Supplementary Material (ESI) for *CrystEngComm*


**Supporting Information**

# A novel (4, 8)-connected 3D polyoxometalate-based metal-organic framework containing an in situ ligand

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**Materials.** High purity graphite powder (average particle 1-2 um) was obtained from Aldrich. Nujol was purchased from Beijing Chemical Plant and used as received. Other chemicals were of analytical grade and used without further purification.

**General Characterization and Physical Measurements.** Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. P, W, and Cu were determined by a Leaman inductively coupled plasma (ICP) spectrometer. The FT-IR spectra was recorded from KBr pellets in the range 4000–400 $cm^{-1}$ on a Mattson Alpha-Centauri spectrometer. TGA was performed on a Perkin–Elmer TG-7 analyzer heated from room temperature to 1000$^{o}$C under nitrogen. EPR spectrum was obtained on a Japanese JES-FE3AX spectrometer at 293 K. Cyclic voltammograms (CV) were recorded on a 384B polarographic analyzer. A typical three-electrode cell having a CPE working electrode, a platinum counter electrode, and a silver/silver chloride reference electrode was used for the voltammetry experiments.

**Fabrication of the 1-modified carbon paste electrode and the bare carbon paste electrode.** The **1**-modified carbon paste electrode was fabricated as follows: 1.0g graphite powder was added to the solution of 2mL acetone containing 30mg **1** and the mixture was ultrasonically mixed for 3min, followed by evaporation of acetone, which produced rather homogenously covered graphite particles. To the graphite particles 0.67mL Nujol was added and stirred with a glass stick. The homogeneous mixture was used to pack a 3mm inner diameter glass tube to a length of 0.8 cm from one of its ends. In addition, a little extra mixture was retained on the top of the electrode, and the mixture in the tubes was pressed lightly on smooth plastic paper with a copper stick through the back. The electrical contact was established with the copper stick. The surface of the carbon paste electrode was wiped with weighting paper.

**Synthesis of 2**: The procedure for the formation of compound **1** was employed, but $H_3PW_{12}O_{40}$ was replaced by $H_3PMo_{12}O_{40}$. Red crystals of **2** were collected in 56.6% yield based on $Cu(NO_3)_2{\cdot}3H_2O$. Elemental analyses Calcd for $C_{64}H_{84}Cu_4F_8Mo_{24}N_{26}O_{88}P_2$ ($M$ = 5396.23): C, 14.25; H, 1.57; N, 6.75. Found: C, 14.22; H, 1.659; N, 6.77%. IR ($cm^{-1}$): 3450, 3124, 1619, 1526, 1502, 1422, 1382, 1276, 1211, 1120, 1062, 967, 882, 660.

**Crystallographic data for 2:** ($C_{64}H_{84}Cu_4F_8Mo_{24}N_{26}O_{88}P_2$), $M$ = 5396.23, triclinic, space group $P\bar{1}$, $a$ = 14.501(3) Å, $b$ = 15.205(4) Å, $c$ = 16.228(4) Å, $\alpha$ = 80.506(3)º, $\beta$ = 89.984(3)º, $\gamma$ = 75.230(3)º, $V$ = 3409.2(14) $Å^3$, $Z$ = 1, F(000) = 2580, $D_{calcd}$ = 2.628 $gcm^{-3}$, $R1(wR2)$ = 0.0643 (0.1694) ($I>2\sigma(I)$) and GOF = 1.029. A total of 12120 data were measured in the range $1.27< \theta <25.40$º. The data were collected at 273(2) K on a Bruker Apex CCD diffractometer with graphite-monochromated MoKα radiation ($\lambda$ = 0.71073 Å) at 293K. CCDC 679711.

