

含 2,6-二(甲基苯并咪唑)吡啶钴、镨配合物的合成、 结构、电化学性质和理论计算研究

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摘要: 以 2,6-二(甲基苯并咪唑)吡啶和 2,2'-联吡啶为配体, 合成了一个钴的配合物 $[\text{Co}(\text{mbzimpy})(\text{bipy})\text{Cl}]\text{ClO}_4 \cdot 1.3\text{H}_2\text{O}$ (**1**) 和一个镨的配合物 $[\text{Pr}(\text{mbzimpy})_2(\text{NO}_3)_2]\text{ClO}_4 \cdot 2\text{CH}_3\text{COCH}_3$ (**2**), (mbzimpy =2,6-bis(methylbenzimidazol-2-yl)pyridine, bipy =2,2'-bipyridine) 并利用单晶衍射对其结构进行了表征。还对配合物 **1** 和 **2** 的荧光和电化学性质进行了研究。晶体结构中 C-H...O 氢键和 π - π 芳环堆积作用将每个单核分子连接成一个三维的空间结构。配合物 **1** 的 TD-DFT 理论计算的结果表明: 实验得到的紫外谱图和理论计算的紫外谱图较好地吻合。通过循环伏安图可以了解金属中心的氧化和还原电子对。在不同偶极矩的溶剂中研究其荧光性能。

关键词: 2,6-二(甲基苯并咪唑)吡啶; 晶体结构; 氢键; DFT 理论计算; 电化学性质

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Cobalt(II), Praseodymium(III) Complexes Based on a Rigid 2,6-Bis(methylbenzimidazol-2-yl)pyridine: Syntheses, Structures, Properties and DFT Calculations

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Abstract: Two compounds constructed with mbzimpy, namely, $[\text{Co}(\text{mbzimpy})(\text{bipy})\text{Cl}]\text{ClO}_4 \cdot 1.3\text{H}_2\text{O}$ (**1**), $[\text{Pr}(\text{mbzimpy})_2(\text{NO}_3)_2]\text{ClO}_4 \cdot 2\text{CH}_3\text{COCH}_3$ (**2**), (mbzimpy = 2,6-bis(methylbenzimidazol-2-yl)pyridine, bipy =2,2'-dipyridine) has been synthesized and characterized by single crystal X-ray diffraction. Compounds **1** and **2** are characterized by fluorescence spectral, electrochemical analysis. The weak interactions in the structures include the C-H...O hydrogen bonds and π - π stacking interactions which connect the mononuclear fragments into the 3D frameworks. For **1**, TD-DFT calculations have been performed to obtain their UV-Vis absorption spectra, and satisfactory theoretical-experimental agreement was achieved. Electrochemical investigations using cyclic voltammetry indicate the metal centre reduction and oxidation couples. The fluorescence properties were studied in solvents with different dipole moments. CCDC: 833929, **1**; 827577, **2**.

Key words: 2,6-bis(methylbenzimidazol-2-yl)pyridine; crystal structure; hydrogen bond; DFT calculation; electrochemical property

In the recent years, metal-organic coordination polymers have attracted great attention in the field of coordination chemistry as an emerging class of inorganic-organic hybrid materials. It is not only because of the fascinating architectures and complicated topologies, but also for the interesting potential applications, such as gas storage and separation, luminescence, magnetic materials and catalysis technologies^[1-4]. In most of the coordination polymers reported, the N-donor ligands, including pyridine and azole-based ligands play an important role in the construction of metal-organic complexes with novel structures^[5-8]. Especially, 2,6-bis-(benzimidazol-2-yl)pyridine (bzimpy) and its derivatives, which possess some advantages such as the ease of synthesis, stability, wide possibilities of coordination and their diverse applications^[9-12], have attracted great research interest recently. The significance of the hydrogen bonding interactions along with weak C-H $\cdots\pi$ and $\pi\cdots\pi$ interactions as a directing tool in the organization of molecules has been recognized in both chemistry and biology and thus implicated successfully in the crystal engineering and supramolecular assemblies^[13]. Understanding of the tridentate ligands packing is important because of material properties for applications, and governed by the way in which their constituent molecules are arranged.

