Polyhedron 171 (2019) 338-343

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Tunable excitation-dependent emissions in mixed-ligand Cd(II) complexes



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ARTICLE INFO

Article history: Received 9 May 2019 Accepted 21 July 2019 Available online 29 July 2019

Keywords: Luminescence Charge transfer Exciplex Coordination compound X-ray structure

ABSTRACT

Two Cd(II) coordination compounds, i.e. $[Cd(HL)(phen)_2(H_2O)]$ ·HL·3H₂O (**1**) and $\{[Cd(HMeL)_2(4,4'-bipy) (H_2O)]$ ·H₂O]_n (**2**) and (where HL = *N*-carboxymethyl-*N*-phenyliminoacetato, HMeL = *N*-carboxymethyl-*N*-(*m*-methylphenyl)iminoacetato, 4,4'-bipy = 4,4'-bipyridine and phen = phenanthroline) have been synthesized and characterized by elemental analysis, IR and single-crystal X-ray diffraction methods. The photoluminescence properties and mechanisms, studied by means of solid state absorption, excitation/emission spectra, time-resolved lifetime techniques, and density functional theory (DFT) calculations, indicate that the emissions of both compounds originate from a combination of exciplex and charge-transfer complex. Interestingly, both compounds exhibit excitation-dependent emissions, which can be used to fine-tune their emission wavelengths.

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1. Introduction

Luminescent metal-organic complexes have attracted enormous attention because of their potential applications in lightemitting devices, luminescent sensors, biomedical imaging and so on [1]. It has been revealed that the luminescence of such materials can arise from organic ligand(s), metal ion(s), ligand to metal charge transfer (LMCT), metal to ligand charge transfer (MLCT), and even guest molecules [2]. Compared to many examples of the ligand-centered luminescence, the exciplex/excimer and charge transfer emissions from complexes formed between ligands or ligand/guest molecules are much less studied [3], although such behavior has been frequently accessible in pure organic luminescence [4]. In metal-organic materials, supramolecular interactions $(\pi \cdots \pi \text{ and } C - H \cdots \pi \text{ interactions})$ drive organic chromophores in a close proximity, which makes the formation of charge-transfer complex (CTC) and exciplex easy. However, these species are usually unwanted because they often reduce the emission efficiency [5]. More efforts have been made to prevent the formation of these species [6]. However, it has been recently reported that the formation of exciplex could actually enhance the emission, in some cases [7]. Moreover, these species have exhibited potential applications. For example, Maji and co-workers studied the detection of ions and

Zaworotko utilized exciplex emission to probe the structures of some organic complexes [9]. White light-emitting materials could also be achieved by using the exciplex emission [10]. Furthermore, tunable emissions of materials would be realized by varying the excitation wavelength when CTC and exciplex coexist and have enough energy difference. Therefore, more luminescent compounds exhibiting the exciplex/excimer and charge transfer emission are worth studying to render new functional metal–organic materials. On the other hand, the excitation-dependent emission phenomenon has been attracting increasing current attention [11] as

aromatic amine using the exciplex emission [8]; Wagner and

nomenon has been attracting increasing current attention [11] as it is a convenient way to fine-tune the emission property of luminescent materials, and also provides important examples of anti-Kasha rules which state that the emissions always come from the lowest excited state (S_1 or T_1). Most of the excitation-dependent emission systems so far reported are the nanomaterials (such as carbon dots), the corresponding metal coordination compounds have been relatively much less studied, and pure organic materials are emerging.

