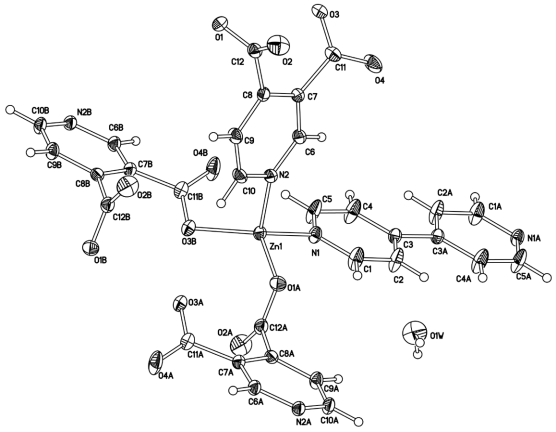
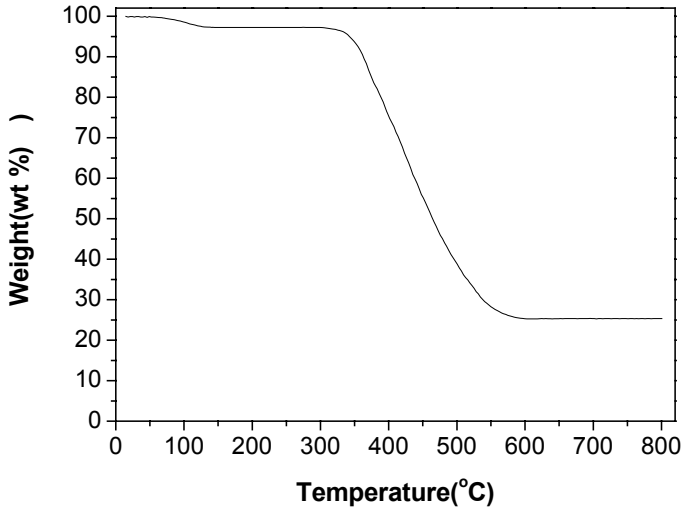
Supporting Information for "Designed double layer assembly: a three-dimensional open framework with two types of cavities by connection of infinite two-dimensional bilayer, Xinlong Wang, Chao Qin, Enbo Wang,* Yangguang Li, Changwen Hu and Lin Xu, *Chemical Communications*"

SI 1: asymmetric unit of 1

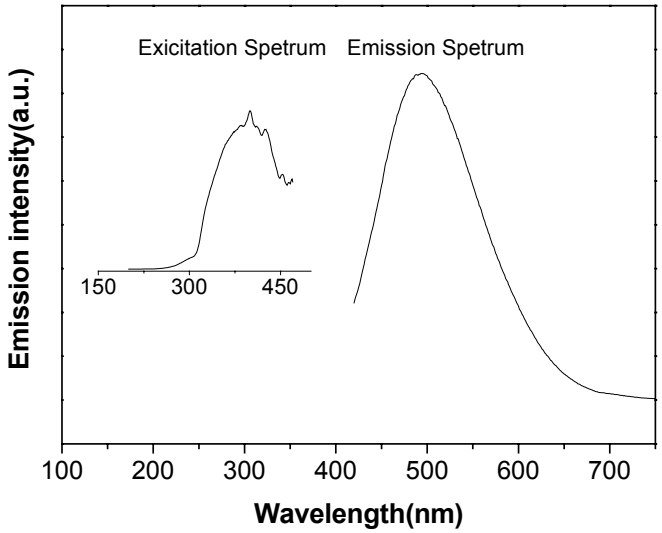


SI 2: TGA curve of 1



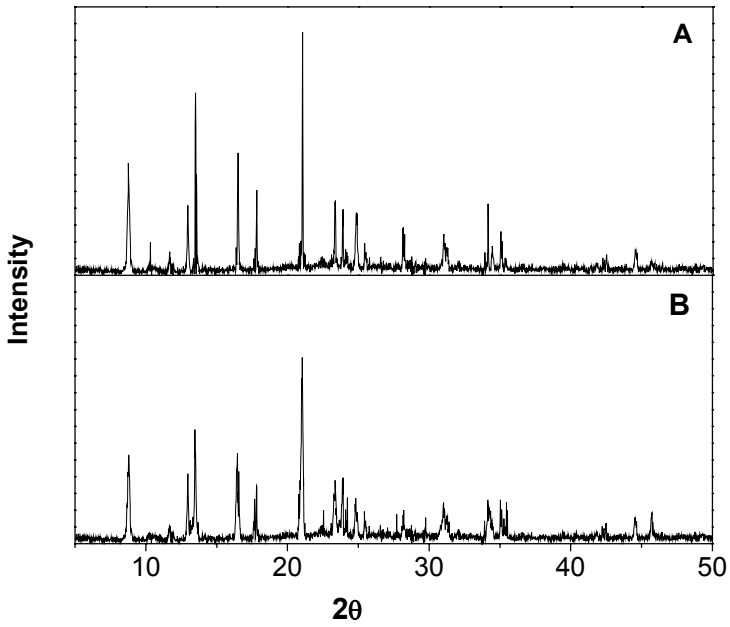
Thermogravimetric analysis (TGA) was performed in air at a heating rate of 10℃ /min on a polycrystalline sample of compound **1**. The result showed that the first weight loss of 2.71% occurred between 60℃ and 120℃, corresponding to the removal of the guest water molecules (Calcd 2.83%). The second weight loss starts at ca. 332℃ up to 590℃ corresponding to the release of organic groups. The remaining weight of 25.34% corresponds to the percentage (25.51%) of Zn and O components, indicating that the final product is ZnO.

