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An Effective Strategy to Boost the Robustness of Metal-Organic Framework via Introducing Size-Matching Ligand Braces

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ELECTRONIC SUPPLEMENTARY INFORMATION

General methods

Commercially available reagents were purchased as high purity from Fisher Scientific and used without further purification. 9,10-anthracenedicarboxylic acid (H_2adc) was synthesized using the similar procedures as reported.[1] Thermogravimetric analysis (TGA) was performed under nitrogen on a TA Instrument Q50 from 25°C to 800 °C at the speed of 10 °C/min. FT-IR data were recorded on a PerkinElmer Spectrum Two instrument in a range from 4000 to 500 cm^{-1} and a resolution of 4 cm-1. Powder X-ray diffraction patterns were collected on a Bruker D8 Advance X-ray diffractometer (CuKα = 1.54178 Å), at 40 kV, 40 mA with a scan speed of 0.5 s/step and a step size of 0.02 in 2θ at room temperature. Gas adsorption isotherms were collected using a Micromeritics surface area analyzer ASAP-2020. Before the measurements, the freshly prepared samples of complex **1** and **2** were exchanged with HPLC-grade methanol for 3 days, and then activated with the "degas" port under the vacuum at 30 °C for 3 hours. CO_2 gas adsorption isotherms were collected at 195 K using an acetone-dry ice bath, 273K using a water-ice bath and at 298K with a water bath. The O_2, N_2, and H_2 adsorption isotherms were measured at 77K using a liquid nitrogen bath.

Single-crystal X-ray crystallography.

The single crystal X-ray data for complex **1** and **2** were collected using Bruker-AXS

SMART-APEXII diffractometer (CuKα = 1.54178 Å). Indexing was performed using APEX2 (Difference Vectors method).[2] Data integration and reduction were performed using SaintPlus 6.01.[3] Absorption correction was performed by multi-scan method implemented in SADABS.[4] Space groups were determined using XPREP implemented in APEX2.[2] Structures were solved using SHELXS-97 (direct methods) and refined using SHELXL-97 (full-matrix least squares on F^2) contained in Win GX[5,6,7,8] and Olex2 programs.[9] All non-H atoms were found in the difference Fourier map. The atoms from adc ligands, metal ions, 4,4'-bpy ligands, μ_3-O and oxygen atoms of coordinated solvent molecules were refined anisotropically. Due to the disorder, the assignment of counterions was tentative. It has been assumed the dimethyl ammonium cation is a product of decomposition of DMA molecule and that those two share the position in the crystal structure. The geometry of disordered partially-occupied counter ions and coordinated DMA molecules were refined with restraints/constraints (DFIX, DELU, SIMU, DANG, FLAT, EXYZ, EADP, ISOR), in order to idealize the models of these ions and molecules. For complex **2** the solvent molecules were modeled as O atoms. Hydrogen atoms were placed in geometrically calculated positions and included in the refinement process using riding model with isotropic thermal parameters: Uiso(H) = 1.2Ueq(-CH). Crystal data and refinement conditions of complex **1** and **2** are shown in Table S1 and S2, respectively.

Preparation of complexes 1 and 2.

Complex **1**: *N*,*N*-dimethylacetamide (DMA, 0.5 mL) solution containing H_2adc (5 mg, 0.019 mmol) was mixed thoroughly with *N*,*N*-dimethylacetamide (DMA, 0.25 mL) solution containing $Co(NO_3)_2 \cdot 6H_2O$ (11 mg, 0.038 mmol), and then three drops of HBF_4 were added. The mixture was sealed in a Pyrex tube, heated at 120 °C for 3 days and then cooled to room temperature. The orange block crystals were obtained with a yield of 45% based on H_2adc.

Complex **2**: A mixture of *N*,*N*-dimethylacetamide (DMA, 0.5 mL) solution containing H_2adc (5 mg, 0.019 mmol) and DMA (0.25 mL) solution containing 4,4'-bpy (3 mg, 0.019 mmol) was mixed thoroughly with DMA (0.25 mL) solution containing $Co(NO_3)_2 \cdot 6H_2O$ (11 mg, 0.038 mmol), and then four drops of HBF_4 were added. The mixture was sealed in a Pyrex tube, heated at 120 °C for 4 days and then cooled to room temperature. The red block crystals were obtained

with a yield of 51% based on H_2adc.

