Design and Synthesis of Squaramide-Based MOFs as Efficient MOF-supported Hydrogen-Bonding Organocatalysts

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SUPPORTING INFORMATION

General Materials and Methods. Unless otherwise noted, all starting materials were obtained from commercial suppliers (Sigma-Aldrich, Acros Organics, Spectrum, Omnisolv, and others), and used without further purification. ¹H NMR spectroscopy was measured on a Varian Mercury-400 NMR spectrometer, chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0 ppm for TMS. ESI-MS was performed using a ThermoFinnigan LCQ-DECA mass spectrometer, and the data was analyzed using the Xcalibur software suite. Inductively coupled plasma optical emission spectrometer (ICP-OES) was tested on a Perkin Elmer Optima 3000 ICP Emission Spectrometer (the concentration of the MOFs were 600-800 ppb). Centrifugation was performed using a Beckman Coulter Microfuge Lite Centrifuge, with a fixed-angle rotor at 6000 rpm for 2 min. FTIR data were collected at ambient temperature on a Bruker ALPHA FTIR Spectrometer from 4000 cm⁻¹ and 400 cm⁻¹, and experimental backgrounds were corrected using The following indications are used to characterize OPUS software package. absorption bands: strong (s), medium (m), weak (w), and broad (br).

Energy Dispersed X-ray Spectroscopy (EDX). Approximately 1-3 mg of $Cu(dbda)_x(tptc)_{1-x}$ (x = 1, 0.75, 0.49, 0.18, 0) were transferred to conductive carbon tape on a sample holder disk, and coated using a Ir-sputter coating for 8 sec. A Philips XL ESEM instrument was used for acquiring images using a 7.5 kV energy source under vacuum.

Thermalgravimetric Analysis (TGA). Approximately 5-10 mg of dried MOFs sample was used for TGA measurements. Samples were analyzed under a stream of N₂ (80 mL/min) using a Mettler Toledo TGA/DSC STARe System running from room temperature to 800 °C with a scan rate of 5 °C/min.

Powder X-ray Diffraction (PXRD) Analysis. As-synthesized MOFs were isolated by filtration and air-dried for 5 min prior to data collection. The samples were spread on a zero field sample holder. PXRD data were collected at ambient temperature on a Bruker D8 Advance diffractometer at 40 kV, 40 mA for Cu K α (λ =1.5418 Å), with a scan speed of 0.2 sec/step, a step size of 0.04° in 2 θ , and a 2 θ range of 5 to 40°.

BET Surface Area Analysis. Low-pressure gas adsorption measurements were measured with an ASAP 2020 surface area and pore size analyzer. Before gas sorption tests, as-synthesized MOFs were been soaked in 10.0 mL MeOH (refreshed every 24 h) for 3 d. Approximately 60-80 mg of each MOFs were transferred to preweighed sample tubes and evacuated on a vacuum line for 1 h at room temperature, and subsequently degassed at 60 °C on an ASAP 2020 Adsorption analyzer for 10 h. The sample tube was reweighed to obtain a consistent mass for the degassed sample. UHP grade (99.999%) N₂ were used for all measurements. The sample temperature was maintained at 77 K (liquid nitrogen bath).

Single-Crystal X-ray Diffraction (XRD). The suitable crystals (~20 μ m × 20 μ m × 20 μ m) of **Zn(dbda)** and **Cu(dbda)** were selected and diffraction data was collected on a Bruker Apex diffractometer using Mo K α (λ = 0.71073 Å) radiation. Metal

atoms were found in the Fourier difference map and refined anisotropically. The disordered solvent molecules within the framework were treated with the "SQUEEZE" protocol in PLATON to account for electron density.^{1, 2} The structure was solved by direct methods using SHELXTL and refined by full-matrix least squares on F^2 using SHELX-97.³ Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Hydrogen atoms were placed in calculated positions. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited in the Cambridge Crystallographic Data Center (CDCC) as CCDC 1472314 and 1472315.

MOF Digestion and Analysis by ¹**H NMR.** ~5 mg of $Cu(dbda)_x(tptc)_{1-x}$ (x = 0.75, 0.49, 0.18) was dried in air and digested with sonication in 750 µL DMSO- d_6 and 10 µL of 35% DCl.

