Electronic Supplementary Material (ESI) for CrystEngComm

List of figures and tables in Supporting Information

Synthesis of UiO-66: The chemicals and solvent used in the synthesis process were DMF (dimethylformamide, 99%), BDC (1,4-benzenedicarboxylic acid, 98.9%) and ZrCl4. All reagents and solvents were used as received from commercial suppliers without further purification. 0.053g of ZrCl4 and 0.034g BDC were mixed in 18ml of DMF for a solvothermal process in an autoclave at 393 K for 24 h. Then as-synthesized Zr-MOF was immersed in DMF for 5 d. After separation by centrifugation, the solid sample was dried under vacuum at 463 K for 48 h. In order to remove the solvent molecules from the framework, the sample were treated at 573k for 24h under N_2 flow to form the final product (calcined UiO-66). The structure was stable during the heat treatment. (Figure S1)

Figure S1 Powder X-ray diffraction (PXRD) of as synthesized (red) and calcined (blue) UiO-66 samples.

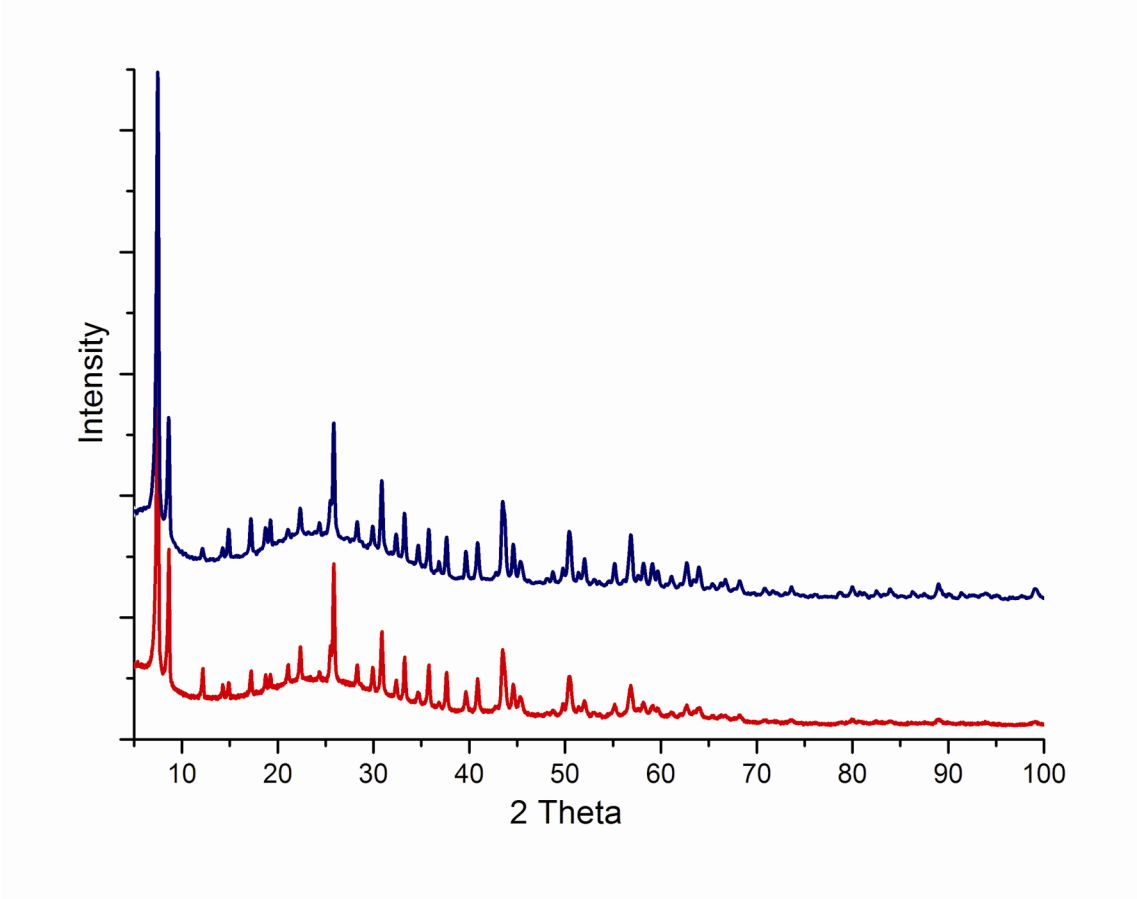


Figure S2 TEM image of synthesized UiO-66

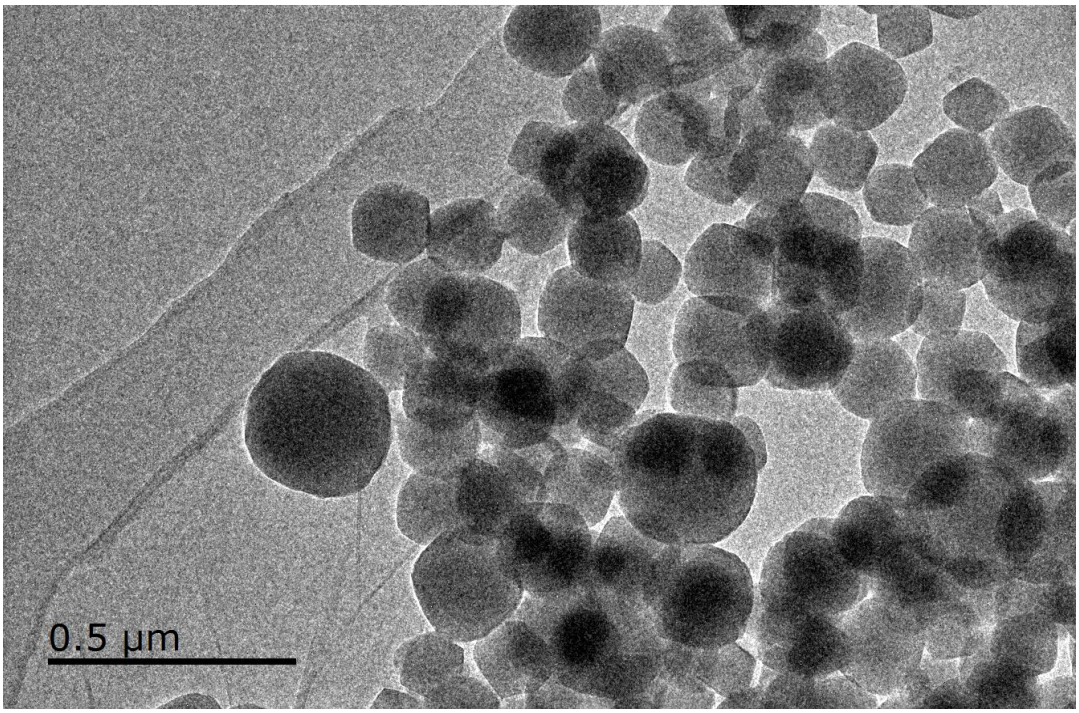


Figure S3 Reconstructed reciprocal lattices for a unit cell determination

Screen copy of RED software shows a dataset with 576 ED frames from 115° rotation range. Only strong reflections were used in the lattice refinement.

