

A Three-Dimensional Supramolecular Network Constructed from Ti(III) Doped Doubly Bridged Molecular Ribbons *catena-bis*(μ -pyrazine-2,3-dicarboxylato-N,O,O')-Titanium(III)_{0.15}zinc(II)_{0.85} and Hydrated Proton *via* Hydrogen Bonding

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Received: 24 August 2013;

Accepted: 5 October 2013;

Published online: 16 July 2014;

AJC-15573

In the title Ti^{III} doped Zn^{II} complex, Ti_{0.15}Zn_{0.85}(C₆H₂N₂O₄)₂[(H₃O)_{1.85}(H₂O)_{0.15}] (**1**), obtained during exploring new photochromic materials based on Ti^{III/IV} ion, the coordination polyanion ribbons constructed by pyrazine-2,3-dicarboxylato (2,3-PZDC) ligands is balanced with the close-by hydronium cations. The asymmetric unit consists of a half metal center (composed of 15 % Ti^{III} and 85 % Zn^{II}) on the symmetry axis, a 2,3-PZDC ligand and one hydronium cation (2.91 H atoms disordered at three sites). The Ti^{III}/Zn^{II} ion is coordinated by four 2,3-PZDC ligands, giving a distorted Ti(Zn)N₂O₄ octahedral coordination geometry. The 2,3-PZDC ligand adopts a bridged 3-coordinated mode with one N and 2-carboxyl O atoms biting one metal center and the other 3-carboxyl O atom coordinating a adjacent metal. In addition, the connected mode of 2,3-PZDC ligand could append a π - π stacking interaction of two pyrazine within the doubly ribbons and especially append three strong hydrogen bonding interactions with hydronium cations. These hydrogen bonding interactions play a key role not only in the formation of the three-dimensional supramolecular network but also to the good thermal stability of the molecular structure. The optical absorption properties of powder samples of the title compound have also been studied and the colored profile of the sample also confirms the presence of the Ti^{III} ion, just like a sapphire.

Keywords: Ti^{III} doped Zn^{II} complex, Hydrogen bonding, Supramolecular network, Optical absorption.

INTRODUCTION

Pigments and dyes are very important materials due to their widely applications in numerous industrial fields, *e.g.*, decoration, printing, textile and photo-electric industry, *etc.*¹⁻⁵. Besides well known organic forms, inorganic forms have also been receiving much attention due to not only their industrial applications but also their color transformation derived from the change of ionic valence or its coordination environment. A well known example is the allochroic silica gel which display blue or pink depended on the water absorption, *i.e.*, the coordination change of cobalt ions⁶. Recently, Subramanian *et al.*^{7,8} discovered that substitution of Mn³⁺ into the trigonal-bipyramidal sites of oxides with YInO₃ or YbFe₂O₄-related structure produces an intense blue color.

Titanium is also an interesting element for it can be oxidized from +3 to +4 oxidation state with a significant transformation in color (purple to colorless). Yao *et al.*^{9,10} have found that TiO₂ can be colored by band gap excitation due to the trapping of electrons as Ti³⁺ species in bulk particles or in

a dried gel, though this photochromism is hardly observed in the absence of a hole scavenger in single crystals at room temperature^{9,10}. These are so-called photochromic materials, a new type of pigment/dye, which have attracted much attention due to their wide range of applications, *e.g.*, for self-developing photography, protective materials, reusable information storage media, data display, optical signal processing, chemical switch for computer, smart window, *etc.*¹⁰⁻¹². Although most photo-chromic materials are organic so far, inorganic materials have some advantages over the organic counterparts due to their better thermal stability, strength, chemical resistance and *etc.*. Yao *et al.*¹⁰ also demonstrated that doped titanium oxide may be competent for developing good photochromic pigment/dye. In this work, we reacted pyrazine-2,3-dicarboxylate (2,3-PZDC) with a titanium(IV) salt and a zinc salt and successfully obtained a new polymeric phase of the Ti^{III} doped Zn^{II} complex, Ti_{0.15}Zn_{0.85}(C₆H₂N₂O₄)₂[(H₃O)_{1.85}(H₂O)_{0.15}] (**1**), composed of a doubly ribbon polyanion and corresponding hydronium cations with three strong hydrogen bondings fusing them together.

