Synthesis, structure, properties and a theoretical study of $[ZnCl_2(4,4'\text{-bipy})]_n$

Yiming Xie* and Jihuai Wu

College of Materials Science and Engineering, Huaqiao University, Quanzhou, Fujian 362021, P.R. China

The compound $[ZnCl_2(4,4'\text{-bipy})]_n$, has been synthesised via hydrothermal reaction and structurally characterised. It crystallises in the space group *Cc* of the monoclinic system: a = 15.883(5), b = 25.656(5), c = 14.642(6) Å, β = 110.321(4)°, V = 5595(3) Å^3, $C_{10}H_8Cl_2N_2Zn$, M_r = 292.45 g mol^{-1}, D_c = 1.736 g cm^{-3}, S = 1.003, μ(Mo$K\alpha$) = 2.636 mm^{-1}, F(000) = 2920, R = 0.0471 and wR = 0.0946. The complex has a one-dimensional zigzag chain-like structure. Photoluminescent investigation reveals that it displays a strong emission in the purple region and molecular orbital (MO) calculation indicates that the emission originates from the ligand-to-ligand charge-transfer (LLCT) transition.

Keywords: bipy, crystal structure, inorganic–organic hybrid, LLCT, metal halide

Inorganic–organic hybrid materials have been of great interest owing to their intriguing structural features and potential in various applications, such as electrical conductivity, photochemistry, ion exchange, catalysis, biochemistry, nonlinear optical behaviour.[1,2] A large variety of ligands containing bridging functionalities such as carboxylates, phosphonates, or 4,4'-bipy has been exploited to prepare novel inorganic-organic hybrid materials. Being an important class of inorganic-organic hybrid materials, metal halide–bipy (bipy = 4,4'-bipyridine) systems have attracted more and more attention in recent years not only for their intrinsic aesthetic appeals, but also for their various potential applications, as well as the special coordination modes of bipy.

Recently, huge structures of metal halide-bipy materials were reported,[3-5] showing various architectures with discrete, one-(1-D), two-(2-D), and three-dimensional (3-D) connections between inorganic and organic species. However, among the known metal halide-bipy materials, group 12 metal halide-bipy materials are relatively rare and some of them possess fluorescent properties. For most of these complexes, the luminescent mechanism is usually metal-to-ligand charge-transfer (MLCT) transition[6,7] or ligand-to-metal charge-transfer (LMCT) transition,[8,9] while ligand-to-ligand charge-transfer (LLCT) transition[10,11] is rarely documented in metal halide–bipy systems.

Our recent efforts in synthesising novel goup 12 metal-based complexes have focused largely on the systems containing bifunctional ligands, such as 4,4'-bipy. Here we describe the synthesis and characterisation of a bipy-containing zinc chloride complex $[ZnCl_2(4,4'\text{-bipy})]_n$ (**1**). The electronic transition in the photoluminescent process of **1** has been studied by means of time-dependent density functional theory (TDDFT) calculation.

Experimental

Materials and instrumentation

All reactants of A.R. grade were obtained commercially and used without further purification. Elemental analyses of carbon, hydrogen and nitrogen were carried out with an Elementar Vario EL III microanalyser. The IR spectra were recorded on a PE Spectrum-One FT-IR spectrophotometer over the frequency range 4000–400 cm^{-1} using the KBr pellet technique. The solid-state fluorescent study was conducted at room temperature on an Edinburgh FLS920 fluorescence spectroscopy instrument.

Calculation details

Time-dependent density functional theory (TDDFT) calculation was performed, employing the Gaussian03 suite of programs.[12] Calculation on the electronic ground state of **1** was carried out using B3LYP density functional theory. "Double-ζ" quality basis sets was employed for the C, H, N (6-31G) and the Zn and Cl (LANL2DZ). The electron density diagrams of molecular orbital were obtained with the ChemOffice Ultra 7.0 graphics program.

