[Electronic Supporting Information to accompany]

A catalytically active vanadyl(catecholate)-decorated metal organic framework via post-synthesis modifications

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S1. Materials and Methods

O,*O*'-Di(*tert*-butyl-dimethylsilyl)dopamine was synthesized according to literature protocol.[S1] Unless otherwise stated, all reagents were used as received. Terephthalic acid, $Cr(NO_3)_3 \cdot 9H_2O$, aqueous HF (48 wt%), potassium ferricyanide (III), *tert*-butyldimethylsilyl chloride, imidazole, vanadyl acetylacetonate, naphthalene, thioanisole, *tert*-butyl hydroperoxide (5-6 M in nonane), aqueous hydrogen peroxide (30 wt%), 2-(methylthio)ethylamine, and NaH were purchased from Sigma-Aldrich (Milwaukee, WI). Dopamine·HCl and ammonium fluoride were purchased from Alfa Aesar. Ferric chloride and ethanol (absolute) were purchased from Mallinckrodt. Concentrated sulfuric acid was purchased from VWR. Chromium ICP standard was purchased from Ultra Scientific. Vanadium and silicon ICP standards were purchased from Fluka Analytical. Sulfur ICP standard was purchased from Ricca Chemicals Co. (Arlington, TX).

Ultrapure deionized water (18.2 MΩ•cm resistivity) was obtained from a Millipore Milli-Q Biocel A10 instrument (Millipore Inc., Billerica, MA). Solvents were purchased from either Sigma-Aldrich or Fisher Scientific. Dry solvents were prepared by passing HPLC-grade solvents through a Dow-Grubbs solvent system installed by Glass Contours (now SG Water USA, Nashua, NH). All dry solvents were collected under inert gases, degassed under vacuum, and stored under nitrogen in a Strauss flask prior to use.

Centrifugation was carried out in an Eppendorf Centrifuge 5804 R, Model AG 22331 (Hamburg, Germany) equipped with an F34-6-68 rotor. Unless otherwise stated, all centrifugations were carried out at 5200 rcf for 20 minutes.

Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku X-ray Diffractometer Model ATX-G (Tokyo, Japan) equipped with an 18 kW Cu rotating anode, MLO monochromator, and a high-count rate scintillation detector. Measurements were made over a range of $1° < 2\theta < 20°$ in 0.05° step width with a 2 deg/min scanning speed.

N_2 adsorption and desorption isotherm measurements were performed on a Micromeritics Tristar II 3020 (Micromeretics, Norcross, GA) at 77K. Before each run, samples were activated at 150 °C for 24 h under high vacuum on a MasterPrep (Quantachrome Instruments, Boynton Beach, FL). Between 30-60 mg of samples was used in each measurement. Data were analyzed using the ASAP 2020 software (Micromeretics, Norcross, GA). Brunauer-Emmet-Teller (BET) surface areas for N_2 isotherms were calculated in the range of $0.02 < P/P_0 < 0.2$. All the gases used for the adsorption and desorption measurements were Ultra High Purity Grade 5 and were obtained from Airgas Specialty Gases (Chicago, IL).

TGA experiments were performed on a Mettler Toledo TGA/DSC 1 Star^e System (Schwerzenbach, Switzerland) interfaced with a PC using Star^e software (version 9.10). Samples were placed in alumina pans and heated at a rate of 10 °C/min from 25-700°C under a nitrogen atmosphere.

In a typical Prussian Blue screening,[S2] MOF samples (~1 mg) were suspended in a solution of deionized water (460 μL), ferric chloride (20 μL, 1.5 x 10^{-2} M), and potassium ferricyanide (20 μL, 1.5 x10^{-2} M). The blank sample, free of MOF analyte, gave a yellow solution that turned green over time. Dopamine-modified samples turned blue instantaneously after suspension indicating the presence of catechol moieties which reduced Fe^{III} to Fe^{II} followed by subsequent binding of Fe^{II} to potassium ferricyanide to form the visible Prussian blue complex.

