Supporting Information for:

NOVEL METAL-ORGANIC FRAMEWORKS BASED ON 5-BROMONICOTINIC ACID: MULTIFUNCTIONAL MATERIALS WITH H_2 PURIFICATION CAPABILITIES

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Luminescence Properties

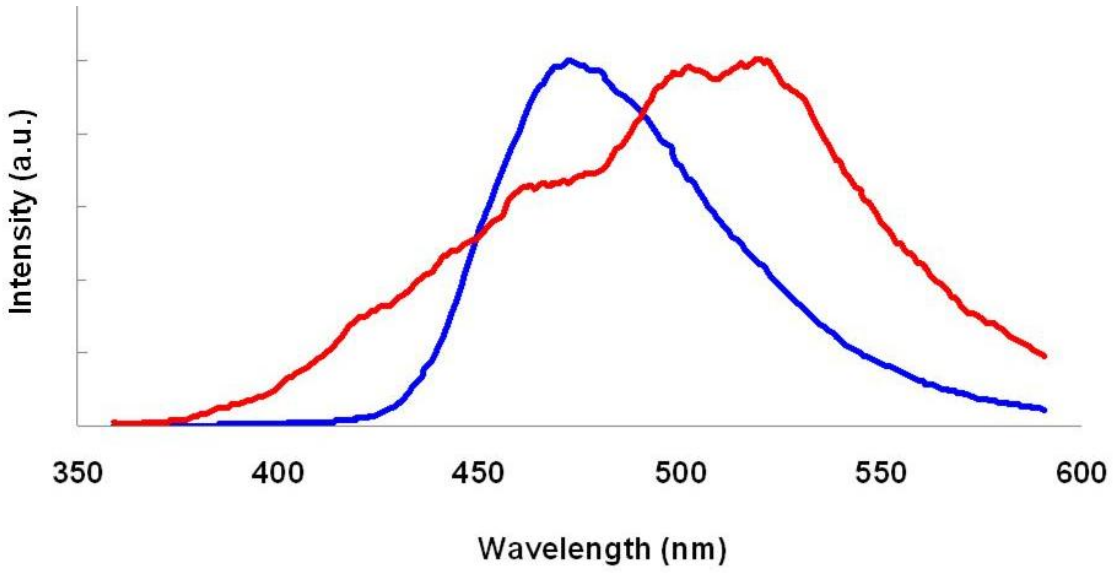

Figure S1. The emission spectra of **1,** red line, and 5-BrNic, blue line, in solid state at room temperature.

Crystal Data

Crystal Data. **1**: $[Cd(C_{12}H_6N_2O_4Br_2)]$, M = 514.41, monoclinic, space group *P21/n*, a = 11.2814(12), b = 9.9474(11), c = 13.2863(15) Å, β = 108.7840(10), V = 1411.6(3) Å^3, Z = 4, ρ_{calcd} = 2.421 g cm^{-3}, μ(Mo-$K\alpha$) = 7.223 mm^{-1}, R_{int} = 0.0341, T = 293 K, $R1(F_o)$ = 0.0323, ($wR2(F_o^2)$ = 0.0723) with a goodness-of-fit on F^2 1.021. **2**: $[Co(C_{24}H_{12}N_4O_8Br_4)(H_2O)]$, M = 939.89, monoclinic, space group *C2/c*, a = 15.0926(18), b = 16.9747(18), c = 14.4400(16) Å, β = 120.52(4), V = 3186.9(6) Å^3, Z = 4, ρ_{calcd} = 1.959 g cm^{-3}, μ(Mo-$K\alpha$) = 6.109 mm^{-1}, R_{int} = 0.0964, T = 293 K, $R1(F_o)$ = 0.0669, ($wR2(F_o^2)$ = 0.2040) with a goodness-of-fit on F^2 1.064. Data were collected by $\omega/2\theta$ scans ($2\theta_{max}$ = 51.98º and 36.58º for **1** and **2**, respectively) on a Bruker APEXII diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined on F2 by the SHELX-97 program.

