Supporting information

Syntheses, Structures and Properties of a Series of Polyazaheteroaromatic Core-Based Zn(II) Coordination Polymers Together with Carboxylate Auxiliary Ligands

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Table S1. Selected Bond Lengths [Å] and Bond Angles [deg] for Complexes **1** - **6**[a]

		1	
Zn(1)-N(1)	2.001(16)	Zn(1)-O(2)	1.982(14)
O(2)#1-Zn(1)-O(2)	95.18(8)	O(2)#1-Zn(1)-N(1)	106.34(7)
O(2)-Zn(1)-N(1)	123.71(7)	N(1)-Zn(1)-N(1)#1	103.38(10)
		2	
Zn(1)-O(1)	1.9666(13)	Zn(1)-O(2)#1	1.9547(13)
Zn(1)-N(3)	1.9963(17)	Zn(1)-N(1)#2	1.9774(15)
O(2)#1-Zn(1)-O(1)	122.94(6)	O(2)#1-Zn(1)-N(1)#2	96.89(6)
O(1)-Zn(1)-N(1)#2	99.46(6)	O(2)#1-Zn(1)-N(3)	110.68(6)
O(1)-Zn(1)-N(3)	104.29(6)	N(1)#2-Zn(1)-N(3)	123.71(7)
		3	
Zn(1)-O(1)	1.9303(17)	Zn(1)-N(1)	2.010(2)
Zn(1)-N(5)#1	2.013(2)	Zn(1)-N(7)#2	2.038(2)
Zn(2)-O(3)#3	1.9439(17)	Zn(2)-N(11)	1.970(2)
Zn(2)-N(10)#4	2.047(2)	Zn(2)-N(3)	2.079(2)
O(1)-Zn(1)-N(1)	128.85(9)	O(1)-Zn(1)-N(5)#1	96.48(8)
N(1)-Zn(1)-N(5)#1	106.87(8)	O(1)-Zn(1)-N(7)#2	106.07(8)
N(1)-Zn(1)-N(7)#2	106.11(9)	N(5)#1-Zn(1)-N(7)#2	111.96(9)
O(3)#3-Zn(2)-N(11)	126.25(9)	O(3)#3-Zn(2)-N(10)#4	106.15(8)
N(11)-Zn(2)-N(10)#4	119.10(9)	O(3)#3-Zn(2)-N(3)	100.81(8)
N(11)-Zn(2)-N(3)	103.54(9)	N(10)#4-Zn(2)-N(3)	93.61(9)
		4	
Zn(1)-O(1)	1.941(2)	Zn(1)-N(11)#1	2.000(2)
Zn(1)-N(1)	2.002(3)	Zn(1)-N(9)#2	2.030(3)
Zn(2)-O(6)#3	1.953(2)	Zn(2)-N(7)	1.969(3)
Zn(2)-N(4)	1.997(3)	Zn(2)-N(5)#4	2.008(3)
O(1)-Zn(1)-N(11)#1	106.48(10)	O(1)-Zn(1)-N(1)	126.08(10)
N(11)#1-Zn(1)-N(1)	115.30(11)	O(1)-Zn(1)-N(9)#2	105.22(10)
N(11)#1-Zn(1)-N(9)#2	104.09(10)	N(1)-Zn(1)-N(9)#2	96.31(11)
O(6)#3-Zn(2)-N(7)	108.92(11)	O(6)#3-Zn(2)-N(4)	110.02(12)

N(7)-Zn(2)-N(4)	121.34(11)	O(6)#3-Zn(2)-N(5)#4	97.61(11)
N(7)-Zn(2)-N(5)#4	106.56(11)	N(4)-Zn(2)-N(5)#4	109.74(11)

