<Supporting Information>

3,6-Connected Metal–Organic Frameworks Based on Triscarboxylate as a 3-Connected Organic Node and a Linear Trinuclear $Co_3(COO)_6$ Secondary Building Unit as a 6-Connected Node

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Table S1. Crystal data and structure refinement for **l** and **2**.

	l	**2**
Empirical formula	$C_{86}H_{102}N_8O_{20}Co_3$	$C_{62}H_{48}N_2O_{14}Co_3$
Formula weight	1744.55	1221.81
Temperature, K	193(2)	173(2) K
Crystal system	Monoclinic	Trigonal
Space group	$P2_1/n$	$P3_221$
Unit cell dimensions, Å, °	a = 12.341(3), α = 90	a = 25.472(4), α = 90
	b = 25.960(5), β = 98.81(3)	b = 25.472(4), β = 90
	c = 13.670(3), γ = 90	c = 13.143(3), γ = 120
Volume, $Å^3$	4327.9(15)	7385(2)
Z	2	3
Density (calculated), Mg/m^3	1.339	0.824
Absorption coefficient, mm^{-1}	0.642	0.539
F(000)	1830	1881
Crystal size, mm^3	0.56 x 0.10 x 0.08	1.12 x 0.84 x 0.56
Theta range for data collection, °	3.02 to 27.48	3.17 to 25.00
Reflections collected	41331	84810
Independent reflections	9878 [R(int) = 0.0744]	8672 [R(int) = 0.0990]
Completeness, %	99.7	99.7
Max. and min. transmission	0.9504 and 0.7151	0.7523 and 0.5836
Data / restraints / parameters	9878 / 48 / 652	8672 / 88 / 413
Goodness-of-fit on F^2	1.082	1.024
Final R indices [I>2sigma(I)]	R1 = 0.0433, wR2 = 0.0829	R1 = 0.0800, wR2 = 0.2238
R indices (all data)	R1 = 0.0912, wR2 = 0.1099	R1 = 0.0872, wR2 = 0.2319
Absolute structure parameter	-	0.48(2)
Largest diff. peak and hole, $e \cdot Å^{-3}$	0.600 and –0.765	0.660 and –0.451

Table S2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

1		**2**	
Co(1)-O(1)	2.159(2)	Co(1)-O(1)	2.096(4)
Co(1)-O(3)#1	2.049(2)	Co(1)-O(3)#4	2.137(4)
Co(1)-O(4)#2	2.045(2)	Co(1)-O(4)#2	2.121(4)
Avg.	2.085(65)		2.118(21)
Co(2)-O(1)	2.155(2)	Co(2)-O(1)	2.233(4)
Co(2)-O(2)	2.222(2)	Co(2)-O(2)	2.055(4)
Co(2)-O(4)#1	2.038(2)	Co(2)-O(4)#4	1.970(4)
Co(2)-O(6)#2	2.067(2)	Co(2)-O(6)#2	1.972(4)
Co(2)-O(7)	2.079(2)	Co(2)-O(7)	2.038(5)
Co(2)-O(8)	2.110(2)		
Avg.	2.112(67)		2.054(107)
O(1)#5-Co(1)-O(1)	180.0	O(1)-Co(1)-O(2)#2	173.6(2)
O(1)-Co(2)-O(2)	60.01(7)	O(2)-Co(2)-O(1)	60.90(14)
O(3)#1-Co(1)-O(1)	87.40(8)	O(1)-Co(1)-O(3)#4	87.94(15)
		O(1)-Co(1)-O(3)#5	87.30(15)
O(4)#1-Co(2)-O(1)	100.13(8)	O(4)#4-Co(2)-O(1)	89.74(16)
O(5)#2-Co(1)-O(1)	92.30(7)	O(1)-Co(1)-O(5)#2	91.64(14)
		O(1)-Co(1)-O(5)#3	92.86(15)
O(6)#2-Co(2)-O(1)	93.68(7)	O(6)#2-Co(2)-O(1)	93.79(16)
O(7)-Co(2)-O(1)	160.70(8)	O(7)-Co(2)-O(1)	167.26(19)
O(8)-Co(2)-O(1)	96.59(8)		
O(4)#1-Co(2)-O(2)	**157.61(8)**	**O(4)#4-Co(2)-O(2)**	**125.7(2)**
O(6)#2-Co(2)-O(2)	**95.26(8)**	**O(6)#2-Co(2)-O(2)**	**112.62(18)**
O(7)-Co(2)-O(2)	101.38(8)	O(7)-Co(2)-O(2)	106.7(2)
O(8)-Co(2)-O(2)	84.21(8)		
O(3)#1-Co(1)-O(3)#4	180.0	O(3)#4-Co(1)-O(3)#5	84.3(2)
O(5)#2-Co(1)-O(3)#1	95.73(8)	O(5)#2-Co(1)-O(3)#4	92.31(14)
O(5)#2-Co(1)-O(3)#4	84.27(8)	O(5)#3-Co(1)-O(3)#4	176.52(15)
O(4)#1-Co(2)-O(6)#2	**96.34(9)**	**O(4)#4-Co(2)-O(6)#2**	**114.0(2)**
O(4)#1-Co(2)-O(7)	99.09(9)	O(4)#4-Co(2)-O(7)	96.4(2)