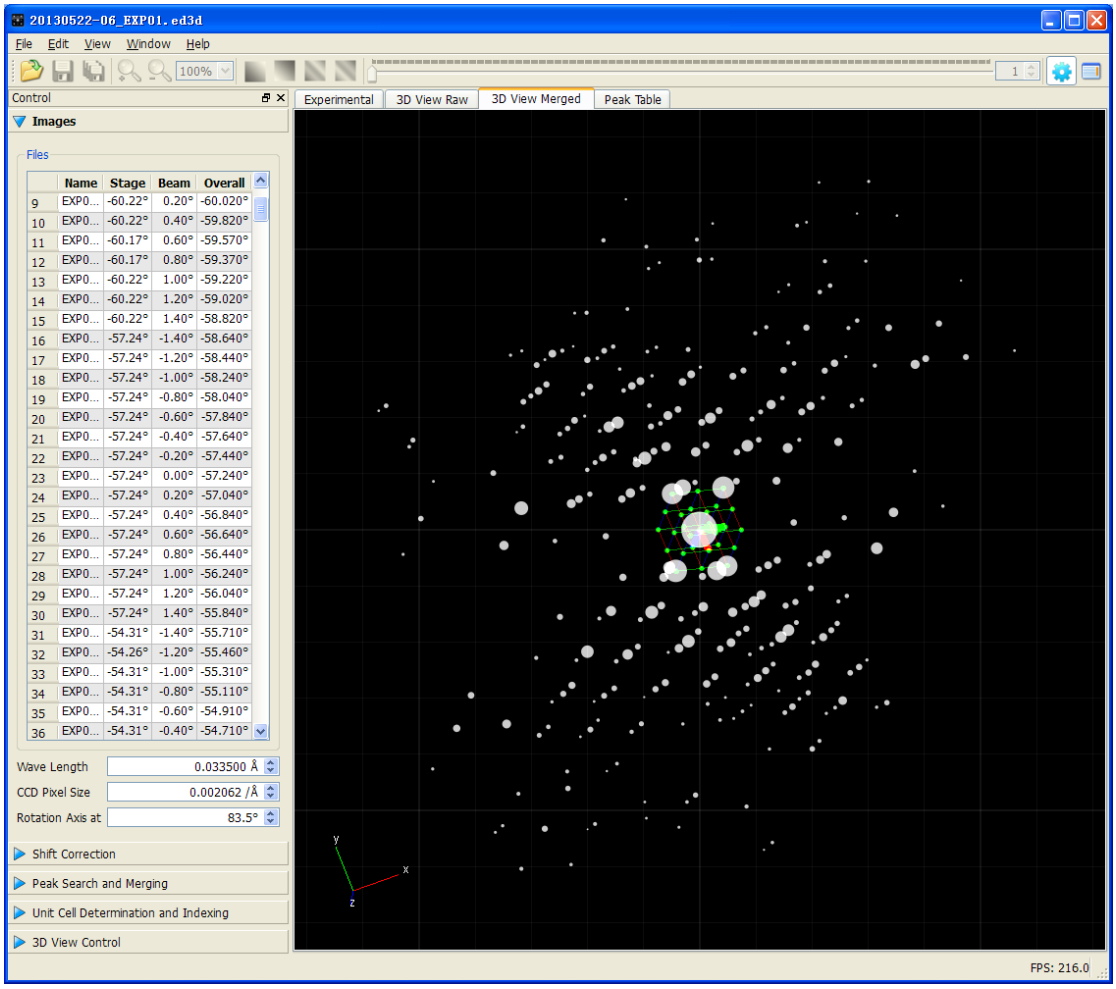


Figure S4 Image processing and projection symmetry determination

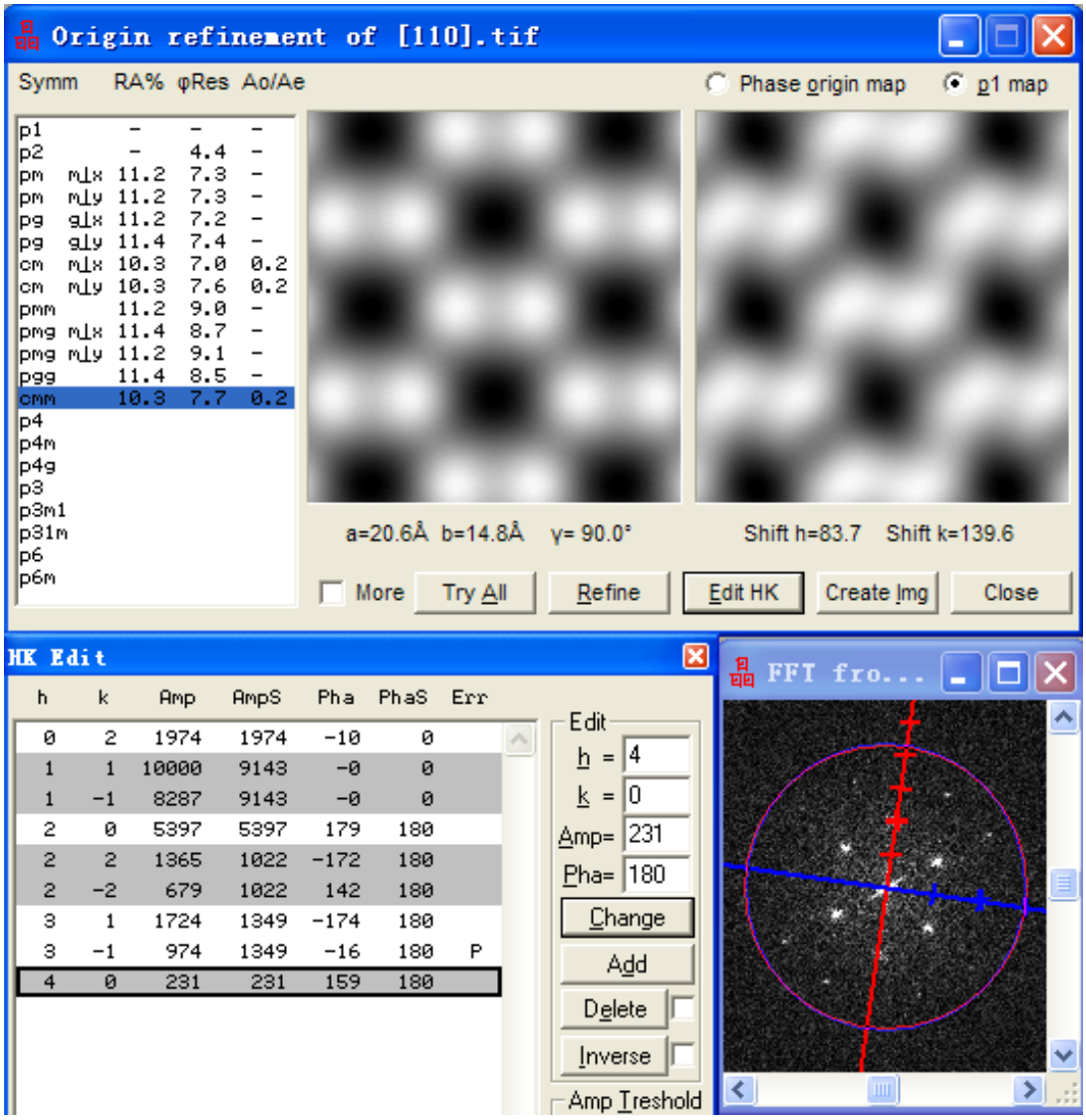


Figure S5 N_2 adsorption isotherm

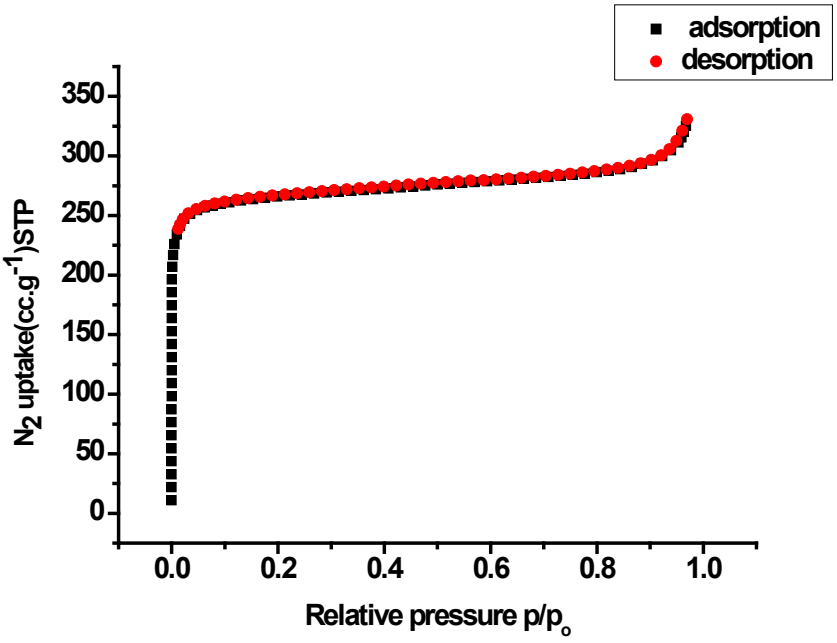
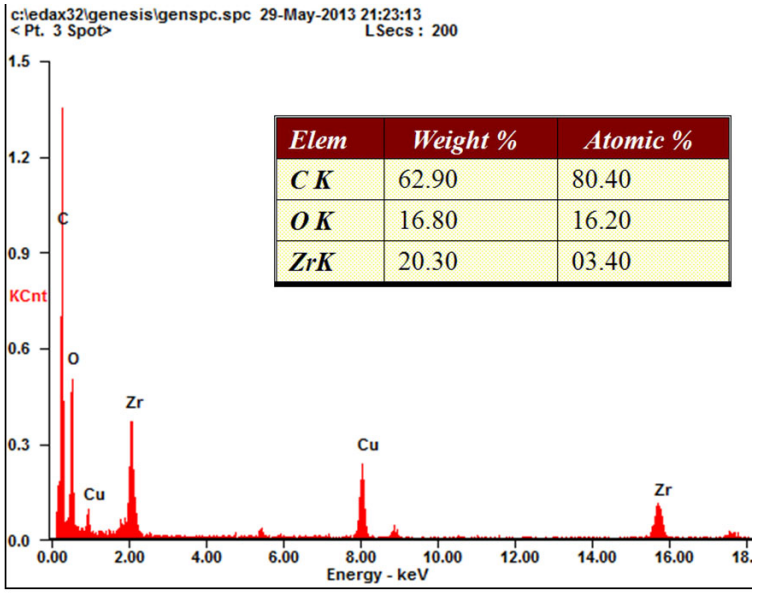


Figure S6 Energy-dispersive X-ray spectroscopy (EDS) analysis for UiO-66 suggested an O/Zr atomic ratio about 4.8. The C peak was influenced by the TEM grid.



Elem	Weight %	Atomic %
C K	62.90	80.40
O K	16.80	16.20
ZrK	20.30	03.40

Structure solution and refinement of PXRD： The structure model resolved from EDT was used as the starting model of refinements. Rietveld refinements resulted in a crystal structure model indicator (R = 0.065) and profile factors (RP = 0.049 and RWP = 0.064). Figure S7 shows the observed, calculated and difference diffraction profiles from the Rietveld analysis of UiO-66. Table S4 and Table S5 list the crystallographic data and atom coordinates.

Figure S7 Final Rietveld plots of the calcined UiO-66 showing observed (pink line), calculated (yellow line), and difference (white line) curves.

