Supplementary Materials

A Highly Stable Porous Multifunctional Co(II) Metal-Organic Framework

Showing Excellent Gas Storage Applications and Interesting Magnetic Properties

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Experimental Section

Materials and Synthesis. All chemicals were purchased commercially and used without further purification. **H_6L** was synthesized by a modified procedure previously documented.[1]

Elemental analyses of C, H and N in the solid samples were performed with a VarioEL analyzer. Energy Disperse Thermogravimetric and differential thermal analysis (TG-DTA) data were recorded on a Thermal Analysis Instrument (SDT 2960, TA Instruments, New Castle, DE) from room temperature to 700 °C with a heating rate of 10 °C/ min under air atmosphere. Powder X-ray power diffraction (XRD) patterns were performed on a D8 Focus (Bruker) diffractometer and D8 advance X-ray powder diffractometer with Cu Kα radiation Field-emission (λ = 0.15405 nm, continuous, 40 kV, 40 mA, increment = 0.02°). FT-IR spectra were recorded in the range of 4000-650 cm^{-1} on a Nicolet 7600 FT-IR spectrophotometer (diamond). Magnetic susceptibility measurements were carried out on a Quantum Design MPMSXL SQUID magnetometer and PPMS-9T system. The raw data were corrected for the susceptibility of the container and the diamagnetic contributions of the sample using Pascal constants. The gas adsorption isotherms for N_2 at 77 K, H_2 at 77 K, CO_2 at 273 K and 298 K were performed on ASAP 2050 V1.01 E and Autosorb MP-1 apparatuses at 1 atm.

Prior to the measurement of gas adsorption, some preparatory work has been done. The

as-synthesized sample of **Co₃(L)(dib)•2H₂O•6DMF (1)** was immersed into anhydrous methanol for 3 days, methanol was refreshed three times during the exchange. Then similar immersion was utilized to treat the sample with dichloromethane to remove methanol molecules. After the removal of dichloromethane by centrifuging, the wet sample was dried under vacuum at 130 °C for 8 h to yield an activated **1** (denoted as **1a**).

Synthesis of Co₃(L)(dib)•2H₂O•6DMF (1): $Co(NO_3)_2 \cdot 6H_2O$ (0.12 mmol, 35.0 mg), H_6L (0.04 mmol, 39.0 mg), dib (0.08 mmol, 16.8 mg) in mixed N,N'-Dimethylformamide (DMF, 6 mL)/ distilled water (H_2O, 1 mL) solvent were placed in a 20 ml vial, and then sealed. The sample was heated at 130 °C for three days; cooled to room-temperature slowly. After washed by distilled water, red brick crystals were obtained, yield 52.7 mg (72% based on Co). Its purity was confirmed by X-ray power diffraction (XRD). Anal. Calcd (%) for **1** $C_{82}H_{96}Co_3N_{10}O_{27}$ (Mr = 1830.48): C, 53.8; H, 5.29; N, 7.65. Found: C, 53.1; H, 5.33; N, 7.69.

X-ray crystal structure determination

The data collection for **1** was carried out on a Bruker Apex II CCD diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) at 273 K. The diffraction data were integrated by using the SAINT program, which were also used for the intensity corrections for the Lorentz and polarization effects. Absorption correction was applied using multi-scan program SADABS.[2] The structure was solved by direct methods. All atoms were refined anisotropically on F^2 by full-matrix least squares using SHELXTL-97.[3] Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. All hydrogen atoms of organic molecules were placed by geometrical considerations and were added to the structure factor calculation. The remained solvent molecules (9 DMF and 43 H_2O molecules) in the channels of **1** were disordered and could not be modeled properly, and the contribution of their electron density was removed by the SQUEEZE routine in PLATON, combining the results of thermogravimetric analysis. The formula for **1** was also determined by combining single-crystal structure, elemental microanalysis and TGA. A summary of the crystallographic data is listed in Table S1. Selected bond distances and angles are given in Table S2, respectively.

