Variation of Topologies and Entanglements in Metal-Organic Frameworks with mixed tris[4-(1H-imidazol-1-yl)phenyl]phosphine oxide and dicarboxylate ligands

Yingying Sun,[†] Xiaojie Chen,[‡] Fengyuan Wang,[†] Ruidan Ma,[†] Xianmin Guo,*[,†] Shaowen Sun,[†] Huadong Guo,*[,†] and Eugeny V. Alexandrov *[,§,‖]

[†]*Department of Chemistry, Changchun Normal University, Changchun 130032, People's Republic of China*

‡ *State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, Changchun 130012, People's Republic of China*

§ *Samara State Technical University, Molodogvardeyskaya St. 244, Samara 443100, Russia*

‖ *Samara Center for Theoretical Material Science (SCTMS), Samara University, Moskovskoe shosse 34, 443086 Samara, Russia*

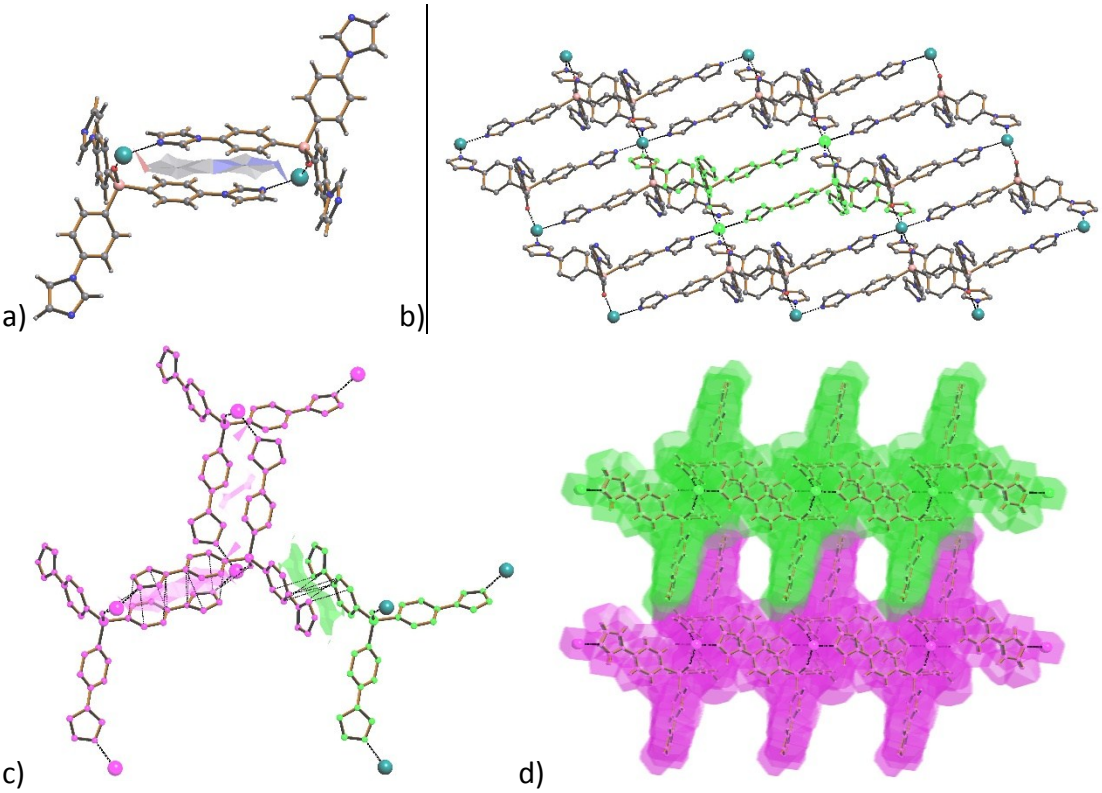

Fig. S1. The 4-ring $\{Cd(tipo\text{-}O)\}_2$ (a), Cd-tipo layer (b), environment of tipo ligand (c), and packing of Cd-tipo layers (d) in compound 2.

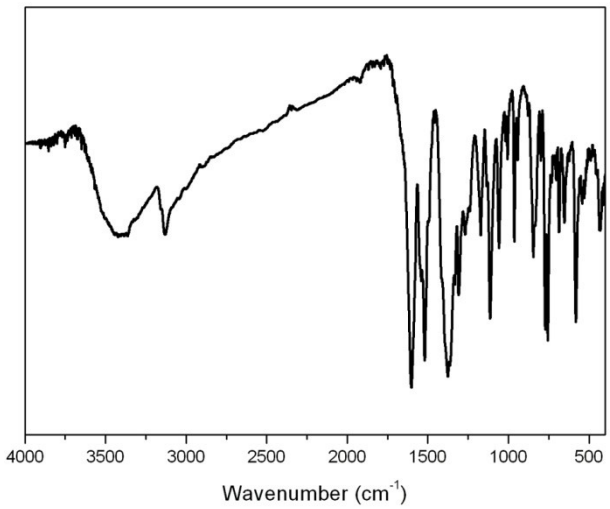

Fig. S2. IR spectra for as-synthesized **1**.

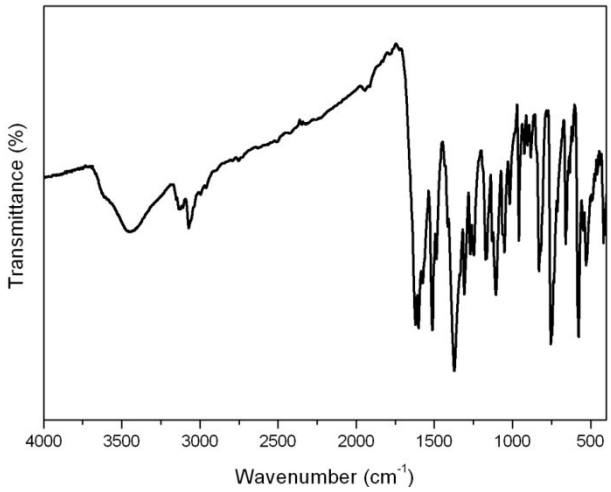

Fig. S3. IR spectra for as-synthesized **2**.

