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Computational and spectroscopic studies of the imidazole-fused phenanthroline derivatives containing phenyl, naphthyl, and anthryl groups

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ABSTRACT

Three N,N-bidentate ligands, 2-phenyl-1H-imidazo[4,5-f][1,10]phenanthroline (**1**), 2-(2-naphyl)-1H-imidazo[4,5-f]phenanthroline (**2**), and 2-(2-anthryl)-1H-imidazo[4,5-f]phenanthroline (**3**) have been synthesized and characterized. Effects of aryl subsistiuents (phenyl, naphthyl, and anthryl) on the photophysical properties of these ligands in solution have been studied. Ligand **1** exhibit the main absorption band at 283 nm with the shoulder bands at 300–350 nm and these bands are assigned as the typical $\pi\rightarrow\pi^*_{(\mathrm{imPhen})}$ state (imPhen = 1H-imidazo[4,5-f][1,10]phenanthroline). A similar absorption spectrum was also observed in the case of **2,** in which the charge transfer (CT) state should be considered. **3** shows the slightly different absorption properties compared to that of **1** and **2**. The highest-lying absorption band at 257 nm is assigned as a mixed $\pi\rightarrow\pi^*_{(\mathrm{imPhen})}/\pi\rightarrow\pi^*_{(\mathrm{Anth})}$ (Anth = anthracene) state. Additionally, the characteristic absorption band of anthryl group with three vibronic bands at 352, 367, and 386 nm also observed in the visible region range from 340 to 400 nm. **1** shows the typical ligand-centered $^1\pi\rightarrow\pi^*$ emission, while **2** and **3** emit 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.

1. Introduction

The transition metal complexes have received much current interest owing to their unique photophysical properties such as the MLCT visible absorption, relatively long-lived excited lifetimes, and high luminescence efficiency, and so on [1–5]. Their photophysical properties are sensitive to the coordinated ligand system and can easily be modulated by an appropriate choice and combination of ligands and ligand substituents. Until now, the number of ligands with different structural and electronic properties have been designed and synthesized in order to tune the photophysical properties of these complexes [6–12]. Among them, the most commonly used ligands are based on 1,10-phenanthroline (Phen) due to their rigid planar, hydrophobic, electro-poor heteroaromatic system [13,14]. Additionally, the utilization of the functionalized Phen or its derivatives provides further options to tune the optical and electrical properties [15–20].

As a Phen derivative, 1H-imidazo[4,5-*f*][1,10]phenanthroline (imPhen) is an appealing ligand [21,22]. The fused imidazole ring provides a more π-delocalized molecular skeleton, and consequently has a positive impact on the photophysical proprieties of the corresponding complexes. Meanwhile, imPhen ligands 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 corroding metal complex emission. A large number of metal complexes of imPhen such as those of Ru(II), Ir(III), Pt(I), Re(I), and Cu(I), have been reported and shown interesting photophysical properties [23–30]. However, the electrical structures and the photophysical properties of these ligands seem deficient compared to that of Phen [31,32] and the origin of these spectroscopic properties remains unexplored. Therefore, a deep understanding of fundamental

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photophysical properties of imPhen ligand with new molecular structures is desired to furthermore guide the future molecular design of new complexes.

Herein, the photophysical properties of three imPhen derivatives with phenyl, naphthyl, and anthryl groups (Chart 1) were studied by exploiting their optical absorption and photoluminescent spectra. 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.

2. Experimental

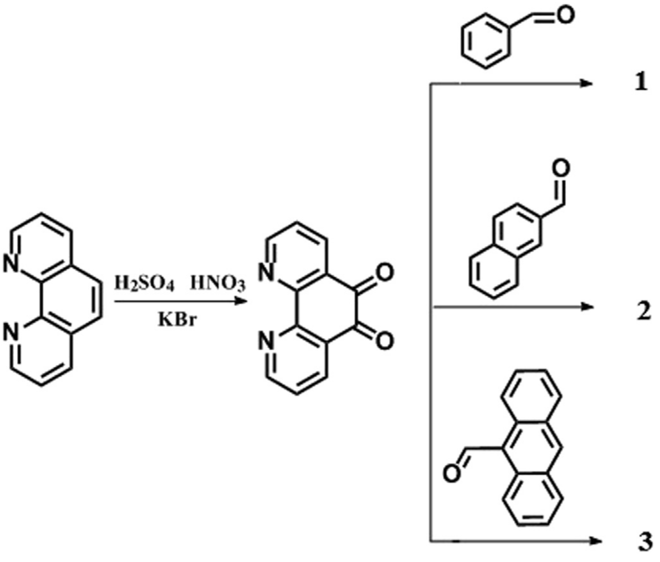
2.1. Materials and methods

1,10-phenanthroline (Phen), 2,9-dimethyl-1,10-phenanthroline, Ethylenediamine, Potassium bromide were purchased from Aladdin-reagent Co. and used without further purification. Concentrated sulfuric and nitric acids were purchased from Sinopharm Chemical Reagent Co. The solvent dichloromethane used for UV–vis absorption and emission spectroscopy was obtained from Shanghai Vita Chemical Reagent Co., Ltd (99.9%. HPLC grade). ^{1}H NMR spectra were performed in a Bruker AV400 MHz spectrometer, using tetramethylsilane (TMS) as internal reference. DMSO-d$_6$ was used as the solvents. UV–vis absorption spectra were measured using a Perkin Elmer Lambda-900 spectrophotometer. Fluorescence spectra were determined with a Hitachi F-4500 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. 2,9-Dimethyl-1,10-Phenanthroline-5,6-dione