*Synthesis of $[ZnCl_2(4,4'\text{-bipy})]_n$ (**1**):* $ZnCl_2$ (1 mmol, 136 mg), 4,4'-bipy (1 mmol, 156 mg) and distilled water (10 ml) were loaded into a Teflon-lined stainless steel autoclave (25 ml) and kept at 453 K for 10 days. After slowly cooling the vessel to room temperature at a rate of 8 K/h, colourless crystals suitable for X-ray analysis were obtained. Yield: 76% (based on zinc). Anal. Calcd for $C_{10}H_8Cl_2N_2Zn$: C, 41.03; H, 2.74; N, 9.57. Found: C, 41.11; H, 2.72; N, 9.53%. IR peaks (cm^{-1}): 3059(s), 2322(m), 1602(s), 1537(w), 1462(vs), 1413(m), 1386(m), 1322(vs), 1214(w), 1074(m), 1037(s), 1004(w), 805(vs), 741(m), 623(s) and 493(m).

X-ray structure determination

The intensity data set was collected on Rigaku Mercury CCD X-ray diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) by using a ω scan technique. CrystalClear software was used for data reduction and empirical absorption corrections.[13] The structure was solved by the direct methods using the Siemens SHELXTLTM Version 5 package of crystallographic software.[14] The difference Fourier maps based on these atomic positions yield all the atoms. The structures were refined using a full-matrix least-squares refinement on $F2$. A summary of crystallographic data and structure analysis is listed in Table 1, and selected bond distances and bond angles are given in Table 2.

Results and discussion

The IR spectra of **1** show the bands in the range of 500–1700 cm^{-1} that are attributed to bipy.

X-ray diffraction analysis reveals that complex **1** features a zigzag chain structure. The tetrahedral zinc atoms are coordinated by two bridging 4,4'-bipy molecules and two terminal chlorine atoms with the bond lengths of Zn–N and Zn–Cl being of 2.023(3)–2.099(3) and 2.204(2)–2.246(2)Å, respectively. The Zn–N distances are normal and comparable with those in the literature.[15,16] The bond angles of

Table 1 Summary of crystallographic data and structure analysis for **1**

Formula	$C_{10}H_8Cl_2N_2Zn$
FW	292.45
colour	Colourless
Crystal size/mm^3	0.30 0.18 0.15
Crystal system	
Space group	Cc
a (Å)	15.883(5)
b (Å)	25.656(5)
c (Å)	14.642(6)
β (°)	110.321(4)
V (Å^3)	5595(3)
Z	20
$2\theta_{max}$ (°)	50
Reflections collected	20816
Independent, observed reflections (R_{int})	12367, 3286 (0.0344)
D_{Calcd} (g cm^{-3})	1.736
μ(mm^{-1})	2.636
T (K)	293(2)
F(000)	2920
R^1, wR^2	0.0471, 0.0946
S	1.003
Largest and mean Δ/σ	0.001, 0
$\Delta\rho$(max/min) (e/Å^3)	0.573/–0.342

---

* Correspondent. E-mail: xym8790@yahoo.com.cn

Table 2 Selected bond lengths (Å) and bond angles (°)

