Electronic Supplementary Information

Metallomacrocycle-supported interpenetration networks assembled from binary N-containing ligands

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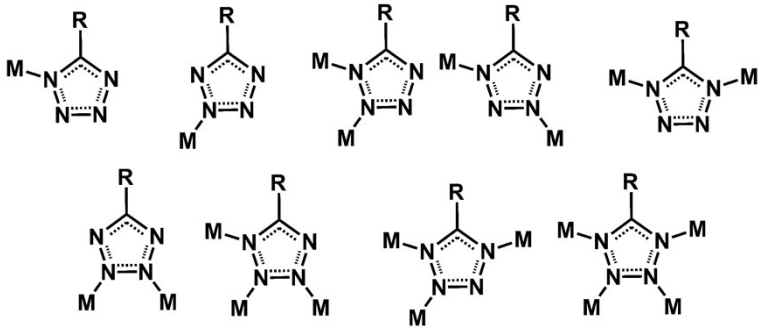

Scheme S1. Diverse coordination modes of tetrazole group previously reported.

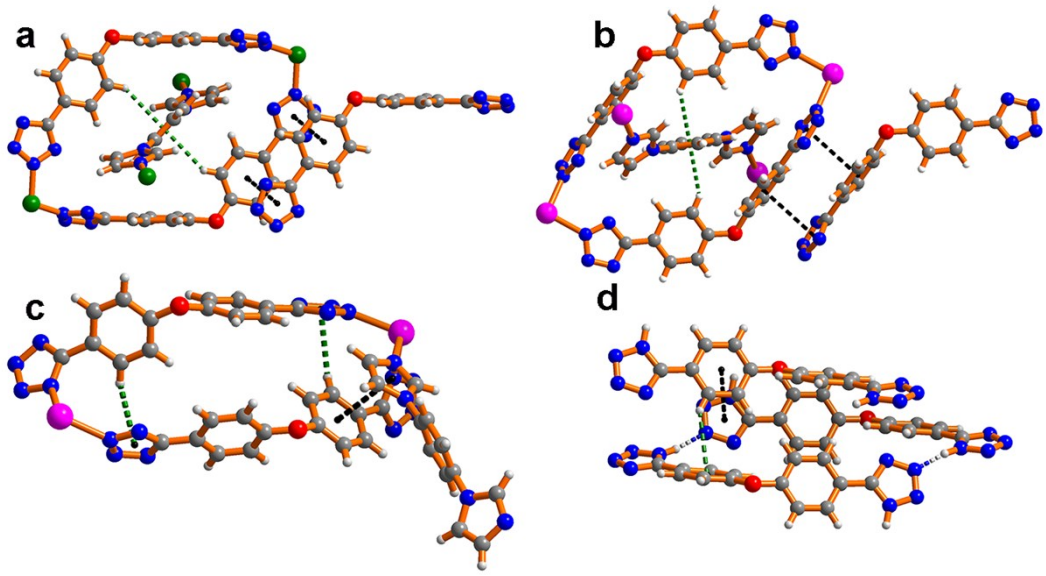

Figure S1. The weak interactions between the neighboring btzb and bib ligands in compounds **1-3** (a-c, respectively) and H_2btzb (d) (π-π and C-H···π interactions are indicated using black and yellow dash lines, respectively).

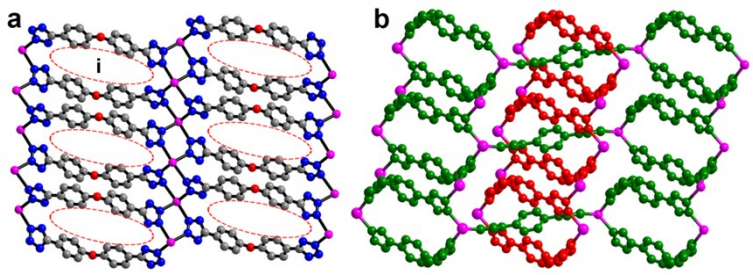

Figure S2. X-ray crystal structure of **2** showing (a) metallomacrocycle (i) in a two-dimensional layer and (b) an interpenetration fragment in **2**.