EXPERIMENTAL

All chemicals were obtained from commercial sources and used as received. Elemental analysis for C, H and N were performed on an Elementar Vario MICRO analytic instrument.

Synthesis of $\text{Ti}_{0.15}\text{Zn}_{0.85}(\text{C}_6\text{H}_2\text{N}_2\text{O}_4)_2[(\text{H}_3\text{O})_{1.85}(\text{H}_2\text{O})_{0.15}]$ (1): The title compound **1**, was synthesized by the solution reaction of tetrabutyl titanate (102 mg, 0.3 mmol), zinc sulfate (57 mg, 0.2 mmol) and pyrazine-2,3-dicarboxylate (50 mg, 0.3 mmol) in 6 mL water and 2 mL hydrochloric acid at room temperature. The filtered solution was placed in a beaker and evaporated slowly. After several days, pale purple crystals of **1** were obtained in a yield of 40 % (26 mg upon ligand). Anal. calc. for $\text{C}_{12}\text{H}_{9.85}\text{N}_4\text{O}_{10}\text{Ti}_{0.15}\text{Zn}_{0.85}$ (%): C, 33.30; H, 2.28; N, 12.94; O, 36.97. Found: C, 33.10; H, 2.03; N, 12.74; O, 37.26. The ratio of two metal elements, Ti: Zn, is also confirmed by EDS measurement on this purple crystals. Samples suitable for single-crystal X-ray diffraction were selected directly from the crop obtained from the reaction.

Single crystal structure determination: X-ray intensity data for **1** were collected on a pale purple crystal (0.33 mm \times 0.24 mm \times 0.15 mm) at 293 (2) K on a Rigaku RAXIS-RAPID CCD area detector diffractometer using graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.071075$ nm). The structure was solved using direct methods and refined by full-matrix least-squares techniques. All non-hydrogen atoms were assigned anisotropic displacement parameters in the refinement. All hydrogen atoms were located from difference Fourier peaks and refined isotropically without any restraint. The structure was refined on F^2 using SHELXTL-97 software package¹³ without any unusual events. The crystal and refinement details for compound **1** are listed in Table-1. Selected bond lengths and angles are given in Table-2.

RESULTS AND DISCUSSION

The structure of **1** is isomorphous with the pure zinc compound, $\text{Zn}(2,3\text{-PZDC})_2(\text{H}_3\text{O})_2$, while the crystal color of **1** is purple for the presence of Ti^{3+} instead of colorless as pure zinc crystal¹⁴. Additionally, the cell volume also becomes a few bigger when the Ti^{3+} ions replace the Zn^{2+} sites, the difference is about 7\AA^3 between our experiment and Gryz's reported value. As shown in Fig. 1, the asymmetric unit of **1** contains a half metal ion (composed of 15 % Ti^{3+} and 85 % Zn^{2+}), a 2,3-PZDC ligand and one hydronium cation (2.91 H atoms disordered at three sites). A twofold symmetry axis falls at the metal center. Each metal center is six-coordinated in a distorted octahedral environment surrounded by two sets of $\text{O}_{\text{carboxylate}}$ & $\text{N}_{\text{pyrazine}}$ atoms from two different 2,3-PZDC ligands with a chelated so far mode and the other two $\text{O}_{\text{carboxylate}}$ atoms from another two 2,3-PZDC ligands. In this $\text{Ti}(\text{Zn})\text{N}_2\text{O}_4$ octahedron, the M-O distances (Table-2) are similar to those reported in compound $\text{Zn}(2,3\text{-PZDC})_2(\text{H}_3\text{O})_2$ ¹⁴. On the other hand, the 2,3-PZDC ligand is versatile and could bridge metal ions into multifarious structures with six potential coordination sites¹⁴⁻¹⁶. In this case, the 2,3-PZDC adopts a bridged 3-coordinated mode to the metal center (Fig. 2), with one N and one 2-carboxyl O atoms biting one metal center and the other 3-carboxyl O atom coordinating a adjacent metal. This coordination model is same as that in other cases of zinc complexes¹⁶⁻¹⁹. In addition,

