The impact of an isoreticular expansion strategy on the performance of iodine catalysts supported in multivariate zirconium and aluminum metal-organic frameworks

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Supplementary Information

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S1 Experimental Details

S1.1 General Methods

Aluminum chloride hexahydrate (99.0%, Acros Organics), zirconium tetrachloride (98.0%, Merck KGaA), 4-tert-butylcatechol (99.0%, Acros Organics), 3,5-di-tert-butylcatechol (99.0%, Acros Organics), hydroquinone (>99.5%, Merck KGaA), catechol (99%, Alfa Aesar), 4methylcatechol (98%, Acros Organics), 2,5-dibromohydroguinone (97%, Alfa Aesar), 2,5-Alfa dichlorohydroquinone (97%, Aesar), methylhydroquinone (>98.0%, TCI), bromohydroquinone (94%, Acros Organics), 2,5-di-tert-butylhydroquinone (97%, Ark Pharm, Inc.), tert-butylhydroquinone (97%, Acros Organics), chlorohydroquinone (90%, Acros Organics), N,N-dimethylformamide (DMF, >99.9%, EMD Millipore), hydrochloric acid (36.5-38.0%, BDH), isopropanol alcohol (99.5%, BDH), dichloromethane (99.9%, Fisher Scientific), dimethyl-[1,1'biphenyl]-4,4'-dicarboxylate (>97%, Browm molecular), [1,1'-biphenyl]-4,4'-dicarboxylic acid (97%, Ark Pharm), tetrahydrofuran (99.0%, Fisher Scientific), nitric acid (68.0-70.0%, AR® ACS, Macron Fine Chemicals[™]), meta-chloroperoxybenzoic acid (70.0-75.0%, Acros Organics), 2,2,2trifluoroethanol (>99%, Sigma-Aldrich), potassium hydroxide (≥85.0%, Fisher Scientific), sulfuric acid (96.0%, J.T.Baker), magnesium sulfate anhydrous (≥99.0%, J.T.Baker), dimethyl sulfoxide-d₆ (DMSO-d₆, >99.0%, Cambridge Isotope Laboratories), methylsulfonylmethane (>99.0%, TCI), tin mossy (95.5%, Alfa Aesar), tert-butyl hydroperoxide (70.0% aq. sol., Alfa Aesar), ethanol (99.5%, Pharmco-AAPER), methanol (>99.9%, Fisher Scientific), nitromethane (>98.0%, Alfa Aesar), deuterium oxide (>99.0%, Cambridge Isotope Laboratories), sodium deuteroxide solution 40 wt. % in D₂O (>99.0%, Acros Organics), potassium iodide (>99.0%, Fisher Scientific), sodium bisulfite

(98.5%, Fisher Scientific) and sodium nitrite (>99.0%, J.T.Baker) were used as purchased without further purification. All measurements, unless noted otherwise, were carried out at 298 K and NMR chemical shifts were given in ppm. The ¹H NMR spectra were referenced to the residual ¹H residue in the deuterated solvent. All IR spectra were obtained using a Nicolet iS 5 FT-IR spectrometer equipped with a diamond ATR accessory.

S2 Synthesis

S2.1 Preparation of Iodo-Functionalized Linker.

All the ligands were synthesized using earlier reported procedures with some minor adaptations (Scheme S1).^{1–3}



Scheme S1. Multi-step synthesis of I-BPDC.

Dimethyl 2-nitro-[1,1'-biphenyl]-4,4'-dicarboxylate¹: (i) A cold solution of nitric acid (56%, 2.6 mL) and concentrated sulfuric acid (3.2 mL) was added dropwise to a solution of dimethyl [1,1'-biphenyl]-4,4'-dicarboxylate (5.00 g, 18.5 mmol) in 50 mL of concentrated sulfuric acid once solution is clear at 0 °C under intense stirring. The reaction mixture turned yellow while the temperature was maintained at 0 °C for 5 h. The solution was then poured onto crushed ice at which point a milky white solid precipitated. The solids were separated by filtration and washed with water. The solid was dissolved in hot isopropanol and the desired product was collected after recrystallization occurred at 40 °C (Yield: 4.9 g, 86%). ¹H NMR (DMSO-d₆, 400 MHz), δ : 3.89

(s, 3H), 3.94 (s, 3H), 7.56 (d, 2H, J = 8 Hz), 7.76 (d, 1H, J= 8 Hz), 8.05 (d, 2H, J= 8 Hz), 8.29 (dd, 1H, J= 4.0 Hz), 8.31 (d, J = 4.0 Hz, 1H), 8.50 (s, 1H). (Figure S1)



Figure S1.¹H NMR spectrum of 2-nitro-[1,1'-biphenyl]-4,4'-dicarboxylate in DMSO-d₆.

Dimethyl 2-amino-[1,1'-biphenyl]-4,4'-dicarboxylate³: (ii) To a solution of dimethyl 2-nitro-[1,1'-biphenyl]-4,4'-dicarboxylate (2.45g, 7.77 mmol) in methanol (100 mL), tin powder (5.53g, 46.6 mmol) was added in small portions. hydrochloric acid (1 M, 150 mL) was slowly added and the reaction mixture was heated under reflux condition for 2 h. The solution was then poured onto crushed ice at which point a yellowish solid precipitated upon addition of 1 M aq. NaOH. The product was extracted with warm ethyl acetate and was recrystallized from hot ethanol.

dried under reduced pressure (Yield: 1.64 g, 74%). ¹H NMR (DMSO-d₆, 400 MHz), δ: 3.85 (s, 3H), 3.89 (s, 3H), 7.27 (d, 1H, J=8 Hz), 7.43 (d, 1H, J=4 Hz), 7.45 (d, 1H, J=4 Hz), 7.63 (d, 2H, J=8 Hz), 8.05 (d, 2H, J=12 Hz). (Figure S3)



Figure S2. ¹H NMR spectrum for synthesized dimethyl 2-amino-[1,1'-biphenyl]-4,4'- dicarboxylate in DMSO-d₆.

