



Experimental and theoretical investigations on spectroscopic properties of the imidazole-fused phenanthroline and its derivatives



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ABSTRACT

Two phenanthroline derivatives, 1H-imidazo[4,5-f][1,10]phenanthroline (**imPhen**) and 2-(9H-fluorene-2-yl)-1H-imidazo[4,5-f][1,10]phenanthroline (**Flu-imPhen**), have been synthesized and characterized and the corresponding absorption and emission spectroscopic properties have been studied in CH₂Cl₂ solution. The **imPhen** exhibits the main two absorption bands at 282 nm and 229 nm and these bands are assigned as the typical $\pi \rightarrow \pi^*$ (Phen) state. In addition, the weak absorption bands at 313 nm associated with a shoulder near 302 nm were assigned to the $\pi \rightarrow \pi^*$ (Phen) state with partial charge transfer (CT) character. A similar absorption spectra are observed in the case of the **Flu-imPhen** in the region of 200–300 nm, while the region of 300–400 nm of the spectra are dominated by the characteristic $\pi \rightarrow \pi^*$ transition of the fluorene moiety. **imPhen** shows the typical ligand-centered $^1\pi \rightarrow \pi^*$ emission, while **Flu-imPhen** emits from the mixed $^1\pi \rightarrow \pi^*/CT$ states. Density functional theory (DFT) and time-dependent density functional theory (TDDFT) were employed to rationalize the photophysical properties of these ligands studied. The theoretical data confirm the assignment of the experimental absorption spectra and the nature of the emitting states.

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1. Introduction

1,10-Phenanthroline (**Phen**), a nitrogen-containing heterocyclic compound, has been extensively used as a basic ligand to prepare the transition metal complexes due to its strong coordination ability and rigid planar skeleton [1,2]. Transition metal complexes containing Phen-based ligands are of great interest in organic light-emitting diodes (OLEDs), solar cells, sensors, and photocatalysis [3–9]. Up to now, the great versatility of Phen ligands for structural modifications has been utilized to prepare a huge number of phosphorescent transition metal complexes with extensive tuning of photophysical properties [10–15].

One of the closely relevant derivatives of the Phen ligand is 1H-imidazo[4,5-f][1,10]phenanthroline (**imPhen**) (Fig. 1) [16,17]. The fused imidazole ring provides a more π -delocalized molecular skeleton, and consequently has a positive impact on the photophysical properties of the corresponding complexes. Meanwhile, the imPhen ligand can be easily substituted with electron-withdrawing or -donating groups, and these substitutions have an important effect on their HOMO and LUMO energies and consequently on the corresponding metal complex emission. In a recent paper [18], effects of phenyl, naphthyl, and anthryl substituents on HOMO and LUMO energies of

the imPhen ligand have been demonstrated, thus allowing the corresponding Cu(I) complex emissions to be tuned [19]. Although the wide variety of complexes containing imPhen ligands and their derivatives have been reported [20–24], very few studies have focused on the photophysical properties of those ligands compared to that of the parent Phen [25,26]. Hence, fundamental insights into the electronic structures and photophysical properties of the imPhen ligands are highly favored to guide the future molecular design of new complexes.

Fluorene, consisting of biphenyl units with rigid and planar structure, is a robust chromophore and has been extensively explored in luminescent materials used as an active component due to its unique photophysical properties, such as large band gaps, π -donating ability, high emission efficiency, and high thermal stability [27–32]. To the best of our knowledge, however, the fluorene moiety has never been attached to the imPhen ligand and introduction of the fluorene group into the imPhen ligand should result in significant changes in the photophysical properties. Herein, the imPhen ligand and its derivatives containing the fluorene moiety (see Fig. 1) were synthesized and their photophysical properties were investigated. The emphasis is being given a detailed analysis of the structural and spectral properties of those ligands. Meanwhile, the assignment of the electronic absorption and emission spectra were also investigated using density functional theory (DFT) and time-dependent density functional theory (TDDFT), and the results are compared with the corresponding experimental data.

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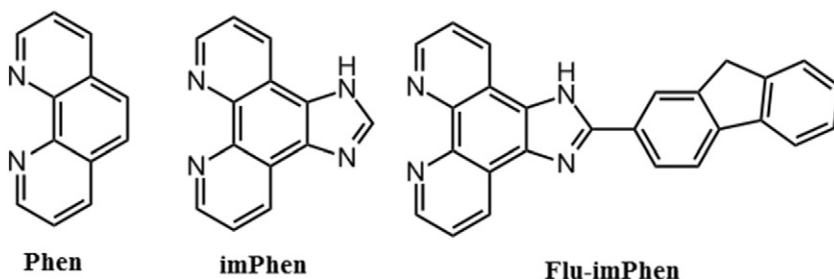


Fig. 1. Molecular structures of the phenanthroline derivatives studied in this study.

2. Experimental

2.1. Materials and methods

1,10-Phenanthroline (**Phen**), potassium bromide, ammonium acetate, methanol, 2-fluorencarboxaldehyde, anhydrous magnesium sulfate, sodium hydroxide, concentrated sulfuric acid and nitric acid et al. were purchased from Sinopharm Chemical Reagent Co. All other chemicals were analytical grade reagents.

