Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information (ESI)

Contents

1. Experimental Section

1.1. Reagents and materials

All reagents and materials are of analytical grade and used as received from commercial sources without further purification. H_4EBTC was synthesized according to the method published before.[1]

1.2. Physical measurements

Thermal gravimetric analyses (TGA) were performed using a DTA–TGA 2960 thermogravimetric analyzer in nitrogen atmosphere with a heating rate of 10 °C/min from 30 to 800 °C. Powder X–ray diffraction (PXRD) data and variable temperature powder X–ray diffraction (VT PXRD) data were recorded on a Bruker D8 Discover diffractometer with Cu Kα (λ = 1.54056 Å) radiation with a scan speed of 5 °/min and a step size of 0.02° in 2θ. Elemental analyses (C, H and N) were carried out on a Perkin–Elmer 240 analyzer. The IR spectra were obtained on a NICOLET iS10 spectrometer in the 4000–400 cm^{-1} region. UV/visible absorbance was collected in the solid state at room temperature on a Perkin–Elmer Lambda 950 UV/vis spectrometer equipped with Labsphere integrating over the spectral range 200–800 nm using BaSO4 as reflectance standards. Steady state emission and excitation spectra were recorded for the solid samples on an F–7000 FL spectrophotometer equipped with a 150 W Xenon lamp as an excitation source at room temperature. The photomultiplier tube (PMT) voltage was 700 V in all the measurements. The scan speed was 1200 nm/min. The variable temperature luminescence study was performed on a Fluorolog–3–TAU fluorescence spectrophotometer. The phosphorescence lifetime measurement was measured by a single–photon counting spectrometer using an Edinburgh FLS920 spectrometer equipped with a continuous Xe900 xenon lamp.

2. Preparation and characterization of 1

[Mg(H EBTC)(DMF)$_2$] (1). A solution of $Mg(NO_3)_3 \cdot 6H_2O$ (15 mg, 0.056 mmol), H_4EBTC (5 mg, 0.014 mmol), DMF (0.4 mL), CH_3OH (0.10 mL), HNO_3 (0.02 mL, 1M in DMF) and H_2O (0.10 mL) were mixed and sealed in a 10 mL Teflon–lined autoclave and heated to 85 °C for 24 h. Colorless hexagonal–shaped crystals were achieved after slowly cooled to room temperature (yield: 70 % based on Mg). Anal. Calcd for $C_{24}H_{22}MgN_2O_{10}$: C, 55.14; H, 4.24; N, 5.36. Found: 55.06; H, 4.10; N, 5.15. Selected IR data (KBr pellet, cm^{-1}): 3390 (b), 2931 (w), 1663(s), 1558 (w), 1496 (w), 1437 (w), 1384 (s), 1254 (m), 1103 (s), 786 (s).

3. Crystal Structure Determination

Suitable single crystal of **1** was carefully selected under an optical microscope and glued to thin glass fibers. Single crystal X–ray diffraction data were collected on a Bruker Smart Apex II CCD diffractometer at 293 K using graphite monochromated Mo/Kα radiation (λ = 0.71073 Å). Data reductions and absorption corrections were performed with the SAINT[2] and SADABS2[3] software packages, respectively. Structures were solved by a direct method using the SHELXL–97 software package.[4] The non–hydrogen atoms were anisotropically refined using the full–matrix least–squares method on F^2. All hydrogen atoms were placed at the calculated positions and refined riding on the parent atoms.

CCDC–1441925 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif. The crystallographic data and details of structural refinement for **1** are listed in Table S1 and selected bond distances and angles are summarized in Table S2.