Aromatic iminocarboxylic acids ArN(CH₂COOH)₂ are excellent ligands towards metal complexes as they exhibit multiple coordination modes [12]. The electron-rich ArN moieties of these ligands act as electron donors when suitable electron acceptors are present. An analysis of the literature shows that when auxiliary ligands such as phenanthroline, 4,4'-bipyridine, or 2,2'-bipyridine are present, the corresponding complexes of Zn(II) and Cd(II)







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exhibit much longer wavelength emission than those of the ligands [12b,c,e-g], however, such phenomena and the emission mechanisms have not been understood comprehensively. Recently we reported such a zinc coordination compound with 4,4'-bipyridine as the auxiliary ligand (acceptor) which exhibits reversible thermochromism and exciplex emission [13]. In this paper we utilized N-phenyliminodiacetic acids as the main ligands, and phenanthroline/4,4'-bipyridine as the auxiliary ligands, to obtain two metal-organic complexes, [Cd(HL)(phen)₂(H₂O)]·HL·3H₂O (1) and $\{ [Cd(HMeL)_2(4,4'-bipy)(H_2O)] \cdot H_2O \}_n$ (2). It is found that the emissions of both compounds can be tuned by varying the excitation light. The luminescent mechanisms were studied by a combination of solid state absorption and excitation/emission spectra, fluorescence lifetime techniques and DFT calculations, which indicate that the emissions arise from both exciplex and charge-transfer complexes.

2. Experimental

2.1. General methods

The ligands H₂L and H₂MeL were prepared by the reactions of aniline or *m*-methylaniline with chloroacetic acid under basic conditions, respectively, according to the literature [14]. $Cd(NO_3)_2$. 4H₂O, 4,4'-bipy and phen₁H₂O were commercially purchased and used without further purification. Elemental analyses were performed on an Elementar Vario EL III Analyzer. PXRD patterns were recorded on a Bruker D8 diffractometer. IR spectra were measured on a Perkin Elmer Spectrum RX I spectrometer. UV-Vis diffuse reflectance spectra were recorded on a Shimadzu UV-3101PC spectrometer with an integration sphere attachment, and BaSO₄ was used as the reference. Excitation and emission spectra were measured on an Edinburgh FLS 920 fluorimeter, using a front-face solid sample configuration. The fluorescence decay curves were measured by means of the time-correlated single-photon-counting technique with a hydrogen lamp as excitation light source, and the data were analyzed using the software supplied by Edinburgh Instruments. This software allows the simulation of the multiexponential decay curves:

$$R(t) = A + B_1 e^{-t/\tau_1} + B_2 e^{-t/\tau_2} + \cdots$$

where *B* is pre-exponential factor, τ is the characteristic lifetime, and *A* is an additional background. The results are evaluated using global x^2 and local residuals.

2.2. Synthesis of $[Cd(HL)(phen)_2(H_2O)] \cdot HL \cdot 3H_2O(1)$

A solution of Cd(NO₃)₂·4H₂O (0.156 g, 0.5 mmol) in 20 mL of water/ethanol (1:1, *V/V*) was added dropwise to a solution of H₂L (0.208 g, 1 mmol) in 20 mL of water/ethanol (1:1, *V/V*). After stirring at 80 °C for 30 min, phenanthroline monohydrate (0.194 g, 1 mmol) was added to the reaction mixture which was further stirred for 1 h. The resulting mixture was filtered while hot to produce a yellowish filtrate, and brown crystals (0.288 g, 60% yield based on Cd) suitable for X-ray diffraction started to grow once the filtrate was cooled to room temperature. *Anal.* Calc. for C₄₄H₄₄N₆O₁₂Cd, C, 54.98; H, 4.61; N, 8.74; found: C, 54.84; H, 4.40; N, 8.79; IR (KBr, cm⁻¹): 3436, 2924, 1698, 1600, 1508, 1427, 1194, 846, 730.

2.3. Synthesis of $\{[Cd(HMeL)_2(4,4'-bipy)(H_2O)] \cdot H_2O\}_n$ (2)

Pale yellow crystals of **2** suitable for X-ray diffraction were obtained by similar procedures to those described for **1**, with H₂MeL (0.474 g, 2 mmol), Cd(NO₃)₂·4H₂O (0.310 g, 1 mmol) and 4,4'-bipy (0.160 g, 1 mmol). Yield: 0.378 g, 50% yield based on Cd.