upon a supramolecular view, the connected mode of 2,3-PZDC ligand should append a π - π stacking interaction and three strong hydrogen bonding interactions (Fig. 2). The π - π stacking interaction is an offset face-to-face fashion concerning to two adjacent pyrazine rings (ring A and ring B) in an independent doubly ribbon (Fig. 3). The ring A (N1-C2-C3-N2-C5-C6) [symmetry code: (x, y, z)] is exactly parallel (angel 0°) to the pyrazine ring B [symmetry code: (-x, 1 - y, -z)] with a separation of 3.29136 \AA . Comparing with the previously reported case²⁰⁻²¹, the π - π stacking interaction must be strong here. And this π - π stacking interaction should contribute to the formation of the doubly ribbon structure. Between these ribbons, hydronium cations all connect to them *via* three strong hydrogen bonding interactions, thus, a three-dimensional supramolecular network is formed (Fig. 4). The hydrogen-bonding data (Table-3) are in the range of ordinary examples and have been examined by the PLATON program²²⁻²⁵. As shown in Fig. 3 and Fig. 5, there are four O4 atoms in one repeat unit of the doubly ribbon and these O4 atoms connect four adjacent ribbons at four directions (cross-shaped model) all through $\text{O5-H5}\cdots\text{O4}$ and $\text{O5-H3}\cdots\text{O2}$ hydrogen bonds. Thus, the O4 atom and O4' atom (O4' generated by just shifting one repeat unit) connect same ribbon (Fig. 6) and the three-dimensional supramolecular network is formed finally.

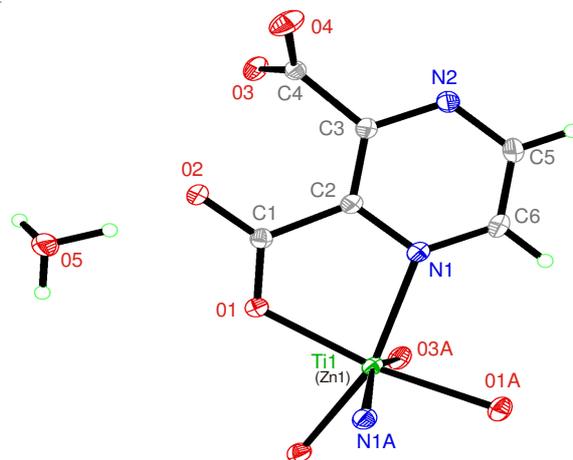


Fig. 1. Asymmetric structure of (**1**), with displacement ellipsoids drawn at the 30 % probability level and H atoms shown as small spheres of arbitrary radii

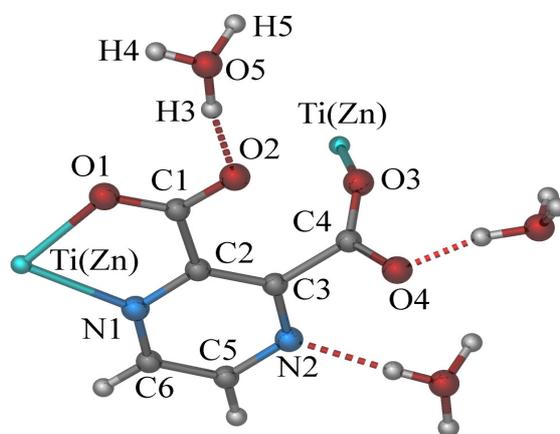


Fig. 2. Full coordination and hydrogen bonding model for the 2,3-PZDC ligand in (**1**)

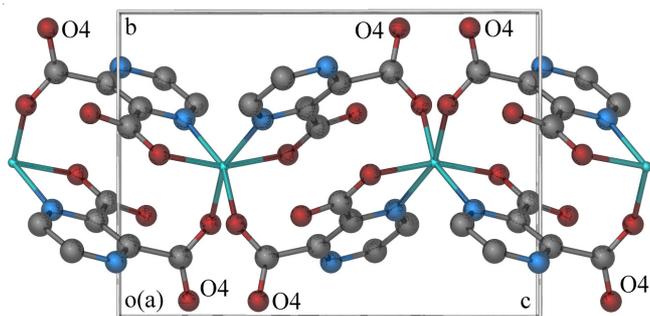


Fig. 3. A part of the doubly ribbon structure of (1), viewed along the *a* direction

