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以四氟苯甲酸根及联吡啶为配体的铜配合物的合成、晶体结构及量子化学研究

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摘要：水热条件下，合成了一个新的单核铜(Ⅱ)配合物 $[Cu(TFBA)(2,2'\text{-bipy})(H_2O)_2](TFBA)$(HTFBA=2,3,4,5-四氟苯甲酸,2,2′-bipy=2,2′-联吡啶),并通过元素分析、红外光谱,热重分析和 X-射线单晶衍射对其进行了表征。铜(Ⅱ)分别与来自 1 个 2,2′-bipy 的 2 个氮原子、1 个 2,3,4,5-四氟苯甲酸根的 1 个氧原子和 2 个水分子中的 2 个氧原子配位,形成变形的四方锥的配位构型。配合物通过强的 O–H…O 氢键作用形成了二聚体结构,该二聚体又通过分子间弱的 C–H…O 氢键和 C–H…π 作用形成了一维链状结构。对配合物中$[Cu(TFBA)(2,2'\text{-bipy})(H_2O)_2]^+$进行了量子化学从头计算,探讨了配合物的稳定性、分子轨道能量以及一些前沿分子轨道的组成特征。

关键词：2,3,4,5-四氟苯甲酸；2,2′-联吡啶；铜(Ⅱ)配合物；晶体结构；从头计算

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Hydrothermal Synthesis, Crystal Structure and Quantum Chemistry of Cu(Ⅱ) Complex with Tetrafluorobenzoate and Bipyridine

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Abstract: The title complex $[Cu(TFBA)(2,2'\text{-bipy})(H_2O)_2](TFBA)$ (HTFBA=2,3,4,5-tetrafluorobenzoic acid, 2,2′-bipy=2,2′-bipyridine) was hydrothermally synthesized by the reaction of cupric acetate monohydrate with HTFBA and 2,2′-bipy in the solvent mixture of methanol and water. It was characterized by elemental analysis, IR spectra, TG and X-ray single crystal diffraction. The copper(Ⅱ) ion is five-coordinated with two nitrogen atoms from one 2,2′-bipy, one oxygen atom from one TFBA and two water oxygen atoms, forming a distorted square-pyramidal configuration. A dimer structure was formed by strong O–H…O hydrogen bonds. Weak intermolecular C–H…O hydrogen bonds and C–H…π stacking interactions further link the dimer into one-dimensional chain. Furthermore, Density functional theory (DFT) calculations of the structures, stabilities, orbital energies, composition characteristics of some frontier molecular orbitals and Mulliken charge distributions of the $[Cu(TFBA)(2,2'\text{-bipy})(H_2O)_2]^+$ cation were performed by means of Gaussian 03W package and taking B3LYP/

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lanl2dz basis set. CCDC: 848788.

Key words: 2,3,4,5-tetrafluorobenzoic acid; 2,2′-bipyridine; copper(Ⅱ) complex; crystal structure; *ab initio* method

0 Introduction

The design and synthesis of metal-organic coordination polymers have received considerable attention due to their diversity structures and potential applications such as catalytic, conductive, luminescent, magnetic, spin-transition, non-linear optical or porous functional materials[1-12].

Benzoic acid and its derivatives which commonly possess multiple coordination modes are excellent candidates for constructing supramolecular metal complexes through selective and directional non-covalent forces such as hydrogen bonding[13]. On the other hand, the chelating aromatic amine 2,2′-bipyridine (2,2′-bipy) and 1,10-phenanthroline (phen) as co-ligands can increase the stability of the crystal structure by $\pi\cdots\pi$ and C–H$\cdots\pi$ interactions[11].

In order to obtain further information about the complex construction with rigid benzoic acid ligand, we selected 2,3,4,5-tetrafluorobenzoic acid (HTFBA) and 2,2′-bipy as ligands, and obtained a new complex [Cu(TFBA)(2,2′-bipy)(H_2O)$_2$](TFBA) prepared by hydrothermal method. We report here the synthesis and crystal structure. Furthermore, quantum chemistry calculation was performed to disclose the stability, molecular orbital energy and frontier orbital constitution.