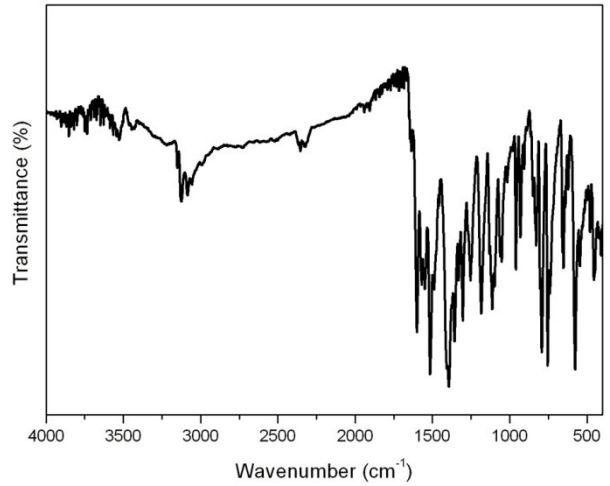

Fig. S4. IR spectra for as-synthesized **3**.

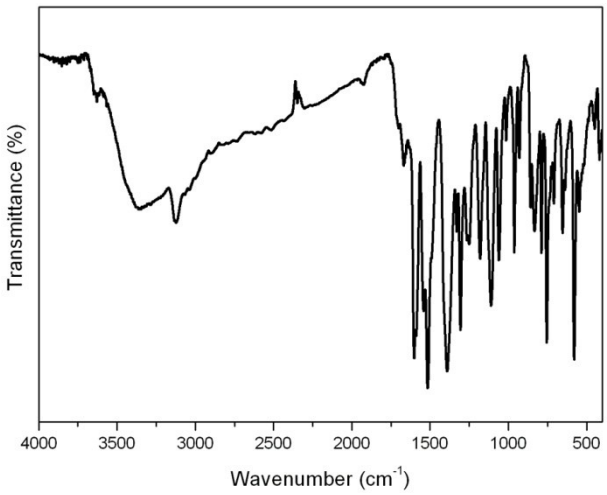

Fig. S5. IR spectra for as-synthesized **4**.

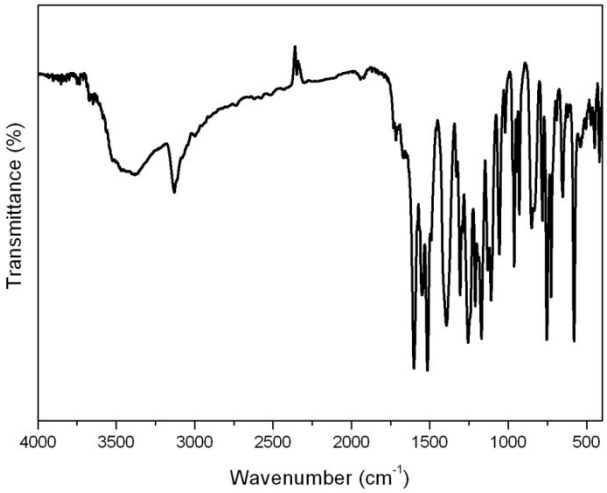

Fig. S6. IR spectra for as-synthesized **5**.

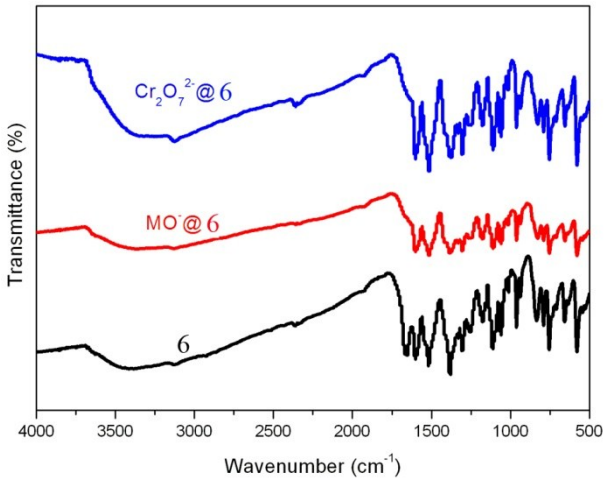

Fig. S7. IR spectra for: as-synthesized **6**, MO^-@**6** obtained in a 5.0×10^{-5} M aqueous solution for 20 minutes and $Cr_2O_7^{2-}$@**6** obtained in a 200 mg/L $K_2Cr_2O_7$ aqueous solution for 20 minutes.

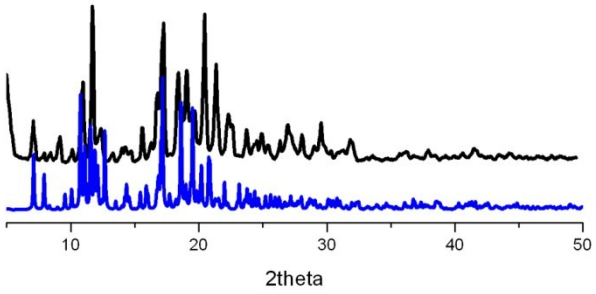

Fig. S8. PXRD patterns of the simulated **1** (blue), as-synthesized **1** (black).

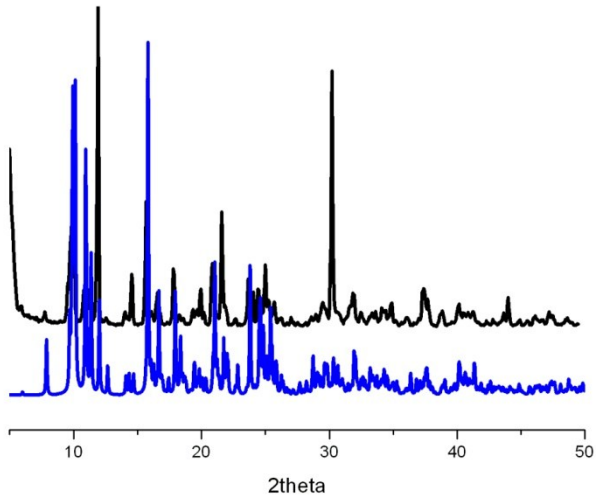

Fig. S9. PXRD patterns of the simulated **2** (blue), as-synthesized **2** (black).