**The choice of space group for 1:**

Because three space groups of Immm, I222 and Imm2 show the same systematic absences, we have tried to solve the structure with space groups I222 and Imm2. The results indicate the crystallographical disorder still occurs. In other word, we obtain

the same result with three space groups (Immm, I222 and Imm2), which show the same disordered structure. In addition, when $(E^2-1) \approx 0.97$, it suggests the space group is centrosymmetry; when $(E^2-1) \approx 0.74$, it suggests the space group is non-centrosymmetry. The value of $(E^2-1)$ in the compound **1** is 0.977. So we consider that the space group for **1** is centrosymmetry, and Immm is the best choice.

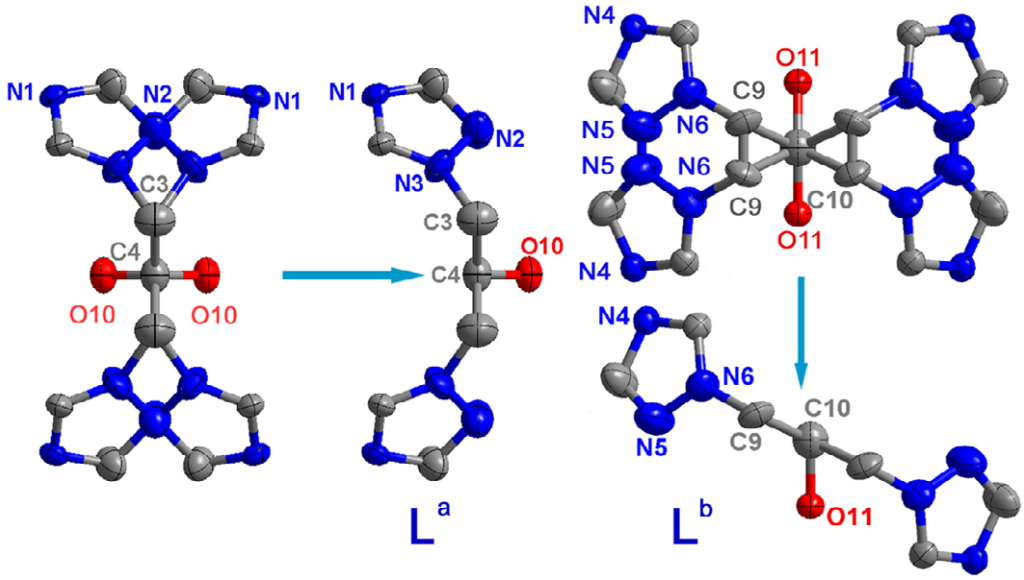
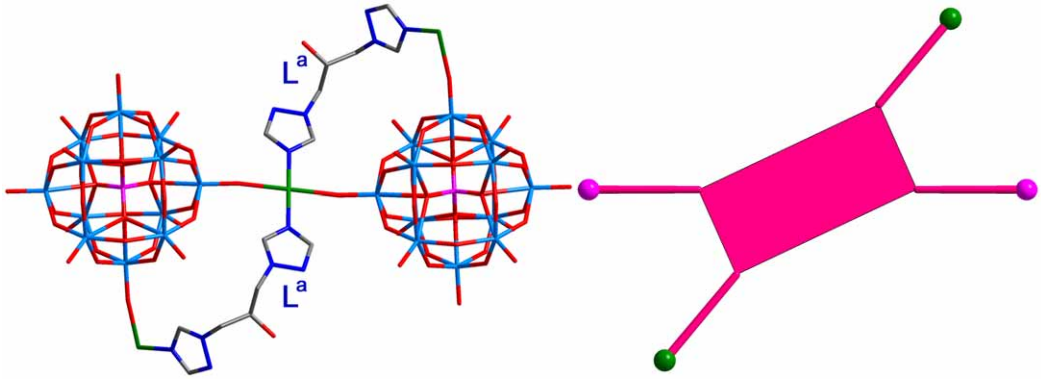
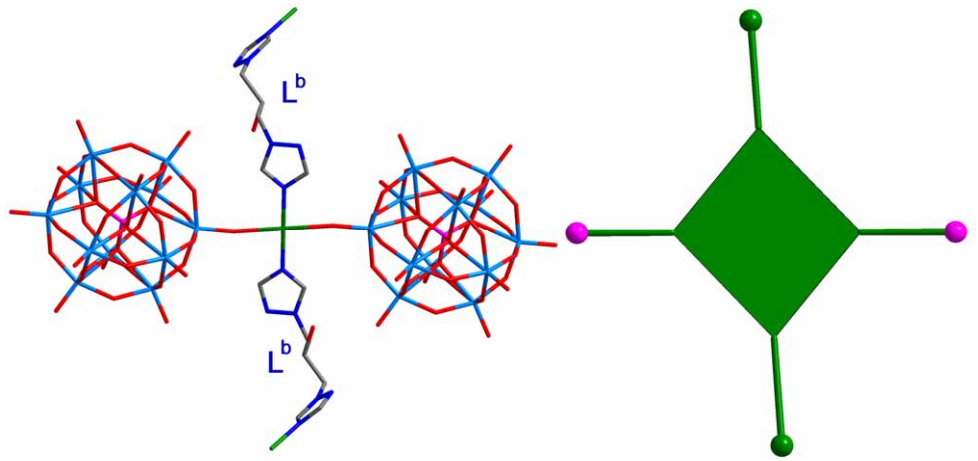