In order to get deeper insights on this effect, we have utilized the rigid trident ligand 2,6-bis(methylbenzimidazol-2-yl)pyridine constructing the new coordination polymers with the transition metals and lanthanide metals, some of which has been reported displaying potential applications of water oxidations^[14-15], catalytic activities^[16-17] and so on. Recently, two compounds were synthesized in our current studies. Herein, we report the preparation, crystal structure, electrochemical properties of these compounds. The calculations of UV-Vis absorption spectra completed by TD-DFT computation of compound **1** have been investigated.

1 Experimental

1.1 Materials and physical methods

All reagents and solvents employed are of

analytical grade and without further purification. The ligand 2,6-bis(methylbenzimidazol-2-yl)pyridine (bzimpy) was synthesized following the reported methods^[18]. Elemental analyses were performed with a Perkin-Elmer 240. IR spectra were measured as KBr pellets on a Nicolet FT-170SX spectrometer in the range of 400~4 000 cm⁻¹. Photoluminescence analyses were performed on a Cary-Eclipse fluorescence spectrometer. The UV-Vis spectra were measured on UV-2450 spectrophotometer. The electrochemical experiments were performed with a Chi-730C electrochemistry station at room temperature, using three-electrode system with a glassy carbon working electrode, a platinum counter electrode and a saturated calomel reference electrode (SCE).

1.2 Synthesis of [Co(mbzimpy)(bipy)Cl]ClO₄·

1.3H₂O (**1**)

The ligand mbzimpy (67.8 mg, 0.2 mmol) and bipy (31.3 mg, 0.2 mmol) were dissolved in hot acetone (10 mL), then mixed with a solution of Co(NO₃)₂·6H₂O (47.4 mg, 0.2 mmol) in methanol (5 mL) and stirred for 10 min. 28 mg NaClO₄ (0.2 mmol) in methanol (2 mL) was added to the above solution and stirred for another 8 h at 50 °C. The solution was filtered, evaporated in the air and prismatic orange crystals of **1** were formed after four weeks. Yield: 76%. Elemental analysis result for C₃₁H_{27.6}Cl₂CoN₇O_{5.3}(%): Calcd.: C, 52.23; H, 3.90; N, 13.75; Found: C, 52.46; H, 3.59; N, 14.01. IR (KBr, cm⁻¹): 3 529w, 3 404w, 2 975w, 2 885w, 1 602m, 1 572w, 1 509w, 1 478s, 1 414m, 1 328m, 1 092s, 925w, 874w, 809m, 749s, 623s.

1.3 Synthesis of [Pr(mbzimpy)₂(NO₃)₂]ClO₄· 2CH₃COCH₃ (**2**)

The same synthetic procedure reported for **1** was used to prepare **2**, except that Co(NO₃)₂·6H₂O was replaced by Pr(NO₃)₃·6H₂O (0.089 0 g, 0.2 mmol) to produce small prismatic white crystals of **2**. Yield: 42%. Elemental analysis result for C₄₈H₄₆ClN₁₂O₁₂Pr (%): Calcd.: C, 49.73; H, 4.00; N, 14.50; Found: C, 48.87; H, 4.11; N, 13.89. IR (KBr, cm⁻¹): 3 368w, 2 972w, 2 884w, 1 602m, 1 572m, 1 473s, 1 414m, 1 381m, 1 304w, 1 283m, 1 095s, 1 028m, 1 003w, 913w, 866w, 817w, 748s, 620m.

