

## Supporting Information for

### **Two new metal-chalcogenide-cluster-based frameworks with single metal ion of $Zn^{2+}/(Sb^{3+})$ serving as inter-cluster linker**

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## Experimental section

### Chemicals and instrumentation

Zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 99.9%), stannous chloride ( $\text{SnCl}_2$ , 99%), sublimed sulfur (S, 99.5%), diantimony trioxide ( $\text{Sb}_2\text{O}_3$ , 99.9%), 1,2-diaminopropane (1,2-DMP, 97%), ethylenediamine (EDA, 98%), and N-aminoethylpiperazine (AEP, 99%). All chemicals were purchased commercially and used without further purification.

Room-temperature powder X-ray diffraction (PXRD) data were carried out on a desktop diffractometer (D2 PHASER, Bruker, Germany) using  $\text{Cu-K}\alpha$  ( $\lambda = 1.54184 \text{ \AA}$ ) radiation operated at 30 kV and 10 mA. The crystals were ground into fine powders for several times before the test. Energy dispersive spectroscopy (EDS) analysis were performed on scanning electron microscope (SEM) equipped with energy dispersive spectroscopy detector (ZEISS EVO 18). Elemental analysis (EA) of C, H, and N was performed on VARIO EL III elemental analyzer. Thermogravimetric Analysis (TGA) measurements was performed with a Shimadzu TGA-50 system under nitrogen flow with heating rate of  $10^\circ\text{C}/\text{min}$ .

### Synthesis of MCCF-22

A mixture of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (97 mg, 0.325 mmol),  $\text{SnCl}_2$  (57 mg, 0.3 mmol), S (96 mg, 3mmol), 1,2-DMP (3.0 mL) and EDA (1.0 mL) was stirred in a 23 mL Teflon-lined stainless steel autoclave for 20 minutes. Then the autoclave was sealed and reaction at  $180^\circ\text{C}$  for 7 days. Subsequently, the autoclave was cooled to room temperature. Those raw products were washed several times by ethanol and filtered off. Finally, light pink octahedral crystals were obtained (yield:  $\sim 65$  mg). Elemental analysis, *Calcd.* (wt %): C, 11.34; N, 10.47; H, 3.83; *Found* (wt %): C, 11.28; N, 10.39; H, 3.95.

### Synthesis of MCCF-23

A mixture of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (149 mg, 0.5 mmol),  $\text{SnCl}_2$  (57 mg, 0.3 mmol),  $\text{Sb}_2\text{O}_3$  (35 mg, 0.12 mmol), S (96 mg, 3 mmol), 1,2-DMP (1.0 mL), and AEP (3.0 mL) was stirred in a 23 mL Teflon-lined stainless steel autoclave for 20 minutes, then the autoclave was sealed and reaction in a  $180^\circ\text{C}$  oven for 8 days. Subsequently, the autoclave was cooled to room temperature. Those raw products were washed several

times by ethanol and filtered off. Finally, light pink block crystals were obtained (yield: ~24 mg). Elemental analysis, *Calcd.* (wt %): C, 20.95; N, 12.46; H, 4.79; *Found* (wt %): C, 21.05; N, 12.81; H, 4.93.

### **Single crystal X-ray diffraction characterization**

The single-crystal X-ray diffraction (SCXRD) measurements on **MCCF-22** and **MCCF-23** were carried out on a Bruker smart CPAD diffractometer controlled using graphite-monochromated Mo-K $\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation at 120 K under N<sub>2</sub>. The structures were solved by direct method using SHELXS-2014 and the refinements against all reflections of the compound were performed using SHELXS-2014. All the Zn, Sn, S, O, and Sb atoms were refined anisotropically. In these compounds, protonated amines were seriously disordered and could not be located. Therefore, we use the SQUEEZE routine of PLATON and refined further by using the data generated to remove the diffuse electron densities resulting from these molecules from the data. The CCDC number is 2036235 for **MCCF-22**, 2036236 for **MCCF-23**.

### **UV-Vis absorption measurement**

Room-temperature UV-Vis diffusion reflectance spectra of power samples were recorded on a SHIMADZU UV-3600 UV-Vis-NIR spectrophotometer. The absorption spectra were calculated from reflectance spectra by using the Kubelka-Munk function:  $F(R) = (1-R)^2/2R$ , where R is the reflection coefficient.

