**Spectrometric measurements and DFT studies
on new complex of copper (II) with
2-(E)-9-ethyl-3-(2-(6-(4-methylpyridin-2-yl)pyridin-3-yl)vinyl)-9H-carbazole**

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Abstract:

The molecular structure of a new coordination compound of copper (II) with (E)-9-ethyl-3-(2-(6-(4-methylpyridin-2-yl)pyridin-3-yl)vinyl)-9H-carbazole ($[\text{Cu}_2(\text{emppc})_2\text{Cl}_2]\text{Cl}_2$) was optimized with B3LYP/LanL2DZ, PBE1PBE/LanL2DZ and M062X/LanL2DZ theoretical level. The ligand, (E)-9-ethyl-3-(2-(6-(4-methylpyridin-2-yl)pyridin-3-yl)vinyl)-9H-carbazole (emppc), binds to Cu(II) ions with a bi-dentate mode, two Cl^- serve as bridging ligand, each Cu(II) ion has a highly distorted tetrahedron coordination geometry. With M062X/LanL2DZ theoretical level, the calculated interaction energies of Cu(II) with coordination atoms N are between 183.3-200.0 kJ/mol for α spin and 319.4-324.9 kJ/mol for β spin, and interaction energies of Cu(II) with coordination atoms Cl atom are 248.0-252.4 kJ/mol for α spin and 332.6-333.6 kJ/mol for β spin. The experimental Fourier transform infrared spectrum was assigned. The calculated IR based on B3LYP/LanL2DZ, PBE1PBE/LanL2DZ and M062X/LanL2DZ methods were performed and compared with experimental results. The UV-Vis experimental spectrum of $[\text{Cu}_2(\text{emppc})_2\text{Cl}_2]\text{Cl}_2$ was measured in methanol solution. The calculated electronic spectra was performed with TD/M062X and PCM-TD/M062X methods with LanL2DZ basis set. Calculated vibration wavenumbers, UV-Vis absorption wavelengths are in good agreement with the experimental results. The nature bond orbital analysis and temperature dependence of the thermodynamic properties were calculated with the same methods.

Keywords: vibrational spectra; electronic spectra; NBO; DFT; $[\text{Cu}_2(\text{emppc})_2\text{Cl}_2]\text{Cl}_2$

1. Introduction

2,2'-Bipyridine and its derivatives are a kind of well known bidentate chelating agent for transition metal ions mainly for its availability, strong redox stability and relative ease of functionalization[1-4] and still continues to be of considerable interest

as versatile starting material for organic, inorganic and supramolecular chemistry[5-9]. Their abilities to absorb visible light to act as electron reservoirs are promising factors in their applications as photosensitizers. For example, the ruthenium complexes with 2,2'-bipyridine derivatives are generally recognized as a class of the most excellent dye for dye-sensitized solar cells. Grätzel research group[10] reported cis-bis(2,2'-bipyridyl-4,4'-dicarboxylate)(SCN)₂ ruthenium(II)(N3) in 1993, the compound gives the photoelectric energy conversion efficiency reached 10%. If butyl ammonium salt introduced to N3, the photoelectric conversion efficiency reached 11.18% [11].

Transition metal complexes of 2,2'-bipyridine and their derivatives are of great interest also due to their ability to undergo facile electrochemical processes and can be used as efficiently catalysis. Lehn[12] reported the earliest metal complexes [Re(bpy)(CO)₃Cl₂], the compound shown efficiently to catalyze the electrochemical conversion of CO₂ to CO. Kubiak[13] demonstrated that the activity of this complex could be vastly improved by utilizing a modified bpy ligand containing tert-butyl groups. More recently, Shunsuke Sato[14] reported an efficient photocatalyst, [Ir-Meppy], which has the TNCO value up to 50, and the quantum yield FCO up to 0.21.

Transition metal complexes of 2,2'-bipyridine and their derivatives has become one of the most powerful and extensively used tools fluorescent imaging and sensing in cell biology, physiology, and related areas of the biomedical sciences [15]. For example, Puckett and Barton found that the introduction of more lipophilic bipyridyl ligands improved uptake and allowed luminescence imaging to be carried out without the need for membrane permeation they studied a series of analogues of [Ru(bpy)₂(dppz)]²⁺ (dppz=1,3-di(2-pyridyl)benzene) [16], these compounds exhibited high cellular luminescence, detectable even using concentrations less than 1 μM. Hagimori [17] reported a high-affinity and low-molecular-weight fluorescent sensor based on a 2,2'-bipyridine scaffold, which functions as both the chelating moiety for Zn²⁺ and the fluorophore, was developed and evaluated in biological applications.

Further, transition metal complexes of 2,2'-bipyridine and their derivatives can be used widely in extraordinary molecular architectures [18-20]. Many of these compounds have been designed to be used in the assembly of 0-D to 3-D polymeric complexes which consist of mononuclear building blocks bridged by transition metal

or lanthanide ions[21-24]. Highlights include single molecule magnets[25,26], metal-organic frameworks[27,28] and materials which display organic electronic[29], spin crossover [30] and luminescence[31].

Although new developments in synthesis and applications have been reported, the spectroscopic properties of such compounds were not extensively studied [32,33]. Herein, we describe our results on a new binuclear compound, $[\text{Cu}_2(\text{emppc})_2\text{Cl}_2]\text{Cl}_2$, concerning the structural, vibrational and electronic analyses through spectral measurements. Density Functional theory calculations have been performed to support our wavenumber assignments. The redistribution of Electron Density (ED) in various bonding, antibonding orbitals and E(2) energies have been calculated by natural bond orbital (NBO) analysis to provide evidence of stabilization originating from the hyperconjugation and various intramolecular interactions. UV-Vis spectra were measured in methanol solution. The transition energies and oscillator strengths were calculated with time dependent (TD) method to assign of charge transference (CT) electronic bands. To our best knowledge, this is the first report on the synthesis, spectral measurements and computational study of this compound. The calculated results were compared with the observed spectra. Calculated vibration wavenumbers, UV-Vis absorption wavelengths are in good agreement with the experimental results.