Anal. Calc. for $C_{32}H_{36}CdN_4O_{10}$, C, 51.31; H, 4.84; N, 7.48; found: C, 51.34; H, 4.77; N, 7.44; IR (KBr, cm⁻¹): 3434, 2956, 2922, 1728, 1609, 1582, 1410, 1328, 774, 678.

2.4. Single-crystal X-ray crystallography

Data collection was performed with suitable crystals on an Oxford Diffraction Gemini E diffractometer with graphitemonochromated Mo K α radiation ($\lambda = 0.71073$ Å, ω scan mode). The structures were solved by Direct Methods and expanded using Fourier difference techniques with the SHELXL program package [15]. The non-hydrogen atoms were refined anisotropically by fullmatrix least-squares calculations on F^2 . The details of the data collection and refinement of the complexes are shown in Table S1, and the selected bond lengths and angles are presented in Table S2.

3. Results and discussion

3.1. Crystal structures

The brown crystals of 1 and pale yellow crystals of 2 were obtained by the reactions of iminocarboxylic acids (H₂L/H₂MeL), 4,4'-bipy/phen and Cd(NO₃)₂ in water–ethanol media, respectively. According to the single crystal X-ray structural analyses, 1 is a discrete mononuclear complex with phen as the auxiliary ligand (Fig. 1). The Cd center in **1** coordinates to two phen, a HL moiety and an aqua ligand, adopting a slightly distorted octahedral geometry. The HL ligand coordinates to the Cd(II) in a monodentate manner via one oxygen atom, and the other HL moiety acts as a counter anion. The bond angles around the uncoordinated N1 atom (119.0°, 119.8° and 120.2°) and N2 atom (119.2°, 119.7° and 120.8°) are all near to 120°, and the N-C bond lengths (N1-C5 1.392 Å, N2–C15 1.382 Å) are between those of a single (1.47– 1.50 Å) and a double bond (1.34–1.38 Å) [16], which indicates that both the N1 and N2 atoms adopt an sp² hybridization and are conjugated to the phenyl ring, making the HL moiety electron-rich in nature

In compound **2**, a coordination polymer, each seven-coordinate metal center binds two HMeL moieties, two pyridine and an aqua ligand (Fig. 1). Each HMeL ligand coordinates to the metal center in a bidentate way and the two HMeL moieties point to the opposite directions relative to the metal ion. The bond angles around the uncoordinated N1 (120.2°, 118.0° and 121.8°) and N2 atoms (121.4°, 118.8° and 119.2°), and the N1–C5 (1.383 Å) and N2–C16 (1.392 Å) bond lengths suggest that both N atoms are conjugated to the phenyl rings, as in compound **1**.

3.2. Fluorescence spectroscopy

The phase purity of **1** and **2** was confirmed by the comparison of the PXRD patterns of the as-synthesized samples with those simulated from the single crystal X-ray data (Fig. S1). The photoluminescent emission spectra of solid 1 and 2 were studied at ambient temperature and the results are shown in Fig. 2. Both complexes show broad structureless emission bands. Interestingly, the emission maxima of 1 change from 556 nm to 625 nm gradually upon varying the excitation wavelengths from 300 to 520 nm (Fig. 2a and Table 1), exhibiting obvious excitation-dependent emissions. As a result, the emission colors are tuned from green yellow to red. The excitation spectra of 1 (Fig. 2b), obtained by setting 556 and 625 nm as the emission wavelengths, respectively, are much different, especially in the relative intensity of each peak/wavelength. Obviously, the emission intensity at 556 nm reaches the maximum by excitation at 394 nm. The emission at 625 nm displays the strongest intensity upon excitation at



Fig. 1. Crystal structures of 1 and 2 (hydrogen atoms are omitted for clarity).



Fig. 2. Solid state emission (a, c) and excitation (b, d) spectra of crystalline 1 (a, b) and 2 (c, d).