1.4 Crystal structure determination and refinement

For X-ray diffraction analyses, single crystals of dimension 0.28×0.25×0.23 mm for **1** and 0.22×0.22×0.19 mm for **2** were mounted on a glass rod. The crystal data were collected with a Rigaku Saturn 724+ CCD area detector system using graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0.071\ 073$ nm) at 193 K. The numbers of observed and unique reflections are 11 942 and 3 439 ($R_{\text{int}}=0.027\ 6$) for **1** and 21 377 and 8 311 ($R_{\text{int}}=0.020\ 5$) for **2**. Absorption corrections were applied using the multi-scan technique^[19]. The structure was solved by direct methods of SHELXS-97^[20] and refined by full-matrix least-squares methods on F^2 using the SHELXTL-97 program package^[21]. The hydrogen atoms were generated geometrically and refined isotropically using the riding model, and the solvent water molecules in **1** are highly disordered, SQUEEZE subroutine of the PLATON software suit was used to remove the scattering from the highly disordered guest

molecules^[22]. Intensity data were corrected for factors and empirical absorption. The crystallographic data, bond lengths and angles, hydrogen bonds are listed in Table 1, Table 2 and Table 3.

CCDC: 833929, **1**; 827577, **2**.

1.5 Computational details

Density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations were performed to characterize the experimental absorption spectra by using the Gaussian 09 program^[23]. The model compound was optimized at the UPBEPBE/6-31G*+LanL2DZ* level due to odd electrons of compound **1**. The unrestricted doublet wave function of **1** in DMF (dielectric constant, $\varepsilon=36.71$) solution was test to be stable with the framework of the polarized continuum model (PCM) using PBE functional^[24]. Here, the basis set 6-31G*+LanL2DZ* (using 6-31G* basis set for C, N, Cl, and H atoms, adding the f -type polarization function to Co atom at the basis set LanL2DZ) was employed in view of the

Table 1 Crystal data and structure refinements for **1** and **2**

Compound	1	2
Empirical formula	C ₃₁ H _{27.6} Cl ₂ CoN ₇ O _{5.3}	C ₄₈ H ₄₆ ClN ₁₂ O ₁₂ Pr
Formula weight	712.83	1 159.33
Temperature / K	193	193
Crystal system	Trigonal	Triclinic
Space group	$R\bar{3}m$	$P\bar{1}$
a / nm	3.084 9(3)	1.088 3(2)
b / nm	3.084 9(3)	1.088 3(2)
c / nm	1.054 0(2)	1.611 1(3)
α / (°)		91.78
β / (°)		105.44
γ / (°)		105.95(3)
D_c / (g·cm ⁻³)	1.226	1.573
Z	9	2
$F(000)$	3 289	1 180
Reflections collected	11 942	21 377
Unique reflections	3 439	8 311
μ / mm ⁻¹	0.627	1.126
Goodness-of-fit on F^2	1.071	1.010
R_1 [$I>2\sigma(I)$]	0.047 5	0.028 8
wR_2 [$I>2\sigma(I)$]	0.138 2	0.063 1
R_1 (all data)	0.049 0	0.030 8
wR_2 (all data)	0.139 6	0.064 2
$(\Delta\rho)_{\text{max}}, (\Delta\rho)_{\text{min}}$ / (e·nm ⁻³)	291, -359	822, -570

Table 2 Selected bond lengths (nm) and angles (°) for **1** and **2**

Compound 1					
Co(1)-N(11)	0.211 0(5)	Co(1)-N(2)	0.213 5(5)	Co(1)-N(3)	0.211 8(3)
Co(1)-N(4)	0.210 1(5)	Co(1)-Cl(2)	0.241 6(2)		
N(4)-Co(1)-N(3)	75.70(9)	N(3)-Co(1)-N(3)	150.57(17)	N(11)-Co(1)-N(3)	103.81(9)
N(4)-Co(1)-N(2)	96.49(17)	N(11)-Co(1)-N(2)	76.96(17)	N(3)-Co(1)-N(2)	88.23(10)
N(4)-Co(1)-Cl(2)	90.45(12)	N(3)-Co(1)-Cl(2)	93.50(9)	N(2)-Co(1)-Cl(2)	173.06(14)
Compound 2					
Pr(1)-O(1)	0.254 6(2)	Pr(1)-O(2)	0.258 7(2)	Pr(1)-O(4)	0.254 4(2)
Pr(1)-N(1)	0.262 6(2)	Pr(1)-N(2)	0.267 5(2)	Pr(1)-N(3)	0.262 6(2)
N(5)-Pr(1)-N(2)	172.04(7)	O(1)-Pr(1)-N(5)	69.19(7)	O(4)-Pr(1)-N(1)	85.81(7)
O(5)-Pr(1)-N(5)	68.07(7)	N(12)-Pr(1)-N(5)	61.57(7)	N(4)-Pr(1)-N(5)	62.69(8)
O(2)-Pr(1)-N(2)	70.17(7)	N(1)-Pr(1)-N(2)	62.12(7)	N(3)-Pr(1)-N(2)	61.30(7)
N(12)-Pr(1)-N(2)	111.71(7)	O(5)-Pr(1)-N(1)	130.43(7)	O(1)-Pr(1)-N(4)	83.70(7)

