Supporting Information for

Nanoporous Metal-organic Framework as Renewable Size-selective Hydrogen-Bonding Catalyst in Water

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Materials and Methods.

Reagents and chemicals: All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. 3,4-diethoxy-3-cyclobutene-1,2-dione, 3-aminobenzoic acid, 1-Phenyl-1,3-butanedione, Dibenzoylmethane, Ethyl acetoacetate, 2,4-Pentanedione, Methyl acetoacetate, tert-Butyl acetoacetate, trans-β-Nitrostyrene, trans-4-Methoxy-β-nitrostyrene, β,4-Dinitrostyrene, (E)-1-Methyl-4-(2-nitrovinyl)benzene, trans-3-Bromo-β-nitrostyrene and trans-2-Bromo-β-nitrostyrene were purchased from Beijing Innochem Science & Technology Co.,Ltd.

Instruments and spectroscopic measurements: The elemental analyses of C, H and N were performed on a Vario EL III elemental analyzer. 1H NMR spectra were measured on a Bruker-400 spectrometer with Me₄Si as an internal standard. X-Ray powder diffraction (XRD) patterns of the Zn–DBDA was recorded on a Rigaku D/max-2400 X-ray powder diffractometer (Japan) using Cu–Kα (λ =1.5405 Å) radiation. Thermogravimetric analysis (TGA) was carried out at a ramp rate of 5 °C/min in a nitrogen flow with a Mettler-Toledo TGA/SDTA851 instrument. FT-IR spectra were recorded as KBr pellets on Bruker Optics TENSOR 27 FT-IR spectrophotometer. The Zn²⁺ content before and after catalytic were measured by Inductively Coupled Plasma Spectrometer (Perkin Elmer). The solution fluorescent spectra were measured on Jasco V-530. Both excitation and emission slit widths were 2.5 nm, and fluorescence measurements were carried out in a 1 cm quartz cuvette with stirring the suspension of Zn–DBDA. Gas adsorption isotherms were obtained using a Belsorp-mini volumetric adsorption instrument from BEL Japan Inc. using the volumetric technique. For the Gaussian calculations, we used the popular B3LYP functional combined with the standard basis set 6-31G(d,p). The starting structures of Zn–DBDA is their crystallographic geometries, considering the experimental results, the Gaussian calculations are only performed for the 1:1 complexes, including the geometry optimization and vibrational spectral analysis.
Synthesis of the \( \text{H}_2\text{dbda} \) (3,3'-(3,4-dioxocyclobut-1-ene-1,2-diyl)bis(azanediyl))dibenzoic acid) ligand.

\[
\begin{align*}
\text{3-Aminobenzoic acid (576 mg, 4.2 mmol), Zn(CF}_3\text{SO}_3)_2 \text{ (145 mg, 0.4 mmol), and} \\
\text{3,4-diethoxy-3-cyclobutene-1,2-dione (295 uL, 2 mmol) was added into 19.0 mL toluene and 1.0 mL} \\
\text{NMP. After heating to reflux at 100 °C for 24 h under a N}_2 \text{ atmosphere, a yellow precipitate was} \\
\text{harvested by filtration and washed with MeOH (10 mL). To further purify the product, the yellow solid} \\
\text{was stirred in boiling MeOH (20 mL) for 5 min and then isolated by vacuum filtration, and washed with} \\
\text{MeOH (3 × 5 mL). This purification procedure was repeated two more times, and the product was dried at} \\
\text{80 °C for 12 h. Yield: 0.6 g (85%) based on 3,4-diethoxy-3-cyclobutene-1,2-dione.} \\
\text{^1H NMR (400 MHz, DMSO-}d_6\text{): } \delta \text{ 11.36 (s, 2H), 8.13 (s, 2H), 7.99 (d, } J = 8.0 \text{ Hz, 2H), 7.63 (d, } J = 8.0 \text{ Hz, 2H), 7.50 (t, } J = \\
\text{8.0 Hz, 2H). ESI-MS (m/z): [M]^- \text{ calculated for } [\text{C}_{18}\text{H}_{11}\text{N}_2\text{O}_6^-] 351.3, \text{ found 350.9.}}
\end{align*}
\]
X-ray Crystallography (Single-crystal diffraction) and Characterizations of Zn–DBDA.