1 Experimental

1.1 Materials and physical measurements

All reagents and solvents used for the syntheses were commercially available and were used without further purification. IR spectra were recorded on a Nicolet 6700 spectrometer with KBr pellets in the 4 000~400 cm^{-1} region. Crystal structure determination was carried out on a Bruker Smart APEX Ⅱ CCD diffractometer. C, H and N elemental analyses were performed on a PE-2400 (Ⅱ) apparatus. Thermogravimetric analysis (TG) data were collected on a METTLER TGA/DSC 1100 instrument under nitrogen atmosphere with a heating rate of 10 ℃·min^{-1}.

1.2 Synthesis of [Cu(TFBA)(2,2′-bipy)(H_2O)$_2$](TFBA)

A mixture of Cu(OAc)$_2$·H_2O (0.199 g, 1.0 mmol), HTFBA (0.682 5 g, 2.0 mmol), 2,2′-bipy (0.1562 g, 1.0 mmol), Et_3N (1.0 mmol, 0.14 mL) were added into a mixed solvent of 10 mL anhydrous methanol and 5 mL water and stirred for 0.5 h. Then the mixture was transferred and sealed into a 23 mL Teflon-lined stainless steel autoclave, which was heated at 140 ℃ for 3 d and then cooled to room temperature. The green crystals were obtained in 47% yield (based on Cu). Anal. Calcd. for $C_{24}H_{14}CuF_8N_2O_6$(%): C, 44.91; H, 2.20; N, 4.36; Found(%): C, 44.87; H, 2.15; N, 4.43. IR (KBr, ν/cm^{-1}): 3 417, 1 596, 1 474, 1 381, 1 260, 1 102, 907, 759, 707.

1.3 Crystal structure determination

The single crystals of the title complex with approximate dimensions of 0.25 mm×0.20 mm×0.15 mm was placed on a Bruker Smart APEX Ⅱ CCD diffractometer. The diffraction data were collected at 295 K using a graphite-monochromatic Mo $K\alpha$ radiation (λ=0.071 073 nm) with the φ-ω scan mode in the range of 1.97°≤θ≤25.05°. The correction for Lp factors was applied. The structure was solved by direct methods with SHELXS-97 program[14] and refined by full-matrix least-squares techniques on F^2 with SHELXL-97[15]. All non-hydrogen atoms were treated anisotropically. The organic hydrogen atoms were placed in calculated positions with fixed isotropic thermal parameters and included in structure factor calculations in the final stage of full-matrix least-squares refinement. The water hydrogen atoms were located in the difference Fourier map and refined isotropically. All calculations were performed using the SHELXL programs. The final R=0.045 2, wR=0.099 7 (w=1/[$\sigma(F_o)$+(0.035 3P)^2+0.000 1P], where P=(F_o^2+2F_c^2)/3), S=1.093, $(\Delta/\sigma)_{max}$=0.000, $(\Delta\rho)_{max}$=580 and $(\Delta\rho)_{min}$=−703 e·nm^{-3}. The crystallographic data and structure refinements for the complex are

summarized in Table 1. The selected bond lengths and bond angles of the title complex are listed in Table 2, and the hydrogen bond details in Table 3.

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Table 1　Crystal data and structure refinements of the title complex

Empirical formula	$C_{24}H_{14}CuF_8N_2O_6$	Z	2
Formula weight	641.91	μ / mm^{-1}	1.044
Size / mm	0.25×0.20×0.15	D_c / (g·cm^{-3})	1.821
θ range for data collection / (°)	1.97 to 25.04	F(000)	642
Crystal system	Triclinic	Reflections collected	6100
Space group	$P\bar{1}$	Independent reflections (R_{int})	4 106 (0.057 9)
a / nm	0.764 09(10)	Goodness of fit on F^2	1.093
b / nm	1.1240 1(14)	R_1, wR_2 ($I>2\sigma(I)$)	0.045 2, 0.099 7
c / nm	1.4.809 9(18)	R_1, wR_2 (all data)	0.060 3, 0.102 8
V / nm^3	1.171 0(3)	$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ / (e·nm^{-3})	580, −703