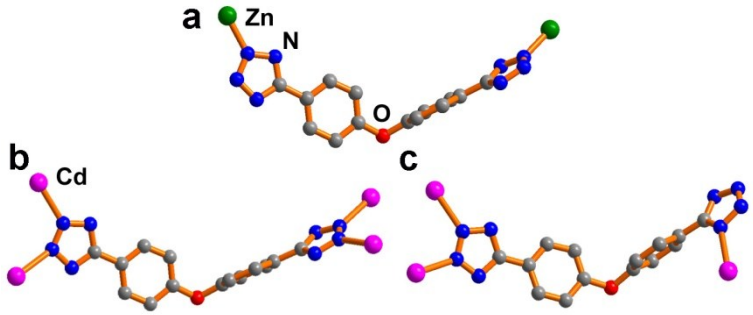

Figure S3. Coordination modes (a-c) of btzb ligand for **1**-**3**, respectively.

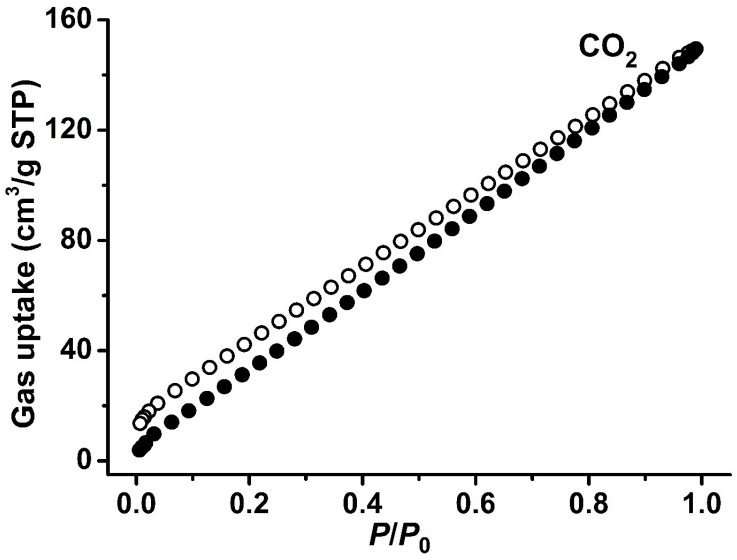

Figure S4. CO_2 sorption isotherms of **3** at 196 K (solid symbols: adsorption, open symbols: desorption).

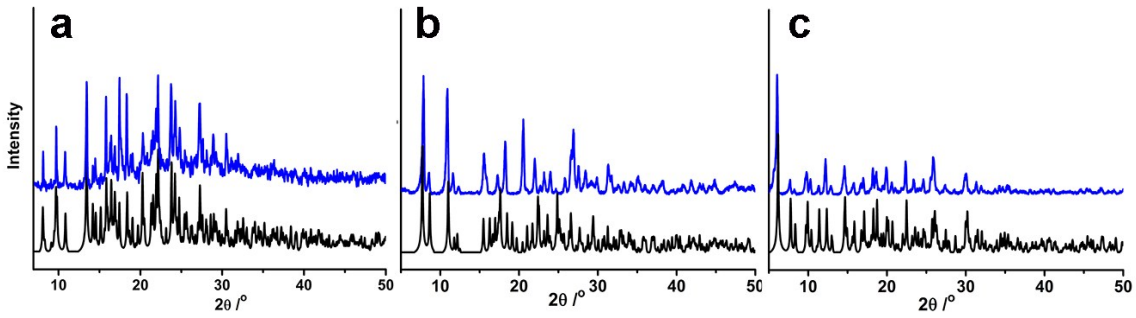

Figure S5. Powder X-ray diffraction profiles for as-synthesized **1-3** (a-c, respectively) (blue line) in comparison with simulated powder patterns based on their single-crystal structures (black line).

Table S1. Selected bond distances (Å) and bond angles (°).

