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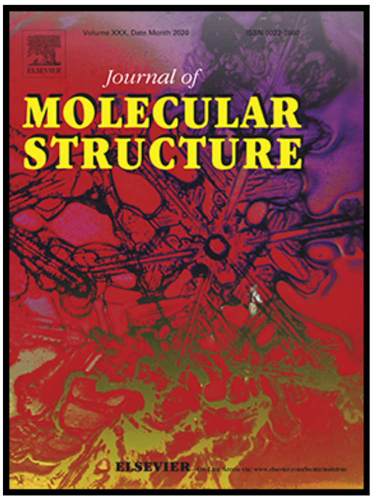

Crystal structure, thermal behavior, luminescence and theoretical calculation of a new Pb(II) coordination complex

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Highlights

- One new Pb(II) complex has been synthesized with DIPT and HL.
- The complex **1** has been characterized by IR and single crystal X-ray diffraction.
- The PXRD, TGA, UV and Luminescent property were also investigated.
- The calculated absorption value is in closed the experimental result.
- Intermolecular hydrogen bonding give rise to 2D supramolecular arrangements.

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Crystal structure, thermal behavior, luminescence and theoretical calculation of a new Pb(II) coordination complex

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Abstract: In this report, a new coordination complex Pb(CDIPT)$_2$(L)$_2$ (CDIPT= 10-chloro-2-(2,4-dichlorophenyl)-1H-imidazo[4,5-f]-[1,10]phenanthroline, HL= 2,4-dichlorophenyl acrylic acid) has been synthesized and fully characterized by elemental analysis, IR spectroscopy, UV spectrum, single-crystal X-ray diffraction analysis, luminescence spectra, TGA and powder X-ray diffraction. The structural analysis showed that the complex **1** is a zero dimensional structure with seven coordinated Pb(II) ion. And further, the adjacent complex units are extended into a 2D supramolecular network through the H-bonds [N(4)-H(4)···O(4) and N(7)-H(7)···O(1)]. The luminescence explorations demonstrated that complex **1** has good optical properties. In addition, the quantum chemistry calculations were performed with the Gaussian09 program.

Keywords: Crystal structure; Pb(II) complex; Luminescence; Quantum chemistry calculations

1. Introduction

Coordination complexes are crystal materials with periodic network formed by self-assembly of metal ions or metal clusters and organic ligands. Coordination complexes have become a hot topic in the field of new materials due to their adjustable structures, high crystallinity and controllable porosity. [1-6]. Coordination complexes can be divided into one-dimensional chain structure, two-dimensional layer structure and three-dimensional network [7-9]. And now, it is easy to acquire the different coordination complexes with desired structures and properties. There are lots of methods to synthesize the coordination complexes such as evaporative solvent method, diffusion method, hydrothermal or solvent-thermal method, ultrasonic and microwave method etc. [10-12].

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The center metal ions and organic ligands show the decisive role for the structures and functions of targeted coordination complexes [13-15]. The selection of metal centers of coordination complexes almost covers all metals, including main group elements, transition elements, lanthanide metals, etc. [16-22]. The different valence states and coordination capacities of different metal ions can also affect the structures and properties of materials. For organic ligand's selection, the transition from the earliest easily collapsed nitrogen heterocyclic ligands to the stable carboxylic acid ligands [23]. In order to solve the collapse of coordination complexes which were removing guest molecules, chemists began to synthesized coordination complexes with one or more functional groups based on anion and neutral ligands. The combination of different functional groups greatly expanded the application scope of coordination complexes [24]. Due to large specific surface area, adjustable channel, easy functionalization and interesting topological structure, researchers have made great advances in fields such as molecular magnetics, photoluminescence, ion exchange, gas storage, and catalysis.[25-34].

Heterocyclic compounds play an important role in coordination chemistry [35-39]. 1,10-phenanthroline and its derivatives [39] have been widely studied on account of their unique structures and properties. Each 1,10-phenanthroline molecule is composed of three aromatic rings, which has strong conjugation and is easy to coordinate with a variety of metal ions to produce complexes with unique functions. Because it has a good conjugated system, which can increase the thermal stability and fluorescence intensity of coordination complexes [41-43]. Therefore, it has widespread applications in optical, magnetic and fluorescent materials.

β-substituted phenylacrylic acid has good coordination ability and thermal stability. For example, S. Han, etc. [44] investigated the synthesis, crystal structure and theoretical calculation of triphenyltin (IV) polymer based on 2,4-dichlorophenylacrylic acid. H. Y. Sun, etc. [45] successfully synthesized a novel Co(II) by using 2-(2,4-dichlorophenyl)-1H-imidazo[4,5-f]-[1,10]phenanthroline as the N-heterocyclic ligand and the 3-(2-chlorophenyl)acrylic acid. Therefore, it is meaningful to study the β-substituted phenylacrylic acid as carboxylic acid ligand in coordination complexes.

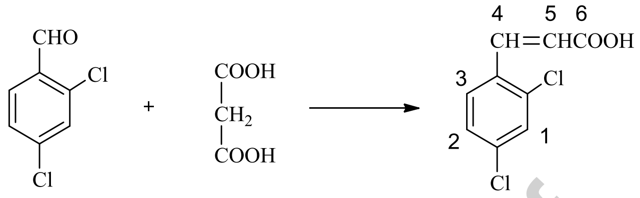
In order to further exploring the structural type of the coordination complex and the coordination mode of central Pb(II) ions, our group synthesized a Pb(II) coordination complex using 2,4-dichlorophenyl acrylic acid (HL) and 2-(2,4-dichlorophenyl)-1H-imidazo[4,5-f]-[1,10]phenanthroline (DIPT).

2. Experimental

2.1 Synthesis of 2, 4-dichlorophenyl acrylic acid

The synthesis of HL (Route 1): A mixture of 3.7 g malonic acid (0.035 mol), 4 mL pyridine, 8 mL toluene, 5.7 g 2, 4-Dichlorobenzaldehyde (0.033 mol), 0.35 mL aniline (catalytic) are added in a round-bottom flask, added. The mixed solution was refluxed for 3-4 h under electromagnetic stirring, taken away the solvent by vacuum distillation, added K_2CO_3 solution and ethyl acetate, then stirred for

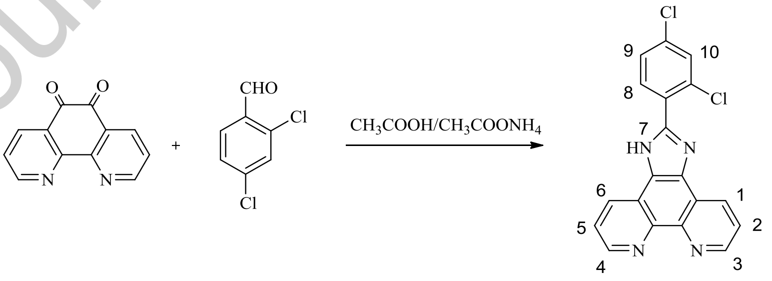
15 minutes. The organic layer was neutralized by HCl solution and the resulting solid was washed, filtered and dried, then obtained target compound. Productivity: 64.6%. Elemental analysis: calcd. (%) for $C_9H_6O_2Cl_2$: C, 49.80; H, 2.79; found (%): C, 48.04; H, 2.81. IR (KBr, cm^{-1}): 2823(w), 2567(w), 1690(s), 1619 (m), 1579(m), 1469(m), 1211(m), 982(m), 862(m), 815(m), 769(m). ^1H NMR (DMSO, ppm, 400Hz) : 12.71 (s, 1H, H_6), 7.96 (d, ^3J(H-H) = 8.0 Hz, 1H, H_3), 7.81 (d, ^3J(H-H) = 16.0 Hz, 1H, H_4), 7.72(s, 1H, H_1), 7.48 (d, ^3J(H-H) = 8.0 Hz, 1H, H_2), 6.65 (d, ^3J(H-H) = 16.0 Hz, 1H, H_5).