Table 2　Selected bond lengths (nm) and angles (°) for the title complex

Cu(1)-O(1)	0.195 4(2)	Cu(1)-N(1)	0.201 4(3)	C(11)-O(2)	0.122 8(4)
Cu(1)-O(1W)	0.223 7(2)	Cu(1)-N(2)	0.199 7(3)	C(18)-O(3)	0.123 5(4)
Cu(1)-O(2W)	0.195 8(2)	C(11)-O(1)	0.127 5(4)	C(18)-O(4)	0.125 1(4)
O(1)-Cu(1)-O(2W)	94.62(9)	O(1W)-Cu(1)-O(2W)	95.53(9)	N(1)-Cu(1)-N(2)	80.77(11)
O(1)-Cu(1)-N(2)	90.96(10)	O(1W)-Cu(1)-N(1)	89.73(10)	N(1)-Cu(1)-O(2W)	91.25(10)
O(1W)-Cu(1)-O(1)	102.54(9)	O(1W)-Cu(1)-N(2)	94.82(10)		

Table 3　Hydrogen bond lengths and angles for the title complex

D–H…A	d(D-H) / nm	d(H…A) / nm	d(D…A) / nm	∠DHA / (°)
O(1W)–H(2W)…O(4)	0.085	0.189	0.274 1(3)	177.5
O(2W)–H(4W)…O(2)	0.085	0.174	0.257 2(3)	165.8
O(1W)–H(1W)…O(3)A	0.085	0.196	0.280 0(3)	170.3
O(2W)–H(3W)…O(4)A	0.085	0.178	0.259 9(3)	161.9
C(4)–H(4)…O(1W)B	0.093	0.258	0.344 8(4)	156.0
C(8)–H(8)…O(3)C	0.093	0.253	0.317 1(4)	126.6

Symmetry transformations used to generate equivalent atoms: A: $-x+1$, $-y$, $-z+1$; B: $-x+1$, $-y+1$, $-z+1$; C: x, $y+1$, z.

2　Results and discussion

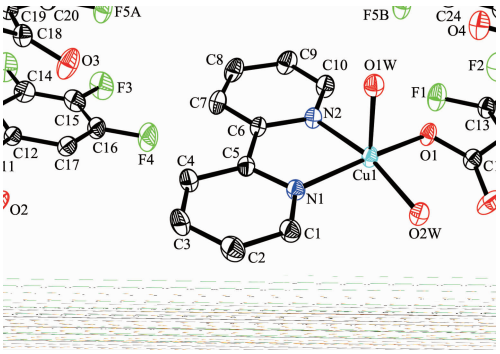
2.1　IR spectra

In the IR spectra, the wide adsorption peak at about 3 417 cm^{-1} is characteristic of ν(O-H) group in H_2O. The strong peaks at 1 596 and 1 381 cm^{-1} are attributed to $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$, respectively. The value of $\Delta[\nu_{as}(COO^-)-\nu_s(COO^-)]$ is 215 cm^{-1}, which is larger than 200 cm^{-1}, indicating that the monodentate coordination mode[16] of the carboxyl group to the metal atom. In addition to the above, the characteristic 2,2′-bipy adsorption peaks at 1 474 and 759 cm^{-1}, suggesting the existence of coordinate bonds between Cu(Ⅱ) and 2,2′-bipy ligand. The above analysis is consistent with the crystal determination.

2.2　Crystal structural

The crystallographic analysis has revealed that the complex crystallizes in the triclinic system with space group $P\bar{1}$. The asymmetric unit in the complex contains one Cu(Ⅱ) atom, one 2,2′-bipy ligand, one TFBA ligand, two coordinated water molecules and one free TFBA. As shown in Fig.1, the Cu(Ⅱ) atom is coordinated by one oxygen atom from one monodentate TFBA, two nitrogen atoms from one 2,2′-bipy and two oxygen atoms from two waters, forming a distorted square-pyramidal coordination geometry. One F and one H of the