O(4)#1-Co(2)-O(8) 88.39(9)
O(5)#2-Co(1)-O(5)#3180.0 O(5)#2-Co(1)-O(5)#391.1(2)

O(6)#2-Co(2)-O(7) 82.40(8) O(6)#2-Co(2)-O(7) 93.9(2)
O(6)#2-Co(2)-O(8)167.77(8)
O(7)-Co(2)-O(8) 85.72(8)

Symmetry transformations used to generate equivalent atoms for **1**:
#1 x+1,y,z+1 #2 -x+3/2,y+1/2,-z+3/2 #3 x+1/2,-y+3/2,z+1/2
#4 -x+1,-y+2,-z+1 #5 -x+2,-y+2,-z+2 #6 x-1,y,z-1
#7 -x+3/2,y-1/2,-z+3/2
Symmetry transformations used to generate equivalent atoms for **2**:
#1 y,x,-z #2 -x+y,-x,z-2/3 #3 -x,-x+y,-z+2/3
#4 x-y+1,-y+1,-z+1/3 #5 -y+1,x-y+1,z-1/3 #6 x-y,-y+1,-z+1/3
#7 -x+y,-x+1,z+1/3 #8 -y,x-y,z+2/3

Table S3. The close contacts (Å) between the doubly interconnected two 3-connected ligands of **2**.

		1	
C(6) ⋯ C(21) #1	3.298(6)	C(9) ⋯ C(14) #1	3.334(8)
C(14) ⋯ C(14) #1	3.387(9)	C(24) ⋯ C(25) #1	3.427(8)

Symmetry transformations used to generate equivalent atoms for **2**: #1 -x,-x+y,-z+2/3