Dimethyl 2-iodo-[1,1'-biphenyl]-4,4'-dicarboxylate¹: (iv) A solution of dimethyl 2-amino-[1,1'biphenyl]-4,4'-dicarboxylate (1.50 g, 5.3 mmol) in ultrapure water/HCl (100 mL, 1:1 v:v), was cooled to 0-5 °C. A cold solution of sodium nitrite (1.1 g, 15.9 mmol) in ultrapure water (5mL) was added dropwise to the suspension over 2 h. The reaction mixture was stirred at 0-5 °C for an additional 60 min and then poured into a solution of potassium iodide (8.34 g, 50.3 mmol) in ultra-pure water (10 mL). The color of the solution changed to dark brown and the reaction mixture was started to bubble. The reaction mixture was stirred at 60 °C for 24 h. Sodium hydrogen sulfite was added in portions to stirring reaction mixture until the dark color turned to light brown. The resulting solid was filtered and then dissolved in dichloromethane and washed with water. The aqueous phase was further extracted with water (2x). The organic phases were combined and dried over MgSO₄ before being taken to dryness to yield a brown crystalline solid. (Yield: 1.51 g, 72%). ¹H NMR (DMSO-d₆, 400 MHz), δ : 3.89 (s, 6H), 7.50 (d, 1H, J=8 Hz), 7.52 (d, 2H, J=8 Hz), 8.03 (d, 1H, J=8 Hz), 8.06 (d, 2H, J=8 Hz), 8.49 (s, 1H). (Figure S3)



Figure S3. ¹H NMR spectrum of dimethyl 2-iodo-[1,1'-biphenyl]-4,4'-dicarboxylate in DMSO-d₆. **2-iodo-[1,1'-biphenyl]-4,4'-dicarboxylic acid**²: (v) Dimethyl 2-iodo-[1,1'-biphenyl]-4,4'dicarboxylate (1.50 g, 3.79 mmol) was dissolve in 20 mL of tetrahydrofuran (THF). A solution of potassium hydroxide (0.22 g, 3.79 mmol) in 20 mL water was added and the reaction mixture was refluxed for 20 h. The THF was removed under reduced pressure and 6M HCl was added until the solution had a pH of 1. The solid was filtrated and washed with water and dried under vacuum (Yield: 1.3 g, 93%).¹H NMR (NaOD/ D₂O, 400 MHz), δ : 6.82 (d, 1H, J=8 Hz), 6.87 (d, 2H, J= 8 Hz), 7.35 (dd, 1H, J=8 Hz), 7.39 (d, 2H, J= 8 Hz), 7.89 (d, J= 2 Hz, 1H). ¹H NMR (DMSO-d₆, 400 MHz), δ :





Figure S4. ¹H NMR spectrum of 2-iodo-[1,1'-biphenyl]-4,4'-dicarboxylic acid in DMSO-d₆. S2.2 Synthesis of UiO-67 25%-I.

UiO-67 25%-I was prepared via solvothermal methods adapted from the previously reported method for UiO-67.^{4,5} Zirconium tetrachloride (0.46 g, 2.0 mmol) was added to (60 mL) DMF. The mixture of [1,1'-biphenyl]-4,4'-dicarboxylic acid (0.364 g, 1.50 mmol) and 2-iodo-[1,1'-biphenyl]-4,4'-dicarboxylic acid (0.364 g, 1.50 mmol) and 2-iodo-[1,1'-biphenyl]-4,4'-dicarboxylic acid (0.184 g, 0.500 mmol) were dissolved in DMF (10 mL) with a small amount of ultrapure water (0.050 mL, 2.8 mmol) and this was added to the first solution. The reaction S10

mixture was heated in a round bottom flask fitted with a condenser at 95 °C for 100 h to yield a light brown solid as UiO-67 25%-I MOFs. The solid was washed with hot DMF (x3) and soaked in hot methanol (x1) overnight prior to being heated at 160 °C for 24 hours under vacuum. (Yield: 0.63 g)

S2.3 Synthesis of UiO-67 100%-I.

UiO-67 100%-I was prepared via solvothermal methods adapted from the previously reported method for UiO-67.^{4,5}. Zirconium tetrachloride (0.067 g, 0.28 mmol) was added in an 8-dram vial. A solution of hydrochloric acid (12 M, 0.5 mL) in (5 mL) DMF was added to the vial containing Zirconium tetrachloride. 2-iodo-[1,1'-biphenyl]-4,4'-dicarboxylic acid (0.136 g, 0.37 mmol) were dissolved in (10 mL) DMF and this was added to the first solution. The reaction mixture was placed pre-heated oven at 80 °C for 18 h to yield a brown solid as UiO-67 100%-I MOFs. The solid was washed with hot DMF (x3) and soaked in hot methanol (x1) overnight prior to being heated at 160 °C for 24 hours under vacuum. (Yield: 0.22 g)

S2.4 Synthesis of DUT-5 25%-I.

