Research Paper

Journal of Chemical Research

Journal of Chemical Research
2019, Vol. 43(1-2) 58–62

DOI: 10.1177/1747519819831886
journals.sagepub.com/home/chl
SAGE

Preparation, photoluminescence, semiconductor properties, and theoretical calculations for a novel zinc zero-dimensional structure complex

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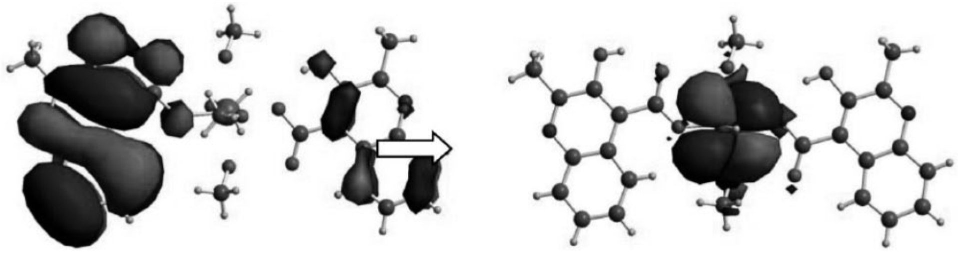
Abstract

The complex [$Zn(CH_3OH)_4(MCA)_2$] (3-hydroxy-2-methylquinoline-4-carboxylic acid) has been synthesized through hydrothermal reactions and characterized by single-crystal X-ray diffraction. Its solid-state photoluminescence spectrum shows an emission in the blue region, which is assigned to ligand-to-metal charge transfer on the basis of time-dependent density functional theory calculations. Solid-state diffuse reflectance measurements show the existence of a narrow optical band gap of 1.73 eV.

Keywords

ligand-to-metal charge transfer, photoluminescence, semiconductor, time-dependent density functional theory, zinc



A novel zinc(II) complex shows blue violet photoluminescence emission, which can be attributed to ligand-to-ligand charge transfer (LMCT), as revealed by TDDFT calculations. Solid-state diffuse reflectance measurement shows the existence of a narrow optical band gap of 1.73 eV.

Introduction

In recent years, more and more coordination compounds possessing group-12 elements (Zn, Cd, and Hg) have been synthesized, because such compounds may possess attractive physicochemical properties and useful applications in many fields such as photoluminescent materials, photoelectric materials, nonlinear optics materials, and semiconductors, as well as their relevance to the important role played in biological systems by zinc.[1–4]

Quinoline carboxylic acids, as O-donor ligands, are very interesting units in the construction of inorganic–organic hybrid compounds with extended structures because of their carboxyl oxygen atoms and hydroxyl oxygen atoms, which bridge metal ions.[5–8] Up to now, there are few reports on the complexes of quinoline carboxylic acids.

Based on this, we are interested in the crystal engineering of group-12 element-containing compounds with 3-hydroxy-2-methylquinoline-4-carboxylic acid (HMCA) as a ligand. We report the solvothermal synthesis, X-ray crystal structure, photoluminescent, and semiconductor properties, as well as time-dependent density functional theory (TDDFT) calculations for a novel zinc complex [$Zn(CH_3OH)_4(MCA)_2$] (**1**) (HMCA), which has a zero-dimensional (0D) isolated structure.

Experimental

General procedure

The reagents and chemicals for the synthesis of the title compound were analytical reagent grade, commercially available and applied without further purification. Infrared spectra were obtained with a PE Spectrum-One Fourier-transform infrared (FT-IR) spectrometer using KBr disks.

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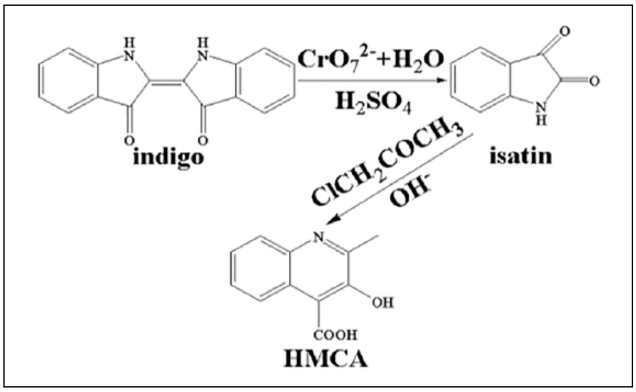

Scheme 1. Reaction route.