Table 3 Intermolecular hydrogen bond lengths (nm) and bond angles (°) for **1** and **2**

D-H...A	<i>d</i> (D-H)	<i>d</i> (H...A)	<i>d</i> (D...A)	∠DHA
Compound 1				
C(9)-H(9)···O(3)	0.093	0.259	0.351 1(1)	173
C(10)-H(10)···O(1)	0.093	0.255	0.321 2(2)	128
Compound 2				
C(5)-H(5)···O(11) ⁱ	0.093	0.246	0.333 0(5)	155
C(9)-H(9)···O(3) ⁱⁱ	0.093	0.253	0.325 8(4)	135
C(20)-H(12A)···O(4) ⁱⁱⁱ	0.093	0.256	0.346 9(4)	159
C(21)-H(21A)···O(2) ⁱⁱ	0.093	0.249	0.340 12(4)	160
C(24)-H(24)···O(11) ^{iv}	0.093	0.251	0.338 8(5)	158
C(26)-H(26)···O(3) ^{iv}	0.093	0.253	0.339 4(4)	154
C(31)-H(31)···O(7) ^v	0.093	0.258	0.335 4(6)	141
C(36)-H(36)···O(13) ^{vi}	0.093	0.238	0.330 6(4)	172
C(41)-H(41A)···O(11)	0.096	0.252	0.348 0(5)	174
C(41)-H(41C)···O(8)	0.096	0.255	0.348 9(5)	167
C(63)-H(63A)···O(7)	0.096	0.254	0.344 6(8)	157

Semmetry codes: ⁱ $x, -1+y, z$; ⁱⁱ $2-x, -y, 1-z$; ⁱⁱⁱ $1-x, -y, 1-z$; ^{iv} $2-x, 1-y, 1-z$; ^v $1-x, 1-y, -z$; ^{vi} $1-x, -y, -z$.

influence of d and f functions on the absorption spectra. The exponent (2.780) of f orbital for Co atom was selected as those in previous works^[25]. The vertical electronic excitation energies of **1** in DMF were then obtained through TD-DFT/PCM calculation at the same level.