Fourier-transformed infrared (FTIR) spectroscopy was performed on a Thermo Nicolet Nexus 870 FTIR spectrometer (Thermo Scientific, Waltham, MA), using either KBr pellets or disposable polyethylene IR cards. Frequencies are given in reciprocal centimeters (cm^{-1}). The FTIR spectra were analyzed using EZ Omnic software (Thermo Scientific, Waltham, MA).

^{1}H and ^{13}C NMR spectra were recorded on a Bruker 500 FT-NMR spectrometer (499.773 MHz for ^{1}H, 125.669 MHz for ^{13}C). ^{1}H NMR data are reported as follows: chemical shift (multiplicity (b = broad singlet, s = singlet, d = doublet, dd = doublet of doublets, ddd = doublet of doublets of doublets, t = triplet, q = quartet, and m = multiplet), integration, and peak assignments, coupling constants). ^{1}H and ^{13}C chemical shifts are reported in ppm from TMS with the residual solvent resonances as internal standards.

Inductively coupled plasma optical-emission spectroscopy (ICP-OES) was conducted on a Varian Vista-MDX model ICP-OES spectrometer (Varian, Walnut Creek, CA) equipped with a CCD detector and argon plasma to cover the 175-to-785 nm spectral range. Samples (1-3 mg) were digested in 1 mL of a mixture of 3:1 v/v conc. H_2SO_4:H_2O_2 (30 wt% in H_2O) or 4:1 v/v conc. HNO_3:H_2O_2 (30 wt% in H_2O) (for S analysis) and heated in a Biotage (Uppsala, Sweden) SPX microwave reactor (software version 2.3, build 6250) at 180 °C (160 °C for S digestion) until the solution became clear. The acidic solution was diluted to 25 mL with ultrapure deionized H_2O and analyzed for Cr (205.506 and 206.158 nm), V (292.401 and 309.310 nm), Si (185.005 and 212.412 nm), and/or S (181.972 nm) content as compared to standard solutions.

Gas chromatography was performed on an Agilent Technologies 6890N Network GC system equipped with an FID detector and HP-5MS capillary column (30 m × 320 μm × 0.25 μm film thickness). Analysis parameters were as followed: initial temperature = 50 °C, initial time = 3 minutes, ramp = 10 °C/min, final temperature = 200 °C, final time = 10 minutes. Elution times (min) = 10.6 (sulfide); 12.4 (naphthalene); 14.6 (sulfoxide); 15.6 (sulfone). Sulfoxidation product concentration was calculated based on calibration curves using naphthalene as internal standard.

S2. Synthesis of small molecules, MIL-101 (Cr) and modified MIL-101 (Cr) materials

MIL-101 (Cr). MIL-101 (Cr) was synthesized using a modification of a reported procedure.[S3] Chromium nitrate nonahydrate (3 g, 7.50 mmol), terephthalic acid (1.25 g, 7.52 mmol), HF (48 wt%, 0.068 mL, 1.9 mmol), and H_2O (36 mL, 2 mol) were placed inside an 100-mL autoclave and sealed. The autoclave was heated at 220 °C in a safety (non-runaway) oven for 8 h before being slowly cooled to room temperature. The autoclave was unsealed and the reaction mixture was filtered through a coarse fritted funnel to removed unreacted, crystallized terephthalic acid. The filtrate was then centrifuged. After decanting the mother liquor, the leftover MIL-101 (Cr) was subjected to the following work-up steps:

1. The collected MIL-101 (Cr) pellet was resuspended in a mixture of 95:5 v/v of ethanol:water (~ 25 mL) and heated at 70 °C in a closed vessel for 24 h while stirring. The resulting suspension was removed from the heating bath and centrifuged before being decanted.
2. The collected MIL-101 (Cr) pellet was resuspended in 1 M *aqueous* NH_4F solution (25 mL) and heated at 70 °C in a closed vessel for 24 h while stirring. The resulting suspension was removed from the heating bath and centrifuged before being decanted.
3. The collected MIL-101 (Cr) pellet was resuspended in ultrapure deionized water (25 mL) and heated at 70 °C in a closed vessel for 24 h while stirring. The resulting suspension was removed from the heating bath and centrifuged before being decanted. This last wash was repeated once more before the solution was filtered through a fine-fritted funnel to give a bluish-green powder. Yield = ~ 50% based on Cr content, as determined by ICP-OES.