The DUT-5 25%-I framework was prepared by adapting the reported procedure for DUT-5.^{6,7} Preparation of DUT-5 25%-I was carried out under solvothermal conditions in a 100 mL round bottom flask using aluminum chloride hexahydrate (0.51 g, 2.1 mmol), [1,1'-biphenyl]-4,4'- dicarboxylic acid (0.294 g, 1.2 mmol), 2-iodo-[1,1'-biphenyl]-4,4'-dicarboxylic acid (0.149 g, 0.4 mmol), and (75 mL) DMF. The chloride salt was chosen as the nitrate salt used in the original procedure led to oxidation of the iodine-functionalized linker. The flask was fitted with a condenser and heated at 120 °C for 24 h. The as-synthesized MOF, DUT-5 25%-I (as), was

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obtained after filtering and washing with hot DMF. To empty the pores of residual materials, the as-synthesized MOF was washed with DMF (x3) and soaked for overnight in hot methanol (x1) prior to being heated at 160 °C for 24 hours under vacuum. (Yield: 0.51 g)

S2.5 Synthesis of DUT-5 100%-I.

The DUT-5 100%-I framework was prepared by adapting the reported procedure for DUT-5.^{6,7} Preparation of DUT-5 25%-I was carried out under solvothermal conditions in a 100 mL round bottom flask using aluminum chloride hexahydrate (0.51 g, 2.1 mmol), 2-iodo-[1,1'-biphenyl]-4,4'-dicarboxylic acid (0.779 g, 1.6 mmol), and (75 mL) DMF. The flask was fitted with a condenser and heated at 120 °C for 24 h. The as-synthesized MOF, DUT-5 100%-I (as), was obtained after filtering and washing with hot DMF. To empty the pores of residual materials, the as-synthesized MOF was washed with DMF (x3) and soaked for overnight in hot methanol (x1) prior to being heated at 160 °C for 24 hours under vacuum. (Yield: 0.63 g)

S3 Crystallography

S3.1 Powder X-ray Diffraction

The diffraction patterns were collected on a Rigaku Ultima III powder diffractometer. X-ray diffraction patterns were obtained by using 2θ - θ scans with a range of 5-30°, step size = 0.05°, and scan time of 1 second/step. The X-ray source was Cu K α radiation (λ =1.5418 Å) with an anode voltage of 40 kV and a current of 44 mA. The beam was then discriminated by Rigaku's Cross Beam optics to create a monochromatic parallel beam. Diffraction intensities were recorded on a scintillation detector after being filtered through a Ge monochromator. Powder mounts were prepared by packing the powder into a well on a glass slide.

S4 Characterization

S4.1 NMR Digestions

NMR digestions were performed on the MOFs to establish the ratio that the different ligands were incorporated and to ensure that no ligand decomposition had taken place. Digested solutions of UiO-67 25%-I and DUT-5 25%-I were prepared by soaking 5-10 mg of MOF in 570 μ L D₂O and 200 μ L of NaOD solution (40 wt. % in D₂O) for 18 h followed by sonication for 2 h. The solutions were then filtered to remove the inorganic salts (Figure S5) and the resulting clear solutions were analyzed by ¹H NMR (Figure S6-7).



Figure S5. Di-ATR FTIR of activated UiO-67 25%-I before (black) and after (blue) digestion.

Spectra are plotted as attenuation.



Figure S6. ¹H NMR spectrum for digested DUT-5 25%-I in 570 μ L D₂O and 200 μ L of NaOD solution 40 wt. % in D₂O. (A: D₂BPDC, B: D₂IBPDC)

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Figure S7. ¹H NMR spectrum for digested UiO-67 25%-I in 570 μ L D₂O and 200 μ L of NaOD solution 40 wt. % in D₂O. (A: BPDC⁻², B: IBPDC⁻²)

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S4.2 Nitrogen Adsorption

Nitrogen sorption measurements were performed at 77 K on a Quantichrome Autosorb iQ (ASiQ) gas sorption analyzer. Approximately 20 mg of the MOFs were added to a preweighed 6 mm sample cell. All samples were activated under vacuum at 200 °C for ~10 hours. The sample weight was then collected. The surface areas, pore volumes and pore size were calculated using the DFT method in the Quantachrome ASiQwin software. The NLDFT equilibrium (cylinder/slit) model was chosen for the pore volume measurements.



Figure S8. Pore size distribution of DUT-5 25%-I (top) and UiO-67 25%-I (bottom) (77 K) S16

S5 Catalytic Experiments

S5.1 Typical Catalytic Reaction Procedure

In a typical catalytic reaction, the catalyst (20 mol%), co-oxidant (0.579 mmol, 0.0999), and substrate (0.145 mmol, 0.0160 g) were mixed in the specified solvent or solvent mixture (4.0 mL) along with the internal standard (methylsulfonylmethane) in a 2-dram clear glass vial. The vial was charged with a Teflon coated stir bar and placed on a hot plate preheated to 50 °C. After the specified time had been reached, the catalyst was separated by centrifugation, the liquid was decanted and 3 drops were taken for analysis. The collected sample was dissolved in the DMSO- d_6 to determine the catalytic conversion and yield via integration of the relevant peaks in the ¹H NMR spectrum (see Figures S10 and S11). All control reactions were done in the absence of MOF.



Figure S9. Observed products in the catalytic oxidation reaction of hydroquinone.



Figure S10. Representative ¹H NMR of hydroquinone in acetonitrile reaction mixture in DMSO-d₆ with MSM as internal standard for analysis of product distribution.



Figure S11. Zoom in of representative ${}^{1}H$ NMR of hydroquinone reaction mixture with products of over oxidation in DMSO-d₆ with MSM as internal standard.