Table S1. **Summary of Crystal Data and Structure Results for 1.**

Compound	**1**
chemical formula	$C_{82}H_{96}Co_3N_{10}O_{27}$
structural formula	Co₃(L)(dib)•2H₂O•6DMF
fw	1830.48
Temperature (K)	273(2)
a (Å)	30.190(5)

b (Å)	19.637(3)
c (Å)	16.038(3)
α (°)	90
β (°)	108.829(3)
γ (°)	90
V (Å^3)	8999(3)
Z	4
space group	$C2/c$
crystal system	monoclinic
2θ max (deg)	52.28
μ(Mo-Kα) mm^{-1}	0.627
D (g/cm^3)	1.351
F(000)	3820
Reflections collected/unique	24499/8868 [R$_{int}$ = 0.0921]
Final R indices [I>2sigma(I)] ^{a}	R$_1$ = 0.0896, wR$_2$ = 0.2453
R indices (all data)	R$_1$ = 0.1405, wR$_2$ = 0.2842
GOF	0.959
Largest diff. peak and hole	2.108 and -0.632 e.A^{-3}

^{a}R$_1$ = Σ||Fo| -|Fc||/Σ|Fo|, wR$_2$ = {Σw[(Fo)^2 -(Fc)^2]^2/Σw[(Fo)^2]^2}$^{1/2}$.

Table S2. Selected bond lengths for **1**.

Co(1)-O(9)#3	2.028(4)	Co(2)-O(10)#1	1.987(4)
Co(1)-O(9)#1	2.028(4)	Co(2)-N(1)	2.043(5)
Co(1)-O(4)#4	2.098(4)	Co(2)-O(3)	2.085(5)
Co(1)-O(4)	2.098(4)	Co(2)-O(7)#2	2.086(5)
Co(1)-O(7)#5	2.146(5)	Co(2)-O(4)	2.257(5)
Co(1)-O(7)#2	2.146(5)	Co(2)-O(6)#2	2.364(6)
O(1)-C(2)#3	1.429(7)	C(31)-C(32)#6	1.372(9)
O(6)-Co(2)#7	2.364(6)	O(7)-Co(1)#5	2.146(5)
O(7)-Co(2)#7	2.086(5)	O(9)-Co(1)#3	2.028(4)

|			
O(10)-Co(2)#8	1.987(4)		
O(9)#3-Co(1)-O(9)#1	180	O(4)-Co(1)-O(7)#5	98.41(19)
O(9)#3-Co(1)-O(4)	89.79(16)	O(9)#1-Co(1)-O(7)#2	88.45(16)
O(9)#1-Co(1)-O(4)	90.21(16)	O(4)-Co(1)-O(7)#2	81.59(19)
O(4)#4-Co(1)-O(4)	180	O(7)#5-Co(1)-O(7)#2	180
O(9)#1-Co(1)-O(7)#5	91.55(16)	Co(2)#7-O(7)-Co(1)#5	97.0(2)
C(2)#3-O(1)-C(2)	113.3(7)	N(1)-Co(2)-O(6)#2	86.3(2)
O(10)#1-Co(2)-N(1)	90.3(2)	O(3)-Co(2)-O(6)#2	88.4(3)
O(10)#1-Co(2)-O(3)	134.6(3)	O(7)#2-Co(2)-O(6)#2	57.19(19)
N(1)-Co(2)-O(3)	100.5(2)	O(4)-Co(2)-O(6)#2	113.96(19)
O(10)#1-Co(2)-O(7)#2	95.45(19)	Co(1)-O(4)-Co(2)	93.40(17)
N(1)-Co(2)-O(7)#2	130.9(2)	O(3)-Co(2)-O(4)	59.91(17)
O(3)-Co(2)-O(7)#2	109.0(2)	O(7)#2-Co(2)-O(4)	79.27(17)
O(10)#1-Co(2)-O(4)	89.39(18)	O(10)#1-Co(2)-O(6)#2	136.6(2)
N(1)-Co(2)-O(4)	149.6(2)		

Symmetry transformations used to generate equivalent atoms:

#1 x+1/2, -y+3/2, z-1/2; #2 x+1/2, -y+3/2, z+1/2; #3 -x+1, y, -z+3/2; #4 -x+3/2, -y+3/2, -z+1; #5 -x+1, y, -z+1/2; #6 -x+3/2, -y+1/2, -z+1; #7 x-1/2, -y+3/2, z-1/2; #8 x-1/2, -y+3/2, z+1/2.
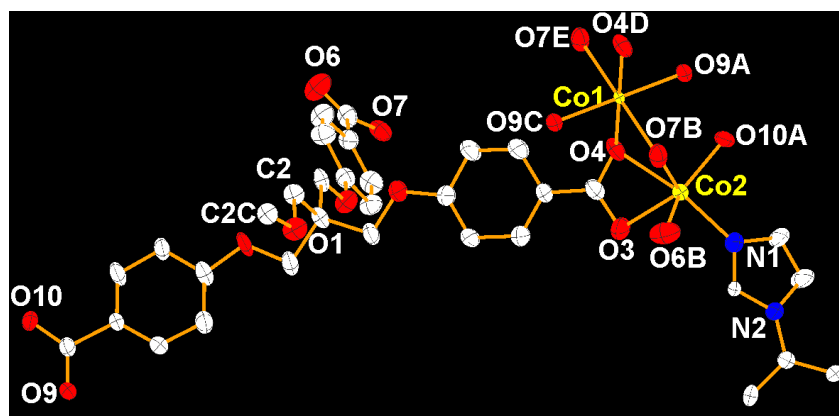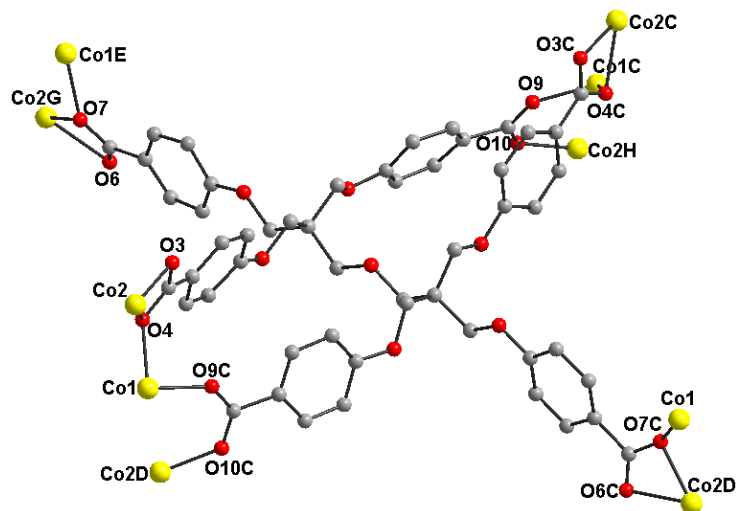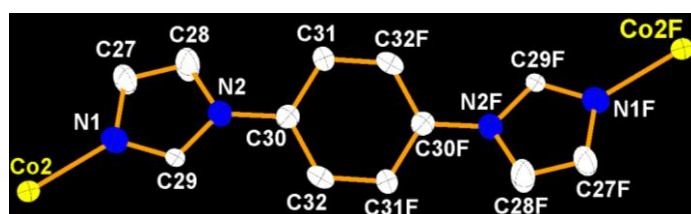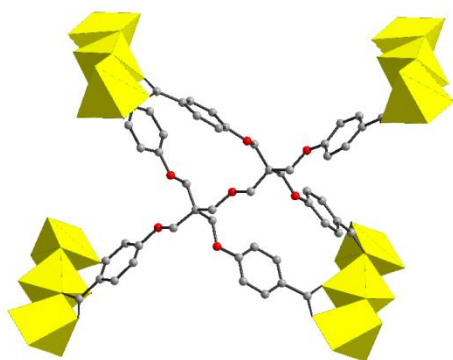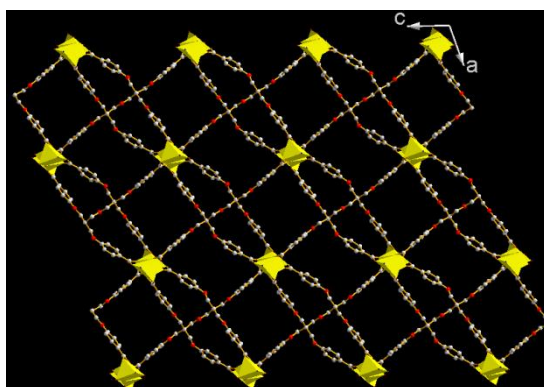

