Supporting Information

Structural Variety in Calcium Metal-Organic Frameworks with a Tetratopic Carboxylate Ligand

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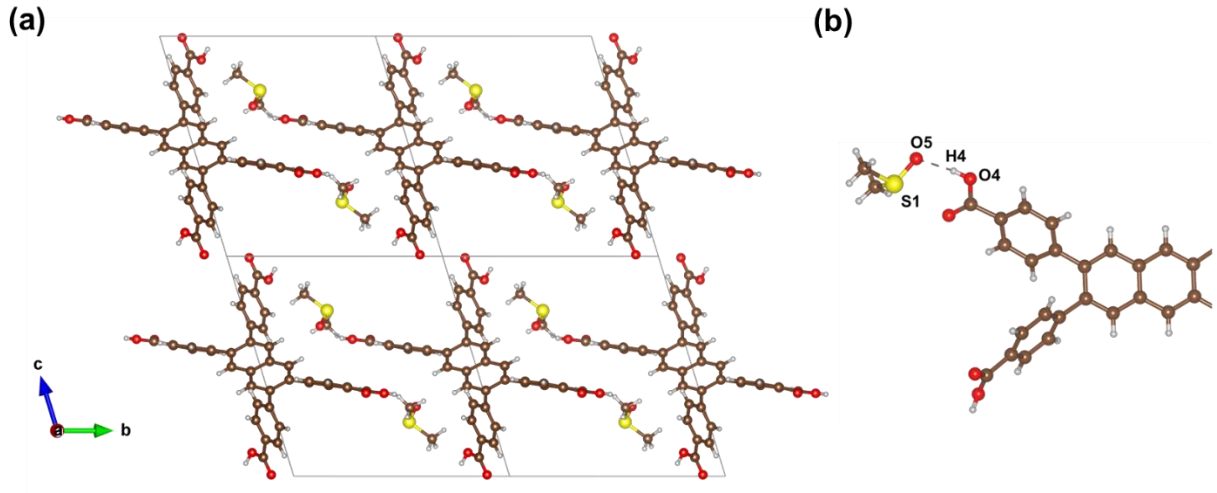

Figure S1. (a) Crystal structure of ligand $[H_4NTTB](DMSO)_2$ viewed from *a* crystallographic axis. (b) Coordination environment of carboxylic acid group to DMSO. Hydrogen bond interaction between the hydroxyl group of the carboxylic acid and the oxygen atom of DMSO (O4-H···O5), with an intermolecular distance of 2.59 Å. Atom colour scheme: carbon (brown), hydrogen (light gray), oxygen (red), sulfur (yellow).