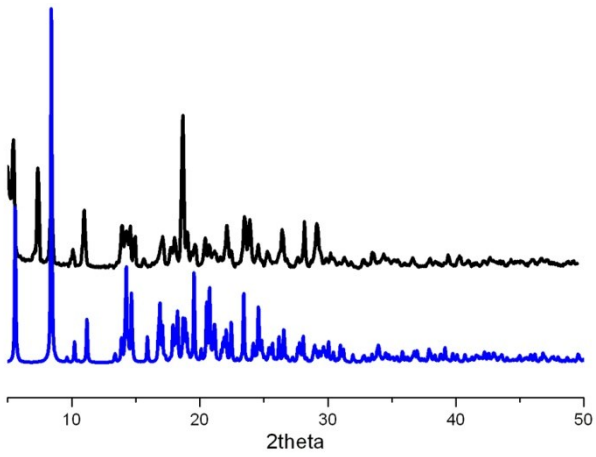

Fig. S10. PXRD patterns of the simulated **3** (blue), as-synthesized **3** (black).

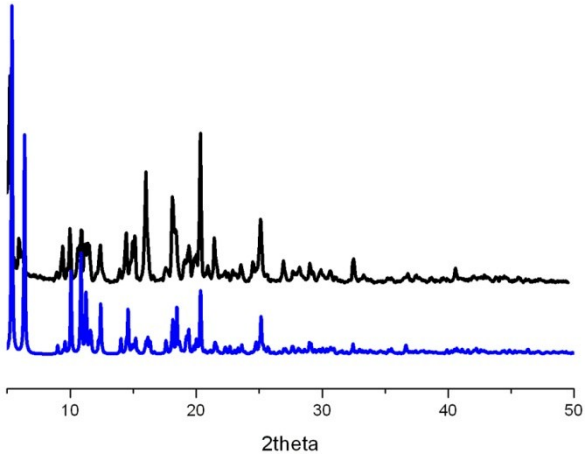

Fig. S11. PXRD patterns of the simulated **4** (blue), as-synthesized **4** (black).

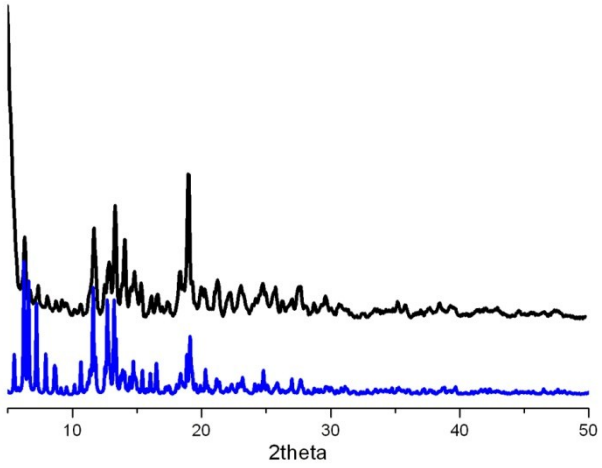

Fig. S12. PXRD patterns of the simulated **5** (blue), as-synthesized **5** (black).

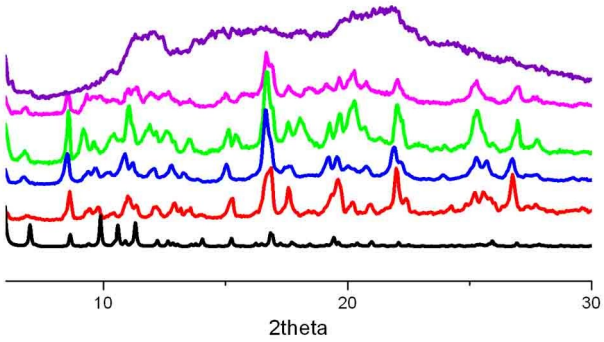

Fig. S13. PXRD patterns of the simulated **6** (black), as-synthesized **6** (red), **6** immersed in water after one week (blue), MO^-@**6** (green), $Cr_2O_7^{2-}$@**6** (pink) and desolvated **6** (violet).

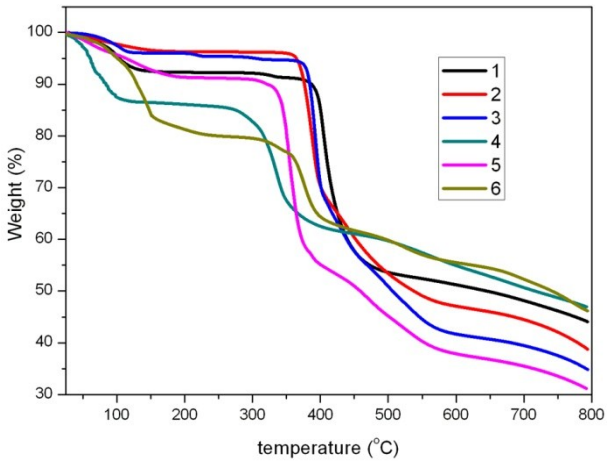

Fig. S14. The TGA curves of **1-6**.

Table S1. Crystal and Structure Refinement Data for Compounds **1-6**.

param	1	2	3	4	5	6
formula	$C_{55}H_{47}N_6O_{15}PZn_2$	$C_{78}H_{62}N_{12}O_{18}P_2Cd_3$	$C_{78}H_{60}N_{12}O_{13}P_2Cd_2$	$C_{86}H_{92}N_{12}O_{25}P_2Cd_2$	$C_{88}H_{78}F_{12}N_{12}O_{20}P_2Cd_2$	$C_{76}H_{74}N_{16}Ni_2O_{18}P_2$
fw	1193.69	1854.53	1660.12	1980.45	2138.36	1678.87
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a	9.953(5)	11.2136(6)	10.889(5)	10.088(5)	16.2201(8)	11.0519(6)
b	12.572(5)	11.2212(6)	10.961(5)	15.743(5)	16.5015(8)	14.6451(8)
c	22.406(5)	14.7386(8)	15.897(5)	18.126(5)	19.5574(10)	17.8325(9)
α (deg)	86.109(5)	92.5440(10)	83.872(5)	111.637(5)	97.7280(10)	66.6520(10)
β(deg)	85.452(5)	95.8890(10)	87.251(5)	100.107(5)	106.9440(10)	76.5310(10)
γ (deg)	82.818(5)	90.3370(10)	74.609(5)	94.589(5)	97.7670(10)	81.1240(10)
V	2768.1(19)	1851.40(17)	1818.5(13)	2601.2(17)	4877.3(4)	2570.9(2)
Z	2	1	1	1	2	1
D_{calcd} (g cm^{-3})	1.432	1.663	1.532	1.264	1.456	0.910
GOF on F^2	1.056	1.062	1.030	0.979	0.929	0.945
R_1/wR_2[I≥2sigma(I)]	0.0481/0.1301	0.0255/0.0606	0.0613/0.1688	0.0443/0.1167	0.0563/0.1377	0.0478/0.1165
R_1/wR_2 (all data)	0.0718/0.1393	0.0298/0.0623	0.0903/0.11919	0.0631/0.1235	0.1003/0.1524	0.0693/0.1225

Table S2. Ring links for polycatenated array of 3,3,4L34 nets in structure of compound 1.