Route 1

2.2 Synthesis of 2-(2,4-dichlorophenyl)-1H-imidazo[4,5-f][1,10]phenanthroline

The synthesis of DIPT (Route 2): A mixture of 2.2 mL 2,4-dichlorobenzaldehyde (0.020 mol) , 4.20 g 1,10-Phenanthroline-5,6-dione (0.020 mol), 5.0 g ammonium acetate (0.060 mol), 40 mL glacial acetic acid were added in a round-bottom flask and the reaction was monitored by TLC technique. After the reaction ended, reaction mixture was extracted by dichloromethane and resultant products was purified by column chromatography (benzene : ethyl acetate = 9 : 1). Productivity: 69.8%. Elemental analysis: calcd. (%) for $C_{19}H_{10}Cl_2N_4$: C, 62.48; H, 2.76; N, 15.34. found (%): C, 62.04; H, 2.08; N, 14.88. IR (KBr, cm^{-1}): 3379(w), 1672(s), 1554(m), 1096(m), 803(m), 738(m), 562(m). ^1H NMR (DMSO, ppm, 400 Hz): 13.97 (s, 1H, H_7), 9.07(d, 2H, H_3,H_4), 8.89 (d, 2H, H_1,H_6), 7.98 (d, ^3J(H-H) = 8.0 Hz, 1H, H_8), 7.92 (s, 1H, H_{10}), 7.84(s, 2H, H_5,H_2),7.69 (d, ^3J(H-H) = 8.0 Hz, 1H, H_9).



Route 2

2.3 Synthesis of complex 1

The synthesis of complex **1**: 83.44 mg $PbCl_2$ (0.0003 mol), 219.13 mg DIPT (0.0006 mol) and 83.44 mg HL (0.0003 mol) were mixed according to the material ratio of 1 : 2 : 1, added 36 mL tap water and stirred thoroughly at room temperature for 20min. Then adjusted pH=6.5 with NaOH solution. The reaction mixture crystallized in a 50 mL Teflon-lined autoclave for 5 days at 160 ℃, and

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then cooled to room temperature at 5 ℃/h. A large number of yellow block crystals were obtained at the bottom of the kettle, washed with distilled water and dried naturally with a yield of 6.8% (in terms of Pb). The experimental value of element analysis is (%): C, 46.69; H, 1.94; N, 5.05. The theoretical value of element analysis is (%): C, 46.71;H, 1.95;N, 5.00.

2.4 physical measurements

The IR spectrum was described through Perkin-Elmer 240C spectrometer in the range of 4000~400 cm^{-1}. The UV spectrum was carried out a JASCO V-770 ultraviolet spectrophotometer in the range of 200~800nm. TGA was performed using a Rigaku Thermo Plus-EVO analyzer in nitrogen with a heating rate of 10 ℃/min. The luminescence spectra for the powdered solid samples were measured at room temperature and the spectra were collected with a Hitachi F-4600 fluorescence spectrometer. Powder X-ray diffraction (PXRD) data was recorded on a Rigaku model RINT Ultima III diffractometer by depositing powder on glass substrate, from 2θ = 1.5° up to 60° with 0.02° increment. The date of ^{1}H NMR were obtained Bruker AVANCE III HD 400M. The quantum chemistry calculation of complex **1** was performed with the Gaussian09 program [46] at the B3LYP/GenECP level (the 6-31+G(d) basis set for C, H, O, N, Cl) and LANL2DZ basis set for Pb). The initial state structure for the title complex **1** was obtained from the X-ray refinement data (cif). The initial state structure we adopted the approximate structure model was not optemized, while the triplet state structure is optemized at the same level.

2.5 X-ray crystallography

Crystal structure measurement was performed on a Bruker SMART APEX II CCD diffractometer equipped with a graphite-monochromatic Mo Kα (λ = 0.71073 nm) radiation by using the φ and ω scan mode at 296 (2) K [47]. The structure was solved by direct methods with SHELXS program [48] and refined with SHELXL-2016/6 [49] by full-matrix least-squares techniques on F^2. All non-hydrogen atoms were refined anisotropically. Crystallographic data and Structure Refinement parameters for the complex **1** in Table 1. Selected bond lengths (**Å**) and bond angles (°) are in Table 2. Hydrogen bond lengths (**Å**) and bond angles (°) are listed are in Table 3. The Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre: deposition numbers CCDC 1977916. These data may be obtained free of charge from the Cambridge Crystallographic Data Center through http:// www.ccdc.cam.ac.uk/data_request/cif.

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Table 1. Crystallographic data and Structure Refinement parameters for the complex 1.

Empirical formula	$C_{56}H_{28}Cl_{10}N_8O_4Pb$
Formula weight	1438.55
Temperature	296(2) K
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	$Pn2_1a$
a (Å)	33.112(3)
b (Å)	14.3543(15)
c (Å)	11.3282(12)
α (º)	90
β (º)	90
γ (º)	90
Volume (Å^3)	5384.3(10)
Z	4
Density (Mg/m^3) calculated	1.775
Absorption coefficient (mm^{-1})	3.687
F(000)	2816
Crystal size (mm^3)	0.28 × 0.26 ×0.25
Theta range (°)	1.878-25.009
Limiting indices	$-39 \leq h \leq 39$, $-17 \leq k \leq 14$, $-13 \leq l \leq 12$
Reflections collected / unique	27332 / 8580 [R_{int} = 0.0479]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6914 / 5 / 629
Goodness-of-fit on F^2	1.048
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0410, wR_2 = 0.0939
R indices (all data)	R_1 = 0.0575, wR_2 = 0.0999
Largest diff. peak and hole (e Å^{-3})	0.623 and -1.344

Table 2. Selected Bond Lengths (Å) and Bond Angles (°)

Bond	**Dist.**	**Bond**	**Dist.**	**Bond**	**Dist.**
Pb-O(1)	2.486(9)	Pb-O(3)	2.643(9)	Pb-N(6)	2.795(5)
Pb-N(1)	2.527(4)	Pb-N(2)	2.549(5)	Pb-N(5)	2.709(6)
Angle	**(°)**	**Angle**	**(°)**	**Angle**	**(°)**
O(1)-Pb-O(3)	90.4(3)	O(1)-Pb-N(1)	76.1(3)	O(1)-Pb-N(2)	79.8(3)
O(1)-Pb-N(6)	147.3(3)	O(1)-Pb-N(5)	126.3(3)	O(3)-Pb-N(6)	105.5(3)
O(3)-Pb-N(5)	134.7(3)	N(1)-Pb-O(3)	141.1(3)	N(1)-Pb-N(6)	73.6(3)
N(1)-Pb-N(2)	63.9(3)	N(1)-Pb-N(5)	79.4(3)	N(2)-Pb-O(3)	78.0(3)
N(2)-Pb-N(6)	75.9(3)	N(2)-Pb-N(5)	128.6(3)	N(5)-Pb-N(6)	59.3(3)

Table 3. Hydrogen Bond Lengths (Å) and Bond Angles (°)

D–H···A	**d(D–H)**	**d(H···A)**	**d(D···A)**	**∠DHA**
N(4)-H(4)···O(4)	0.86	1.88	2.731(17)	170.7
N(7)-H(7)···O(1)	0.86	2.14	2.898(14)	147.3

