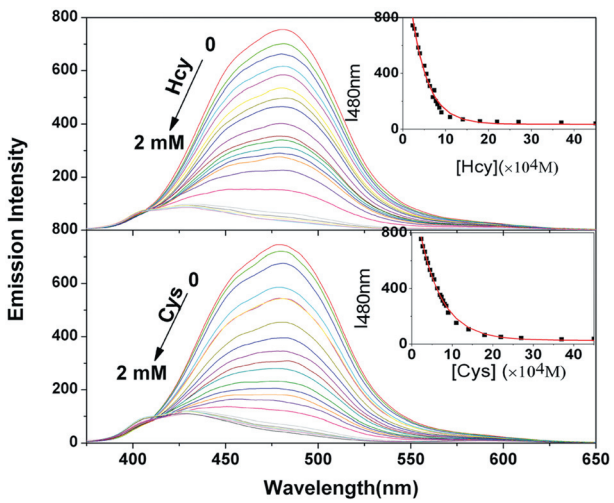


Fig. 3 Changes in the phosphorescence emission spectra of **1** (4.5 μM) with various amounts of Hcy and Cys (0–2 mM) (λ_{ex} = 360 nm).

Electronic absorption spectral response of 1 to Cys/Hcy. The recognition of Cys/Hcy by **1** is studied here by UV-Vis absorption. Fig. 4 shows the change in the UV-Vis spectrum when the Cys/Hcy solutions were added to the DMF–HEPES buffer

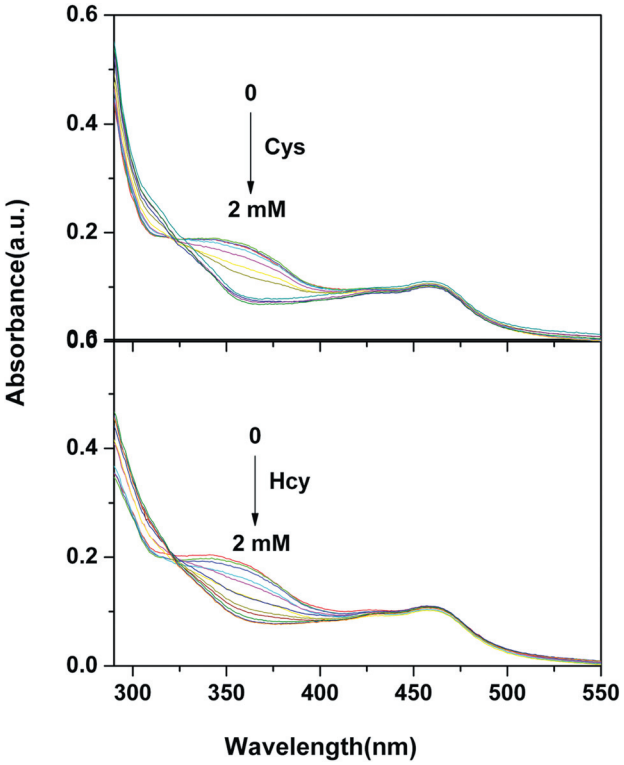


Fig. 4 Changes in UV-Vis absorption spectra of **1** (4.5 μM) in DMF–HEPES buffer (50 mM, pH 7.0, 10 : 1 v/v) with various amounts of Hcy/Cys (0–2 mM).

(10 : 1, v/v) containing the probe **1** (4.5 μM). As the concentration of Cys/Hcy increased, the bands at 325–400 nm decreased gradually until the amount of Cys/Hcy added reached 400 equiv. Because the bands are related to the n–π* transition of the aldehyde moiety, and the final absorption mode is similar to that of **2**, it can be inferred that the addition of Cys/Hcy leads to a change in the aldehyde group.