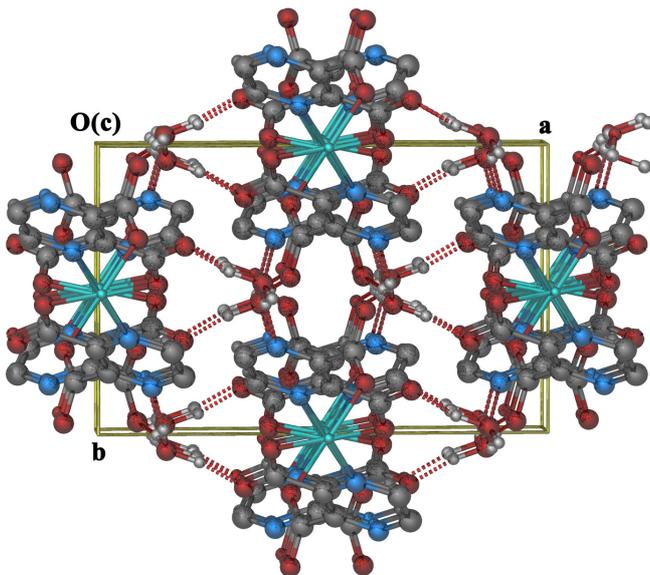


Fig. 4. Three-dimensional supramolecular network diagram for (1), viewed along the *c* direction

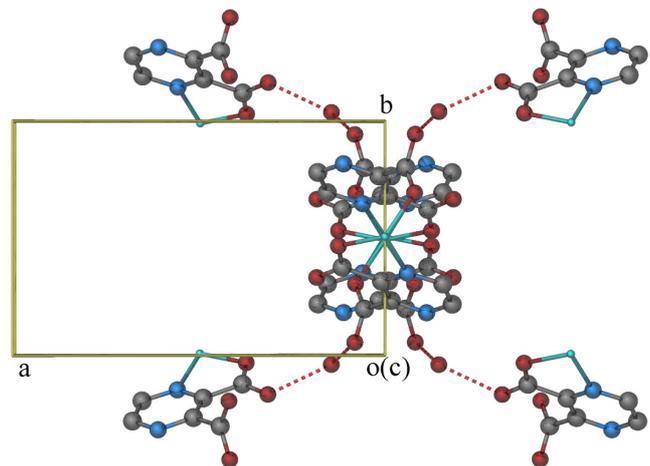


Fig. 5. Connection model of one ribbon with four adjacent ribbons

The UV-visible diffuse-reflectance spectrum of **1** was measured on the as-synthesized powder sample (qualified by powder X-ray diffraction, Fig. 7) and is plotted in Fig. 8 as $F(R)^2$ vs. wavelength, according to the Kubelka-Munk function²⁵. There are two obvious absorption bands in the spectrum. One strong band located in the region 200 nm to 350 nm can be assigned to the transition of ligands between different energy levels. The remaining very weak band from

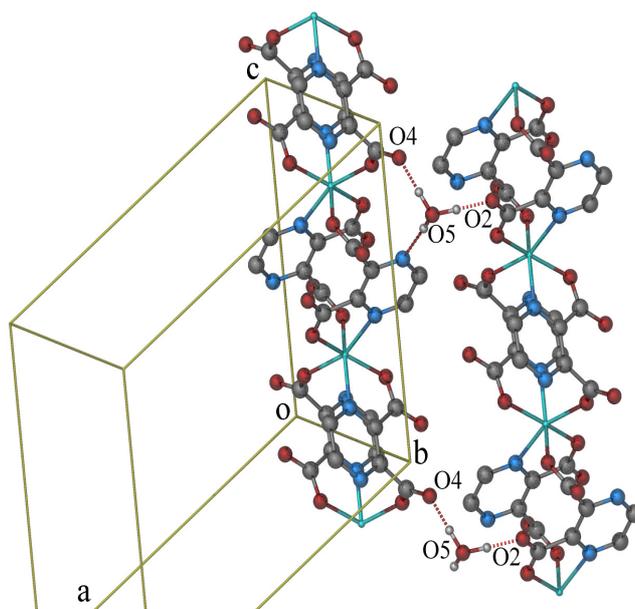


Fig. 6. Connection fashion of two near-by ribbons, the hydrogen bonds shown as dash lines