3. Results and discussion

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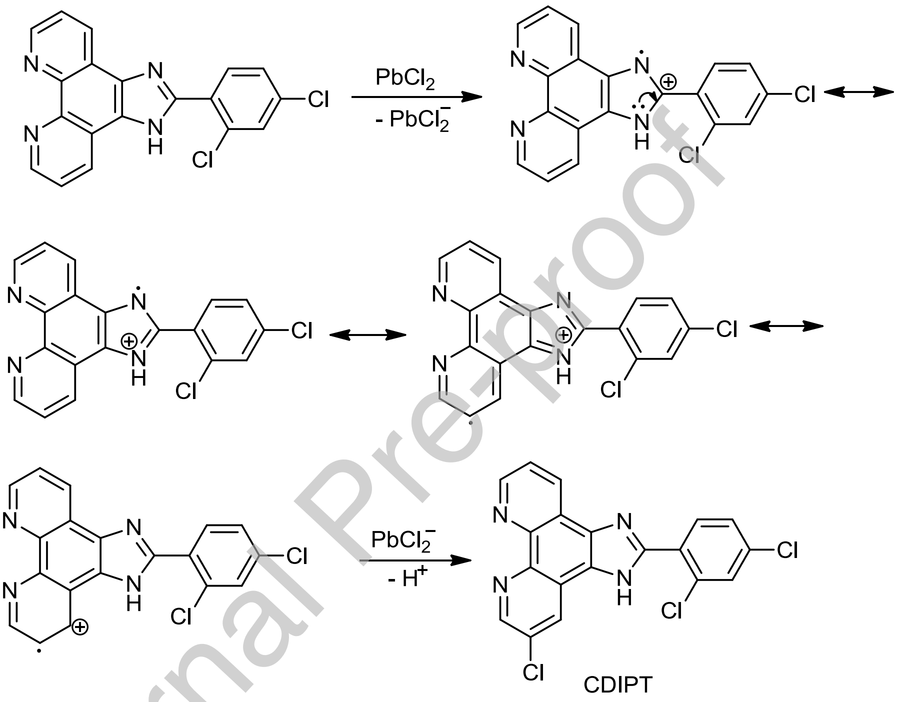
3.1 Description of crystal structure

It's interesting that a hydrogen atom on the carbon at position 10 of the DIPT ligand was replaced by a chlorine atom. According to references[50-51], the Speculative principle is as follows (Route 3): under a definite temperature and pressure, $PbCl_2$ as a single electron transfer reagent, captures a single electron on the imidazole ring and causes the DIPT ligand to generate free radical positive ions. The corresponding resonance formula reacts with $PbCl_2^-$ and obtains the 10-chloro-2-(2,4-dichlorophenyl)-1H-imidazo[4,5-f][1,10]phenanthroline (CDIPT).



Route 3

The structure of complex **1** is described in **Fig. 1**, each central Pb(II) is seven-coordinated by four nitrogen atoms (N1, N2, N5, N6) from two CDIPT ligands and three carboxylate oxygen atoms (O1, O2, O3) from two different deprotonation of HL, it can be regarded as a distorted heptacoordinate pentagonal bipyramid in **Fig. 2.** Deprotonation of HL has two coordination modes: monodentate bridging and bidentate chelating coordination. The structure analysis shows that the complex **1** is a zero dimensional structure. There exist hydrogen bonds [N(4)-H(4)···O(4) and N(7)-H(7)···O(1)] between the two bridging ligands CDIPT and deprotonation of HL in the complex **1**, there are intermolecular which stabilizes the structure and promote the formation of 2D supramolecular network (**Fig. 3 and 4)**.

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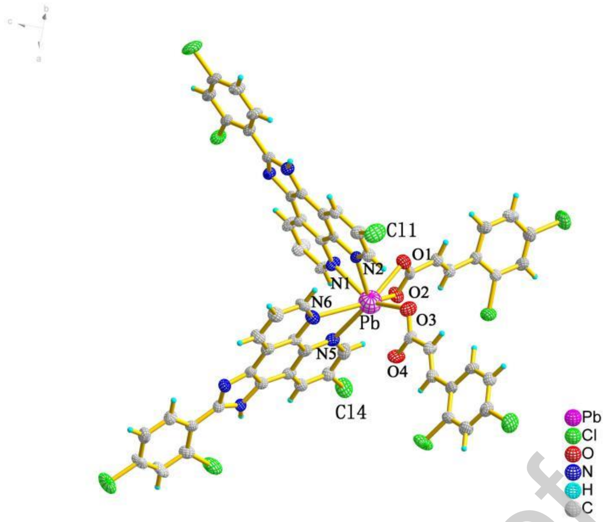

Fig. 1 Crystal structure of the complex 1.

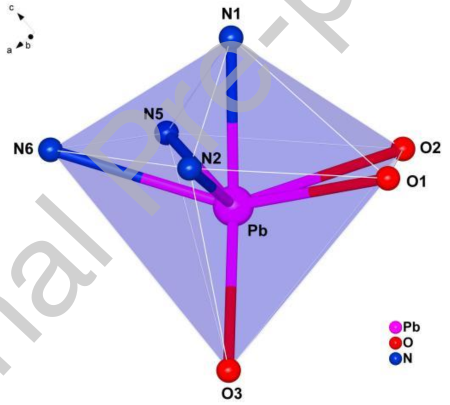

Fig. 2 Coordination environment of the Pb^{2+}.

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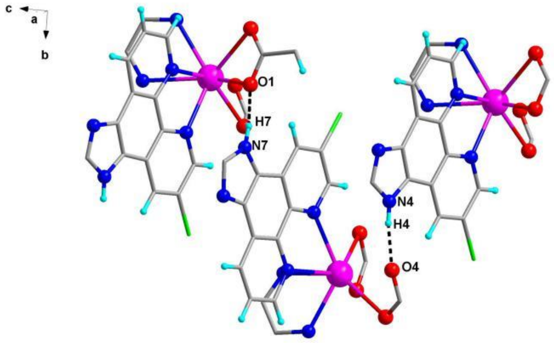

Fig. 3 Hydrogen bond linking of neighboring molecules (Some atoms are omitted).

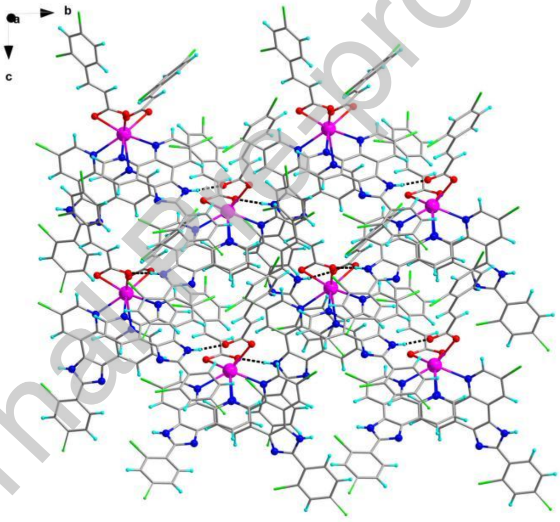

Fig. 4 The 2D structure of complex 1 .

3.2 IR spectrum

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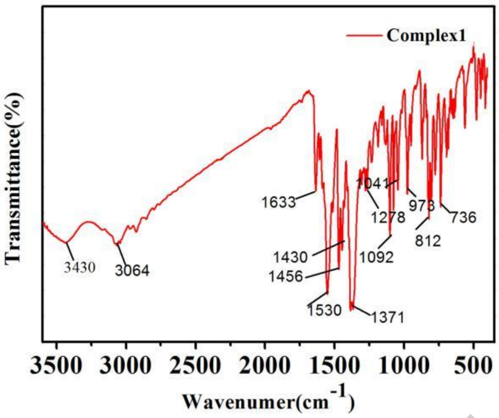

Fig. 5 IR spectra of complex 1.