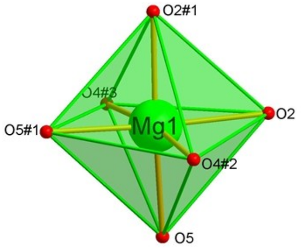
Table S1: Crystallographic data and structural refinements for **1**

Formula	$C_{24}H_{22}MgN_2O_{10}$
Formula weight	522.75
CCDC no.	1441925
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Crystal size /mm	0.21×0.20×0.19
Crystal system	Monoclinic
Space group	*C2/c*
a / Å	10.717(8)
b / Å	23.114(18)
c / Å	10.070(8)
α/ (°)	90

β / (°)	104.780(14)
γ/ (°)	90
V / Å^3	2412(3)
Z	4
$F(000)$	1088
$\theta_{\mathrm{min,max}}$/°	1.76–28.28
GOF	1.032
$R_1{}^{a}$, w$R_2{}^{b}$ [$I > 2\sigma(I)$]	0.0470, 0.1300

$^{a}R_1=\sum||F_0|-|F_c|/\sum|F_0|$; $^{b}wR_2=\{\sum[w(F_0{}^2-F_c{}^2)^2]/\sum[w(F_0{}^2)^2]\}^{1/2}$

Table S2: Selected bond lengths (Å) and angles (°) in **1**



bond lengths					
Mg1–O2	2.070(18)	Mg1–O2#1	2.070(18)	Mg1–O5	2.072(20)
Mg1–O5#1	2.072(20)	Mg1–O4#2	2.102(20)	Mg1–O4#3	2.102(20)
bond angles					
O2–Mg1– O2#1	87.225(56)	O2#1–Mg1–O4#3	87.280(56)	O4#3–Mg1–O5#1	87.896(63)
O5–Mg1–O4#3	87.053(63)	O2#1–Mg1–O4#2	98.232(57)	O2#1–Mg1–O5#1	88.517(80)
O5–Mg1– O5#1	96.392(67)	O4#2–Mg1–O4#3	172.420(56)	O2#1–Mg1–O5	172.358(64)

Symmetry transformations used to generate equivalent atoms for **1**: #1=1–x, y, –0.5–z; #2=0.5–x, 0.5–y, –z; #3=0.5+x, 0.5–y, –0.5+z.

4. Crystal Structure Descriptions

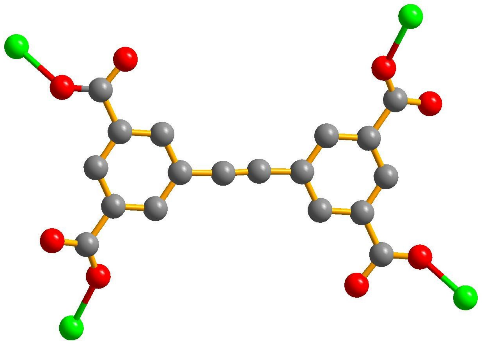


Fig. S1 Coordination modes of the ligand in **1** (all hydrogen atoms were omitted for clarity).

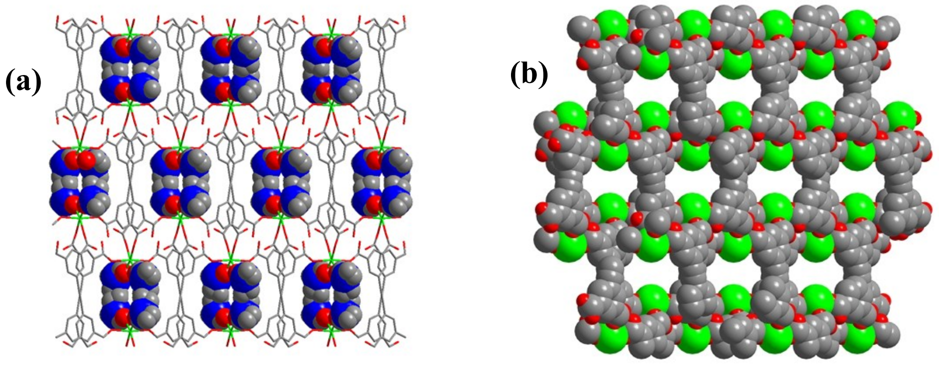


Fig. S2 The 3D framework of **1** (a) showing 1D channels filled with disordered DMF solvents and (b) space filled representation without DMF solvents along c axis (all hydrogen atoms are omitted for clarity).