General Procedure for Catalysis Experiments. Indole (18 mg, 0.15 mmol), β nitrostyrene (15 mg, 0.1 mmol), and 5 mol% MOF catalyst were added to 1.0 mL of dry CHCl₃ in a 8.0 mL glass vial. A freeze-pump-thaw method was used to degas the system. The vial was connected to a Schlenk line, and liquid nitrogen in a dewar was used to freeze the solution. When the solvent was frozen, the frozen solution was placed under vacuum for 10 min, then purged with nitrogen, and then thawed until the solvent melted. The reaction mixture was incubated at 50 °C for 24 h under After cooling down, the solution was evaporated under vacuum to remove the N₂. solvent and 750 µL CD₂Cl₂ was used to dissolve the product for ¹H NMR analysis. The reaction was monitored by ¹H NMR spectroscopy via the integration of α -vinyl and β -vinyl proton of β -nitrostyrene (δ 8.02 – 8.07 ppm) and the resulting aliphatic proton of the product 3-(2-nitro-1-phenylethyl)-1*H*-indole (δ 4.95 – 5.25 ppm). То test recyclability, the supernatant was separated from the catalyst by centrifugation. The solid catalysts were washed with MeOH (3×5 mL) and soaked in the MeOH for 24 h. After soaking, the solids were centrifuged and dried in air. The dried MOFs were directly used for the next run of Friedel-Crafts catalysis.

Synthesis of Squaramide Ligand and MOFs.

Synthesis of 5,5'-((3,4-dioxocylcobut-1-ene-1,2-diyl)bis(azanediyl))diisophthalic acid (H_4 dbda). H_4 dbda ligand was synthesized according to a literature procedure (Fig. S1).⁴ 5-Amino-isophthalic acid (761 mg, 4.2 mmol), $Zn(CF_3SO_3)_2$ (145 mg, 0.4 mmol), and 3,4-diethoxy-3-cyclobutene-1,2-dione (295 uL, 2 mmol) was added into 19.0 mL toluene and 1.0 mL NMP. After heating to reflux at 100 °C for 24 h under a N₂ atmosphere, a yellow precipitate was harvested by filtration and washed with MeOH (10 mL). To further purify the product, the yellow solid was stirred in boiling MeOH (20 mL) for 5 min and then isolated by vacuum filtration, and washed with MeOH $(3 \times 5 \text{ mL})$. This purification procedure was repeated two more times, and the product was dried at 80 °C for 12 h. Yield: 1.41 g (80%) based on 3,4diethoxy-3-cyclobutene-1,2-dione. ¹H NMR (400 MHz, DMSO- d_6): δ 10.24 (s, 2H), 8.13 (d, J = 20 Hz, 6H). ESI-MS (m/z): [M]⁻ calculated for [C₂₀H₁₁N₂O₁₀]⁻ 439.32,

found 439.23.

Synthesis of Zn(dbda). A mixture of Zn(NO₃)₂·6H₂O (60 mg, 0.20 mmol) and H₄dbda (22 mg, 0.05 mmol) in 2.0 mL of DMF and 0.2 mL EtOH was sealed in a 20 mL glass vial and heated to 80 °C for 24 h. After cooling, pale-yellow block crystals were collected by filtration. The crystals were washed with DMF (3×5 mL) and stored in DMF. Yield: 20 mg (67% based on H₄dbda). IR: $\tilde{v} = 3196$ (br), 1788 (w), 1552 (m), 1360 (s), 898 (w), 771 (m), 710 (w), 662 (w).