**Fig. S1** ORTEP view of two kinds of distorted L ligands ($L^a$ and $L^b$). The C1, C2, C3, C4, N1, N2, N3 and O10 atoms of $L^a$, and C7, C8, C9, C10, N4, N5, N6 and O11 atoms of $L^b$ are dually disordered, and the crystallographic mirror planes pass through the N2, C3 and C4 for $L^a$, and the centers of the centrosymmetrically related N5 and C9, and C10 atom of $L^b$, respectively.

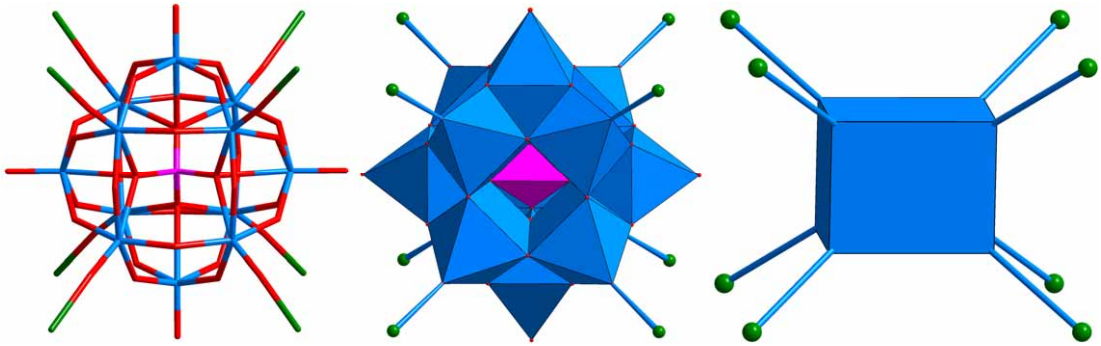



(a)