***O,O'*-di(*tert*-butyl-dimethylsilyl)dopamine or $(TBDMS)_2$dopamine (1)**. Compound **1** was synthesized according to a literature protocol.[S1] The product was isolated as an oil with ~ 10 wt% of unreacted TBDMS-Cl and solvent based on NMR analysis. This material was used in the next step without further purification. ^{1}H NMR (500 MHz, DMSO-d_6): δ 6.78 (d, 1H, J = 7.98 Hz, Ar), 6.70-6.66 (m, 2H, Ar), 2.74 (t, 2H, J = 7.28 Hz, CH_2NH_2), 2.56 (t, 2H, J = 7.28 Hz CH_2Ph), 0.97, 0.97 (2s, 18H, SiC(CH_3)$_3$), 0.19, 0.18 (2s, 12H, SiCH_3). ^{13}C NMR (125 MHz, DMSO-d_6): δ 145.81, 144.24, 135.65, 121.84, 121.34, 120.58 (C_{Ar}), 43.72 (CH_2NH_2), 38.81(CH_2Ph), 25.80, 25.80 (SiC(CH_3)$_3$), 18.19, 18.16 (SiC(CH$_3$)$_3$), -4.13, -4.17 ppm (SiCH_3).

Free-base dopamine (2). In a dry box, dopamine·HCl (2.5 g, 13.2 mmol) was dissolved in MeOH (20 mL) and THF (20 mL). NaH (316 mg, 13.2 mmol) was then added slowly. The reaction mixture was left to stir at room temperature for two days before being filtered through a fine-fritted funnel to remove unreacted starting materials and salts. The filtrate was dried under vacuum to give **2** as a white powder (2.01 g, 99% yield). ^{1}H NMR (500 MHz, DMSO-d_6): δ 6.63 (d, 1H, J = 7.94 Hz, Ar), 6.56 (d, 1H, J = 1.92 Hz, Ar), 6.42 (dd, 1H, J = 7.95, 1.89 Hz, Ar), 2.70 (t, 2H, J = 7.38 Hz, CH_2NH_2), 2.47 (t, 2H, J = 7.38 Hz CH_2Ph). ^{13}C NMR (125 MHz, DMSO-d_6): δ 145.08, 143.45, 130.59, 119.21, 116.03, 115.48 (C_{Ar}), 43.39 (CH_2NH_2), 38.22 ppm (CH_2Ph).

Dop-MIL-101 (Cr). MIL-101 (Cr) (100 mg) was dehydrated at 150 °C under vacuum for 24 h in a 6 dram vial and allowed to cool slowly to 50 °C. Free-base dopamine (**2**) (44.8 mg (0.292 mmol), where x = 2 equivalents per chromium cluster) was suspended in anhydrous THF (5 mL) and added to the dehydrated MIL-101 (Cr) and left to stir at 50 °C for 24 h. The reaction mixture was filtered over a fine-fritted funnel to remove unreacted **2**. The sample powder was washed twice in EtOH (10 mL) at 50 °C for 24 h and dried over vacuum filtration to give a brown powder that gave a positive Prussian blue test (Fig. S6).

$(TBDMS)_2$dop$_x$-MIL-101 (Cr). MIL-101 (Cr) (100 mg) was dehydrated at 150 °C under vacuum for 24 h in a 6 dram vial and allowed to cool slowly to 50 °C. $(TBDMS)_2$-dop **(1)** (27.9 mg (0.073 mmol), 55.8 mg (0.146 mmol), and 111 mg (0.292 mmol) for ½, 1, and 2 theoretical equivalents of **1** per chromium cluster, respectively) was dissolved in anhydrous THF (5 mL) and added to the dehydrated MIL-101 (Cr). The reaction mixture was allowed to stir at 50 °C for 24 h. The resulting material was collected over a fine-fritted funnel to remove unreacted **1**. The sample powder was washed twice in EtOH (10 mL) at 50 °C for 24 h and dried over vacuum filtration to give a brownish powder with a 0.05 $(TBDMS)_2$dop/Cr ratio (0.1 Si/Cr ratio) (based on ICP-OES).