### **Preparation of ITO electrode of MCCF-22 and MCCF-23**

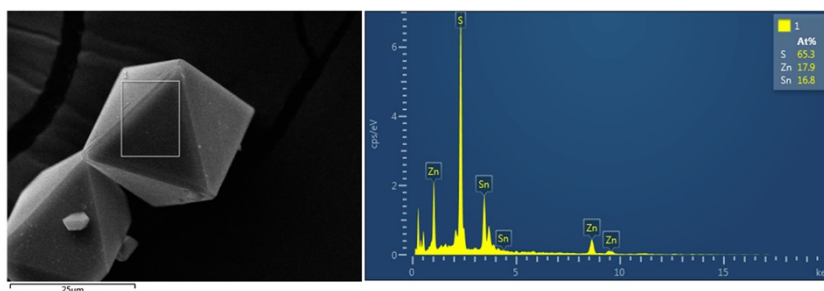
Typical preparation of ITO electrode of **MCCF-22** and **MCCF-23**: 25.0 mg of ground **MCCF-22** or **MCCF-23** powder were added to a solution of 5.0 mg Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O in 50 mL of isopropanol. The sealed mixture solution was stirred for 12h in the darkness, and then ultrasonically vibrated for 20 minutes before electrophoretic deposition. The clean and smooth Pt plate electrode and ITO conductive glass were used as anode and cathode, respectively. Constant working voltage was set up to 30 V and the entire electro-deposition process lasted for 30 minutes. Finally, the obtained ITO electrode was washed with ethanol three times in order to remove residual isopropanol and Mg(NO<sub>3</sub>)<sub>2</sub> salt left in the surface.

### **Transient photocurrent and electrochemical impedance spectroscopy measurement**

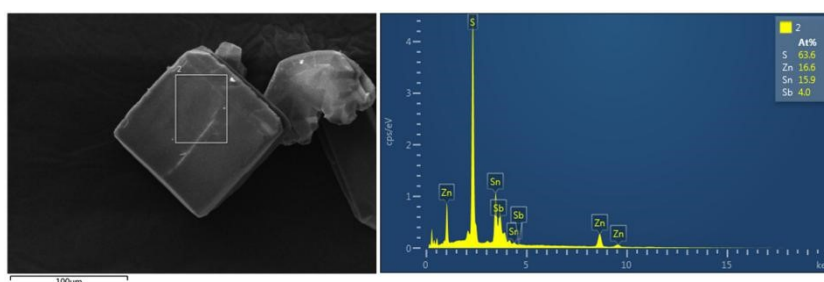
The transient photocurrent and electrochemical impedance spectroscopy (EIS) experiments were carried out on a CHI760E electrochemistry workstation in a standard three-electrode configuration. The sample coated ITO glass electrode (effective area about 1 cm<sup>2</sup>), the saturated calomel electrode (SCE), and the Pt plate electrode were used as the working electrode, reference electrode and auxiliary electrode, respectively. The light source is a 150 W high pressure xenon lamp with a horizontal of 25 cm away from the surface of the ITO working electrode. Sodium sulphate aqueous solution (0.5 M, 100 mL) was used as the supporting electrolyte.

### **MB Photodegradation Process**

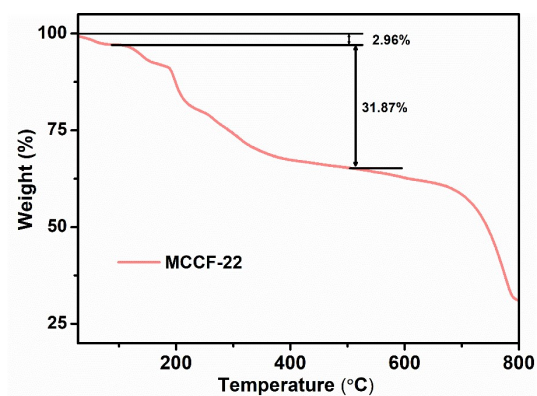
Under full-spectra irradiation, the catalytic activities of **MCCF-22** and **MCCF-23** were evaluated by the degradation reactions of MB dye. The power samples (5 mg) were immersed in 10 mL of MB ( $1.9 \times 10^{-5}$  mol·L<sup>-1</sup>) aqueous solution in a transparent glass sample bottle and stirred for 30 min and remained for 60 min before irradiation in the darkness to reach the adsorption/desorption equilibrium. During irradiation, 3 mL of suspension was sucked up from the reaction reactor at certain interval times and analyzed on a UV-1800 UV-vis spectrophotometer.