S5.2 Results of All Catalytic Experiments

Table S1. The results of catalytic oxidation of hydroquinone (HQ) to benzoquinone (BQ) for UiO-67 0%-I, and DUT-5 0%-I, UiO-67 25%-I, DUT-5 25%-I and control in the presence of 20 mol% catalyst, 2.9 equivalent meta-chloroperbenzoic acid (mCPBA), 4 mL nitromethane at 50 °C for 60 minutes.

Sample	Time (min)	Solvent	Normalized integrated intensity of MSM	Normalized integrated intensity of HQ	Normalized integrated intensity of BQ	Normalized integrated intensity of products 3 and 4	Total normalized integrated intensity of reactants and products	Yield (%)	Conversion (%)
Control			1.00	0.85	0.08	0.06	0.99	8	15
UiO-67 0%-I			1.00	0.84	0.08	0.07	0.99	8	16
DUT-5 0%-I	60	NM	1.00	0.81	0.08	0.09	0.99	8	18
UiO-67 25%-I			1.00	0.12	0.84	0.03	0.99	83	86
DUT-5 25%-I			1.00	0.13	0.82	0.04	0.99	81	85

Sample	Temp. (°C)	Solvent	Normalized integrated intensity of MSM	Normalized integrated intensity of HQ	Normalized integrated intensity of BQ	Normalized integrated intensity of products 3 and 4	Total normalized integrated intensity of reactants and products	Yield (%)	Conversion (%)
Control			1.00	0.93	0.03	0.03	0.99	3	7
DUT-5 25%-I	24		1.00	0.72	0.22	0.06	1.00	22	28
UiO-67 25%-I			1.00	0.49	0.36	0.15	1.00	36	51
Control		INIVI	1.00	0.85	0.08	0.06	0.99	8	15
DUT-5 25%-I	50		1.00	0.13	0.82	0.04	0.99	81	85
UiO-67 25%-I			1.00	0.12	0.84	0.03	0.99	83	86

Table S2. Catalytic oxidation of hydroquinone (HQ) to benzoquinone (BQ) in the presence of 20 mol% UiO-67 25%-I and DUT-5 25%-I, 2.9 equivalent meta-chloroperbenzoic acid (mCPBA) at 50 $^{\circ}$ C and room temperature in 4 mL nitromethane for 60 minutes.

Sample	Time (min)	Solvent	Normalized integrated intensity of MSM	Normalized integrated intensity of HQ	Normalized integrated intensity of BQ	Normalized integrated intensity of products 3 and 4	Total normalized integrated intensity of reactants and products	Yield (%)	Conversion (%)
Control			1.00	1.00	0.00	0.00	1.00	0	0
UiO-67 25%-I	10		1.00	0.86	0.14	0.00	1.00	14	14
Control		E+OU	1.00	1.00	0.00	0.00	1.00	0	0
UiO-67 25%-I	20	ELUH	1.00	0.83	0.16	0.00	0.99	16	17
Control			1.00	1.00	0.94	0.06	1.00	6	6
UiO-67 25%-I	60		1.00	0.81	0.18	0.00	0.99	18	19
Control			1.00	0.90	0.10	0.00	1.00	10	10
UiO-67 25%-I	10		1.00	0.38	0.61	0.00	0.99	61	62
Control			1.00	0.85	0.14	0.00	0.99	14	15
UiO-67 25%-I	20	TFE	1.00	0.37	0.61	0.00	0.98	62	63
Control			1.00	0.72	0.28	0.00	1.00	28	28
UiO-67 25%-I	60		1.00	0.32	0.68	0.00	1.00	68	68

Table S3. Effect of 2,2,2-Trifluoroethanol (TFE) on catalytic oxidation of hydroquinone (HQ) to benzoquinone (BQ) in the presence of 20 mol% UiO-67 25%-I, 2.9 equivalent meta-chloroperbenzoic acid (mCPBA), 4 mL specified solvent at 50 °C for 60 minutes.

Table S4. Catalyst mol% variation for catalytic oxidation of hydroquinone (HQ) to benzoquinone (BQ) using 2.9 equivalent mCPBA in 4 mL nitromethane at 50 °C for 60 minutes.

Sample	Catalyst (mol %) based on I	Normalized integrated intensity of MSM	Normalized integrated intensity of HQ	Normalized integrated intensity of BQ	Normalized integrated intensity of products 3 and 4	Total normalized integrated intensity of reactants and products	Yield (%)	Conversion (%)
Control	0	1.00	0.85	0.08	0.06	0.99	8	15
	20	1.00	0.12	0.84	0.03	0.99	83	86
UiO-67 25%-I	10	1.00	0.12	0.84	0.03	0.99	83	86
	5	1.00	0.40	0.58	0.00	0.98	58	60
	20	1.00	0.13	0.82	0.04	0.99	81	85
DUT-5 25%-I	10	1.00	0.31	0.58	0.11	1.00	58	69
	5	1.00	0.56	0.33	0.10	0.99	33	44

Table S5. Catalytic oxidation of hydroquinone (HQ) to benzoquinone (BQ) in the presence of 20 mol% UiO-67 25%-I, UiO-67 100%-I, DUT-5 25%-I, DUT-5 100%-I, and 2.9 equivalent meta-chloroperbenzoic acid (mCPBA) at 50 °C in 4 mL acetonitrile for 60 minutes.