5

N(1)-Zn(1)	2.152(4)	Zn(1)-O(1)	1.982(4)
O(4)-Zn(2)#1	1.982(4)	O(6)-Zn(2)#2	1.938(4)
O(8)-Zn(1)#3	2.042(4)	Zn(1)-N(6)#4	2.004(4)
Zn(1)-O(3)#3	2.173(4)	Zn(2)-N(5)	2.003(4)
Zn(2)-O(5)	1.981(4)	Zn(2)-O(4)#1	1.982(4)
O(1)-Zn(1)-N(6)#4	123.73(17)	O(1)-Zn(1)-O(8)#3	123.34(16)
N(6)#4-Zn(1)-O(8)#3	112.42(17)	O(1)-Zn(1)-N(1)	88.83(16)
N(6)#4-Zn(1)-N(1)	99.96(18)	O(8)#3-Zn(1)-N(1)	88.61(18)
O(1)-Zn(1)-O(3)#3	91.04(16)	N(6)#4-Zn(1)-O(3)#3	90.74(17)
O(8)#3-Zn(1)-O(3)#3	80.79(16)	N(1)-Zn(1)-O(3)#3	167.21(16)
O(6)#5-Zn(2)-O(5)	102.68(19)	O(6)#5-Zn(2)-O(4)#1	128.17(15)
O(5)-Zn(2)-O(4)#1	104.22(17)	O(6)#5-Zn(2)-N(5)	114.94(17)
O(5)-Zn(2)-N(5)	98.54(19)	O(4)#1-Zn(2)-N(5)	103.77(17)

6

Zn(1)-O(2)	1.942(5)	Zn(1)-N(5)#1	1.999(6)
Zn(1)-N(1)	2.024(6)	Zn(1)-N(13)	2.052(6)
Zn(2)-O(5)#2	1.950(5)	Zn(2)-N(11)#1	1.975(6)
Zn(2)-N(3)	2.011(6)	Zn(2)-N(7)	2.011(6)
Zn(3)-N(17)#1	2.002(6)	Zn(3)-N(10)#3	2.039(7)
Zn(3)-O(3)	2.039(6)	Zn(3)-N(16)#4	2.044(6)
O(2)-Zn(1)-N(5)#1	111.6(2)	O(2)-Zn(1)-N(1)	115.0(2)
N(5)#1-Zn(1)-N(1)	109.1(2)	O(2)-Zn(1)-N(13)	109.2(2)
N(5)#1-Zn(1)-N(13)	110.6(3)	N(1)-Zn(1)-N(13)	100.7(3)
O(5)#2-Zn(2)-N(11)#1	104.9(2)	O(5)#2-Zn(2)-N(3)	104.3(2)
N(11)#1-Zn(2)-N(3)	117.8(2)	O(5)#2-Zn(2)-N(7)	110.6(2)
N(11)#1-Zn(2)-N(7)	112.2(2)	N(3)-Zn(2)-N(7)	106.7(3)
N(17)#1-Zn(3)-N(10)#3	107.8(3)	N(17)#1-Zn(3)-O(3)	112.4(3)

N(10)#3-Zn(3)-O(3)	130.1(3)	N(17)#1-Zn(3)-N(16)#4	110.2(2)
N(10)#3-Zn(3)-N(16)#4	101.3(3)	O(3)-Zn(3)-N(16)#4	91.5(2)
N(17)#1-Zn(3)-O(4)	98.3(2)	N(10)#3-Zn(3)-O(4)	88.5(2)
O(3)-Zn(3)-O(4)	58.0(2)	N(16)#4-Zn(3)-O(4)	144.9(2)

[a] Symmetry transformations used to generate equivalent atoms:

For **1**: #1 -x+2,y,-z+1/2. For **2**: #1 -x+1,-y+2,-z+1; #2 -x+3/2,y+1/2,-z+3/2. For **3**: #1 x+1,y,z; #2 x+1,y,z-1; #3 -x+2,-y+2,-z+1; #4 -x+1,-y+1,-z+2. For **4**: #1 x+1,y,z-1; #2 x+1,-y+1/2,z-1/2; #3 -x,-y+1,-z; #4 -x,-y+1,-z+1. For **5**: #1 -x+1,-y+1,-z; #2 x+1,y-1,z-1; #3 -x+1,-y,-z; #4 -x-1,-y+1,-z+1; #5 x-1,y+1,z+1. For **6**: #1 x+1,y,z; #2 -x+1,-y+1,-z+1; #3 x+1,y+1,z+1; #4 -x+2,-y+2,-z+1.