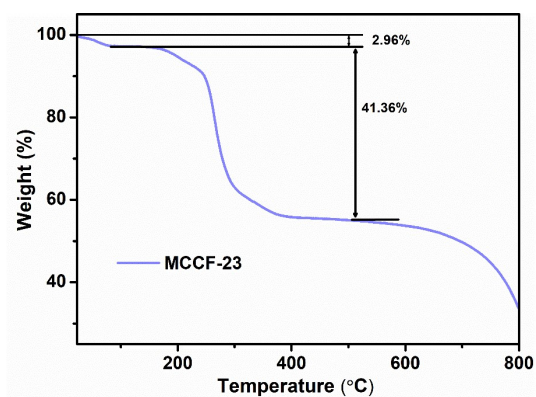
**Fig. S1** Left: SEM image of as-synthesized **MCCF-22**. Right: EDS of **MCCF-22**.



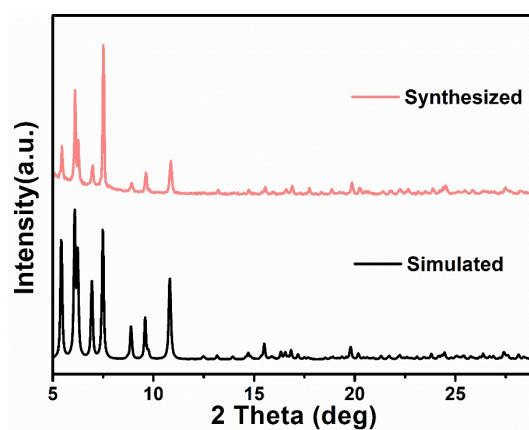
**Fig. S2** Left: SEM image of as-synthesized **MCCF-23**. Right: EDS of **MCCF-23**.



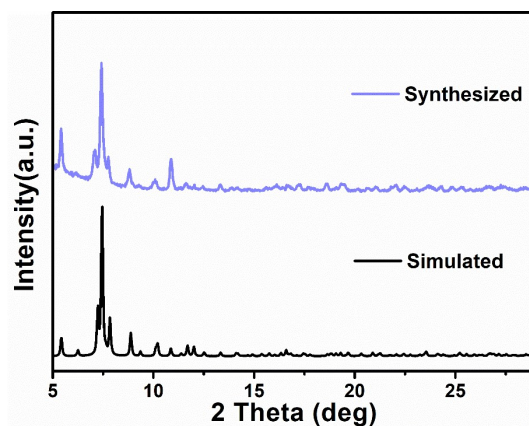
**Fig. S3** TGA curves of **MCCF-22**. The initial gradual weight loss of 2.96% between 25-100°C could be attributed to loss of moisture and solvent adsorbed on the surface of **MCCF-22**. A further abrupt weight loss of 31.87% between 100-500°C are attributed to the carbonization of template and the release of some  $\text{H}_2\text{S}$ .



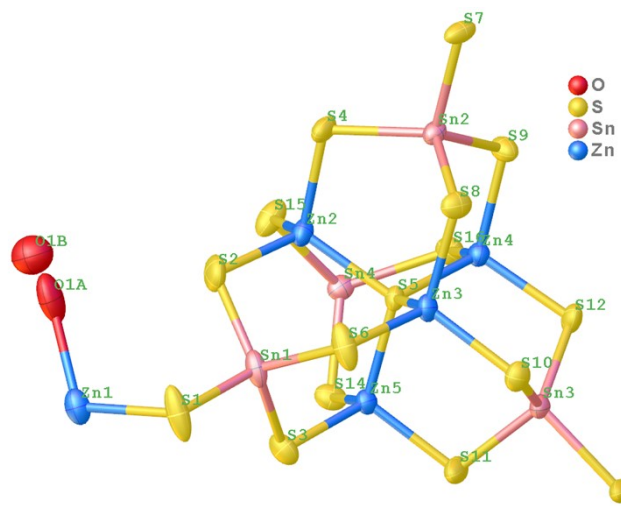
**Fig. S4** TGA curves of **MCCF-23**. The initial gradual weight loss of 2.96% between 25-100°C could be attributed to loss of moisture and solvent adsorbed on the surface of **MCCF-23**. A further abrupt weight loss of 41.36% between 200-500°C are attributed to the carbonization of template and the release of some H<sub>2</sub>S.