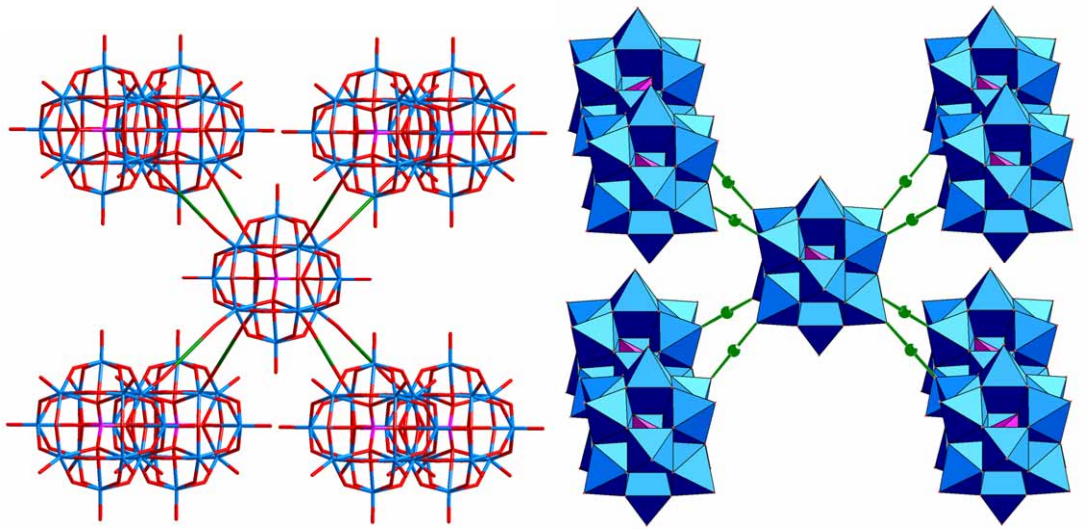

(b)

**Fig. S2** Two kinds of copper coordination modes by $L^a$ and polyanions (a), and $L^b$ and polyanions (b), respectively.



(a) (b) (c)

**Fig. S3** (a) –(c) View of the coordination mode of the Keggin polyanion.



(a) (b)