2. Experimental and calculation

2.1. Synthesis of $[\text{Cu}_2(\text{emppc})_2\text{Cl}_2]\text{Cl}_2$

2.1.1 Synthesis of (E)-9-ethyl-3-(2-(6-(4-methylpyridin-2-yl)pyridin-3-yl)vinyl)-9H-carbazole (emppc)

(E)-9-ethyl-3-(2-(6-(4-methylpyridin-2-yl)pyridin-3-yl)vinyl)-9H-carbazole (emppc) was obtained according to the previous report[34] with slight modification. 1.84 g (10.0 mmol) 4,4'-methyl-2,2'-bipyridine and 2.23g (10 mmol) N-Ethyl-3-carbazolecarboxaldehyde was slowly added into a 100 mL three-necked flask with 20 mL DMF, potassium tert-butoxide was used as catalyst. The mixture was stirred for 20 min at room temperature and heated to 100 °C for 9 h. Yellow powder yielded and recrystallized with ethanol. Yield: 37.2%. ^1H NMR (400 MHz, CDCl_3): δ (ppm) ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.63 (d, 1H, H^6), 8.59 (d, 1H, $\text{H}^{6'}$), 8.55 (d, 1H, H^3), 8.27 (s, 2H, H^3 , Ar), 8.13 (d, 1H, Ar), 7.71 (d, 1H, Ar), 7.66 (d, 1H, H^6), 7.49 (m, 1H, Ar), 7.41 (m, 3H, H^3 , H^5 , Ar), 7.27 (m, 1H, Ar), 4.36 (q, 2H, CH_2 -), 2.45 (s, 3H, CH_3), 1.44 (t, 3H, CH_3). ESI-MS [m/z]: 390.4 [$\text{M}+\text{H}$] $^+$

2.1.2 Preparation of $[\text{Cu}_2(\text{emppc})_2\text{Cl}_2]\text{Cl}_2$

To a solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.275g, 1.0 mmol) in methanol (10 mL), a solution of emppc (0.389 g, 1.0 mmol) in methanol (20 mL) was added dropwise with magnetic stirring. The resulting solution turned brown. The mixture was stirred at room temperature for 3 h and filtered. Deep brown powder yielded and recrystallized with DMF and ethanol. (ca. 86% yield based on emppc). Anal. calcd. for $\text{C}_{56}\text{H}_{46}\text{N}_6\text{Cl}_4\text{Cu}_2$ (%): C, 57.58; H, 3.94; N, 7.20; Found (%): C, 57.36; H, 3.92; N, 7.454. ESI-MS $[\text{m/z}]$: 548.2 $[\text{M}]^{2+}$

2.2. Spectral characterization

The FT-IR spectrum of the title compound was measured on AVATAR360 spectrophotometer in the range of $500\text{--}4000\text{ cm}^{-1}$ at room temperature using KBr pellet technique. The UV-Vis spectrum was recorded on UV-Vis 916 spectrophotometer in the region $225\text{--}600\text{ nm}$ using methanol as solvent.

2.3 Methods of calculation

In recent years, density functional theory (DFT) has emerged as a powerful tool in studying vibrational spectra, electronic spectra, and the physical properties of molecules. The DFT calculations are reported to provide excellent vibrational frequencies of organic compounds and metal complexes[35-38]. Therefore, we have utilized the gradient corrected DFT with the Becke's three-parameter hybrid functional (B3) for the exchange part and the Lee-Yang-Parr (LYP) correlation function, B3LYP [39], PBE1PBE[40] and M062X[41] accepted as a cost-effective approach, for the computation of molecular structure, vibrational frequencies and energies of optimized structures[42,44]. Based on the previous studies[44,45], these methods and a fairly large and flexible basis set LanL2DZ level to perform accurate calculations on the title molecule were chosen. DFT calculations were generally carried out with the spin restricted RDFT approach for closed shell and with the spin unrestricted UDFT approach for open shell compounds. For the investigated complexes, the ground state geometries were calculated in the gas phase using the unrestricted Kohn-Sham formalism (UKS) with unrestricted B3LYP functional (UB3LYP). Geometry optimization proceeded in two steps, firstly, the initial geometry was constructed by MM+ molecular modeling in HyperChem 6.0 package[46]. Then the geometry was optimized by density functional theory (DFT) B3LYP, PBE1PBE and M062X methods with LanL2DZ basis set. The vibrational calculations were performed. No imaginary mode was observed. The study of the molecular orbitals was carried out using the Mulliken population analysis and a

graphical analysis with the Chemcraft and GaussSum[447] programs. The calculations of the transition energies and the oscillator strengths in the UV–Vis spectra were based on the optimized structures. The calculations were carried out using the TD method implemented in the Gaussian09[48]. Transition moment calculations were based on M062X theoretical level. The incorporation of the solvent effect in the TD method, using the polarizable calculation model (PCM)[49], was carried out with methanol. Finally, to corroborate the previous observations, the analysis of the variation of the electronic density of this compound was carried out through natural bond orbital (NBO).

