

Supporting Information

Size-Dependent Catalysis by DABCO-Functionalized Zn-MOF with One-Dimensional Channels

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Experimental Details

Anhydrous toluene, nitromethane, nitroethane, 2-nitropropane, 1-nitropropane, and 1,1,2,2-tetrachloroethane were purchased from Sigma-Aldrich and used as received. Nitrocyclohexane was purchased from TCI. PXRD patterns were obtained by using a Rigaku MiniFlex (30 kV, 15 mA). FT-IR spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR spectrometer.

Catalytic Reactions

Nitroaldol (Henry) reaction: Reagent-grade nitromethane was used without further purification. A mixture of the as-prepared Zn-MOF **1** catalyst (10 mg, 0.0166 mmol) and 4-nitrobenzaldehyde (0.151 g, 1.0 mmol) in nitroalkanes (10 mL) was heated at 60°C with constant stirring for 120 h. The reaction mixture was filtered through a glass frit, and the solids were washed with chloroform and acetone. The solvent was removed from the filtrate by rotary evaporation, and the residue was dried under high vacuum then completely

dissolved in deuterated chloroform (10 mL). The product was analyzed by ^1H NMR spectroscopy on a Varian GEMINI 2000 spectrometer (200 MHz). Distinctive chemical shifts were observed for the aromatic hydrogen atoms of the product. The signals were assigned by comparing the chemical shifts observed for the authentic samples.

Cyanosilylation: A mixture of the as-prepared Zn-MOF **1** catalyst (10 mg), 4-nitrobenzaldehyde (0.151 g, 1.0 mmol), and $(\text{CH}_3)_3\text{SiCN}$ (0.099 g, 1.0 mmol) in dry toluene (10 mL) was heated at 50°C with constant stirring for 24 h. The reaction mixture was then filtered through a glass frit, and the solids were washed with chloroform and acetone. The solvent was removed from the filtrate by rotary evaporation, and the residue was dried under high vacuum then completely dissolved in CDCl_3 . An internal standard, 1,1,2,2-tetrachloroethane (1.0 mmol), was added. The product was analyzed by ^1H NMR spectroscopy on a Varian GEMINI 2000 spectrometer (200 MHz). A distinctive chemical shift of 5.6 ppm was observed for the silyl ether product. The signals were assigned by comparing the chemical shifts observed for the products with literature values. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis of the reaction filtrate was performed at Korea Basic Science Institute (Seoul, Korea) by using a Jobin Yvon 138 Ultrace spectrometer.

Figure S1. The molecular dimensions of 4-nitrobenzaldehyde and various nitroalkanes. In order to estimate the physical dimensions of these molecules, we chose two suitable atoms and calculated their center-to-center distance by Chem3D followed by adding their van der Waals radii.

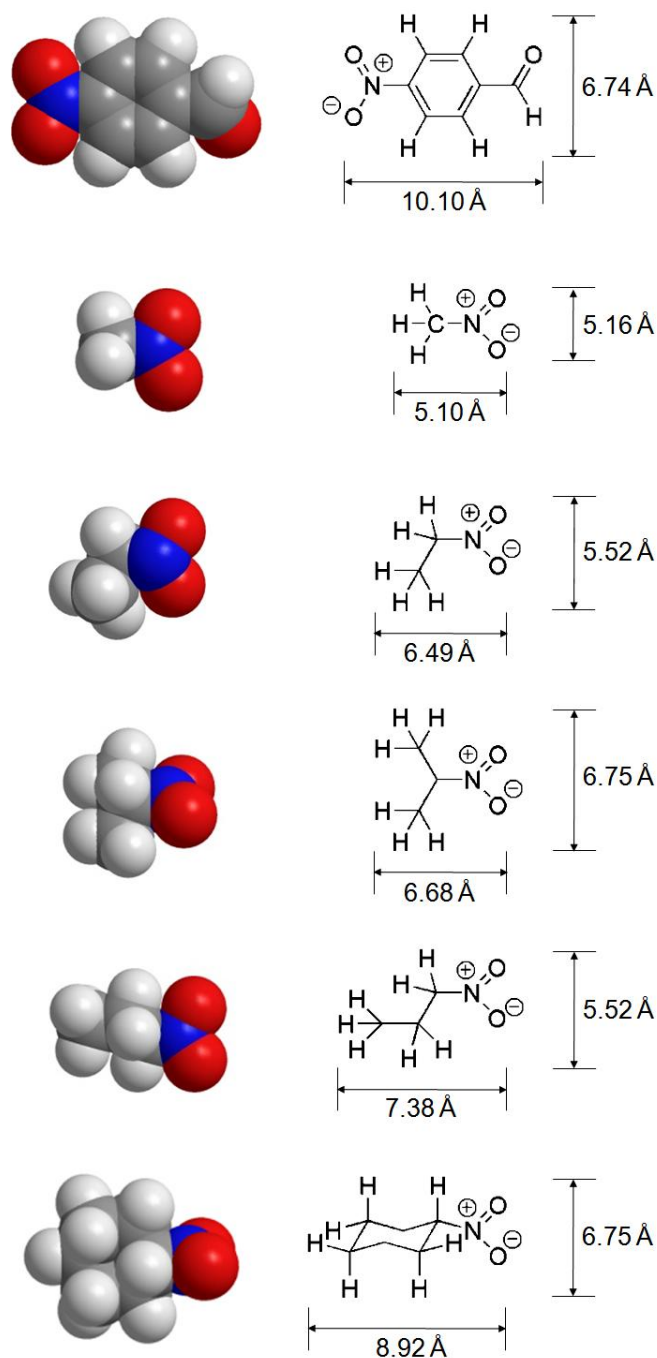


Figure S2. (a) The structures of an individual 2D layer of 3D-like Zn-MOF **1** with different orientations starting from the *a*-axis. (b) Single planar 2D layer shown in (a) along the *b*-axis.

