# A pillared layer MOF with anion-tunable magnetic properties and photochemical [2+2] cycloaddition

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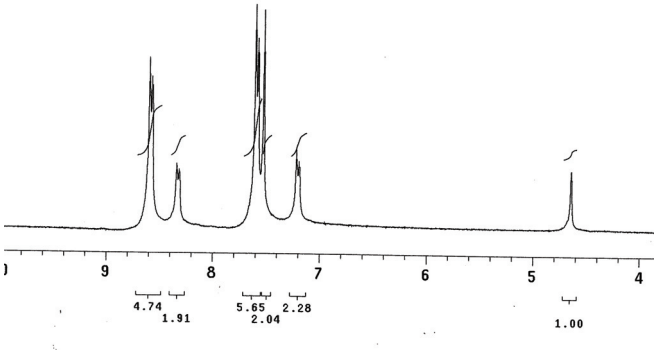
# Supporting Information

**General Remarks.** All starting materials were commercially available, reagent grade, and used as purchased without further purification. $Mn(HCOO)_2{\cdot}2H_2O$ was prepared by reaction of $MnCO_3$ with formate. Elemental analysis of carbon, hydrogen, and nitrogen was carried out with an Elementary Vario EL. The micro-infrared spectroscopy studies were performed on a Magna-IR 750 spectrophotometer in the 4000-500 $cm^{-1}$ region. Variable–temperature magnetic susceptibility, and field dependence of magnetization on a polycrystalline sample and a carefully oriented single crystal were performed on Quantum Design MPMS XL-5 SQUID system and an Oxford Maglab 2000 System. All experimental magnetic data were corrected for the diamagnetism of the sample holders and of the constituent atoms (Pascal's tables). The $^1H$ NMR spectrum was recorded in the Mercury 200 MHz of Varian.

**Synthesis of 1:** A 5 mL solution of $H_2O$ containing $Mn(CHOO)_2{\cdot}2H_2O$ (36.0 mg, 0.20 mmol) and $NaClO_4$ (24.5 mg, 0.20 mmol) was added to 5 mL of hot DMF containing 4,4′-bpe (36.4 mg, 0.20 mmol) and stirred for five minutes and filtered. Slow evaporation for about 1 week gave the pale yellow single crystals of **1**, with a yield of about 50%.

**Solid-state photoreaction**: A crystalline sample of **1** (~30 mg) was placed between two glass slides and was irradiated using an Hg lamp (400 W) for approximately 2 days. The sample turned from light yellow to dark yellow when the irradiation stopped. Then the sample was dissolved in 20 mL methanol, and 20 mg of NaOH was added to the solution. After stirring for 30 minutes, the dark brown precipitate was removed by filtration. The methanol was removed under reduced pressure and the residue was washed by a small amount of water. After drying in the air, the

product (a mixture of 4,4′-bpe and 4,4′-tpcb) was dissolved in D6-DMSO and checked by $^{1}H$ NMR (200 MHz, 298 K).




## Additional figures:

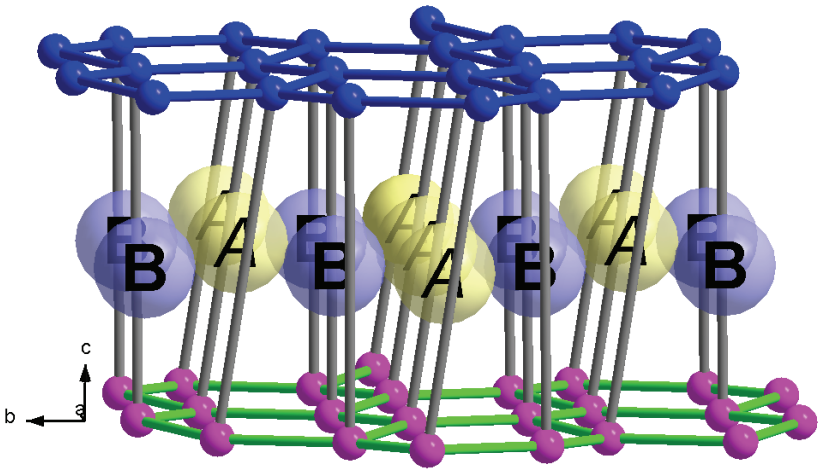



**Figure S1** The 3D topology of **1** with two sites ***A*** and ***B*** from view of *a* axis.

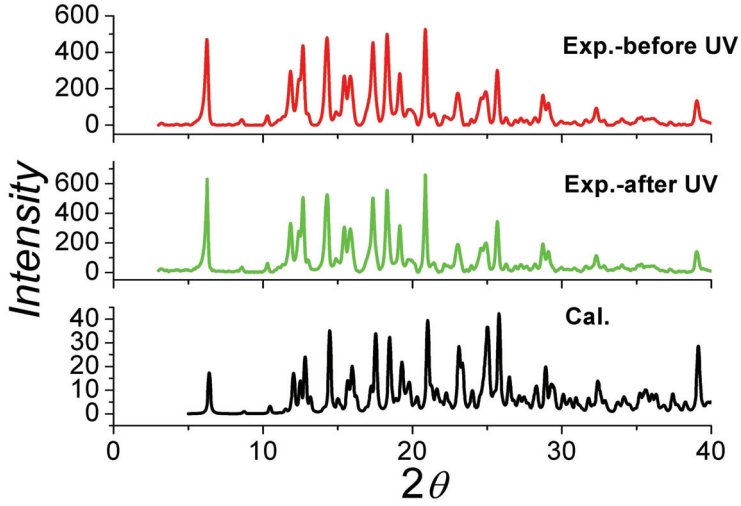



**Figure S2.** The XRD patterns of **1** before and after the photoreaction**,** together with the simulated pattern based on single crystal structure of **1**.