3 Results and discussion

3.1. Structural description

The optimized geometry with atomic numbering scheme for the title compound is shown in Fig. 1. The predicted geometric parameters (bond lengths, bond angles and dihedral angles) of the investigated structures are collected in Table 1. In the complex cation, each Cu(II) is bonded to two Cl⁻ ligand and one emppc ligands which coordinate through two bpy nitrogen atoms, forming five-membered chelate rings. The geometry around the copper atom can be described as a highly distorted tetrahedron. The calculated Cu(II)-N are 2.0398 Å for Cu-N20 and 2.0269 Å for Cu-N25 with B3LYP theoretical level, these values are comparable with the experimental results ca. 2.0 Å in the compound [Cu(2,2'-bipy)(Htda)]_n (2,2'-bipy = 2,2'-bipyridine, Htda=1,2,3-triazole-4,5-dicarboxylate)[50]. The calculated Cu(II)-Cl bond distance are ca. 2.40 Å with B3LYP theoretical level, these values are comparable with the experimental results 2.30 Å in the compound Cu(bpy)₂(μ-Cl)₂Cl₂[51]. The calculated N57–Cu59–Cl09 bond angle 158.4° and N20–Cu54–Cu110 bond angle 158.8°. In the compound, the C5–N9 (1.4137 Å) is typical single bond which is very close to the calculated values in all methods. The calculated bond length of C19–N20 and (1.3467 Å) is shorter than C24–N55 (1.3698 Å) bond length, but significantly longer than the typical C=N double bond since the conjugation effects. [52,53]

3.2. The infrared spectrum of [Cu₂(emppc)₂Cl₂]Cl₂ and DFT calculations

In the present study, we performed a frequency calculation analysis to obtain the spectroscopic signature of the compound. The compound had 324 vibrational normal modes. The selected harmonic vibrational frequencies were given in Table 2. Also, the calculated FT-IR spectra for the compounds were shown in Fig. 2. None of the

predicted vibrational spectra had any imaginary frequency, proving that optimized geometry was located at the lowest point on the potential energy surface. It is well known fact that DFT levels systematically overestimate the vibrational wave-numbers[54]. Therefore, the scaling factor values were used in order to correct anharmonicity and neglected part of electron correlation. The scale factor for the frequencies scaling was used as 0.9650 for B3LYP, 0.9516 for PBE1PBE and 0.9480 for M062X.

The vibrational assignments have been made on the basis of visualization of the atomic displacements in each calculated normal mode and by comparison with the assignments reported earlier for other similar systems [55,56]. As is seen in Fig. 2, The observed bands at 3068, 2976 and 2930 cm^{-1} are the CH stretching mode of C16(17)H, C14H and C46H, the corresponding B3LYP/LanL2DZ calculated values for these vibrations are 3170, 3090 and 3051 cm^{-1} , respectively. The observed values 1615, 1475 and 1413 cm^{-1} and corresponding calculated values 1672, 1527 and 1475 cm^{-1} can be assigned to coupled vibrational modes of CC stretching and CH wagging in plane vibrational modes of carbazole ring. The CC stretching vibrational modes of bpy are found in the observed bands 1588, 1558, 1335, 1287, 1235 and 1179 cm^{-1} , PED analysis found that the first mode is strongly coupled with CH wagging in plane mode of C(bpy)H(PED, 49%), the second mode is coupled with CC stretching mode of carbazole(PED, 19%), CH wagging in plane mode of C(bpy)H(PED, 12%) and CH wagging in plane mode of C(carbazole)H(PED, 14%). The observed band 1085 cm^{-1} and corresponding theoretical value 1133 cm^{-1} can be assigned to the coupled vibrational mode of carbazole ring breath mode(PED, 17%) with CH wagging in plane mode of carbazole(PED, 24%) and the torsion mode of HC95C96H(PED, 22%). The observed band 1026 cm^{-1} and corresponding theoretical value 1075 cm^{-1} can be assigned to the coupled vibrational mode of N90C95 stretching vibrational mode(PED, 15%) with C95C96 stretching vibrational mode(PED, 22%), CCC bending mode of carbazole(PED, 28%) and wagging in plane mode CH in carbazole ring (PED, 47%). Compared with the experimental values for these modes, the calculated results overestimate the frequencies with errors 2.5-4.8%, 3.0-6.9% and 4.3-7.5% for B3LYP, PBE1PBE and M062X, respectively.

3.3. The UV-Vis spectrum of $[\text{Cu}_2(\text{emppc})_2\text{Cl}_2]\text{Cl}_2$ and DFT calculations

3.3.1 Molecular orbitals for $[\text{Cu}_2(\text{emppc})_2\text{Cl}_2]\text{Cl}_2$

The energy levels of the frontier orbital of the compound calculated with

M062X/LanL2DZ theoretical level are listed in Table 3. The 3D plots of the HOMOs and LUMOs of the compound are shown in Fig. 3. The experimental and simulated spectra with M062X/LanL2DZ are shown in Fig. 4. The energy levels of the frontier orbital of the compound are listed in Table 3. For α spin, HOMO, HOMO-3, HOMO-4 and HOMO-5 have >90% contribution of emppc ligand, while HOMO-2 and HOMO-6 have mainly contribution of d orbital of (Cu) along with a significantly contribution of Cl. The LUMO has 98% π (L) character, and delocalized on the emppc ligand. The LUMO+1 electrons are mainly delocalized on the bpy(85.15%) and seldom from Cu d orbital (1.81%). The Koopmans' energy difference between the highest occupied and the lowest unoccupied orbitals, HOMO(α)–LUMO(α) gap, was 3.21 eV for the M062X. For β -spin, HOMO are mainly delocalized on the carbazole ring(80.68%) and some from bpy(8.33%), significant contributions of the d(Cu) orbitals have been found in HOMO-2(47.87%), HOMO-6(68.82 %). The LUMO mainly delocalized on the ligand ring. The LUMO+1 has significantly Cu character along with a significant contribution from Cl(12.57%) and bpy(28.00%). The participation of the metal orbitals were consistent with the evaluation of multiplicity adopts for d^7 Cu (II), duplet for one unpaired electron.