TABLE-1
CRYSTAL DATA, COLLECTION, AND STRUCTURE REFINEMENT PARAMETERS FOR COMPOUND **1**

Parameters	1
Empirical formula	$2(C_6H_2N_2O_4)(Ti_{0.15}Zn_{0.85}) \cdot 1.85(H_2O)_{0.15}(H_2O)$
Formula weight	432.84
Temperature(K)	293(2)
Crystal system	Monoclinic
Space group	C2/c
Crystal size(mm ³)	0.33 × 0.24 × 0.15
Crystal description	Chunk, pale purple
<i>a</i> (Å)	14.499 (3)
<i>b</i> (Å)	8.4426 (17)
<i>c</i> (Å)	12.891 (3)
β (°)	114.53 (3)
Volume V(Å ³)	1435.4 (5)
Z	4
D _{calc} (Mg m ³)	2.003
μ (mm ⁻¹)	1.62
F(000)	875
Final R indices	R1 = 0.0207, wR2 = 0.0489
[I>2 σ (I)] [#]	
R indices (all data) [#]	R1 = 0.0253, wR2 = 0.0507
Goodness-of-fit ^c on F ²	1.107

[#] R1 = $\sum (|F_o| - |F_c|) / \sum |F_o|$; wR2 = $\left\{ \frac{\sum w(F_o^2 - F_c^2)}{\sum w(F_o^2)} \right\}^{1/2}$

TABLE-2
SELECTED BOND LENGTHS (Å) AND ANGLES (°) OF THE COMPOUND **1**

Ti1/Zn1-O1	2.0761 (13)	Ti1/Zn1-O1 ⁱ	2.0761 (13)
Ti1/Zn1-O3 ⁱⁱ	2.0903 (11)	Ti1/Zn1-O3 ⁱⁱⁱ	2.0903 (11)
Ti1/Zn1-N1	2.1879 (12)	Ti1/Zn1-N1 ⁱ	2.1879 (12)
O1 ⁱ -Ti1/Zn1-O1	161.64 (6)	O1 ⁱ -Ti1/Zn1-O3 ⁱⁱⁱ	88.01 (4)
O1-Ti1/Zn1-O3 ⁱⁱ	106.04 (4)	O1 ⁱ -Ti1v-O3 ⁱⁱⁱ	106.04 (4)
O1-Ti1/Zn1-O3 ⁱⁱⁱ	88.01 (4)	O3 ⁱⁱ -Ti1/Zn1-O3 ⁱⁱⁱ	81.64 (6)
O1 ⁱ -Ti1/Zn1-N1	91.71 (4)	O1-Ti1/Zn1-N1	77.26 (4)
O3 ⁱⁱ -Ti1/Zn1-N1	88.28 (5)	O3 ⁱⁱⁱ -Ti1/Zn1-N1	159.15 (4)
O1 ⁱ -Ti1/Zn1-N1 ⁱ	77.26 (4)	O1-Ti1/Zn1-N1 ⁱ	91.71 (4)
O3 ⁱⁱ -Ti1/Zn1-N1 ⁱ	159.15 (4)	O3 ⁱⁱⁱ -Ti1/Zn1-N1 ⁱ	88.28 (5)
N1-Ti1/Zn1-N1 ⁱ	106.61 (6)		

Symmetry codes: (i) $-x, y, -z+1/2$; (ii) $-x, -y+1, -z$; (iii) $x, -y+1, z+1/2$

TABLE-3
HYDROGEN-BOND GEOMETRY (Å, °) OF THE COMPOUND 1

D-H...A	D-H	H...A	D...A	D-H...A
O5-H3...O2	1.02(3)	1.50(3)	2.5057(16)	168(3)
O5-H4...N2i	0.89(2)	1.86(2)	2.7436(18)	175(2)
O5-H5...O4ii	0.98(3)	1.54(3)	2.5021(18)	166(3)

