## Electronic Supplementary Information (ESI) for

## Metallic Coordination Selectivity Effect the Trinuclear M<sub>3</sub>(RCOO)<sub>6</sub> Secondary Building Units of Three Layer Metal-Carboxylate Frameworks

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$\mathbf{I}^{a}$	1	Z		<b>3</b> <sup>c</sup>	<b>I-</b>
Znl-Ol	1.967(1)	Mn1-O1	2.309(3)	Col-O2	2.031(5)
Zn1-O5	1.969(1)	Mn1-O2	2.285(3)	Co1-O5	2.207(5)
Zn1-N1	2.002(1)	Mn1-O3	2.137(3)	Co1-O6	2.157(5)
Zn1-O3#1	1.942(1)	Mn1-O4	2.260(3)	Co1-O7	2.170(7)
Zn2-O2	2.060(1)	Mn1-O6#1	2.128(3)	Co1-N1	2.091(8)
Zn2-O5	2.184(1)	Mn1-O14#2	2.150(3)	Co1-O3#1	2.035(5)
Zn2-O4#2	2.052(1)	Mn2-O2	2.214(3)	Co2-O1	2.055(5)
		Mn2-O5	2.118(2)	Co2-O6	2.144(5)
O1-Zn1-O5	96.59(4)	Mn2-O13#3	2.162(2)	Co2-O4#1	2.055(5)
O1-Zn1-N1	102.33(5)	Mn3-O7	2.133(3)		
O1-Zn1-O3#1	117.31(5)	Mn3-O9	2.217(2)	O2-Co1-O5	155.57(19)
O5-Zn1-N1	127,99(5)	Mn3-011	2.154(2)	O2-Co1-O6	97.33(18)
O3#1-Zn1-O5	112,23(4)	Mn4-08	2,124(3)	02-Co1-07	85 5(2)
O3#1-Zn1-N1	101.07(5)	Mn4-09	2.121(3)	$O_{2}^{2}Co_{1}N_{1}$	104 8(3)
$02_{-}7n2_{-}05$	90 51(4)	Mn4-O10	2.234(3)	02  Col 103#1	98 2(2)
$02-Z_{112}-03$	90.31(4) 84.61(4)	Mn4-010	2.274(3)	$02-001-03\pi1$	90.2(2)
02-Z112-04#2 02 Zn2 02#2	04.01(4)	Mn4-012	2.127(5)	05-C01-07	04.1(2)
02-ZII2-02#3	100.00	M: 4 010	2.109(5)	03-001-INI	50.0(5) 05.0(2)
02-Zn2-05#3	89.49(4)	win4-016	2.25/(5)	05#1-001-05	95.0(2)
02-Zn2-04#1	95.39(4)	01.14.1.00	57 00(0)	06-001-07	85./9(19)
04#2-Zn2-O5	88.36(4)	OI-Mn1-O2	57.88(9)	O6-Co1-N1	156.2(3)
04#1-Zn2-O5	91.64(4)	O1-Mn1-O3	97.71(10)	O3#1-Co1-O6	100.15(19)
Zn1-O5-Zn2	99.55(4)	O1-Mn1-O4	85.81(11)	O7-Co1-N1	86.8(3)
		O1-Mn1-O6#1	151.54(9)	O3#1-Co1-O7	172.2(2)
		O1-Mn1-O14#2	95.59(10)	O3#1-Co1-N1	85.6(3)
		O2-Mn1-O3	155.59(11)	O1-Co2-O6	88.16(18)
		O2-Mn1-O4	88.72(10)	O1-Co2-O4#2	86.7(2)
		O2-Mn1-O6#1	95.84(10)	O1-Co2-O1#3	180.00
		O2-Mn1-O14#2	96.00(9)	O1-Co2-O6#3	91.84(18)
		O3-Mn1-O4	89.82(10)	O4#2-Co2-O1	93.3(2)
		O3-Mn1-O6#1	108.14(11)	Co1-O6-Co2	109.15(18)
		O3-Mn1-O14#2	85 35(10)		
		04-Mn1-06#1	82 63(12)		
		0.4  Mm = 0.014  Hz	175 11(10)		
		04 - 1011 - 014 # 2 06 f-Mn1-014 # 2	98.14(11)		
		$00_1 \text{ min} 014/2$ 02 Mn2 05	02.08(0)		
		$O_2 M_{n2} O_{12\#2}$	92.08(9)		
		$O_2 - M_{m2} - O_1 + 3$	88.08(9)		
		02 - Mii 2 - 03 # 1	07.92(9)		
		02-WIIZ-013#2	91.32(9)		
		05-Mn2-013#3	93.43(9)		
		05-Mn2-013#2	80.56(9)		
		07-Mn3-09	91.09(8)		
		07-Mn3-O11	92.77(8)		
		O9-Mn3-O11	87.69(8)		
		O7#4-Mn3-O9	88.91(8)		
		O7#4-Mn3-O11	87.23(8)		
		O8-Mn4-O9	95.57(9)		
		O8-Mn4-O10	92.41(9)		
		O8-Mn4-O12	106.28(10)		
		O8-Mn4-O15	83.16(10)		
		O8-Mn4-O16	170.07(9)		
		O9-Mn4-O12	93.03(9)		
		09-Mn4-015	164.94(10)		
		09-Mn4-016	89 95(9)		
		$010 Mn_{1-012}$	147 34(10)		
		010 - Mn4 - 012	106.98(10)		
		010  Mm + 013	22 51(10)		
		010-Mn4-016	05.51(10)		
		012-1/114-015	101.75(10)		
		012-Mn4-016	81.59(10)		
			100 (5/15)		
		Mn1-O2-Mn2	108.65(12)		
		Mn3-O9 -Mn4	109.45(9)		

Table S1 Selection bond lengths (Å) and angles (°) for 1-3

<sup>*a*</sup> Symmetry transformations used to generate equivalent atoms: #1 = 1/2+x, 1/2-y, 1/2+z; #2 = 1/2-x, 1/2+y, -1/2-z; #3 = 1-x, 1-y, -z.

<sup>b</sup> Symmetry transformations used to generate equivalent atoms: #1 = 2-x, 1-y, 1-z; #2 = 2-x, 2-y, -z; #3 = x, -1+y, 1+z; #4 = 1-x, 2-y, -z.

<sup>*c*</sup> Symmetry transformations used to generate equivalent atoms: #1 = x,-3/2-y,-1/2+z; #2 = -x,1/2+y,-1/2-z; #3 = -x,-1-y,-1-z.



Figure S1. Powder X-ray diffraction (PXRD) of 3.