Elemental microanalyses of carbon, hydrogen, and nitrogen were performed on an Elementar Vario EL elemental analyzer. ^1H NMR spectra were measured on Bruker Avance 400 MHz instrument with dimethyl sulfoxide (DMSO) as solvent. Photoluminescence measurements were performed on a F97XP photoluminescence spectrometer. Solid-state ultraviolet (UV)-vis reflectance spectroscopy was carried out with a TU1901 UV-Vis spectrometer equipped with an integrating sphere. A $BaSO_4$ plate acted as a 100% reflectance reference, on which the finely ground powder was coated. TDDFT investigations were carried out by means of the Gaussian 03 suite of program packages.

Preparation of HMCA

HMCA was prepared according to the following reaction route (Scheme 1).

Synthesis of isatin. Indigo (262 g) and $K_2Cr_2O_7$ (147 g) were added into H_2O (500 mL) and stirred. After cooling, $K_2Cr_2O_7$ (147 g), H_2O (300 mL) and dil. H_2SO_4 (500 mL) were added and kept stirring at 40°C and 45°C for 1.5 h. Then, the mixture was diluted with twice its volume of H_2O, filtered off, dissolved with a KOH solution, filtered again, acidified by HCl and refiltered. Yield, 230 g (⩾90%); m.p. 210°C; high-resolution mass spectrometry (HRMS) m/z electrospray ionization (ESI) calcd for $C_8H_5NO_2$ ([M+H]+)147.0320, found 147.0826.

Synthesis of HMCA. Isatin (1.0 mol) and KOH (1.0 mol) were dissolved into a sufficient amount of water and filtered. The filtrate and 1.0 mol KOH were added into chloroacetone (2.0 mol), and hydrochloric acid was added dropwise to adjust to pH=7, and the solution was then filtered. Yield ⩾95% and m.p. 225°C. IR peaks (KBr, cm^{-1}): 3433(vs), 3125(w), 3043(w), 2869(w), 2499 (m), 2040(m), 1621(m), 1553 (s), 1500 (m), 1462(m), 1410(m), 1242(vs), 1160(m), 1014(w), 906(m), and 686(s); HRMS m/z (ESI) calcd for $C_{11}H_9NO_3$ ([M+H]+) 203.0582, found 203.0548; ^1H NMR (400 MHz, DMSO) δ 9.15 (s, 1H), 7.93 (d, J=8.2 Hz 1H), 7.64 (t, J=7.7 Hz, 1H), 7.60–7.52 (m, 3H), 2.70 (s, 3H).

The melting points of isatin and HMCA are in reasonable agreement with those reported in the literature.[9]

Preparation of complex 1

HMCA (1 mmol, 203 mg), $(CH_3COO)_2Zn{\cdot}6H_2O$ (0.5 mmol, 109 mg), methanol (9.5 mL) and distilled water (0.5 mL) were mixed in a 25-mL Teflon-lined stainless steel autoclave. The autoclave was heated to 200°C in an oven and kept there for 3 days and then allowed to cool. When the autoclave reached room temperature, yellow block crystals were obtained and used to collect the single-crystal X-ray data. Yield 60% based on $(CH_3COO)_2Zn{\cdot}6H_2O$. IR peaks (KBr, cm^{-1}): 3434(s), 3338(vs), 3122(w), 2962(w), 2740(w), 2500 (s), 2018(w), 1656(m), 1608(s), 1580 (s), 1524(s), 1434(m), 1408(m), 1242(vs), 1158(m), 1019(s), 912(s), 870(s), 812(w), and 764(s); Anal. Calcd for $C_{26}H_{32}N_2O_{10}Zn$: C, 52.23; H, 5.39; N, 4.69; found: C, 52.32; H, 5.31; N, 4.68%.

Table 1. Structure determination summary for complex 1.