Synthesis of $Zn(dbda)_x(tptc)_{1-x}$ (x = 0.75, 0.49, 0.18, 0). These compounds were prepared via the same procedure as **Zn(dbda)** but with different ratio of mixed ligands: H_4 dbda (16 mg, 0.038 mmol) and H_4 tptc (5 mg, 0.0125 mmol); H_4 dbda (11 mg, 0.025 mmol) and H₄tptc (10 mg, 0.025 mmol); H₄dbda (5.5 mg, 0.0125 mmol) and H₄tptc (15 mg, 0.0375 mmol); and H₄tptc (20 mg, 0.050 mmol), respectively. All the harvested crystals were washed with DMF (3×5 mL) and stored in DMF. While the block crystals of Zn(tptc) were colorless, the crystals of $(Zn(dbda)_x(tptc)_1)$ x (x = 0.75, 0.49, 0.18) are pale-yellow. Yield calculated based on the total amount 21 mg (71%) for Zn(dbda)_{0.75}(tptc)_{0.25}, 17 mg (71%) for of combined ligand: Zn(dbda)_{0.49}(tptc)_{0.51}, 21 mg (72%) for Zn(dbda)_{0.18}(tptc)_{0.82}, and 21 mg (73%) for for $Zn(dbda)_{0.75}(tptc)_{0.25}$, $\tilde{v} = 3198$ (br), 1787 (w), **Zn(tptc)**, respectively. IR: 1551 (m), 1364 (s), 1110 (w), 770 (m), 709 (w); for $Zn(dbda)_{0.49}(tptc)_{0.51}$, $\tilde{v} = 3207$ (br), 1614 (w), 1555 (m), 1362 (s), 1109 (w), 770 (m), 714 (m); for $Zn(dbda)_{0.18}(tptc)_{0.82}, \tilde{v} = 3201 (br), 1613 (w), 1547 (m), 1358 (s), 1108 (w), 836 (w),$ 771 (w), 718 (m); for **Zn(tptc)**, $\tilde{v} = 3237$ (br), 1618 (w), 1561 (m), 1448 (w), 1359 (s), 1107 (w), 915 (w), 836 (w), 770 (w), 719 (m).

Synthesis of Cu(dbda) using PSE. 50 mg of Zn(dbda) crystals were placed in 10 mL MeOH containing Cu(NO₃)₂·2.5H₂O (9.3 mg/mL). The solution was incubated at room temperature for 2 d, with a fresh Cu(NO₃)₂·2.5H₂O solution (10 mL) provided every 12 h. The harvested Cu(dbda) crystals were washed with MeOH (3×5 mL) and then immersed in 10 mL of pure MeOH for 2 d with a fresh MeOH solution provided every 12 h. Yield: 51 mg (98%). IR: $\tilde{v} = 3080$ (br), 1789 (w), 1687 (w), 1614 (m), 1366 (s), 901 (w), 765 (m), 716 (w), 666 (w), 475 (w).

Synthesis of Cu(dbda)_{*x*}(**tptc)**_{1-*x*} (*x* = 0.75, 0.49, 0.18, 0) **using PSE**. All of the compounds were prepared via the same procedure as described above for **Cu(dbda)**, but using the corresponding **Zn(dbda)**_{*x*}(**tptc)**_{1-*x*} MOFs instead of **Zn(dbda)** crystals for the metal exchange. Yield: 51 mg (98%) for **Cu(dbda)**_{0.75}(**tptc)**_{0.25}, 52 mg (99%) for **Cu(dbda)**_{0.49}(**tptc)**_{0.51}, 51 mg (98%) for **Cu(dbda)**_{0.18}(**tptc)**_{0.82}, and 52 mg (99%) for **Cu (tptc)**. IR: for **Cu(dbda)**_{0.75}(**tptc)**_{0.25}, $\tilde{v} = 3081$ (br), 1789 (w), 1556 (m), 1361 (s), 901 (w), 766 (m), 717 (m), 475 (w); for **Cu(dbda)**_{0.49}(**tptc)**_{0.51}, $\tilde{v} = 3173$ (br), 1551 (m), 1358 (s), 1079 (w), 836 (w), 767 (m), 719 (w), 475 (w); for **Cu(dbda)**_{0.18}(**tptc)**_{0.82}, $\tilde{v} = 3185$ (br), 1609 (w), 1560 (m), 1449 (w), 1356 (s), 1080 (w), 834 (w), 769 (m), 722 (w), 477 (w); for **Cu (tptc)**, $\tilde{v} = 3211$ (br), 1608 (w), 1572 (m), 1450 (m), 1357 (s), 1081 (w), 915 (w), 834 (w), 769 (m), 723 (w), 485 (w).