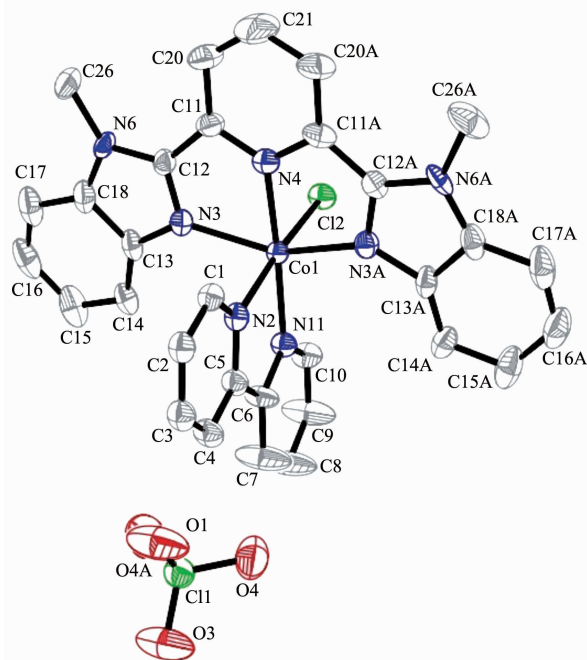
2 Results and discussion

2.1 Crystal structural description of **1**

The perspective view of molecular structure of **1**

with atom numbering scheme is shown in Fig.1. The single-crystal X-ray diffraction study reveals that **1** contains a cation complex [Co(mbzimpy) (bipy)Cl]⁺, which is neutralized by an ClO₄⁻ ions. The Co(II) ion is six coordinated by five nitrogen atoms from the mbzimpy and bipy ligand with chelating mode and one Cl⁻ anion, forming a distorted [CoN₅Cl] octahedral geometry. The axial positions are occupied by nitrogen atoms N4 and N11, with Co1-N4 and Co1-N11 bond lengths of 0.210 1(5) and 0.211 0(5) nm. Slight

distortion is observed in the axial position where N4-Co1-N11 angle is $173.45(16)^\circ$ as opposed to the ideal angle of 180° , which is probably due to the geometric requirements. The equatorial plane is formed by three nitrogen atoms (N3, N3A, N4) and one oxygen atoms Cl2, with Co-N bond distances $d_{\text{Co1-N3}}=0.211\ 8\ (3)\ \text{nm}$, $d_{\text{Co1-N2}}=0.213\ 5\ (5)\ \text{nm}$ as well as $d_{\text{Co1-Cl2}}=0.241\ 60(15)\ \text{nm}$. These bond distances and angles are comparable to those reported for Co(II) complexes of mbzimpy and its derivatives^[26-29]. The counter ClO_4^- anions are evidently strongly associated to cationic complexes by two hydrogen bonds ($\text{C9-H9}\cdots\text{O3}$, $\text{C10-H10}\cdots\text{O1}$). The $\text{C9}\cdots\text{O3}$ and $\text{C10}\cdots\text{O1}$ distances are $0.351\ 1$ and $0.321\ 3\ \text{nm}$, respectively. π - π stacking interactions (Fig.2) are observed between the two mbzimpy parts



Thermal ellipsoids are shown at the 30% probability level

Fig.1 Molecular structure of **1** with atom numbering scheme

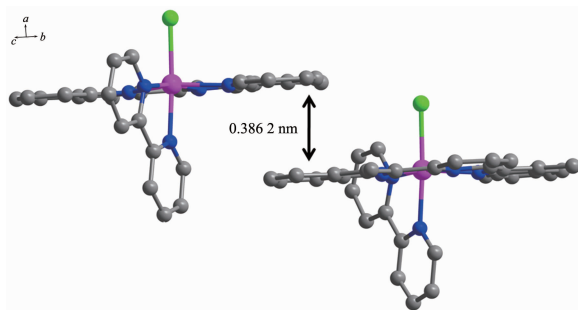
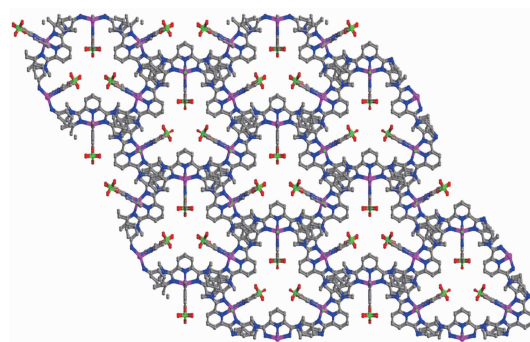


Fig.2 π - π stacking interaction of **1**

from two different neighboring molecules with the centroid to centroid distance of $0.386\ 2\ \text{nm}$ for Cg1 and Cg2 [Cg1=C13~C18, Cg2=N3, N6, C12, C13, C18]. These interactions finally form the 3D framework which shows a porous structure (Fig.3).



