



## Synthesis and Properties of Two Dimensional Wavelike Sheet Coordination Polymer

Z.L. TAO, L.L. LIANG\*, H.B. XUE, Y.L. SI and J. CHEN

Department of Chemistry, Bengbu Medical College, Bengbu 233030, P.R. China

\*Corresponding author: Tel: +86 552 3175259, E-mail: liangjyt@163.com

Received: 19 March 2015;

Accepted: 2 May 2015;

Published online: 29 August 2015;

AJC-17489

A new coordination polymer  $[Zn(C_{14}H_{18}SO_6)(C_{28}H_{22}N_4)]_n$ , has been synthesized under solvothermal conditions and characterized by single crystal X-ray structure analyses, thermogravimetric analyses, powder X-ray diffraction and solid-state photoluminescent measurements. The  $Zn^{2+}$  ion has a square pyramidal coordination and two neighbouring  $Zn^{2+}$  ions are bridged together by four carboxylate groups of 4,4'-dicarboxyldiphenyl sulfone to generate a paddle wheel dinuclear zinc structure. The dizinc paddle wheel is linked by two V-shaped linker 4,4'-dicarboxyldiphenyl sulfone *via* carboxylate groups to form an infinite 1-D chain which is further connected by 4,4'-*bis*(benzimidazole-1-ylmethyl)biphenyl through sharing the dizinc paddlewheel into an infinite 2D sheet framework. The framework is further strengthened by  $\pi$ - $\pi$  interaction between benzimidazol rings of 4,4'-*bis*(benzimidazole-1-ylmethyl)biphenyl ligand and the benzene ring of 4,4'-dicarboxyldiphenyl sulfone ligand. The TG analysis shows that the framework of the complex is stable up to 370 °C. Moreover, the complex exhibits strong photoluminescence in the solid state at room temperature.

**Keywords:** Luminescence, 4,4'-*Bis*(benzimidazole-1-ylmethyl)biphenyl, 4,4'-Dicarboxyldiphenyl sulfone, Zinc complex.

### INTRODUCTION

Great effort has been made to the rapidly expanding field of crystal engineering of coordination polymers due to their structural and topological diversities as well as their potential applications in catalysis, gas storages, sensing small molecules and enantioselective separations<sup>1-6</sup>. However, it is still difficult to accurately predict the structure and functions of coordination polymers as the processes of assembly are influenced by many factors, such as organic linker kinds, solvent systems, metal ions and reaction temperature, *etc.* Among all of the effects, organic ligands play a significant role in constructing various structural configuration and many different shapes, lengths and rigidities of organic ligands have been developed. A large number of mixed-ligand coordination polymers have been reported, which usually reveal greater tunability and diversity of structural frameworks than single ligands<sup>7-9</sup>. V-shaped biphenylene dicarboxylates combined with long linear nitrogenous ligands have been shown interesting structures and properties, such as 4,4'-oxybenzoic acid and 4,4'-dicarboxyldiphenylamine. We have been interested in the study of dicarboxylates and *bis*-imidazole based coordination polymers, resulting in a variety of structures and properties<sup>9-11</sup>. Herein, we employed a V-shaped dicarboxylates ligand 4,4'-dicarboxyldiphenyl sulfone (dcps) combined with a linear semi-rigid ligand 4,4'-*bis*(benzimidazol-1-ylmethyl)biphenyl (bbmb) and successfully synthesized a two dimensional wavelike sheet.

### EXPERIMENTAL

The ligand 4,4'-*bis*(benzimidazole-1-ylmethyl)biphenyl (bbmb) was synthesized according to the reported method<sup>12</sup>. All other starting chemicals were of analytical grade and used without further purification. Powder X-ray diffraction (PXRD) patterns were collected in the  $2\theta = 5-50^\circ$  range with a scan speed of 0.2 sec/deg. on a Bruker D8 diffractometer with  $CuK\alpha$  ( $\lambda = 1.542 \text{ \AA}$ ) radiation equipped with a LynxEye detector at room temperature. Thermogravimetric analyses (TGA) were performed in  $N_2$  atmosphere (a flow rate of 100 mL  $min^{-1}$ ) on a simultaneous SDT 2960 thermal analyzer from 25 °C up to 800 °C, with a heating rate of 10 °C/min. Solid state luminescence spectra for the solid samples were recorded on an AMINCO Bowman Series2 fluorescence spectrophotometer.