Synthesis of Cu(tptc) using solvothermal methods. H_4 tptc (0.05 g, 0.12 mmol) and Cu(NO₃)₂·2.5H₂O (0.1 g, 0.43 mmol) were mixed and dispersed in DMF/1,4-dioxane/H₂O (2:1:1 v/v/v, 15 mL). Then added 2 drops of aqueous HCl (37%). The solution was kept at 80 °C for 3 days. The blue crystalline product was separated by filtration washed by DMF (3×5 mL), and then dried briefly in air (yield: 76 mg, 70%).

Synthesis of $Cu(dbda)_{0.12}(tptc)_{0.88}$, $Cu(dbda)_{0.31}(tptc)_{0.69}$, and Cu(dbda) using solvothermal methods. The mixed-ligand MOFs were prepared via the same procedure as Cu(tptc) but with different ratio of mixed ligands: H₄dbda (13.2 mg, 0.03 mmol) and H₄tptc (36.5 mg, 0.09 mmol); H₄dbda (26.4 mg, 0.06 mmol) and H₄tptc (25.0 mg, 0.06 mmol); and H₄dbda (52.8 mg, 0.12 mmol), respectively. The materials were isolated as blue powders. Yield: 76 mg (69%) for $Cu(dbda)_{0.12}(tptc)_{0.88}$, 70 mg (63%) for $Cu(dbda)_{0.31}(tptc)_{0.69}$, 0% for Cu(dbda).

	Zn(dbda)	Cu(dbda)	
formula	$C_{180}H_{54}N_{18}O_{108}Zn_{18}$	C ₁₉₄ H ₅₄ N ₁₈ O ₁₁₇ Cu ₁₈	
FW	5373.77	5648.54	
<i>T</i> (K)	296(2)	296(2)	
crystal system	Trigonal	Trigonal	
space group	<i>R</i> -3 <i>m</i>	R-3m	
a (Å)	18.816(2)	18.2623(6)	
$b(\mathbf{A})$	18.816(2)	18.2623(6)	
c(Å)	38.416(5)	39.6543(13)	
α (deg)	90.00	90.00	
β (deg)	90.00	90.00	
γ (deg)	120.00	120.00	
$V(Å^3)$	11778(3)	11453.3(8)	
Z	1	1	
$\rho_{\rm calc}$ (g/cm ³)	0.758	0.819	
μ (mm ⁻¹)	0.946	0.870	
index ranges	$-23 \le h \le 22$ $-20 \le k \le 21$ $-48 \le l \le 48$	$-23 \le h \le 23$ $-22 \le k \le 20$ $-50 \le l \le 50$	
reflns collected	14002	28287	
Independent(R_{int})	2950 (0.0458)	2365 (0.0453)	
GOF on F^2	1.184	1.133	
$R_1, \omega R_2[I \ge 2\sigma(I)]$	0.0700, 0.1823	0.0689, 0.2158	
$R_1, \omega R_2$ (all data)	0.0901, 0.1900	0.0784, 0.2267	
largest diff. peak/hole (e/Å3)	1.44, -0.55	1.17, -0.65	

 Table S1.
 Crystal Data and Structure Refinement for Zn(dbda) and Cu(dbda).

Table S2. Metal ion content analysis for $Cu(dbda)_x(tptc)_{1-x}$ (x = 1, 0.75, 0.49, 0.18, 0).

Samples	EDX	ICP-OES	
Cu(dbda)	Cu 99%	Cu>99%	
	Zn 1%	Zn N/A	
Cu(dbda) _{0.75} (tptc) _{0.25}	Cu 100%	Cu >99%	
	Zn 0%	Zn N/A	
Cu(dbda) _{0.49} (tptc) _{0.51}	Cu 92%	Cu >99%	
	Zn 8%	Zn N/A	
Cu(dbda) _{0.18} (tptc) _{0.82}	Cu 92%	Cu >99%	
	Zn 8%	Zn N/A	
Cu(tptc)	Cu 92%	Cu >99%	
	Zn 8%	Zn N/A	

 $N/A = Zn^{2+}$ was below the detection limit of the instrument.