Anions and solvent molecules are omitted for clarity

Fig.3 3D framework of **1** showing porous structure

2.2 Crystal structural description of **2**

Compound **2** consists of one cationic complex $[\text{Pr}(\text{mbzimpy})_2(\text{NO}_3)_2]^+$, one ClO_4^- anion, and two uncoordinated acetone molecules. The cationic complex is ten-coordinated by six nitrogen atoms from two tridentate mbzimpy ligands and four oxygen atoms from the two bidentate nitrate groups. The coordination polyhedron of Pr atom is best described as a distorted bicapped square antiprism (Fig.4). The atoms N4, O5, N12, O1 and N3, O2, N1, O4 form the upper and lower square faces. The nitrogen atoms N2, N5 cap the square faces. The average values of the Pr-O and Pr-N bond lengths are found to be in the normal

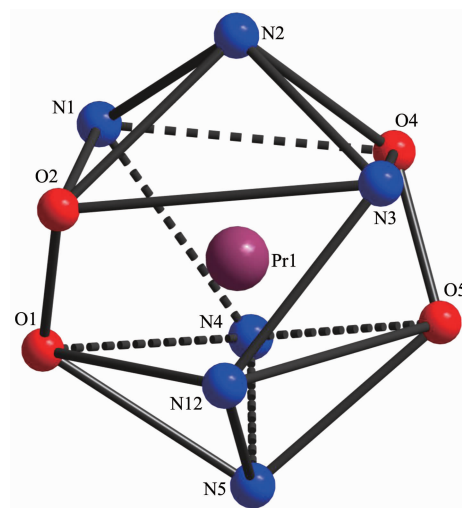


Fig.4 Coordination polyhedra of **2**

range and have a good agreement with those observed for the similar compounds and reported in earlier literatures^[30-31]. In addition, The angle ($\angle N(2)-Pr(1)-N(5)=172.04(7)^\circ$) is significantly distorted from the ideal value of 180° ^[32]. There are $\pi-\pi$ stacking interactions between imidazole rings (Cg3=N4, N13, C34, C35, C50) and benzene rings (Cg4=C35~C39, C50) of each parallel pair of the mbzimpy ligands with centroid...centroid distances of 0.366 1 nm for Cg3...Cg4^{vii} [Symmetry code: ^{vii} 1-x, -y, z] (Fig.5). Finally, the $\pi-\pi$ stacking interactions connect the cationic complexes together, constructing the 3D framework with the help of the C-H...O hydrogen bonds.

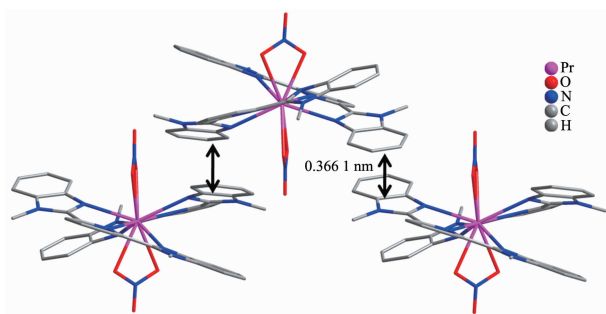


Fig.5 $\pi-\pi$ stacking interactions of **2**

2.3 Electrochemical behavior

The electrochemistry of each complex was examined by cyclic voltammetry (CV) in DMF containing $0.1 \text{ mol} \cdot \text{L}^{-1}$ $[n\text{-Bu}_4\text{N}][\text{ClO}_4]$ (TBAP). Cyclic voltammetry was carried out at 298 K by using an EG&G Princeton Applied Research (PAR) 173 potentiostat/galvanostat or CHI-730C Electrochemical Workstation. A homemade three-electrode cell was used for cyclic voltammetric measurements and consisted of a glassy carbon working electrode, a platinum counter electrode and a homemade saturated calomel reference electrode (SCE). The SCE was separated from the bulk of the solution by a fritted glass bridge of low porosity which contained the solvent/supporting electrolyte mixture. The results of the complex are summarised in Table 4.