V(dop)-MIL-101 (Cr). Dried dop$_x$-MIL-101 (Cr) (50 mg) was evacuated at 150 °C under vacuum for 24 h in a 6 dram vial and allowed to cool slowly to 50 °C. In a separate 6 dram vial, excess $VO(acac)_2$ (55 mg, 0.208 mmol, pre-dried under vacuum for 3 h at 150 °C and cooled to 50 °C) was dissolved in MeOH (8 mL) and added to dop$_x$-MIL-101 (Cr). The reaction mixture was left to stir at 50 °C for 24 h. The metallated dop-MIL-101 (Cr) was filtered over a fine-fritted funnel and washed twice in MeOH (10 mL) at 50 °C for 24 h remove unreacted $VO(acac)_2$. The sample was dried over vacuum filtration to give a dark-brown powder with a V/Cr metallation ratio = 0.13 ± 0.02 (based on ICP-OES)

V(deprot-$(TBDMS)_2$dop$_x$-MIL-101 (Cr). $(TBDMS)_2$dop$_x$-MIL-101 (Cr) (50 mg) was evacuated at 150 °C for 24 h and then cooled to 50 °C in a 6 dram vial. *In situ* deprotection was carried out by addition of excess NH_4F (0.12-1.2 mg, 2-20 ×, 3.2 μmol-0.32 mmol) dissolved in anhydrous MeOH (1 mL). Excess $VO(acac)_2$ (55.8 mg, 0.210 mmol), dried at 150 °C for 3 h, was dissolved in anhydrous MeOH (5 mL) and added to the MIL material. The reaction mixture was left to stir at 50 °C for 24 h. The metallated and deprotected MIL material was filtered over a fine-fritted funnel and washed twice in MeOH (10 mL) at 50 °C for 24 h to remove unreacted $VO(acac)_2$. The sample was dried over vacuum filtration to give a dark-brown powder with a V/Cr metallation ratio = 0.05(based on ICP-OES).

($MeSCH_2CH_2NH_2$)-$(TBDMS)_2$dop-MIL-101 (Cr). $(TBDMS)_2$dop-MIL-101 (Cr) (25 mg) was dehydrated at 150 °C for 24 h in a 6 dram vial. Excess 2-(methylthio)ethylamine (20 mg, 0.219 mmol) was dissolved in anhydrous THF (5 mL) and added to $(TBDMS)_2$dop$_x$-MIL-101 (Cr). The reaction mixture was left to stir at 45 °C for 24 h. The resulting material was collected over a fine-fritted funnel to remove unreacted 2-(methylthio)ethylamine. The sample powder was washed twice in EtOH (10 mL) at 45 °C for 24 h and dried over vacuum filtration to give a dark yellow-brownish powder with a thioamine/Cr loading ratio = 0.61 ± 0.05 (based on ICP-OES).

($MeSCH_2CH_2NH_2$)-dop-MIL-101 (Cr). Dop-MIL-101 (Cr) (100 mg) was dehydrated at 150 °C for 24 h in a 6 dram vial. Excess 2-(methylthio)ethylamine (80 mg, 0.876 mmol) was dissolved in anhydrous THF (10 mL) and added to dop-MIL-101 (Cr). The reaction mixture was left to stir at 45 °C for 24 h. The resulting material was collected over a fine-fritted funnel to remove unreacted 2-(methylthio)ethylamine. The sample powder was washed twice in EtOH (20 mL) at 45 °C for 24 h and dried over vacuum filtration to give a dark yellow-brownish powder with a thioamine/Cr loading ratio = 0.55 ± 0.02 (based on ICP-OES).