SI 3: Fluorescence Spectrum of 1



The emission spectrum of compounds **1** in solid state at room temperature shows that an intense emissions occurring at 497nm (λ_{ex}=399 nm). According to the previous literature, 4,4'-bpy does not emit any luminescence in the range 300-700 nm. In order to understand the nature of the emission band, we analyzed the photoluminescence property of H_2PDB ligand and found that the strongest emission peak for H_2PDB is at about 370 nm which is attributable to the $\pi^* \rightarrow n$ transition. Therefore, according to the literature, the emissions at 497 nm can be assigned to the emission of ligand-to-metal charge transfer (LMCT).

SI 4: XRPD



A: X-Ray Powder diffraction pattern of as-synthesized **1**.
B: X-Ray Powder diffraction pattern of the calcinations product (**1'**) at 120℃ for 2h.

It is nearly the same as that of **1**, indicating that the porous network of **1** is retained after the calcinations and removal of guests.

Elemental analysis for calcinated sample (**1'**): C 46.70%; H 2.30%; N 9.13%.

Calculated framework formula of $[Zn_2(PDB)_2(4,4'\text{-bpy})]_n$: C 46.67%; H 2.27%; N 9.07%. Thus, it can be considered that guest water molecular had been removed in the course of calcinations.

Table 1. Crystal data and structure refinement for **1**.

Identification code	qc22
Empirical formula	C24 H16 N4 O9 Zn2
Formula weight	635.15
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	a = 16.069(3) A alpha = 90 deg. b = 13.635(3) A beta = 111.60(3) deg. c = 11.508(2) A gamma = 90 deg.
Volume	2344.3(8) A^3
Z, Calculated density	4, 1.800 Mg/m^3
Absorption coefficient	2.112 mm^-1
F(000)	1280
Crystal size	0.423 x 0.374 x 0.331 mm
Theta range for data collection	2.41 to 27.43 deg.
Limiting indices	-20<=h<=20, -17<=k<=17, -14<=l<=14
Reflections collected / unique	5113 / 2673 [R(int) = 0.0273]
Completeness to theta = 27.43	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.497 and 0.426
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2673 / 1 / 177
Goodness-of-fit on F^2	1.018
Final R indices [I>2sigma(I)]	R1 = 0.0333, wR2 = 0.1021
R indices (all data)	R1 = 0.0387, wR2 = 0.1068
Largest diff. peak and hole	1.028 and -0.617 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **1**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Zn(1)	3968(1)	2092(1)	9635(1)	26(1)
N(1)	5269(1)	2236(2)	9838(2)	28(1)
N(2)	3319(1)	1207(1)	8123(2)	27(1)
C(1)	5494(2)	2935(2)	9197(3)	44(1)
C(6)	3692(1)	576(2)	7563(2)	27(1)
C(10)	2421(2)	1176(2)	7794(2)	31(1)
C(9)	1894(1)	492(2)	6967(2)	31(1)
O(1W)	5000	4867(3)	7500	66(1)
C(2)	6355(2)	3058(2)	9235(3)	46(1)
C(5)	5914(2)	1645(2)	10540(3)	49(1)
C(4)	6793(2)	1727(3)	10629(3)	50(1)
C(8)	2287(1)	-190(2)	6430(2)	24(1)
C(7)	3213(1)	-127(2)	6707(2)	26(1)
C(12)	1695(1)	-966(2)	5602(2)	29(1)
O(1)	1587(1)	-1698(1)	6214(2)	37(1)
O(2)	1333(2)	-827(2)	4475(2)	52(1)
C(11)	3701(2)	-774(2)	6103(2)	31(1)
O(3)	3379(1)	-1622(1)	5754(2)	35(1)
O(4)	4361(1)	-450(2)	5948(2)	53(1)
C(3)	7031(1)	2446(2)	9965(2)	25(1)

Table 3. Bond lengths [A] and angles [deg] for **1**.