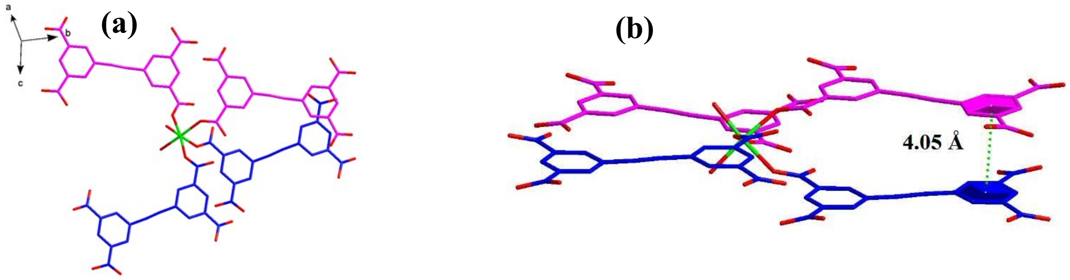


Fig. S3 (a) Crystal packing view of phenyl rings of H_2EBTC^{2-} ligands and (b) dotted lines indicate the nearest centroid−to−centroid distance of two phenyl rings.

5. Characterization Section

5.1 The PXRD Patterns

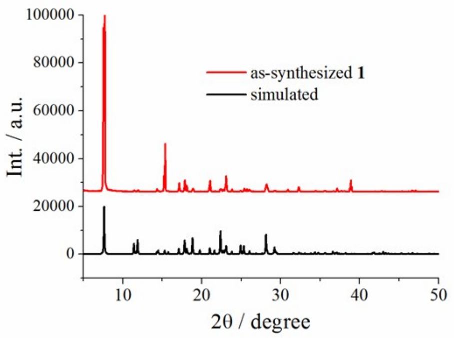


Fig. S4 PXRD patterns of simulated from the X−ray single−crystal structures and as−synthesized samples of **1** at ambient temperature.

The powder X–ray diffraction (PXRD) experiments for compound **1** was carried out carefully to check phase purity at room temperature. The patterns showed that the main peaks of the synthesized MOF were closely consistent with those of the simulations from the single–crystal X–ray diffraction data, which imply high quality of the obtained products (Figure S4).

5.2 The IR Spectra

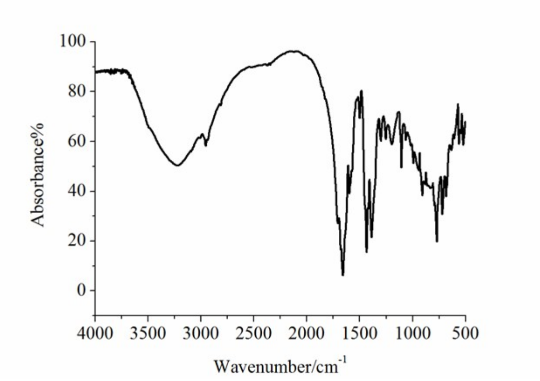


Fig. S5 The IR spectrum of **1** recorded from a KBr pellet.

5.3 Thermogravimetric analysis

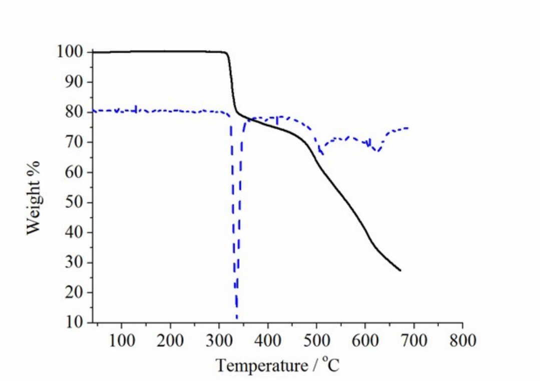


Fig. S6 TG and DTA (dash lines) plots of **1**.