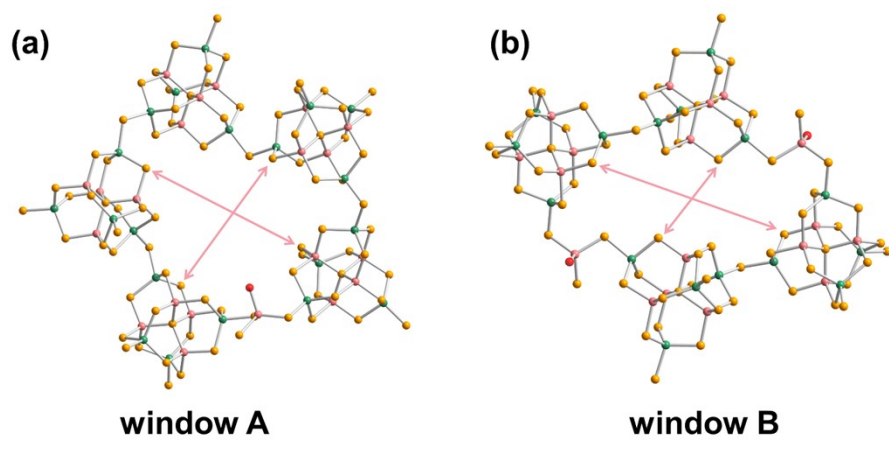
**Fig. S5** The simulated and experimental PXRD patterns of **MCCF-22**.



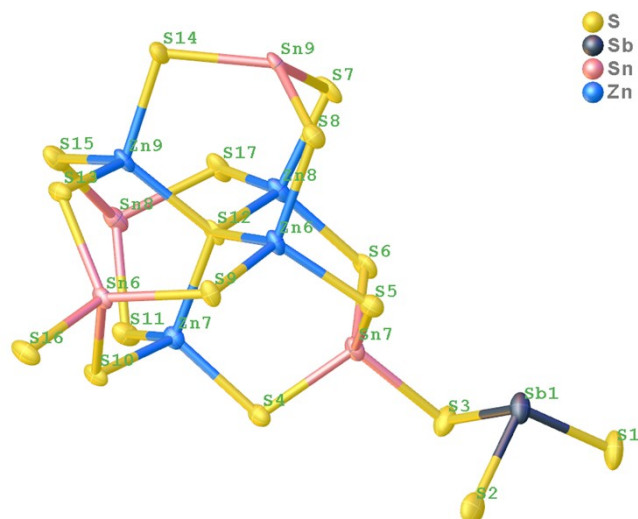
**Fig. S6** The simulated and experimental PXRD patterns of **MCCF-23**.



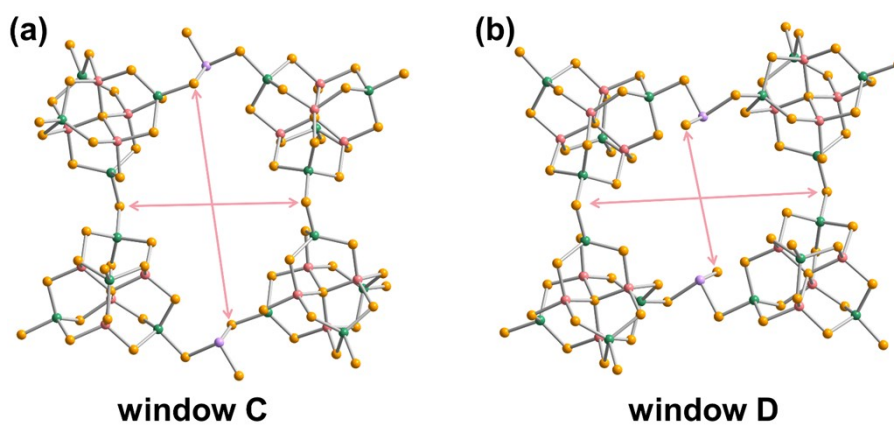
**Fig. S7** The crystallographically asymmetric unit in the framework of **MCCF-22**.



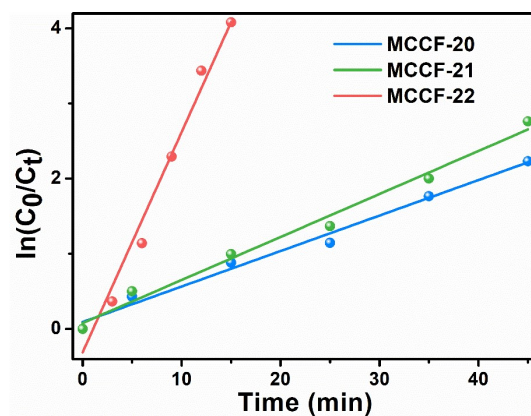
**Fig. S8** Two kinds of windows in **MCCF-22**.