^{1}H NMR spectra and ESI-MS

^{1}H NMR experiments were carried out (Fig. 5) to reveal the sensing mechanism of **1** for Cys/Hcy. When excess Cys/Hcy is added into a DMSO-d_6 solution of **1**, the aldehyde resonance (9.98 ppm) of **1** disappears and two new peaks, centered at 5.84 ppm and 5.65 ppm for **1**-Cys, 5.64 ppm and 5.42 ppm for **1**-Hcy, corresponding to the methine protons of the thiazolidine diastereomer, are observed, consistent with the previous reports.[42–47] This fact indicates that thiazolidine is formed by the interaction of aldehyde with Cys/Hcy. This formation is further characterized by mass spectrometry analysis, in which the peaks at *m*/*z* 451.3 (calcd = 451.49) corresponding to [(**1**-Hcy) – $2PF_6$]$^{2+}$ and 444.4 (calcd = 444.48) corresponding to [(**1**-Cys) – $2PF_6$]$^{2+}$ were clearly observed, respectively (Fig. S4 in ESI†).

Selective optical response of 1 to various amino acids

The fluorescence responses of **1** (4.5 μM) to 250 equiv. of various amino acids as well as thiol biomacromolecules such as

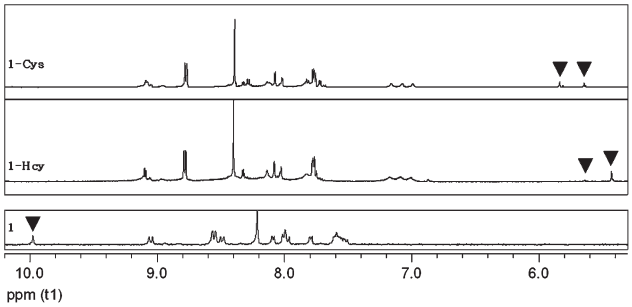


Fig. 5 ^{1}H NMR spectra of **1** in DMSO-d_6 in the absence and presence of Hcy and Cys. The resonance centered at 9.98 ppm corresponds to the aldehyde hydrogen of **1**. The resonances centered at 5.84 ppm and 5.65 ppm for **1**-Cys, and 5.64 ppm and 5.42 ppm for **1**-Hcy correspond to the methine protons of the thiazolidine diastereomer, respectively.

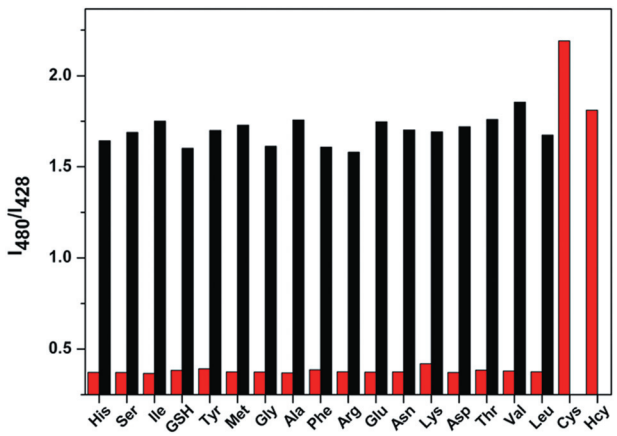


Fig. 6 Luminescent responses of **1** (4.5 μM) in DMF–HEPES buffer (50 mM, pH 7.0, 10 : 1 v/v) to various amino acids at 25 °C. Bars represent the ratio I_{480}/I_{428} of luminescence intensity at 480 to 428 nm. Red bars represent the addition of 2 mM various amino acids to a 4.5 μM solution of **1**. Black bars represent the addition of Cys/Hcy (2 mM) to the above solution, respectively. (λ_{ex} = 360 nm).

2-thiobarbituric acid, thioglycol and GSH, were also investigated (Fig. 6 and 7). In fact, these competitive species do not induce any significant fluorescent changes of **1**, and only Cys/Hcy cause a dramatic change in the fluorescent intensity, and emit a purple fluorescence. Importantly, as a structurally related thiol biomolecule, reduced glutathione (GSH) hardly reacts with **1** under these conditions, which may be due to its steric hindrance. Moreover, in the presence of these competitive species, Cys/Hcy still result in similar fluorescent changes, suggesting that **1** is highly selective for Cys/Hcy.