Crystal data of Zn–DBDA:

\[ \text{C}_{33}\text{H}_{45}\text{N}_{7}\text{O}_{12}\text{Zn}_{1.5}, \text{Mr} = 829.8, \text{Monoclinic, space group } P2(1)/c, a = 5.9994(12), b = 29.661(6), c = 19.068(4) \text{ Å}, \alpha = 90.00, \beta = 90.09, \gamma = 90.00, V = 3393.0(12) \text{ Å}^3, Z = 4, D_c = 1.624 \text{ g cm}^{-3}, \mu(\text{Mo-Kα}) = 1.146 \text{ mm}^{-1}, T = 296(2) \text{ K}. 19212 \text{ unique reflections } [R_{int} = 0.1398 \text{ ]. Final } R_1[\text{with } I > 2\sigma(I)] = 0.0637, wR_2(\text{all data}) = 0.1262, \text{GOOF} = 1.003. \text{CCDC number: 1810642.} \]

Crystallography:

Intensities were collected on a Bruker SMART APEX CCD diffractometer with graphitemonochromated Mo-Kα (λ = 0.71073 Å) using the SMART and SAINT programs. The structure was solved by direct methods and refined on \( F^2 \) by full-matrix least-squares methods with SHELXTL version 5.1. Non-hydrogen atoms of the ligand backbones were refined anisotropically. Hydrogen atoms within the ligand backbones were fixed geometrically at calculated positions and allowed to ride on the parent non-hydrogen atoms. In addition to the two DMF molecules that were modelled, the masking process was used and 478 electrons were found in a volume of 988 Å³ void per unit cell. With \( Z = 4 \) in this case, this is equivalent to the removal of \( 478/4 = 119.5 \) electrons from the formula unit. This is consistent with the presence of \( 3[C_3H_7NO] \) per Formula Unit which account for 480 electrons per unit cell.

Selective bond distance (Å) and angle (°) in Zn–DBDA.

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<th>Zn(1)–O(1WA)</th>
<th>Zn(2)–O(6A)</th>
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Symmetry code A: 2-x, 1-y, 1-z; B: 3-x, -0.5+y, 1.5-z; C: -1+x, 1.5-y, -0.5+z; D: 2-x, -0.5+y, 1.5-z; E: 1-x, 1-y, 1-z.
**Figure S1** The coordination environment of Zn(II) in Zn–DBDA.

**Figure S2** The coordination mode of dbda$^{2-}$ ligands in Zn–DBDA.
**Figure S3** CO$_2$ adsorption/desorption isotherms of Zn–DBDA at 195 K.

**Figure S4** TGA traces of Zn–DBDA ranging from room temperature to 600 °C.
**Figure S5** Powder XRD patterns of Zn−DBDA simulated from single-crystal X-ray diffraction results, the as-synthesized Zn−DBDA and Zn−DBDA treated with water.
**Figure S6** Family of fluorescence spectra of Zn–DBDA (0.55 mM) upon addition of β-nitrostyrene up to 0.23 mM; and the Stern–Volmer plot of Zn–DBDA quenched by β-nitrostyrene, where $I_0$ and $I$ are the fluorescence intensity ratio before and after β-nitrostyrene incorporation, respectively.

![Nitrostyrene](image)

![Stern-Volmer plot](image)

**Figure S7** Family of fluorescence spectra of Zn–DBDA (0.55 mM) upon addition of Hacac up to 1.5 mM; and the Stern–Volmer plot of Zn–DBDA quenched by Hacac, where $I_0$ and $I$ are the fluorescence intensity ratio before and after Hacac incorporation, respectively.

![Hacac](image)

![Stern-Volmer plot](image)
**Figure S8** FT-IR spectra of Zn–DBDA (top), Zn–DBDA obtained after the absorption of $\beta$-nitrostyrene (middle) and $\beta$-nitrostyrene itself (bottom).

![FT-IR spectra of Zn–DBDA](image)

**Figure S9** FT-IR spectra of Zn–DBDA (top), Zn–DBDA obtained after the absorption of Hacac (middle) and Hacac itself (bottom).

![FT-IR spectra of Zn–DBDA](image)
**Figure S10** The $^1$H-NMR spectra of the Zn–DBDA after β-nitrostyrene adsorption (decomposed by DCl).

![Figure S10](image1)

**Figure S11** The $^1$H-NMR spectra of the Zn–DBDA after Hacac adsorption (decomposed by DCl).

![Figure S11](image2)
**Figure S12** Yields of 3-(2-nitro-1-phenylethyl)pentane-2,4-dione catalyzed by Zn–DBDA (violet) and without Zn–DBDA through filtration after 2 hrs of the reaction (green).

![Graph showing yields over time](image)

**Figure S13** Study on recycling of catalyst Zn–DBDA for the heterogeneous Michael addition of acetylacetone with β-nitrostyrene.

![Graph showing cycles and yields](image)