The analysis of the molecular orbitals obtained with the PCM methodology, which incorporate the solvent effect, present some differences of HOMO, LUMO energy in both methods. However, the order of the frontier orbitals was not changed.

3.3.2 Electronic spectra

The electronic absorption spectrum of the ligand and the title compound in methanol solvent was recorded within 225–500 nm range and representative spectrum is given in Fig. 4. For comparison, the calculated UV-Vis with different methods is also showed in the Fig. 4. The energies and oscillator strengths of the title compound in CH₃OH solution listed in Table 4. The UV–Vis absorption spectrum of methanol solution for the ligand shows strong bands around 357, 290 and 240 nm. After complexed with Cu(II), these bands red shift to 415, 297 and 242 nm. The observed band at 415 nm in CH₃OH solution was compared with the theoretical data 412 nm in gas phase and 405 nm in CH₃OH solution for M062X theoretical level. The band was defined as HOMO→LUMO(α), HOMO→LUMO+1(α) and HOMO→LUMO+2(β) and HOMO→LUMO+3(β) was classified as LLCT transition. The experimental band at 297 nm in CH₃OH solution was represented by state in 291 nm for M062X. The

oscillator strength was calculated between 0.5464, and was classified as HOMO→LUMO+2(α), HOMO→LUMO+9(α) and HOMO→LUMO+4(β), HOMO→LUMO+11(β) transition. These states of oscillator strengths between 0.3418 were classified as LLCT transitions.

3. 4. Natural bond orbital analysis

The second order perturbation theory of Fock matrix in the NBO analysis shows strong intramolecular interactions, the interaction energies of the Cu(II) center with coordination atoms are listed in Table 5. With M062X/LanL2DZ method, the interaction energy correspond to the transfer of electrons from LP (1) N20 and N25 to empty orbital of Cu(54) were found to be 187.6 and 183.3 kJ mol⁻¹, respectively, for α spin state and 319.4 and 322.4 kJ mol⁻¹ for β spin state. Almost the same interaction energy was obtained for the interaction energy correspond to the transfer of electrons from LP (1) N56 and N57 to empty orbital of Cu(55). These values indicated that there are strong interaction between center Cu(II) and lone pair of the N atom in bpy. The interaction energies correspond to the transfer of electrons from bpy to empty orbital of Cu(54) were found to be 86.9 kJ mol⁻¹ for α spin state and 89.5 kJ mol⁻¹ for β spin state, while the interaction energies correspond to the transfer of electrons from bpy to empty orbital of Cu(55) were found to be 85.2 kJ mol⁻¹ for α spin state and 75.5 kJ mol⁻¹ for β spin state. There are weakly interaction between Cu(54) and Cu(55), the interaction energies correspond to the transfer of electrons from Cu(54) to empty orbital of Cu(55) were found to be 29.1 kJ·mol⁻¹ for α spin state and 35.4 kJ·mol⁻¹ for β spin state. With B3LYP/LanL2DZ and PBE1PBE/LanL2DZ methods, the calculated values of interaction energies are different, but the trend is consistent. Based on local block eigen vector of the one-particle density matrix, the hybridization and covalent effects for the title complex was analyzed. The bond orbital occupancies, contribution from parent NBO, the natural atomic hybrids were described in Table 6. For example, for C5-N9 bond, with B3LYP/LanL2DZ method, the bond was formed by interaction between a sp^{2.63} (27.56% s, 72.44% p) orbital centered on the C5 and a sp^{2.04} (32.95% s, 67.05% p) orbital on the N9 atom. The molecular orbital can be described as $\sigma_{CN} = 0.3658(sp^{2.63})C + 0.6342(sp^{2.04})N$. This shows a strong polarization directed toward the N atom.

3.6. Thermodynamic Properties

The temperature dependence of the thermodynamic properties heat capacity at

constant pressure (Cp), entropy (S), enthalpy (H) and Gibbs free energy (G) for the title compound were also determined by B3LYP/LanL2DZ method and were listed in Table 9. It can be observed that these thermodynamic functions, Cp, S and H are increasing, while G decreasing with temperature ranging from 100 to 1000 K due to the fact that the molecular vibrational intensities increase with temperature. The correlation equations between heat capacity, entropy, enthalpy and Gibbs free energy with temperatures were filled by quadratic formulas, and the corresponding fitting factors (R^2) for these thermodynamic properties are 0.99909, 0.999234, 0.99182 and 0.99893, respectively. The corresponding fitting equations are as follows and the correlations graphs have are showed in Fig. 5.

$$C_v = 3.1857 + 0.83344 \times T - 3.59263 \times 10^{-4} \times T^2$$

$$S = 95.43554 + 0.87949 \times T - 2.63485 \times 10^{-4} \times T^2$$

$$H = 549.2091 + 0.09554 \times T + 2.11327 \times 10^{-4} \times T^2$$

$$G = 562.10937 + -0.15203 \times T - 2.78164 \times 10^{-4} \times T^2$$

4. Conclusions

The Cu(II) complex with (E)-9-ethyl-3-(2-(6-(4-methylpyridin-2-yl)pyridin-3-yl)vinyl)-9H-carbazole $\text{Cu}_2(\text{emppc})_2\text{Cl}_2\text{]Cl}_2$, was synthesised and investigated. The most important results and conclusions can be summarized as follows:

(1) In the complex cation, Cu(II) is bonded to two Cl^- ligand and two emppc ligands which coordinate through two bpy nitrogen atoms, forming Cl^- bridged binuclear structure. The geometry around the copper atom can be described as a highly distorted tetrahedron.

