Electronic Supplementary Material (ESI) for CrystEngComm
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Electronic Supplementary Information (ESI) for

An unusual (3,6)-connected microporous metal–organic framework based on tetrahedral Zn_4 clusters with selective adsorption of CO_2

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Materials and Methods:

All reagents of A. R. grade employed were commercially available and used without further purification. The FT-IR spectra (KBr pellets) were recorded on a Nicolet Avatar 360 FT-IR Spectrometer in the range of 4000–400 cm^{-1}. The Raman spectra were recorded using an ALMEGA Dispersive Raman spectrometer with the laser wavelength of 532 nm. C, H, and N elemental analyses were determined on an Elementar Vario EL III elemental analyzer. Thermal stability studies were carried out on a NETSCHZ STA–449 C thermoanalyzer under nitrogen atmosphere (40–1000 ^{o}C range) at a heating rate of 10 ºC min^{-1}. The solid-state fluorescence spectra were measured at room temperature using a Cary Eclipse fluorescence spectrophotometer. The excitation slit and emission slit both were 2.5 nm. Powder X-ray diffraction (PXRD) pattern was measured on a Rigaku DMAX 2500 powder diffractmeter at 40 kV and 100 mA using Cu-Kα (λ = 1.54056 Å), with a scan speed of 0.2 s/step and a step size of 0.02°. The simulated powder pattern was calculated using single-crystal X-ray diffraction data and processed by the free Mercury 2.3 program provided by the Cambridge Crystallographic Data Centre.

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Table S1. Crystal data and structure refinements for **1**.

Empirical formula	$C_{48}H_{60}N_{12}O_{35}Zn_{11}$
Formula weight	2084.15
Temperature (K)	298(2)
Crystal system, Space group	Trigonal, *P*-3*c*1
Unit cell dimensions	*a* = 14.3470(18) Å *b* = 14.3470(18) Å *c* = 20.408(2) Å *V* = 3637.9(7) Å^3
Z, Density(cal.)	2, 1.903 g/cm^3
Absorption coefficient	3.652 mm^{-1}
F(000)	2084
Crystal Size (mm)	0.23 × 0.19 × 0.15
Theta range for data collection	1.64 to 25.02
Limiting indices	- 13 <= h <= 17, - 16 <= k <= 10, - 24 <= l <= 24
Reflections collected / unique	14004 / 2152
Data Completeness measured	1.00
Relative Transmission Factor	0.4872 and 0.6104
Refinement Method	Full-matrix least-squares on F^2
Parameter/Restraints/Data(obs.)	2152 / 0 / 186
Goodness-of-fit	1.048
Final R indices ($I > 2\sigma(I)$)	R1 = 0.0662, wR2 = 0.1703
R indices (all)	R1 = 0.1019, wR2 = 0.1920
Largest difference peak	1.714 and -0.749 e·A^{-3}

[a] $R1 = \sum(|F_o| - |F_c|) / \sum|F_o|$, $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{0.5}$.

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Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **1**.

atom	*x*	*y*	*z*	*U*(eq)
Zn(1)	2792(1)	7737(1)	10058(1)	22(1)
Zn(2)	0	6375(1)	12500	31(1)
Zn(3)	3333	6667	8359(1)	26(1)
N(1)	1152(6)	6891(6)	10126(4)	24(2)
N(2)	3544(6)	9352(6)	9922(4)	24(2)
O(1)	3316(5)	7875(5)	9010(3)	24(1)
O(2)	972(5)	6238(7)	13167(3)	40(2)
O(3)	2606(5)	7602(5)	11122(3)	28(2)
O(4)	1344(5)	6748(6)	11900(3)	39(2)
O(5)	3333	6667	10209(5)	23(2)
O(6)	130(30)	7980(19)	12397(17)	27(5)
O(7)	2208(6)	6831(6)	7746(3)	40(2)
C(1)	1175(7)	6390(8)	13769(4)	25(2)
C(2)	1606(7)	6974(7)	11306(5)	25(2)
C(3)	264(7)	6439(7)	9729(4)	23(2)
C(4)	3783(7)	9663(7)	9268(4)	20(2)
C(5)	797(8)	6578(7)	10767(4)	24(2)
C(6)	300(8)	6669(9)	9008(5)	35(2)
C(7)	-50(20)	7520(20)	8848(11)	44(6)
C(8)	650(20)	8623(19)	9179(12)	64(9)
C(7')	610(40)	7850(30)	8855(19)	42(11)
C(8')	-220(40)	8130(40)	9230(20)	64(16)

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Table S3. Selected bond lengths (Å) and bond angles (°) for **1**.