Table S2 Hydrogen bonding data for complexes **1 - 6**

D-H···A	d(D···A) (Å)	∠D-H···A (°)
	Compound **1**	
N2-H2···O5#1	2.688(3)	168
O3-H3A···O1#2	2.610(2)	158
O5-H5A···O4#3	2.765(3)	155
O5-H5···O1#4	2.788(3)	134
	Compound **2**	
N2-H2A···N4#1	2.871(2)	157
C16-H16A···N5#2	3.382(2)	170
	Compound **3**	
N6-H6···O8	2.910(4)	168
O8-H8A···O2	3.007(4)	151
O8-H8B···O5#1	3.043(5)	117
O8-H8B···O6#1	3.174(4)	165
N12-H12A···O7#2	2.905(3)	169
C1-H1···O8	3.163(4)	147
C8-H8···N2#3	3.104(3)	116
C9-H9···O5#1	3.040(3)	123
C11-H11···O7#2	3.360(4)	166
C14-H14···O4#4	3.469(3)	159
C18-H18···N4	3.256(3)	140
	Compound **4**	
N6-H6···O2#1	2.890(4)	167
N8-H8A···O5#2	2.764(4)	172
C5-H5···O2#1	3.227(4)	163
C11-H11···O5#2	3.426(4)	164
	Compound **5**	
N4-H4A···O7#1	2.823(9)	159
O5-H5A···O2#2	2.775(6)	132
O5-H5C···O2#3	2.619(7)	157
C15-H15···O2#4	3.081(8)	122
	Compound **6**	

N6-H6···O6	2.842(9)	170
N12-H12A···O4#1	2.677(11)	133
C5-H5···O2	3.125(11)	163
C10-H10···O1#2	3.028(11)	120
C11-H11···O5#1	3.371(10)	141
C28-H28···N9#3	3.258(11)	128
C29-H29···O1#2	3.233(13)	126
C32-H32···N8#3	3.452(11)	157

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

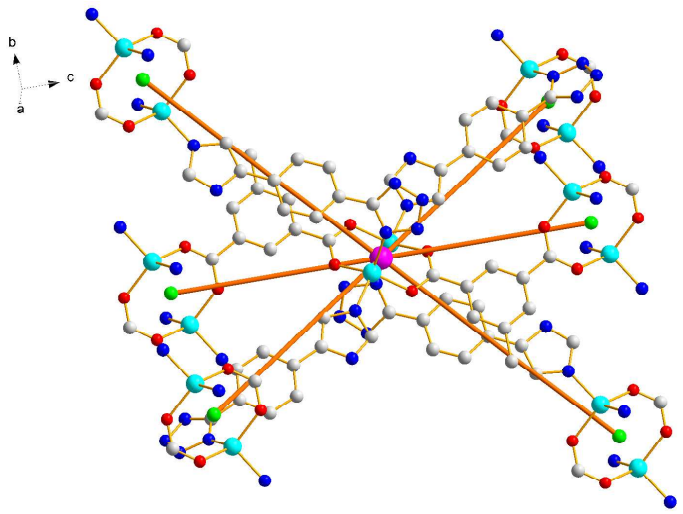


Figure S1 View of the linkage of a binuclear Zn(II) node with six adjacent cores of **2**.

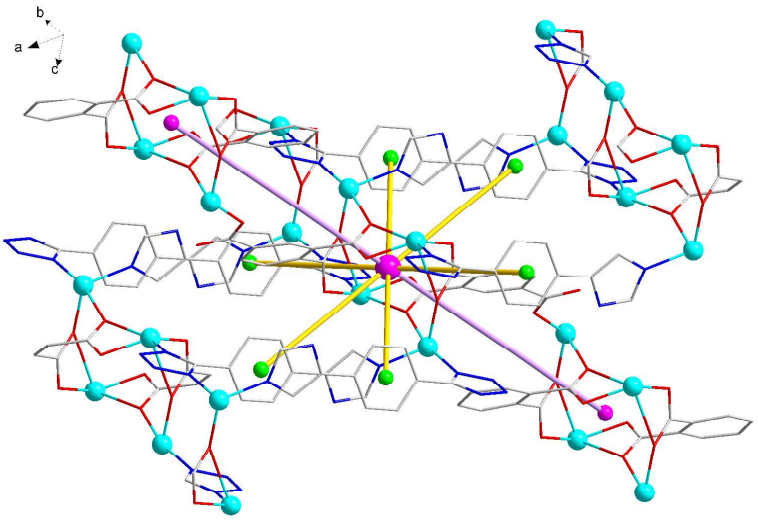


Figure S2 Schematic view of the 8-connected tetranuclear $[Zn_4(COO)_4]$ SBU of **5**.