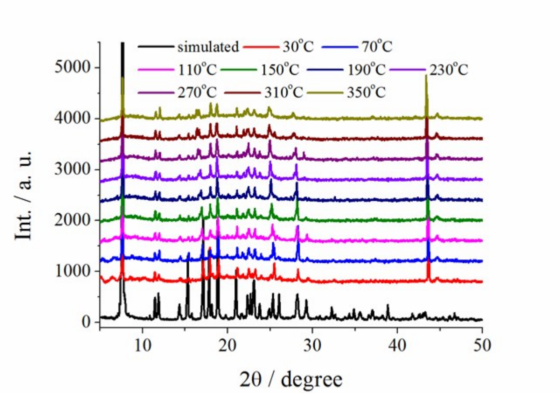


Fig. S7 VT−PXRD patterns for **1** in the temperature range of 30−350 °C.

Moreover, the thermal stability of **1** was also detected *via* thermogravimetric analysis (TGA) and VT−PXRD, which are displayed in Figure S6 and Figure S7 respectively. The thermal analysis of powdered sample of **1** was performed under a nitrogen atmosphere. From the TG curve depicted in Figure S6, **1** is thermally stable up to 310 °C when the coordinated DMF molecules start to release at this temperature and this process is sustained up to ca. 343 °C (calcd. 20.71 %) which corresponds to the removal of one and a half coordinated DMF molecules in the structure (20.95 %). The whole coordinated DMF molecules can be removed at 460 °C according to the TG curve. This temperature is much higher than the pure DMF decomposition temperature (151 °C), and it is a quite rare case that it can be thermally stable to so high temperature (460 °C), indicating that the thermal stability of some small molecules can be enhanced when they are confined in the channels or pores of MOFs. Above this temperature, the framework of **1** begins to collapse upon the coordinated DMF molecules removal. On the basis of the above analysis we can conclude that, in the range 310–460 °C, **1** remains intact after the removal of the coordinated DMF molecules. Among the reported magnesium–based MOFs, they usually have poor thermal stability and **1** is among few samples with good thermal stability.[5]

The results of VT−PXRD measurements of **1** also confirmed the high thermal stability of **1** and the powder diffraction peaks all remained even the temperature is over 343 °C (where one and a half coordinated DMF molecules were removed according to TG result).

5.4 UV–vis spectrum

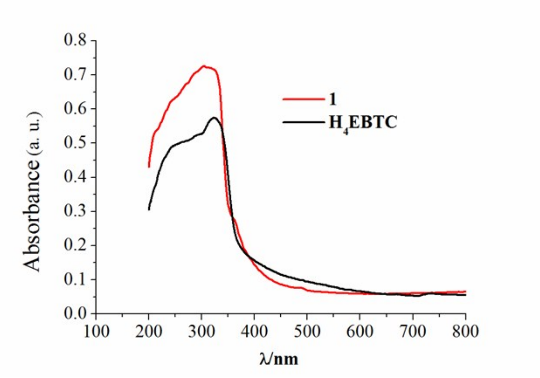


Fig. S8 UV−vis absorption spectra for **1** (red) and the H_4EBTC ligand (black).

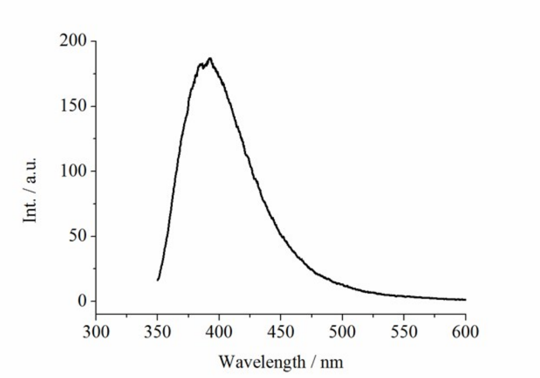


Fig. S9 The solid–state PL spectra of H_4EBTC (λ_{ex}= 278 nm) at room temperature.