(2) The detailed assignments of the experimental infrared spectrum of the title compound have been made on the basis of the theoretical calculations of the $[\text{Cu}_2(\text{emppc})_2\text{Cl}_2]^{2+}$ cation using the unrestricted density functional B3LYP, PBE1PBE and M062X methods with LanL2DZ basis set. The calculated frequencies show good agreement with experiments, the calculated results overestimate the frequencies with errors 2.5-4.8%, 3.0-6.9% and 4.3-7.5% for B3LYP, PBE1PBE and M062X, respectively.

(3) The UV-Vis absorption spectrum of methanol solution for the ligand shows strong bands around 357, 290 and 240 nm. After complexed with Cu(II), these bands red shift to 415, 297 and 242 nm.. The calculated absorbsion bands show good

agreement with experiments.

(4) With NBO analysis, the calculated interaction energies of Cu(II) with ligand's atom N are between 183.3-200.0 kJ·mol⁻¹ for α spin and 319.4-324.9 kJ·mol⁻¹ for β spin.

The results provided helpful information on the rational design of novel polynuclear Cu(II) complexes of bipy derivatives with the specific spectroscopic natures.

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Table 1 Optimized and experimental bond distances (Å)
and bond angles (°) for the compound.

Bond lenth	B3LYP	PBE1PBE	M062X	Bond angle	B3LYP	PBE1PBE	M062X
R(1,2)	1.4098	1.4014	1.3991	A(2,1,6)	118.8	118.8	118.8
R(1,6)	1.4037	1.4007	1.4029	A(7,8,9)	109.2	109.1	109.1
R(2,3)	1.4148	1.4108	1.4135	A(9,8,13)	129.6	129.6	129.5
R(3,4)	1.4075	1.4011	1.3999	A(5,9,8)	108.8	108.9	108.8
R(4,5)	1.4043	1.3989	1.4005	A(21,20,54)	113.3	113.0	112.9
R(5,6)	1.4276	1.421	1.4198	A(21,24,25)	115.3	115.1	115.1
R(5,9)	1.4137	1.4063	1.4059	A(24,25,54)	114.0	113.5	113.2
R(6,7)	1.4615	1.4536	1.4569	A(20,54,25)	81.6	82.9	83.3
R(7,8)	1.4419	1.4361	1.4346	A(25,54,109)	98.1	97.2	96.5
R(8,9)	1.3866	1.3781	1.3801	A(25,54,110)	158.8	163.9	168.4
R(8,13)	1.4116	1.4066	1.4065	A(109,54,110)	89.5	86.7	85.2
R(9,14)	1.4748	1.4637	1.4642	A(56,55,57)	81.6	82.8	83.4
R(10,11)	1.4264	1.4188	1.4148	A(56,55,109)	98.0	97.9	96.9
R(11,12)	1.4322	1.4273	1.4254	A(56,55,110)	159.5	163.7	169.3
R(11,16)	1.4546	1.4456	1.452	A(57,55,109)	158.4	162.3	168.3
R(12,13)	1.3951	1.3893	1.3909	A(109,55,110)	89.4	86.2	85.1
R(14,15)	1.5436	1.5335	1.536	A(55,56,62)	113.3	113.0	112.8
R(16,17)	1.3718	1.3698	1.3651	A(55,57,63)	113.9	113.5	113.2
R(17,18)	1.457	1.4459	1.4512	A(55,57,66)	126.1	126.4	126.6
R(18,19)	1.4226	1.4193	1.4183	A(56,58,59)	122.9	122.9	122.8
R(18,23)	1.4239	1.4203	1.4185	A(56,58,75)	116.2	116.5	116.9
R(19,20)	1.3467	1.3415	1.3448	A(59,58,75)	120.8	120.7	120.3
R(20,21)	1.3693	1.3659	1.3664	D(19,20,54,110)	-21.6	-17.3	-12.6
R(20,54)	2.0398	1.9938	1.9884	D(24,25,54,109)	160.4	165.3	169.7
R(21,22)	1.4105	1.4041	1.4006	D(20,54,109,55)	-119.7	-110.6	-104.4
R(21,24)	1.4784	1.466	1.4739	D(25,54,109,55)	152.5	160.2	167.0
R(22,23)	1.3967	1.3908	1.394	D(110,54,109,55)	-7.7	-4.1	-1.5
R(24,25)	1.3698	1.3657	1.3664	D(20,54,110,55)	169.4	169.8	170.9
R(24,29)	1.4071	1.4012	1.3979	D(25,54,110,55)	-103.8	-100.5	-97.5
R(25,26)	1.3557	1.3524	1.3548	D(109,54,110,55)	7.7	4.1	1.5
R(25,54)	2.0269	1.9844	1.9836	D(109,55,56,58)	-21.8	-18.5	-13.1
R(26,27)	1.3998	1.3928	1.3933	D(109,55,56,62)	157.6	161.6	167.9
R(27,28)	1.4156	1.4114	1.4104	D(110,55,56,58)	88.5	85.2	87.6
R(28,29)	1.4108	1.405	1.4065	D(109,55,57,63)	-90.9	-93.8	-91.3
R(28,46)	1.5108	1.5015	1.5051	D(109,55,57,66)	91.0	88.1	87.2
R(54,109)	2.4076	2.3762	2.3728	D(110,55,57,63)	159.0	163.2	170.3
R(54,110)	2.402	2.3721	2.3722	D(110,55,57,66)	-19.2	-14.9	-11.2
R(55,56)	2.0402	2	1.9882	D(56,55,109,54)	168.5	168.3	170.9
R(55,57)	2.0279	1.9891	1.983	D(57,55,109,54)	-104.1	-100.7	-98.1
R(55,109)	2.4038	2.3846	2.3724	D(56,55,110,54)	-119.4	-109.3	-103.3
R(55,110)	2.4087	2.3885	2.375	D(57,55,110,54)	152.1	158.7	166.9
R(56,58)	1.3466	1.3413	1.3444	D(109,55,110,54)	-7.7	-4.1	-1.5

Table 2 Experimental and calculated IR vibrational frequencies (cm⁻¹) and intensity of the title compound.