As shown in Fig.6, **1** exhibits two one-electron reversible reduction and one irreversible one-electron oxidation. The first reduction at $E_{1/2} = -0.57 \text{ V}$ is assigned to the $\text{Co}^{\text{II}}/\text{Co}^{\text{I}}$ couple ($\Delta E_p = 80 \text{ mV}$), while the other at $E_{1/2} = -1.27 \text{ V}$ is assigned to the process of

Table 4 Redox and potentials of **1-2** in DMF^a

Compound	E_{pc} / V	E_{pa} / V	$\Delta E_p / \text{mV}$	$E_{1/2} / \text{V}^b$
1	-0.57	-0.49	80	-0.53
	-1.28	-1.19	90	-1.24
	0.57	—	—	—
2	-1.78	—	—	—

^a Potentials are vs $\text{Fc}^{+/0}$ in $0.1 \text{ mol} \cdot \text{L}^{-1}$ TBAP, $T=293 \text{ K}$ ($\text{Fc}^{+/0}$ is the potential of Ferrocene). Scan rate $100 \text{ mV} \cdot \text{s}^{-1}$. Approximate concentrations: $1 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$. ^b $E_{1/2} = 0.5(E_{\text{pc}} + E_{\text{pa}})$.

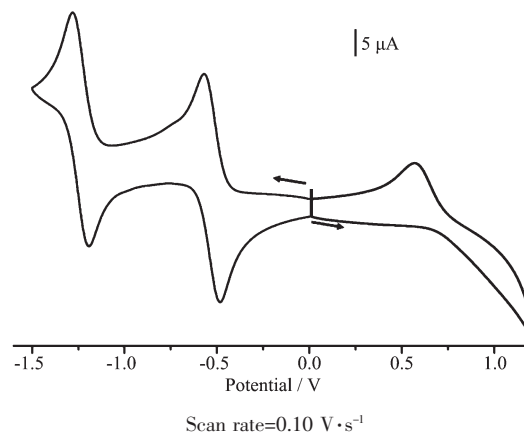


Fig.6 Cyclic voltammogram of **1** in DMF, $0.1 \text{ mol} \cdot \text{L}^{-1}$ TBAP

$\text{Co}^{\text{I}}/\text{Co}^0$ ($\Delta E_p = 90 \text{ mV}$). The metal-based oxidation of the coordination center attributes to the irreversible couple $\text{Co}^{\text{II}}/\text{Co}^{\text{III}}$ ($E_{\text{pc}} = 0.57 \text{ V}$). The electrochemical results show that the ligand can stabilize the reduction states of cobalt, which due to the π^* nature of the ligand^[33]. Compound **2** displays a CV wave for $\text{Pr}^{\text{III}}/\text{Pr}^{\text{II}}$, and the CV wave for the process $\text{Pr}^{\text{III}}/\text{Pr}^{\text{II}}$ falls at potentials near -1.78 V (Fig.7).

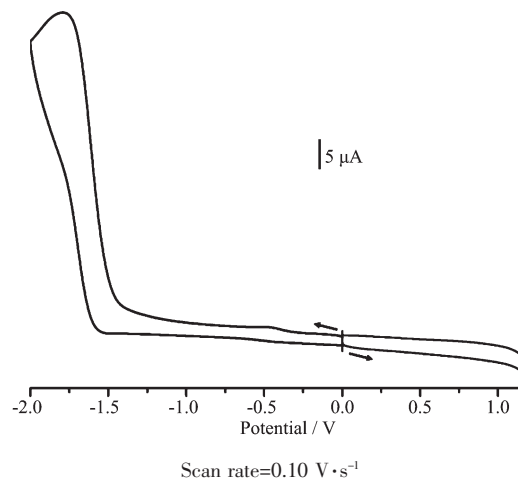
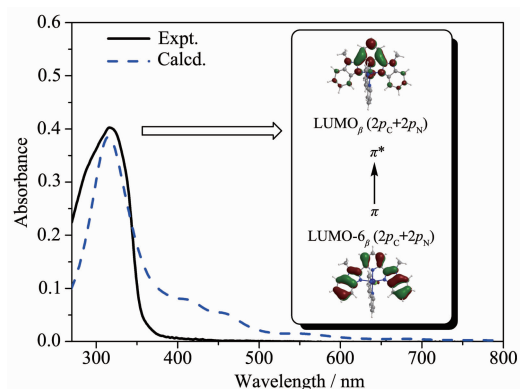


