Supporting Information For

Cleavage of C–C σ bond between two phenyl groups under mild conditions during the construction of Zn(II) organic frameworks

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EXPERIMENTAL SECTION

Materials and Measurements. All reagents and solvents were commercially available and were used without further purification. Infrared spectra were obtained in KBr discs on a Nicolet Avatar 360 FTIR spectrometer in the 400-4000 cm^{-1} region. Elemental analyses (C, H and N) were performed with a PerkinElmer 2400C Elemental Analyzer. 1 H NMR spectra were recorded on Varian instrument (400 MHz) and (100 MHz). Thermal gravimetric analyses (TGA) were carried out in nitrogen stream using a Netzsch TG209F3 equipment at a heating rate of 5 °C/min. Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 ADVANCE X-ray powder diffractometer (Cu Kα,1.5418 Å). All the gas sorption isotherms were measured by using a ASAP 2020M adsorption equipment.

Synthesis of [Zn(dbba)(Hbpe)]·H_2O (1). A mixture of $Zn(NO_3)_2·6H_2O$ (59.5 mg, 0.2 mmol), H_3dbba (26.2 mg, 0.1 mmol), and bpe (18.2 mg, 0.1 mmol) in H_2O/DMF (4/1, v/v 5 mL) was placed in a screw-capped vial in an oven at 105 ºC for 72 h, and then cooled to room temperature at a rate of 0.5 °C min^{-1}. The resulting colorless block crystals of **1** were isolated by washing with H_2O/DMF, and dried in air. The yield was *ca*. 20.2 mg (67.6%). Anal. Calcd for $C_{27}H_{20}ZnN_2O_7$: C, 58.98; H, 3.67; N, 5.10%. Found: C, 59.06; H, 3.55; N, 5.02%.

Synthesis of [Zn(bdc)$(bpe)_{0.5}$]·H_2O·DMF (2). A mixture of $Zn(NO_3)_2·6H_2O$ (59.5 mg, 0.2 mmol), H_3dbba (26.2 mg, 0.1 mmol), and bpe (18.2 mg, 0.1 mmol) in DMF (5 mL) was placed in a screw-capped vial in an oven at 105 ºC for 48 h, and then cooled to room temperature at a rate of 0.5 °C min^{-1}. The resulting colorless block crystals of **2** were isolated by washing with DMF, and dried in air. The yield was *ca*. 28.5 mg (86.4%). Anal. Calcd for $C_{17}H_{18}ZnN_2O_6$: C, 49.59; H, 4.41; N, 6.80%. Found: C, 49.68; H, 4.30; N, 6.69%.

Crystallography

Diffraction data were collected at 296(2) K with a Mo Kα radiation (λ = 0.71073 Å) on a Bruker-AXS SMART CCD area detector diffractometer. Absorption corrections were carried out utilizing SADABS routine.[1] The structures were solved by the direct methods and refined using the SHELXTL program package.[2] All non-hydrogen atoms were refined anisotropically with the hydrogen atoms added to their geometrically ideal positions and refined isotropically. The contribution of the disordered solvent molecules in **2** was subtracted from the reflection data by the SQUEEZE method as implemented in PLATON program.[3] The final formulas of **1** and **2** were

determined by combining the single-crystal structures, elemental microanalyses and TGA data. Selected crystallographic data and structure refinement results are listed in Table S5.

1 Bruker. *SADABS*, *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconson, USA, 2002.

2 Sheldrick, G. M. *SHELXL-97, program for the refinement of the crystal structures*. University of Göttingen, Germany, 1997.

3 Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7−13.