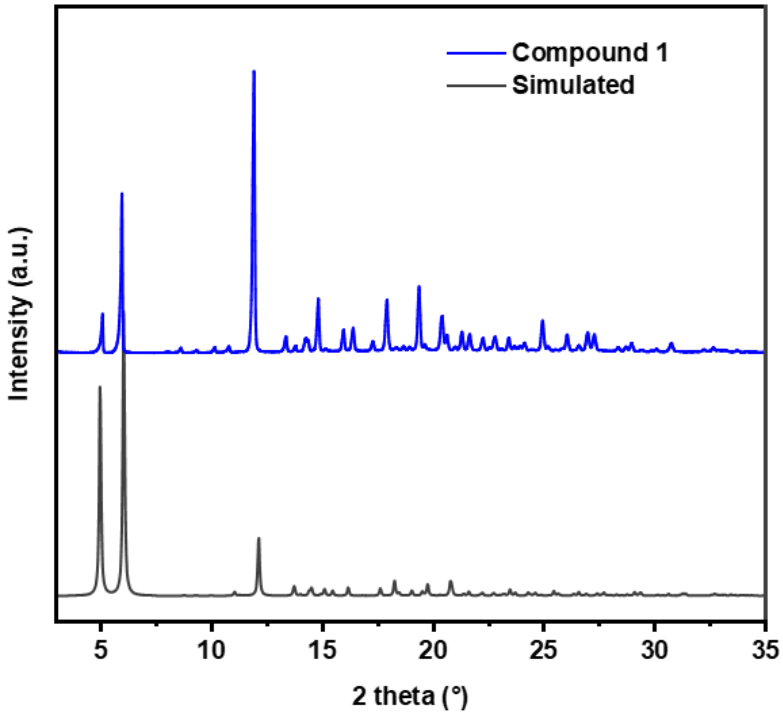

Figure S2. Powder XRD pattern of as-synthesised compound **1** compared with simulated pattern from the single-crystal structure.

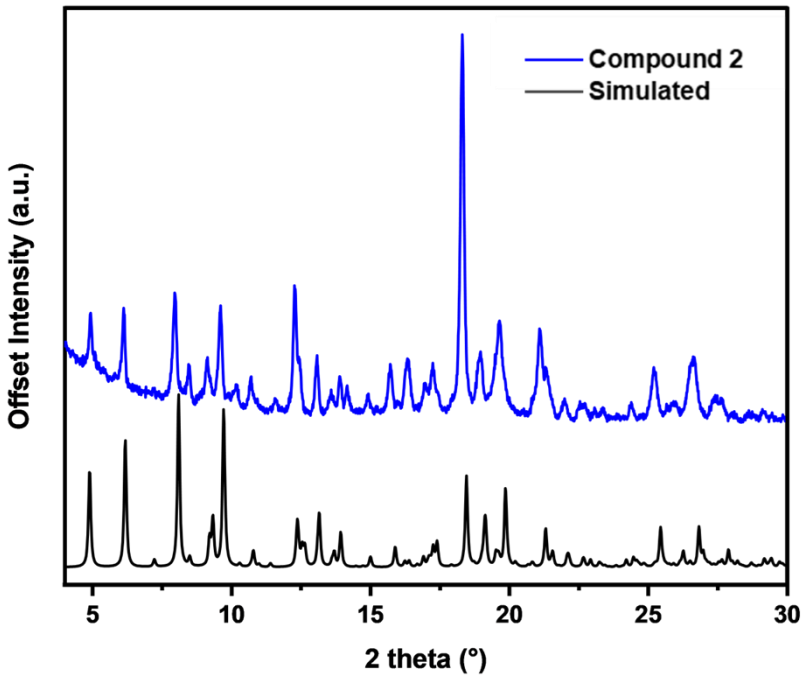

Figure S3. Powder XRD pattern of as-synthesised compound **2** compared with simulated pattern from the single-crystal structure.

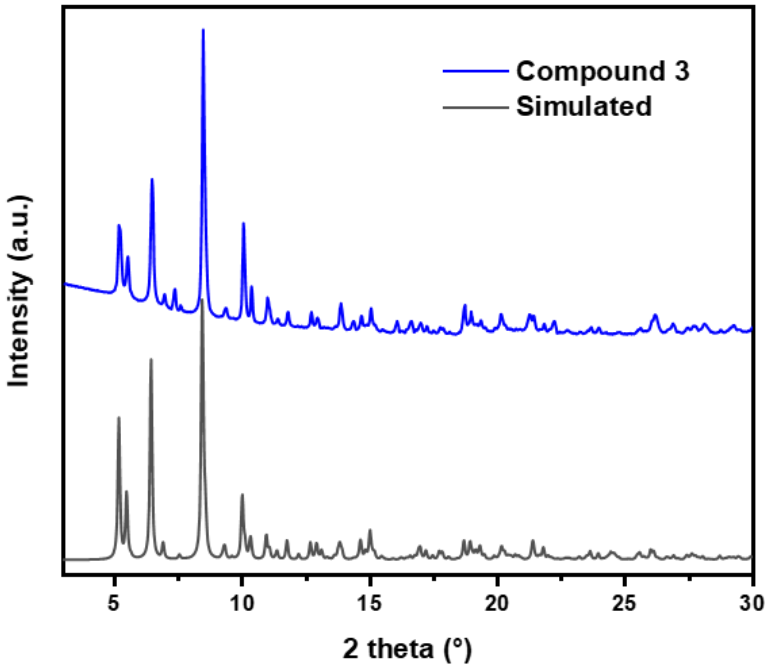

Figure S4. Powder XRD pattern of as-synthesised compound **3** compared with simulated pattern from the single-crystal structure.