B3LYP			PBE1PBE			M06X			Exp. IR	Assign.(PED) ^a
Wavel ength	Intensi ty	Scaled wavel ength	Wavel ength	Intensi ty	Scaled wavel ength	Wavel ength	Intensi ty	Scaled wavel ength		
550	4.4	531	557	1.6	530	560	27.3	531	536	δCCC(carbazole)(11) τCCC(Carbazole) (41)
571	23.1	551	579	47.9	551	589	11.5	558	557	δCCC(carbazole)(12)+τCCC (Carbazole) (35)+ωCC(Carbazole)H(44)
652	21.0	629	653	21.1	621	654	20.6	620	627	τCCC(Carbazole) (35), ωCC(Carbazole)H(41)
773	10.8	746	782	8.2	744	784	21.3	743	748	δCCC(bpy)(14)+ δCCC(carbazole)(40)
850	32.4	820	854	36.3	813	862	40.0	817	829	ωC(carbazole)H(81))
885	3.4	854	890	111.5	847	898	8.9	851	853	ωC(carbazole)H(76)
914	4.8	882	918	121.4	874	921	10.4	873	880	τC58(60)C59C74H(13)+ τC59C74C79H(10)+ τC82C79C74H(16)
960	15.4	926	979	19.4	932	980	14.8	929	934	vC14C15(33)+δC14C15H(2 2)+ τHC14C15H(8)
999	9.2	964	1002	9.5	954	1014	12.5	961	969	τHCC(Carbazole)H(77)
1075	18.2	1037	1094	11.7	1041	1099	17.7	1042	1026	vN90C95(15)+ vC95C96(22)+δCCC(carbaz ole)(28)+p CC(carbazole)H (47.5)
1133	15.4	1093	1160	24.2	1104	1166	266.7	1105	1085	pCC(Carbazole)H(24)+ring breath (carbazole)(17)+ τHC95C96H(22)
1164	62.6	1123	1179	127.7	1122	1183	22.0	1121	1123	pcc(bpy)H(25)+p CC(carbazole)H(20)+τHC95 C96H(12)
1190	74.5	1148	1202	568.4	1144	1208	239.0	1145	1155	pCC(bpy)H(25)+p CC(carbazole)H (20.3) +τHC95C96H(12)
1221	188.1	1178	1236	176.4	1176	1233	543.0	1169	1179	vCC(bpy)(18)+ pcc(bpy)H(17)+p CC(carbazole)H(48)
1262	137.5	1218	1282	69.4	1220	1279	142.5	1212	1217	vCC(carbazole)(15)+ ωcc(carbazole)H(12)+p CC(bpy)H(35)
1283	110.5	1238	1299	479.0	1236	1297	6.5	1230	1235	vCC(bpy)(14)+ pC16C17H(41.8)+p CC(bpy)H(20)
1330	174.5	1283	1350	377.0	1285	1349	41.3	1279	1287	C63N57(10)vCC(bpy)(14)+ vCC(Carbazole)(12)+ pCC79H(16)p C(carbazole)H (40)
1382	74.4	1334	1409	135.9	1341	1402	44.5	1329	1335	vCC(bpy)(12)+pN9C14H (10) + pCC(bpy)H(40)
1438	85.7	1388	1448	11.3	1378	1451	19.5	1376	1389	vCC(carbazole)(11)+p C(bpy)H(27), pC74C79H(37)
1475	61.9	1423	1501	447.6	1428	1500	263.7	1422	1413	vCC(carbazole)(13)+p C(carbazole)H(69)
1527	92.3	1474	1547	36.2	1472	1551	11.0	1470	1475	CC(carbazole)(25),p C(carbazole)H(43)
1544	77.5	1490	1559	34.6	1484	1569	53.8	1487	1491	ωHC14C15H(45), ωC5(8)N9C14H(18)
1604	115.9	1548	1635	61.9	1556	1646	257.3	1560	1558	vCC(bpy)(17), vCC(carbazole)(19),pδCC(b py)H(12)

										δ CC(carbazole)H(14)
1650	224.2	1592	1683	254.8	1602	1694	174.5	1606	1588	vCC(bpy)(38), ρ CC(bpy)H(49)
1672	2848.3	1613	1707	4459.6	1624	1723	16.6	1633	1615	vCC(carbazole)(31)+ ρ HCC(carbazole)(34)
3051	8.2	2944	3079	3.4	2930	3076	18.4	2916	2930	vC46H(100)
3090	314.0	2982	3113	364.9	2962	3111	36.0	2949	2976	vC14H(96)
3170	99.4	3059	3199	6.3	3044	3200	7.0	3034	3068	vC16(17)H (97)

^aAbbreviation/symbols: ν , stretching; δ , bending in-plane; τ , torsion; ω , wagging out-of-plane; ρ , wagging in-plane; PED: potential energy distribution

Table 3 The energy levels (eV) of the frontier orbitals of the title compound calculated with M062X/LanL2DZ theoretical level.

