Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

for

A boracite metal-organic framework displaying selective gas sorption and guest-dependent spin-crossover behaviour

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Contents:

Experimental Section:

General procedures: All starting materials were obtained commercially and were used without further purification. Elemental analyses for C, H, N were performed on a Vario EL III elemental analyzer. Thermogravimetric analyses were performed on a NETZSCH TG 209 thermobalance in a nitrogen atmosphere, sample was placed in alumina containers and data were recorded at 10 °C/min between 20 and 200 °C. The IR spectra were recorded in range of 400–4000 cm^{-1} on a Nicolet 5DX spectrometer (KBr pellets). Small angle X-ray scattering data were collected on Anton Paar SAXSess-mc2 system. Scanning electron microscopy (SEM) images were obtained on a Hitachi S4800 scanning electron microscope with a field emission electron gun. Gas adsorption measurements were performed in the Micromeritics ASAP2020 system. Magnetic susceptibility data under 0.5 T applied field were collected using a Quantum Design MPMS XL7 SQUID magnetometer, samples were immersed in solvents while measuring. The diamagnetic correction was performed by a rough estimation ($\chi_d = M_r \times 10^{-6}$ cm^3 mol^{-1}, M_r is the molecular weight. O. Kahn, *Molecular Magnetism*, Wiley-VCH Inc., 1993).

Synthesis of $[\{Fe(NCS)_2\}_3(C_{21}H_{15}N_3)_4]\cdot(H_2O)_{10}(CH_2Cl_2)_{15}(C_2H_5OH)_{60}$ [1·*x*(guest)]. A solution of 1,3,5-tris(4-pyridyl)benzene (TPB, 6.2 mg, 0.02 mmol) in dichloromethane (4.0 mL) and ethanol (1.0 mL) was placed in the bottom of a test tube (inner diameter 1.2 cm × length 14 cm), after 2 mL ethanol was added as buffering solvent freshly prepared solution of $Fe(NCS)_2$ in ethanol (0.04 M, 1 mL) was layered. The test tube was sealed and put in refrigeratory (8 °C). Red block crystals of **1**·*x*(guest) formed in four days. Yield: ~35% based on TPB. Elemental analysis: calcd.: C 45.25%, H 7.93%, N 4.22%; found: C 45.09%, H 8.06%, N 4.62%. IR (KBr pellet, cm^{-1}): 3432(s), 2925(w), 2854(w), 2053(m), 1633(m), 1610(m), 1404(w), 1387(m), 1122(w), 1072(w), 813(s), 626(w), 524(w).

Preparation of activated sample $1\cdot H_2O$. The solvent molecules in sample **1**·*x*(guest) were exchanged with acetone for three times, then the samples were treated with supercritical CO_2 over a period of 6 hours, during this time the liquid CO_2 was vented under positive pressure for five minutes each hour, and then the temperature was heated to 40 °C for one hour, giving activated product $\mathbf{1}\cdot(H_2O)_{10}$. Elemental analysis for $\mathbf{1}\cdot(H_2O)_{10}$: calcd.: C 55.90%, H 4.17%, N 13.04%; found: C 56.00%, H 4.18%, N 12.82%.

X-ray Crystallography:

X-ray crystallographic data for **1**·*x*(guest) were collected with a Cu K_α radiation source (λ = 1.54178 Å) by using Oxford Gemini S Ultra diffractometers, equipped with graphite monochrometor. Crystal size is 0.3 × 0.2 × 0.1 mm^3. The structure was solved by direct methods and refined by full matrix least-square calculations (F^2) by using the SHELXTL-97 software.[1] All non-hydrogen atoms were refined in the anisotropic approximation against F^2 for all reflections. All hydrogen atoms were added by riding model. The contribution of highly disordered solvent molecules was treated using SQUEEZE procedure implemented in PLATON program.[2]

1. M. Sheldrick, SHELXS-97: Programs for crystal structure analysis, University of Göttingen, Göttingen (Germany), 1997.

2. A. L. Spek, *Acta Cryst.* **1990**, *A46*, 194-201.

Crystallographic data for **1**·*x*(guest): $C_{225}H_{470}Cl_{30}Fe_3N_{18}S_6$, M_r = 5971.60, cubic, $Fm\bar{3}m$, T = 120(2) K, a = 37.4447(4) Å, V = 52501.4(10) Å^3, Z = 12, ρ_{calcd} = 2.266 g cm^{-3}, μ(CuK_α) = 7.907, F(000) = 38280, final R_1 ($I > 2\sigma(I)$), wR_2 (all data) = 0.1294, 0.3696, GOF = 1.133. T = 173(2) K, a = 38.6149(2) Å, V = 57579.1(5) Å^3, Z = 12, ρ_{calcd} = 2.067 g cm^{-3}, μ(CuK_α) = 7.210, F(000) = 38280, final R_1 ($I > 2\sigma(I)$), wR_2 (all data) = 0.1526, 0.3615, GOF = 2.690. All disordered solvent molecules were not included in the formula unit as determined by the X-ray analysis.