Zn(1)-N(1)	2.043(8)	Zn(1)-O(5)	2.0612(19)	Zn(3)-O(1)	2.194(6)
Zn(1)-N(2)	2.027(8)	Zn(2)-O(2)	2.026(7)	Zn(3)-O(7)	2.147(7)
Zn(1)-O(1)	2.243(6)	Zn(2)-O(4)	2.115(7)		
Zn(1)-O(3)	2.184(6)	Zn(2)-O(6)	2.228(11)		
N(2)-Zn(1)-N(1)	119.0(3)	O(3)-Zn(1)-O(1)	167.5(2)	O(7)-Zn(3)-O(7)#2	89.4(3)
N(2)-Zn(1)-O(5)	133.5(2)	O(2)#1-Zn(2)-O(2)	127.7(5)	O(7)-Zn(3)-O(1)	87.7(3)
N(1)-Zn(1)-O(5)	107.4(2)	O(2)#1-Zn(2)-O(4)	89.6(3)	O(7)#2-Zn(3)-O(1)	96.0(3)
N(2)-Zn(1)-O(3)	102.1(3)	O(2)-Zn(2)-O(4)	80.1(3)	O(7)#3-Zn(3)-O(1)	173.8(3)
N(1)-Zn(1)-O(3)	80.1(3)	O(4)-Zn(2)-O(4)#1	156.6(5)	O(1)-Zn(3)-O(1)#3	87.1(2)
O(5)-Zn(1)-O(3)	81.9(3)	O(2)#1-Zn(2)-O(6)	114.6(13)	Zn(3)-O(1)-Zn(1)	130.0(3)
N(2)-Zn(1)-O(1)	78.7(3)	O(2)-Zn(2)-O(6)	117.3(14)	Zn(1)-O(5)-Zn(1)#3	117.81(14)
N(1)-Zn(1)-O(1)	110.6(3)	O(4)-Zn(2)-O(6)	95.3(6)		
O(5)-Zn(1)-O(1)	88.5(3)	O(4)#1-Zn(2)-O(6)	108.1(6)		

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

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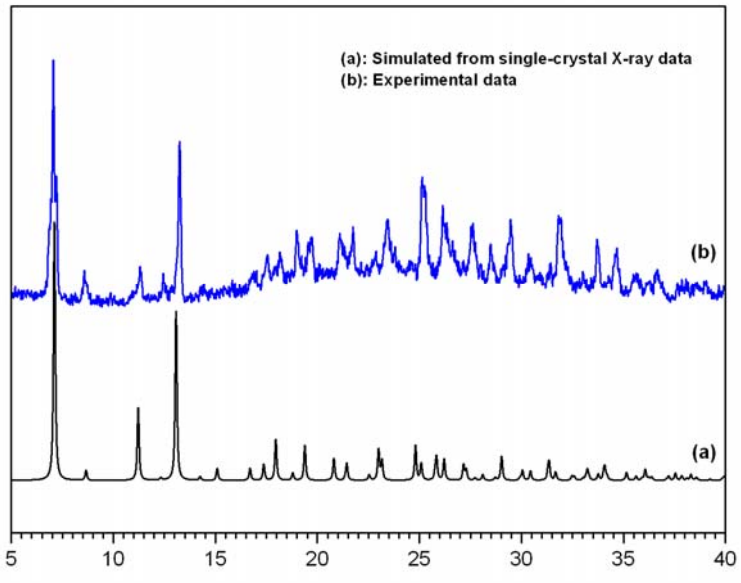

Fig. S1 X-ray powder diffraction patterns for **1**.