(a)
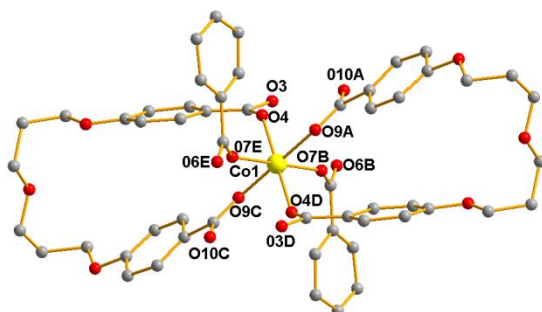
(b)
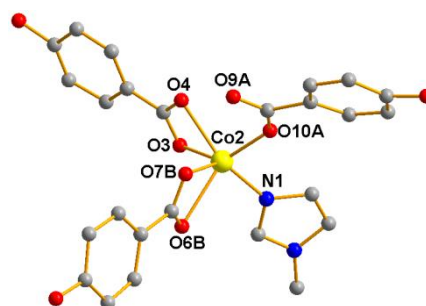
(c)

(d)

(e)

Fig. S1 The asymmetric unit of **1** (a), and coordination mode of Co(1) (b), Co(2) (c), H_6L ligand (d) and dib ligand (e). Symmetry code: A x+1/2, -y+3/2, z-1/2; B x+1/2, -y+3/2, z+1/2; C -x+1, y, -z+3/2; D -x+3/2, -y+3/2, -z+1; E -x+1, y, -z+1/2; F -x+3/2, -y+1/2, -z+1; G x-1/2, -y+3/2, z-1/2; H x-1/2, -y+3/2, z+1/2.
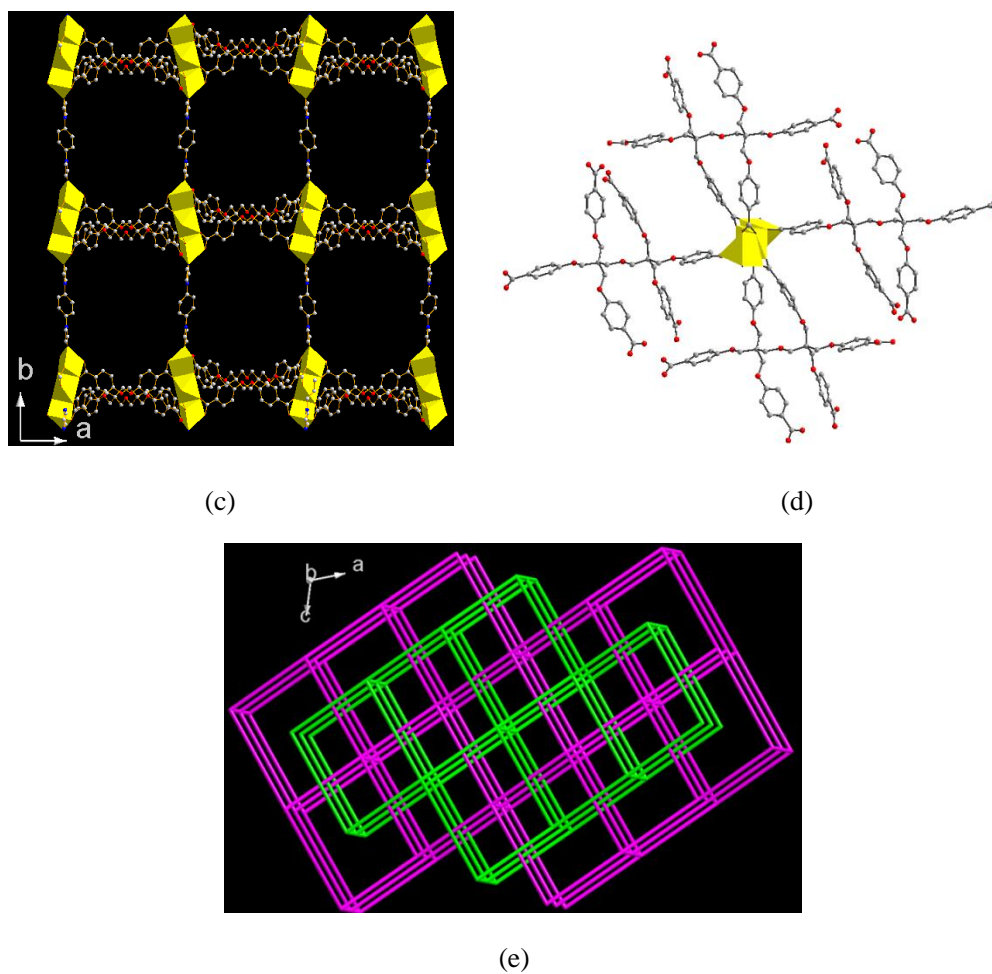