Fig.7 Cyclic voltammogram of **2** in DMF, $0.1 \text{ mol} \cdot \text{L}^{-1}$ TBAP

2.4 DFT calculations and electronic structure

The theoretical absorption spectrum of compound **1** obtained from TD-DFT/PCM calculation at the UPBEPBE /6-31G* + LanL2 DZ* level is in good agreement with the experimental observation, as displayed in Fig.8. The lowest dipole-allowed absorption band is mainly assigned to be $\pi \rightarrow \pi^*$ transitions. As schematically illustrated in the inset of Fig.9, the π and π^* orbitals are dominated by the p orbitals of mbzimpy.



Lorentzian function is adopted with the spectral line width set to be 120 nm; Theoretical spectrum is systematically left-shifted by 105 nm from TD-DFT excitation energies

Fig.8 Absorption spectra of **1** obtained from experimental observation and TD-DFT/PCM calculation at the UPBE/LanL2DZ(f)+6-31G(d) level

2.5 Photoluminescent properties

Coordination polymers with lanthanide metal centers and conjugated organic linkers are promising candidates for luminescent materials, which have been investigated owing to their fluorescent properties and potential applications. As we see from Fig.9, The fluorescence spectra recorded for various solvents such as n-hexane, acetone, ethanol, methanol and acetonitrile have slightly different shapes. The fluorescence emissions were observed between 368 and 390 nm in these solvents. In the case of the solute molecule having different dipole moments in the electronically excited state and the ground state, absorption of light induces changes of the local electric field and gives rise to a reorganization of solvent molecules within a sphere of action surrounding the excited chromospheres molecule^[34].

The central wavelengths shift towards long wavelengths for increasing solvent's orientation polarizability. This is because the lowest-energy state of the first excited state lowered in a polar solvent. The larger the dipole moment is, the lower the excited state will be^[35].

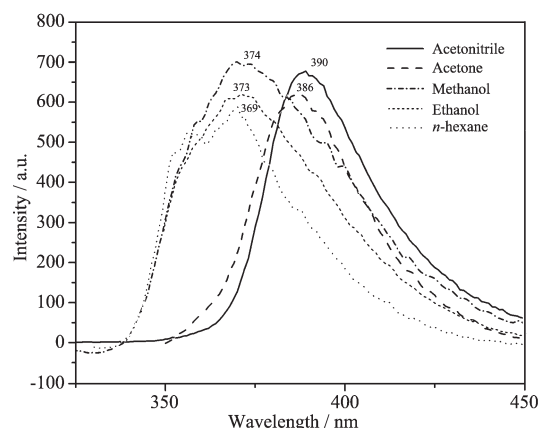


Fig.9 Fluorescence spectra of **2** in different solvents

3 Conclusions

We have synthesized and characterized two new supramolecular compounds. TD-DFT calculations using PBEPBE functional fit very well with the experimentally observed electronic and UV-Vis spectrum. Electrochemical investigations using cyclic voltammetry indicate the metal centre reduction couples. Compound **1** gives two one-electron metal-based reduction process $\text{Co}^{\text{II}}/\text{Co}^{\text{I}}$ and $\text{Co}^{\text{I}}/\text{Co}^0$ and one-electron oxidation $\text{Co}^{\text{II}}/\text{Co}^{\text{III}}$. While **2** has one-electron reduction process $\text{Pr}^{\text{III}}/\text{Pr}^{\text{II}}$. Especially, these cyclic voltametric analyses of the compounds provide further support to the studies of compounds with mbzimpy and its derivatives. Furthermore, by studying the uorescence shifts of **2** in solvents with different dipole moments, we found these compounds could be applied in the area of luminescent materials in further studies.

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