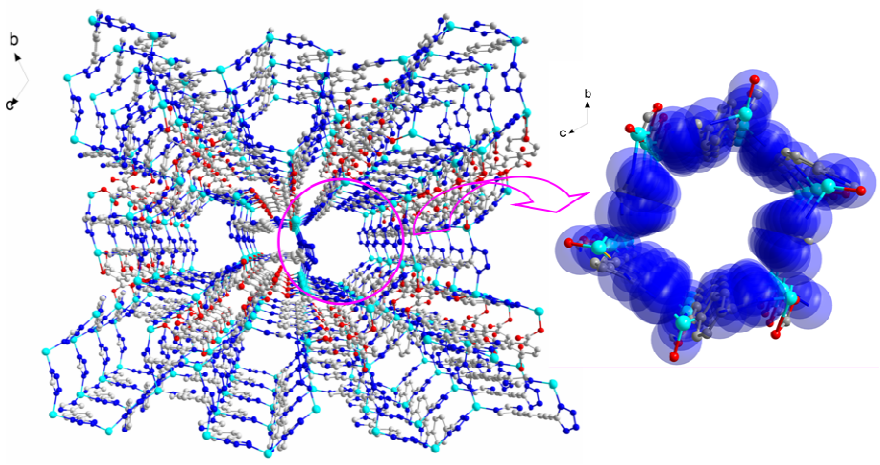


Figure S3 The pores of framework decorated with uncoordinated tetrazole-N atoms in **6**.