IR spectra of complex **1** was shown in **Fig.5**. From the infrared spectra of complex **1**, the main characteristic peaks of complex **1** are 3430, 3064, 1633, 1530, 1456, 1430, 1371, 1278, 1092, 1041, 973, 812,736 cm^{-1}. At 3430 cm^{-1}, the absorption peak is wide and scattered, which indicates that the complex **1** contains water. The peak at 3064 cm^{-1} is mainly the stretching vibration of C-H(-C=C-H) [52]. At 1633, 1530 cm^{-1}, they should be attributed to the asymmetric stretching vibration absorption peak of C=O on the carboxyl group, and at 1456, 1430 cm^{-1}, they should be classified as the symmetric stretching vibration absorption peak of C=O, indicating that the carboxyl group in the ligand participates in coordination [53] and the coordination pattern of carboxyl group are single dentate bridging and double dentate chelating. The peak at 1371 cm^{-1} should be attributed to the stretching vibration of C-N. Around 1092 cm^{-1}, this region mainly includes the in-plane bending vibration of C-H [54], stretching vibration of C-Cl, and single-bond skeleton vibration of C-C. At 812 and 736 cm^{-1}, there are the characteristic peaks of substituted aromatic ring [55]. It is consistent with the results of elemental analysis and single crystal structure analysis of the complex **1**.

3.3 UV spectrum and Fluorescence spectrum

Its solid UV spectrum and fluorescence spectrum are studied. The relationship between structure and property is discussed.

The UV spectrum was used to test the wavelength range of 200-800 nm, as shown in **Fig. 6**. The ligand HL has a strong absorption peak at 200-380 nm, the DIPT has a strong absorption peak at 200-450 nm. Similarly, the complex **1** has shown strong peak at 200-500nm can be assigned to π→π* transition of the aromatic ring and n→π* transition of the carboxyl, one weaker peak at 500-520 nm and presumably originates from metal-to-ligand transition. The shift in the position and strength of the characteristic absorption peaks are due to the redistribution of the electron cloud and electron transfer between the ligands and metal ions after the coordination between the metal ions and ligands.

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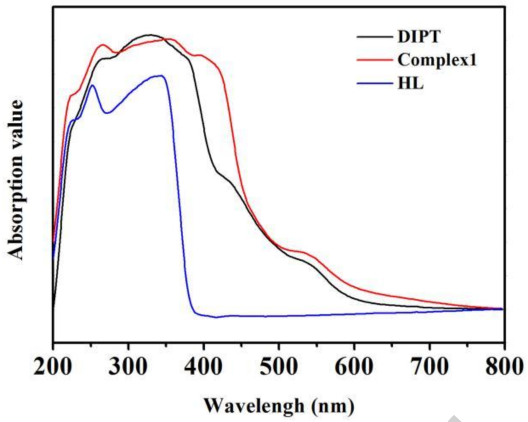

Fig. 6 UV spectrum of the ligands and complex 1

The solid state luminescent properties of complex **1**, ligand HL and DIPT have been tested at room temperature and the fluorescence emission spectra of them are illustrated in **Fig. 7**. the excitation wavelength of HL, DIPT and complex **1** has also tested (insert of Fig.7). The emission peak of the ligand HL is located at 408 nm (excitation at 320 nm) and the ligand DIPT is located at 426 nm (excitation at 352 nm), the emission spectrum of complex **1** shows a maximum emission wavelength at 481 nm (excitation at 384 nm). Compared to the ligand DIPT and HL, complex **1** exhibits a significant red shift, which can be assigned to the formation of the complex. Fluorescence analysis showed that the complex had good optical properties and could be used as a potential optical material [56].

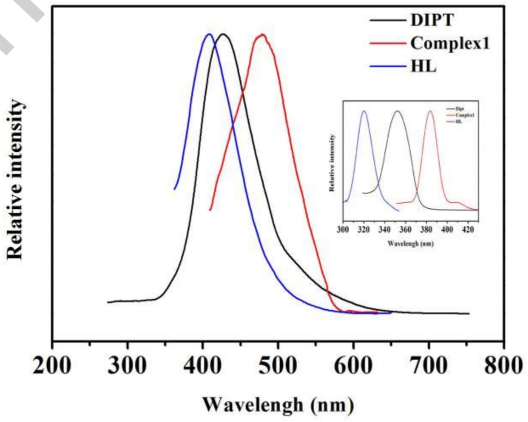

Fig. 7 Emission spectrum of ligands and complex 1 in solid state.

3.4 PXRD and Thermal Analyses

PXRD of complex **1** was carried out at room temperature in order to confirm the phase purity in

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Fig. 8. The experimental PXRD pattern is closely matched with the simulated pattern from single-crystal structure, revealing the good phase purity of the bulk crystalline material.

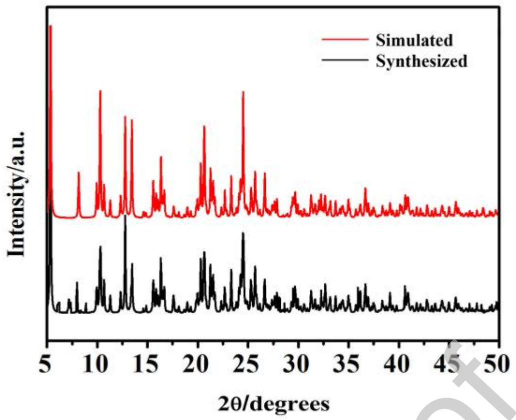

Fig.8 PXRD patterns of complex 1.

The TGA experiment was performed under N_2 atmosphere at a heating rate of 10 ℃/min. As shown in **Fig. 9**, the anhydrous complex **1** begins to decompose at 270 ℃ and ends above 470 ℃. Within the temperature range of 50-800 ℃, only one section of weightlessness of complex **1** corresponds to the loss of organic ligands, and the final residual is the oxide of Pb. The weightlessness of the whole process is 85.12 % (theoretical estimate of 84.48%). In conclusion, the thermal data is in reasonable agreement with the crystal structure analysis and complex **1** exhibited good thermal stability.