Ring 1	Ring 2	Cross	Link	Hopf	Mult
6a	6b	1	1	*	4
6a	8a	1	1	*	8
6a	8b	1	1	*	4
6a	8c	1	1	*	8
6a	8d	1	1	*	4

6b	6a	1	1	*	4
6b	8a	1	1	*	8
6b	8b	1	1	*	4
6b	8c	1	1	*	8
6b	8d	1	1	*	4
8a	6a	1	1	*	4
8a	6b	1	1	*	4
8a	8c	1	1	*	8
8b	6a	1	1	*	4
8b	6b	1	1	*	4
8b	8c	1	1	*	8
8c	6a	1	1	*	4
8c	6b	1	1	*	4
8c	8a	1	1	*	8
8c	8b	1	1	*	4
8c	8d	1	1	*	4
8d	6a	1	1	*	4
8d	6b	1	1	*	4
8d	8c	1	1	*	8

Table S3. Eleven examples of mixed 3D+2D coordination polymers

CSD Code	Name of compound	Ref.		Network periodicity	Underlying net
AQIXUU	$[Co_{10}(OH)_{18}(pip)][Co_2(C_2O_4)_3]$ (pip=piperazine)	18a	$[Co_{10}(OH)_{18}(pip)]_n^{2n+}$	3D	3,4,6-c net, point symbol $(4.6^2)_3(4^3)_6(4^5.6^7.8^3)_3(4^6.6^6.8^3)(6^3.14^3)$
			$[Co_2(C_2O_4)_3]_n^{2n-}$	2D (001)	**hcb**
CAVWIH	$[Cu^I_2(bbtz)_3][Cu^{II}(bbtz)_2(Mo_8O_{26})]$ (bbtz = 1,4-bis-(1,2,4-triazol-1-ylmethyl)benzene)	18b	$[Cu^{II}(bbtz)_2(Mo_8O_{26})]_n^{2n-}$	3D	**pcu**
			$[Cu^I_2(bbtz)_3]_n^{2n+}$	2D (10-1)	3-coord. net*
ETAXAZ	$[Co(bdc)(dia)(H_2O)][Co(bdc)(dia)_2]\cdot H_2O$ (dia = 9,10-di(1H-imidazol-1-yl)anthracene)	18c	$[Co(bdc)(dia)_2]$	3D	**pcu**
			$[Co(bdc)(dia)(H_2O)]$	2D (010)	**sql**
GUXQUM	$[(CH_3)_2NH_2][Zn_2(bdc)(btb)][Zn_3(btb)_2(H_2O)_2]\cdot 4DMA\cdot 2C_2H_5OH\cdot 7H_2O$ (H_3btb = benzene-1,3,5-tribenzoic acid)	18d	$[Zn_2(BDC)(BTB)]_n^{n-}$	3D	**hms**
			$[Zn_3(BTB)_2(H_2O)_2]_n$	2D (001)	3,6L66 (double **hcb**)
IDEYOF	$[Ni(4,4'\text{-bpy})_2(H_2PO_4)_2]\cdot C_4H_9OH\cdot H_2O$ (4,4'-bpy = 4,4'-bipyridine)	18e	$[Ni(4,4'\text{-bpy})_2(H_2PO_4)_2]_n$	3D	**cds**
			$[Ni(4,4'\text{-bpy})_2(H_2PO_4)_2]_n$	2D (001)	**sql**
IMULEH	$[Co(mpe)_2(NCS)_2]$ (mpe = 1-methyl-1,2-bis(pyrid-4-yl)ethene-N,N')	18f	$[Co(mpe)_2(NCS)_2]_n$	3D	2-fold **cds**
			$[Co(mpe)_2(NCS)_2]_n$	2D (001)	**sql**
IZEVAM	$[Cu_4Cl_6(hmt)][Cu_3(OH)(hmt)]\cdot(H_2O)_3$	18g	$[Cu_4Cl_6(hmt)]_n^{2n-}$	3D	**lon**

			$[Cu_3(OH)(hmt)]_n^{2n+}$	2D (001)	**hcb**
LODTOO	$[Cu^{I}_3(btmb)_3][\{Cu^{II}(btmb)_2\}\{PMo_{12}O_{40}(VO)_2\}]\cdot H_2O$ (**1**) (btmb = 1,4-bis(1,2,4-triazol-1-ylmethyl)benzene)	18h	$[\{Cu^{II}(btmb)_2\}\{PMo_{12}O_{40}(VO)_2\}]_n^{3n-}$	3D	**pcu**
			$[Cu^{I}_3(btmb)_3]_n^{3n+}$	2D (10-1)	2-loop **hcb**
QIWQES	$\{[Cu_2(IN)_4(H_2O)_3][Cu_2(IN)_4(H_2O)_2]\}\cdot 3H_2O$ (IN = isonicotinate)	18i	$[Cu_2(IN)_4(H_2O)_3]_n$	3D	**cds**
			$[Cu_2(IN)_4(H_2O)_2]_n$	2D (10-1)	**sql**
SOFNUY	$[Zn(dap)_2][AlB_5O_{10}]$ (dap=1,3-diaminopropane)	18j	$[AlB_5O_{10}]_n^{2n-+}$	3D	**dia**
			$[Zn(dap)_2]_n^{2n+}$	2D (001)	**sql**
XEPFOP	$[Pb_3(tpphz)_2(ocd)_3]\cdot 2H_2O$ (H_2ocd = octanedioic acid, tpphz = tetrapyrido[3,2-*a*:2′,3′-*c*:3″,2″-*h*:2‴,3‴-*j*]phenazine)	18k	$[Pb_2(tpphz)(ocd)_2]_n$	3D	**pcu**
			$[Pb(tpphz)(ocd)]_n$	2D (001)	**sql**

* Topology can not be determined due to disorder

Table S4. Ring-links for 4-fold 3,5T1 underlying net of compound **4**.