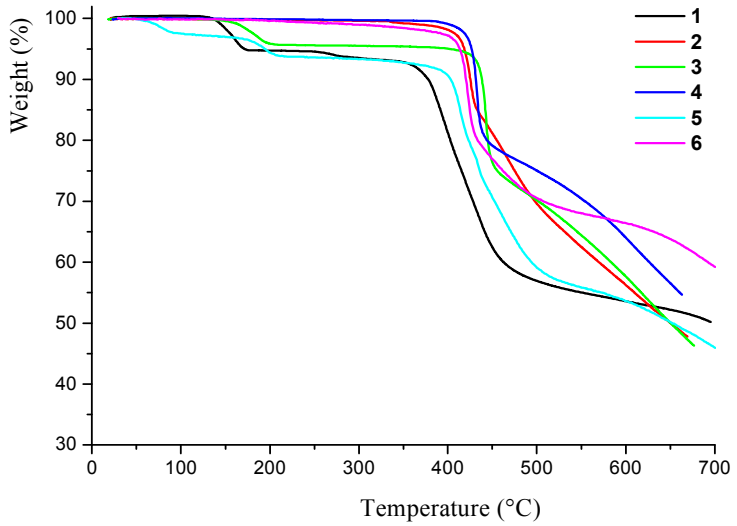
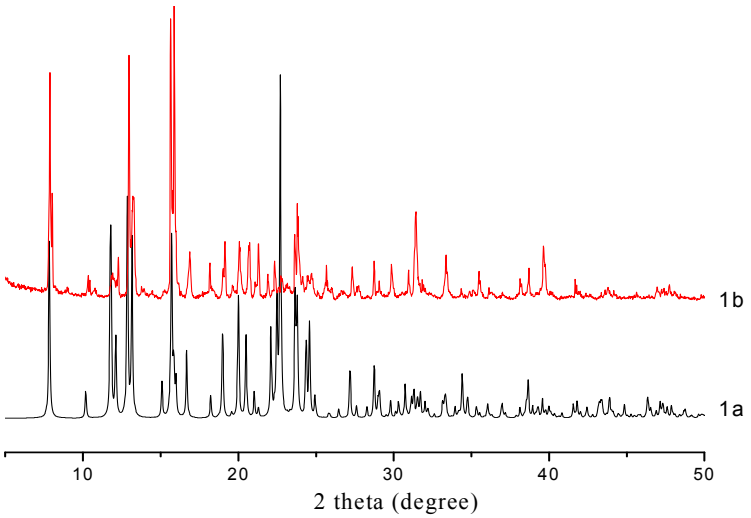
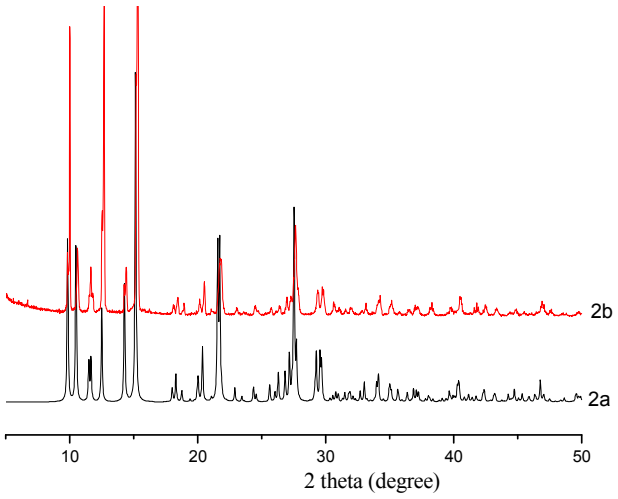
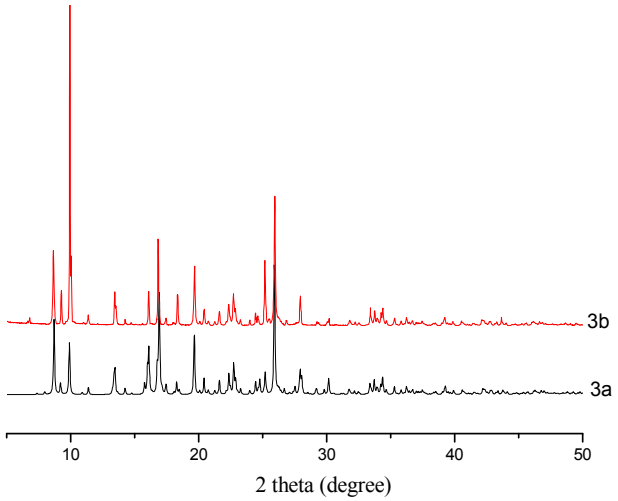
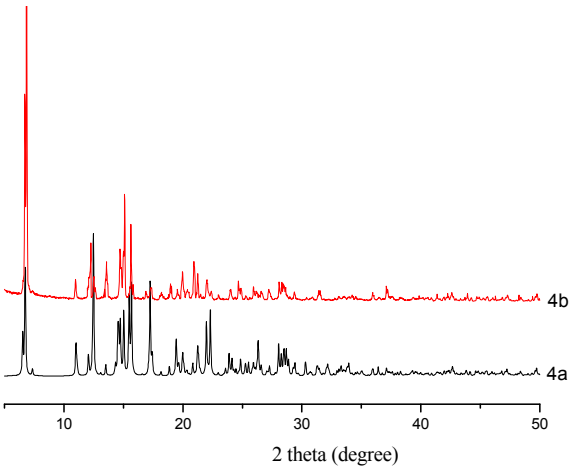


Figure S4 The TG curves of **1 - 6**.




2b
2a
10
20
30
40
50
2 theta (degree)


3b
3a
10
20
30
40
50
2 theta (degree)


4b
4a
10
20
30
40
50
2 theta (degree)