A round-bottom flask containing 2,9-dimethyl-1,10-phenanthroline (3.35 g, 16 mmol) and potassium bromide (19.0 g, 160 mmol) was cooled in an ice bath. Concentrated sulfuric acid (60 mL) and concentrated nitric acid (30 mL) were added dropwise. The reaction mixture was heated under reflux for 3 h, then cooled to room temperature and the solution poured slowly into deionized water (800 mL), neutralized with sodium bicarbonate and extracted with CH_2Cl_2. After washed with water and dried, the chloroform was removed under reduced pressure to leave a yellow residue which was recrystallized from dioxane. Yield: 78% (3.5 g). ^{1}H NMR (400 MHz, DMSO-d$_6$): 8.20–8.22 (dd, 2H), 8.59–8.61 (dd, 2H), 2.82 (s,6H).



Scheme 1. The synthetic pathways of ligands.

2.2.2. 2-phenyl-1H-imidazo[4,5-f][1,10]phenanthroline (**1**)

A mixture of 1,10-Phenanthroline-5,6-dione (104 mg, 0.50 mmol), benzaldehyde (72 mg, 0.68 mmol), ammonium acetate (805 mg, 11.3 mmol), and glacial acetic acid (13 mL) was refluxed for 4 h and then cooled to room temperature. It was diluted with water and dropwise addition of concentrated aqueous ammonia gave a yellow precipitate, which was collected, washed with water, and dried. The crude product obtained was purified by chromatography on silica gel, prepared in a 8:1 mixture of CH_2Cl_2 and methanol. Yield: 96 mg (65%). ^{1}H NMR (400 MHz, DMSO): 13.76 (s, 1H)9.02 (d, J = 8.0 Hz, 2H), 8.93 (d, J = 8.0 Hz, 2H), 8.29 (d, J = 7.9 Hz, 2H), 7.82 (dd, J = 7.9, 4.4 Hz, 2H), 7.61 (t, J = 7.5 Hz, 2H), 7.51 (t, J = 7.2 Hz, 1H).

2.2.3. 2-(2-naphyl)-1H-imidazo[4,5-f]phenanthroline (**2**)

The synthetic procedure was the same as that for compound **1** except for that 106 mg (0.68 mmol) 2-naphthaldehyde was used for the reaction. Yiedl: 95 mg (55%). ^{1}H NMR (400 MHz, DMSO-d$_6$): 13.76 (s, 1H) 9.10–9.02 (m, 2H), 8.98 (d, *J* = 7.2 Hz, 2H), 8.83 (s, 1H), 8.45 (d, *J* = 8.5 Hz, 1H), 8.14 (dd, *J* = 16.6, 8.0 Hz, 2H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.86 (dd, *J* = 7.9, 4.2 Hz, 2H), 7.63 (p, *J* = 8.4 Hz, 2H).

2.2.4. 2-(9-anthryl)-1H-imidazo[4,5-f]phenanthroline (**3**)

The synthetic procedure was the same as that for **1** except for that 140.2 mg (0.68 mmol) 9-anthrylaldehyde was used for the reaction and the reaction mixture was refluxed for 6 h. Yiedl: 89 mg (45%). ^{1}H NMR (400 MHz, DMSO-d$_6$): 14.16 (s, 1H), 9.02 (d, J = 4.1 Hz, 2H), 8.90 (d, J = 8.1 Hz, 1H), 8.85 (s, 1H), 8.72 (d, J = 7.3 Hz, 1H), 8.20 (d, J = 8.4 Hz, 2H), 7.79 (dd, J = 8.0, 4.4 Hz, 2H), 7.74 (d, J = 8.7 Hz, 2H), 7.60–7.52 (m, 2H), 7.52–7.44 (m, 2H).

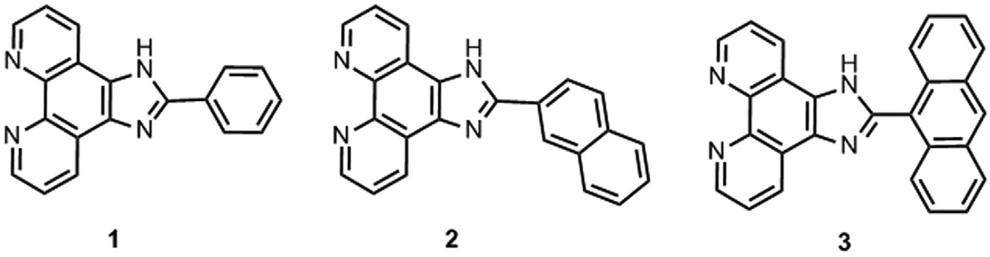


Chart 1. Molecular structures of the phenanthroline derivates studied in this study.