Table 1	
Photophysical data of 1 .	

$\lambda_{\rm ex}$ (nm)	$\lambda_{\rm em}$ (nm)	Lifetime contribution (%)		
		$\tau_1 = 0.98 \text{ ns}$	$\tau_2 = 5.51 \text{ ns}$	$\tau_3 = 23.17 \text{ ns}$
300	556	9.15	20.65	70.20
400	585	17.15	26.02	56.83
420	592	29.43	33.41	37.16
460	598	57.65	35.76	6.59
480	602	65.64	32.69	1.67
520	625	68.10	31.90	0

510 nm. These results demonstrate that the emissions of **1** result from several electronic transitions. The emission properties of **2** (Fig. 2c) are much different from those of **1**. The emission color

keeps essentially green-yellow. There is only a slight bathochromic shift of 7 nm upon changing the excitation wavelengths from 300 to 460 nm (Table 2). When the excitation wavelength is further

Table 2		
Photophysical	data	of 2 .

$\lambda_{\rm ex}$ (nm)	$\lambda_{\rm em}$ (nm)	Lifetime contribution (%)		
		$\tau_1 = 1.72 \text{ ns}$	$\tau_2 = 6.22 \text{ ns}$	$\tau_3 = 33.65 \text{ ns}$
300	540	0	0	100
400	540	0	2.12	97.88
440	542	5.97	5.53	88.50
460	547	19.95	12.75	67.30

increased, **2** keeps emission silent, in agreement with the excitation spectrum (Fig. 2d) which shows that the emission of **2** can not be induced by light with a wavelength longer than 460 nm.

Though the emission behaviors of **1** and **2** are different, both of them have far red-shifted emission maxima when compared with those of the ligands. As shown in Fig. S2, H2L, H2MeL and 4,4'-bipyridine exhibit emission maxima at 351, 364, and 367 nm, respectively. Phenanthroline monohydrate shows a vibrational emission spectrum with three peaks at 363, 379 and 401 nm (Fig. S2), the same as that reported for phen in the literature [17]. Compared with those of the ligands, the emission bands of **1** and **2** are red-shifted by at least 155 and 173 nm, respectively, which is rare in Cd(II) coordination compound [2b].

3.3. Mechanism of emission

To get insights into the photoluminescence mechanisms, density functional theory (DFT) calculations were carried out to investigate the electronic structures of **1** and **2**, and the selected molecular orbitals are listed in Fig. S4. The results show the electron density distribution of the HOMO is located on the ArN moieties, whereas the electron density distribution of the LUMO is governed by phen and 4,4'-bipy, respectively, and the Cd(II) ion does not notably contribute to the frontier orbitals (Fig. S4), in both **1** and **2**. Moreover, it was reported that the complex $[Cd(L)(H_2O)]$. H₂O, without auxiliary ligand as compared to **1** and **2**, exhibits an emission peak at 464 nm [12b]; and the coordination compound of Zn(II) and 4,4'-bipy has even higher energy emission centered at 398 and 422 nm than that of $[Cd(L)(H_2O)] \cdot H_2O$ [18]. Moreover, Maji and George et al. reported that the excited N,N'-dimethylaniline-phen charge-transfer complex exhibits an emission maximum at 576 nm [8b], similar to those of 1. Therefore, the emission bands of 1 and 2 should be assigned to the transitions between the ArN and phen/4,4'-bipy moieties, in which the ArN moieties act as electron donor (D) and phen/4,4'-bipy as electron acceptor (A) in the photoluminescence process.