Complex **1**			
Zn(1)-N(11)	1.979(4)	Zn(1)-N(2)	1.992(4)
Zn(1)-N(9)	1.993(4)	Zn(1)-N(7)#4	1.997(4)
N(7)-Zn(1)#4	1.997(4)		
N(11)-Zn(1)-N(2)	114.88(16)	N(11)-Zn(1)-N(9)	115.90(15)
N(2)-Zn(1)-N(9)	104.39(16)	N(11)-Zn(1)-N(7)#4	109.29(17)
N(2)-Zn(1)-N(7)#4	105.09(16)	N(9)-Zn(1)-N(7)#4	106.44(16)
Complex **2**			
Cd(1)-N(9)	2.236(2)	Cd(1)-N(2)	2.250(2)
Cd(1)-N(7)#2	2.259(2)	Cd(1)-N(6)#3	2.352(2)
Cd(1)-N(3)#4	2.478(2)	N(3)-Cd(1)#4	2.478(2)
N(6)-Cd(1)#3	2.352(2)	N(7)-Cd(1)#5	2.259(2)
N(9)-Cd(1)-N(2)	117.26(8)	N(9)-Cd(1)-N(7)#2	128.04(8)
N(2)-Cd(1)-N(7)#2	113.70(8)	N(6)#3-Cd(1)-N(3)#4	175.08(8)
N(9)-Cd(1)-N(6)#3	91.34(8)	N (2)-Cd(1)-N(6)#3	95.34(8)
N(7)#2-Cd(1)-N(6)#3	93.46(7)	N(9)-Cd(1)-N(3)#4	87.42(8)
N(2)-Cd(1)-N(3)#4	89.45(8)	N(7)#2-Cd(1)-N(3)#4	83.58(7)
Complex **3**			
N(12A)-Cd(1)#1	2.179(12)	N(2)-Cd(1)#2	2.403(5)
N(3)-Cd(1)#3	2.345(5)	N(8)-Cd(1)	2.317(4)
Cd(1)-N(12)#4	2.377(8)	Cd(1)-N(12A)#4	2.179(12)
Cd(1)-N(3)#3	2.345(5)	Cd(1)-N(2)#5	2.403(5)
O(1)-Cd(1)	2.463(4)		

N(12A)#4-Cd(1)-N(9A)	79.0(6)	N(12A)#4-Cd(1)-N(8)	102.1(4)
N(9A)-Cd(1)-N(8)	173.0(4)	N(12A)#4-Cd(1)-N(9)	90.2(5)
N(12)#4-Cd(1)-O(1)	90.8(2)	N(2)#5-Cd(1)-O(1)	80.87(14)
N(3)#3-Cd(1)-O(1)	173.55(14)	N(9)-Cd(1)-O(1)	80.2(2)
N(8)-Cd(1)-O(1)	85.35(14)	N(9A)-Cd(1)-O(1)	87.8(4)
N(8)-Cd(1)-N(3)#3	99.49(15)	N(9)-Cd(1)-N(3)#3	94.0(2)
N(9)-Cd(1)-N(2)#5	81.6(2)	N(12)#4-Cd(1)-N(2)#5	171.1(2)
N(8)-Cd(1)-N(2)#5	83.05(15)	N(3)#3-Cd(1)-N(2)#5	95.41(16)
N(9A)-Cd(1)-N(2)#5	94.3(4)	N(12A)#4-Cd(1)-N(2)#5	165.3(4)
N(3)#3-Cd(1)-N(12)#4	93.1(3)	N(9)-Cd(1)-N(12)#4	100.3(3)
N(8)-Cd(1)-N(12)#4	93.1(2)	N(9A)-Cd(1)-N(12)#4	88.6(5)

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

Table S2. Hydrogen bonding interactions of **1.**

D-H···A	distance of D···A (Å)	angle of D-H···A (o)
O2-H2A···O3#1	2.960(7)	136.1
O4-H4B···O2#1	3.122(9)	132.2
O2-H2B···N4	2.978(5)	134.2
O3-H3B···N1	3.200(7)	167.5
O4-H4A···N3#2	2.856(10)	147.2
O3-H3C···N5#3	3.336(11)	161.5

Symmetric code: #1: -x, 1-y, 1-z; #2: x, 1+y, z, #3: -x, 1-y, -z.