Cycle 1	Cycle 2	Chain	Cross	Link	Hopf	Mult
4a	6b	inf.	1	1	*	2
4a	8a	inf.	1	1	*	2
4a	8b	inf.	1	1	*	4
4a	8c	inf.	1	1	*	2
4a	8d	inf.	1	1	*	4
4a	8e	inf.	1	1	*	2
4a	8f	inf.	1	1	*	2
4b	6a	inf.	1	1	*	2
4b	8a	inf.	1	1	*	2
4b	8b	inf.	1	1	*	4
4b	8c	inf.	1	1	*	2
4b	8d	inf.	1	1	*	4
4b	8e	inf.	1	1	*	2
4b	8f	inf.	1	1	*	2
6a	4b	inf.	1	1	*	2
6a	6b	inf.	1	1	*	2
6a	8a	inf.	1	1	*	4
6a	8b	inf.	1	1	*	8
6a	8c	inf.	1	1	*	4
6a	8d	inf.	1	1	*	8
6a	8e	inf.	1	1	*	4
6a	8f	inf.	1	1	*	4
6b	4a	inf.	1	1	*	2
6b	6a	inf.	1	1	*	2
6b	8a	inf.	1	1	*	4
6b	8b	inf.	1	1	*	8
6b	8c	inf.	1	1	*	4

6b	8d	inf.	1	1	*	8
6b	8e	inf.	1	1	*	4
6b	8f	inf.	1	1	*	4
8a	4a	inf.	1	1	*	2
8a	4b	inf.	1	1	*	2
8a	6a	inf.	1	1	*	4
8a	6b	inf.	1	1	*	4
8a	8b	inf.	1	1	*	4
8a	8c	inf.	1	1	*	6
8a	8d	inf.	1	1	*	12
8a	8e	inf.	1	1	*	4
8a	8f	inf.	1	1	*	6
8b	4a	inf.	1	1	*	2
8b	4b	inf.	1	1	*	2
8b	6a	inf.	1	1	*	4
8b	6b	inf.	1	1	*	4
8b	8a	inf.	1	1	*	1
8b	8a	inf.	3	1	*	1
8b	8b	inf.	1	1	*	3
8b	8b	inf.	3	1	*	1
8b	8c	inf.	1	1	*	6
8b	8d	inf.	1	1	*	12
8b	8e	inf.	1	1	*	2
8b	8f	inf.	1	1	*	6
8c	4a	inf.	1	1	*	2
8c	4b	inf.	1	1	*	2
8c	6a	inf.	1	1	*	4
8c	6b	inf.	1	1	*	4
8c	8a	inf.	1	1	*	6
8c	8b	inf.	1	1	*	12
8c	8d	inf.	1	1	*	2
8c	8d	inf.	3	1	*	2
8c	8e	inf.	1	1	*	6
8c	8f	inf.	1	1	*	2
8c	8f	inf.	3	1	*	2
8d	4a	inf.	1	1	*	2
8d	4b	inf.	1	1	*	2
8d	6a	inf.	1	1	*	4
8d	6b	inf.	1	1	*	4
8d	8a	inf.	1	1	*	6
8d	8b	inf.	1	1	*	12
8d	8c	inf.	1	1	*	2
8d	8d	inf.	1	1	*	3

8d	8d	inf.	3	1	*	1
8d	8e	inf.	1	1	*	6
8d	8f	inf.	1	1	*	1
8d	8f	inf.	3	1	*	1
8e	4a	inf.	1	1	*	2
8e	4b	inf.	1	1	*	2
8e	6a	inf.	1	1	*	4
8e	6b	inf.	1	1	*	4
8e	8a	inf.	1	1	*	2
8e	8a	inf.	3	1	*	2
8e	8b	inf.	1	1	*	2
8e	8b	inf.	3	1	*	2
8e	8c	inf.	1	1	*	6
8e	8d	inf.	1	1	*	12
8e	8f	inf.	1	1	*	6
8f	4a	inf.	1	1	*	2
8f	4b	inf.	1	1	*	2
8f	6a	inf.	1	1	*	4
8f	6b	inf.	1	1	*	4
8f	8a	inf.	1	1	*	6
8f	8b	inf.	1	1	*	12
8f	8c	inf.	1	1	*	4
8f	8d	inf.	1	1	*	4
8f	8e	inf.	1	1	*	6

Table S5. The four examples of observed 4-fold interpenetrating 3,5T1 nets.

RISBOM	catena-((\m~3~-4-(Pyridin-4-yl)-N,N-bis(4-(pyridin-4-yl)phenyl)aniline)-(\m~2~-fumarato)-cadmium).	F.D Meng, L. Qin, M.D. Zhang, H.G. Zheng, Crytengcomm, 2014, 16, 698.	C2/c	4	Ib	18,36,44-c HRN
HEDSOA	catena-((\m~3~-4-(Pyridin-4-yl)-N,N-bis(4-(pyridin-4-yl)phenyl)aniline)-(\m~2~-cyclohexane-1,4-dicarboxylato)-cadmium).	M.D. Zhang, C.M. Di, L. Qin, X.Q. Yao, Y.Z. Li, Z.J. Guo, H.G. Zheng. Cryst. Growth. Des., 2012, 12, 3957.	C2/c	4	Ib	18,36,44-c HRN
YICGUO	catena-(bis(\m~3~-tris(4-(4-Pyridyl)phenyl)amine)-(\m~2~-terephthalato-O,O')-(\m~2~-terephthalato-O,O',O'',O''')-di-cobalt).	M.D. Zhang, L. Qin, H.T. Yang, Y.Z.Li, Z.J. Guo, H.G. Zheng. Zheng. Cryst. Growth. Des., 2013, 13, 1961.	P-1	4	Ib	18,36,44-c HRN
UWAPOZ	catena-[(\m-tris(4-(4H-1,2,4-triazol-4-yl)phenyl)amine)-bis(\m-thiophene-2,5-dicarboxylato)-di-cadmium(ii)].	Y. Shen, C.C. Fan, Y.Z. Wei, J. Du, H.B. Zhu, Y. Zhao. Zheng. Cryst. Growth. Des., 2016.	C2/c	4	Ib	18,36,44-c HRN

Table S6. Selected bond distances (Å) and angles (°) for **1**.