	Zn(dbda)	Cu(dbda)	
Metal-Metal bond distanc	2.999 Å	2.629 Å	
Metal-O bond distance	Zn-O (DMF) = $2.004(11)$ Å		
	Zn-O (COO) = 2.036(11) Å	$C_{\rm H} \cap (M_{\rm P} \cap H) = 2.171(5)$ Å	
	Zn-O (COO) = 2.024(10) Å	Cu = O((MEOH) = 2.171(3) Å	
	Zn-O (COO) = 2.049(10) Å	Cu=O(COO) = 1.947(3) A	

 Table S3.
 Summary of unit cells and parameters in Zn(dbda) and Cu(dbda).

Table S4. Friedel-Crafts reaction of indole and β -nitrostyrene in different solvents.

entry	catalyst	solvent	Temp (°C)	time	Yield (%)
1	Cu(dbda)	CH ₃ CN	25	24 h	0
2	Cu(dbda)	Toluene	25	24 h	15
3	Cu(dbda)	CH_2Cl_2	25	24 h	38
4	Cu(dbda)	CHCl ₃	25	24 h	60
5	Cu(dbda)	CH_2Cl_2	35	24 h	61
6	Cu(dbda)	CHCl ₃	35	24 h	79
7	Cu(dbda)	Toluene	50	24 h	88
8	Cu(dbda)	CHCl ₃	50	24 h	99
9	Cu(dbda)	CD_2Cl_2	25	24 h	32



Fig. S1 Preparation of H_4 dbda.



Fig. S2 ¹H NMR spectrum of the H_4 dbda ligand.



Fig. S3 Structure of Zn(dbda) viewed along crystallographic *b*-axis.





Fig. S5 PXRD patterns of Zn(dbda) after activation at 60 °C for 10 h.



Fig. S6 Simulated PXRD pattern (based on XRD, red) of **Zn(dbda)** and assynthesized **Zn(dbda)** upon exposure to various organic solvents for 24 h at room temperature. Abbreviations: EA, ethyl acetate; DCM, dichloromethane; MeOH, methanol; *n*-Hex, *n*-hexane; EtOH, ethanol; Tol, toluene; Diox, 1,4-dioxane; TCM, trichloromethane; NMP, N-methyl-2-pyrrolidone.



Fig. S7 Simulated PXRD patterns (based on XRD, red) of **Zn(dbda)** and assynthesized **Zn(dbda)** upon exposure to water for 3 h.



Fig. S8 ¹H NMR spectrum (400 MHz) of the reaction between indole and β -nitrostyrene with 5 mol% loading of **Zn(dbda)** as catalyst. No reaction was observed under these conditions.



Fig. S9 *Top*: Simulated PXRD patterns (based on XRD, red) of **Zn(dbda)**, and **Zn(dbda)** after catalysis. *Bottom*: As-synthesized **Zn(dbda)** after soaking in CHCl₃ at 50 °C for 8 h.



Fig. S10 Photographs of Cu(dbda) and Zn(dbda) crystals.



Fig. S11 EDX spectra of Cu(dbda), produced by PSE of Zn(dbda).



Fig. S12 Simulated PXRD patterns (based on XRD, red) of **Cu(dbda)**, and assynthesized **Cu(dbda)** upon exposure to various organic solvents for 90 h at room temperature. Abbreviations: EA, ethyl acetate; DCM, dichloromethane; MeOH, methanol; *n*-Hex, *n*-hexane; EtOH, ethanol; Tol, toluene; Diox, 1,4-dioxane; TCM, trichloromethane; NMP, N-methyl-2-pyrrolidone.



Fig. S13 Simulated PXRD patterns (based on XRD, red) of **Cu(dbda)** and **Cu(dbda)** upon exposure to water for 3 h at room temperature.