TDDFT calculations

To further explain the different emission properties of **1** in protic and aprotic solutions, TDDFT calculations at the B3LYP level with a 6-31G(d) basis set for nonmetals and a CC-PVDZ-PP basis set for Ru were performed. Firstly it was supposed that **1** protonated on the imidazole N exists in protic solvent. For theoretical calculations it is difficult to model the same environment

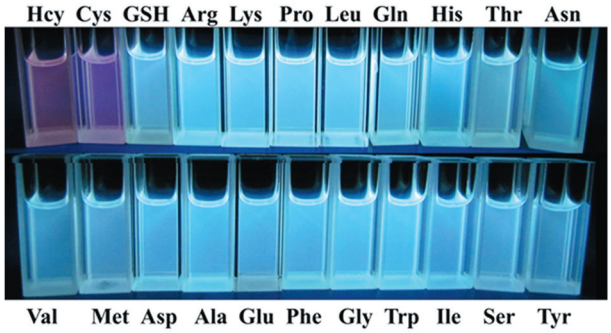


Fig. 7 Photoluminescence observed from the solutions of **1** (4.5 μM) in the presence of different amino acids (2 mM). Excitation wavelength was 365 nm from a portable lamp.

as that in completed experimental conditions, such as the effect of HEPES buffer, hydrogen-bonding, *etc.* The structures are optimized based on **1** and protonated **1** in a vacuum environment. Both complexes were confirmed to be genuine minima on the PES. The important orbitals are shown in Fig. 8. The calculation results show that the emission peak is at 687 nm for the protonated **1**, corresponding to a HOMO − 1 to LUMO MLCT transition. While for **1**, the emission is at 563 nm, corresponding to a HOMO to LUMO LLCT and LC transition. The change trend is consistent with that in the protic and aprotic solvents.

Conclusions

In summary, a novel luminescent ruthenium complex, which displays interesting environment-responsive dual emissive properties, has been discovered. Importantly, the complex could be used to probe Cys/Hcy in both protic and aprotic environments, in which it produces pronounced changes in the emission profiles. We expect that the complex will act as a practical tool for biological sample analysis.

Experimental section

Materials and physical measurements

$Ru(phen)_2Cl_2$ and 4-(1*H*-imidazo[4,5-*f*][1,9]phenanthrolin-2-yl)-benzaldehyde (IPBA) were synthesized using literature methods.[61,62] Unless otherwise stated, all chemical materials were purchased from commercial sources and used without further purification. Here, **1**-Hcy and **1**-Cys represent the adducts of **1** with homocysteine and cysteine, respectively.

NMR spectra were recorded on a Bruker Avance spectrometer (300 MHz). ESI-MS spectra were measured on a Finnigan LCQ system. UV-Vis spectra were recorded on a Hewlett Packard HP-8453 spectrophotometer. Luminescence spectra were recorded on a Perkin-Elmer LS 50B luminescence spectrometer with excitation slits of 5 nm and emission slits of 3 nm.

Synthesis of $[Ru(phen)_2(IPBA)](PF_6)_2$ (1)

Under a nitrogen atmosphere, 32.4 mg of IPBA (0.1 mmol) in 5 mL of EtOH was added to a solution of $Ru(phen)_2Cl_2$ (57 mg,

