Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

A novel metal-organic framework based on bismuth and trimesinic acid: synthesis, structure and properties

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1 Experimental Section

All chemicals used were of analytical grade, and were used without further purification.

1.1 Synthesis of Bi-BTC.

The compound 1 was synthesized by solvothermal method. In the experiment, $Bi(NO_3)_3{\cdot}5H_2O$ (0.2360g, 0.49 mmol) and H_3BTC (0.1930g, 0.92 mmol) were added in a mixture of DMF/MeOH (5mL, 1:3). The solution was then sealed in a 100 mL Teflon-lined autoclave, heated to 120℃ for 45h, kept at this temperature for 12h and then cooled down slowly at the rate of 2℃/min to room temperature. Colorless crystals were washed by DMF, methanol and then dried in air at 60℃.

1.2 Characterization

The X-ray power diffraction (XRD) data of the as-prepared sample was obtained by an X-ray powder diffraction (Bruker AXS D8). Thermogravimetry-differential thermal analysis (TG/DTA) was performed using a Diamond TG/DTA analyzer at a heating rate of 5℃/min in air. Fourier transform infrared (FT-IR) spectra was performed on a Bruker ALPHA-T spectrometer using KBr pellets. The UV-vis diffuse reflectance spectra was determined by a Shimadzu UV 2550 recording spectrophotometer with $BaSO_4$ as a reference. Steady state fluoresce was measured on a high sensitivity fluorescence spectrometer (Edinburgh FS920). The pump source is an Opolette HE 355 II tunable laser system with a laser pulse width of 5 ns and repetition rate of 20Hz.

1.3 Single- Crystal Structure Determination

The data was collected using a Bruker SMART APEXII CCD area detector on a D8 goniometer and with graphite-monochromated and 0.5 mm-Mono Cap-collimated Mo-Kα radiation (λ = 0.71073 Å) at room temperature in ω scan method. The INTEGRATE program in APEX2 software was used for reduction and cell refinement. Multi-scan absorption corrections were applied by the SCALE program for area detector. The structure was solved by the direct method and refined using the

full-matrix least-squares method on F^2 by program SHELX-97. All the atoms were refined anisotropically except hydrogen atoms and hydrogen atoms were placed in idealized positions.

The structure was refined as a twin. The unit cell includes large regions of disordered solvent molecules and could not be modeled properly. PLATON/SQUEEZE was employed to calculate the diffraction contribution from the solvent molecules and, thus produced a set of solvent-free diffraction intensities, and the results were appended to the bottom of the CIF file. According to the SQUEEZE calculations combined with the TG/DTA data, the solvent region are corresponding to nearly 1 DMF and 2 methanol molecules per unit cell. So the tentative formula for this compound is [Bi(BTC)(DMF)]·DMF·2 (CH_3OH). The contents of the solvent region are included in the unit cell contents but not included in the refinement model.

1.3 Photocatalytic reaction

Photocatalytic oxygen production reaction was performed in a top-irradiation vessel which is connected to a glass-enclosed gas circulation system. In the procedure, 50 mg of the sample and 100mg $AgNO_3$ were mixed in 50mL aqueous solution with constant stirring. The reaction temperature was kept at 5℃. The amount of O_2 evolution was determined by a gas chromatograph (Techcomp GC7890Ⅱ).

2 Characterization of Bi-BTC

2.1 Crystal data and structure refinement

Table S1. Crystal data and structure refinement for Bi-BTC

Empirical formula	$C_{17}H_{25}BiN_2O_{10}$
Formula weight	626.19
Temperature	293 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 10.137(2) Å α = 90°
	b = 15.017(3) Å β = 99.441(2)°
	c = 11.422(3) Å γ = 90°
Volume	1715.2(7) $Å^3$
Z	4
Density (calculated)	2.425 $g \cdot cm^{-3}$
Radiation type	Mo Kα
Absorption coefficient (μ)	10.306 mm^{-1}
F(000)	912
Crystal size	0.143 ×0.125 ×0.040 mm^3
ω range for data collection	2.260 to 27.627°
Index ranges	$-13 \leq h \leq 13$, $-19 \leq k \leq 19$, $-14 \leq l \leq 14$
Reflections collected	19035
Independent reflections	19035 [R_{int} = 0.0675]
Final R_1 values [$I > 2\sigma(I)$]	0.0485
Final w$R(F^2)$ values ($I > 2\sigma(I)$)	0.1470
Final R_1 values (all data)	0.0618
Final w$R(F_2)$ values (all data)	0.1592
Goodness of fit on F^2	0.871