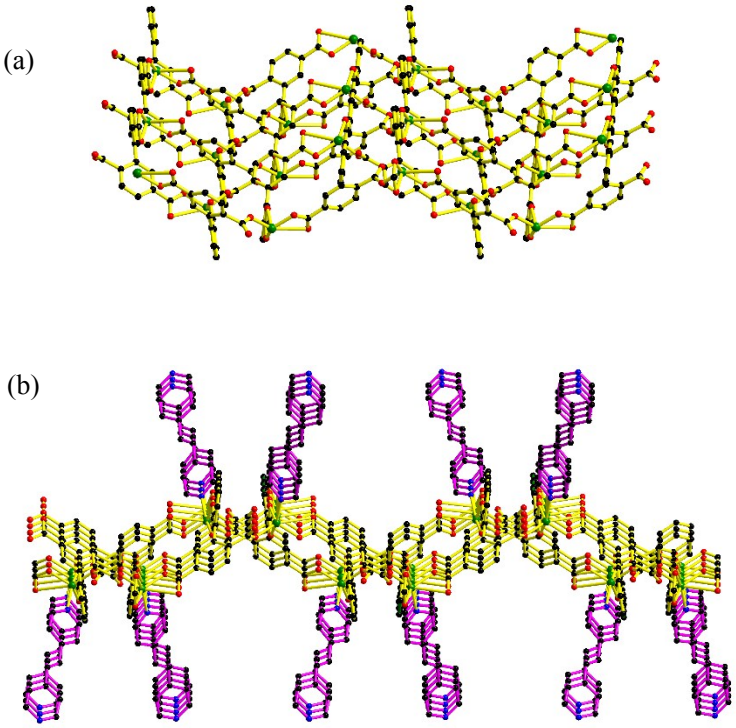
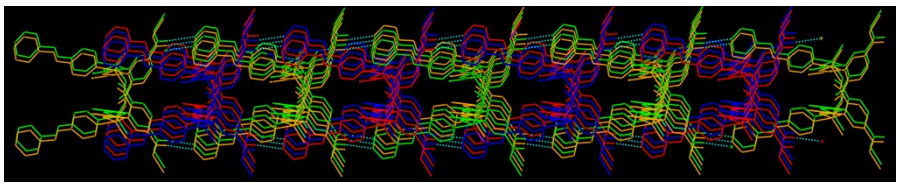
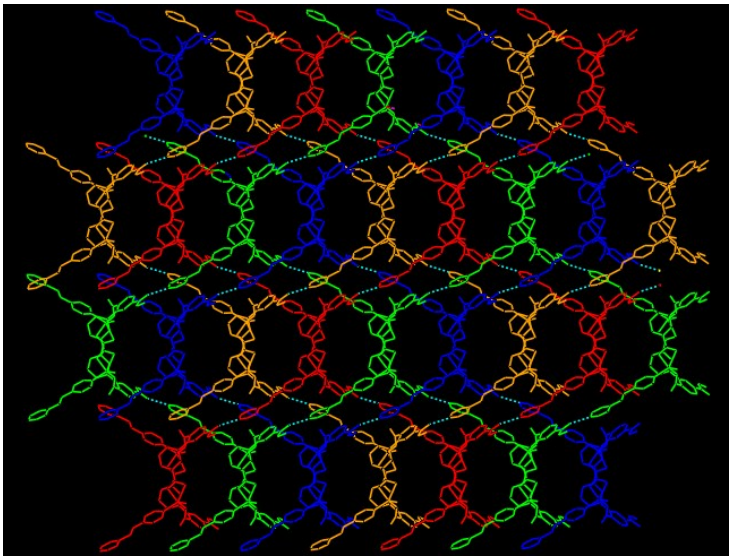


Figure S1. (a) The 2D layer formed by $dbba^{3-}$ and Zn(II) atoms, and (b) the 2D structure of **1** with the $Hbpe^{+}$ ligands are lined in both sides of the layer.