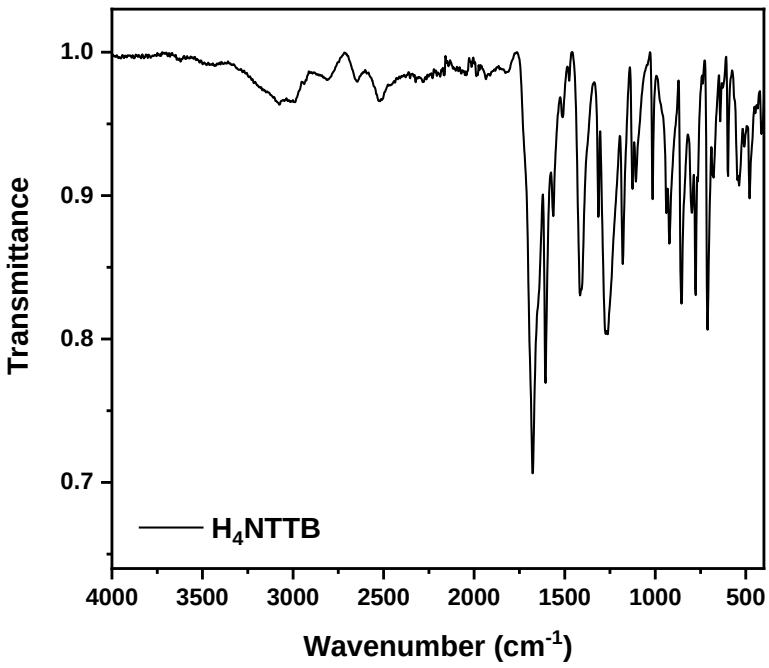

Figure S5. IR spectra of H_4NTTB(DMSO)$_2$.

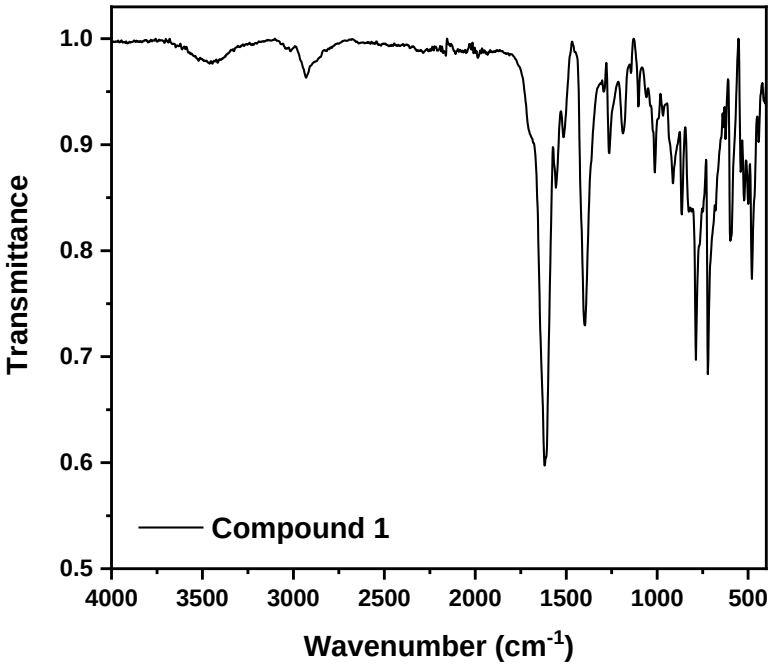

Figure S6. IR spectra of compound **1**.