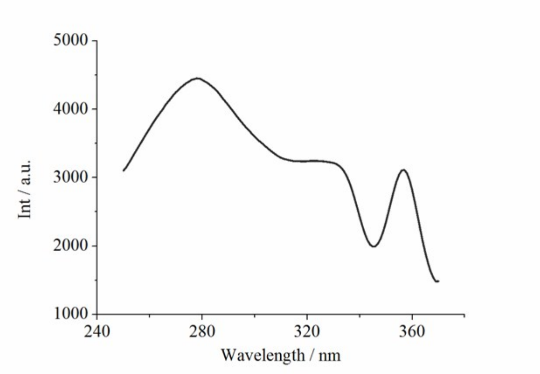


Fig. S10 Solid–state excitation spectra of **1** at room temperature, monitored at 378 nm.

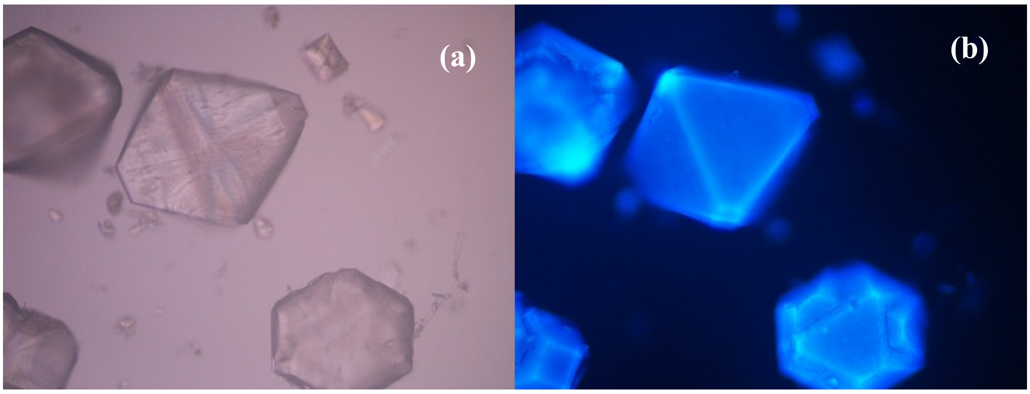


Fig. S11 Photos of crystals of **1** under (a) ambient and (b) 330–380 nm ultraviolet irradiation at room temperature.

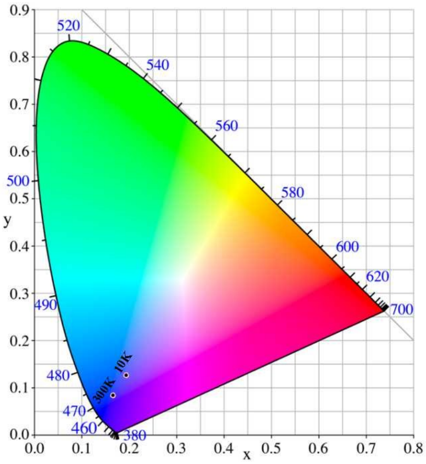


Fig. S12 The CIE coordinates (marked by the circles) for **1** at 300 K and 10 K.

6. References

1. Y. X. Hu, S. C. Xiang, W. W. Zhang, Z. X. Zhang, L. Wang, J. F. Bai and B. L. Chen, *Chem. Commun.,* 2009, **48**, 7551.
2. Bruker, APEX 2, SAINT, XPREP, Bruker AXS Inc., Madison, Wisconsin, USA, 2007.
3. Bruker, SADABS, Bruker AXS Inc., Madison, Wisconsin, USA, 2001.
4. G. M. Sheldrick, SHELXS97 and SHELXL97: Program for the refinement of crystal structure, University of Göttingen, Germany, 1997.
5. (a) Q. Zhai, Q. Lin, T. Wu, S.−T. Zheng, X. Bu and P. Feng, *Dalton Trans.,* 2012, **41**, 2866; (b) N. B. Shustova, A. F. Cozzolino, S. Reineke, M. Baldo and M. Dinca, *J. Am. Chem. Soc.,* 2013, **135**, 13326.