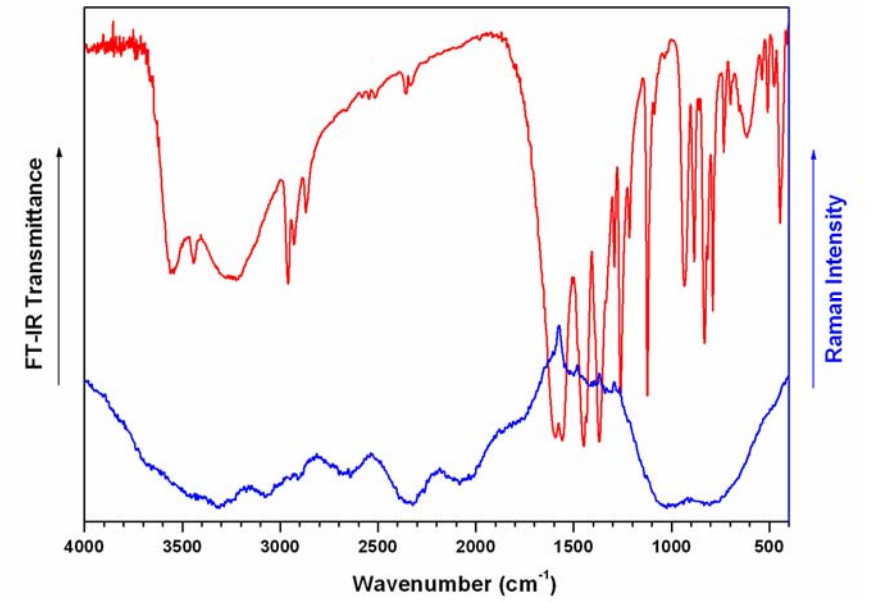

Fig. S2 IR (red) and Raman (blue) spectra for **1**.

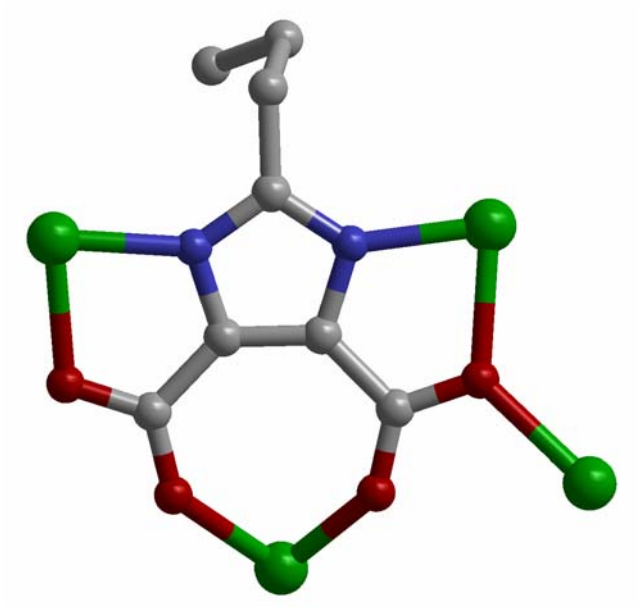

Fig. S3 The linkage between the PIMDC ligand and Zn atoms.