uncoordinated TFBA show disorder over two sites in the title complex. The occupancy factors refined to 0.532(3) and 0.468(3). The equatorial plane is composed of N(1), N (2), O (2) and O (2W), and the axial position is occupied by O (1W). Here, the sum of the angles subtended at the Cu(Ⅱ) atom in the equatorial plane is 357.6° (close to 360°), so that the atoms N (1), N(2), O(2), O(2W) and Cu(1) are almost in the same plane. The equatorial equation is $-6.066\,0x+4.127\,5y+3.948\,0z=2.145\,8$. The deviation of the atoms N (1), N (2), O(2), O(2W) and Cu(1) from equatorial trigonal plane is 0.027 46, 0.000 52, 0.020 87, 0.018 65 and −0.030 20 nm, respectively. The average deviation is 0.022 13 nm. Futhermore, the angles O(1W)-Cu(1)-N(1), O(1W)-Cu(1)-N(2), O(1W)-Cu(1)-O(1) and O(1W)-Cu(1)-O(2W) in the axial place are 89.73(10)°, 94.82(10)°, 102.54(9)° and 95.52(9)°, which deviate from idea value of 90°. So conclusion could be drawn that the central Cu(Ⅱ) atom adopts a distorted square-pyramidal environment.

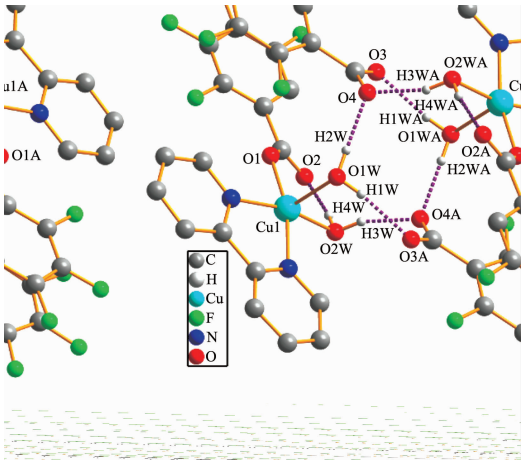


Hydrogen atoms are omitted for clarity

Fig.1 A view of the asymmetric unit of the title complex, showing the atom-labing scheme and 30% thermal ellipsoids

The Cu(1)-N(1), Cu(1)-N(2), Cu(1)-O(1W), Cu(1)-O (2W) and Cu (1)-O (2) bond lengths are 0.201 5(3), 0.201 4(3), 0.199 7(2), 0.223 7(2) and 0.195 8(2) nm, which are fall in the normal Cu-O and Cu-N coordination bonds and comparable to those detected in other related Cu complexes[17-18]. It is worthy to note that the bond lengths between the Cu and the two coordinated waters are significant different. The axial Cu(1)-O(1W) bond lengths is much longer than the equatorial Cu(1)-O(2W) bond lengths. In the coordinated TFBA, the two C-O bond length of carboxyl group (C(11)-O(1) 0.127 5(4) nm and C(11)-O(2) 0.122 8(4) nm) obvious different with the value of Δ=0.004 7 nm, indicating that the monodentate coordination mode[18-19] of the carboxyl group to the Cu(Ⅱ) atom. On the contrary, the bond length of C(18)-O(3) (0.123 5(4) nm) and C(18)-O(4) (0.125 1(4) nm) in the uncoordinated TFBA are nearly identical, suggesting the carboxyl group throughout delocalization of electrons.

As shown in Fig.2, a dimer structure is formed by intramolecular hydrogen bonds (O(1W)−H(2W)⋯O(4) (0.274 1 nm, 177.5°) and O(2W)−H(4W)⋯O(2)(0.257 2 nm, 165.8°)), and intermolecular hydrogen bonds O(1W)−H(1W)⋯O(3)^{A} (0.280 0 nm, 170.3°, symmetry code: A: $-x+1, -y, -z+1$). The dimer structure is further extended into a one-dimensional (1D) infinite chain through C−H⋯O interaction between the coordinated 2,2′-bipy ligand and water molecule (C(4)−H(4)⋯O(1W)^{B} 0.344 8(4) nm, 156.90°, symmetry code: B: $-x+1, -y+1, -z+1$ and C(8)−H(8)⋯O(3)^{C} 0.317 1(4) nm, 126.6°, symmetry code: C: $x, y+1, z$), as depicted in Fig. 3. Besides the hydrogen bonding interactions, C−H⋯π stacking interaction presents among the adjacent 2,2′-bipy (C(7)−H(7)⋯Cg1^{B} 0.369 37(4) nm and(C(3)−H(3)⋯Cg2^{B} 0.364 78(4) nm, symmetry code: B: $-x+1, -y+1, -z+1$) further stabilizes the crystal structure.