**Fig. S4** (a) and (b) Eight Keggin polyanions being linked to one Keggin polyanion via eight copper cations.

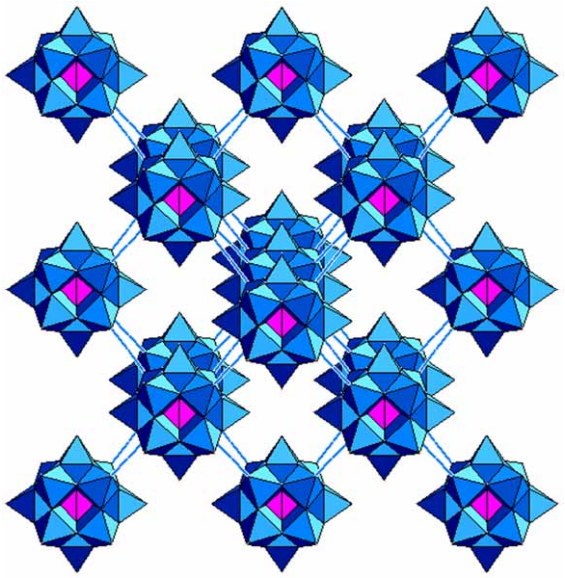


**Fig. S5** Polyhedral representations of the bcu network formed by copper cations and Keggin polyanions.

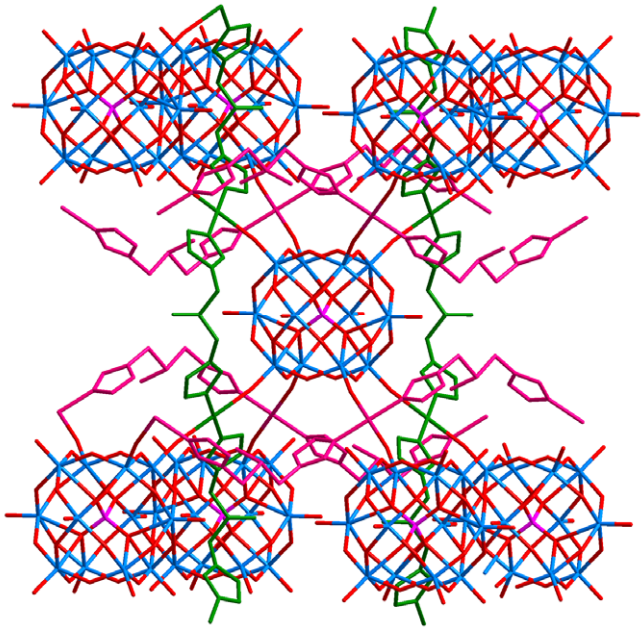
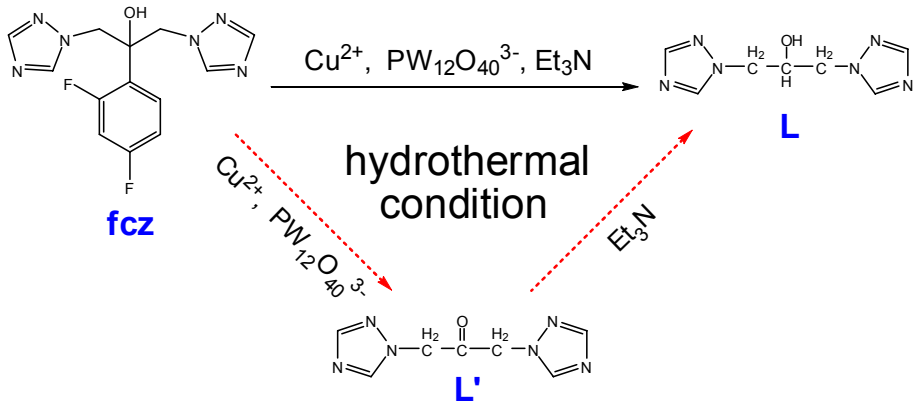


**Fig. S6** View of the 3D framework of compound **1**.




**Scheme S1**. Schematic view of transformation relation from the fcz to the in situ generated ligand L.

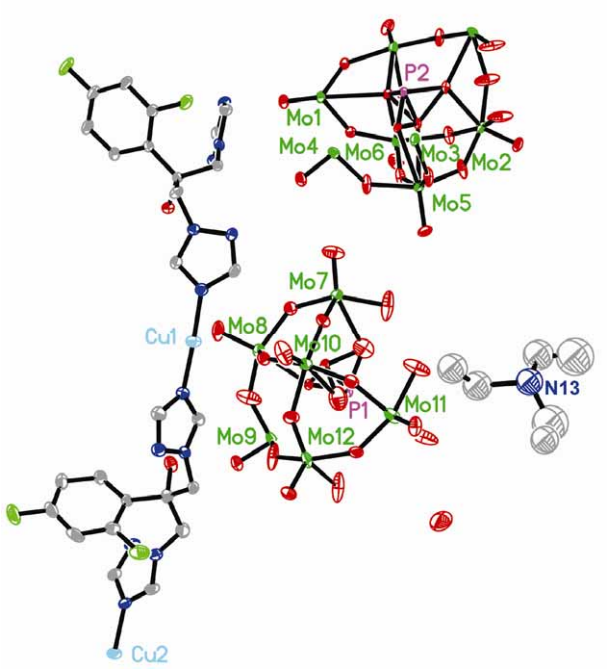
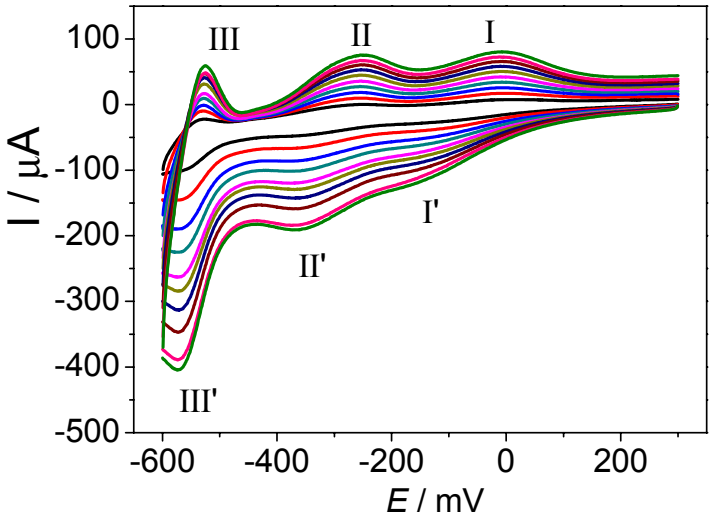