(a)

(b)

(c)   (d)

(e)

Fig. S2 (a and d) The connected node of L ligand (a) and Co$^{II}_3$ SBU (d). (b) The 2D Co-L layer struture along [010] direction. (c) One indenpendent 3D porous single net in **1**. (e) The simplified **fsc** net along [010] direction.
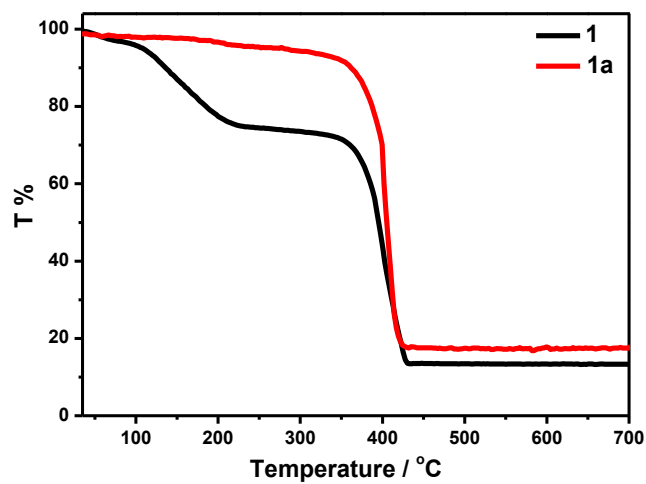

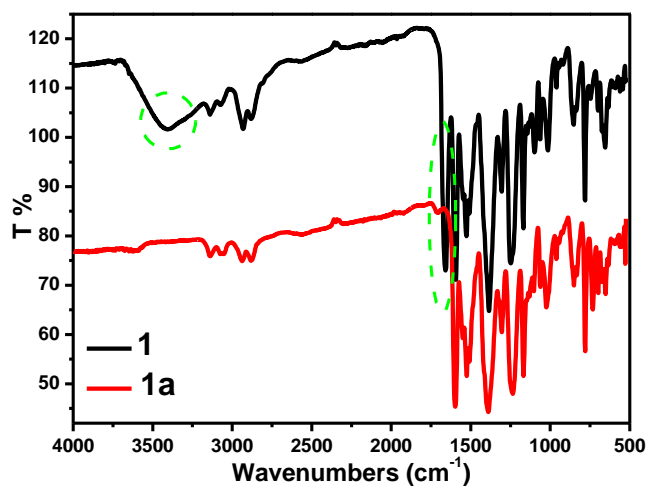Fig. S3 The TGA curves of **1** and activated **1a**.

Fig. S4 The contrastive FT-IR spectra of **1** and activated **1a**.

IR-1: 3403 (m), 3142 (w), 3071 (w), 2935 (w), 2876 (w), 1659 (s), 1594 (s), 1530 (m), 1387 (vs), 1308 (m), 1243 (s), 1172 (m), 1100 (w), 1015 (m), 963 (w), 853 (m), 781 (m), 703 (w), 658 (m).