(a)



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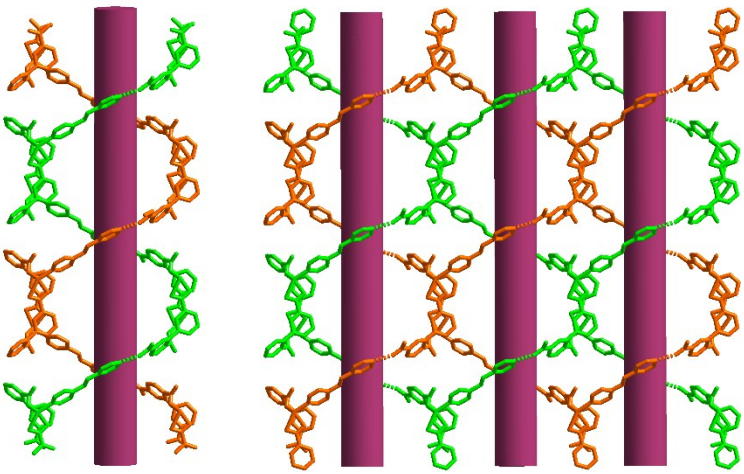


(c)

Figure S2. (a, b) View of the four-fold interpenetrated structure along a-axis b-axis, and (c) the 2-fold right-handed 2_1 helical chains and its expand layer are formed by interlayer hydrogen bonds along a-axis. The dotted lines represent the hydrogen bonds.

Table S1. The results of some solvents used in the reaction system

Solvent	Result/Complex	Solvent	Result
H_2O	**1**	DMA	**2**
DMF	**2**	DEF	**2**

Table S2. Using different zinc salts for preparing complex **2**.

Zinc salt	Result	Notes
$Zn(NO_3)_2·6H_2O$	Pure and good quality, complex **2**	H_3dbba (0.1 mmol) bpe (0.1 mmol) Zinc salt (0.2 mmol) in DMF T = 105 ºC reaction time = 72 h
$Zn(ClO_4)_2·6H_2O$	Pure and good quality, complex **2**	
$Zn(Ac)_2·2H_2O$	Pure and good quality, complex **2**	
$ZnCl_2$	Large number of small crystal	
$ZnSO_4·7H_2O$	Large number of small crystal with small impurity	
$5ZnO·2CO_2·4H_2O$	Large number of small crystal	

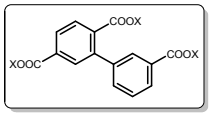
Table S3. The effect of reaction temperatures for preparing complex **2**.