A mixture of 4,4'-*bis*(benzimidazole-1-ylmethyl)biphenyl (bbmb), 4,4'-dicarboxyldiphenyl sulfone (dcps) and  $Zn(NO_3)_2 \cdot 6H_2O$  (a molar ratio of 1:1:1) and the solvent of  $H_2O/DMF$  (3:1, v/v, 4 mL) was sealed in a 20 mL PTFE-lined stainless-steel vessel under autogenous pressure and heated at 130 °C for 72h. Large quantities of colourless block crystals were obtained and crystals were filtered off, washed with distilled water and dried under ambient conditions. The yield of the reaction was about 59 % based on Zn. IR: (KBr pellet,  $cm^{-1}$ ): 3410w, 3031w, 1648s, 1564m, 1498m, 1399s, 1296w, 1950w, 1160s, 1097m, 1009m, 926m, 850m, 740s, 692w, 619m, 577m, 497m.

## RESULTS AND DISCUSSION

X-ray crystallographic analyses reveal that complex crystallizes in the triclinic space group  $P-1$  with one crystallographically independent  $Zn^{2+}$  cation, one bbmb ligand and two halves dcps ligand in the asymmetric unit (Fig. 1). The  $Zn^{2+}$  ion has a square pyramidal coordination, with four O atoms from two dcps ligands occupying the equatorial sites and one N atom from bbmb ligand located on the axial positions. The Zn-O bond lengths range from 2.313 (3) to 2.488 (3) Å and the Zn-N distances are 2.340 (3) and 2.315 (3) Å. Two neighbouring  $Zn^{2+}$  ions are bridged together by four carboxylate groups of four dcps linkers to generate a paddle wheel dinuclear  $[Zn_2(O_2CR)_4]$  unit. The distance of the Zn...Zn intra paddle wheel is 2.95 Å. The dizinc paddle wheel unit is linked by two V-shaped linker dcps *via* carboxylate groups to form an infinite 1-D chain along the *b* axis with a square unit (Fig. 2a). The two chains are further linked by bbmb sharing the dizinc paddle wheel into an infinite wavelike sheet framework in the *bc* plane (Fig. 2b, 2c). It is noteworthy that the nearby benzimidazol rings of bbmb ligand of one sheet and the benzene ring of dcps ligand of the other sheet are parallel with each other. The centroid-to-centroid distance of the benzene ring is 3.5329(4) Å and interplane angle is  $10.308(86)^\circ$  (Fig. 2d). The whole sheet structure is stabilized by the intermolecular  $\pi-\pi$  interactions. There are also uncoordinated bbmb ligands located among the layers and the nearby two benzimidazol rings of the free bbmb ligand are offset parallel with each other. The centroid-to-centroid distance of the phene ring is 3.7927(4) Å and interplane angle is  $0^\circ$  (Fig. 3). Thus the free bbmb ligands are further connected through weak  $\pi-\pi$  interaction stabilizing the structure<sup>13</sup>.

Luminescent properties of compounds are of great current interest due to their various potential applications in chemical