Symmetry codes: (i) $x-1/2, y-1/2, z$; (ii) $-x-1/2, y-1/2, -z-1/2$

450 nm to 650 nm ($\lambda_{\text{max}} = 540$ nm) is assigned to a *d-d* transition of the titanium^{III} ion, which also have been found in many sapphires. This optical absorption transition is similar to the colored state of those photochromic TiO₂ materials^{9,10} and is consistent with the pale purple color of the compound (Fig. 9). We have also examined its photochromism by heating powder/crystal sample or irradiating them under UV light, but there is no obvious color change observed. It maybe due to the large charge difference between Zn^{II} and Ti^{IV}. Because this difference could elevate the barrier that resist Ti^{III} to convert into Ti^{IV} state. Moreover, the photoluminescence of powder sample has also been observed though its emission intensity is weak (Fig. 10). It should be derived from the emission of ligand itself while affected by the Ti^{III}.

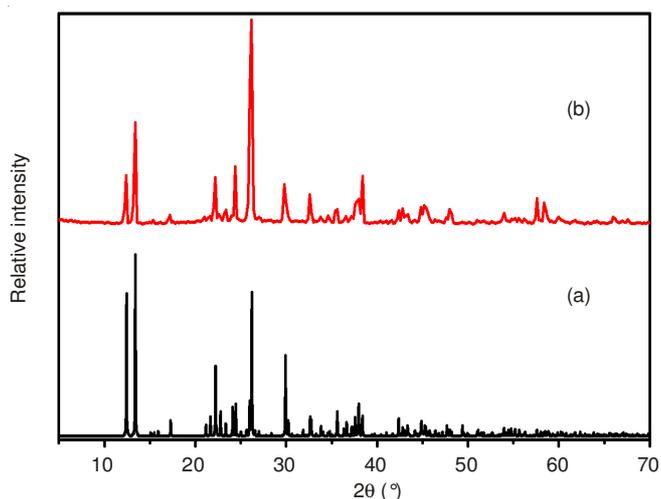


Fig. 7. Powder sample is qualified by PXRD test for compound (1): (a) for simulated data from single-crystal data, (b) for experimental data

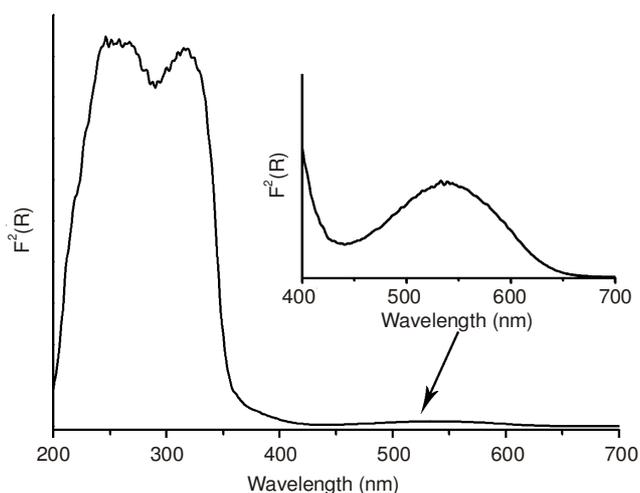


Fig. 8. A plot of $F(R)^2$ vs. wavelength for compound (1). The inset shows the spectrum feature of the *d-d* transition for clarity