Additional figures :

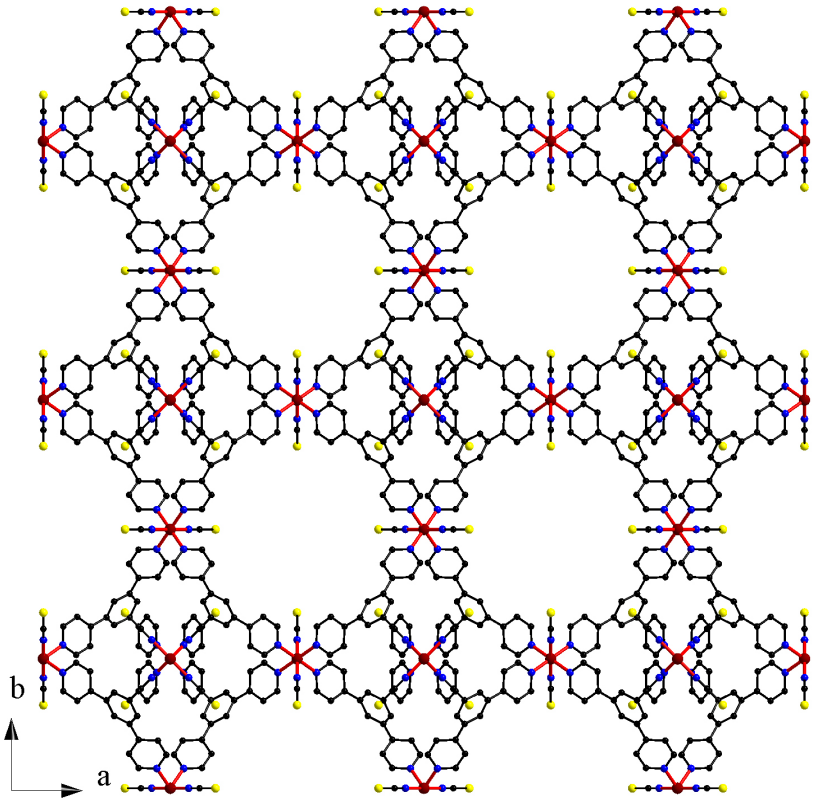
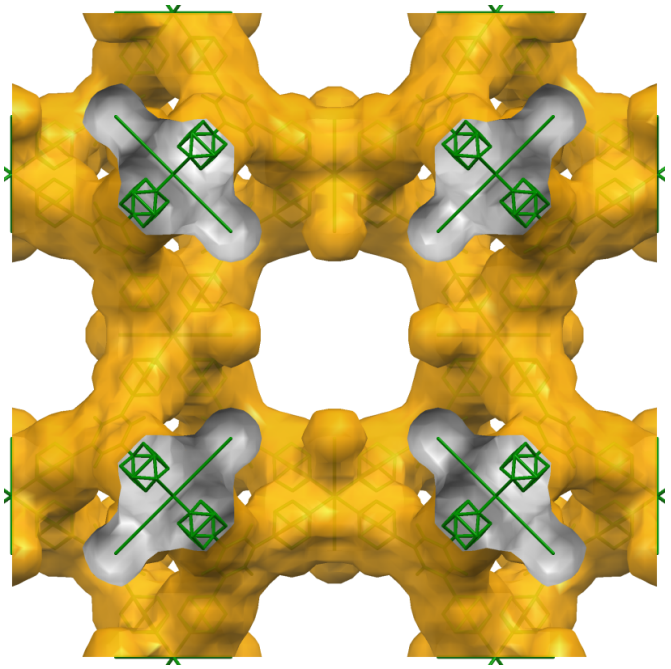
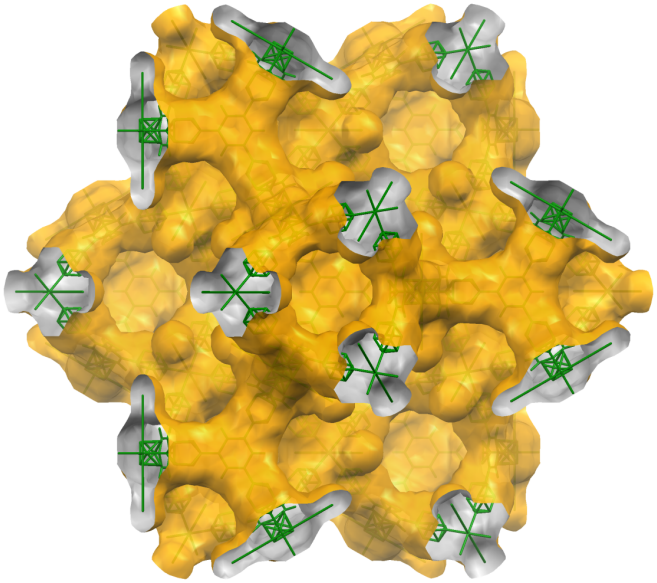