Zn(1)-O(1)#1	1.9573(18)	C(1)-C(2)-C(3)	120.1(2)
Zn(1)-O(3)#2	1.9659(17)	N(1)-C(5)-C(4)	123.0(2)
Zn(1)-N(1)	2.025(2)	C(3)-C(4)-C(5)	120.0(2)
Zn(1)-N(2)	2.0590(19)	C(9)-C(8)-C(7)	118.3(2)
N(1)-C(5)	1.327(3)	C(9)-C(8)-C(12)	117.83(19)
N(1)-C(1)	1.334(3)	C(7)-C(8)-C(12)	123.88(19)
N(2)-C(6)	1.341(3)	C(6)-C(7)-C(8)	117.96(19)
N(2)-C(10)	1.350(3)	C(6)-C(7)-C(11)	118.94(19)
C(1)-C(2)	1.379(4)	C(8)-C(7)-C(11)	123.1(2)
C(6)-C(7)	1.387(3)	O(2)-C(12)-O(1)	126.9(2)
C(10)-C(9)	1.377(3)	O(2)-C(12)-C(8)	120.3(2)
C(9)-C(8)	1.391(3)	O(1)-C(12)-C(8)	112.66(19)
C(2)-C(3)	1.382(3)	C(12)-O(1)-Zn(1)#3	121.08(16)
C(5)-C(4)	1.381(3)	O(4)-C(11)-O(3)	123.9(2)
C(4)-C(3)	1.381(3)	O(4)-C(11)-C(7)	118.8(2)
C(8)-C(7)	1.404(3)	O(3)-C(11)-C(7)	117.3(2)
C(8)-C(12)	1.505(3)	C(11)-O(3)-Zn(1)#4	105.44(15)
C(7)-C(11)	1.509(3)	C(4)-C(3)-C(2)	116.7(2)
C(12)-O(2)	1.226(3)	C(4)-C(3)-C(3)#5	121.5(3)
C(12)-O(1)	1.269(3)	C(2)-C(3)-C(3)#5	121.8(3)
O(1)-Zn(1)#3	1.9573(18)	N(1)-Zn(1)-N(2)	109.54(8)
C(11)-O(4)	1.222(3)	C(5)-N(1)-C(1)	117.4(2)
C(11)-O(3)	1.270(3)	C(5)-N(1)-Zn(1)	123.59(17)
O(3)-Zn(1)#4	1.9659(17)	C(1)-N(1)-Zn(1)	118.95(16)
C(3)-C(3)#5	1.488(4)	C(6)-N(2)-C(10)	117.75(19)
O(1)#1-Zn(1)-O(3)#2	111.15(7)	C(6)-N(2)-Zn(1)	127.22(15)
O(1)#1-Zn(1)-N(1)	103.72(8)	C(10)-N(2)-Zn(1)	114.33(15)
O(3)#2-Zn(1)-N(1)	133.01(8)	N(1)-C(1)-C(2)	122.9(2)
O(1)#1-Zn(1)-N(2)	94.38(8)	N(2)-C(6)-C(7)	123.7(2)
O(3)#2-Zn(1)-N(2)	98.37(8)	N(2)-C(10)-C(9)	122.5(2)
		C(10)-C(9)-C(8)	119.7(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,y+1/2,-z+3/2 #2 x,-y,z+1/2

#3 -x+1/2,y-1/2,-z+3/2 #4 x,-y,z-1/2

#5 -x+3/2,-y+1/2,-z+2

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **1**.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Zn(1)	22(1)	25(1)	35(1)	-1(1)	15(1)	-1(1)
N(1)	18(1)	33(1)	34(1)	6(1)	10(1)	-1(1)
N(2)	25(1)	25(1)	33(1)	-4(1)	15(1)	-2(1)
C(1)	22(1)	54(2)	57(2)	30(1)	15(1)	9(1)
C(6)	23(1)	28(1)	34(1)	-2(1)	14(1)	1(1)
C(10)	26(1)	32(1)	38(1)	-6(1)	18(1)	3(1)
C(9)	22(1)	36(1)	39(1)	-6(1)	15(1)	-1(1)
O(1W)	49(2)	70(2)	67(2)	0	10(2)	0
C(2)	26(1)	56(2)	57(2)	35(1)	17(1)	5(1)
C(5)	26(1)	51(2)	74(2)	36(2)	23(1)	4(1)
C(4)	24(1)	54(2)	73(2)	39(2)	18(1)	8(1)
C(8)	23(1)	24(1)	26(1)	3(1)	11(1)	0(1)
C(7)	25(1)	25(1)	31(1)	-1(1)	14(1)	1(1)
C(12)	26(1)	30(1)	34(1)	-3(1)	14(1)	1(1)
O(1)	41(1)	27(1)	47(1)	-6(1)	23(1)	-11(1)
O(2)	54(1)	56(1)	33(1)	-5(1)	3(1)	2(1)
C(11)	30(1)	33(1)	32(1)	-5(1)	12(1)	4(1)
O(3)	45(1)	29(1)	40(1)	-6(1)	25(1)	2(1)
O(4)	35(1)	58(1)	79(2)	-30(1)	37(1)	-10(1)
C(3)	20(1)	29(1)	27(1)	1(1)	9(1)	-3(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **1**.

	x	y	z	U(eq)
H(1A)	5051	3358	8703	53
H(6A)	4307	611	7761	33
H(10A)	2149	1633	8137	37
H(9A)	1279	487	6770	37
H(1)	5493	5195	8201	98
H(2A)	6481	3553	8768	55
H(5A)	5769	1154	10992	59
H(4A)	7223	1298	11137	60