Zn(1)-N(1)	2.051(2)	Zn(2)-N(4)#2	2.001(3)
Zn(2)-N(6)#5	1.986(3)	Zn(1)-O(3)	1.972(2)
Zn(1)-O(8)#4	2.033(2)	Zn(1)-O(9)#4	2.377(2)
Zn(1)-OW1	1.970(2)	Zn(2)-O(5)	1.948(2)
Zn(2)-O(6)	1.999(2)	OW1-Zn(1)-O(3)	122.79(10)
OW1-Zn(1)-O(8)#4	121.96(10)	O(3)-Zn(1)-O(8)#4	106.49(9)
OW1-Zn(1)-N(1)	99.98(10)	O(3)-Zn(1)-N(1)	106.13(9)
O(8)#4-Zn(1)-N(1)	93.25(10)	OW1-Zn(1)-O(9)#4	90.61(10)
O(3)-Zn(1)-O(9)#4	89.58(8)	O(8)#4-Zn(1)-O(9)#4	59.08(9)
N(1)-Zn(1)-O(9)#4	151.52(9)	OW1-Zn(1)-C(55)#4	108.61(10)
O(3)-Zn(1)-C(55)#4	98.16(9)	O(8)#4-Zn(1)-C(55)#4	29.96(9)
N(1)-Zn(1)-C(55)#4	123.05(10)	O(9)#4-Zn(1)-C(55)#4	929.15(9)
O(5)-Zn(2)-N(6)#5	119.47(10)	O(5)-Zn(2)-O(6)	99.57(9)
N(6)#5-Zn(2)-O(6)	113.30(11)	O(5)-Zn(2)-N(4)#2	105.38(10)
N(6)#5-Zn(2)-N(4)#2	115.82(12)	O(6)-Zn(2)-N(4)#2	100.55(11)

Symmetry transformations used to generate equivalent atoms: #1 x+1,y-2,z, #2 -x-2,-y+1,-z, #3 x-1,y+1,z-1, #4 x-1,y+2,z, #5 x+1,y-1,z+1.

Table S7. Selected bond distances (Å) and angles (°) for **2**.

Cd(1)-N(1)	2.3300(18)	Cd(1)-N(6)#4	2.3793(16)
Cd(1)-O(9)#1	2.2989(14)	Cd(2)-O(1)	2.2526(17)
Cd(2)-O(2)#6	2.2081(17)	Cd(2)-O(3)	2.2789(17)
Cd(2)-O(4)#6	2.2203(17)	Cd(2)-O(5)	2.2004(19)

O(9)#1-Cd(1)-O(9)#2	180.0	O(9)#1-Cd(1)-N(1)	85.32(6)
O(9)#2-Cd(1)-N(1)	94.68(6)	O(9)#1-Cd(1)-N(1)#3	94.68(6)
O(9)#2-Cd(1)-N(1)#3	85.32(6)	N(1)-Cd(1)-N(1)#3	180.00(5)
O(9)#1-Cd(1)-N(6)#4	87.55(6)	O(9)#2-Cd(1)-N(6)#4	92.45(5)
N(1)-Cd(1)-N(6)#4	86.19(6)	N(1)#3-Cd(1)-N(6)#4	93.81(6)
O(9)#1-Cd(1)-N(6)#5	92.45(5)	O(9)#2-Cd(1)-N(6)#5	87.55(6)
N(1)-Cd(1)-N(6)#5	93.81(6)	N(1)#3-Cd(1)-N(6)#5	86.19(6)
N(6)#4-Cd(1)-N(6)#5	180.000(1)	O(5)-Cd(2)-O(2)#6	121.95(9)
O(5)-Cd(2)-O(4)#6	112.78(9)	O(2)#6-Cd(2)-O(4)#6	88.95(9)
O(5)-Cd(2)-O(1)	87.19(9)	O(2)#6-Cd(2)-O(1)	149.93(8)
O(4)#6-Cd(2)-O(1)	85.62(9)	O(5)-Cd(2)-O(3)	94.62(8)
O(2)#6-Cd(2)-O(3)	85.61(9)	O(4)#6-Cd(2)-O(3)	150.38(8)
O(1)-Cd(2)-O(3)	84.69(9)		

Symmetry transformations used to generate equivalent atoms: #1 x,y-1,z, #2 -x+1,-y+2,-z+1, #3 -x+1,-y+1,-z+1, #4 -x,-y+2,-z+1, #5 x+1,y-1,z, #6 -x,-y+2,-z+2, #7 -x,-y+1,-z+2, #8 -x+1,-y+2,-z+2, #9 x,y+1,z, #10 x-1,y+1,z.

Table S8. Selected bond distances (Å) and angles (°) for **3**.

Cd(1)-N(1)	2.290(5)	Cd(1)-N(6)#4	2.249(5)
Cd(1)-O(1)	2.175(5)	Cd(1)-O(3)	2.340(5)
Cd(1)-O(4)	2.354(5)	O(1)-Cd(1)-N(6)#4	127.6(2)
O(1)-Cd(1)-N(1)	96.97(19)	N(6)#4-Cd(1)-N(1)	96.64(19)
O(1)-Cd(1)-O(3)	92.5(2)	N(6)#4-Cd(1)-O(3)	139.1(2)

N(1)-Cd(1)-O(3)	84.53(19)	O(1)-Cd(1)-O(4)	113.5(2)
N(6)#4-Cd(1)-O(4)	96.00(18)	N(1)-Cd(1)-O(4)	128.41(19)
O(3)-Cd(1)-O(4)	55.01(17)		

Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y,-z+1, #2 -x+1,-y+2,-z+1, #3 x,y,z-1, #4 x,y,z+1.

Table S9. Selected bond distances (Å) and angles (°) for **4**.

Cd(1) - N(2)	2.328(3)	Cd(1)-N(4)#5	2.338(2)
Cd(1)-N(6)#4	2.314(3)	Cd(1)-O(2)	2.301(3)
Cd(1)-O(3)	2.295(2)	Cd(1)-O(4)	2.629(3)
O(3)-Cd(1)-O(2)	133.24(10)	O(3)-Cd(1)-N(6)#4	85.59(9)
O(2)-Cd(1)-N(6)#4	140.87(10)	O(3)-Cd(1)-N(2)	90.10(12)
O(2)-Cd(1)-N(2)	86.53(14)	N(6)#4-Cd(1)-N(2)	89.25(13)
O(3)-Cd(1)-N(4)#5	103.74(9)	O(2)-Cd(1)-N(4)#5	86.54(10)
N(6)#4-Cd(1)-N(4)#5	88.25(9)	N(2)-Cd(1)-N(4)#5	165.70(11)
O(3)-Cd(1)-O(4)	51.85(9)	O(2)-Cd(1)-O(4)	83.87(10)
N(6)#4-Cd(1)-O(4)	134.66(8)	N(2)-Cd(1)-O(4)	103.85(12)
N(4)#5-Cd(1)-O(4)	87.82(9)		

Symmetry transformations used to generate equivalent atoms: #1 -x+3,-y+1,-z+1, #2 -x+1,-y-1,-z, #3 x,y,z+1, #4 -x+1,-y+1,-z+1, #5 x,y,z-1.