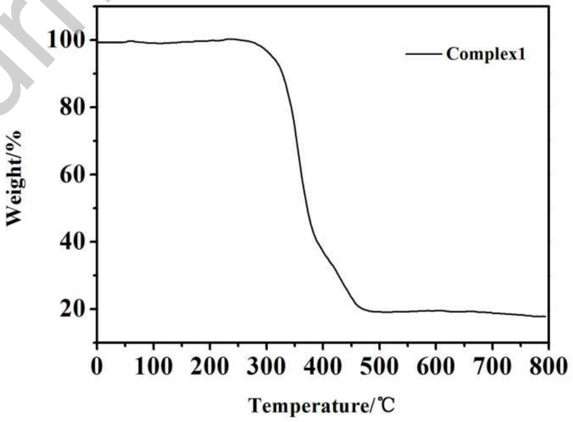

Fig. 9 TGA curves of complex 1

3.5 Theoretical Calculation

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The calculation covered 107 atoms, 1508 basis functions, 2860 primitive gaussians, 313 α electrons and 313 β electrons for the model of complex **1**. The total molecular energy is =-203942.207 eV, the energies of HOMO and LUMO are -3.126 eV and -5.344 eV, respectively, with the ΔE (E_{LUMO}-E_{HOMO}) value to be 2.219 eV. Selected atom net charges and electronic configuration of the title complex at the B3LYP/(6-31 + G(d) (for C, H, O, N and Cl) and LANL2DZ (for Pb) levels are listed in Table **4**. The calculation results show that electronic configurations of the central Pb atom is $6S^{1.96}6p^{0.53}7p^{0.02}$, N atoms are $2S^{1.38\sim1.39}2p^{4.04\sim4.08}3S^{0.01}3p^{0.01\sim0.02}47p^{0.01}$and those of O and Cl atoms are $2S^{1.70\sim1.72}2p^{4.99\sim5.06}3S^{0.01}3p^{0.02\sim0.03}3d^{0.01\sim0.02}$and $3S^{1.86\sim1.87}3p^{25.11\sim5.12}3d^{0.01}$. It can be concluded from the calculation that the coordination of Pb(II) ion with N and O atoms is mainly on the 2s and 2p orbitals. All O atoms give electrons to the Pb(II) ion in the 2s, 2p, 3d orbitals and form coordination bonds. N atoms form coordination bonds with Pb(II) ion through 2s, 2p and 3p orbitals. So the Pb(II) ion gets some electrons from the O atoms of the deprotonation of HL ligand and the N atoms of the CDIPT ligand. N1, N2, N5, N6, O1, O2, O3 have more negative charges, generally speaking, the more negative charges, the stronger nucleophilicity, the stronger its ability to form coordination complexes with the metals. Thus, according to valence-bond theory the atomic net charge distribution in the HL and CDIPT show obvious covalent interactions between the coordinated atoms and Pb(II) ion.

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Table 4 Selected atom net charges and electronic configuration of complex 1 at the B3LYP/(6-31 +G(d) (for C, H, O, N and Cl) and Lanl2dz (for Pb) levels

Atom	**Charge**	**Electron configuration**
Pb	1.494	[core]6S(1.96)6p(0.53)7p(0.02)
N1	-0.493	[core]2S(1.38)2p(4.08)3p(0.02)4p(0.01)
N2	-0.483	[core]2S(1.39)2p(4.07)3p(0.02)
N5	-0.463	[core]2S(1.39)2p(4.04)3S(0.01)3p(0.02)4p(0.01)
N6	-0.460	[core]2S(1.39)2p(4.05)3p(0.02)
O1	-0.776	[core]2S(1.71)2p(5.03)3p(0.02)3d(0.01)
O2	-0.797	[core]2S(1.71)2p(5.04)3p(0.03)3d(0.02)
O3	-0.778	[core]2S(1.70)2p(5.06)3d(0.01)
O4	-0.722	[core]2S(1.72)2p(4.99)3S(0.01)
Cl1	0.016	[core]3S(1.86)3p(5.11)3d(0.01)
Cl4	-0.003	[core]3S(1.87)3p(5.12)3d(0.01)

UV spectral analysis of complex **1** has been investigated by TD-DFT method **(Fig. 10)**. It can be seen from the UV visible spectra, the calculated absorption maximum values has been found to be 341nm. The calculated absorption value is in good agreement with the experimental result.

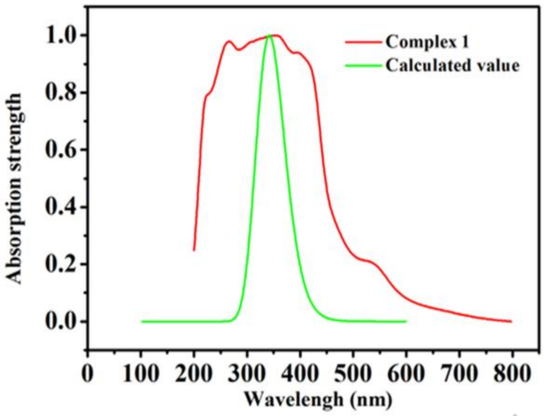

Fig. 10 Calculated and experimental absorption values of complex 1.

The 341 nm absorption peak is mainly due to the transition of electrons from the HOMO-2 orbital to the LUMO orbital, it contributed 56.43 % of the main absorption peak. The others, HOMO-3 → LUMO, 4.84 %; HOMO-1 → LUMO, 3.37 %; HOMO-1 → LUMO+1, 31.17 %; HOMO-1 → LUMO+3, 4.19%. According to molecular orbital theory, HOMO has the important role of giving electrons first, while LUMO receiving electrons. The HOMO and LUMO are presented in **Fig. 11**, The HUMO-2 orbital electron cloud is provided by the double bond carbon atoms on the deprotonation of HL ligand molecule and the whole CDIPT molecule, after absorbing the light energy, it jumped to the CDIPT ligand molecule on the LUMO orbital.

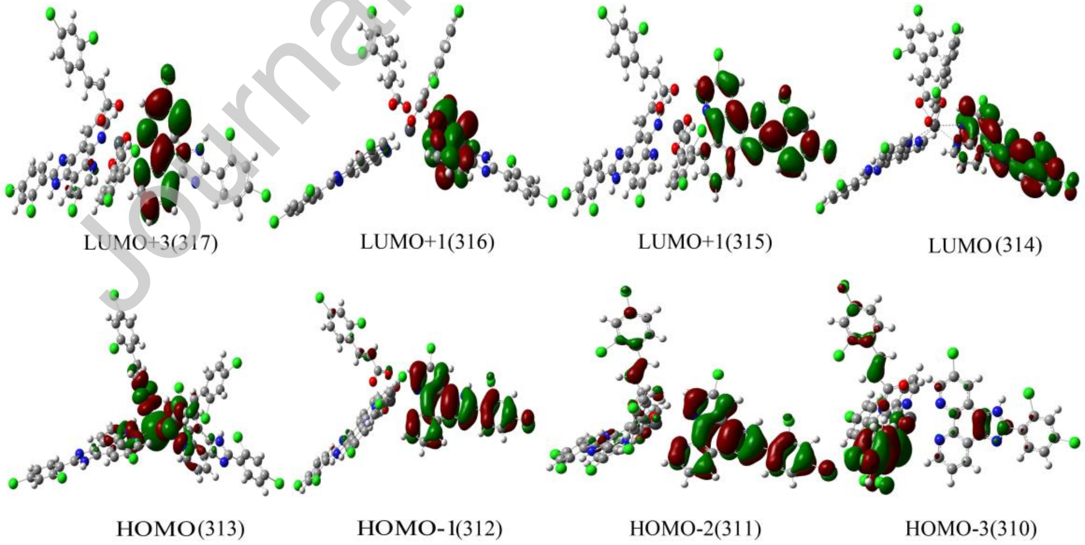

Fig. 11 The molecular orbitals of the complex 1.

In the emission spectrum, complex 1 has the maximum luminescence intensity at 481 nm. In calculation, the optemized triplet state has an emission peak of 532.9 nm as a difference between

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triplet and ground singlet states at ground state molecular geometry, it is very close to the experimental results. And the calculation indicates that the complex **1** emitted fluorescence.

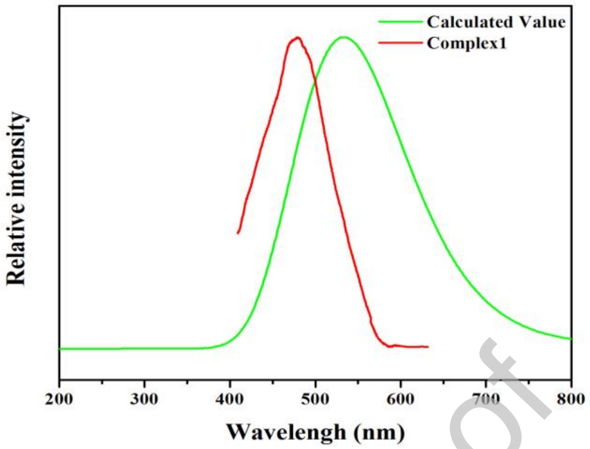

Fig. 12 Calculated and experimental emission peak of complex 1.