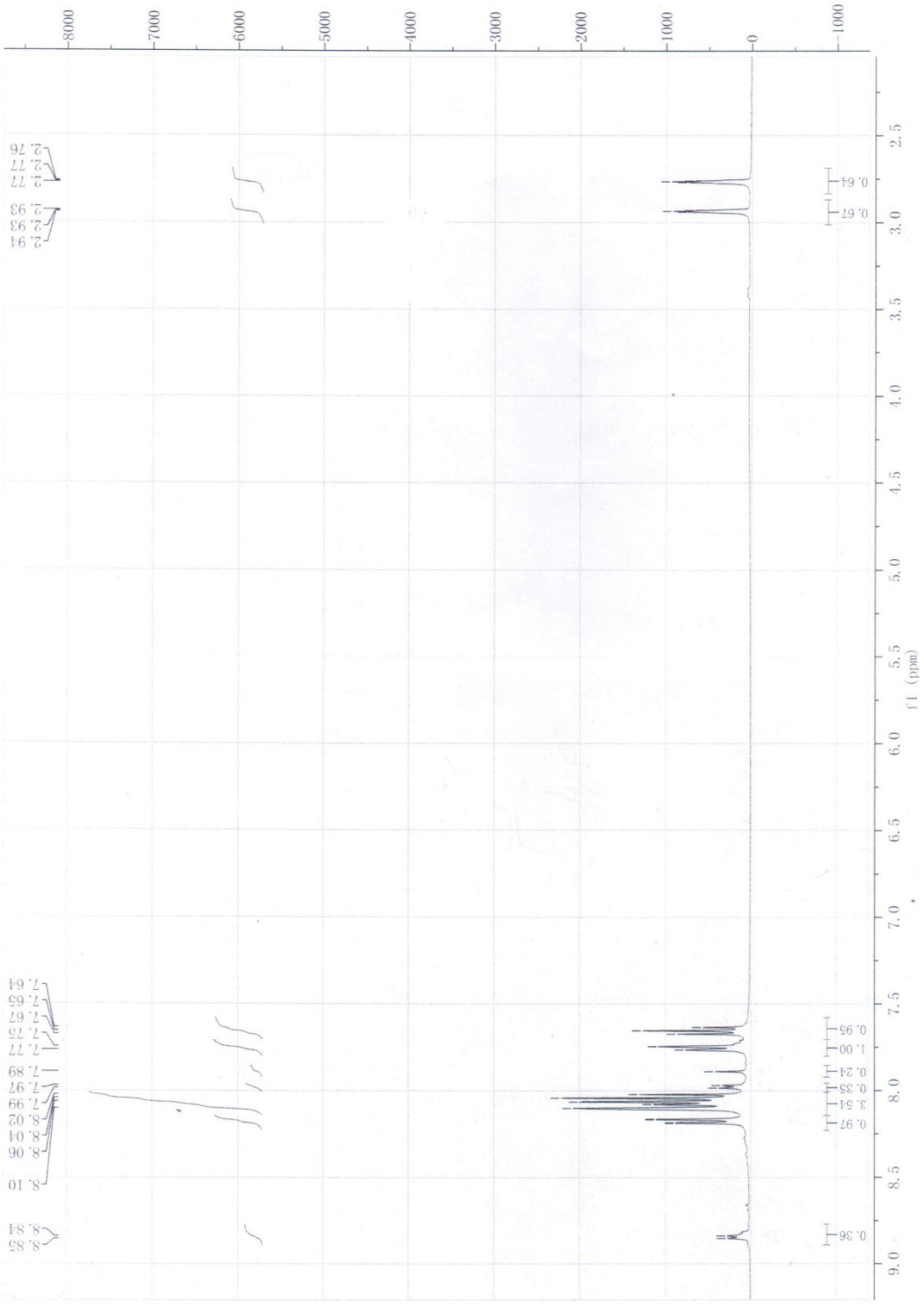
Temperature/ºC	Reaction time/h	Result
50	72	Light yellow solution
70	72	Orange yellow solution, small crystals
90	72	Yellow solution, large crystals
105	72	Yellow solution, very large crystals

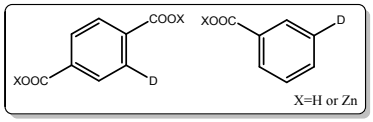
Table S4. The effect of reaction times for preparing complex **2**.