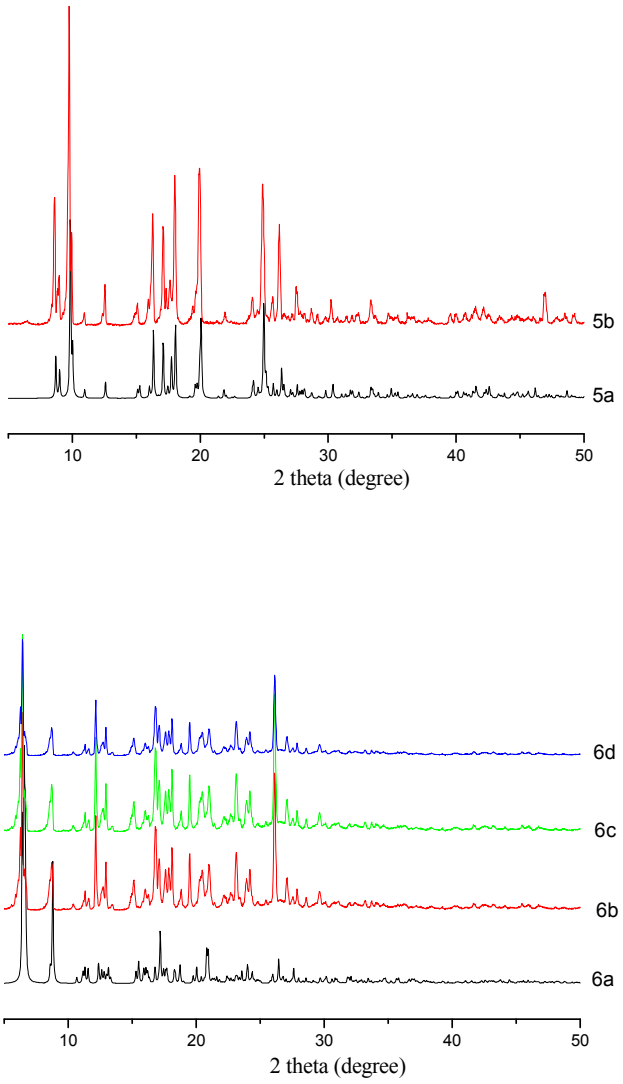


Figure S5 The X-ray powder diffraction patterns of complexes **1** – **6**: a – simulated; b – as-synthesized; c –the actived phase at 140ºC; d –the actived phase at 180ºC.

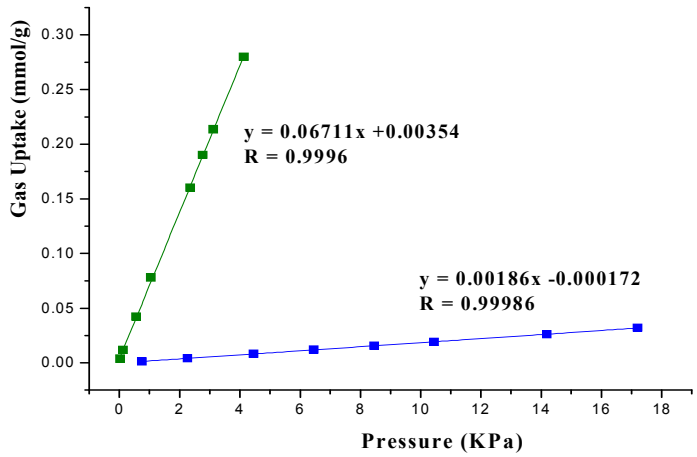


Figure S6 The fitting initial slope for CO_2 and N_2 isotherms collected at 273 K (CO_2: green; N_2: blue).

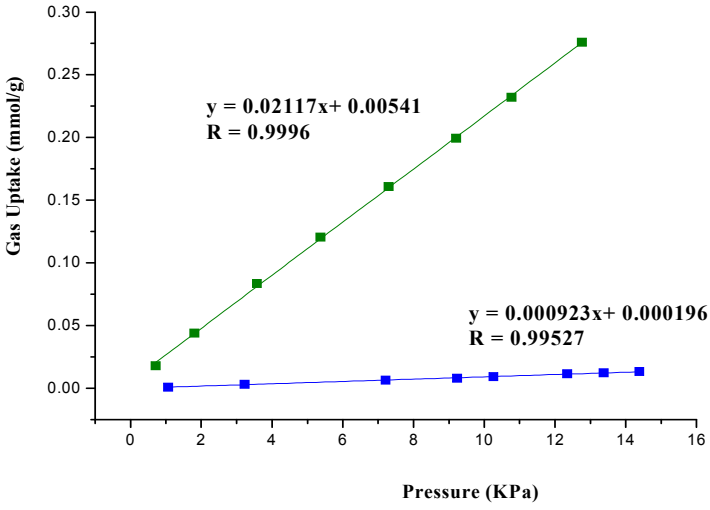


Figure S7 The fitting initial slope for CO_2 and N_2 isotherms collected at 298 K (CO_2: green; N_2: blue).