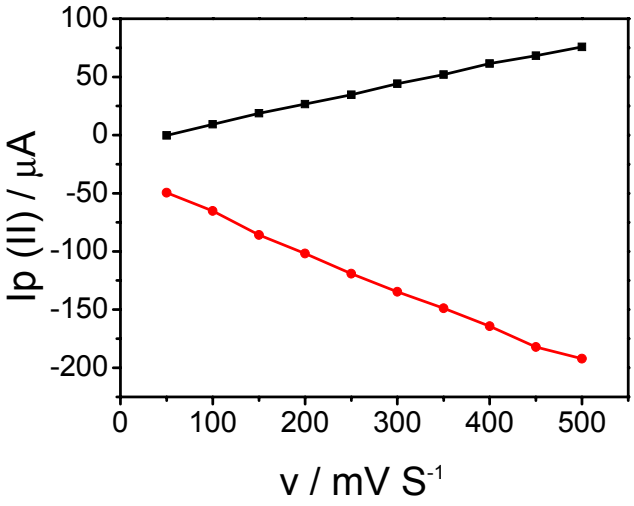

**Fig. S7** ORTEP diagram of the asymmetric unit of **2** with thermal ellipsoids at 20% probability displacement, the hydrogen atoms are omitted for clarity.

When $H_3PMo_{12}O_{40}$ instead of $H_3PW_{12}O_{40}$ was used under the same hydrothermal conditions, compound **2** has been obtained. X-ray diffraction analysis reveals that compound **2** contains two kinds of $Cu^{I}$ ions, two kinds of fcz ligands, two kinds of $[PMo_{12}O_{40}]^{3-}$ polyanions and one kind of protonated $Et_3N$ molecule. In addition, when $H_4SiMo_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ instead of $H_3PW_{12}O_{40}$ are used under the same hydrothermal conditions, six novel compounds have been obtained and reported in the

Dalton Trans by us. In these compounds, fcz ligands have been observed, which indicates C-C bond cleavage dose not exist.




(a)




(b)

**Fig. S8** (a) Cyclic voltammograms of the **1**-CPE in 1 M $H_2SO_4$ solution at different scan rates (from inner to outer: 50, 100, 150, 200, 250, 300, 350, 400, 450 and 500 $mV \cdot s^{-1}$). (b) View of the plots of the anodic and the cathodic peak II-II' currents against scan rates.

The electrochemical behavior of **1**-modified carbon paste electrode (**1**-CPE) was also studied. Figure S8 shows the cyclic voltammetric behavior for **1**-CPE in 1 M $H_2SO_4$ aqueous solution at different scan rates. It can be seen that in the potential range +300 mV to -600 mV, three reversible redox peaks appear and the peak potentials $E_{1/2} = (E_{pa}+E_{pc})/2$ are -548, -303 and -71 mV (100 $mV \cdot s^{-1}$), respectively. Redox peaks I/I', II/II' and III/III' correspond to three consecutive two-electron process, respectively. The approximate proportionality of the reduction peak current to the scan rate up to 500 $mVs^{-1}$ indicates that the redox process is surfacecontrolled.[5]

In addition, the peak-to-peak separations between the corresponding anodic and cathodic peak increase with increasing scan rate, which may be according to the following reasons: (a) the reduction of compound **1** immobilized in the CPE is accompanied by the evolution of protons from solution to maintain charge neutrality. The encapsulation of **1** particles into a CPE may slow down the penetration rate of protons from solution into the particles and thus decrease the electron exchange rate to some extent. With increasing scan rate, the diffusion rate of the protons into the particles begins to determine the electrochemical reduction rate. (b) The electron exchange rate between the insoluble solid **1** particles and the electrode may be slower than the rate between the soluble POM anions and the electrode.[6]