Fig. S14 ¹H NMR spectrum (400 MHz) monitoring the reaction between indole and β -nitrostyrene in CH₃CN, toluene, CH₂Cl₂, CD₂Cl₂, and CHCl₃ solvents. The reaction was carried out using 5 mol% of **Cu(dbda)** catalyst in 1 mL of solvent for 24 h at the temperature indicated in the figure. The reaction in CD₂Cl₂ was performed under the same condition as reported in reference 20 of the main text (*J. Am. Chem. Soc.*, 2015, **137**, 919-925).



Fig. S15 ¹H NMR spectrum (400 MHz) monitored the reaction between indole and β -nitrostyrene with no catalyst, H₄dbda, Cu(NO₃)₂, and **Cu(dbda)** at 50 °C for 24 h (5 mol% loading of catalyst).



Fig. S16 *Left*: ¹H NMR spectrum (400 MHz) of the reaction between indole and β -nitrostyrene from 30 min to 24 h using 5 mol% of **Cu(dbda)** catalyst at 50 °C. *Right*: Graphical depiction of the reaction conversion at each time point (black line). A test was performed with the same catalysis procedure where the reaction progress was measured after 30 min, and then the MOF was removed using a PTFE microfilter. The reaction progress was again measured after another 23.5 h, which showed no progression of the reaction (red line, and top ¹H NMR spectrum at left).



Fig. S17 *Left*: ¹H NMR spectrum (400 MHz) of catalyst recycling performed with 5 mol% of **Cu(dbda)** in CHCl₃ at 50 °C for 24 h. *Right*: Graphical depiction of the reaction yield for each run.



Fig. S18 PXRD patterns of **Cu(dbda)**, simulated, (based on XRD, red) experimental **Cu(dbda)** before catalysis (black), and experimental **Cu(dbda)** catalyst after 5 reaction cycles (blue).



Fig. S19 ¹H NMR spectra (400 MHz) monitoring the reaction between indole and substituted β -nitrostyrene using 5 mol% of **Cu(dbda)** in CHCl₃ at 50 °C for 24 h.



Fig. S20 EDX spectra of the Cu(dbda)_{0.75}(tptc)_{0.25}.



Fig. S21 EDX spectra of the Cu(dbda)_{0.49}(tptc)_{0.51}.



Fig. S22 EDX spectra of the Cu(dbda)_{0.18}(tptc)_{0.82}.



Fig. S23 EDX spectra of the Cu(tptc).



Fig. S24 Simulted PXRD patterns of Cu(dbda) and Cu(tptc) (based on XRD, red and purple), and as-synthesized $Cu(dbda)_x(tptc)_{1-x}$ (x = 1, 0.75, 0.49, 0.18, 0).



Fig. S25 ¹H NMR spectra (400 MHz) collected to determine the ratio of ligands present in $Cu(dbda)_x(tptc)_{1-x}$ (x = 0.75, 0.49, 0.18).



Fig S26. Simulted PXRD patterns of **Cu(dbda)** and **Cu(tptc)** (based on XRD, red and purple), and as-synthesized **Cu(dbda)**_x(tptc)_{1-x} (x = 0.12, 0.31, 0) using a modification of a direct solvothermal method from the literature).⁵



Fig S27. ¹H NMR spectra (400 MHz) collected to determine and compare the ratio of ligands present in $Cu(dbda)_x(tptc)_{1-x}$ (x = 0.49, 0.18, PSE method) and $Cu(dbda)_x(tptc)_{1-x}$ (x = 0.31, 0.12, direct solvothermal method).



Fig. S28 ¹H NMR spectra (400 MHz) monitoring the reaction between indole and substituted β -nitrostyrene using 5 mol% of Cu(dbda)_x(tptc)_{1-x} in CHCl₃ at 50 °C for 24 h.



Fig. S29 TGA traces of $Zn(dbda)_x(tptc)_{1-x}$ (x = 1, 0.75, 0.49, 0.18, 0).



Fig. S30 TGA traces of $Cu(dbda)_x(tptc)_{1-x}$ (x = 1, 0.75, 0.49, 0.18, 0).

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Fig. S31 Proposed mechanism of the reaction between indole and β -nitrostyrene catalyzed by Cu(dbda). Reproduced from reference 6.

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