4. Conclusion

In this work, a new 0 dimensional Pb(II) complex has been successfully synthesized by using DIPT as a nitrogen-donor ligand and HL as an oxygen-donor carboxylic acid. The complex **1** was analyzed by single-crystal X-ray diffraction analysis and the result showed that seven coordination Pb(II) presents a distorted heptacoordinate pentagonal bipyramid structure. The complexes formed a two-dimensional network by intermolecular hydrogen bonds. The calculation results showed reasonable electronic configurations of the central Pb atom and the existence of the coordination bond in the complex is fully confirmed. The theoretical results of the calculated absorption and emission values are close to those of experiments. In addition, the complex which has good thermal stability and red shift in solid state, is expected to be further applied in the future.

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Author Contributions Section

He Wang : Investigation,Synthesized, Writing- Reviewing, Editing
Shuang Han: Investigation,Collecting data,Validation
Linan Dun: Investigation, Characterized
Baosheng Zhang: Investigation, Characterized
Xue Chen: Investigation, Characterized
Jiajun Wang: Conceptualization, Methodology, Investigation
Chuanbi Li: Conceptualization, Methodology, Investigation
Chunling Liu: Supervision, Conceptualization, Methodology, Investigation, Editing

Declaration of interests

☑ 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.

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REFERENCES

[1] C.Gao, J.Wang, H.Xu, Y.Xiong, Coordination chemistry in the design of heterogeneous photocatalysts. Chem.Soc.Rev. 46(2017)2799-2823. https://doi.org/10.1039/C6CS00727A

[2] A.Q.Wu, Y.Li, F.K.Zheng, Guo, J.S.Huang, Different molecular frameworks of zinc(II) and cadmium(II) coordination polymers constructed by flflexible double betaine ligands, Cryst. Growth Des. 6 (2006) 444-450. https://doi.org/10.1021/cg050378e

[3] D.Yuan, Y.Li, W.Li, S.Li, Structures and properties of large supramolecular coordination complexes predicted with the generalized energy-based fragmentation method, Phys.Chem.Chem.Phys. 2018(20)28894-28902. https://doi.org/10.1039/C8CP05548C

[4] A.J.Timmons, M.D.Symes, Converting between the oxides of nitrogen using metal–ligand coordination complexes, Chem.Soc.Rev. 44(2015)6708-6722. https://doi.org/10.1039/C5CS00269A

[5] J.Crassous, Chiral transfer in coordination complexes: towards molecular materials, Chem.Soc. Rev. 38(2009)830-845. https://doi.org/10.1039/B806203J

[6] Y.Mao, Q.Kong, B.Guo, X.Fang, X.Guo, L.Shen, A.Michel, Chen.L, Polypyrrole-iron-oxygen coordination complex as high performance lithium storage material, Energy Environ.Sci. 4(2011)3442-3447. https://doi.org/10.1039/C1EE01275D

[7] F.A.Mautner, R.C.Fischer, K.Reichmann, E.Gullett, K.Ashkar, S.S.Massoud, Synthesis and characterization of 1D and 2D cadmium(II)-2,2′-bipyridine-N,N′-dioxide coordination polymers bridged by pseudohalides, J.Mol.Struct. 1175(2019) 797-803. https://doi.org/10.1016/j.molstruc.2018.08.022

[8] S.Gayen, D.Saha, S.Koner, Quinoline derivative containing monomeric and polymeric metal carboxylates: Synthesis, crystal structure and gas adsorption study over a 2D layered framework, J.Mol.Struct. 1162(2018)10-16. https://doi.org/10.1016/j.molstruc.2018.02.090

[9] G.G.Sezer, O.Z.Yeşilel, O.Büyükgüngör, Two 3D Zinc(II) coordination frameworks constructed from pyrazine-2,3-dicarboxylate and 1,2-bis(4-pyridyl)ethylene, J.Mol.Struct. 1137(2017)562-568. https://doi.org/10.1016/j.molstruc.2017.02.077

[10] J.A.Brant, Y.Liu, D.F.Sava, D.Beauchamp, M.Eddaoudi, Single-metal-ion-based molecular building blocks (MBBs) approach to the design and synthesis of metal–organic assemblies. J.Mol.Struct. 796(2006)160-164. https://doi.org/10.1016/j.molstruc.2006.02.064

[11] V.V.Butova, M.A.Soldatov, A.A.Guda, K.A.Lomachenko, C.Lamberti, Metal-organic frameworks: Structure, properties, methods of synthesis and characterization, Russ.Chem.Rev. 85(2016) 280-307. https://doi.org/10.1070/rcr4554

[12] T.Uemura, N.Yanai, S.Kitagawa, Polymerization reactions in porous coordination polymers, Chem.Soc.Rev. 38 (2009) 1228-1236. https://doi.org/10.1039/B802583P

[13] B.C.Félix-Sonda, J.Rivera-Islas, D.Herrera-Ruiz, H.Morales-Rojas, H.Höpfl, Nitazoxanide cocrystals in combination with succinic, glutaric, and 2,5-dihydroxybenzoic acid, Cryst.Growth Des. 14(2014)1086-1102. https://doi.org/10.1021/cg4015916

[14] Y.Tümer, N.Asmafiliz, Z.Kılıç, T.Hökelek, L.Y.Koç, L.Açık, M.L.Yola, A.O.Solak, Y.Öner, D.Dündar, M. Yavuz, Phosphorus–nitrogen compounds: Part 28. Syntheses, structural characterizations, antimicrobial and cytotoxic activities, and DNA interactions of new phosphazenes bearing vanillinato and pendant ferrocenyl groups, J.Mol.Struct. 1049 (2013)112-124. https://doi.org/10.1016/j.molstruc.2013.06.036

[15] H.Agarkar, D.Das, The photo-switching study of guest 2-(phenylazo)pyridine(PAP) embedded in solid host material MOF-5, J.Mol.Struct. 1184(2019)435-442. https://doi.org/10.1016/j.molstruc.2019.02.059

[16] Kh.S.Abou-El-Sherbini, M.M.Hassanien, Synthesis of controlled-pore silica glas functionalized with quercetin and its application for the separation and preconcentration of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II), Sep.Sci.Technol. 39(2004)1177-1201. https://doi.org/10.1081/SS-120028578

[17] R.F.V.Souza, W.F.Giovani, Synthesis, spectral and electrochemical properties of Al(III) and Zn(II) complexes with flavonoids, Spectrochim. Acta A. 61(2005)1985-1990. https://doi.org/10.1016/j.saa.2004.07.029

[18] M.Ghoreishi Amiri, G.Mahmoudi, A.Morsali, A.D.Hunter, M.Zeller, Zinc(II) nitrite coordination polymers based on rigid and flexible organic nitrogen donor ligands, CrystEngComm. 9(2007)686-697. https://doi.org/10.1039/B701711A

[19] H.Sadeghzadeh, A.Morsali, P.Retailleau, Ultrasonic-assisted synthesis of two new nano-structured 3D lead(II) coordination polymers: precursors for preparation of PbO nano-structures, Polyhedron. 29(2010)925-933. https://doi.org/10.1016/j.poly.2009.10.026