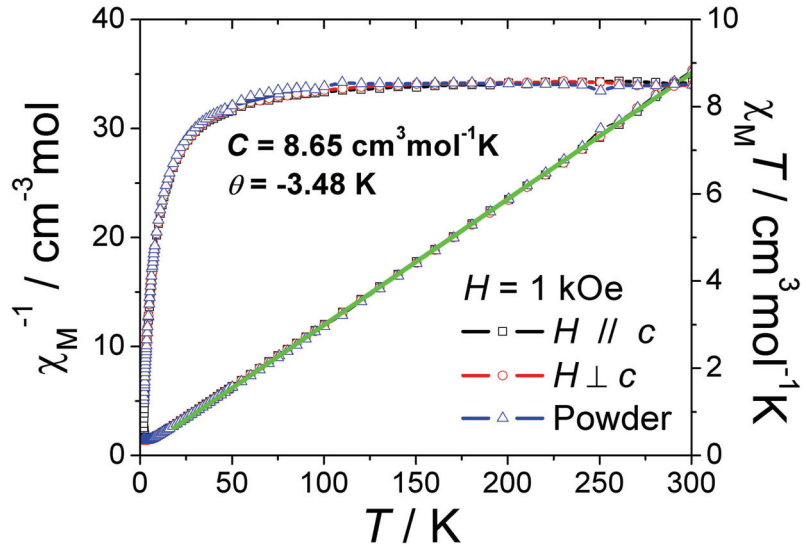



**Figure S3**. Temperature dependence of $\chi T$ and $\chi^{-1}$ of **1** at $H$ = 1 kOe from 2-300 K. The line across $\chi^{-1}$ is the fit of Curie-Weiss law. The data were measured on a single crystal ($H$ // $c$ and $H \perp c$) and a powder sample.

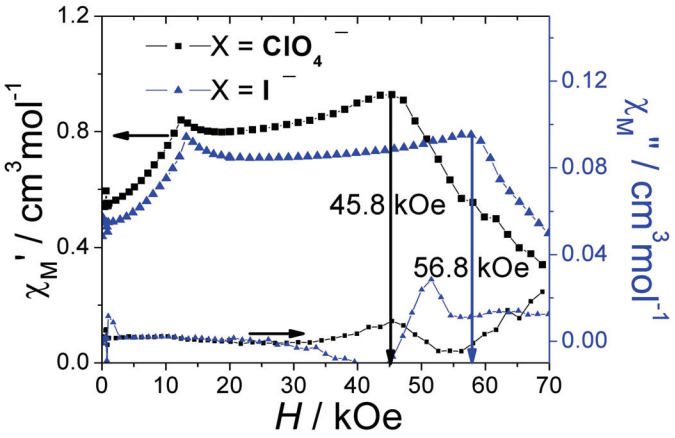



**Figure S4.** The field dependence of the *ac* susceptibilities at 1.8 K of **1** with anions $ClO_4^-$ and $I^-$ in site *A*.

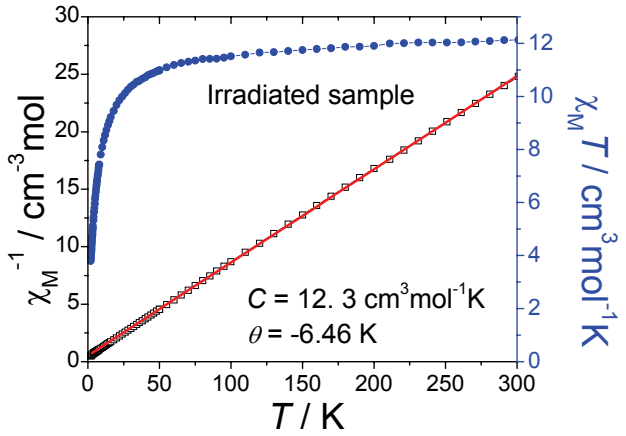



**Figure S5.** Temperature dependence of $\chi T$ and $\chi^{-1}$ of the irradiated sample at $H$ = 1 kOe from 2-300 K.

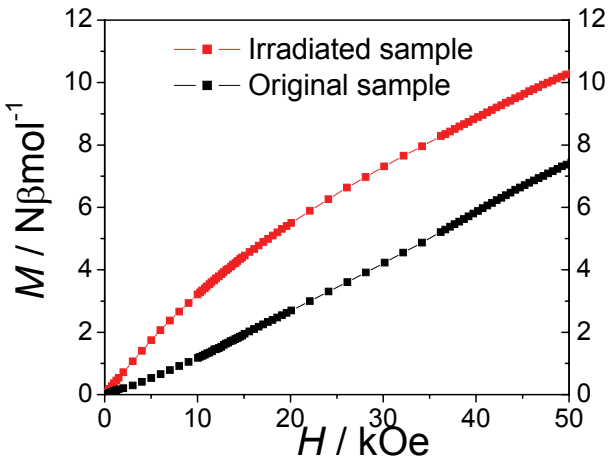



**Figure S6.** Field dependent magnetizations at 2 K for the irradiated and original samples.