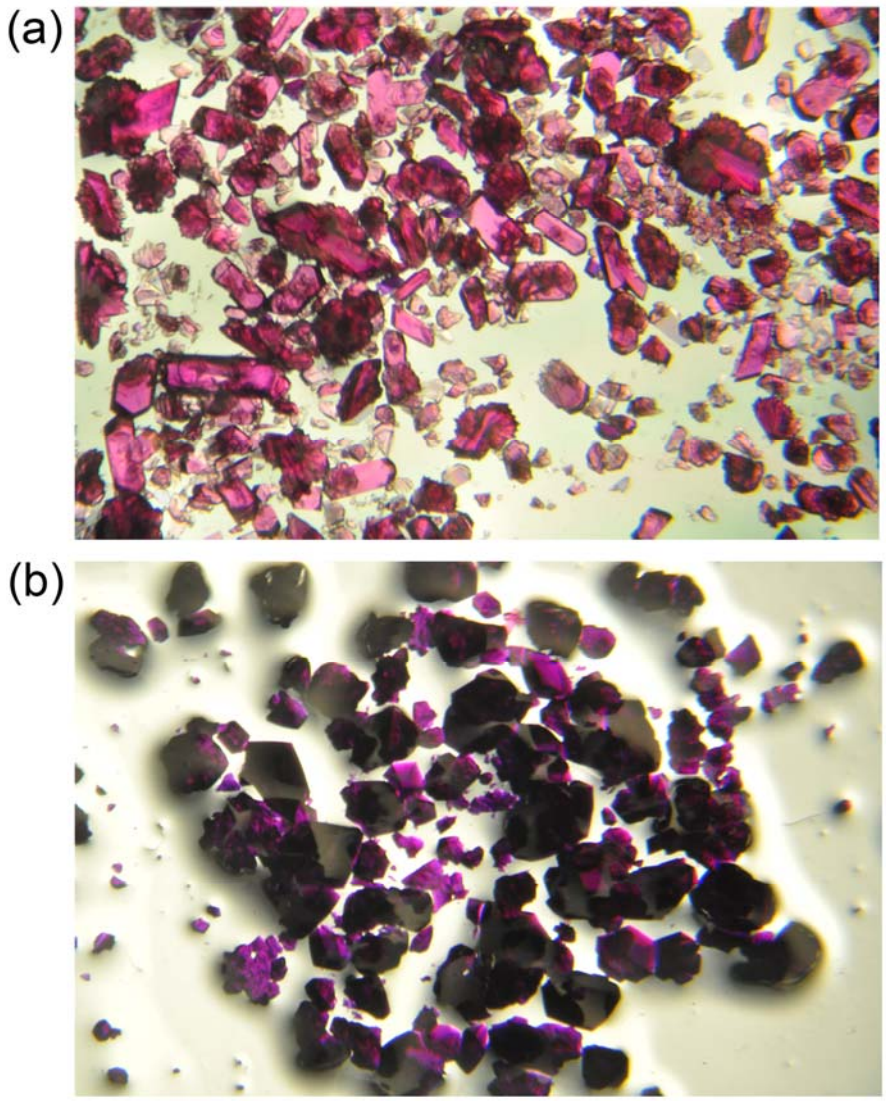

Figure S1. Optical microscopic photographs of (a) **1** and (b) **2**.

