Electronic Supplementary Material (ESI) for CrystEngComm

Stoichiometry, Temperature, Solvent, Metal-Directed Syntheses of Metal-Organic Frameworks Based on Flexible V-Shaped Methylenebis(3,5-dimethylpyrazole) and Various Aromatic Dicarboxylate Acids

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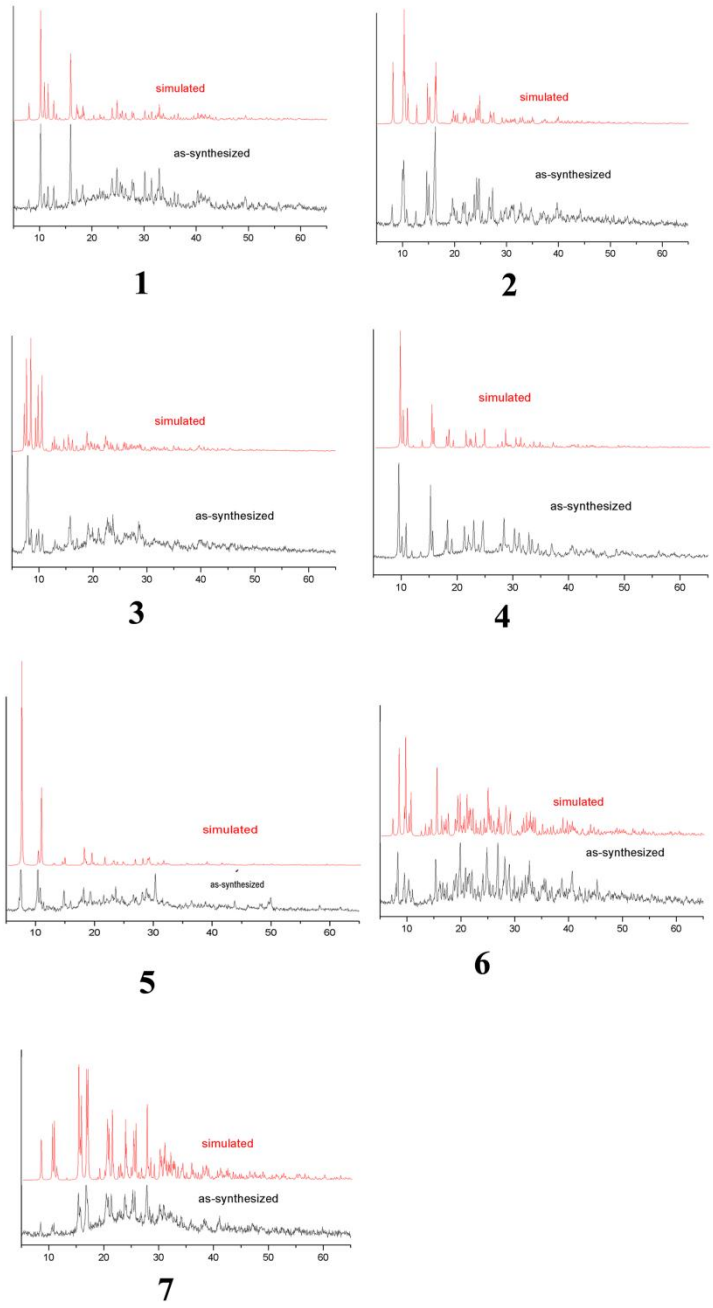