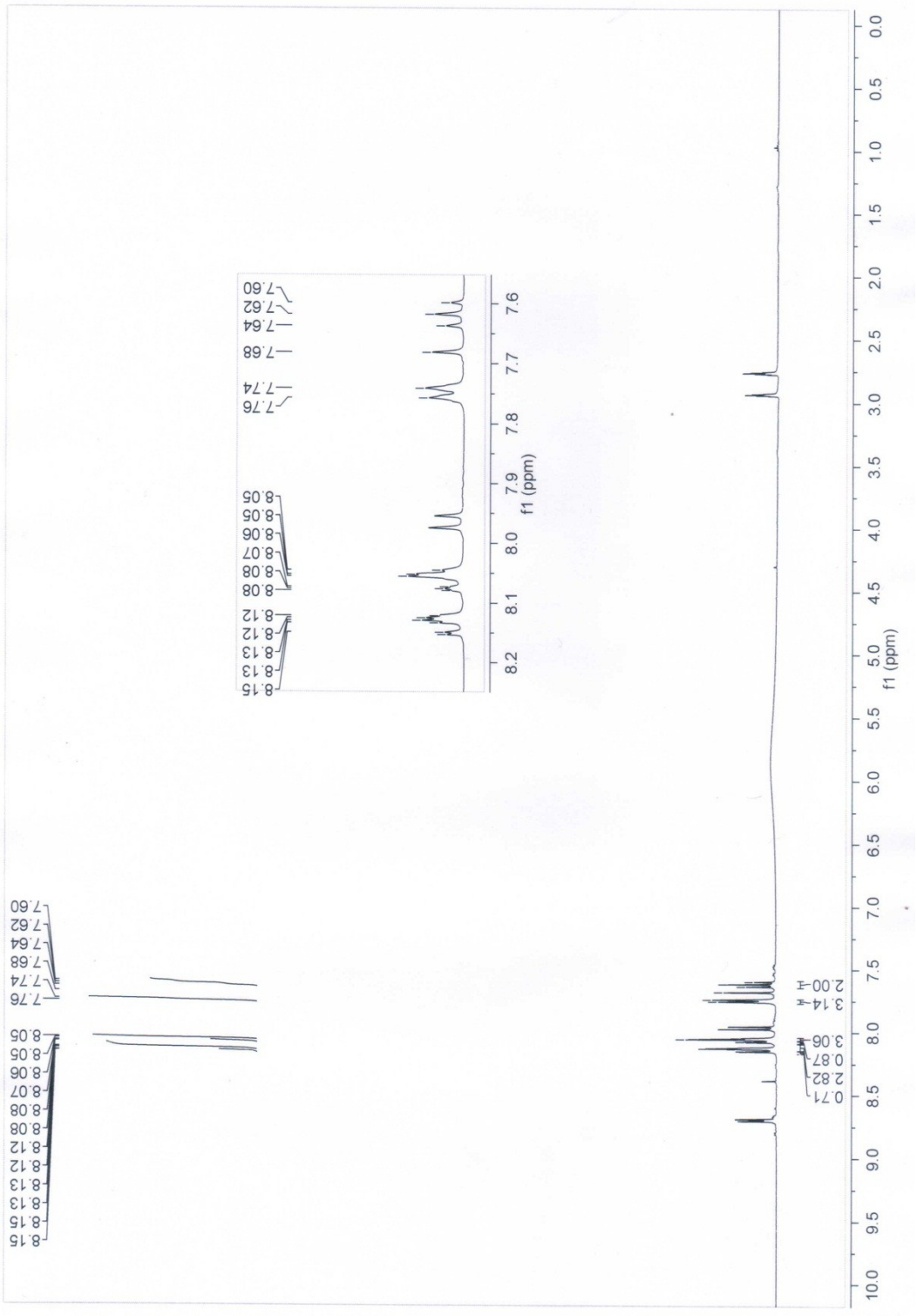
Temperature/ºC	Reaction time/h	Result
105	0	Colorless transparent liquid
105	2	Light yellow transparent liquid
105	6	Deep yellow transparent liquid
105	8	Yellow turbid liquid
105	10	Yellow transparent liquid
105	12	Yellow transparent liquid, crystals

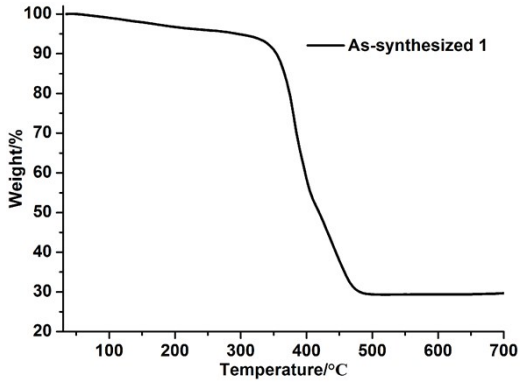
Figure S3. Copies of 1 H spectra:



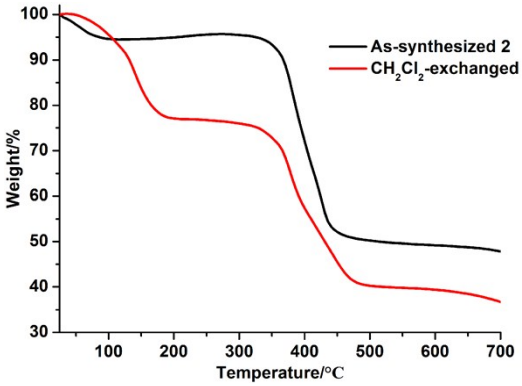



COOX
XOOC
D
XOOC
D
X=H or Zn


8.15
8.13
8.13
8.12
8.12
8.08
8.08
8.07
8.06
8.05
8.05
7.76
7.74
7.68
7.64
7.62
7.60
f1 (ppm)
0.71
2.82
0.87
3.06
3.14
2.00
f1 (ppm)

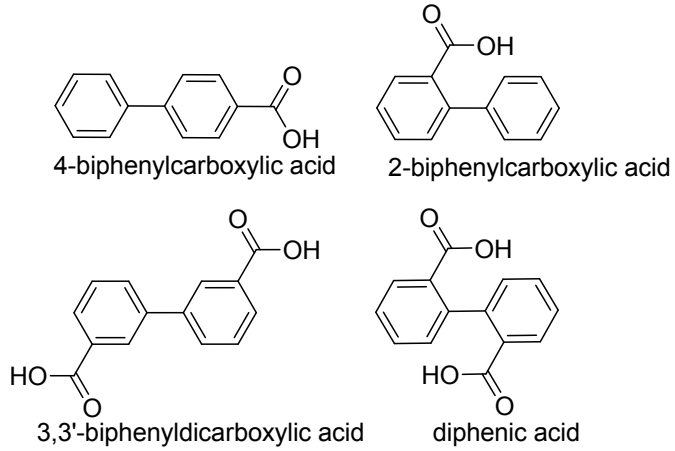


(a)



(b)

Figure S4. TGA plots for the as-synthesized **1**, **2** and the CH_2Cl_2-exchanged sample. For **1**, a total weight loss of 3.4% at 32−210 ºC, corresponding to the loss of $1H_2O$ guest molecules per formula unit (calc. 3.3%). Then, the structure without the solvent molecules is maintained until 340 °C. For **2**, a total weight loss of 22.8 % at 25−200 ºC, corresponding to the loss of 1DMF and $1H_2O$ guest molecules per formula unit (calc. 22.1%). Then, the desolvated framework is stable until 350 °C. For the CH_2Cl_2-changed sample $[Zn(bdc)(bpe)_{0.5}]\cdot H_2O$, the initial weight loss of 5.2% from 25−90 ºC should be attributed to the H_2O guest molecules per formula unit (calc. 5.6%), then followed by a plateau of stability from 90 to 350 °C.



Scheme S1 The other biphenylcarboxylic acids were used in the reaction.

Table S5. Crystal data and structure refinements for **1** and **2**

Complex No.	**1**	**2**
Empirical formula	$C_{27}H_{20}N_2O_7Zn$	$C_{14}H_9NO_4Zn$
Formula mass	549.84	320.61
Temperature [K]	296(2)	296(2)
Crystal system	Orthohombic	Tetragonal
Space group	$P2_12_12$	P_4/mmm
a [Å]	15.7341(18)	10.8088(15)
b [Å]	19.190(2)	10.8088(15)
c [Å]	8.3925(10)	16.283(5)
α [deg]	90.00	90.00
β [deg]	90.00	90.00
γ [deg]	90.00	90.00
V [Å^3]	2534.0(5)	1902.3(7)
Z	4	2
$D_{calcd.}$[g·cm^{-3}]	1.436	0.560
μ [mm^{-1}]	1.018	0.649
GOF on F^2	1.079	1.145
reflns collected/ unique	12774/4502	10471/1203
R_{int}	0.0668	0.0841
R_1[a], wR_2[b] [I>2 σ(I)]	0.0702, 0.1932	0.0863, 0.2481
R_1, wR_2 (all data)	0.1014, 0.2214	0.0968, 0.2583

[a] $R_1 = \Sigma||F_o| - |F_c|)/\Sigma|F_o|$; [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$