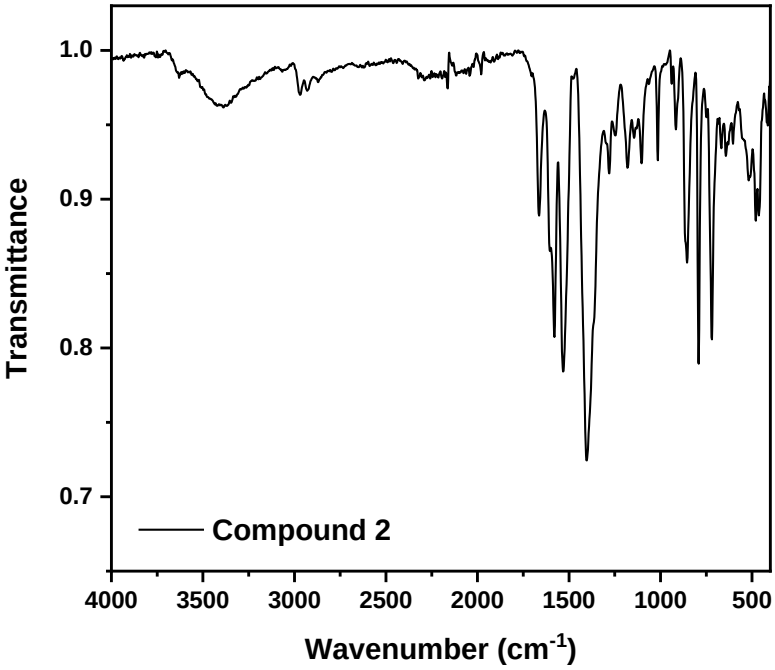

Figure S7. IR spectra of compound **2**.

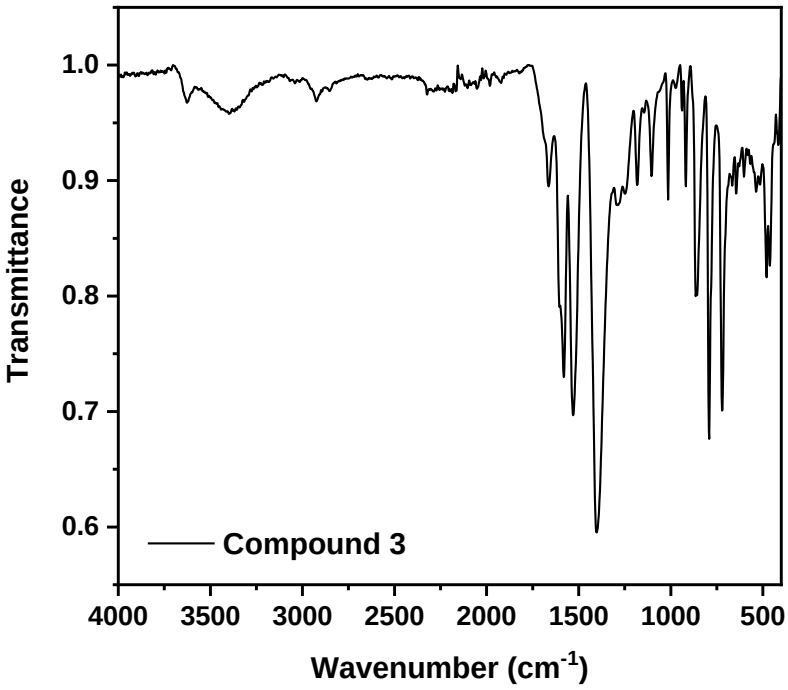

Figure S8. IR spectra of compound **3**.