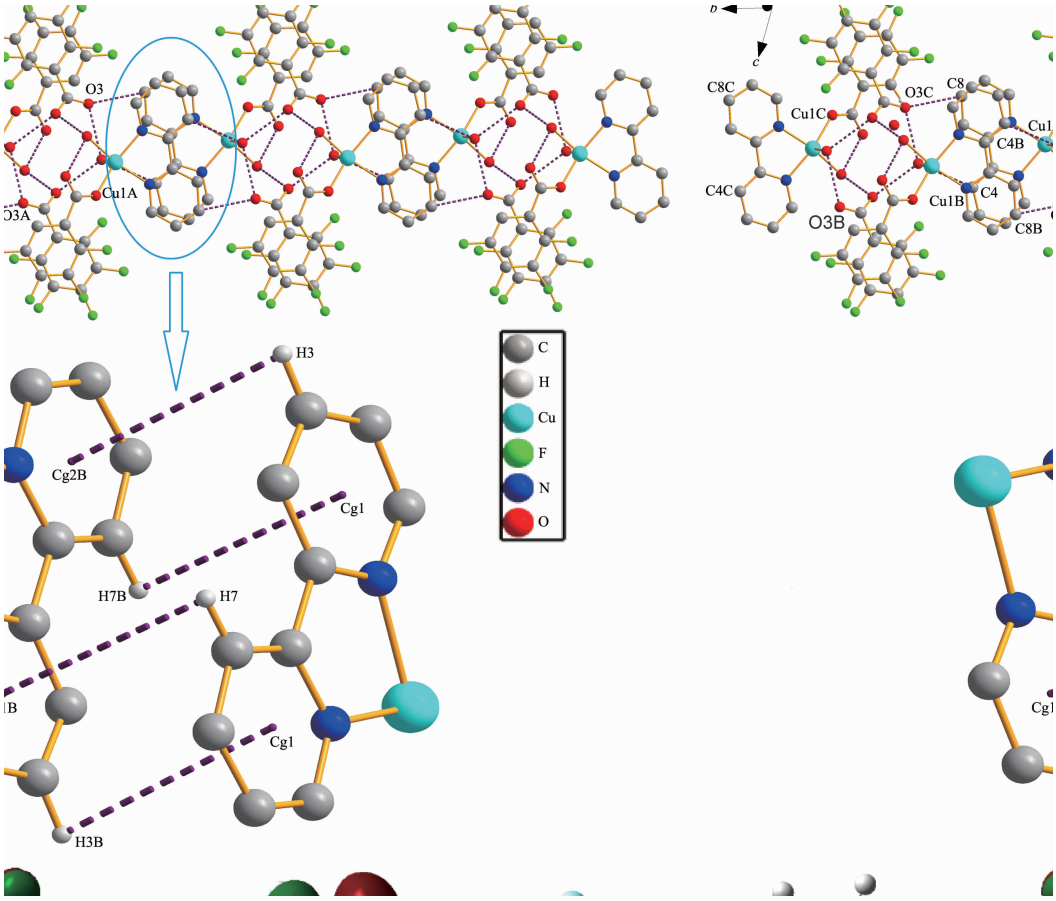


Hydrogen atoms not included in hydrogen bonding are omitted for clarity; Symmetry code: A: $-x+1, -y, -z+1$

Fig.2 Dimer structure of the title complex formed by O−H⋯O hydrogen bonds

2.3 Thermal analysis

Thermal stability studies were performed for the title complex. The first weight loss of 5.51% (calcd.