The transition between a donor (D) and an acceptor (A) usually gives rise to the charge-transfer emission, as well as that of exciplex when D and A are both aromatic species [19]. Exciplex and CTC generally coexist and are connected in the excited state [19a,20]. Thus it is difficult to distinguish these emissions. However the existence of each emissive species could be explored by choosing the excitation wavelength, i.e. direct excitation of one of the moieties (donor or acceptor) would yield the exciplex $(A-D)^*_{EX}$ as the main species (Eq. (1)), and the excited CT $((A^{\delta-}-D^{\delta+})^*_{CT})$ would arise mainly when the CT $((A^{\delta-}-D^{\delta+})^*_{CT})$ absorption band is excited (Eq. (2)) [19b,20a].

$$\mathbf{A} + \mathbf{D} \stackrel{n\nu_1}{\rightleftharpoons} \mathbf{A}^* + \mathbf{D} \rightleftharpoons (\mathbf{A} - \mathbf{D})^*_{\mathbf{EX}}$$
(1)

$$\mathbf{A} + \mathbf{D} \rightleftharpoons \left(\mathbf{A}^{\delta^{-}} - \mathbf{D}^{\delta^{+}}\right)_{\mathrm{CT}} \xrightarrow{h\nu_{2}} \left(\mathbf{A}^{\delta^{-}} - \mathbf{D}^{\delta^{+}}\right)_{\mathrm{CT}}^{*}$$
(2)

To verify the existence of CTC, the solid state absorption of **1**, **2** and the ligands were studied (Fig. 3). The emergence of a new absorption band in the low energy region is the feature of a CTC



Fig. 3. Solid state absorption spectra of 1 (a), 2 (b) and the corresponding ligands.

in materials [19]. The ligands H_2L , H_2MeL and phenanthroline monohydrate show absorption bands in the UV region and that of 4,4'-bipy is below 450 nm, whereas 1 exhibits a new strong absorption band tailing to 700 nm, which confirm the existence of CTC. The CT absorption band of 2 is much weaker than that of 1. These results are consistent with those of the emission and excitation spectra mentioned above, which show that 1 can be excited effectively by light with a wavelength longer than 460 nm, but 2 can not be excited under the same conditions.

The reason of the different absorption behaviors of **1** and **2** can be ascribed to the aromatic stacking interactions in **1** and **2** as shown in Fig. 4, as the intensity of CT absorption is highly governed by the aromatic stacking interactions, i.e. $\pi \cdots \pi$ and $C-H \cdots \pi$ interactions between the chromophores in metal–organic structures [8a]. It was found the $\pi \cdots \pi$ and/or $C-H \cdots \pi$ interactions exist between the chromophores in both complexes. As shown in Fig. 4a, two phen (A) and PhN (I) moieties from four molecules of **1** are connected via $\pi \cdots \pi$ interactions (the A···A centroid···centroid distance 3.69 Å, A···I centroid···centroid distance 3.67 Å), which are further connected by two phen (B) moieties, through $\pi \cdots \pi$ interaction (the B···B centroid···centroid distance 3.57 Å) and the $C-H \cdots \pi$ interactions (the C26···centroid distance 3.75 Å) to form a 1D chain structure. The 1D chains are linked into a 2D layer by the HL moieties (II) through $C-H \cdots \pi$



Fig. 4. $\pi \cdots \pi$ and/or C-H $\cdots \pi$ interactions in 1 and 2 (only chromophores are displayed for clarity), (a) 1D chain and (b) 2D layer formed in 1, (c) zigzag chain formed in 2.

interactions (C43…centroid distance 3.67 Å, C22…centroid distance 3.53 Å, Fig. 4b).

In **2** there are no $\pi \cdots \pi$ interactions, but edge-to-face C—H $\cdots \pi$ interactions between the chromophores exist. The C18—H $\cdots \pi$ (C18 \cdots centroid distance 3.58 Å) and C29—H $\cdots \pi$ (C29 \cdots centroid distance 3.54 Å) interactions between the benzene and the pyridine rings form a zigzag chain (Fig. 4c). Clearly the D–A interactions in **1** are much stronger than those in **2**. Such difference in the intermolecular interactions leads to the difference in the absorption spectra that **1** has a strong CT absorption but **2** has only a weak one.