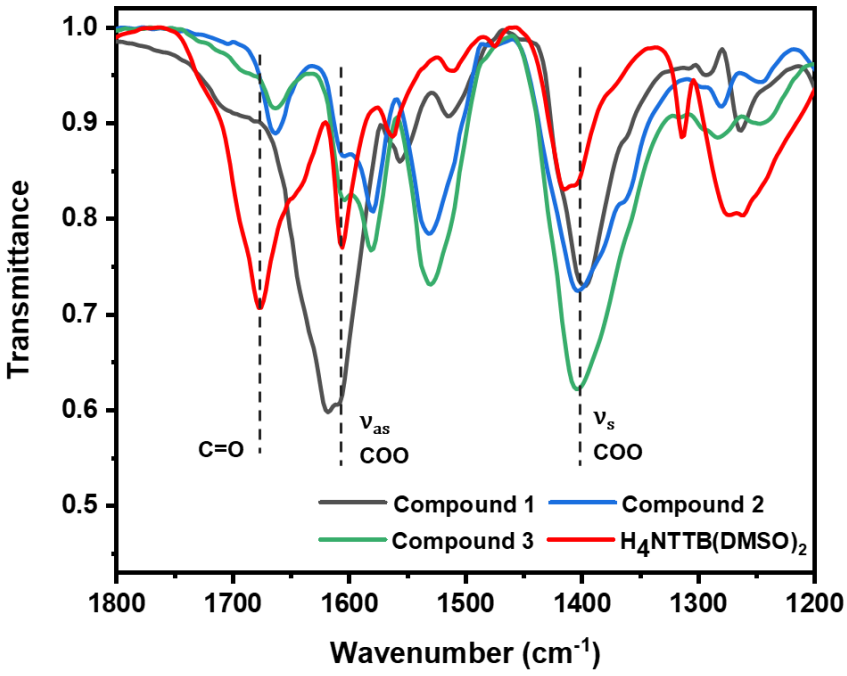

Figure S9. Carboxylate region of the IR spectra.