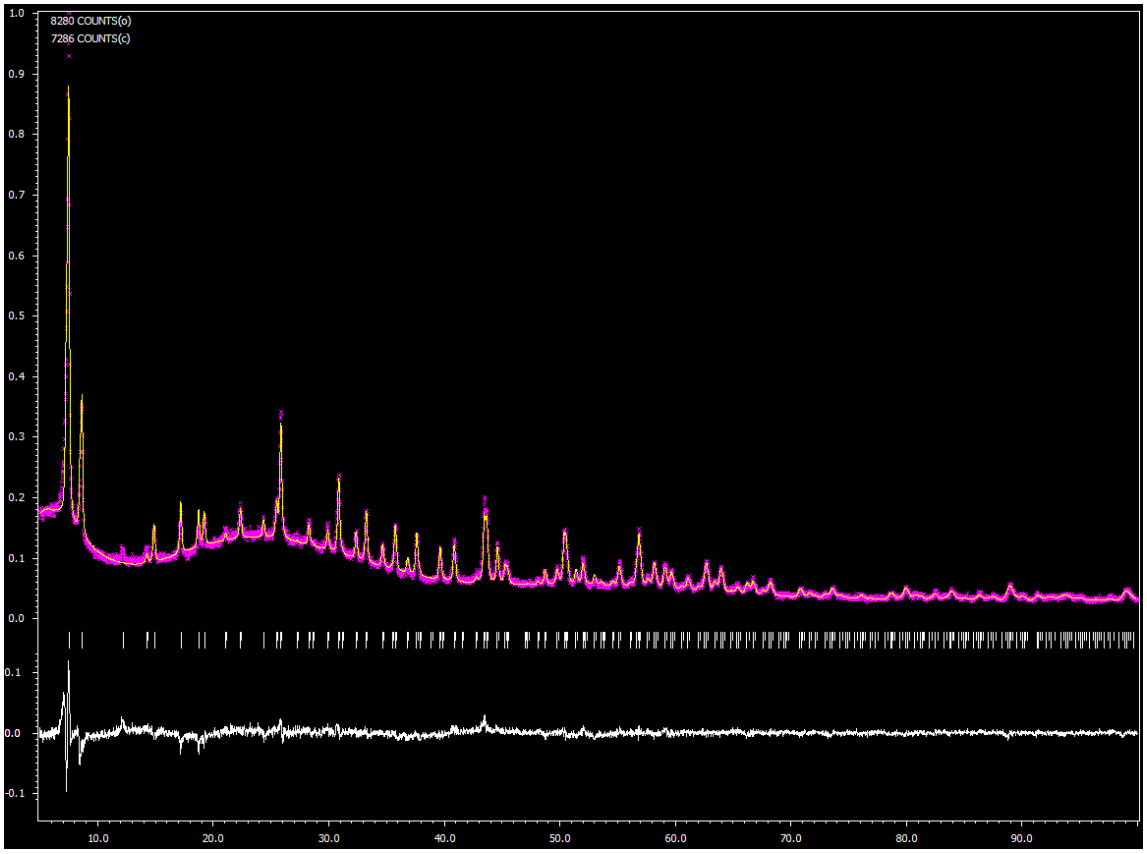


Table S1. Observed reflections from HRTEM

2D index		3D index			Deduced amplitudes and phases from *cmm* plane group				
H	K	h	k	l	Amp_{exp}	$Amp_{cal}{}^{\$}$	Pha_{exp}	$Pha_{cal}{}^{\$}$	*d*
0	2	2	-2	0	1974	1974	-10	0	7.35
1	1	1	-1	1	10000	9143	0	0	12.01
1	-1	-1	1	1	8287	9143	0	0	12.01
2	0	0	0	2	5397	5397	179	180	10.40
2	2	2	-2	2	1365	1022	-172	180	6.00
2	-2	-2	2	2	679	1022	142	180	6.00
3	1	1	-1	3	1724	1349	-174	180	6.27
3	-1	-1	1	3	974	1349	-16	180	6.27
4	0	0	0	4	231	231	159	180	5.20

Amp_{exp} and Pha_{exp}, experimental amplitudes and phases

$Amp_{cal}{}^{\$}$ and $Pha_{cal}{}^{\$}$ symmetry deduced amplitudes and phases

Although the (004) reflection was observed in a weak amplitude, it was considered in the reconstruction of 3D potential map because of the acceptable phase residual.