Table S10. Selected bond distances (Å) and angles (°) for **5**.

N(1)-Cd(1)	2.325(3)	Cd(1)-N(10)#1	2.282(3)
Cd(1)-N(12)#5	2.318(4)	N(6)-Cd(2)	2.277(3)
N(7)-Cd(2)	2.291(3)	Cd(2)-N(4)#6	2.318(3)

O(2)-Cd(1)	2.302(4)	O(5)-Cd(1)	2.571(3)
O(6)-Cd(1)	2.297(3)	Cd(2)-O(3)#4	2.365(3)
Cd(2)-O(4)#4	2.406(3)	Cd(2)-O(8)#6	2.352(3)
N(10)#1-Cd(1)-O(6)	146.07(11)	N(10)#1-Cd(1)-O(2)	130.67(15)
O(6)-Cd(1)-O(2)	83.24(15)	N(10)#1-Cd(1)-N(12)#5	84.85(13)
O(6)-Cd(1)-N(12)#5	93.64(13)	O(2)-Cd(1)-N(12)#5	95.73(18)
N(10)#1-Cd(1)-N(1)	84.44(12)	O(6)-Cd(1)-N(1)	91.96(13)
O(2)-Cd(1)-N(1)	95.72(16)	N(12)#5-Cd(1)-N(1)	167.77(14)
N(10)#1-Cd(1)-O(5)	92.57(11)	O(6)-Cd(1)-O(5)	53.51(10)
O(2)-Cd(1)-O(5)	136.69(14)	N(12)#5-Cd(1)-O(5)	89.83(13)
N(1)-Cd(1)-O(5)	84.77(11)	N(6)-Cd(2)-N(7)	168.87(12)
N(6)-Cd(2)-N(4)#6	88.17(11)	N(7)-Cd(2)-N(4)#6	86.63(11)
N(6)-Cd(2)-O(8)#6	88.22(12)	N(7)-Cd(2)-O(8)#6	88.21(12)
N(4)#6-Cd(2)-O(8)#6	133.31(11)	N(6)-Cd(2)-O(3)#4	101.91(11)
N(7)-Cd(2)-O(3)#4	88.29(11)	N(4)#6-Cd(2)-O(3)#4	94.26(10)
O(8)#6-Cd(2)-O(3)#4	131.94(11)	N(6)-Cd(2)-O(4)#4	90.40(12)
N(7)-Cd(2)-O(4)#4	99.26(12)	N(4)#6-Cd(2)-O(4)#4	147.44(11)
O(8)#6-Cd(2)-O(4)#4	79.11(11)	O(3)#4-Cd(2)-O(4)#4	54.31(10)

Symmetry transformations used to generate equivalent atoms: #1 x,y-1,z-1, #2 x+1,y,z, #3 x-1,y+1,z+1, #4 x,y+1,z+1, #5 x+1,y-1,z-1, #6 x-1,y,z.

Table S11. Selected bond distances (Å) and angles (°) for **6**.

Ni(1)-N(1)	2.0719(19)	Ni(1)-N(4)#2	2.0602(19)
Ni(1)-N(6)#3	2.0621(18)	Ni(1)-O(1)	2.0608(16)

OW1-Ni(1)	2.1068(16)	Ni(1)-OW2	OW2-Ni(1)
N(4)#2-Ni(1)-O(1)	89.60(7)	N(4)#2-Ni(1)-N(6)#3	178.96(8)
O(1)-Ni(1)-N(6)#3	90.70(7)	N(4)#2-Ni(1)-N(1)	90.91(8)
O(1)-Ni(1)-N(1)	88.92(7)	N(6)#3-Ni(1)-N(1)	90.10(7)
N(4)#2-Ni(1)-OW2	91.53(7)	O(1)-Ni(1)-OW2	90.80(7)
N(6)#3-Ni(1)-OW2	87.47(7)	N(1)-Ni(1)-OW2	177.55(7)
N(4)#2-Ni(1)-OW1	88.92(7)	O(1)-Ni(1)-OW1	177.70(6)
N(6)#3-Ni(1)-OW1	90.76(7)	N(1)-Ni(1)-OW1	92.86(7)
OW2-Ni(1)-OW1	87.49(7)		

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y,-z+1; #2 -x+1,-y+1,-z+2; #3 -x+1,-y+2,-z+1.

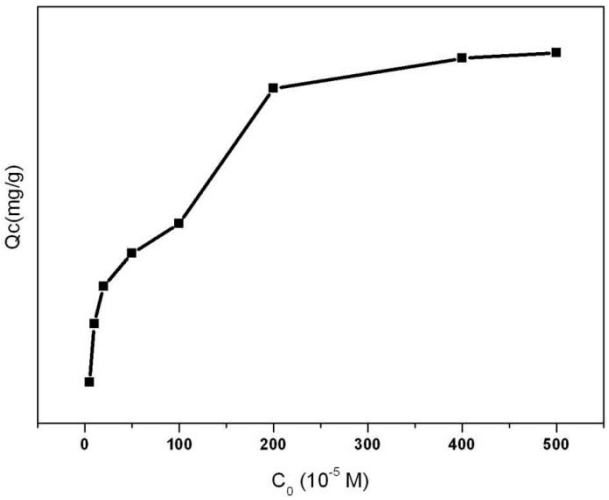

Fig. S15. Adsorption isotherms for MO adsorption over 1h, C_0: the initial concentration of adsorbate, Qc: the amount of MO adsorbed.