¹H NMR spectra were performed in a Bruker AV400 MHz spectrometer, using tetramethylsilane (TMS) as internal reference. DMSO and CDCl₃ were used as solvents. The mass of molecular was measured by amaZon SL. UV-vis absorption spectra were measured using a PerkinElmer Lambda-900 spectrophotometer. Fluorescence spectra were determined with a Hitachi F-4600 fluorescence spectrophotometer. Photoluminescence (PL) quantum yields were determined using a Hamamatsu system for absolute PL quantum yield measurements (type C11347). Fluorescent lifetimes were measured with a compact fluorescent lifetime spectrometer (Hamamatsu, C11367, Japan).

2.2. Synthetic procedure

2.2.1. 1,10-Phenanthroline-5,6-dione

5.0 g (25.2 mmol) of 1,10-phenanthroline monohydrate was dissolved in 60 mL of concentrated sulfuric acid and 2.9 g (25.2 mmol) of potassium bromide was slowly added at 0 °C. 30 mL of concentrated nitric acid was added dropwise to the mixture and the resulting mixture was stirred for 6 h at 100 °C. Then, the mixture was poured into the ice (400 g) and neutralized with aq 40% KOH solution until the pH = 7. After cooled to room temperature, the turbid solution was filtered. The aqueous solutions were extracted with CH₂Cl₂, dried over anhydrous magnesium sulfate and filtered. The solvent was evaporated under reduced pressure, and the product was recrystallized from methanol to give the pure dione (3.28 g, 62%). ¹H NMR(400 MHz, CDCl₃): δ = 9.11–9.13 (dd, 2H), 8.50–8.52 (dd, 2H), 7.59–7.61 (dd, 2H). MS: *m/z* = 210.04 (M⁺).

2.2.2. 1H-imidazo[4,5-f][1,10]phenanthroline (**imPhen**)

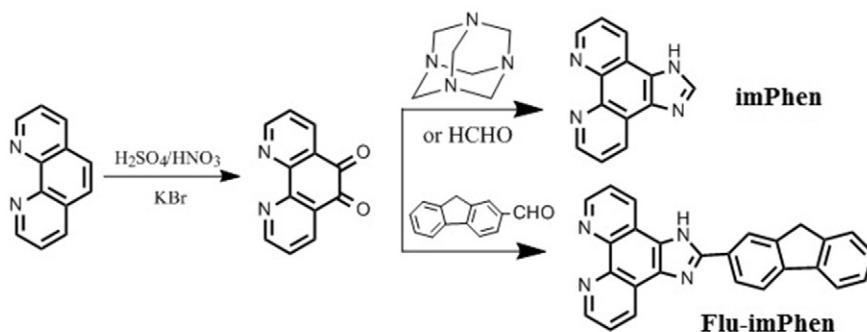
A round-bottom flask containing 1,10-phenanthroline-5,6-dione (2.5 mmol, 0.525 g), ammonium acetate (50 mmol, 3.88 g), hexamethylenetetramine (5 mmol, 0.70 g) and glacial acetic acid (7 mL) was refluxed for 1 h, then cooled to room temperature and the solution poured slowly into water (25 mL). Concentrated aqueous ammonia was added dropwise to the solution and gave a yellow precipitate, filtered and washed with water. The crude product was purified by silica gel column chromatography (methanol) to give the compound (0.25 g, 50%) ¹H NMR (400 MHz, DMSO): δ = 13.75 (s, 1H), 9.05 (s 2H), 8.84 (s, 2H), 8.48 (s, 1H), and 7.84 (s, 2H). MS: *m/z* = 220.1 (M⁺).

2.2.3. 2-(9H-fluoren-2-yl)-1H-imidazo[4,5-f][1,10]phenanthroline (**Flu-imPhen**)

The compound was prepared according to the method used for imPhen by using 1,10-phenanthroline-5,6-dione (1 mmol, 0.21 g), ammonium acetate (20 mmol, 1.55 g), fluorene-2-carboxaldehyde (1 mmol, 0.194 g) and glacial acetic acid (15 mL). Purification by silica gel column chromatography (CH₂Cl₂/methanol, 8:1) to give the compound (0.24 g, 63%) ¹H NMR(400 MHz, DMSO): δ = 13.80 (s, 1H), 8.95–9.15 (dd, 4H), 8.54 (s, 1H), 8.35–8.40 (d, 1H), 8.13–8.20 (d, 1H), 8.00–8.05 (d, 1H), 7.90 (s, 2H), 7.65–7.72 (t, 1H), 7.37–7.53 (m, 2H), and 4.14 (s, 2H). MS: *m/z* = 384.33 (M⁺).

2.3. DFT calculations

All calculations were performed using the Gaussian 09 [33] program package. The ground state geometries (*S*₀) of **Phen**, **imPhen**, and **Flu-imPhen** were optimized with DFT theory using the B3LYP density functional [34,35] with a 6–31G* basis set [36,37] using the polarized continuum model (PCM) [38] in CH₂Cl₂ media, while the excited state geometries (*S*₁) were optimized with TDDFT method [39,40] at the same condition. On the basis of the optimized ground geometries, the TDDFT method associated with PCM in CH₂Cl₂ media was used to simulate the absorption spectra of compounds studied. The first 100 singlet vertical excitations were obtained from the TDDFT output file to



Scheme 1. The synthetic pathways of **imPhen** and **Flu-imPhen**.

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