Zn(1)–N(1)	2.090(3)	Cl(1)–Zn(1)–Cl(2)	127.36(6)
Zn(1)–N(2)	2.072(3)	N(4)–Zn(2)–N(3)	107.5(1)
Zn(1)–Cl(1)	2.228(2)	N(4)–Zn(2)–Cl(4)	107.2(1)
Zn(1)–Cl(2)	2.212(2)	N(3)–Zn(2)–Cl(4)	105.8(1)
Zn(2)–N(3)	2.087(3)	N(4)–Zn(2)–Cl(3)	103.8(1)
Zn(2)–N(4)	2.046(3)	N(3)–Zn(2)–Cl(3)	103.5(1)
Zn(2)–Cl(3)	2.246(2)	Cl(3)–Zn(2)–Cl(4)	127.84(5)
Zn(2)–Cl(4)	2.219(1)	N(6)–Zn(3)–N(5)	107.3(1)
Zn(3)–N(5)	2.099(3)	N(6)–Zn(3)–Cl(5)	106.6(1)
Zn(3)–N(6)	2.032(3)	N(5)–Zn(3)–Cl(5)	105.0(1)
Zn(3)–Cl(5)	2.204(2)	N(6)–Zn(3)–Cl(6)	104.9(1)
Zn(3)–Cl(6)	2.230(1)	N(5)–Zn(3)–Cl(6)	104.5(1)
Zn(4)–N(7)	2.086(3)	Cl(5)–Zn(3)–Cl(6)	127.28(6)
Zn(4)–N(8)	2.023(3)	N(8)–Zn(4)–N(7)	108.1(1)
Zn(4)–Cl(7)	2.230(2)	N(8)–Zn(4)–Cl(8)	104.8(1)
Zn(4)–Cl(8)	2.227(2)	N(7)–Zn(4)–Cl(8)	104.0(1)
Zn(5)–N(9)	2.050(3)	N(8)–Zn(4)–Cl(7)	106.4(1)
Zn(5)–N(10)#1	2.067(3)	N(7)–Zn(4)–Cl(7)	104.5(1)
Zn(5)–Cl(9)	2.221(2)	Cl(7)–Zn(4)–Cl(8)	127.87(7)
Zn(5)–Cl(10)	2.241(2)	N(9)–Zn(5)–N(10)#1	109.6(1)
N(1)–Zn(1)–N(2)	109.6(1)	N(9)–Zn(5)–Cl(9)	106.5(1)
N(2)–Zn(1)–Cl(2)	106.3(1)	N(10)#1–Zn(5)–Cl(9)	105.7(1)
N(1)–Zn(1)–Cl(2)	106.1(1)	N(9)–Zn(5)–Cl(10)	104.2(1)
N(2)–Zn(1)–Cl(1)	103.4(1)	N(10)#1–Zn(5)–Cl(10)	102.9(1)
N(1)–Zn(1)–Cl(1)	103.4(1)	Cl(9)–Zn(5)–Cl(10)	127.25(6)

Symmetry codes: #1 *x*–1/2, –*y*+3/2, *z*–1/2.

Cl–Zn–Cl, N–Zn–Cl and N–Zn–N range from 102.9(1) to 127.87(7)° with an average value of 109.3(1)°. The two μ_2-4,4'-bipy ligands around a zinc (II) ion are nearly perpendicular to each other with the N–Zn–N bond angles ranging between 107.3(1) and 109.6(1)°. The zinc (II) ions, separated at *ca* 11.198, 11.200 and 11.204 Å, respectively, are bridged by μ_2-4,4'-bipy ligands to form the inorganic-organic hybrid polymeric chains running along the [1, 0, 1] direction (Fig. 1). There are no hydrogen bonds and π...π stacking interactions between the hybrid chains, so the molecules are stacked together *via* van de Waals' force (Fig. 2).

Note that in the title complex the Zn…Zn distances range from 11.198 to 11.204 Å, obviously shorter than the values of 11.249–12.359 Å in the refs 15 and 16. In **1**, every two bridging 4,4'-bipy ligands surrounding one zinc ion form an obtuse angle of 107.3(1)–109.6(1)°, similar to the values of 96.915–99.118° in ref. 15 but different from the values of 177.906–180.0° in ref. 16, because in ref. 16 the complexes features a straight linear chain-like structure while in **1** and ref. 15 the complexes are have a zigzag chain-like structure.

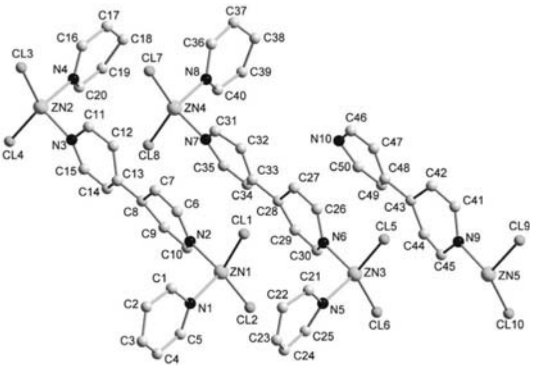

Fig. 1 ORTEP drawing of **1** with 35% thermal ellipsoids.