Table S12 Comparison of the adsorption capacities of MO onto some typical adsorbents

Adsorbents	Adsorption capacity (mg g-1)	Ref.
MIL-100(Fe)	1045	M. Tong, D. Liu, Q. Yang, S. Devautour-Vinot, G. Maurin and C. Zhong, J. Mater. Chem. A, 2013, 1, 8534.
$[Cd_3(TCA)_2(bimb).(DMA)_6]_n$	748	L. Wen, X. Wang, H. Shi, K. Lv and C. Wang, RSC Adv., 2016, 6, 1388.
Porous carbon	680	H. Li, Z. Sun, L. Zhang, Y. Tian, G. Cui and S. Yan, Colloids Surf., A, 2016, 489, 191.
MOF-235	477	E. Haque, J. W. Jun and S. H. Jhung, J. Hazard. Mater., 2011, 185, 507.

MIL-100(Cr)	212	M. Tong, D. Liu, Q. Yang, S. Devautour-Vinot, G. Maurin and C. Zhong, J. Mater. Chem. A, 2013, 1, 8534.
Amino-MIL-101(Al)	188	E. Haque, V. Lo, A. I. Minett, A. T. Harris and T. L. Church, J. Mater. Chem. A, 2014, 2, 193.
ED-MIL-101	160	E. Haque, J. E. Lee, I. T. Jang, Y. K. Hwang, J.-S. Chang, J. Jegal and S. H. Jhung, J. Hazard. Mater., 2010, 181, 535
CP1	779	J. Zhang, C.C. Wang, P. Wang and Y.L. Cao, RSC Adv., 2016, 6, 73595.
UiO-67-bpy-Me	357	L. Xu, Y.P. Luo, L. Sun, S. Pu, M. Fang, R.X. Yuan and H. B. Du, Dalton. Trans., 2016, 45, 8614.
Compound 6	157.6	This work

The evaluation of $NO_3^-/Cr_2O_7^{2-}$ exchange capacity of 6.

The anion-exchange capacity of **6** was evaluated by measuring the decolorization rate of aqueous $K_2Cr_2O_7$ solution, which was calculated by the following formula:

$$Q_e = \frac{(C_0 - C_e)V}{m}$$

where C_0 and Ce (mg/L) are the initial and equilibrium Cr(VI) concentration, respectively. V (mL) is the volume of Cr(VI) solution, m(mg) is the mass of adsorbent.

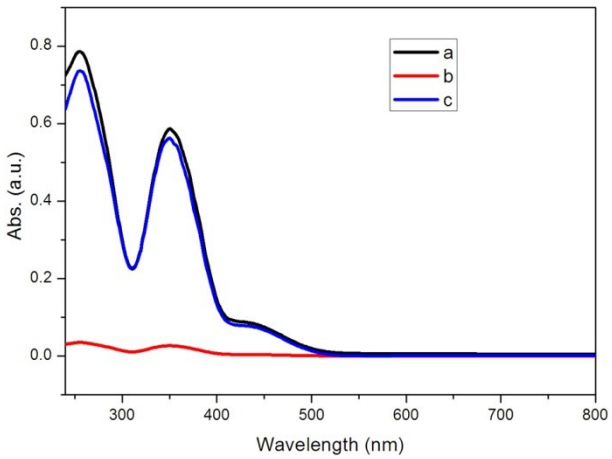

Fig. S16. (a) UV-vis adsorption spectra of $Cr_2O_7^{2-}$ solution without **6**. (b) UV-vis adsorption spectra of $Cr_2O_7^{2-}$ solution after ion-exchange with **6**. (c). UV-vis adsorption spectra of $Cr_2O_7^{2-}$ solution after the releasing process in the presence of a 200-fold molar excess of KNO_3.

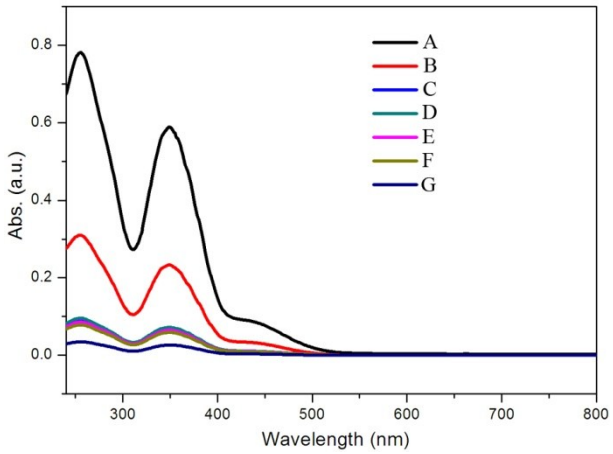

Fig. S17. The UV-vis absorbance spectra of $Cr_2O_7^{2-}$ on the selective trapping of **6**. **(A)**: the UV-vis absorbance spectra of the $K_2Cr_2O_7$ solution (50 mg L^{-1}); **(B)**: the UV-vis absorbance spectra of the $K_2Cr_2O_7$ solution after ion exchange with 5-fold molar excess of SO_4^{2-}; (**C-F**): the UV-vis absorbance spectra of the $K_2Cr_2O_7$ solution after ion exchange with 5-fold molar excess of Cl^-, Br^-, I^- or NO_3^-; (**G**) the UV-vis absorbance spectra of the $K_2Cr_2O_7$ solution after ion exchange with the crystals.

Table 13. Comparison of $Cr_2O_7^{2-}$ adsorption capacity for MOF-based adsorbents.

MOF-type Adsorbents	Uptake capacity (mg g^{-1})	Ref
SLUG-21	60.0	H. H. Fei, M. R. Bresler, S. R. J. Oliver, *J. Am. Chem. Soc*., 2011, **133**, 11110
3-D Dy-MOFs	62.9	P. F. Shi, B. Zhao, G. Xiong, Y. L. Hou and P. Cheng, *Chem.Cummun.*, 2012, **48**, 8231
$Zn_{0.5}Co_{0.5}$-SLUG-35	68.5	H. H. Fei, C. S. Han, J. C. Robins and S. R. J. Oliver, *Chem. Mater.*, 2013, **25**, 647
FIR-53	74.2	H. R. Fu, Z. X. Xu and J. Zhang, *Chem. Mater.*, 2015, **27**, 205
FIR-54	103.1	H. R. Fu, Z. X. Xu and J. Zhang, *Chem. Mater.*, 2015, **27**, 205
ZJU-101	243	Q. Zhang, J. C. Yu, J. F. Cai, L. Zhang, Y. J. Cui, Y. Yang, B. L. Chen and G. D. Qian, *Chem. Commun.*, 2015, **51**, 14732
6	99.5	This work