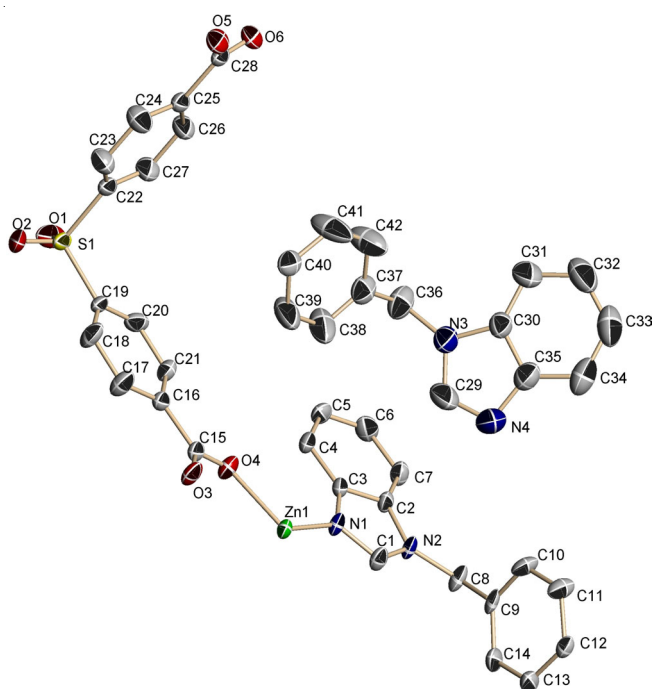


Fig. 1. Coordination environment of the Zn atom in (I), showing the atom numbering scheme. Displacement ellipsoids are drawn at the 30 % probability level

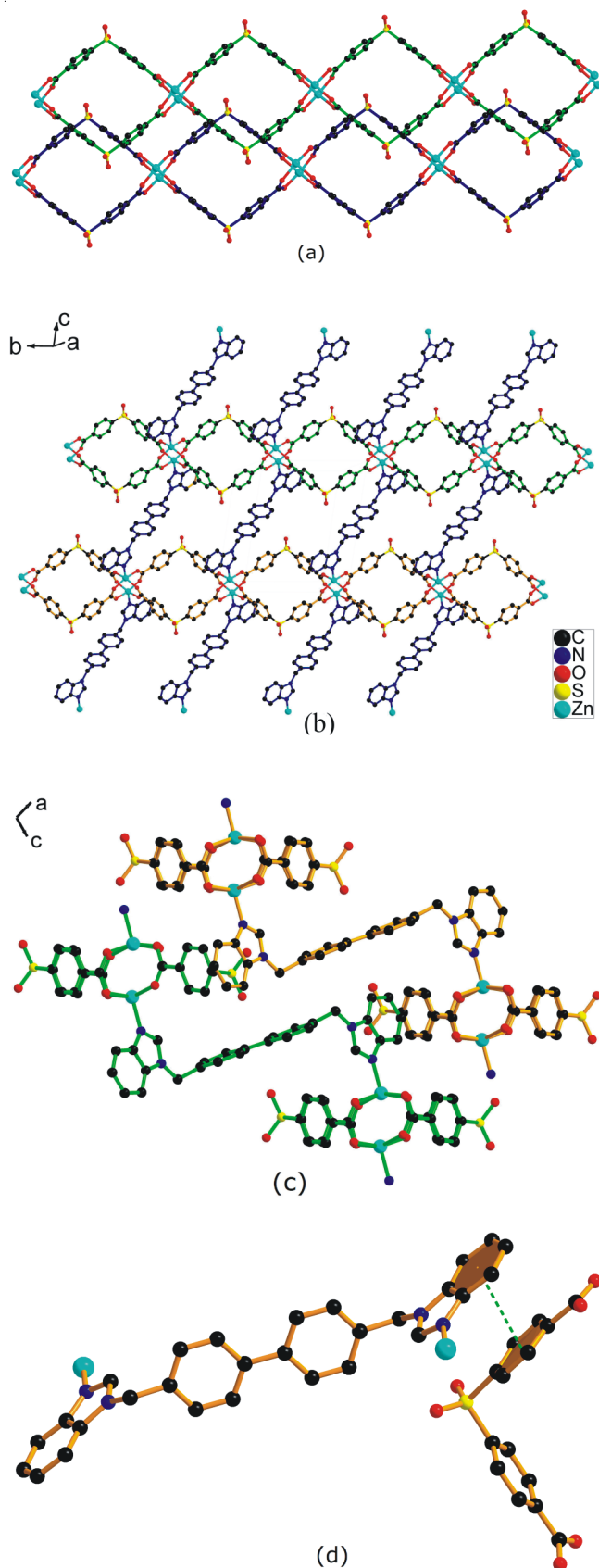


Fig. 2. (a) Two infinite 1-D chains formed by the dizinc paddle wheel SBU and V-shaped linker dcps; (b) The two chains are further linked by ligand bbmb; (c) Packing diagram of the structure showing the infinite wavelike sheet viewed along the *b* axis; (d) The  $\pi-\pi$  interaction between the benzimidazol rings of bbmb ligand and the benzene ring of dcps ligand