Orbital	α spin E(eV)	Cu	Cl	carba zole	bpy	C16=C17 (C74=C79)	β spin E(eV)	Cu	Cl	carbazole	bpy	C16=C17 (C74=C79)
LUMO+6	-4.256	0.16	0.00	0.27	96.80	1.94	-4.775	1.53	0.11	25.37	68.75	3.76
LUMO+5	-4.783	0.30	0.02	12.18	81.90	5.33	-5.134	1.86	0.14	2.32	92.97	2.23
LUMO+4	-4.804	1.74	0.09	2.44	92.78	2.47	-5.165	0.19	0.03	89.05	8.56	1.89
LUMO+3	-5.136	1.54	0.15	35.25	56.65	5.81	-6.335	4.29	1.08	5.19	81.67	6.74
LUMO+2	-5.167	0.13	0.02	91.81	6.80	1.01	-6.372	0.85	0.13	21.78	53.71	23.16
LUMO+1	-6.378	1.81	3.13	4.94	85.15	6.71	-7.557	57.73	12.57	0.36	28.00	0.44
LUMO	-6.408	0.48	0.07	25.33	46.42	27.43	-7.581	0.90	0.28	71.96	11.66	14.31
HOMO	-9.617	0.01	0.01	80.91	8.1	9.97	-9.618	0.01	0.00	80.68	8.33	9.97
HOMO-1	-9.670	0.04	0.02	97.31	1.1	1.4	-9.670	9.53	3.22	79.50	6.09	1.37
HOMO-2	-10.185	52.73	17.51	0.11	28.66	0.13	-10.185	47.87	15.91	9.27	25.98	0.33
HOMO-3	-10.286	0.02	0.02	67.38	15.29	17.15	-10.286	0.04	0.02	67.84	14.97	16.99
HOMO-4	-11.045	2.04	0.27	43.02	35.75	18.54	-11.045	7.36	1.42	44.31	35.30	11.19
HOMO-5	-11.129	0.69	0.39	57.73	28.18	12.59	-11.129	0.59	0.41	56.46	28.81	13.31
HOMO-6	-12.210	67.99	13.51	5.3	12.37	0.21	-12.209	68.82	14.35	3.85	12.03	0.41

Table 4 Experimental and calculated absorption wavelengths, energies and oscillator strengths of the title compound in CH₃OH solution

Gas OrbitalOcc.	Energy (eV)	Wavelen gth (nm)	Os.	CH ₃ OH solution Orbital Occ.	Energy	Wavelen gth	Os.	exp	Assign
HOMO(α)→LUMO+1(α)(0.5914)	2.5312	489.83	0.9033						LLCT MLCT
HOMO-5(β)→LUMO(β)(0.4882)									
HOMO(β)→LUMO+3(β)(0.5717)									
HOMO-2(α)→LUMO(α)(-0.2713)	3.0084	412.13	0.1109	HOMO(α)→LUMO(α)(-0.4456)	3.0599	405.19	1.4508	415	MLCT LLCT
HOMO-13(β)→LUMO(β) (0.6792)				HOMO(α)→LUMO+1(α)(0.4651)					
HOMO-1(β)→LUMO+3(β)(0.2290)				HOMO(β)→LUMO+2(β)(-0.4604)					
				HOMO(β)→LUMO+3(β)(0.4518)					
HOMO-3(α)→LUMO+1(α)(0.4339)	3.8478	322.22	0.3004						LLCT MLCT
HOMO-6(β)→LUMO+2(β)(0.1836)									
HOMO -3(β)→LUMO+3(β)(0.4316)									
HOMO-24(β)→LUMO+1(β)(-0.1786)	3.9566	313.36	0.1639	HOMO(α)→LUMO+2(α)(-0.2686)	4.2659	290.64	0.5464	297	LLCT
HOMO-15(β)→LUMO+1(β)(0.8591)				HOMO(α)→LUMO+9(α)(0.2637)					
				HOMO(β)→LUMO+4(β)(-0.2747)					
				HOMO(β)→LUMO+11(β)(0.2836)					
				HOMO-4(α)→LUMO(α)(-0.2323)	4.4691	277.43	0.3418		LLCT

				HOMO-4(α) $\rightarrow$ LUMO+1(α)(-0.2301)						
				HOMO-19(β) $\rightarrow$ LUMO(β)(0.4059)						
				HOMO-4(β) $\rightarrow$ LUMO+3(β)(-0.2343)						
HLMO-1(α) $\rightarrow$ LUMO+5(α)(-0.3087)	4.9660	249.66	0.1672	HOMO-3(α) $\rightarrow$ LUMO+6(α)(0.2845)	4.8155	257.47	0.3679		LLCT	
HOMO-1(α) $\rightarrow$ LUMO+13(α)(0.3775)				HOMO-25(β) $\rightarrow$ LUMO(β)(0.3261)						
HOMO-1(β) $\rightarrow$ LUMO+8(β)(-0.2968)				HOMO-3(β) $\rightarrow$ LUMO+8(β)(0.2568)						
HOMO-1(β) $\rightarrow$ LUMO+13(β)(0.3727)										
HOMO-1(α) $\rightarrow$ LUMO+6(α)(0.4352)	5.0048	247.73	0.2135	HOMO-32(β) $\rightarrow$ LUMO(β)(-0.3179)	5.0449	245.76	0.3295	242	LLCT	
HOMO-1(α) $\rightarrow$ LUMO+12(α)(0.2424)				HOMO-26(β) $\rightarrow$ LUMO+1(β)(0.3771)						
HOMO-1(β) $\rightarrow$ LUMO+6(β)(0.3259)				HOMO-2(β) $\rightarrow$ LUMO+10(β)(-0.1855)						