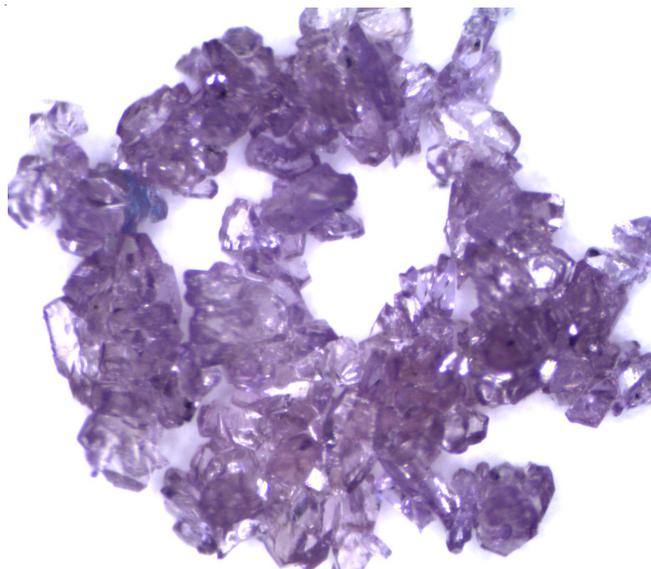


Fig. 9. Pale purple is obvious in the crystal profile of (1)

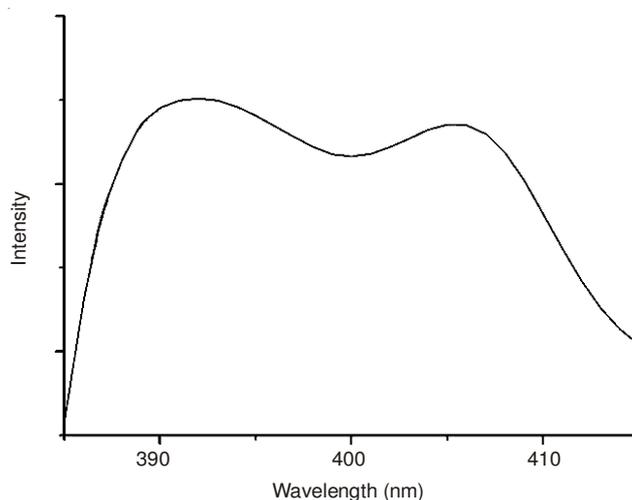


Fig. 10. Solid state photoluminescent spectrum measured at room temperature

For investigating the thermal stability of **1**, the simultaneous thermogravimetric (TG) and differential scanning calorimetry (DSC) measurements were carried out on the powder sample. As show in Fig. 11, the compound is stable until about 220 °C followed by two obvious weight-loss steps. The weight loss in the range 220-280 °C (30 %) corresponds to the release of the hydronium cation and one carboxyl group (calculated value 29.2 %). After about 290 °C, the sample undergoes a continuous decomposition up to about 1000 °C, during which the organic ligand was fully released. The final weight loss of about 80 % was consistent with a residual of ZnO mixed some TiO₂ (expected loss 80 %). In general, its thermal stability is good and the high decomposition temperature should be due to the strong hydrogen bonds.

Conclusion

In conclusion, we have synthesized the Ti^{III} doped Zn^{II} complex, Ti_{0.15}Zn_{0.85}(C₆H₂N₂O₄)₂[(H₃O)_{1.85}·(H₂O)_{0.15}]. Its optical absorption properties and the colored profile both confirm the presence of the Ti^{III} ion. This new polymeric phase of the Ti^{III}

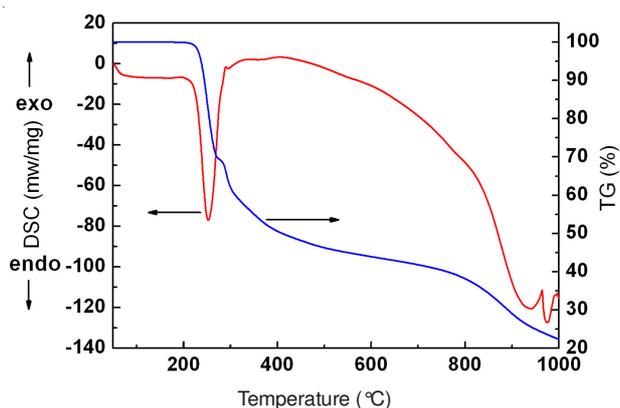


Fig. 11. Simultaneous TG and DSC curves of compound (1) recorded on a polycrystalline sample under the argon atmosphere

doped Zn^{II} complex exhibits a three-dimensional supramolecular network structure, which composes of the doubly ribbon polyanion and corresponding hydronium cations with three strong hydrogen bonding fusing them together. These hydrogen bonding interactions should also play a key role to the good thermal stability of the molecular structure.