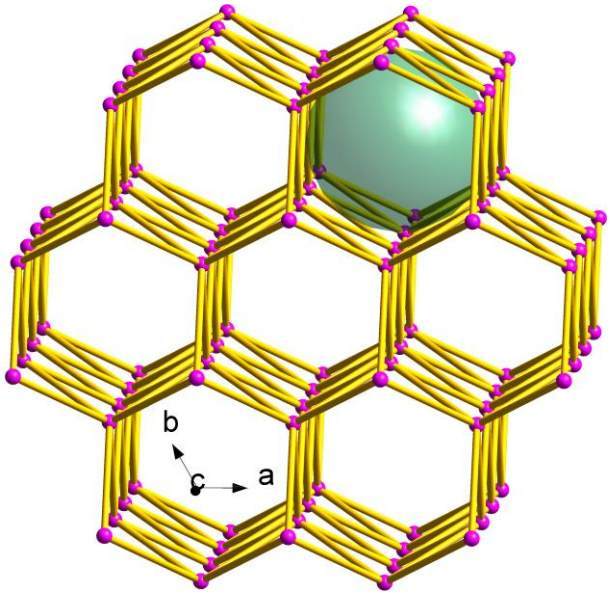


Fig. S1 View of the topological network of complex **1**.

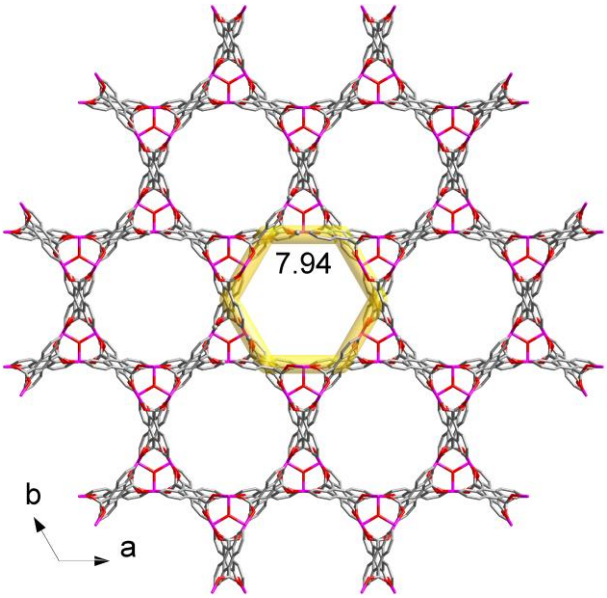


Fig. S2 View of 3D architecture with 1D channels by remove the coordinated DMA molecules in complex **1**.

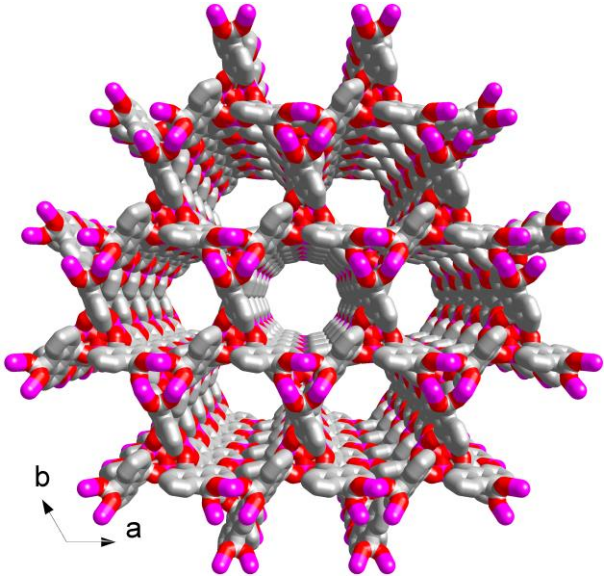


Fig. S3 The 1D nanochannels with terminal DMA removed from tricobalt SBUs in complex **1** .