Magnetic Properties

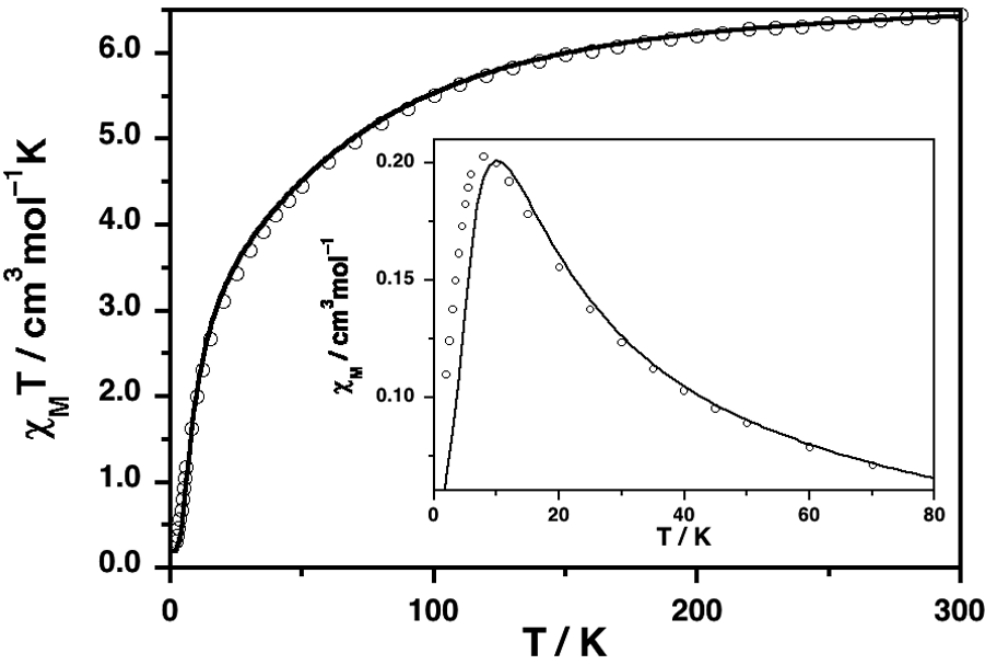

Figure S2. Temperature dependence of $\chi_M T$ (Δ) and χ_M (○, inset) for **2**. The solid lines correspond to the best fit.

Experimental Isotherms

Excess H_2 adsorption isotherms at 77 K were obtained over the 0-20 bar pressure range by volumetric analysis (PCI instrument from Advanced Materials Corp., Pittsburgh, PA). The non-ideality of hydrogen was taken into account by using the Peng-Robinson equation of state.[1] Prior to the measurements, samples were activated on a high vacuum line (10^{-4} mbar) at 120 C overnight.

Computational Details

The material was characterized geometrically, starting from the crystallographic coordinates. The geometric pore size distribution was calculated, which is related to the diameter of the largest sphere that can fit into the cavities without overlapping with any of the framework atoms[17] and the accessible surface area[2] using different probe molecules (Figure S1). Additionally, hydrogen adsorption at 77 K on **2** was studied using grand canonical Monte Carlo (GCMC) simulations (Figure S2).[3] In the grand canonical ensemble, the chemical potential, the volume, and the temperature are kept fixed as in adsorption experiments. An atomistic model was used for **2**, with the atoms frozen at the crystallographic positions. In the simulation, hydrogen molecules were randomly moved, rotated, inserted, and deleted, allowing the number of molecules in the framework to fluctuate. The chemical potential was related to the system pressure by the Peng-Robinson equation of state.[4] The standard 12-6 Lennard-Jones (LJ) potential was used to model the interatomic interactions. The parameters for the framework atoms were obtained from the UFF force field,[5] while molecular hydrogen was modeled by two LJ spheres (σH=2.72Å, εH/kB = 10.00 K, dH-H=0.74Å)[6, 7]. The Lorentz_Berthelot mixing rules were employed to calculate the mixed parameters. Interactions beyond 17 Å were neglected for the simulations. Quantum effects were taken into account using the Feynman-Hibbs effective potential method,[8,] which is sufficiently accurate at 77 K.[6,9,10] A total number of 2×10^7 Monte Carlo steps were performed. The first 50% was used for system equilibration, carefully ensuring that thermodynamic equilibrium was reached, while the remaining steps were used to calculate the ensemble averages.