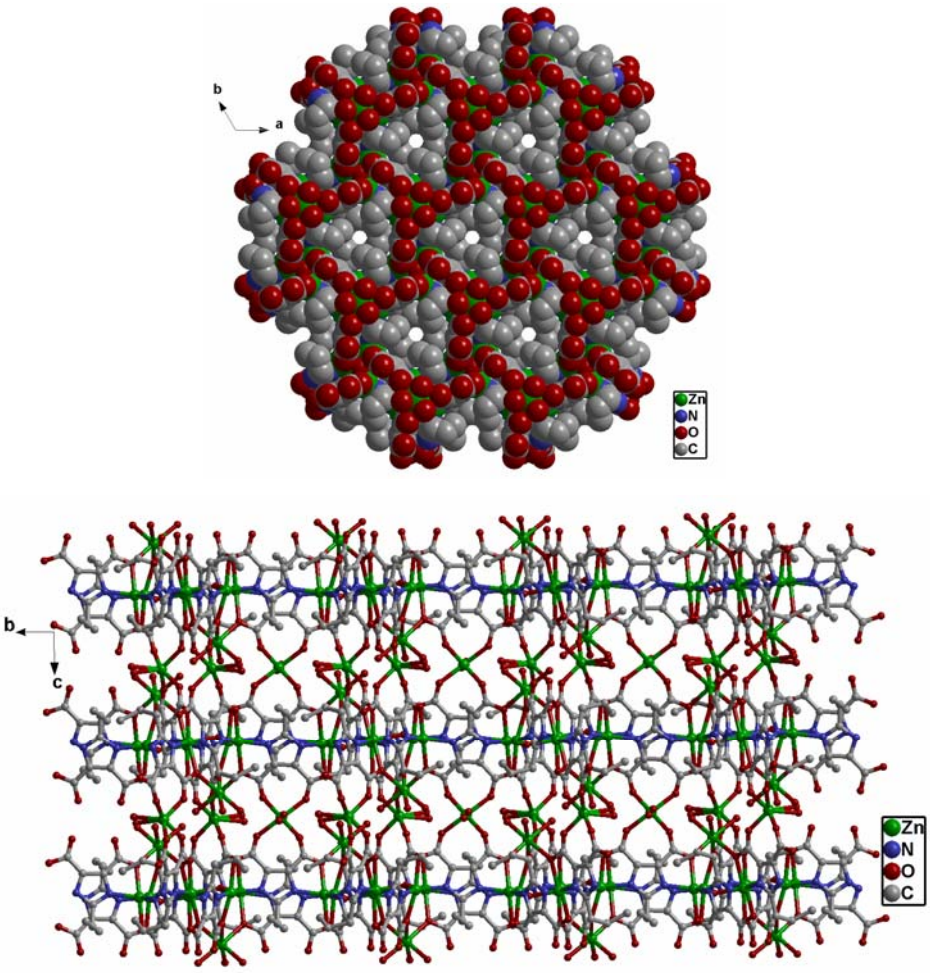

Fig. S4 The space-filling (top) and ball-stick diagrams (bottom) for the 3D framework of **1** viewed from different directions.

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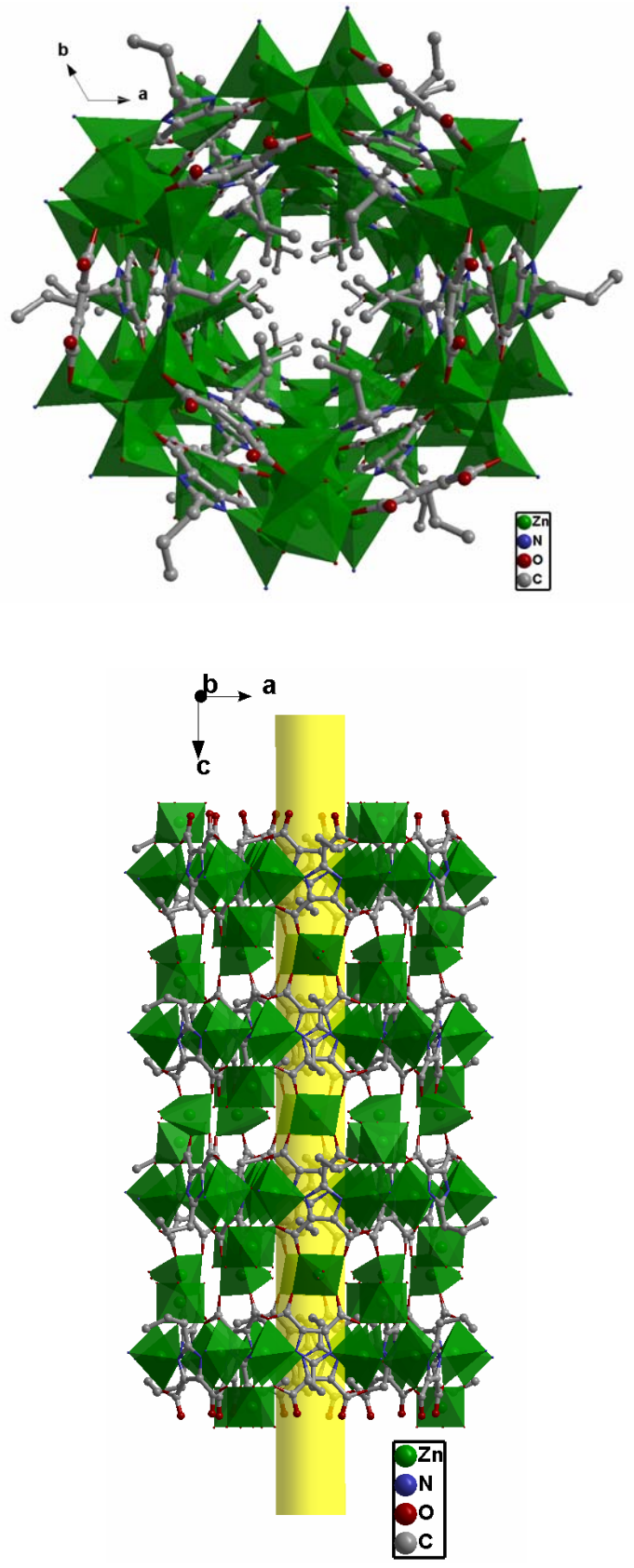

Fig. S5 The 1D channel in the 3D framework of **1** viewed from *c*- and *b*-directions, respectively.