Sample	Catalyst (mol %) based on I	Normalized integrated intensity of MSM	Normalized integrated intensity of HQ	Normalized integrated intensity of BQ	Normalized integrated intensity of products 3 and 4	Total normalized integrated intensity of reactants and products	Yield (%)	Conversion (%)
Control	0	1.00	0.99	0.00	0.00	0.99	0	0
UiO-67 25%-I		1.00	0.71	0.29	0.00	1.00	29	29
UiO-67 100%-I		1.00	0.83	0.17	0.00	1.00	17	17
DUT-5 25%-I	20	1.00	0.05	0.94	0.00	0.99	94	95
DUT-5 100%-I		1.00	0.11	0.87	0.00	0.98	87	89

Table S6. Catalytic oxidation of hydroquinone (HQ) to benzoquinone (BQ) in the presence of 20 mol% UiO-67 25%-I, UiO-67 100%-I, DUT-5 25%-I, DUT-5 100%-I, and 2.9 equivalent meta-chloroperbenzoic acid (mCPBA) at 50 °C in 4 mL nitromethane for 60 minutes.

Sample	Catalyst (mol %) based on I	Normalized integrated intensity of MSM	Normalized integrated intensity of HQ	Normalized integrated intensity of BQ	Normalized integrated intensity of products 3 and 4	Total normalized integrated intensity of reactants and products	Yield (%)	Conversion (%)
Control	0	1.00	0.85	0.08	0.06	0.99	8	15
UiO-67 100%-I	20	1.00	0.60	0.23	0.15	0.98	23	40
DUT-5 100%-I	20	1.00	0.12	0.70	0.17	0.99	71	86

Table S7. Catalytic oxidation of 2,5-di-tert-butylhydroquinone to the corresponding oxidation product in the presence of 20 mol% UiO-67 100%-I, DUT-5 100%-I, and 2.9 equivalent meta-chloroperbenzoic acid (mCPBA) at room temperature in 4 mL nitromethane for 60 minutes.

Sample	Catalyst (mol %) based on I	Normalized integrated intensity of MSM	Normalized integrated intensity of HQ	Normalized integrated intensity of BQ	Normalized integrated intensity of products 3 and 4	Total normalized integrated intensity of reactants and products	Yield (%)	Conversion (%)
Control	0	1.00	0.58	0.41	0.00	0.99	41	42
UiO-67 100%-I	20	1.00	0.40	0.48	0.12	1.00	48	68
DUT-5 100%-I	20	1.00	0.35	0.49	0.14	0.98	49	65



Figure S12. The size effect of substrate on the catalytic activity of UiO-67 100%-I and DUT-5 100%-I, in the presence of 20 mol% MOFs, and 2.9 equivalent meta-chloroperbenzoic acid (mCPBA) at room temperature in 4 mL nitromethane for 60 minutes.

Table S8. Control reactions for catalytic oxidation of hydroquinone (HQ) to benzoquinone (BQ) in the presence of 2.9 equivalent meta-chloroperbenzoic acid (mCPBA) at 50 °C in 4 mL solvent for 60 minutes.

Sample	Solvent	Normalized integrated intensity of MSM	Normalized integrated intensity of HQ	Normalized integrated intensity of BQ	Normalized integrated intensity of products 3 and 4	Total normalized integrated intensity of reactants and products	Yield (%)	Conversion (%)
NO MOF		1.00	0.85	0.08	0.06	0.99	8	15
UiO-67 0%-I	NM	1.00	0.84	0.08	0.07	0.99	8	16
DUT-5 0%-I		1.00	0.81	0.08	0.09	0.99	8	18
NO MOF		1.00	0.99	0.00	0.00	0.99	0	0
UiO-67 0%-I	ACN	1.00	0.99	0.00	0.00	0.99	0	0
DUT-5 0%-I		1.00	0.94	0.04	0.01	0.99	4	6

S5.3 Experimental procedure for recyclability test of multivariate MOFs.

The recyclability tests for UiO-67 25%-I and DUT-5 25%-I was performed in the presence of ~2.9 equiv. metachloroperbenzoic acid

(mCPBA) in 4 mL nitromethane (NM) at 50 °C for 60 minutes as shown in Table S4. After each run, the catalyst was separated using centrifugation and the liquid was decanted and 5 drops of liquid were dissolved in 0.5 mL DMSO-d₆ to determine the catalytic conversion and yield of catalytic conversion of hydroquinone (HQ) to benzoquinone (BQ). The leftover catalyst was washed three

times with nitromethane. A 1.00 mL solution containing MSM and HQ was added to the catalyst followed by 2.9 equivalent of metachloroperbenzoic acid (mCPBA), and 4 mL nitromethane (NM). The closed cap 2-dram clear glass vial was placed on the hot plate when the temperature was 50 °C for 60 minutes.

Table S9. The recyclability test for catalysts with 2.9 equivalent meta-chloroperbenzoic acid (mCPBA) in 4 mL nitromethane at 50 °C for 60 minutes.

Sample	Run	Normalized integrated intensity of MSM	Normalized integrated intensity of HQ	Normalized integrated intensity of BQ	Normalized integrated intensity of products 3 and 4	Total normalized integrated intensity of reactants and products	Yield (%)	Conversion (%)
Control	-	1.00	0.86	0.08	0.06	1.00	8	15
	1 st	1.00	0.12	0.84	0.03	0.99	83	86
	2 nd	1.00	0.14	0.75	0.11	1.00	75	86
UiO-67 25%-I	3 rd	1.00	0.14	0.76	0.10	1.00	76	86
	4 th	1.00	0.14	0.74	0.12	1.00	76	86
	1 st	1.00	0.13	0.82	0.04	0.99	81	85
	2 nd	1.00	0.15	0.81	0.00	0.96	80	85
DUT-5 25%-I	3 rd	1.00	0.16	0.81	0.00	0.97	80	84
	4 th	1.00	0.18	0.80	0.00	0.98	79	82



Figure S13. SEM analysis for UiO-67 25%-I before (a, b) and after the 4th run (c, d) of the catalytic oxidation of hydroquinone (HQ) to benzoquinone (BQ).