Table S2: EDT data collection, crystal data and structure refinement information of UiO-66

Tilt angle (°)	-60.00 to +55.00
Tilt step (°)	0.2
No. of RED frames	576
Exposure time/frame (s)	3.0
a (Å)	20.1346
b (Å)	20.296
c (Å)	20.5957
α (°)	89.1785
β (°)	89.7794
γ (°)	89.3767
Completeness (d ≥ 0.90 Å) (%)	68.1
Completeness (d ≥ 1.10 Å) (%)	99.6
R_{int}	0.1623
No. of non-zero reflections	542
No. of independent reflections	262 (Theory No.: 385)
h	$-12 \le h \le 14$
k	$-14 \le k \le 16$
l	$-4 \le l \le 8$
The second dataset:	
Tilt angle (°)	-60.00 to +50.00
Tilt step (°)	0.2
No. of RED frames	550
Exposure time/frame (s)	3.0
a (Å)	20.2960
b (Å)	20.0968
c (Å)	20.5826
α (°)	90.2799
β (°)	90.8565
γ (°)	89.4241
Completeness (d ≥ 1.45Å) (%)	100
Completeness (d ≥ 1.14Å) (%)	61.6
No. of non-zero reflections	386
No. of independent reflections	109 (Theory No.: 177)
h	$-17 \le h \le 14$
k	$-8 \le k \le 8$
l	$-15 \le l \le 13$

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Crystallographic information

Formula	$Zr_{24}\ O_{120}\ C_{192}\ H_{96}$
Z	1
Number of unique atoms	6
Space group	*Fm*-3*m*
Refined cell parameter: *a* (Å)	20.7782 (from PXRD)
*R*1 (The first dataset)	0.35
*R*1 (Merged dataset)	0.32
Data for Refinement (Å)	$2.5 \leq d \leq 1.38$

Table S3: Atom positions, selected bond lengths and angles from the EDT structure solution.

Atom positions

Atom	*x*	*y*	*z*	*U*(eq)	*site occupancy*
C(3)	0.1994(1)	0.5000	0.3006(1)	0.156(4)	1
C(2)	0.2670(3)	0.5000	0.3157(4)	0.156(4)	1
C(1)	0.1484(1)	0.5000	0.3516(1)	0.156(4)	1
O(1)	0.1738(3)	0.5000	0.4092(2)	0.102(5)	1
O(2)	0.0695(4)	0.5695(4)	0.5695(4)	0.160(16)	0.75
Zr	0.1210(3)	0.5000	0.5000	0.076(3)	1

Selected bond lengths (Å)

Zr - O2	2.308(7)
Zr – O1	2.184(5)
O1 - C1	1.310(5)
C1 – C3	1.501(4)
C2 – C3	1.441(6)
C2 – C2	1.431(13)

Selected angles (°)

C2 – C3 – C2	115.2(7)
C2 – C3 – C1	122.4(3)
O1 – C1 – O1	137.6(6)
O1 – C1 – C3	111.2(3)

Table S4. Information for the Rietveld refinement of PXRD

Formula	$Zr_{24}\ O_{120}\ C_{192}\ H_{96}$
Formula weight	6512.10
Temperature (K)	298
Wavelength (Å)	1.5405981
Range of 2θ (°)	5-100
Space group	*Fm*-3*m* (225)
Cell parameter *a* (Å)	20.7782(7)
Volume ($Å^3$)	8970.7(5)
Z	1
Number of unique atoms	6
R_p	0.049
R_{wp}	0.064
R	0.065

Table S5. A comparison of atom positions resolved from PXRD and EDT

	Coordination table from Rietveld refinement (PXRD)			Differences of atom positions (EDT *vs* PXRD)		
	x	*y*	*z*	Δx	Δy	Δz
C3	0.2004(3)	0.5000	0.2996(3)	0.0010	0.0000	0.0010
C2	0.2673(4)	0.5000	0.3176(3)	0.0003	0.0000	0.0019
C1	0.1480(3)	0.5000	0.3520(3)	0.0004	0.0000	0.0004
O1	0.1757(4)	0.5000	0.4092(2)	0.0019	0.0000	0.0000
O2	0.0590(6)	0.5590(6)	0.5590(6)	0.0105	0.0105	0.0105
Zr	0.1190(2)	0.5000	0.5000	0.0020	0.0000	0.0000