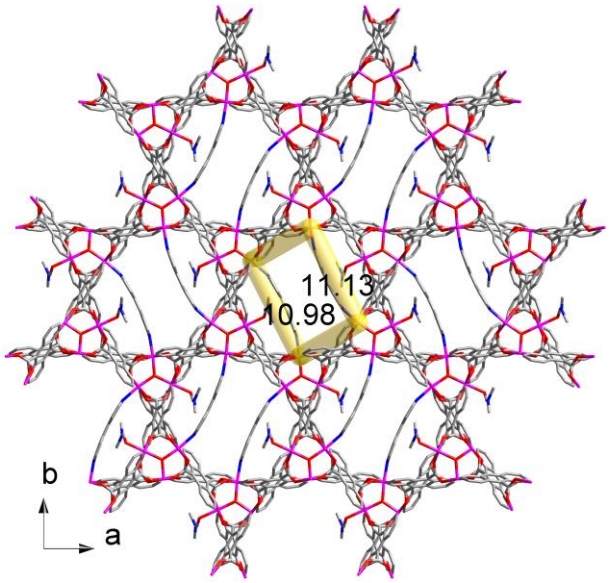


Fig. S4 View of 3D architecture with 1D channels decorated bpy in complex **2**.

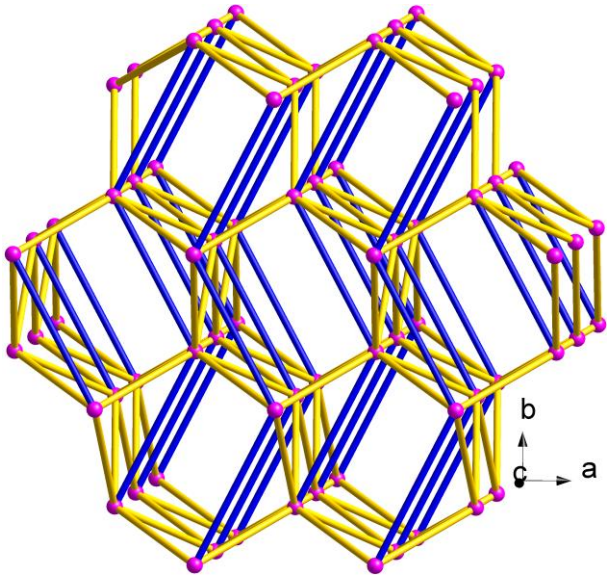


Fig. S5 View of the topological network of complex **2**.