Figure S1. PXRD patterns of complexes **1-7.**

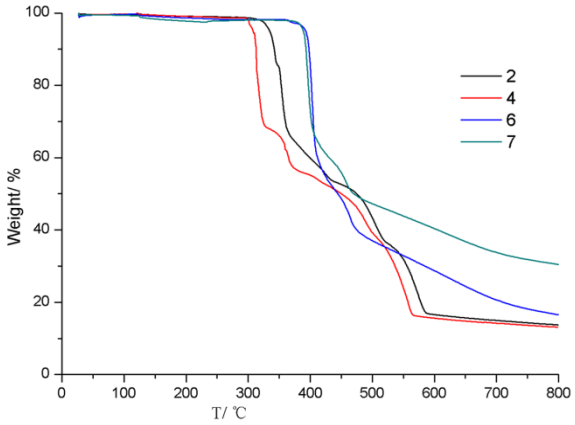
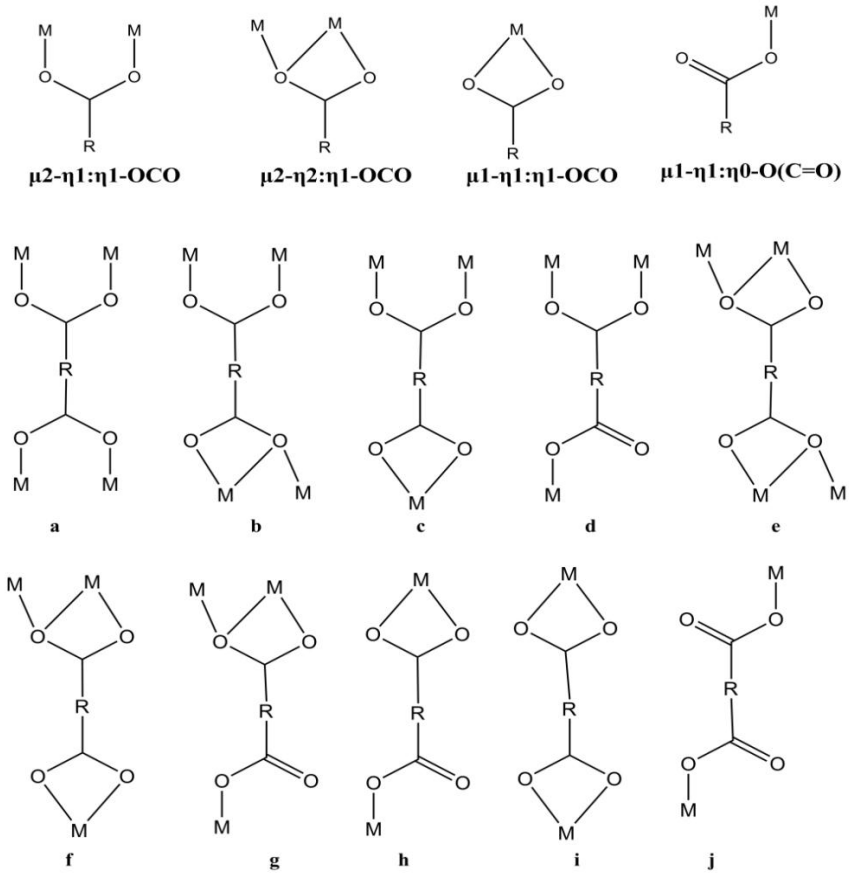


Figure S2. TGA cures for complexes **2**, **4**, **6** and 7.



Scheme **S1**. Coordination modes of carboxylate observed in complexes **1**-**7**, and the combination of R (= naphthyl or substituted phenyl) spacers and above four carboxylate coordination modes produces ten possible bridging modes of completely deprotonated dicarboxylates, four of which (a, h, i, j) are observed in **1**-**7**.

Bond Distance	(Å)	Bond Distance	(Å)
Cd(1)-O(7)#1	2.197(4)	Cd(2)-O(8)#1	2.199(4)
Cd(1)-O(3)	2.210(4)	Cd(2)-O(5)#3	2.227(4)
Cd(1)-O(1)	2.222(4)	Cd(2)-N(1)	2.231(5)
Cd(1)-N(3)#2	2.221(4)	Cd(2)-O(4)	2.240(4)
Cd(1)-O(6)#3	2.295(4)	Cd(2)-O(2)	2.280(4)
Cd(2)-O(8)#1	2.199(4)		
Bond Angle	(°)	Bond Angle	(°)
O(7)#1-Cd(1)-O(3)	147.8(2)	O(8)#1-Cd(2)-O(5)#3	90.0(2)
O(7)#1-Cd(1)-O(1)	96.8(2)	O(8)#1-Cd(2)-N(1)	100.55(18)
O(3)-Cd(1)-O(1)	85.53(19)	O(5)#3-Cd(2)-N(1)	104.06(18)
O(7)#1-Cd(1)-N(3)#2	94.29(19)	O(8)#1-Cd(2)-O(4)	159.3(2)
O(3)-Cd(1)-N(3)#2	114.89(19)	O(5)#3-Cd(2)-O(4)	85.83(19)
O(1)-Cd(1)-N(3)#2	111.25(17)	N(1)-Cd(2)-O(4)	100.13(17)
O(7)#1-Cd(1)-O(6)#3	87.1(2)	O(8)#1-Cd(2)-O(2)	86.41(19)
O(3)-Cd(1)-O(6)#3	83.15(18)	O(5)#3-Cd(2)-O(2)	141.00(19)
O(1)-Cd(1)-O(6)#3	164.32(18)	N(1)-Cd(2)-O(2)	114.8(2)
N(3)#2-Cd(1)-O(6)#3	83.44(17)	O(4)-Cd(2)-O(2)	84.21(18)