Empirical formula	$C_{26}H_{32}N_2O_{10}Zn$
Color and habit	Yellow block
Crystal size (mm)	0.17 × 0.08 × 0.05
Crystal system	Triclinic
Space group	P_1
a (A)	7.8511(3)
b (A)	8.9457(3)
c (A)	10.5008(3)
α (°)	74.749(3)
β (°)	86.959(3)
γ (°)	70.118(4)
V (Å^3)	668.59(4)
Z	1
Formula weight	597.91
$d_{calcd.}$ (g cm^{-3})	1.485
Absorption coefficient(mm^{-1})	0.979
F(000)	312
Reflections measured	7434
Index ranges of measured data	$-9<=h<=9$, $-10<=k<=10$, $-12<=l<=12$
Independent reflections	4174 (Rint=0.0198)
Observed reflection	3972 (>2sigma(I))
Relative transmission factor	0.910–0.952
Parameter/restraints/data (obs.)	353/3/3972
Final R indices (obs.)	$R_1=0.0354$, $wR_2=0.0909$
S	1.115
Largest and mean Δ/σ	0, 0
$\Delta\rho$ (max, min) (e Å^{-3})	0.448, −0.542

X-ray structural determination

The X-ray diffraction data were collected on a SuperNova charge-coupled device (CCD) X-ray diffractometer with a carefully selected single crystal (dimensions of 0.17 × 0.08 × 0.05 mm). The X-ray source was graphite monochromated Mo-$K\alpha$ radiation with $\lambda=0.71073$ Å. The reduction and empirical absorption correction of the diffraction data were carried out with the CrystalClear software. The crystal structure is solved by direct methods and the Siemens SHELXTL™ V5 software[10] and refined with a full-matrix least-squares refinement on F^2. All non-hydrogen atoms were located on the difference Fourier maps with applied anisotropic refinement. The hydrogen atoms were theoretically attached to their parent atoms and included in the structural factor calculations with assigned isotropic thermal parameters.[11] Reflections measured were 7434; the final $R=0.0354$ for 353 parameters and 3972 observed reflections with $I>2\sigma(I)$ and $wR=0.0909$ ($w=1/(\sigma^2(Fo^2)+(0.0536P)^2+0.0977P)$, where

Table 2. Selected bond lengths (Å) and bond angles (°) for complex **1**.

Distance	(Å)	Distance	(Å)
Zn(1)-O(3)	2.061(4)	Zn(1)-O(8)	2.097(4)
Zn(1)-O(10)	2.097(4)	Zn(1)-O(7)	2.136(4)
Zn(1)-O(5)	2.098(4)	Zn(1)-O(9)	2.157(4)
Angle	**(°)**	**Angle**	**(°)**
O(3)-Zn(1)-O(10)	92.47(16)	O(5)-Zn(1)-O(7)	89.39(16)
O(3)-Zn(1)-O(5)	179.5(2)	O(8)-Zn(1)-O(7)	89.23(16)
O(10)-Zn(1)-O(5)	87.33(16)	O(3)-Zn(1)-O(9)	90.84(16)
O(3)-Zn(1)-O(8)	87.25(16)	O(10)-Zn(1)-O(9)	88.73(17)
O(10)-Zn(1)-O(8)	178.2(2)	O(5)-Zn(1)-O(9)	89.64(15)
O(8)-Zn(1)-O(5)	92.97(16)	O(8)-Zn(1)-O(9)	89.47(17)
O(3)-Zn(1)-O(7)	90.14(15)	O(7)-Zn(1)-O(9)	178.3(2)
O(10)-Zn(1)-O(7)	92.57(16)		

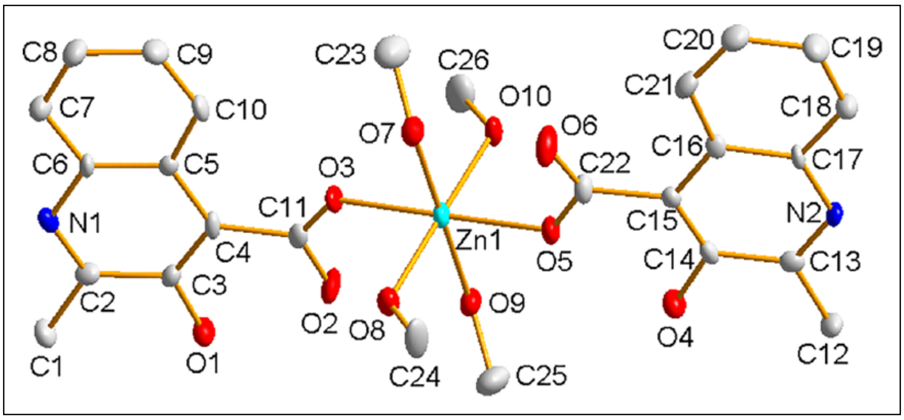

Figure 1. An ORTEP drawing of compound **1** with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

$P=(Fo^2+2Fc^2)/3)$; $S=1.115$, $(\Delta\rho)_{max}=0.448$, $(\Delta\rho)_{min}=-0.542\,e\,Å^{-3}$ and $(\Delta/\sigma)_{max}=0$. The selected bond distances and angles are shown in Table 1. Selected bond lengths and bond angles are presented in Table 2.