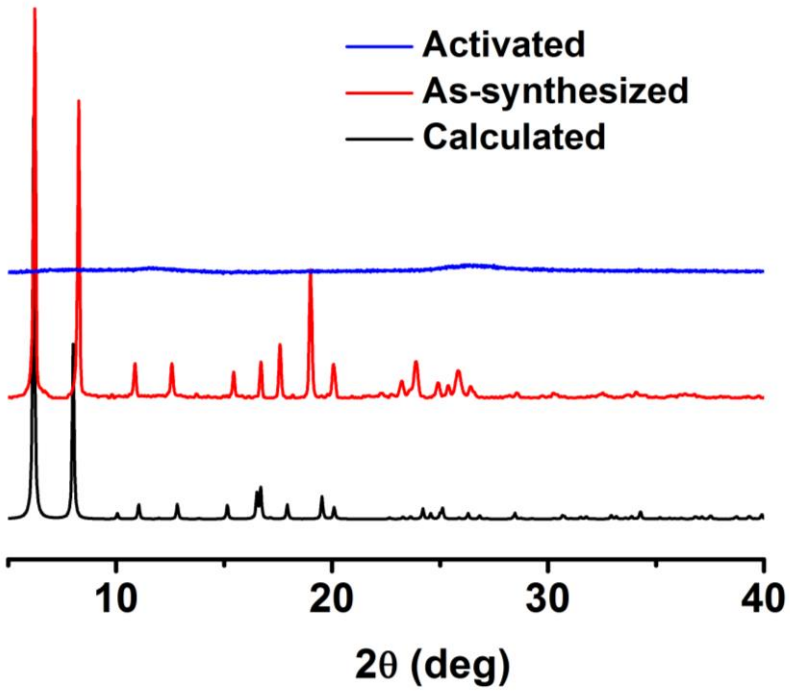


Fig. S6 The PXRD patterns of complexes **1**

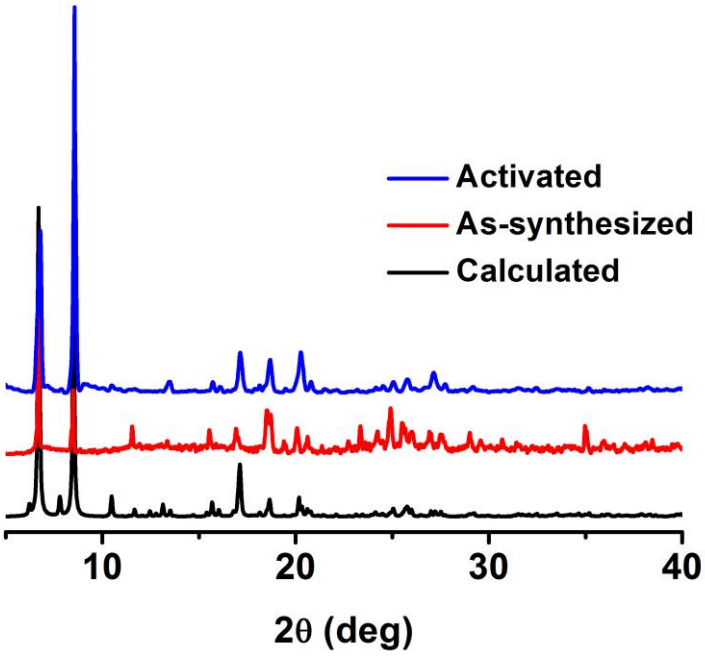


Fig. S7 The PXRD patterns for complex **2**.

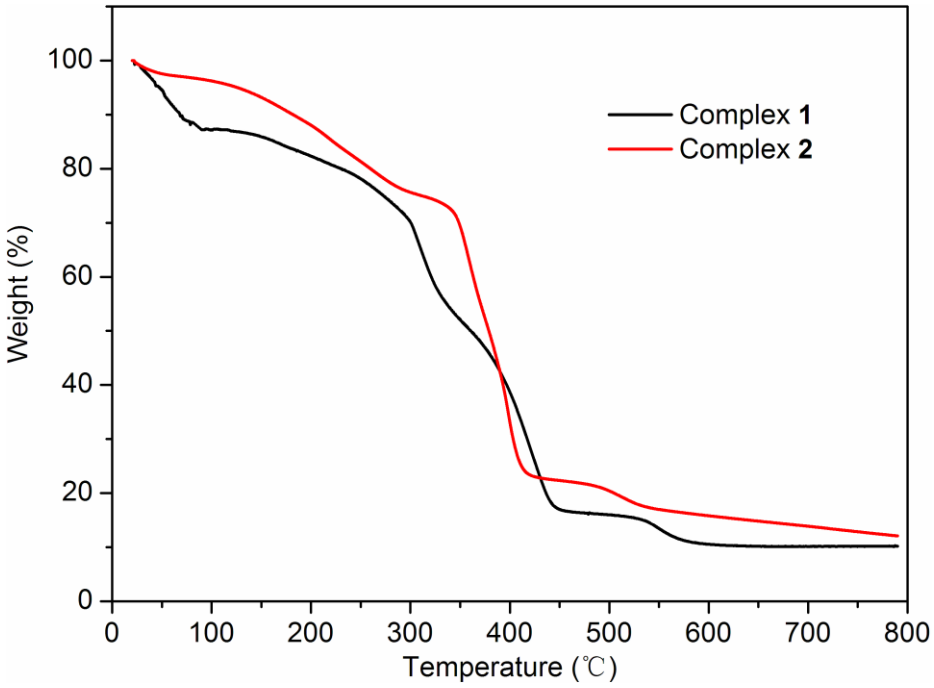


Fig. S8 The TGA curves of complexes **1** and **2**.