Hydrogen atoms are omitted for clarity; Symmetry code: A: $-x+1, -y, -z+1$; B: $-x+1, -y+1, -z+1$; C: $x, y+1, z$

Fig.3　1D chain structure of the title complex constructed by O–H…O, C–H…O and C–H…π stacking interaction

5.61%) between 96 and 108 ℃ corresponds to the release of coordinated water molecules in the complex. The further decomposition occurred in the range of 193~452 ℃, which may be attributed to the elimination of 2,2′-bipy and TFBA. The remaining products may be CuO (obsd. 11.98%, calcd. 12.39%).

2.4　Energy and constitution of FMOs

According to the coordination determined by X-ray determination, the single point energy and frontier molecular orbitals (FMOs) were calculated at the B3LYP/lanl2dz level with Gaussian 03W[19] program. 41 atoms, 291 basis functions, 780 primitive gaussians, including 108 occupied orbitals, are involved in the calculation.

The calculations indicate that the total molecular energy is −1 661.316 765 06 a.u and the energy of the highest occupied orbital (HOMO) −0.371 92 a.u. Both of them are relatively low, suggesting a good stability of the title complex. And the energy of the lowest unoccupied orbital (LUMO) is −0.219 27 a.u. The calculated HOMO-LUMO energy gap is 0.152 65 a.u. From the viewpoint of oxidation/reduction or charge transfer, the title complex is difficult to lose electron for oxidization.

In order to disclose the electronic structure and bonding character of the title complex, systematical analysis on the molecular orbitals has been carried out. Here, the orbital component was assigned according to the percentage of orbital coefficient quadratic sum and normalization. For the convenience of discussion, the atoms of the title complex are divided into seven groups: (a) Cu atom, (b) F atoms, (c) N atoms (d) carboxyl O atoms(O(Ⅰ)), (e) water O atoms(O(Ⅱ)), (f) C atoms on the benzene ring (C(Ⅰ)), (g) C atoms on the 2,2′-bipy ring (C(Ⅱ)), (h) hydrogen atom H. Five frontier occupied and unoccupied orbitals were taken into account in this paper, and the calculation results are shown in Table 4 and Fig.4.

Table 4 Some calculated frontier molecular orbital composition of the title complex

MO	ε / Hartree	Cu / %	N / %	O(Ⅰ) / %	O(Ⅱ) / %	F / %	C(Ⅰ) / %	C(Ⅱ) / %	H / %
104	−0.398 9	5.392 1	5.656 3	53.060 1	13.484 3	0.373 3	18.225 7	2.855 8	0.952 3
105	−0.393 0	0.333 1	3.846 1	0.617 4	0.047 2	0.010 7	0.069 2	95.067 1	0.009 2
106	−0.390 4	16.273 3	16.363 5	35.467 3	7.140 6	0.564 5	15.589 4	7.488 1	1.113 4
107	−0.378 9	0.065 8	0.005 8	6.578 3	0.108 5	23.314 9	69.881 5	0.034 6	0.010 7
108HOMO	−0.371 9	0.050 0	0.018 0	0.800 8	0.019 2	28.649 9	70.280 1	0.172 9	0.009 1
109LUMO	−0.219 3	1.337 6	26.686 8	0.089 5	0.411 0	0.006 6	0.218 9	71.171 9	0.077 7
110	−0.184 3	0.571 5	5.229 4	0.016 7	0.075 8	0.002 2	0.095 1	93.941 6	0.067 6
111	−0.176 0	0.533 3	2.307 2	14.676 7	0.482 7	4.029 3	70.384 8	7.337 1	0.250 8
112	−0.175 1	0.342 4	19.511 5	1.328 6	0.040 3	0.331 7	6.343 0	72.073 8	0.028 7
113	−0.131 4	0.013 9	0.025 1	0.270 3	0.019 4	7.304 0	92.095 4	0.230 4	0.041 5