Substrate	Sample	Temp. (°C)	Normalized integrated intensity of MSM	Normalized integrated intensity of substrate	Normalized integrated intensity of desired product	Normalized integrated intensity of byproducts	Total normalized integrated intensity of reactants and products	Yield (%)	Conversion (%)
2.5	Control		1.00	0.94	0.05	0.00	0.99	5	6
2,5- dibromohydroguinono	DUT-5 25%-I	50	1.00	0.03	0.94	0.00	0.97	94	97
dibromonydroquinone	UiO-67 25%-I		1.00	0.16	0.82	0.02	1.00	82	84
	Control		1.00	0.75	0.07	0.18	1.00	7	25
ЭГ	DUT-5 25%-I		1.00	0.01	0.97	0.00	0.98	97	99
2, J- dichlorohydroguinone	UiO-67 25%-I	50	1.00	0.13	0.86	0.00	0.99	86	87
ultinoi onyul oquinone	MIL-53 25%-I		1.00	0.62	0.2	0.18	1.00	20	38
	UiO-66 25%-I		1.00	0.14	0.68	0.18	1.00	68	86
	Control		1.00	0.71	0.07	0.21	0.99	7	29
2-	DUT-5 25%-I		1.00	0.04	0.92	0.01	0.97	92	96
bromohydroquinone	UiO-67 25%-I	50	1.00	0.15	0.80	0.04	0.99	80	85
	MIL-53 25%-I		1.00	0.38	0.26	0.36	1.00	26	62
	UiO-66 25%-I		1.00	0.1	0.63	0.26	0.99	63	90
2 chlorobydroguinono	Control		1.00	0.75	0.24	0.00	0.99	24	25
2-chioronyuroquinone	DUT-5 25%-I	50	1.00	0.00	0.96	0.003	0.98	96	100
	UiO-67 25%-I		1.00	0.22	0.76	0.02	1.00	76	78
2 E di tort	Control		1.00	0.50	0.50	0.00	1.00	50	50
butylcatechol	DUT-5 25%-I	24	1.00	0.08	0.79	0.12	0.99	79	92
Julyicalection	UiO-67 25%-I		1.00	0.00	0.77	0.2	0.97	77	100
4-tert-butylcatechol	Control		1.00	0.80	0.04	0.14	0.98	5	20

Table S10. Catalytic oxidation of hydroquinone and catechol derivatives in the presence of 20 mol% UiO-67 25%-I and DUT-5 25%-I as catalysts, 2.9 equivalent meta-chloroperbenzoic acid (mCPBA), 4 mL nitromethane for 60 minutes.