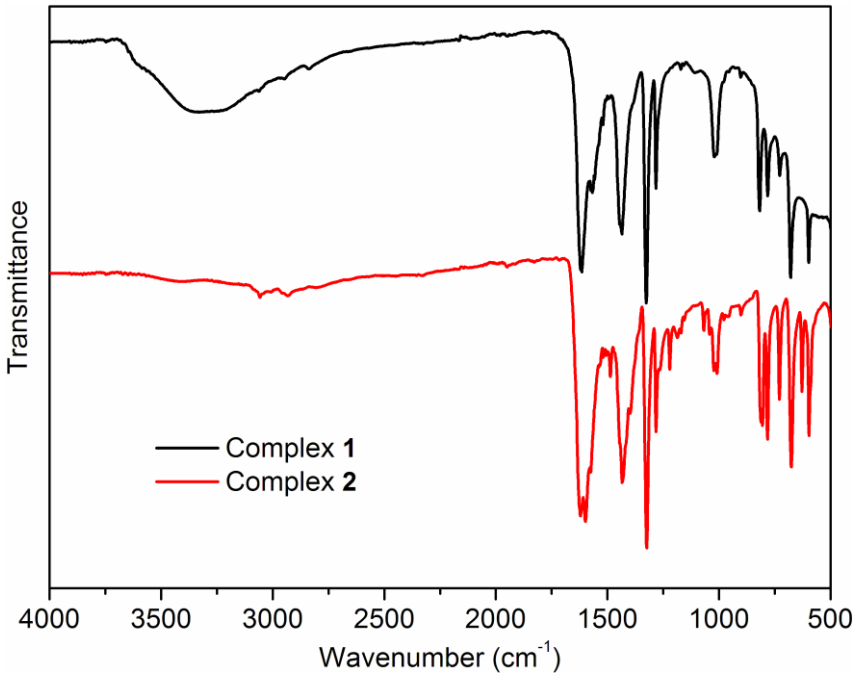
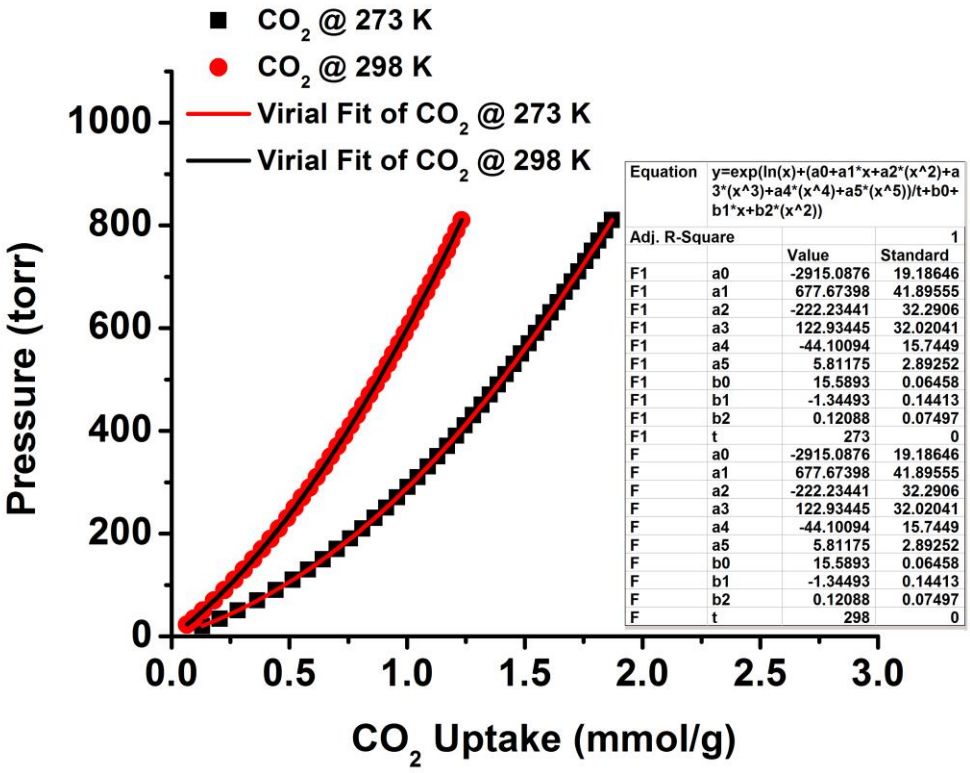


Fig. S9 The FT-IR spectra of complexes **1** and **2**.



Equation	y=exp(ln(x)+(a0+a1*x+a2*(x^2)+a3*(x^3)+a4*(x^4)+a5*(x^5))/t+b0+b1*x+b2*(x^2))		
Adj. R-Square			1
		Value	Standard
F1	a0	-2915.0876	19.18646
F1	a1	677.67398	41.89555
F1	a2	-222.23441	32.2906
F1	a3	122.93445	32.02041
F1	a4	-44.10094	15.7449
F1	a5	5.81175	2.89252
F1	b0	15.5893	0.06458
F1	b1	-1.34493	0.14413
F1	b2	0.12088	0.07497
F1	t	273	0
F	a0	-2915.0876	19.18646
F	a1	677.67398	41.89555
F	a2	-222.23441	32.2906
F	a3	122.93445	32.02041
F	a4	-44.10094	15.7449
F	a5	5.81175	2.89252
F	b0	15.5893	0.06458
F	b1	-1.34493	0.14413
F	b2	0.12088	0.07497
F	t	298	0

Fig. S10 The plots of virial equation of complex **2**.