Results and discussion

X-ray single-crystal diffraction analysis reveals that complex **1** is composed of an electronically neutral isolated (0D) $[Zn(CH_3OH)_4(MCA)_2]$ structure, as shown in Figure 1. Complex **1** crystallizes in the $P1$ space group of the triclinic system with one formula unit in one cell. The zinc ion is surrounded by six oxygen atoms from two ligands and four methanol molecules, yielding an octahedral geometry. The bond lengths of Zn–O of 2.061(4) and 2.157(4) Å are normal and comparable with those reported in the literature.[12] The results of a bond valence calculation reveal that all zinc ions are in a +2 oxidation state. The top and bottom planes of the zinc ions are defined by O(3), O(7M), O(10M) and O(5), O(8M), and O(9M) atoms, respectively. The bond distances of $Zn–O_{Methanol}$ are 2.136(4) Å, 2.097(4) Å, 2.157(4) Å, and 2.097(4) Å, while those of $Zn–O_{HMCA}$ are 2.061(4) Å and 2.098(4) Å. The bond distances of Zn–O are in the normal range and comparable with those reported in the previous studies.[13–16] The bond angle of O–Zn–O resides in a wide range of 86.25(16)°–178.3(2)°. No π–π stacking interactions can be found between the HMCA ligands in complex **1**, whereas some hydrogen bonds exist between the hydrogen and oxygen in the HMCA molecule. Supramolecular layers via Van der Waals attraction complete a crystal packing structure, as presented in Figure 2.

Photoluminescence measurements

To our knowledge, zinc and HMCA complexes can generally exhibit photoluminescence emission bands. Based on this consideration, and in order to reveal its potential photoluminescent properties, we carried out photoluminescence measurements on complex **1** in the solid state at room temperature and the experimental results are presented in Figure 3. It is obvious that the photoluminesent spectrum of complex **1** displays an effective energy absorption residing in the wavelength range of 310–350 nm. Upon the emission of 491 nm, the excitation spectrum shows a band at 322 nm. We further measured the corresponding photoluminescence emission spectrum of complex **1**. Upon excitation at 322 nm, the emission spectrum is characterized by a sharp band at 491 nm in the blue region of the spectrum. As a result, the title complex is a potential blue photoluminescent material.[17]