Table S1 Selected Bond Lengths (Å) and Bond Angles (°) for **1**

Symmetry codes: #1 *x*-1/2, -*y*+1/2, z-1/2; #2 *x*, *y*-1, *z*; #3 *x*+1/2,-*y*+1/2, *z*-1/2.

Bond Distance	(Å)	Bond Distance	(Å)
Cd(1)-O(1B)	2.180(17)	Cd(1)-O(1A)	2.23(2)
Cd(1)-O(3A)	2.07(3)	Cd(1)-O(4A)	2.404(12)
Cd(1)-N(1)	2.219(5)	Cd(1)-O(3B)	2.476(17)
Cd(1)-N(3)#1	2.265(6)	Cd(1)-O(4B)	2.53(2)
Bond Angle	(°)	Bond Angle	(°)
N(1)-Cd(1)-N(3)#1	102.6(2)	O(1B)-Cd(1)-O(3B)	92.1(7)
O(1B)-Cd(1)-N(1)	129.2(6)	O(3A)-Cd(1)-O(4A)	57.4(6)
O(3A)-Cd(1)-N(1)	112.1(10)	N(1)-Cd(1)-O(3B)	97.9(6)
O(1B)-Cd(1)-N(3)#1	93.9(5)	N(3)#1-Cd(1)-O(3B)	147.9(6)
O(3A)-Cd(1)-N(3)#1	128.7(9)	O(1B)-Cd(1)-O(4B)	118.7(10)
O(3A)-Cd(1)-O(1A)	107.5(9)	N(1)-Cd(1)-O(4B)	105.3(6)
N(1)-Cd(1)-O(1A)	114.1(6)	N(3)#1-Cd(1)-O(4B)	100.3(6)
N(3)#1-Cd(1)-O(1A)	90.4(6)	O(3B)-Cd(1)-O(4B)	50.0(7)
N(1)-Cd(1)-O(4A)	106.2(4)	O(1A)-Cd(1)-O(4A)	139.6(7)
N(3)#1-Cd(1)-O(4A)	77.6(4)		

Table S2 Selected Bond Lengths (Å) and Bond Angles (°) for **2**

Symmetry code: #1 -*x*+3/2, *y*+1/2,-*z*+1/2.