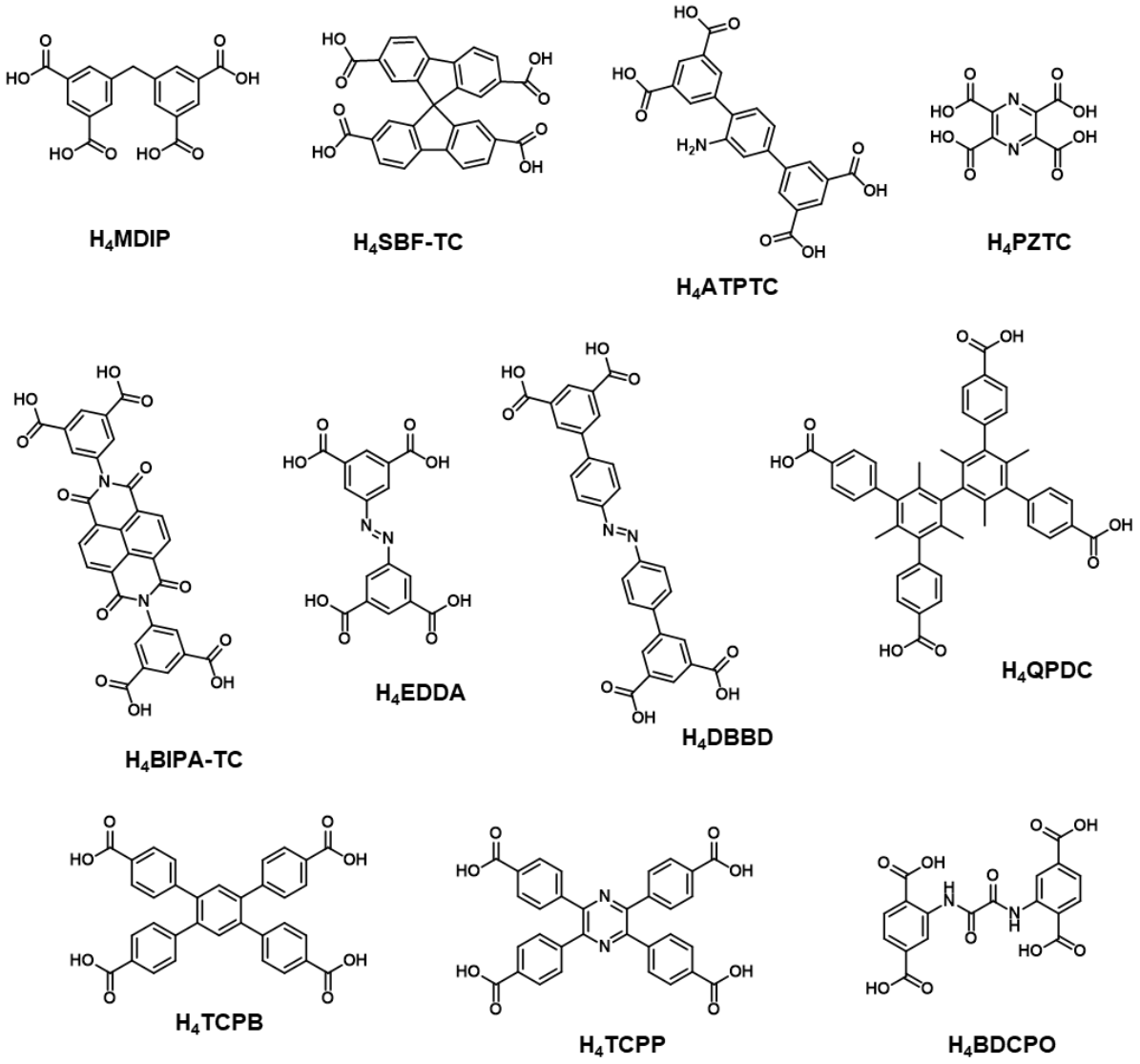

Figure S10. Tetracarboxylic acid linkers used for Ca MOFs. H_4MDIP = 5,5'-methylenediisophthalic acid, H_4SBF-TC = 9,9′-spirobi[9H-fluorene]-2,2′,7,7′-tetracarboxylic acid, H_4ATPTC = 2'-amino-[1,1':4',1"-terphenyl]-3,3",5,5"-tetracarboxylic acid, H_4PZTC = pyrazine-2,3,5,6-tetracarboxylic acid, H_4BIPA-TC=5,5'-(1,3,6,8 tetraoxobenzo[lmn][3,8] phenanthroline-2-7-diyl)bis-1,3-benzene dicarboxylate, H_4EDDA = (E)-5,5′-(diazene-1,2-diyl) diisophthalic acid, H_4DBBD = (E)-4′,4‴-(diazene-1,2-diyl)bis(([1,1′-biphenyl]-3,5-dicarboxylic acid)), H_4QPDC = 5',5''-bis(4-carboxyphenyl)-2',2'',4',4'',6',6''-hexamethyl-[1,1':3',1'':3'',1'''-quaterphenyl]-4,4'''-dicarboxylic acid, H_4TCPB = 1,2,4,5-tetrakis(4-carboxyphenyl)benzene, H_4TCPP = 2,3,5,6-tetrakis(4-carboxyphenyl)-pyrazine, H_4BDCPO = N,N'-bis(2,4-dicarboxyphenyl)-oxalamide

Table S1. Refined lattice parameters of as-synthesised structures from powder diffraction.

Compound	**1**	**2**	**3**
Crystal system	monoclinic	triclinic	triclinic
Space group	*C*2/*c*	$P\bar{1}$	$P\bar{1}$
a [Å]	19.0999(44)	11.1743(23)	18.5258(37)
b [Å]	34.9893(11)	14.7249(70)	19.2690(23)
c [Å]	10.7928(17)	18.3581(50)	20.9806(55)
α [°]	90	98.988(38)	65.837(4)
β [°]	120.406(4)	91.779(14)	67.884(8)
γ [°]	90	99.277(2)	85.359(6)
V [Å^3]	6220.73(20)	2939.64(98)	6306.73(32)
R_{wp} [%]	16.6	6.4	7.2
GoF	9.7	2.1	2.3