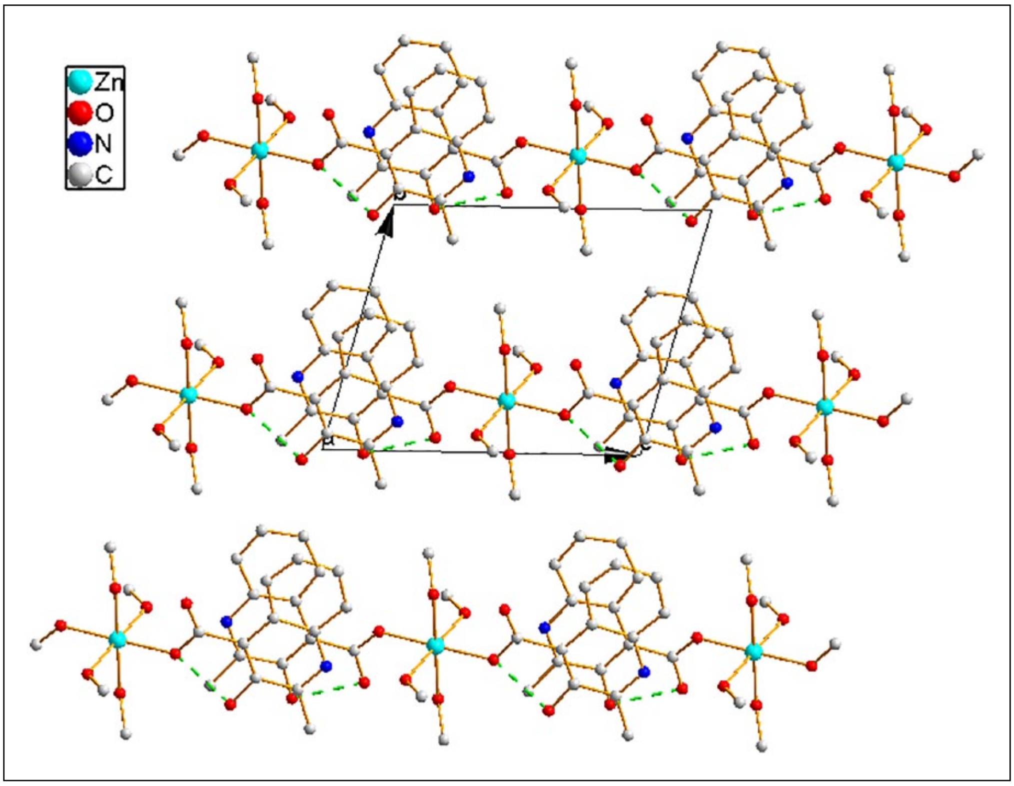

Figure 2. Packing diagram of compound **1** with the dashed lines representing the hydrogen bonding interactions (Å, °): O(1)-H(1D)···O(2) 2.515(6), 146; O(4)-H(4A)···O(5) 2.524(6), 146; C(10)-H(10A)···O(3) 2.816(7), 125; C(21)-H(21A)···O(6) 2.836(8), 124.

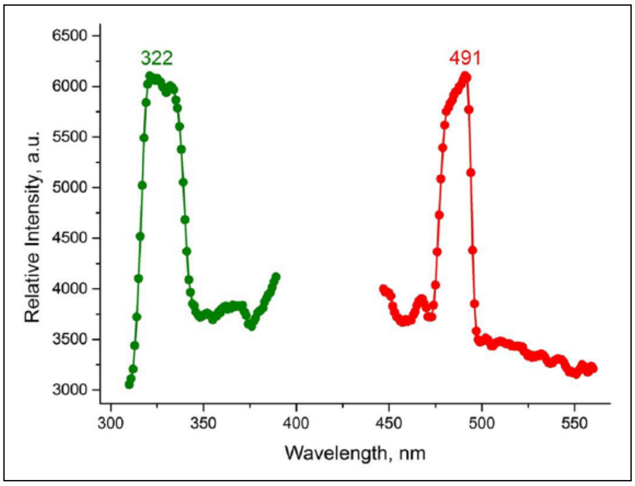

Figure 3. Solid-state photoluminescence spectra of **1** measured at room temperature (green curve = excitation; red curve = emission).

Note. Coloured version of this figure is available online.

Theoretical calculations

In order to reveal the nature of the photoluminescence emission of complex **1**, TDDFT calculations were performed using the B3LYP function (Figure 4). The single-crystal X-ray diffraction data set of complex **1** was used to truncate the ground-state geometry for the calculation. Based on the geometry, a TDDFT study was carried out by means of the Gaussian 03 suite of programs, and the results reveal the characteristics of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of complex **1**. Clearly, it can be seen that the electron density distribution of the singlet state of HOMO is located totally on the ligand moieties. However, the electron density population of the singlet state of the LUMO resides completely on the zinc moiety. In light of this observation, the essence of the photoluminescence emission of complex **1** can be attributed to ligand-to-metal charge transfer (LMCT) from the HOMO of the HMCA to the LUMO + 1 of the Zn.