To gain further information on the emissive species involved in the photophysical processes of **1** and **2**, the time-resolved fluorescence spectra were measured by changing the excitation wavelength, and the corresponding emission maxima were used as emission wavelength. The fluorescence decay curves clearly show the emissions of both **1** and **2** are from multiple components (Fig. 5). It was found that almost all the fluorescence decay curves of **1** could be analyzed with three components, and the lifetimes are $\tau_1 = 0.98$, $\tau_2 = 5.51$, $\tau_3 = 23.17$ ns, respectively (Figs. S5–10). The contributions of each lifetime change regularly with the increasing excitation wavelengths (Table 1). The contributions of the longest lifetime τ_3 decrease gradually from the dominant 70.20% (excitation at 300 nm) to zero (excitation at 520 nm). When the wavelength of the excitation light is shorter than 420 nm, τ_3 is dominant. According to the absorption and excitation spectra, the ArN moieties and/or phen are excited in such situations. As illustrated in Eq. (1), τ_3 attributes to the emission of the exciplex. The contribution change of τ_1 is opposed to that of τ_3 , it is dominant when **1** is excited with a wavelength longer than 460 nm, obviously in such situations the CT absorption bands are excited, so τ_1 should be assigned to the emissions from CTC. As to τ_2 , it's contribution first increases and then decreases, reaching the maxima with an excitation light at 460 nm. The energy of 460 nm light can not excite the ArN and phen moieties, thus τ_2 should come from a different type of CT emission from that of τ_1 . These results including exciplex and CTCs, these components have different emission wavelengths but are partially overlapped which brings about the tunable emissions of **1**.

The fitting results for the fluorescence decay curves of **2** are shown in Figs. S11–14 and Table 2. Triexponential functions with $\tau_1 = 1.72$ ns, $\tau_2 = 6.22$ ns, $\tau_3 = 33.65$ ns, respectively, are needed to fit the curve with excitation wavelength longer than 440 nm. The emission excited at 400 nm need a biexponential function to be fit with identical lifetimes of τ_2 and τ_3 , and the fit of that excited at 300 nm need a monoexponential function, and the value of the lifetime is the same as that of τ_3 . Considering the excitation wavelengths, τ_3 should belong to the emission of exciplex. It is obvious that τ_3 is dominant in all the situations, which implies the emissions of **2** mainly come from the exciplex formed between the ArN and 4,4'-bipy moieties. Comparing the emission behaviors of



Fig. 5. Fluorescence decay curves of 1 (a) and 2 (b) with different excitation wavelengths (the emission maxima were used for each curve).

both **1** and **2**, a conclusion could be reached that the C–H \cdots π interactions between the corresponding donors and acceptors favor the formation of exciplex rather than CTC in similar systems.

4. Conclusions

Two luminescent Cd(II) metal complexes were synthesized and structurally characterized and their photophysical properties were studied. They exhibit a relatively wide-scope red-shifted emissions covering green to red region compared with those of the ligands. The mechanistic studies suggest that CTC and exciplex are formed in the excited states for both compounds. The aromatic stacking interactions in the solid state structures position the electron donors (the ArN moieties) and acceptors (the auxiliary ligands) in a close proximity, promoting the emission behavior of these metal complexes. It is due to the multiple components involved that the emissions of both compounds can be tuned by simply varying the excitation wavelengths. We believe that CTC and exciplex emissions would be a general phenomenon in similar molecular systems. Further work in this direction with different ligands and metal ions are under way in our lab.

Acknowledgments

The authors thank the Natural Science Foundation of Shandong Province (ZR2009BL008) and the Science and Technology Program of University of Jinan (grant XKY1906) for support of this work. We also thank Prof. Jean F. Halet and his associates for the attempts to simulate the emission spectra of **1**.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

CCDC 1533758 and 1533759 contains the supplementary crystallographic data for 1 and 2, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data to this article can be found online at https://doi.org/10.1016/j.poly.2019. 07.028.

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