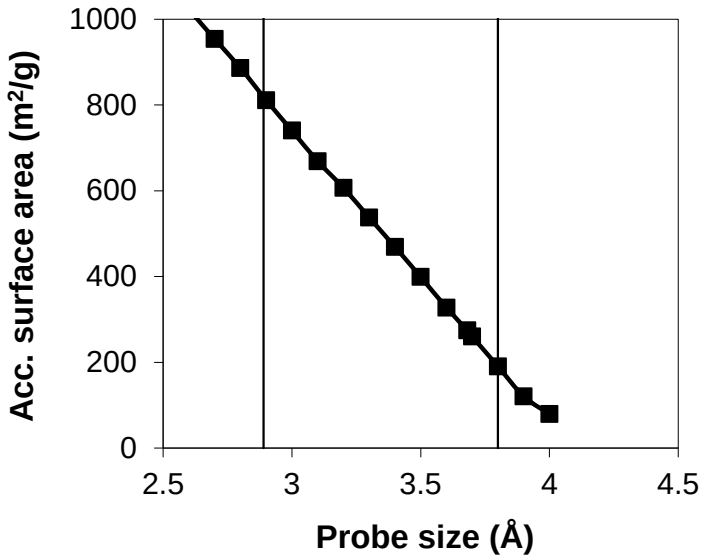

Figure S3. Accessible surface area of **2** obtained with different probe molecules with a diameter ranging between 2.6 and 4.0 Å Vertical lines show the kinetic diameter of H_2 (2.89 Å) and CH_4 (3.8 Å), and so the accessible surface areas for this compound.

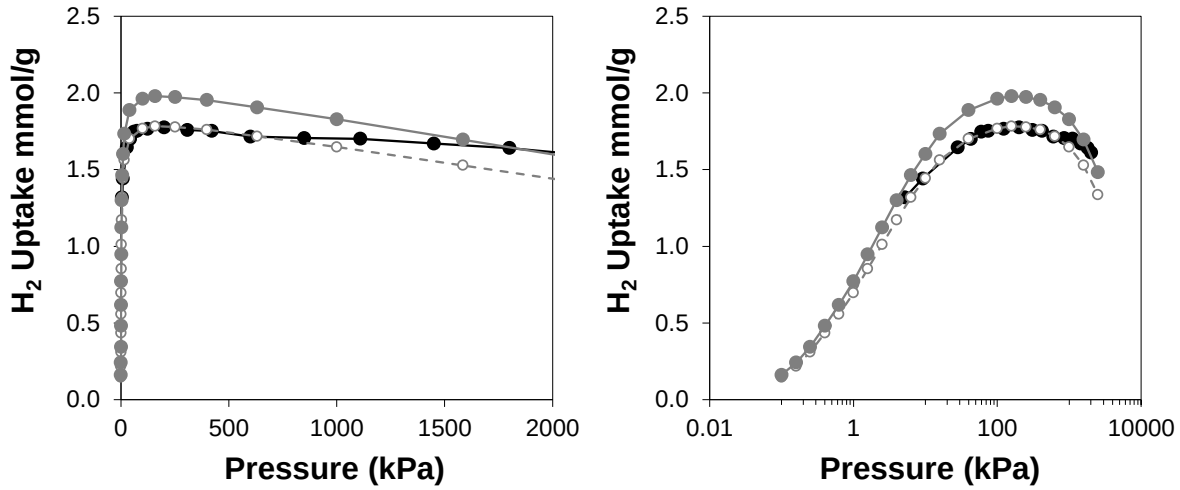

Figure S4. *(left)* Experimental, black closed circles, and simulated, grey closed circles, H_2 isotherms at 77 K on **2**. Scaled ($\prod$ = 0.91) simulated isotherms, grey open circles. *(right)* Semilog representation of the H_2 isotherms.

References

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