**Fig. S9** The crystallographically asymmetric unit in the framework of **MCCF-23**.

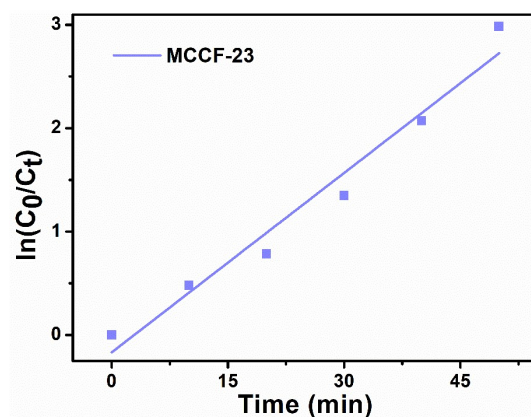


**Fig. S10** Two kinds of windows in **MCCF-23**.

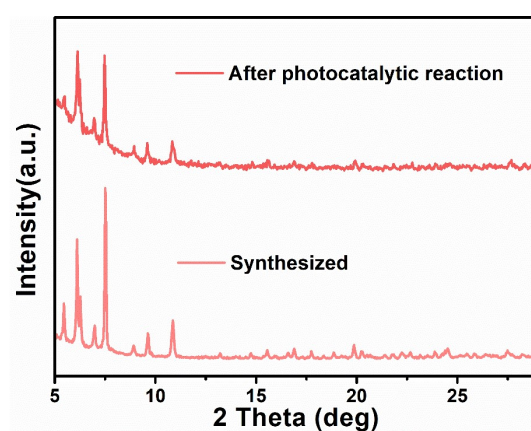


**Fig. S11** The calculated degradation rate of MB over **MCCF-22**, **MCCF-20**, and **MCCF-21**.

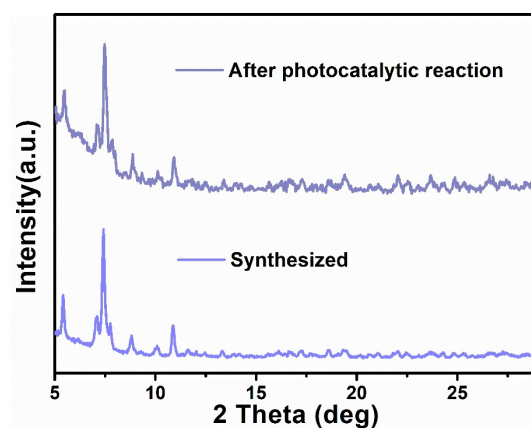




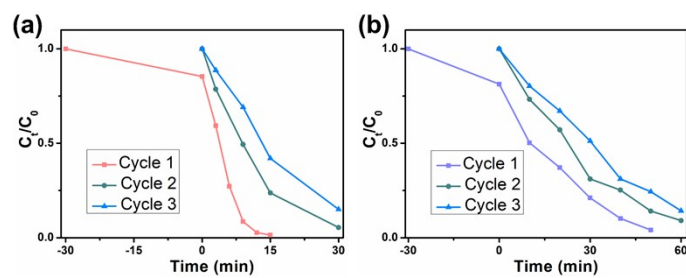
**Fig. S12** The calculated degradation rate of MB over **MCCF-23**.



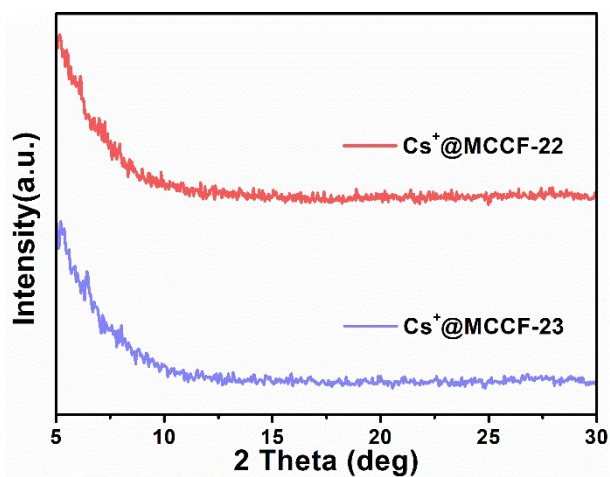
**Fig. S13** XRD patterns of **MCCF-22** before and after photocatalytic reactions.