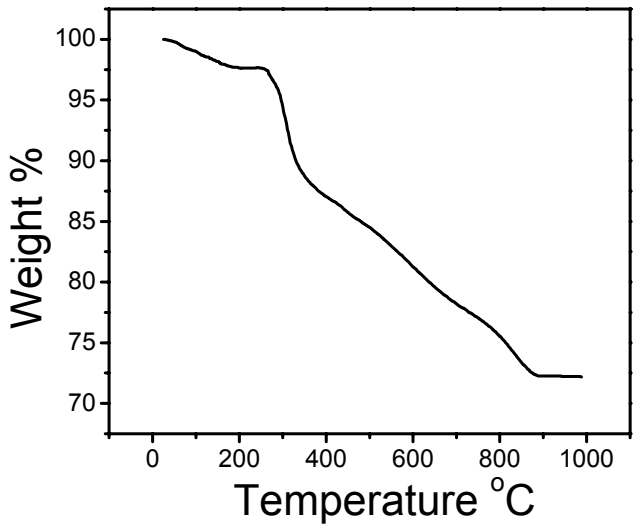



**Fig. S9** TGA curve of **1**.

In order to characterize the compound more fully in terms of thermal stability, its thermal behavior was studied by TGA. The weight loss corresponding to the release of one water molecule is observed from room temperature to 185 °C (obsd 2.42 %, calcd 2.69 %). The anhydrous composition begins to decompose at 256 and ends above 885 °C.

**The bond valence sum calculations for compound 1:**

The value of BVS[1] for Cu centers coordinated by $L^a$ is +0.934, and that by $L^b$ is +0.948, which suggests that the Cu atoms exhibit oxidation state of +1. In the polyanion, one $W^{VI}$ atom is reduced to $W^V$ and shows one-electron-reduced, so the polyanion is $[PW^VW^{VI}_{11}O_{40}]^{4-}$. Such an explanation requires a detailed analysis of charge conservation,[2-4] which agrees with the result of EPR (Fig. S10).

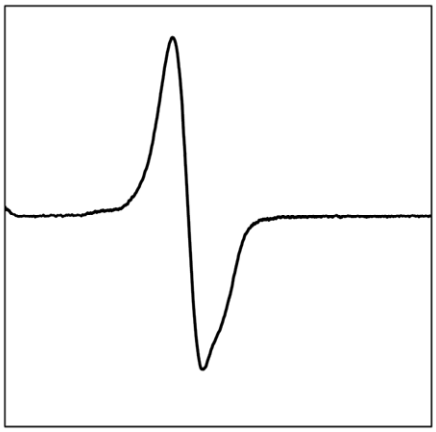


**Fig. S10** EPR spectrum of **1**.

References

1 The valence sum calculations are performed on a program of bond valence calculator, version 2.00 February 1993, written by C. Hormillosa with assistance from S. Healy, distributed by I. D. Brown.

2 Y. Xu, J. Q. Xu, K. L. Zhang, Y. Zhang and X. Z. You, *Chem. Commun.,* 2000, 153.

3 E. Burkholder, V. Golub, C. J. O'Connor and J. Zubieta, *Inorg. Chem. Commun.*, 2004, **7**, 363.

4 H. Jin, X. L. Wang, Y. F. Qi and E. B. Wang, *Inorg. Chim. Acta*, 2007, **360**, 3347.

5 L. Cheng, X. M. Zhang, X. D. Xi and S. J . Dong, *J. Electroanal. Chem*., 1996, **407**, 97.

6 Z. G. Han, Y. L. Zhao, J. Peng, Q. Liu and E. B. Wang, *Electrochim*. *Acta*, 2005, **51**, 218.