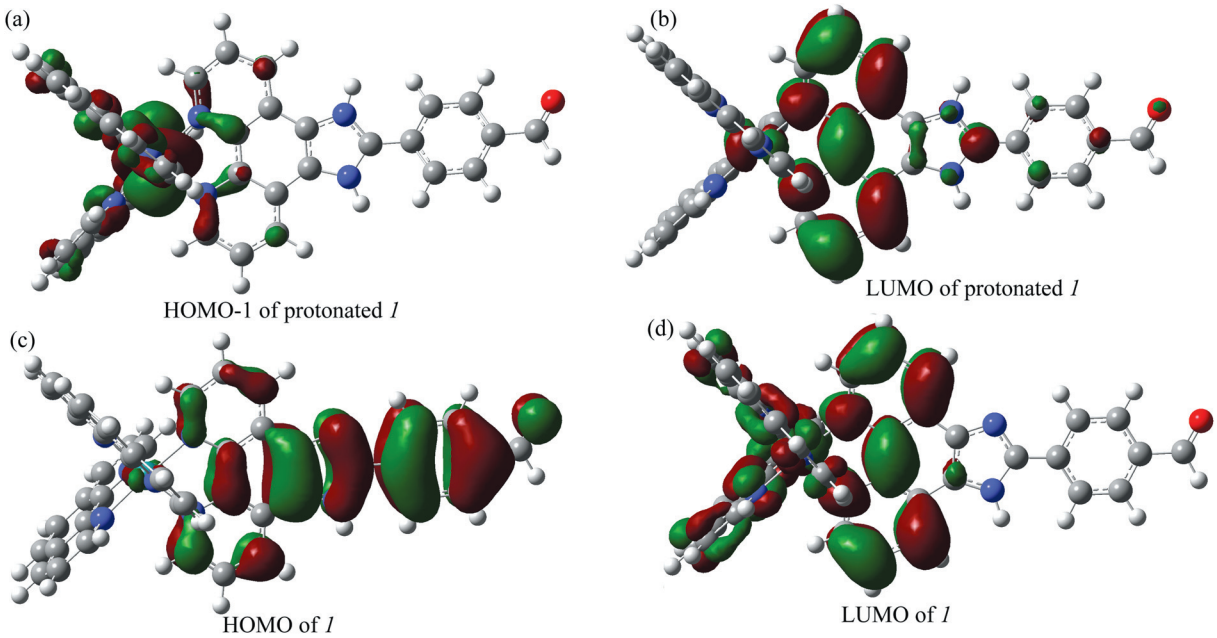


Fig. 8 Important orbitals of protonated **1** and **1** based on TDDFT.

0.1 mmol) in 2.5 mL H_2O. The reaction mixture was refluxed for 5 h, and then cooled to room temperature. After EtOH was evaporated, a small amount of water was added. The precipitation was filtered off. The addition of a saturated solution of NH_4PF_6 into the orange filtrate yielded red precipitation of the product. ^{1}H NMR (300 MHz, CD_3CN): δ = 9.98 (s, 1H, CHO), 9.05 (d, 2H, ^2J = 8.2 Hz), 8.55 (d, 4H, ^2J = 8.2 Hz), 8.49 (d, 2H, ^2J = 8.2 Hz), 8.22 (s, 4H), 8.09 (d, 2H, ^2J = 5.0 Hz), 8.01–7.96 (m, 4H), 7.79(d, 2H, ^2J = 5.0 Hz), 7.62–7.51 (m, 6H). ESI-MS (*m*/*z*): 393.4 (calcd = 392.9) corresponding to $[M - 2PF_6]^{2+}$. EA: (cal) C, 48.32; N, 10.24; H, 2.76 (found) C, 48.30; N, 10.54; H, 2.94%.

Amino acid titration of 1

Typically, the samples containing different concentrations of amino acids were kept at 37 °C overnight before the UV-Vis absorption and photoluminescence spectra of the samples were recorded. For luminescence measurements, excitation was provided at 360 nm, and emission was collected from 370 to 700 nm. The concentration of **1** in all experiments was kept at 4.5 μM.

Acknowledgements

The authors gratefully acknowledge financial support of this work from the National Natural Science Foundation of China (Nos: 20601018, 21071092), the Shanxi Provincial Natural Science Foundation for Youth (No: 2009021006-3), the Program for the Top Young Academic Leaders of Higher Learning Institutions of Shanxi (TYAL), and Shanxi Province Graduate Innovation and Creativity Funds (20103014).

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