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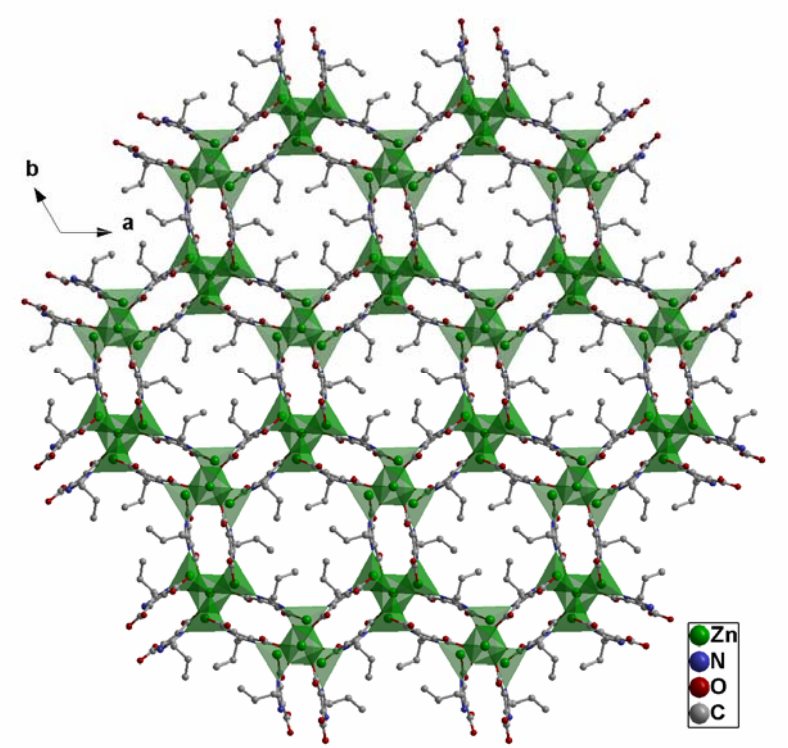

Fig. S6 The 2D layer generated by the tetrahedral subunits.