Bond Distance	(Å)	Bond Distance	(Å)
Cd(1)-O(2)	2.242(3)	Cd(1)-O(10)#1	2.546(5)
Cd(1)-N(2)	2.257(4)	Cd(2)-O(6)	2.252(3)
Cd(1)-N(3)	2.287(4)	Cd(2)-N(7)#2	2.256(4)
Cd(1)-O(9)	2.315(4)	Cd(2)-O(3)	2.303(3)
Cd(1)-O(10)	2.536(5)	Cd(2)-N(6)#2	2.318(4)
Cd(2)-O(4)	2.568(3)	Cd(2)-O(5)#3	2.409(3)
Bond Angle	(°)	Bond Angle	(°)
O(2)-Cd(1)-N(2)	147.92(15)	O(9)-Cd(1)-O(10)#1	113.92(15)
O(2)-Cd(1)-N(3)	106.26(14)	O(10)-Cd(1)-O(10)#1	70.25(18)
N(2)-Cd(1)-N(3)	89.92(14)	O(6)-Cd(2)-N(7)#2	100.09(14)
O(2)-Cd(1)-O(9)	85.85(16)	O(6)-Cd(2)-O(3)	87.69(12)
N(2)-Cd(1)-O(9)	122.62(17)	N(7)#2-Cd(2)-O(3)	166.40(14)
N(3)-Cd(1)-O(9)	89.31(16)	O(6)-Cd(2)-N(6)#2	106.18(14)
O(2)-Cd(1)-O(10)	100.31(15)	N(7)#2-Cd(2)-N(6)#2	89.09(14)
N(2)-Cd(1)-O(10)	88.59(16)	O(3)-Cd(2)-N(6)#2	99.51(13)
N(3)-Cd(1)-O(10)	130.99(15)	O(6)-Cd(2)-O(5)#3	92.93(12)
O(9)-Cd(1)-O(10)	52.14(16)	N(7)#2-Cd(2)-O(5)#3	86.56(13)
O(2)-Cd(1)-O(10)#1	74.36(16)	O(3)-Cd(2)-O(5)#3	81.89(12)
N(2)-Cd(1)-O(10)#1	79.98(16)	N(6)#2-Cd(2)-O(5)#3	160.86(13)
N(3)-Cd(1)-O(10)#1	156.62(15)	O(6)-Cd(2)-O(4)	140.85(12)
N(6)#2-Cd(2)-O(4)	80.76(13)	N(7)#2-Cd(2)-O(4)	118.74(13)
O(5)#3-Cd(2)-O(4)	85.03(11)	O(3)-Cd(2)-O(4)	53.27(11)

Table S3 Selected Bond Lengths (Å) and Bond Angles (°) for **3**

Symmetry codes: #1 -*x*+1,-*y*,-*z*+1; #2 *x*, *y*, *z*-1; #3 -*x*+1,-*y*-1,-*z*.

Bond Distance	(Å)	Bond Distance	(Å)
Cd(1)-N(3)#1	2.333(2)	Cd(1)-O(1)	2.3526(17)
Cd(1)-N(3)#2	2.333(2)	Cd(1)-N(1)	2.389(2)
Cd(1)-O(1)#3	2.3526(17)	Cd(1)-N(1)#3	2.389(2)
Bond Angle	(°)	Bond Angle	(°)
N(3)#1-Cd(1)-N(3)#2	90.39(11)	O(1)-Cd(1)-N(1)	79.21(7)
N(3)#1-Cd(1)-O(1)#3	89.00(7)	N(3)#1-Cd(1)-N(1)#3	167.31(8)
N(3)#2-Cd(1)-O(1)#3	89.57(7)	N(3)#2-Cd(1)-N(1)#3	94.17(8)
N(3)#1-Cd(1)-O(1)	89.57(7)	O(1)#3-Cd(1)-N(1)#3	79.22(7)
N(3)#2-Cd(1)-O(1)	89.00(7)	O(1)-Cd(1)-N(1)#3	102.32(7)
O(1)#3-Cd(1)-O(1)	177.97(9)	N(1)-Cd(1)-N(1)#3	83.88(10)
N(3)#1-Cd(1)-N(1)	94.17(8)	O(1)#3-Cd(1)-N(1)	102.32(7)
N(3)#2-Cd(1)-N(1)	167.31(8)		

Table S4 Selected Bond Lengths (Å) and Bond Angles (°) for **4**

Symmetry codes: #1 *x*, *y*+1, *z*; #2 -*x*, *y*+1, -*z*-1/2; #3 -*x*, *y*, -*z*-1/2.