	DUT-5 25%-I	24	1.00	0.08	0.62	0.27	0.97	63	92
	UiO-67 25%-I		1.00	0.09	0.9	0.00	0.99	90	91
2 E di tart	Control		1.00	0.58	0.41	0.00	0.99	41	42
Z,S-UI-LEIL-	DUT-5 25%-I	24	1.00	0.26	0.69	0.10	0.96	70	74
butyinyuroquinone	UiO-67 25%-I		1.00	0.27	0.64	0.08	0.99	65	73
Teat	Control		1.00	0.68	0.3	0.00	0.98	31	32
Tert-	DUT-5 25%-I	24	1.00	0.53	0.39	0.06	0.98	39	47
butyinyuroquinone	UiO-67 25%-I		1.00	0.51	0.42	0.06	0.99	42	49
	Control		1.00	0.72	0.21	0.06	0.99	21	28
4-methylcatechol	DUT-5 25%-I	24	1.00	0.34	0.46	0.19	0.99	47	66
	UiO-67 25%-I		1.00	0.13	0.62	0.25	1.00	62	87
	Control		1.00	0.69	0.3	0.00	0.99	29	31
Methylhydroquinone	Control DUT-5 25%-I	24	1.00 1.00	0.69 0.42	0.3 0.49	0.00 0.10	0.99 0.92	29 50	31 58
Methylhydroquinone	Control DUT-5 25%-I UiO-67 25%-I	24	1.00 1.00 1.00	0.69 0.42 0.40	0.3 0.49 0.54	0.00 0.10 0.06	0.99 0.92 1.00	29 50 54	31 58 60
Methylhydroquinone	Control DUT-5 25%-I UiO-67 25%-I Control	24	1.00 1.00 1.00 1.00	0.69 0.42 0.40 0.85	0.3 0.49 0.54 0.00	0.00 0.10 0.06 0.15	0.99 0.92 1.00 0.98	29 50 54 0	31 58 60 16
Methylhydroquinone	Control DUT-5 25%-I UiO-67 25%-I Control DUT-5 25%-I	24 24	1.00 1.00 1.00 1.00 1.00	0.69 0.42 0.40 0.85 0.71	0.3 0.49 0.54 0.00 0.12	0.00 0.10 0.06 0.15 0.14	0.99 0.92 1.00 0.98 0.97	29 50 54 0 13	31 58 60 16 29
Methylhydroquinone	Control DUT-5 25%-I UiO-67 25%-I Control DUT-5 25%-I UiO-67 25%-I	24 24	1.00 1.00 1.00 1.00 1.00 1.00	0.69 0.42 0.40 0.85 0.71 0.32	0.3 0.49 0.54 0.00 0.12 0.48	0.00 0.10 0.06 0.15 0.14 0.19	0.99 0.92 1.00 0.98 0.97 0.99	29 50 54 0 13 48	31 58 60 16 29 68
Methylhydroquinone Catechol	Control DUT-5 25%-I UiO-67 25%-I Control DUT-5 25%-I UiO-67 25%-I Control	24 24	1.00 1.00 1.00 1.00 1.00 1.00 1.00	0.69 0.42 0.40 0.85 0.71 0.32 0.88	0.3 0.49 0.54 0.00 0.12 0.48 0.00	0.00 0.10 0.06 0.15 0.14 0.19 0.12	0.99 0.92 1.00 0.98 0.97 0.99 1.00	29 50 54 0 13 48 0	31 58 60 16 29 68 12
Methylhydroquinone Catechol	Control DUT-5 25%-I UiO-67 25%-I DUT-5 25%-I UiO-67 25%-I UiO-67 25%-I DUT-5 25%-I	24 24	1.00 1.00 1.00 1.00 1.00 1.00 1.00 1.00 1.00 1.00	0.69 0.42 0.40 0.85 0.71 0.32 0.88 0.32	0.3 0.49 0.54 0.00 0.12 0.48 0.00 0.41	0.00 0.10 0.06 0.15 0.14 0.19 0.12 0.26	0.99 0.92 1.00 0.98 0.97 0.99 1.00 0.99	29 50 54 0 13 48 0 42	31 58 60 16 29 68 12 68
Methylhydroquinone Catechol	Control DUT-5 25%-I UiO-67 25%-I DUT-5 25%-I UiO-67 25%-I DUT-5 25%-I DUT-5 25%-I UiO-67 25%-I	24 24 50	1.00 1.00 1.00 1.00 1.00 1.00 1.00 1.00 1.00 1.00 1.00	0.69 0.42 0.40 0.85 0.71 0.32 0.88 0.32 0.12	0.3 0.49 0.54 0.00 0.12 0.48 0.00 0.41 0.56	0.00 0.10 0.06 0.15 0.14 0.19 0.12 0.26 0.31	0.99 0.92 1.00 0.98 0.97 0.99 1.00 0.99 0.99	29 50 54 0 13 48 0 42 56	31 58 60 16 29 68 12 68 88
Methylhydroquinone Catechol	Control DUT-5 25%-I UiO-67 25%-I DUT-5 25%-I UiO-67 25%-I DUT-5 25%-I UiO-67 25%-I UiO-67 25%-I MIL-53 25%-I	24 24 50	1.00 1.00 1.00 1.00 1.00 1.00 1.00 1.00 1.00 1.00 1.00 1.00 1.00 1.00	0.69 0.42 0.40 0.85 0.71 0.32 0.88 0.32 0.12 0.86	0.3 0.49 0.54 0.00 0.12 0.48 0.00 0.41 0.56 0.6	0.00 0.10 0.06 0.15 0.14 0.19 0.12 0.26 0.31 0.06	0.99 0.92 1.00 0.98 0.97 0.99 1.00 0.99 0.99 0.99	29 50 54 0 13 48 0 42 56 6	31 58 60 16 29 68 12 68 88 88 13

S5.4 Split test for multivariate MOFs.

In order to study of any possible leaching of incorporated linkers in the MOFs during catalytic oxidation reaction of hydroquinone to benzoquinone split test was done with 1 equivalent methylsulfonylmethane (MSM) as internal standard, 1 equivalent hydroquinone (HQ) as substrate, ~ 2.9 equivalent meta-chloroperbenzoic acid (mCPBA) as co-oxidant in 4 mL nitromethane (NM). The split test for UiO-67 25%-I and DUT-5 25%-I was done at 50 °C. For each catalyst, two reactions were running under the same condition simultaneously. After 30 minutes one of the reactions was interrupted and the catalyst was separated using centrifugation. The hot filtrate was immediately transferred to another vial and the reaction was then allowed to continue under the same conditions. After 60 minutes no significant yield and conversion change was observed following filtration. The observed catalytic yields and conversions are summarized in Table S6

Table S11. Split test of DUT-5 25%-I and UiO-67 25%-I, 2.9 equivalent meta-chloroperbenzoic acid (mCPBA) in 4 mL nitromethane at 50 °C at specified time of reactions.

Sample	Time (min)	Normalized integrated intensity of MSM	Normalized integrated intensity of HQ	Normalized integrated intensity of BQ	Normalized integrated intensity of products 3 and 4	Total normalized integrated intensity of reactants and products	Yield (%)	Conversion (%)
Control	10	1.00	0.91	0.06	0.03	1.00	6	9
	30	1.00	0.90	0.06	0.03	0.99	7	10
	60	1.00	0.86	0.08	0.06	1.00	8	15
DUT-5 25%-I	10	1.00	0.63	0.30	0.06	0.99	30	37
	30	1.00	0.53	0.47	0.00	1.00	47	47
Filtration was done after 30 minutes	60	1.00	0.44	0.47	0.08	0.99	47	56
DUT-5 25%-I	60	1.00	0.13	0.82	0.04	0.99	81	85
UiO-67 25%-I	10	1.00	0.59	0.37	0.00	0.97	38	41
	30	1.00	0.53	0.45	0.00	0.98	45	47
Filtration was done after 30 minutes	60	42.5	0.55	0.45	0.00	1.00	45	47
UiO-67 25%-I	60	1.00	0.12	0.84	0.03	0.99	83	86



Figure S14. Split test for catalysts UiO-67 25%-I (yellow) and DUT-5 25%-I (Red), filtered UiO-67 25%-I (dotted green) and DUT-5 25%-I (dotted blue) after 30 minutes.