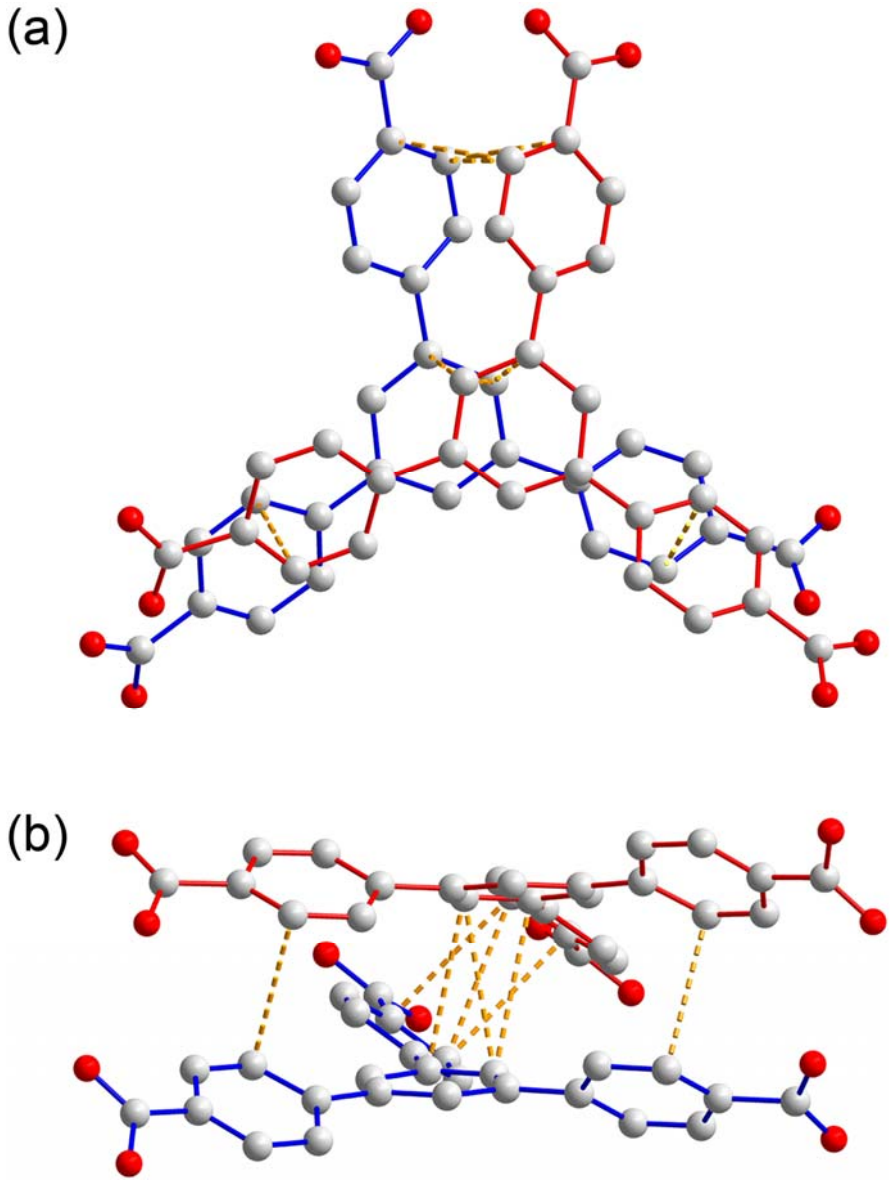

Figure S2. Stacking interaction between the doubly interconnected two 3-connected ligands of **2** in (a) top and (b) side views. The close contacts were represented in dotted lines.

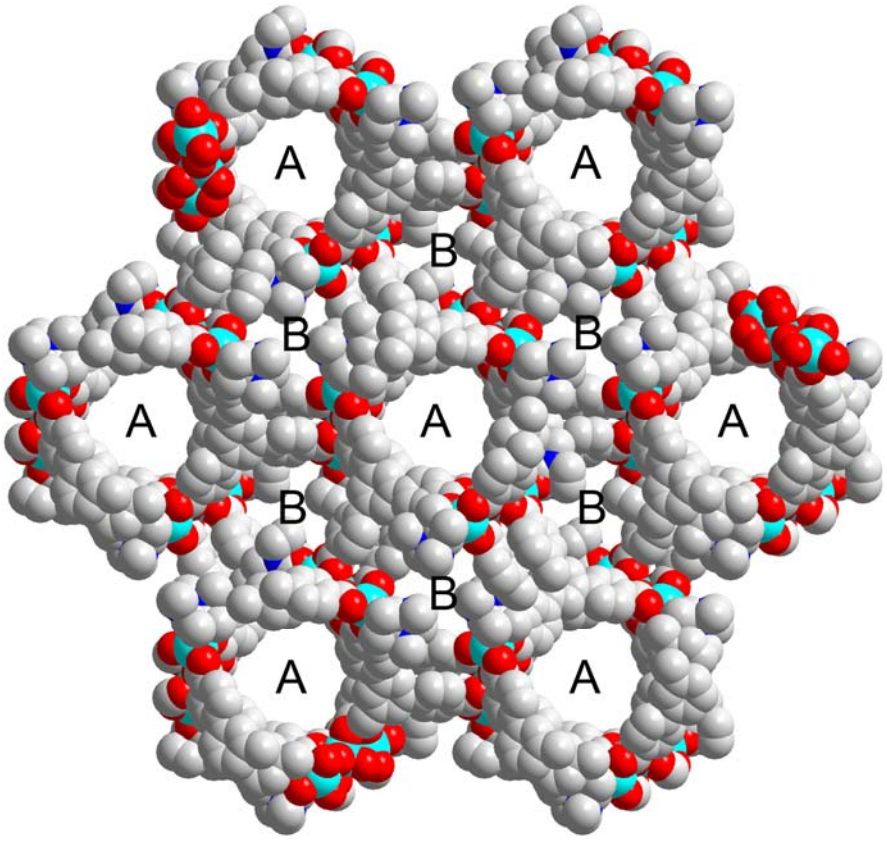

Figure S3. CPK packing diagram of **2** with the two different types of solvent channels, A and B.