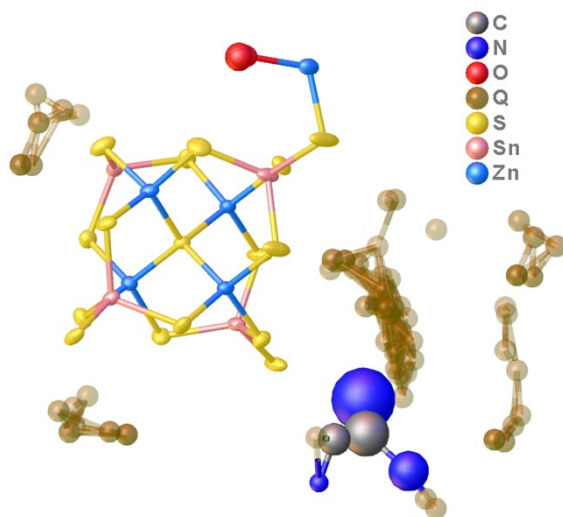
**Fig. S14** XRD patterns of **MCCF-23** before and after photocatalytic reactions.



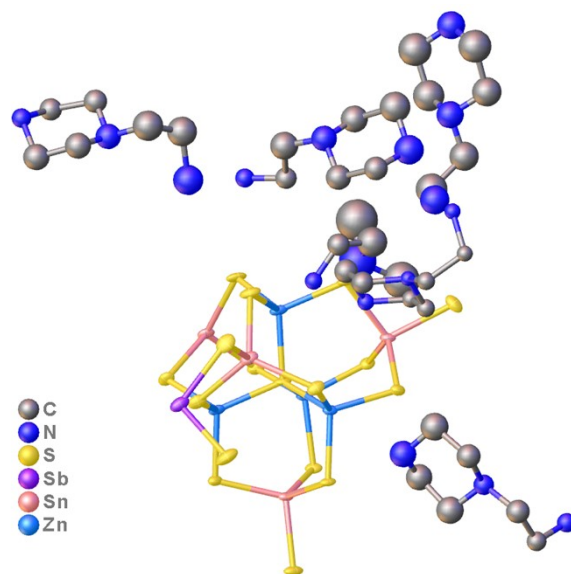
**Fig. S15.** Cycling tests of photocatalytic activity of (a) **MCCF-22** and (b) **MCCF-23**.



**Fig. S16.** PXRD patterns of **MCCF-22** and **MCCF-23** after  $Cs^+$  exchange.



**Fig. S17.** High disordered protonated amines in **MCCF-22**.



**Fig. S18.** The AEP molecules in **MCCF-23**.

**Table S1** Crystallographic data and structure refinement parameters of **MCCF-22** and **MCCF-23**.

Compounds	MCCF-22	MCCF-23
Crystal system	trigonal	monoclinic
<i>Z</i>	6	4
Space group	<i>R-3c</i> (No.167)	<i>P2<sub>1</sub>/c</i> (No.14)
<i>a</i> (Å)	28.3370(12)	16.8345(13)
<i>b</i> (Å)	28.3370(12)	17.3068(13)
<i>c</i> (Å)	87.124(2)	25.268(2)
$\alpha$ (deg.)	90	90
$\beta$ (deg.)	90	105.005(3)
$\gamma$ (deg.)	120	90
<i>V</i> (Å <sup>3</sup> )	60587(6)	7110.9(10)
<i>F</i> (000)	29832.0	4616.0
<i>T</i> (K)	120(2)	120(2)
<i>D</i> (g cm <sup>-3</sup> )	1.669	2.162
$\mu$ (mm <sup>-1</sup> )	3.480	3.629
Collected refls	106244	105462
Independent refls	12312	13072
GOF on <i>F</i> <sup>2</sup>	0.945	1.106
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> ( <i>I</i> > 2σ( <i>I</i> ))	0.0429, 0.0922	0.0947, 0.2077
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.0737, 0.1022	0.1115, 0.2151

$$R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|, wR_2 = [\sum w(F_0^2 - F_c^2)^2 / \sum w(F_0^2)^2]^{1/2}$$