2.2 XRD pattern

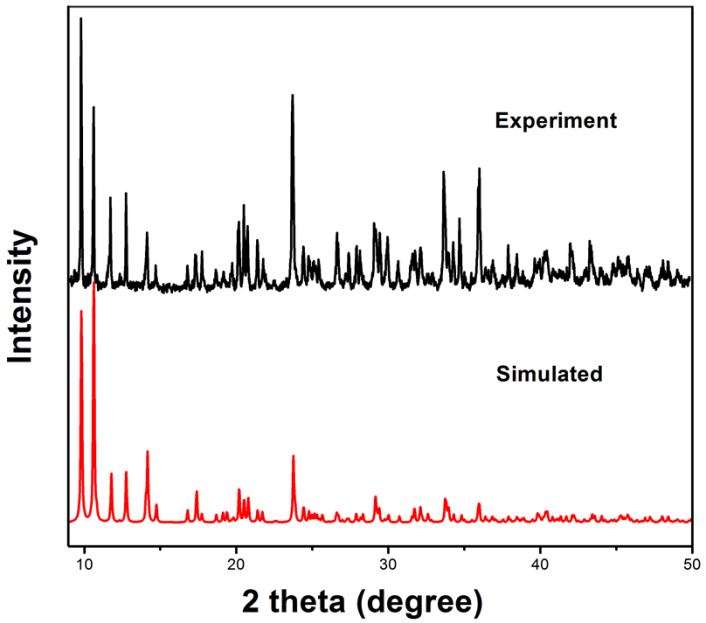

Figure S1. XRD patterns of the as-prepared Bi-BTC.

2.3 The FT-IR spectra of Bi-BTC

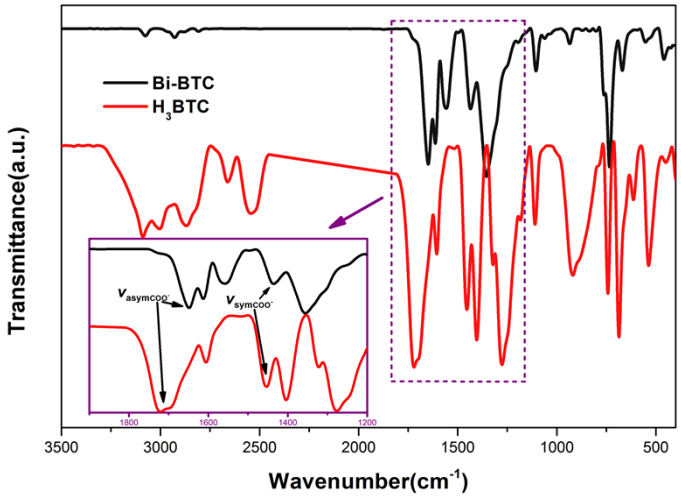

Figure S2. The FT-IR spectra of Bi-BTC

2.4 TG/DTA of Bi-BTC

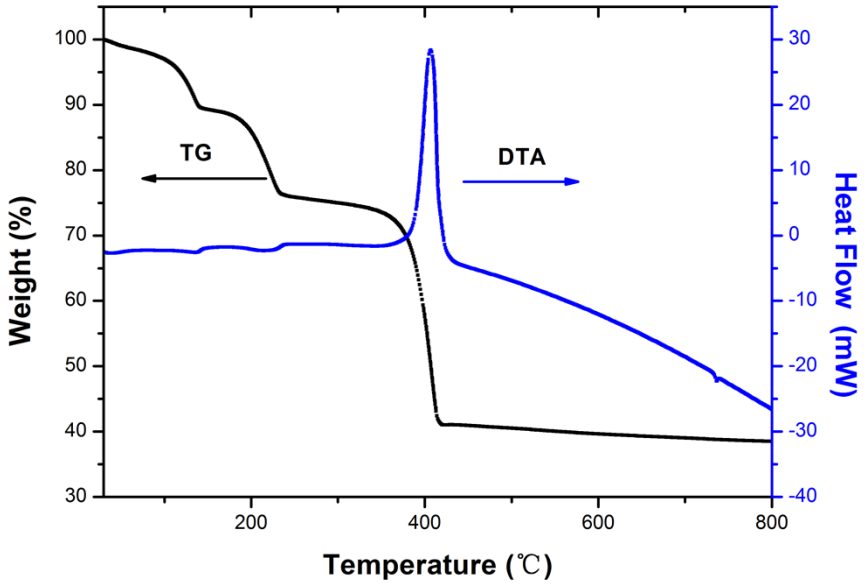

Figure S3. The TG/DTA curve of Bi-BTC.