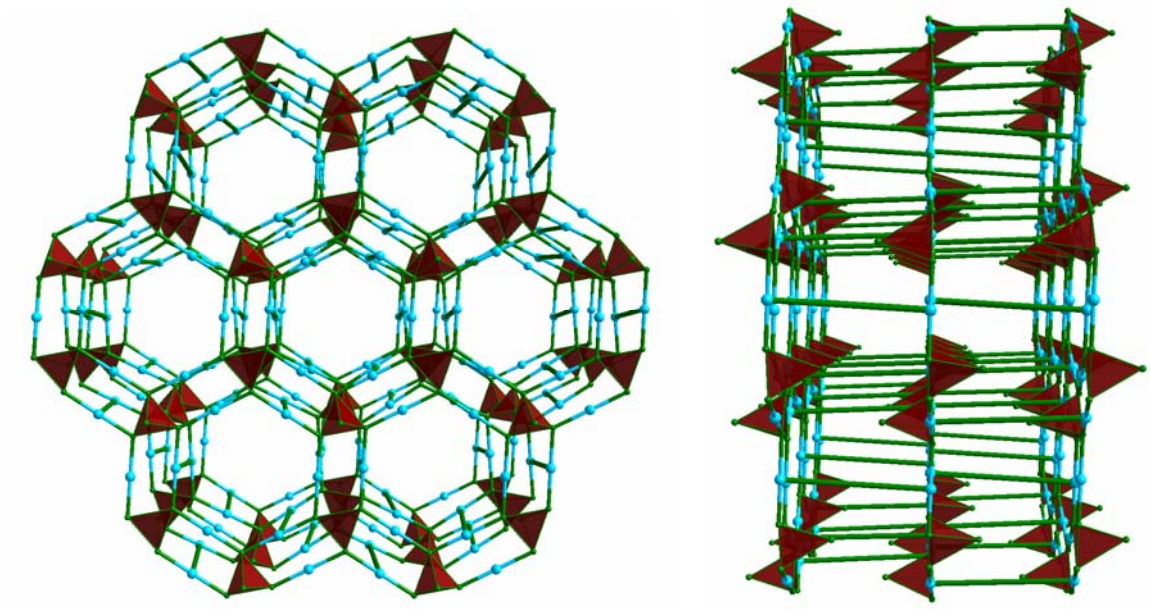

Fig. S7 The polyhedral schematic presentations for the unprecedented (3,6)-connected topology of **1** viewed from different directions.

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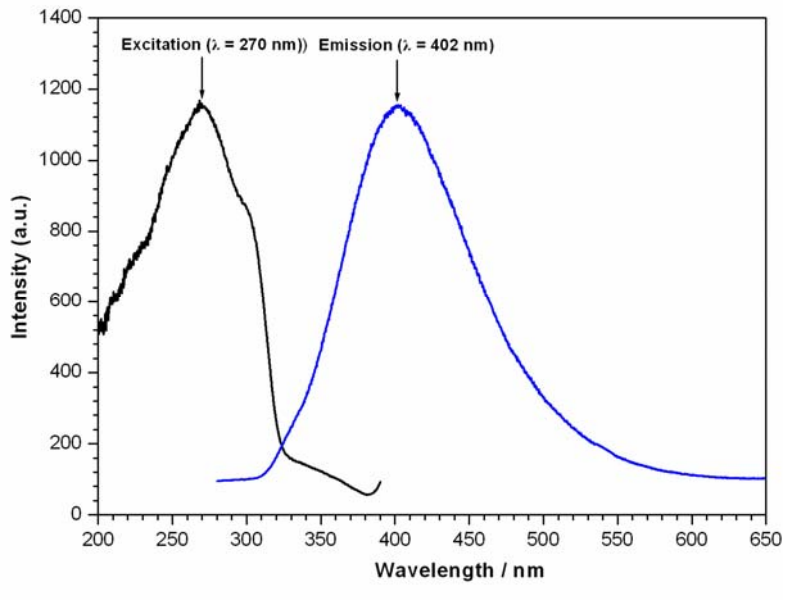

Fig. S8 Solid state excitation and emission spectra of **1** at room temperature.

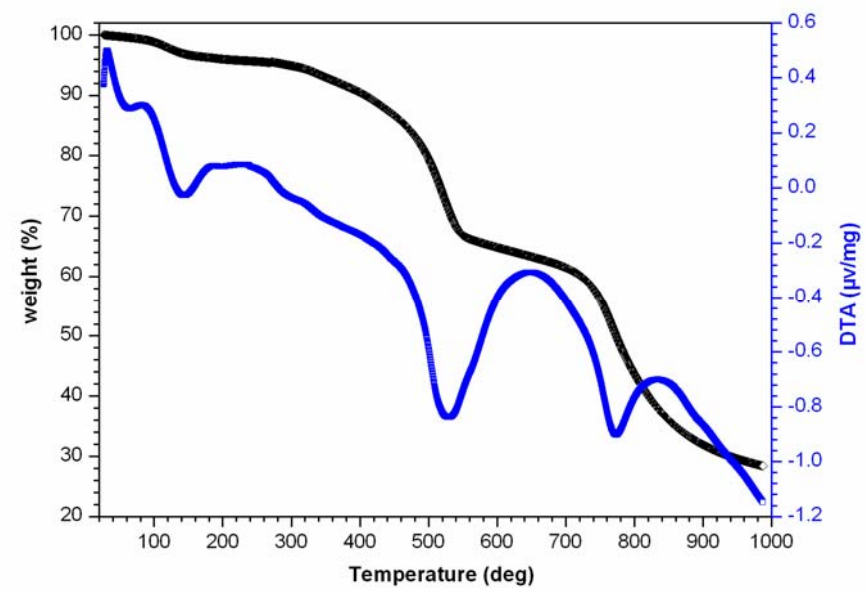

Fig. S9 TG/DTA curves of compound **1**.