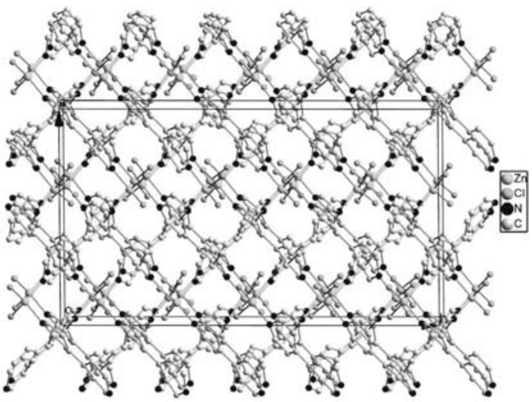

Fig. 2 Packing diagram of **1**.

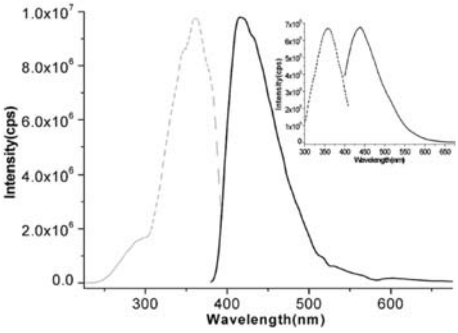

Fig. 3 Solid-state emission and excitation spectra of **1** at room temperature (inner plot: pure bipy ligand). Solid line: emission spectrum; dashed line: excitation spectrum.

The solid-state emission spectra of the title complex were investigated at room temperature. The emission spectrum of the title complex is given in Fig. 3. The fluorescent spectrum study shows that the title complex exhibits a strong purple emission band with a maximum wavelength of 415 nm upon photo-excitation at 362 nm. In order to understand the nature of the luminescence of **1**, the luminescent spectra of pure bipy were also measured under the same conditions. For pure bipy, the emission spectra show one intense emission band in the blue region with the maximum wavelength of 438 nm upon photo-excitation at 357 nm (inner plot of Fig. 3). The obvious discrepancy of the luminescent spectra of **1** and pure bipy suggests that the emission spectra of **1** should not be assigned as an intraligand π…π* transition of the bipy moiety.

To clarify the nature of the fluorescent emissions of **1**, theoretical computation has been performed on **1**. To reduce the complexity of the calculation, complex **1** was truncated into a segment of the 1-D $[ZnCl_2(4,4'\text{-bipy})]_n$ chain, containing one $ZnCl_2$ entity and one 4,4'-bipy ligand. The ground state geometry was adapted from the

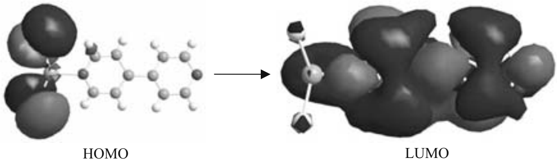

Fig. 4 The electron-density distribution of HOMO (left) and LUMO (right) calculated for 1. The isosurfaces correspond to electronic density differences of –0.015 *e*Å^{-3} and +0.015 *e*Å^{-3}.

truncated X-ray data. On the basis of this geometry, time-dependent DFT (TDDFT) calculation using the B3LYP functional was performed.[17,18] Figure 4 depicts the features of the lowest unoccupied (LUMO) and the highest occupied (HOMO) frontier orbitals of **1**. Apparently, the electron density of the singlet state for the HOMO is located on the chlorine atoms, while that of the LUMO is distributed on the 4,4'-bipy moiety; this suggests that the emission band of **1** can be attributed to the ligand-to-ligand charge transfer (LLCT) (from the HOMO of chlorine atoms to the LUMO of the 4,4'-bipy moiety).