S6 Cyclic Voltammetry

All CV measurements were performed at 298 K with a Pine Research WaveDriver 10 Potentiostat/Galvanostat. The cell contained a glassy carbon working electrode, a Pt wire auxiliary electrode, and a 0.5 mm diameter Ag wire as pseudo-reference electrode. All the potentials were measured in acetonitrile with 0.1 M Bu₄NBF₄. The potentials are reported relative to the Fc/Fc⁺redox couple.

S7 Computational Details and Results

Molecular Mechanics (MM) optimizations were performed on all substrates at the MM2 level of theory. These models were used to evaluate the minimum and maximum radii of the substrates. This analysis was performed by placing a dummy atom at the geometric center of the molecule and increasing its radius until it encompassed the van der Waals representation of the molecule in the Diamond 4 software package. These measurements are shown below in Figure S15. MOF apertures were

estimated by placing a dummy atom in the center of the aperture (structures obtained from experimental structure determinations) and increasing the radius of the atom until it could just fit in the aperture (Figure S16)



Figure S15. Estimated minimum and maximum radii of hydroquinone and catechol derivatives evaluated from MM2 minimized structures.



Figure S16. Estimated pore apertures for DUT-5 0%-I and UiO-67 0%-I (triangular pore).

Density functional theory (DFT) Calculations were performed using the ORCA 4.0 quantum chemistry program package from the development team at the Max Planck Institute for Bioinorganic Chemistry.⁸ The LDA and GGA functionals employed were those of Perdew and Wang (PW-LDA, PW91).⁹ In addition, all calculations were carried out using the Zero-Order Regular Approximation (ZORA).^{10,11} For geometry optimizations, frequencies, and thermochemistry the def2-TZVPP^{12,13} and SARC/J basis sets¹⁴ were used for hydrogen atoms and all other atoms respectively. Spin-restricted Kohn–Sham determinants¹⁵ were chosen to describe the closed shell wavefunctions, employing the RI approximation¹⁶ and the tight SCF convergence criteria provided by ORCA.

S7.1 Optimized Cartesian Coordinates and Energies of HOMOs.

atom	х	У	Z
С	-0.67131	1.226773	0.110787
С	0.721598	1.211468	0.043066
С	1.409741	-0.00342	-0.12921
С	0.656886	-1.18802	-0.22921
С	-0.72811	-1.174	-0.18039
С	-1.40189	0.040172	-0.01054
Н	-1.19693	2.16584	0.257167
I	1.674224	3.080753	0.302326
С	2.89595	-0.08862	-0.26848

Table S12. DFT optimized cartesian coordinates for Me₂IBDC ($E_{HOMO} = -5.9928 \text{ eV}$).

Н	1.18887	-2.12742	-0.35705
Н	-1.30669	-2.09089	-0.26905
С	-2.89379	0.014233	0.042614
0	3.611464	0.771182	-0.7389
0	-3.56338	-0.99761	-0.04167
0	-3.42355	1.252982	0.196244
0	3.36096	-1.28498	0.179942
С	4.783545	-1.46743	0.029794
С	-4.86366	1.290543	0.25541
Н	4.995681	-2.45608	0.442882
Н	5.32777	-0.69142	0.579301
Н	5.066417	-1.41795	-1.02774
Н	-5.22609	0.702481	1.105896
Н	-5.29449	0.886594	-0.66747
Н	-5.12321	2.344835	0.374268

Table S13. DFT optimized cartesian coordinates for Me_2IBPDC ($E_{HOMO} = -6.0337 \text{ eV}$).

atom	х	У	Z
С	-2.82304	1.225915	0.378949
С	-1.4368	1.262487	0.245599
С	-0.67954	0.081448	0.137158
С	-1.38469	-1.13792	0.149533
С	-2.76425	-1.18832	0.283318
С	-3.49492	-0.00167	0.405601
Н	-3.39059	2.148886	0.453695
I	-0.54875	3.183295	0.102359
Н	-0.81314	-2.06207	0.074325
Н	-3.29577	-2.13746	0.301427
С	-4.97509	-0.09741	0.550112
0	-5.59752	-1.14269	0.562015
0	-5.56001	1.122135	0.669394
С	-6.99378	1.091452	0.810667
Н	-7.27888	0.525281	1.704437
Н	-7.45534	0.62515	-0.06699
Н	-7.30055	2.13604	0.899489
С	0.796806	0.035506	0.009668
С	1.383472	-0.63546	-1.07436
С	2.766653	-0.72763	-1.19282
С	3.594438	-0.16091	-0.2153
С	3.014378	0.497361	0.877204
С	1.633503	0.598855	0.986142
Н	0.74429	-1.07312	-1.84031
Н	3.210515	-1.23826	-2.0438

С	5.081019	-0.22929	-0.27826
Н	3.668789	0.921761	1.636163
Н	1.194331	1.10369	1.844454
0	5.824326	0.24412	0.560235
0	5.507498	-0.88802	-1.39196
С	6.931585	-1.01788	-1.5651
Н	7.205228	-0.51098	-2.49694
Н	7.161322	-2.08582	-1.645
Н	7.459724	-0.57318	-0.71655

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