[20] A.A.Soudi, F.Marandi, A.Morsali, L.G.Zhu, $[Pb_2(2,2'\text{-bipy})_2(\mu\text{-}4,4'\text{-bipy})(NO_3)_4]$: A novel hemidirected dimeric mixed-ligands lead(II) complex extended in holodirected two-dimensional polymer by weak $Pb\text{–}O_{nitrate}$ interactions, Inorg.Chem.Commun. 8 (2005)773-776. https://doi.org/10.1016/j.inoche.2005.05.016

[21] H.Ahmadzadi, F. Marandi, A. Morsali, Structural and X-ray powder diffraction studies of nano-structured lead(II) coordination polymer with η2 Pb···C interactions, J.Organomet.Chem. 694(2009)3565-3569. https://doi.org/10.1016/j.jorganchem.2009.07.016

[22] J.X.Li, Z.X.Du, A Binuclear Cadmium(II) Cluster Based on π···π Stacking and Halogen···Halogen Interactions: Synthesis, Crystal Analysis and Fluorescent Properties, J.Clust.Sci. 31(2020)507-511. https://doi.org/10.1007/s10876-019-01666-w

[23] X.X.Xu, Y.Ma, E.B.Wang, Different aliphatic dicarboxylates affected assemble of new coordination polymers constructed from flexible-rigid mixed ligands, J.Solid State Chem. 180(2007)3136-3145. https://doi.org/10.1016/j.jssc.2007.05.033

[24] L.G.Yu, Y.G.Sun, Z.L.Wang, Mixed-ligand strategy affording two new metal-organic frameworks: Photocatalytic, luminescent and anti-lung cancer properties, J.Mol.Struct. 1180(2019)209-214. https://doi.org/10.1016/j.molstruc.2018.11.063

[25] J.N.Clifford, E.Martínez-Ferrero, A.Viterisi, E.Palomares, Sensitizer molecular structure-device efficiency relationship in dye sensitized solar cells, Chem.Soc.Rev. 40(2011)1635-1646. https://doi.org/10.1039/B920664G

[26] M.Gollapalli, M.Taha, H.Ullah, M.Nawaz, L.M.R.AlMuqarrabun, F.Rahim, F.Qureshi, A.Mosaddik, N.Ahmat, K.M.Khan, Synthesis of Bis-indolylmethane sulfonohydrazides derivatives as potent α-Glucosidase inhibitors, Bioorg.Chem. 80(2018)112-120. https://doi.org/10.1016/j.bioorg.2018.06.001

[27] H.Yasui, A.Tamura, T.Takino, H.Sakurai, Structure-dependent metal-lokinetics of antidiabetic vanadyl-picolinate complexes in rats: Studies on solution structure, insulinomimetic activity and metallokinetics, J.Inorg.Biochem. 91(2002)327-338. https://doi.org/10.1016/S0162-0134(02)00443-9

[28] A.A.El-Habeeb, M.S.Refat, Synthesis, structure interpretation, antimicrobial and anticancer studies of tranexamic acid complexes towards Ga(III), W(VI), Y(III) and Si(IV) metal ions, J.Mol.Struct. 1175(2019)65-72. https://doi.org/10.1016/j.molstruc.2018.07.099

[29] S.Gorduk, A.Altindal, Peripherally tetra-substituted metallophthalocyanines bearing carboxylic acid groups for efficient dye sensitized solar cells, J.Mol.Struct. 1196(2019)747-753. https://doi.org/10.1016/j.molstruc.2019.07.027

[30] J.W.Zhang, R.J.Zhang, Y.Man, B.Q.Liu, Y.P.Dong, A new metal-organic framework constructed from Cu(II) and 3-bromo-5-(4-carboxyphenyl)pyridine: Synthesis, structure, photoluminescent and magnetic properties, J.Mol.Struct. 1185(2019)276-280. https://doi.org/10.1016/j.molstruc.2019.02.046

[31] S.Zhao, A novel 3D MOF with rich lewis basic sites as a base catalysis toward knoevenagel condensation reaction, J.Mol.Struct. 1167(2018)11-15. https://doi.org/10.1016/j.molstruc.2018.04.078

[32] L.Yang, L.Guo, Q.Chen, H.Sun, J.Liu, X.Zhang, X.Pan, S.Dai, Theoretical design and screening of panchromatic phthalocyanine sensitizers derived from TT1 for dye-sensitized solar cells, J.Mol.Graph.Model. 34 (2012)1-9. https://doi.org/10.1016/j.jmgm.2011.12.001

[33] H.Furukawa, O.M.Yaghi, Storage of hydrogen, methane, and carbon dioxide in highly porous covalent organic frameworks for clean energy applications, J.Am.Chem.Soc. 131(2009)8875-8883. https://doi.org/10.1021/ja9015765

[34] Y.L.Wu, G.P.Yang, S.Cheng, J.J.Q, Y.Y.Wang, Facile incorporation of Au nanoparticles into an unusual two-fold entangled Zn(II)-MOF with nano-cages for highly efficient CO_2 fixation under the mild conditions, ACS Appl.Mater. Interfaces. 11(2019)47437-47445. https://doi.org/10.1021/acsami.9b17348

[35] H.Pervez, N.Khan, J.Iqbal, S.Zaib, M.Yaqub, M.M.Naseer, Synthesis and in vitro bio-activity evaluation of N4-benzyl substituted 5-chloroisatin-3-thiosemicarbazones as urease and glycation inhibitors, Acta Chim.Slov. 65 (2018)108-118. https://doi.org/10.17344/acsi.2017.3649

[36] C.B.Sangani, N.M.Shah, M.P.Patel, R.G.Patel, Microwave-assisted synthesis of novel 4H-chromene derivatives bearing phenoxypyrazole and their antimicrobial activity assessment, J. Serb.Chem. Soc. 77 (2012) 1165-1174. https://doi.org/10.2298/JSC120102030S

[37] S.Naseem, M.Khalid, M.N.Tahir, M.A.Halim, A.A.C.Braga, M.M.Naseer, Z.Shafiq, Synthesis, structural, DFT studies, docking and antibacterial activity of a xanthene based hydrazone ligand, J.Mol.Struct. 1143(2017)235-244. https://doi.org/10.1016/j.molstruc.2017.04.093

Journal Pre-proof

[38] T.Raj, R.K.Bhatia, A.Kapur, M.Sharma, A.K.Saxena, M.P.S.Ishar, Cytotoxic activity of 3-(5-phenyl-3H-[1,2,4] dithiazol-3-yl)chromen-4-ones and 4-oxo-4H-chromene-3-carbothioic acid N-phenylamides, Eur.J.Med.Chem. 45 (2010)790-794. https://doi.org/10.1016/j.ejmech.2009.11.001

[39] N.Touj, A.Chakchouk-Mtibaa, L.Mansour, A.H.Harrath, J.Al-Tamimi, L.Mellouli, I.Özdemir, S.Yasar, N.Hamdi, Synthesis, spectroscopic properties and biological activity of new Cu(I) N-Heterocyclic carbene complexes, J.Mol.Struct. 1181(2019)209-219. https://doi.org/10.1016/j.molstruc.2018.12.093

[40] M.M.Mohamed. El-Bendary, T.Rüffer, M.N.Arshad, A.M.Asiri, Synthesis and structure characterization of Pt(IV) and Cd(II) 1,10-phenanthroline complexes; fluorescence, antitumor and photocatalytic property, J.Mol.Struct. 1192(2019)230-240. https://doi.org/10.1016/j.molstruc.2019.04.115