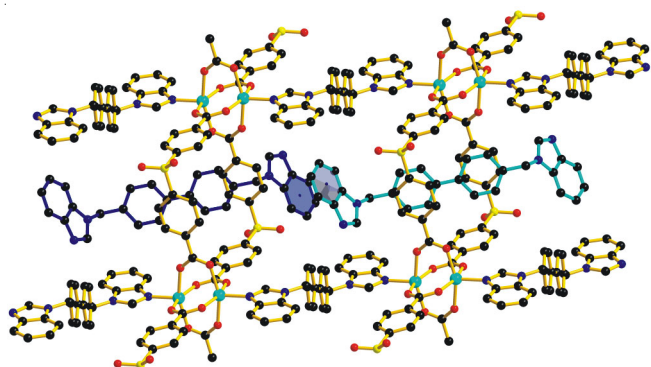


Fig. 3. Free bbmb ligands (blue) located among the layers connecting with each other through weak  $\pi$ - $\pi$  interaction

sensor, photochemistry and electroluminescent display<sup>14</sup>. Considering  $d^{10}$  metal complexes usually exhibit excellent luminescent properties, the photoluminescent properties of the complex, the free ligands of dcds and bbmb have been investigated in the solid state at room temperature. As depicted in Fig 4, emissions of free dcds and bbmb ligands were observed with the emission peak 348 nm ( $\lambda_{\text{ex}} = 317$  nm) and 386 nm ( $\lambda_{\text{ex}} = 346$  nm) respectively, which can be ascribed to the intraligand  $\pi$  to  $\pi^*$  transition. For the complex, excitation of the microcrystalline samples at 298 nm resulted intense fluorescent emissions with a maximum peak of 379 nm, a little shift between the two ligands, which should be attributed to the influence of the coordination effect between ligands and metal ions<sup>15</sup>.

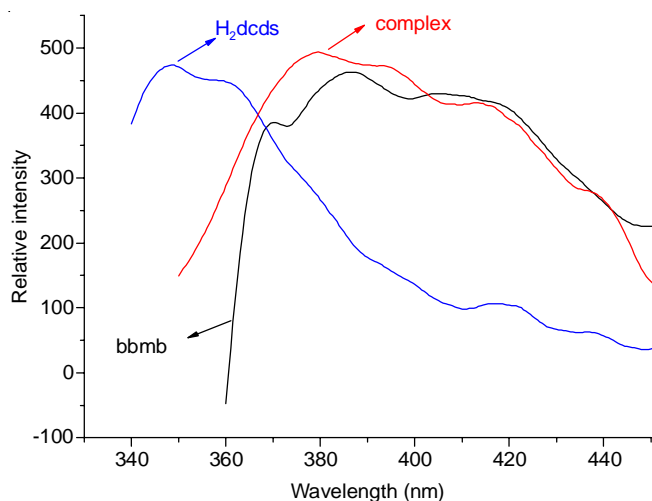


Fig. 4. Solid-state photoluminescent spectra of dcds, bbmb and the complex

Powder X-ray diffraction experiment of the complex was carried out at room temperature. The experimental and simulated XRD patterns are in agreement with each other, confirming the purity of the complex (Fig. 5). Thermal stability of the title complex was examined by TG analysis under  $N_2$  atmosphere in the temperature range of room temperature to 800 °C. TG curve shows no obvious weight loss until 370 °C then the whole framework decomposed.