IR-1a: 3142 (w), 3058 (w), 2940 (w), 2882 (w), 1706 (w), 1600 (s), 1549 (w), 1523 (s), 1392 (vs), 1302 (m), 1236 (s), 1172 (m), 1068 (w), 1023 (m), 963 (w), 852 (m), 781 (m), 730 (w), 696 (w), 651 (w).
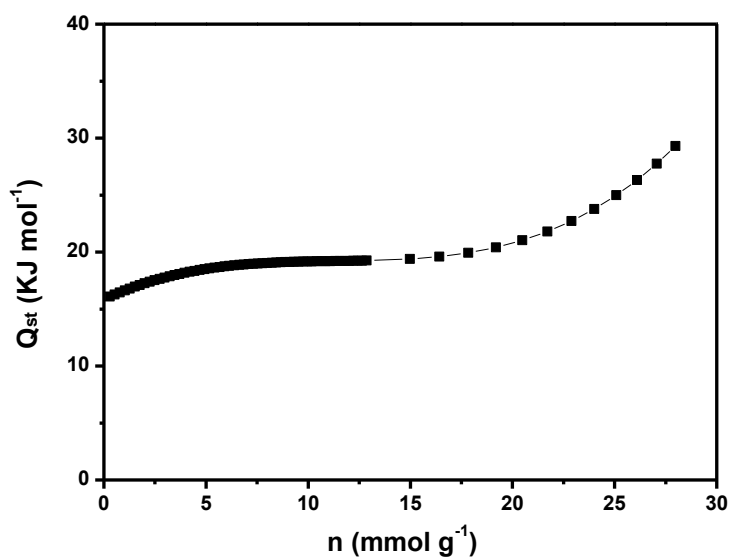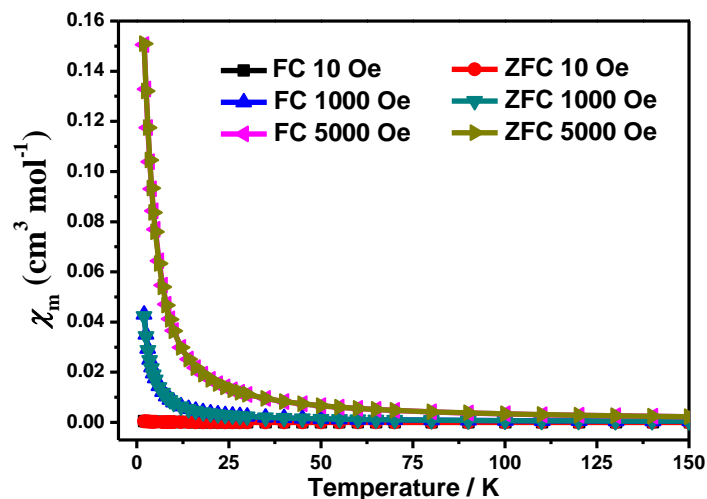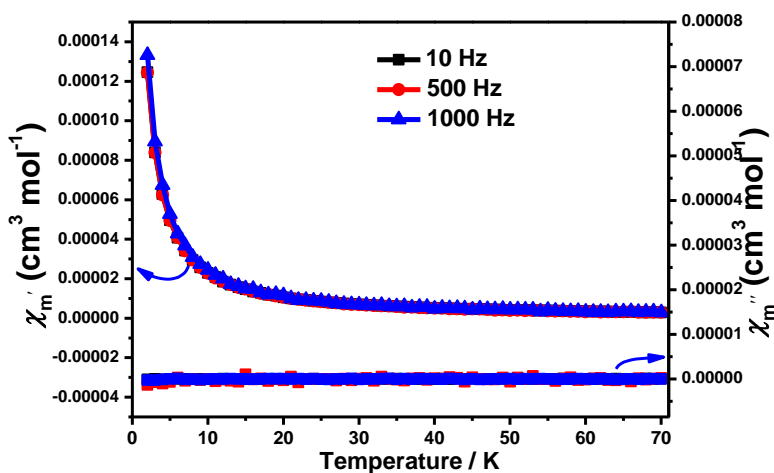

Fig. S5 Isosteric adsorption enthalpies of CO_2 on activated **1a**.

(a)

(b)

Fig. S6 The in-phase χ_m' and out-of-phase χ_m'' components of the ac susceptibility of **1** measured at different frequencies (10, 500, 1000 Hz) in an applied ac field of 3 Oe; and ZFC & FC curves at $H = 10$, 1000 and 5000 Oe from 2 to 150 K.

References:

(1) (a) E. M. D. Keegstra, J. W. Zwikker, M. R. Roest and L. W. Jenneskens, *J. Org. Chem.*, 1992, **57**, 6678-6680; (b) D. Laliberte, T. Maris and J. D. Wuest, *J. Org. Chem.*, 2004, **69**, 1776-1787; (c) H.-Y. Wu, R.-X. Wang, W. Yang, J. Chen and Z.-M. Sun, J. Li, H. Zhang, *Inorg. Chem.*, 2012, **51**, 3103-3107.

(2) G. M. Sheldrick, SADABS; University of Gottingen: Germany, 1996.

(3) (a) G. M. Sheldrick, SHELXS-97, Program for X-ray Crystal Structure Determination; University of Gottingen: Germany, 1997; (b) G. M. Sheldrick, SHELXL-97, Program for

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