

Nitro-functionalized Bis(pyrazolate) Metal-Organic Frameworks as Carbon Dioxide Capture Materials under Ambient Conditions

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Abstract

© 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim The metal-organic frameworks (MOFs) M(BPZNO₂) (M=Co, Cu, Zn; H₂BPZNO₂=3-nitro-4,4'-bipyrazole) were prepared through solvothermal routes and were fully investigated in the solid state. They showed good thermal stability both under a N₂ atmosphere and in air, with decomposition temperatures peaking up to 663 K for Zn(BPZNO₂). Their crystal structure is characterized by 3D networks with square (M=Co, Zn) or rhombic (M=Cu) channels decorated by polar NO₂ groups. As revealed by N₂ adsorption at 77 K, they are micro-mesoporous materials with BET specific surface areas ranging from 400 to 900 m² g⁻¹. Remarkably, under the mild conditions of 298 K and 1.2 bar, Zn(BPZNO₂) adsorbs 21.8 wt % CO₂ (4.95 mmol g⁻¹). It shows a Henry CO₂/N₂ selectivity of 15 and an ideal adsorbed solution theory (IAST) selectivity of 12 at p=1 bar. As a CO₂ adsorbent, this compound is the best-performing MOF to date among those bearing a nitro group as a unique chemical tag. High-resolution powder X-ray diffraction at 298 K and different CO₂ loadings revealed, for the first time in a NO₂-functionalized MOF, the insurgence of primary host-guest interactions involving the C(3)-NO₂ moiety of the framework and the oxygen atoms of carbon dioxide, as confirmed by Grand Canonical Monte Carlo simulations. This interaction mode is markedly different from that observed in NH₂-functionalized MOFs, for which the carbon atom of CO₂ is involved.

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Keywords

adsorption, host-guest interactions, metal-organic frameworks, N ligands, X-ray diffraction

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