Figure S1. View of the three-dimensional structure of **1**·*x*(guest) along the *c*-axis. Hydrogen atoms and guest molecules are omitted for clarity

a)



b)



c)

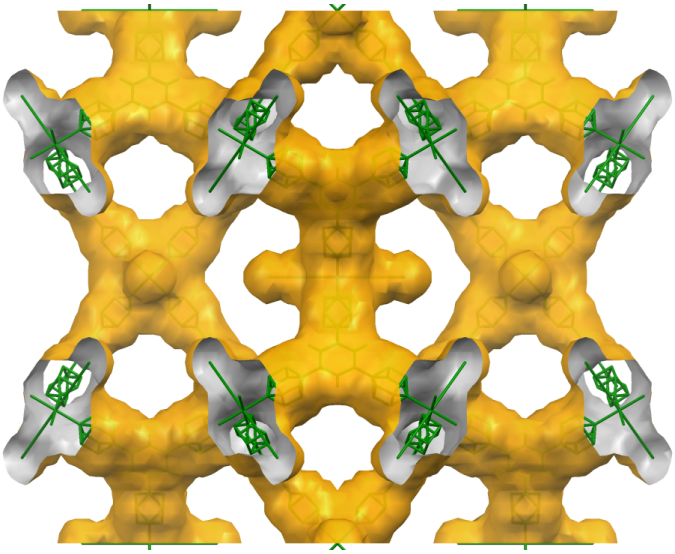


Figure S2. View of the voids and channels in the framework of **1** (a-c).

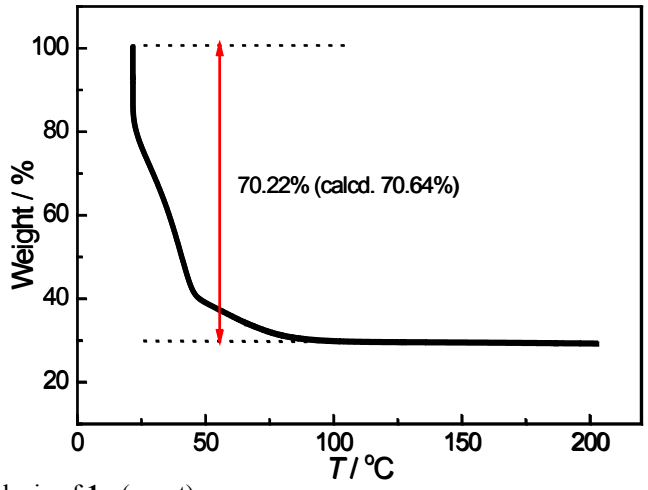


Figure S3. Thermogravimetric analysis of **1**·*x*(guest).

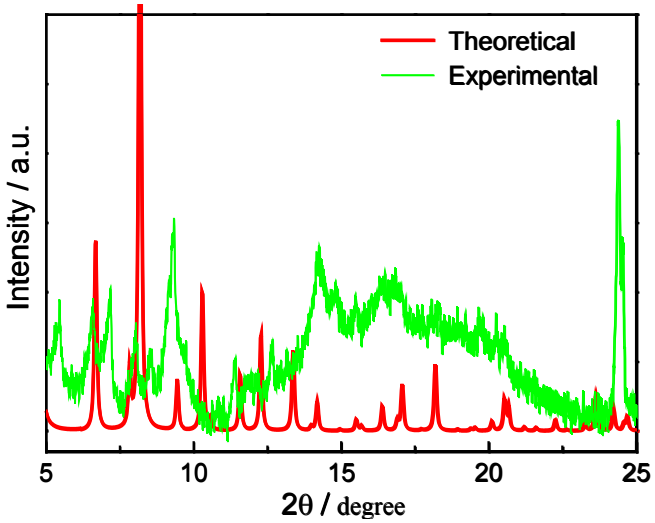


Figure S4. Small-angle X-ray scattering pattern of the activated **1**.

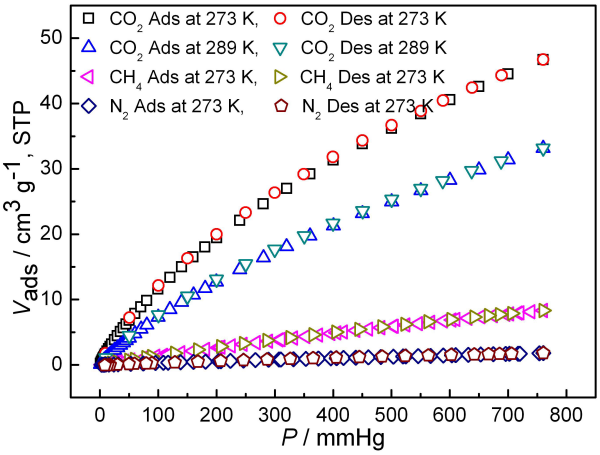


Figure S5. Adsorption-desorption isotherms of CO_2, CH_4 and N_2 in **1**.