Reflectance measurements

Solid-state UV-Vis diffuse reflectance spectra of complex **1** were measured on a powder sample at room temperature. The data set of the solid-state diffuse reflectance spectrum was treated with the Kubelka–Munk function $\alpha/S=(1-R)^2/2R$, where the parameter refers to the absorption coefficient, S is the scattering coefficient that is practically wavelength-independent when the particle diameter is larger than 5 μm, and R is the reflectance. Extrapolating from the linear portion of the absorption edges from the α/S versus energy curve, we obtain the value of the optical band gap. The solid-state UV-Vis diffuse reflectance spectrum reveals that complex **1** possesses a narrow optical band gap of 1.73 eV, as shown in Figure 5. As a result, complex **1** is probably a candidate for narrow band gap semiconductors. The gradual slope of the optical absorption edge of complex **1** indicates that it might be an indirect transition. The optical band gap of 1.73 eV of complex **1** is slightly larger than those of GaAs (1.4 eV), CdTe

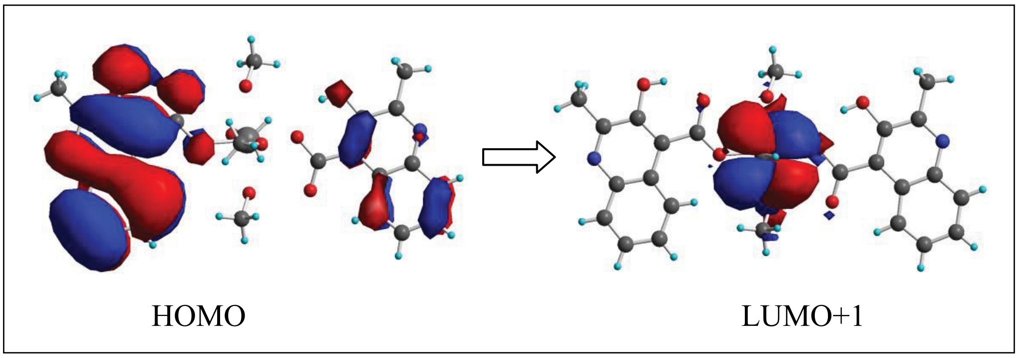

Figure 4. The electron density population of **1**. The isosurfaces correspond to the electronic density differences of −15 e nm^{-3} (blue) and +15 e nm^{-3} (red).
Note. Coloured version of this figure is available online.

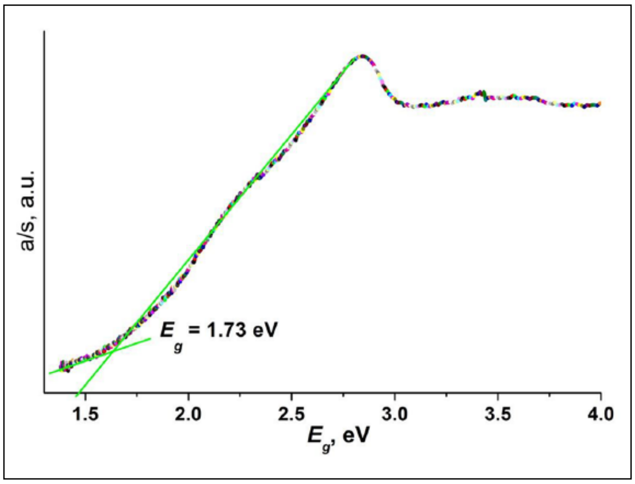

Figure 5. Solid-state diffuse reflectance spectrum of **1**.

(1.5 eV), and CuInS 2 (1.55 eV),[18] all of which are well known as highly efficient narrow band gap photovoltaic materials.

Conclusion

In summary, a novel zinc complex [Zn(CH_3OH)$_4$(MCA)$_2$] (**1**) (HMCA) has been prepared via solvothermal reactions and characterized by single-crystal X-ray diffraction. The solid-state photoluminescence spectrum reveals that it shows an emission in the blue region of the light spectrum. TDDFT calculations reveal that this emission can be attributed to LMCT. Solid-state diffuse reflectance measurements show the existence of a narrow optical band gap of 1.73 eV, suggesting that complex **1** is probably a candidate for narrow band gap semiconductors.

Declaration of conflicting interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

Funding

The author(s) disclosed receipt of the following financial support for the research, authorship and/or publication of this article: This study received financial support from the National Natural Science Foundation of China (51363009, 21764007), Jiangxi Provincial Department of Education's Item of Science and Technology (GJJ160745), the research topics of teaching reform in higher education institutions in Jiangxi (JXJG-17-9-14), the Science and Technology Plan project Fund of Jiangxi Provincial Health Planning Commission(20194083), and Natural Science Foundation Project of Jinggangshan University(JZ09029).

Supplemental material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 1874445. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CBZ 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or online at http://www.ccdc.cam.ac.uk).

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