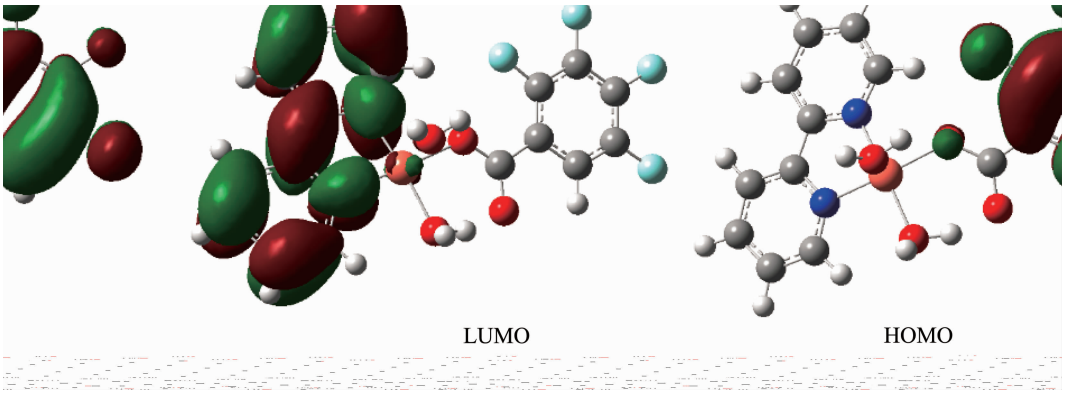


Fig.4 Schematic diagram of the frontier MO for the title complex

As will be seen in Fig.4, the HOMO of the title complex is principally localized among the benzene ring of TFBA, whereas the LUMO is localized approximately on the 2,2′-bipy ring. According to the calculations, in the HOMO, the components of C(Ⅰ) and F are 70.280 1 and 28.649 9%, respectively. The other atoms contribute to the molecular orbital are small. In the LUMO, the contribution of each atom to LUMO changes greatly. The contribution of C (Ⅱ) and N increases to 71.171 9% and 26.686 8%. Upon comparing the orbital component of HOMO and LUMO, it is easy to conclude that when electrons are excited from HOMO to LUMO, they will mainly transmit from TFBA to 2,2′-bipy.

2.5 Mulliken charge distributions

Mulliken charge distributions of all atoms in the complex are calculated and the results were illustrated in Table 4. The result shows that Cu, H and C (non-bonding with H atoms) are all positive. N, O, F and C (bonding with H atoms) are all negative. The net charge of Cu is +0.621 379, deviating from +2. The net charges of N atoms range from −0.306 066 to −0.289 52, O atoms (O (1), O (2), O (1W) and O (2W)) range from −0.477 671, −0.420 365, −0.711 549 to −0.7315 77, showing part electrons of N and O atoms transfer to Cu and then covalent bonds come into being. The analysis

Table 5 Atomic charge populations at B3LYP/Lanl2dz level

Cu(1)	0.621 379	F(1)	−0.206 875	C(4)	−0.263 791	C(11)	0.315 022	H(1)	0.294 840	H(10)	0.333 956
O(1)	−0.477 671	F(2)	−0.176 242	C(5)	0.283 142	C(12)	0.242 370	H(2)	0.263 838	H(17)	0.321 686
O(2)	−0.420 365	F(3)	−0.158 906	C(6)	0.271 720	C(13)	0.122 758	H(3)	0.268 226	H(1W)	0.414 445
O(1w)	−0.711 549	F(4)	−0.187 232	C(7)	−0.265 252	C(14)	0.164 067	H(4)	0.248 174	H(2W)	0.433 335
O(2w)	−0.731 577	C(1)	−0.189 574	C(8)	−0.265 280	C(15)	0.096 739	H(7)	0.246 384	H(3W)	0.414 008
N(1)	−0.306 066	C(2)	−0.153 017	C(9)	−0.157 758	C(16)	0.303 453	H(8)	0.267 008	H(4W)	0.459 633
N(2)	−0.289 582	C(3)	−0.160 705	C(10)	−0.210 062	C(17)	−0.424 545	H(9)	0.266 400		

of the Mulliken charge distributions is consistent with the crystal determination.

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