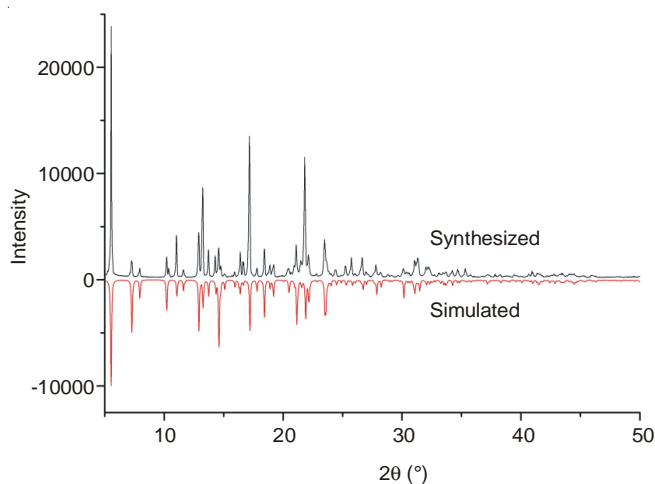


Fig. 5. Powder X-ray diffraction patterns of the complex

## Conclusion

The solvothermal reaction of 4,4'-bis(benzimidazol-1-ylmethyl)biphenyl, 4,4'-dicarboxydiphenyl sulfone and zinc ions afforded a new wavelike sheet complex. The sheet structure is strengthened by  $\pi$ - $\pi$  interaction between benzimidazol rings of bbmb ligand and the benzene ring of dcps ligand. And the free bbmb ligands are also stabilized through weak  $\pi$ - $\pi$  interaction. The complex is stable up to 370 °C and exhibits strong photoluminescence at room temperature.

## ACKNOWLEDGEMENTS

The authors are grateful for financial support from the Natural Science Foundation of Anhui Province (grant No. 1308085QB24) and Anhui Province College Excellent Young Talents Foundation (No. 2013SQRL051ZD).

## REFERENCES

- J.R. Li, J. Sculley and H.C. Zhou, *Chem. Rev.*, **112**, 869 (2012).
- H. Wu, Q. Gong, D.H. Olson and J. Li, *Chem. Rev.*, **112**, 836 (2012).
- M. Zhang, G. Feng, Z. Song, Y.P. Zhou, H.Y. Chao, D. Yuan, T.T. Tan, Z. Guo, Z. Hu, B.Z. Tang, B. Liu and D. Zhao, *J. Am. Chem. Soc.*, **136**, 7241 (2014).
- E. Barea, C. Montoro and J.A. Navarro, *Chem. Soc. Rev.*, **43**, 5419 (2014).
- Y. He, W. Zhou, G. Qian and B. Chen, *Chem. Soc. Rev.*, **43**, 5657 (2014).
- Z. Hu, B.J. Deibert and J. Li, *Chem. Soc. Rev.*, **43**, 5815 (2014).
- L.L. Liang, S.B. Ren, J. Zhang, Y.Z. Li, H.B. Du and X.Z. You, *Cryst. Growth Des.*, **10**, 1307 (2010).
- Z.Q. Shi, Y.Z. Li, Z.J. Guo and H.G. Zheng, *CrystEngComm*, **16**, 900 (2014).
- L. Luo, K. Chen, Q. Liu, Y. Lu, T. Okamura, G.C. Lv, Y. Zhao and W.Y. Sun, *Cryst. Growth Des.*, **13**, 2312 (2013).
- Z.L. Tao, L. Qin and H.G. Zheng, *Wuji Huaxue Xuebao*, **28**, 2109 (2012).
- Z.L. Tao, J.H. Cui, L. Qin and H.G. Zheng, *Wuji Huaxue Xuebao*, **28**, 2633 (2012).
- Z.L. Tao, T.T. Shi, L.L. Liang and H.B. Xue, *J. Synth. Cryst.*, **42**, 371 (2013).
- L. Dobrzànska, G.O. Lloyd, T. Jacobs, I. Rootman, C.L. Oliver, M.W. Bredenkamp and L.J. Barbour, *J. Mol. Struct.*, **796**, 107 (2006).
- C. Janiak, *J. Chem. Soc., Dalton Trans.*, 3885 (2000).
- M.D. Allendorf, C.A. Bauer, R.K. Bhakta and R.J.T. Houk, *Chem. Soc. Rev.*, **38**, 1330 (2009).