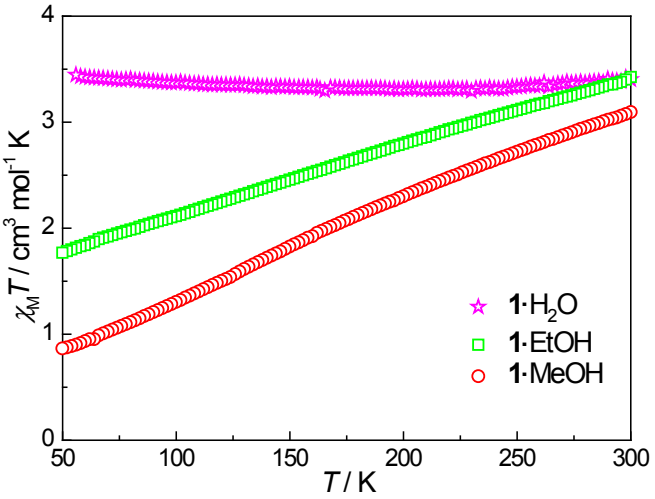


Figure S6. Magnetic properties of **1**·MeOH, **1**·EtOH and **1**·H_2O.

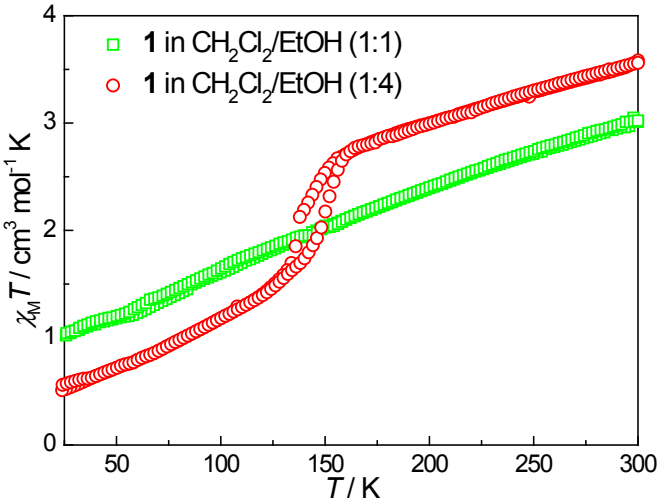


Figure S7. Magnetic properties of **1** in CH_2Cl_2/EtOH at different ratio.

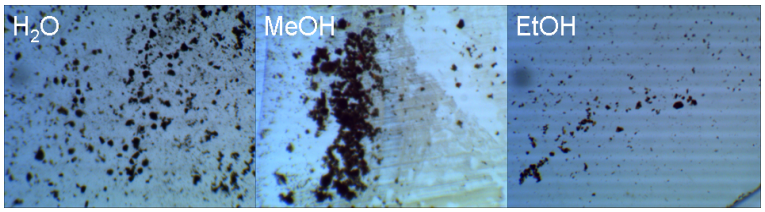


Figure S8. Samples of **1**·MeOH, **1**·EtOH and **1**·H_2O.

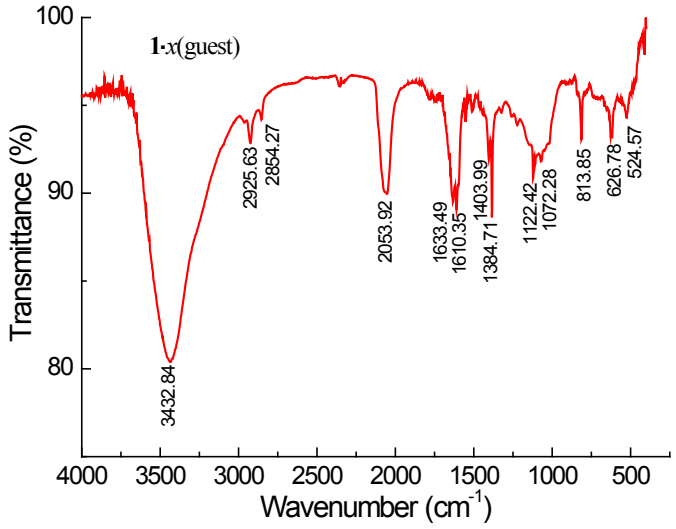


Figure S9. IR spectrum of **1**·*x*(guest).