Table S2. Crystal data and structure refinement details

Compound	**Ligand solvate**	**1**	**2**	**3**
Chemical structure	$H_4NTTB(DMSO)_2$	$Ca(H_2NTTB)(DMA)_2$	$Ca_5(H_2NTTB)(NTTB)_2(H_2O)_8$	$Ca_5(H_2NTTB)(NTTB)_2(H_2O)_5$
Empirical formula	$C_{42}H_{36}O_{10}S_2$	$C_{46}H_{40}CaN_2O_{10}$	$C_{114}H_{78}Ca_5O_{43.8}$	$C_{114}H_{60}Ca_5O_{29}$
Formula weight	764.83	820.88	2348.96	2094.02
Temperature/K	292(2)	100.00(10)	100.00(10)	100(2)
Crystal system	triclinic	monoclinic	triclinic	triclinic
Space group	$P\bar{1}$	*C2/c*	$P\bar{1}$	$P\bar{1}$
a /Å	6.8684(2)	18.6216(6)	11.0429(4)	18.6030(6)
b /Å	13.8322(4)	35.2831(8)	14.6332(5)	19.2334(7)
c /Å	14.4683(5)	10.5028(3)	18.2349(4)	20.9801(7)
α /°	105.538(2)	90	99.017(2)	66.031(4)
β /°	95.126(2)	120.910(3)	91.928(2)	67.392(3)
γ /°	101.433(2)	90	99.224(3)	85.309(3)
Volume /Å^3	1283.19(7)	5920.6(3)	2867.36(16)	6307.5(4)
Z	1	4	1	2
ρ_{calc} g/cm^3	0.990	0.921	1.36	1.103
μ /mm^{-1}	0.148	0.157	2.794	2.397
F(000)	400	1720	1212	2152
Crystal size /mm^3	0.3 × 0.24 × 0.06	0.02 x 0.01 x 0.01	0.2 × 0.1 × 0.02	0.05 × 0.02 × 0.01
Radiation	Mo Kα (λ = 0.71073)	Synchrotron (λ = 0.7293)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2θ range for data collection /°	3.630 to 60.074	4.738 to 55.334	7.256 to 130.178	5.468 to 144.224
Index ranges	-9 ≤ h ≤ 9, -19 ≤ k ≤ 19, -20 ≤ l ≤ 20	-23 ≤ h ≤ 23, -43 ≤ k ≤ 44, -13 ≤ l ≤ 13	-12 ≤ h ≤ 12, -17 ≤ k ≤ 17, -21 ≤ l ≤ 21	-22 ≤ h ≤ 22, -23 ≤ k ≤ 23, -25 ≤ l ≤ 25
Reflections collected	72848	29282	81485	121745
Independent reflections	7485 [R_{int} = 0.059, R_{sigma} = 0.0429]	5127 [R_{int} = 0.2119, R_{sigma} = 0.1908]	9722 [R_{int} = 0.0793, R_{sigma} = 0.0351]	24702 [R_{int} = 0.1301, R_{sigma} = 0.0813]
Data/restraints/parameters	7485/0/248	5127/0/275	9722/44/795	24702/171/1472
Goodness-of-fit on F^2	1.046	0.954	1.035	0.999
Final R indexes [I>=2σ (I)]	R_1 = 0.0724, wR_2 = 0.2249	R_1 = 0.1065, wR_2 = 0.2801	R_1 = 0.0726, wR_2 = 0.2062	R_1 = 0.0900, wR_2 = 0.2569
Final R indexes [all data]	R_1 = 0.0876, wR_2 = 0.2456	R_1 = 0.1461, wR_2 = 0.3090	R_1 = 0.0868, wR_2 = 0.2192	R_1 = 0.1415, wR_2 = 0.2988
Largest diff. peak/hole / e Å^{-3}	0.589/-0.318	0.43/-0.81	0.81/-0.94	0.87/-1.14
CCDC reference	2421323	2421320	2421321	2421322