Table 5 Interaction energies (kJ/mol) of Co(II) with ligands

	B3LYP		M062X		PBE1PBE	
	α	β	α	β	α	β
N(20)-Cu(54)	125.3	132.1	187.6	319.4	306.7	262.8
N(25)-Cu(54)	135.1	138.0	183.3	322.4	262.5	268.9
N(56)-Cu(55)	124.8	131.3	187.3	322.0	173.2	195.6
N(57)-Cu(55)	132.0	136.9	200.0	324.9	178.6	207.0
Cl(109)-Cu(54)	198.9	211.5	250.2	332.6	228.3	293.6
Cl(109)-Cu(55)	196.9	223.8	248.0	333.6	212.9	240.3
Cl(110)-Cu(54)	194.0	184.1	252.4	332.7	223.6	297.2
Cl(110)-Cu(55)	199.5	185.6	250.2	332.7	221.4	266.8
Cu(54)-Cu(55)	11.0	19.5	29.1	35.4	27.8	15.0
Cu(55)-Cu(54)	11.1	21.5	29.3	35.4	26.0	15.7
bpy-Cu(54)	75.4	75.7	86.9	89.5	95.7	96.4
bpy-Cu(55)	76.6	76.2	85.2	75.5	96.4	97.4

Table 6 Bond orbital analysis of title compound with B3LYP/LanL2DZ level of theory

Bond	Occupancy	Atom	Contribution from parent NBO(%)	Atomic hybrid contributions(%)		Hybrid
				s	p	
C1-C2	0.98875	C1	50.71	35.62	64.38	sp ^{1.81}
		C2	49.29	35.55	64.45	sp ^{1.81}
C1-C2	0.84881	C1	48.77	0.00	100.00	sp ^{1.00}
		C2	51.23	0.00	100.00	sp ^{1.00}
C1-C6	0.98675	C1	48.65	35.38	64.62	sp ^{1.83}
		C6	51.35	36.67	63.33	sp ^{1.73}
C2-C3	0.99000	C2	49.93	35.17	64.83	sp ^{1.84}
		C3	50.07	35.37	64.63	sp ^{1.83}
C5-N9	0.98908	C5	36.58	27.56	72.44	sp ^{2.63}
		N9	63.42	32.95	67.05	sp ^{2.04}
N9-C14	0.99224	N9	64.75	33.01	66.99	sp ^{2.03}
		C14	35.25	22.42	77.58	sp ^{3.46}
C8-N9	0.9896	C8	37.10	28.79	71.21	sp ^{2.47}
		N9	62.90	33.92	66.08	sp ^{1.95}
C7-C8	0.97799	C7	49.79	29.98	70.02	sp ^{2.34}
		C8	50.21	33.52	66.48	sp ^{1.98}
C7-C8	0.76033	C7	54.14	0.00	100.00	sp ^{1.00}
		C8	45.86	0.00	100.00	sp ^{1.00}
C7C10	0.98652	C7	50.50	36.75	63.25	sp ^{1.72}
		C10	49.50	36.19	63.81	sp ^{1.76}
C11-C16	0.98542	C11	49.64	32.24	67.76	sp ^{2.10}
		C16	50.36	36.08	63.92	sp ^{1.77}
C16C17	0.98907	C16	49.75	37.29	62.71	sp ^{1.68}
		C17	50.25	37.82	62.18	sp ^{1.64}
C16-C17	0.90387	C16	43.89	0.01	99.99	sp ^{1.00}
		C17	56.11	0.01	99.99	sp ^{1.00}

C17C18	0.98523	C17	47.89	33.83	66.17	sp ^{1.96}
		C18	52.11	35.31	64.69	sp ^{1.83}
C18C19	0.98741	C18	50.53	31.26	68.74	sp ^{2.20}
		C19	49.47	38.90	61.10	sp ^{1.57}
C18C23	0.98648	C18	50.60	33.41	66.59	sp ^{1.99}
		C23	49.40	35.22	64.78	sp ^{1.84}
C19N20	0.99144	C19	36.79	29.93	70.07	sp ^{2.34}
		N20	63.21	38.50	61.50	sp ^{1.60}
C21N20	0.99036	N20	62.29	37.66	62.34	sp ^{1.66}
		C21	37.71	28.33	71.67	sp ^{2.53}
N20-C21	0.88387	N20	64.82	0.00	100.00	sp ^{1.00}
		C21	35.18	0.00	100.00	sp ^{1.00}
C21C24	0.98323	C21	49.72	33.60	66.40	sp ^{1.98}
		C24	50.28	33.39	66.61	sp ^{1.99}
C24N25	0.99070	C24	38.05	28.40	71.60	sp ^{2.52}
		N25	61.95	37.59	62.41	sp ^{1.66}
C26N25	0.99168	N25	63.12	37.47	62.53	sp ^{1.67}
		C26	36.88	29.57	70.43	sp ^{2.38}
C26C27	0.99052	C26	49.90	38.82	61.18	sp ^{1.58}
		C27	50.10	34.04	65.96	sp ^{1.94}
C1H30	0.98858	C1	60.97	28.94	71.06	sp ^{2.46}
		H30	39.03	100.00		s
C14H33	0.98924	C14	61.33	24.32	75.68	sp ^{3.11}
		H33	38.67	100.00		s

Fig. 1 Optimized structure of title compound with B3LYP/LanL2DZ level

Fig 2 Experimental and calculated IR. a) Experimental IR; b) Calculated IR spectra with B3LYP method; c) Calculated IR spectra with PBE1PBE method

Fig.3 Energy levels and the 3D plots of the NHOMO and NLUMO of the compound

Fig. 4 Calculated UV-Vis with B3LYP and PBE1PBE methods.

Fig. 5 The correlation of heat capacity C_v (a), entropy S (b), enthalpy H (c) and Gibbs free energy G (d) with temperature T).

Graphical abstract

Experimental and DFT study of the structural and spectroscopic properties of $[\text{Cu}_2(\text{emppc})_2\text{Cl}_2]\text{Cl}_2$ has been reported