Bond Distance	(Å)	Bond Distance	(Å)
Cd(1)-N(3)#1	2.330(3)	Cd(1)-N(1)	2.365(3)
Cd(1)-N(3)#2	2.330(3)	Cd(1)-O(1)#3	2.397(3)
Cd(1)-N(1)#3	2.365(3)	Cd(1)-O(1)	2.397(3)
Bond Angle	(°)	Bond Angle	(°)
N(3)#1-Cd(1)-N(3)#2	87.66(16)	N(1)#3-Cd(1)-O(1)	102.73(11)
N(3)#1-Cd(1)-N(1)#3	95.98(12)	N(1)-Cd(1)-O(1)	77.95(10)
N(3)#2-Cd(1)-N(1)#3	165.50(11)	N(3)#1-Cd(1)-O(1)#3	91.40(11)
N(3)#1-Cd(1)-N(1)	165.50(11)	N(3)#2-Cd(1)-O(1)#3	87.95(10)
N(3)#2-Cd(1)-N(1)	95.98(12)	N(1)#3-Cd(1)-O(1)#3	77.95(10)
N(1)#3-Cd(1)-N(1)	83.99(15)	N(1)-Cd(1)-O(1)#3	102.73(11)
N(3)#1-Cd(1)-O(1)	87.95(10)	O(1)-Cd(1)-O(1)#3	179.10(13)
N(3)#2-Cd(1)-O(1)	91.40(11)		

Table S5 Selected Bond Lengths (Å) and Bond Angles (°) for **5**

Symmetry codes: #1 *x*, *y*+1, *z*; #2 -*x*, *y*+1, -*z*+1/2; #3 -*x*, *y*, -*z*+1/2.

Bond Distance	(Å)	Bond Distance	(Å)
Cd(1)-O(2)#1	2.228(4)	Cd(1)-O(6)	2.359(3)
Cd(1)-N(26)	2.279(4)	Cd(1)-O(5)	2.437(4)
Cd(1)-N(2)	2.281(4)	Cd(1)-O(1)	2.468(4)
Bond Angle	(°)	Bond Angle	(°)
O(2)#1-Cd(1)-N(26)	106.10(15)	O(6)-Cd(1)-O(5)	54.11(12)
O(2)#1-Cd(1)-N(2)	101.08(15)	O(2)#1-Cd(1)-O(1)	89.66(13)
N(26)-Cd(1)-N(2)	94.13(15)	N(26)-Cd(1)-O(1)	162.87(14)
O(2)#1-Cd(1)-O(6)	152.23(14)	N(2)-Cd(1)-O(1)	89.24(14)
N(26)-Cd(1)-O(6)	82.85(14)	O(6)-Cd(1)-O(1)	80.05(13)
N(2)-Cd(1)-O(6)	104.46(14)	O(5)-Cd(1)-O(1)	78.65(14)
O(2)#1-Cd(1)-O(5)	98.72(13)	N(2)-Cd(1)-O(5)	156.68(14)
N(26)-Cd(1)-O(5)	92.09(15)		

Table S6 Selected Bond Lengths (Å) and Bond Angles (°) for **6**

Symmetry code: #1 -*x*+1, -*y*+1, -*z*+1.

Bond Distance	(Å)	Bond Distance	(Å)
Co(1)-O(2B)	1.91(2)	Co(1)-O(2)	1.975(17)
Co(1)-O(3B)	1.95(3)	Co(1)-N(4)#1	1.984(6)
Co(1)-O(3)	1.94(2)	Co(1)-N(2)	2.010(6)
Bond Angle	(°)	Bond Angle	(°)
O(2B)-Co(1)-O(3B)	101.9(7)	O(3B)-Co(1)-N(4)#1	113.1(8)
O(3)-Co(1)-O(2)	100.8(5)	O(2B)-Co(1)-N(2)	111.7(8)
O(2B)-Co(1)-N(4)#1	108.8(9)	O(3B)-Co(1)-N(2)	114.0(8)
O(3)-Co(1)-N(2)	102.6(7)	N(4)#1-Co(1)-N(2)	107.2(2)
O(2)-Co(1)-N(2)	116.0(6)		

Table S7 Selected Bond Lengths (Å) and Bond Angles (°) for **7**.

Symmetry code: #1 -*x*+1/2, *y*-1/2, -*z*+1/2.

D–H/A	d(H···A)/ Å	D(D···A)/ Å	∠DHA/
For complex **6**			
O4-H4A···O6#1	1.759	2.578	177.79
N1-H31···O1#2	1.995	2.798	155.03
Symmetry transformations to generate equivalent atoms: #1) -*x*,-*y*+1,-*z*+2; #2) -*x*+1,-*y*+1,-*z*+1.			

Table S8. Hydrogen bond distance and angle data for **6.**