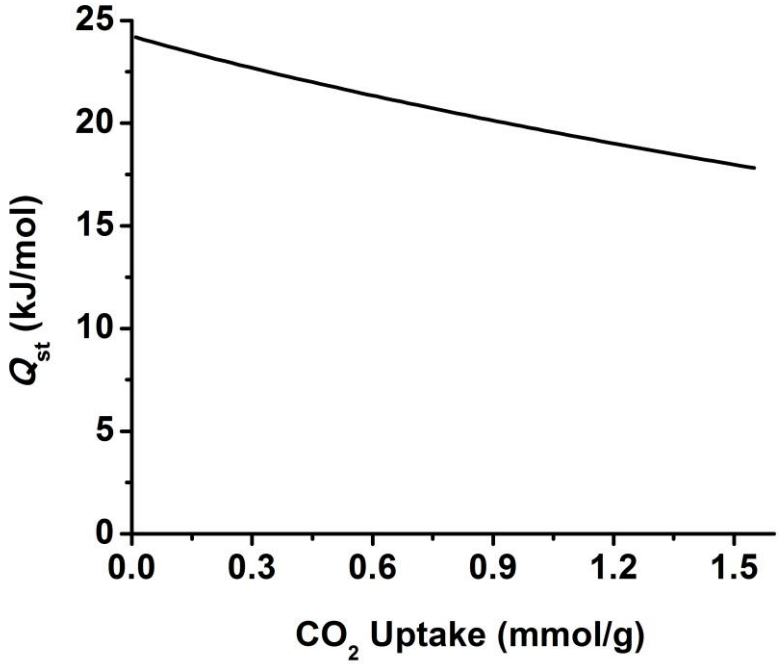


Fig. S11 Heats of adsorption of CO_2 of complex **2** using the virial method.

Table S1. Crystal data and structure refinement for complex 1.	
Identification code	Complex **1**
Empirical formula	$C_{64}H_{24}Co_3N_5O_{18.75}$
Formula weight	1339.75
Temperature/K	233.15
Crystal system	trigonal
Space group	*P*-3$_1$*c*
a/Å	15.3816(3)
b/Å	15.3816(3)
c/Å	16.8215(4)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	3446.66(16)
Z	2
ρ_{calc}g/cm^3	1.291
μ/mm^{-1}	6.182
F(000)	1348.0
Crystal size/mm^3	0.14 × 0.09 × 0.08
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.636 to 133.01
Index ranges	-17 ≤ h ≤ 16, -18 ≤ k ≤ 16, -18 ≤ l ≤ 16
Reflections collected	15678
Independent reflections	1982 [R_{int} = 0.0693, R_{sigma} = 0.0411]
Data/restraints/parameters	1982/80/182
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0571, wR_2 = 0.1561
Final R indexes [all data]	R_1 = 0.0704, wR_2 = 0.1671
Largest diff. peak/hole / e Å^{-3}	0.70/-0.36

Table S2. Crystal data and structure refinement for complex 2.	
Identification code	Complex 2
Empirical formula	$C_{69}H_{32}Co_3N_{5.75}O_{15}$
Formula weight	1358.29
Temperature/K	233.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	15.6069(4)
b/Å	26.4325(8)
c/Å	16.6221(5)
α/°	90
β/°	90.155(2)
γ/°	90
Volume/Å^3	6857.1(3)
Z	4
ρ_{calc}g/cm^3	1.316
μ/mm^{-1}	6.182
F(000)	2749.0
Crystal size/mm^3	0.24 × 0.15 × 0.13
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	8.45 to 137.242
Index ranges	$-18 \leq h \leq 18$, $-31 \leq k \leq 30$, $-19 \leq l \leq 19$
Reflections collected	62684
Independent reflections	12196 [R_{int} = 0.1311, R_{sigma} = 0.1057]
Data/restraints/parameters	12196/149/841
Goodness-of-fit on F^2	1.020
Final R indexes [I>=2σ (I)]	R_1 = 0.0695, wR_2 = 0.1786
Final R indexes [all data]	R_1 = 0.1215, wR_2 = 0.2069
Largest diff. peak/hole / e Å^{-3}	0.85/-0.49

Reference

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