ACKNOWLEDGEMENTS

The authors are grateful for financial support from the National Natural Science Foundation of China (Project 61205184, 11175169), the Foundation of State Key Laboratory of Structural Chemistry (project No. 20110011) and the Natural Science Foundation of Zhejiang Province (Project LY12E02010).

REFERENCES

1. F.J. Duarte and L.W. Hillman, *Dye Laser Principles*, Academic, New York (1990).
2. G. Simon, *Mauve: How One Man Invented a Color that Changed the World*, Faber and Faber (2000).
3. H. Zollinger, *Color Chemistry: Synthesis, Properties and Applications of Organic Dyes and Pigments*, Weinheim: Wiley-VCH, edn 3 (2003).
4. K. Hunger, *Industrial Dyes: Chemistry, Properties, Applications*. Weinheim: Wiley-VCH (2003).
5. M. Balter, *Science*, **325**, 1329 (2009).
6. N.S. Gill, F.B. Taylor, W.E. Hatfield, W.E. Parker, C.S. Fountain and F.L. Bunger, *Inorg. Synth.*, **9**, 136 (1967).
7. A.E. Smith, H. Mizoguchi, K. Delaney, N.A. Spaldin, A.W. Sleight and M.A. Subramanian, *J. Am. Chem. Soc.*, **131**, 17084 (2009).
8. H. Mizoguchi, A.W. Sleight and M.A. Subramanian, *Inorg. Chem.*, **50**, 10 (2011).
9. T. He and J.N. Yao, *Res. Chem. Intermed.*, **30**, 459 (2004).
10. T. He and J.N. Yao, *Prog. Mater. Sci.*, **51**, 810 (2006).
11. J. Lin, W.X. Chai, L. Song, L.S. Qin and K.Y. Shu, *Acta Crystallogr. C*, **65**, 0621 (2009).
12. Y.Y. Yang, W.X. Chai, L. Song and J. Lin, *Acta Crystallogr. C*, **67**, m293 (2011).
13. G.M. Sheldrick, *Acta Crystallogr. A*, **64**, 112 (2008).
14. M. Gryz, W. Starosta and J. Leciejewicz, *J. Coord. Chem.*, **58**, 931 (2005).
15. C.J. O'Connor, C.L. Klein, R.J. Majeste and L.M. Trefonas, *Inorg. Chem.*, **21**, 64 (1982).
16. P. Richard, D. Tranqui and E.F. Bertaut, *Acta Crystallogr. B*, **29**, 1111 (1973).
17. X. Wang, X.Y. Li, Q.W. Wang and G.B. Che, *Acta Crystallogr. E*, **64**, m1078 (2008).
18. J.M. Fang, M.X. Li, X. He, M. Shao, W. Pang and S.R. Zhu, *J. Mol. Struct.*, **921**, 137 (2009).
19. H. Eshtiagh-Hosseini, H. Aghabozorg and M. Mirzaei, *Acta Crystallogr. E*, **66**, m882 (2010).
20. W.X. Chai, J. Lin, L. Song, L.S. Qin, H.S. Shi, J.Y. Guo and K.Y. Shu, *Solid State Sci.*, **14**, 1226 (2012).
21. W.X. Chai, L. Song, J. Lin, K.Y. Shu, L.S. Qin, H.S. Shi and J.Y. Guo, *J. Inorg. Organomet. Polym.*, **22**, 1263 (2012).
22. P. van der Sluis and A.L. Spek, *Acta Crystallogr. A*, **46**, 194 (1990).
23. W.X. Chai, L. Song, H.Y. Shen and K.Y. Shu, *Phosphorus Sulfur Silicon Rel. Elem.*, **184**, 3212 (2009).
24. W.X. Chai, L. Song, K.Y. Shu, H.S. Shi and L.S. Qin, *J. Chem. Crystallogr.*, **40**, 448 (2010).
25. J.J. He, W.X. Chai, L. Song, F. Niu and X.B. Fang, *Acta Crystallogr. C*, **68**, m206 (2012).