In summary, a metal halide 4,4'-bipy complex has been synthesised and characterised. Photoluminescent investigation reveals that the title complex displays a strong emission in purple region, and (MO) calculation leads us to conclude that the emission originates from ligand-to-ligand charge transfer (LLCT) transition. The scope for the syntheses of new metal halide 4,4'-bipy complexes with novel structures and properties appears to be very large, and further systematic experimental and theoretical investigations on this system are in progress.

We gratefully acknowledge the financial support of the NSF of China (50572030), the Foundations of Overseas Chinese Affairs Office of the State Council (07QZR05) and the NSF of Fujian Province (2004HZ01-3).

Received 12 August 2008; accepted 10 November 2008
Paper 08/0118 doi: 10.3184/030823409X393718

References

1 S.I. Stupp and P.V. Braun, *Science*, 1997, **277**, 1242.
2 R. Finn and J. Zubieta, *Chem. Commun.*, 2000, 1321.
3 B.N. Figgis, J.M. Patrick, P.A. Reynolds, B.W. Skelton, A.H. White and P.C. Healy, *Aust. J. Chem.*, 1983, **36**, 2043.
4 J. Lu, C. Yu, T.Y. Niu, T. Paliwala, G. Crisci, F. Somosa and A.J. Jacobson, *Inorg. Chem.*, 1998, **37**, 4637.
5 C.H. Hu, Q. Li and U. Englert, *Cryst.Eng.Comm*., 2003, **5**, 519.
6 T. Rajendran, B. Manimaran, F.Y. Lee, G.H. Lee, S.M. Peng, C.M. Wang and K.L. Lu, *Inorg. Chem*., 2000, **39**, 2016.
7 S.S. Sun, J.A. Anspach, A.J. Lees and P.Y. Zavalij, *Organometallics*, 2002, **21**, 685.
8 J.C. Dai, S.M. Hu, X.T. Wu, Z.Y. Fu, W.X. Du, H.H. Zhang and R.Q. Sun, *New J. Chem*., 2003, **27**, 914.
9 Y.Q. Xu, D.Q. Yuan, B.L. Wu, F.L. Jiang, Y.F. Zhou and M.C. Hong, *Inorg. Chem. Commun*., 2005, **8**, 651.
10 L. Yang, A.M. Ren, J.K. Feng, X.D. Liu, Y.G. Ma and H.X. Zhang, *Inorg. Chem*., 2004, **43**, 5961.
11 L. Yang, A.M. Ren, J.K. Feng, X.J. Liu, Y.G. Ma, M. Zhang, X.D. Liu, J.C. Shen and H.X. Zhang, *J. Phys. Chem. A*, 2004, **108**, 6797.
12 M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C.Strain, O.Farkas, J.Tomasi, V.Barone, M.Cossi, R.Cammi, B.Mennuci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Oritz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B.G. Johnson, W. Chen, M.W. Wong, J.L. Andres, M. Head-Gordon, E.S. Replogle and J.A. Pople, *GAUSSIAN03*, revision C.02; Gaussian, Inc.: Pittsburgh, PA, 2003.
13 Rigaku (2002), CrystalClear Version 1.35, Rigaku Corporation.
14 Siemens(1994), SHELXTLTM Version 5 Reference Manual, Siemens Energy & Automation Inc., Madison, Wisconsin, USA.
15 J.T. Sampanthar and J.J. Vittal, *J. Chem. Soc., Dalton Trans*., 1999, 1993.
16 L. Carlucci, G. Ciani, D.M. Proserpio and A. Sironi, *J. Chem. Soc., Dalton Trans*., 1997, 1801.
17 C. Lee, W. Yang and R.G. Parr, *Phys. Rev. B*, 1988, **37**, 785.
18 C.C. Wang, C.H. Yang, S.M. Tseng, S.Y. Lin, T.Y. Wu, M.R. Fuh, G.H. Lee, K.T. Wong, R.T. Chen, Y.M. Cheng and P.T. Chou, *Inorg. Chem*., 2004, **43**, 4781.