[41] Y.W.Niu, X.Liu, L.Zhao, Y.M.Guo, W.X.Li, M.M.Ma, X.L.Li, Synthesis, structures and photophysical properties of four binuclear Cu(I) complexes of 1H-imidazo[4,5-f][1,10]phenanthroline, Polyhedron. 157(2019)241-248. https://doi.org/10.1016/j.poly.2018.10.016

[42] F.Chen, J.Wang, M.W.Dong, S.L.Zhang, C.P.Wu, J.Q.Liu, Five lanthanide supramolecular frameworks based on mixed 3-(4-hydroxyphenyl)propanoic acid and 1,10-phenanthroline tectons: Crystal structures and luminescent properties, J.Mol.Struct. 1177(2019)117-123. https://doi.org/10.1016/j.molstruc.2018.09.032

[43] S.Hemalatha, J.Dharmaraja, S.Shobana, P.Subbaraj, T.Esakkidurai, N.Raman, Chemical and Pharmacological aspects of Novel Hetero MLB complexes derived from NO_2 type Schiff base and N_2 type 1,10–Phenanthroline ligands, J.Saudi.Chem.Soc. 24(2020)61-80. https://doi.org/10.1016/j.jscs.2019.09.004

[44] S.Han, H.Wang, J.J.Wang, L.N.Dun, C.B.Li, C.L. Liu, Synthesis, crystal structure and theoretical calculation of triphenyltin (IV) polymer based on 2,4-dichlorophenylacrylic acid, Inorg.Nano-Met.Chem. 50(2020)187-193. https://doi.org/10.1080/24701556.2019.1703747

[45] H.Y.Sun, Z.R.Wang, X.Li, S.Han, J.J.Wang, W.F.Li, C.L.Liu, C.B.Li, A novel Co(II) based multifunctional metal-organic framework: synthesis, fluorescence sensing and magnetic analysis, Inorg.Chim.Acta. 486(2019) 750-756. https://doi.org/10.1016/j.ica.2018.11.028

[46] G.W.T.M.J.Frisch, H.B.Schlegel, G.E.Scuseria, M.A.Robb, J.R.Cheeseman, G.Scalmani, V.Barone, B.Mennucci, G.A.Petersson, H.Nakatsuji, M.Caricato, X.Li, H.P.Hratchian, A.F.Izmaylov, J.Bloino, G.Zheng, J.L.Sonnenberg, M. Hada, M.Ehara, K.Toyota, R.Fukuda, J.Hasegawa, M.Ishida, T.Nakajima, Y.Honda, O.Kitao, H.Nakai, T.Vreven, J.A.Jr. Montgomery, J.E.Peralta, F.Ogliaro, M.Bearpark, J.J.Heyd, E.Brothers, K.N.Kudin, V.N.Staroverov, R.Kobayashi, J. Normand, K.Raghavachari, A.Rendell, J.C.Burant, S.S.Iyengar, J.Tomasi, M.Cossi, N.Rega, J.M.Millam, M.Klene, J.E.Knox, J.B.Cross, V.Bakken, C.Adamo, J.Jaramillo, R.Gomperts, R.E.Stratmann, O.Yazyev, A.J.Austin, R.Cammi, C.Pomelli, J.W.Ochterski, R.L.Martin, K.Morokuma, V.G.Zakrzewski, G.A.Voth, P.Salvador, J.J.Dannenberg, S. Dapprich, A.D.Daniels, O.Farkas, J.B.Foresman, J.V.Ortiz, J.Cioslowski, D.J.Fox, Gaussian 09 (Gaussian, Inc., Wallingford CT, 2009).

[47] A.L.Spek, Structure validation in chemical crystallography. Acta Cryst. D. 65(2009)148-155. https://doi.org/10.1107/S090744490804362X

[48] G.M.Sheldrick, SHELXS97 and SHELXL97, University of Göttingen, Germany, 1997.

[49] G.M.Sheldrick,. Crystal structure refinement with SHELXL. Acta Cryst.C. 71(2015)3-8. https://doi.org/10.1107/S2053229614024218

[50] E. Balong-Hergovich, G. Speier, ChemInform Abstract: The Chlorination of Indoles by Copper(II) Chloride. 18(1986)2305-2308. J. CHEM. SOC. PERKIN TRANS. I .https://doi.org/10.1039/P19860002305

[51] D. Y.B., L. Y.C., Progress in the Generation and Structural Study of Origanic Radical Cations, CHINESE J.ORG.CHEM. 10(1990)488-497.

[52] D.Li-Vien, N.B.Colthup, W.G.Fateley, J.G.Grasselli, The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules, Academic Press, Boston, 1991.

[53] S.Lin, L.Zeng, G.Zhang, Y.Liao, D.Gong, Synthesis, characterization and xanthine oxidase inhibition of Cu(II)-chrysin complex, Spectrochim. Acta A Mol. Biomol. Spectrosc. 178(2017)71-78. https://doi.org/10.1016/j.saa.2017.01.056

[54] L.J.Bellamy, The Infrared Spectra of Complex Molecule, third ed., Willey, New York, 1975.

[55] G.Varsanyi, Assignments of Vibrational Spectra of Seven Hundred Benzene Derivatives, vol. 1, Adam Higher, England, 1974.

[56] A.Srivastava, R.Mishra, S.Kumar, K.Dev, P.Tandon, R.Maurya, Molecular structure, spectral investigation (^{1}H NMR, ^{13}CNMR, UV-Visible, FT-IR, FT-Raman), NBO, intramolecular hydrogen bonding, chemical reactivity and first hyperpolarizability analysis of formononetin [7-hydroxy-3(4-methoxyphenyl)chromone]: A quantum chemical study, J.Mol.Struct. 1084(2015) 55-73. https://doi.org/10.1016/j.molstruc.2014.11.070

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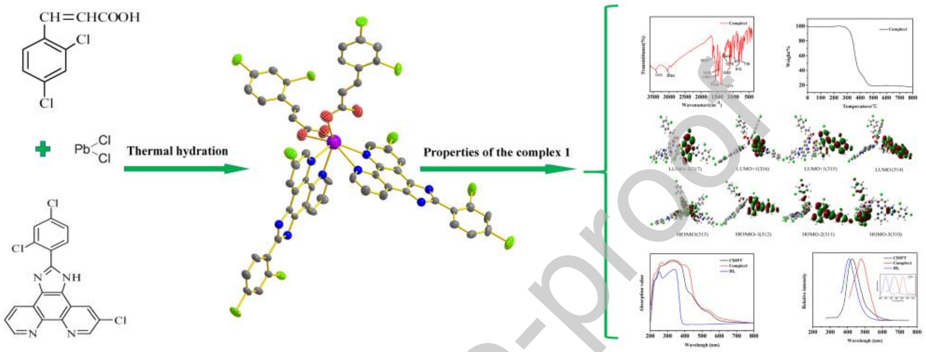
Graphical abstract

A new coordination complex Pb(CDIPT)$_2$(L)$_2$ (**1**) was synthesized with 2-(2,4-dichlorophenyl)-1H-imidazo[4,5-f][1,10]phenanthroline (DIPT) and 2,4-dichlorophenyl acrylic acid(HL). Complex **1** was characterized by elemental analysis, IR spectroscopy, PXRD and single-crystal X-ray diffraction analysis. Each central Pb ion is a distorted heptacoordinate pentagonal bipyramid by four nitrogen atoms from two DIPT ligands and three carboxylate oxygen atoms from two different deprotonation of HL. Based on this, the properties of the complex **1** were further studied, fluorescence spectra showed that the complex has obvious red shift. TGA indicated that the complex has good thermal stability. In addition, the complex was calculated by quantization method. The stability and bonding characteristics of the complex were described, which were in good agreement with the experimental results.



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