S3. Characterization of MIL-101 (Cr) and its derivatives

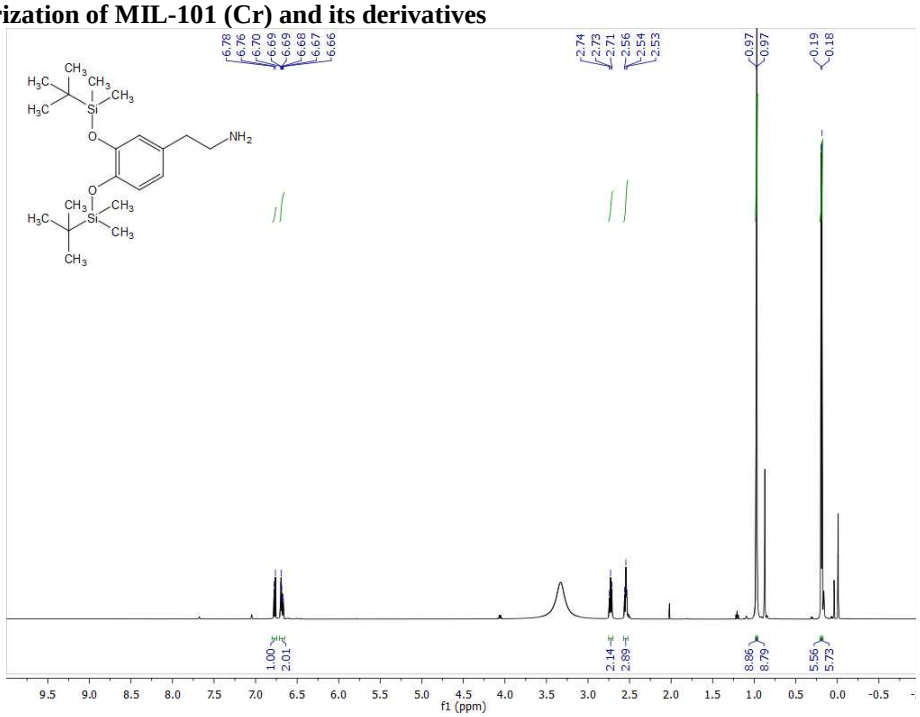

Fig. S1. ^{1}H NMR spectrum of $(TBDMS)_2$dopamine.

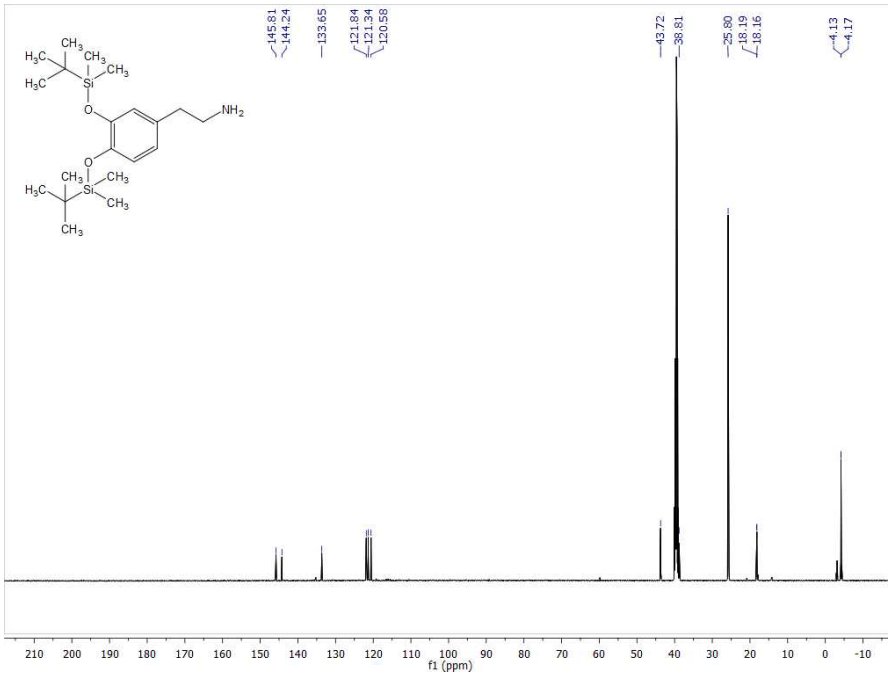

Fig. S2. ^{13}C NMR spectrum of $(TBDMS)_2$dopamine (**1**).

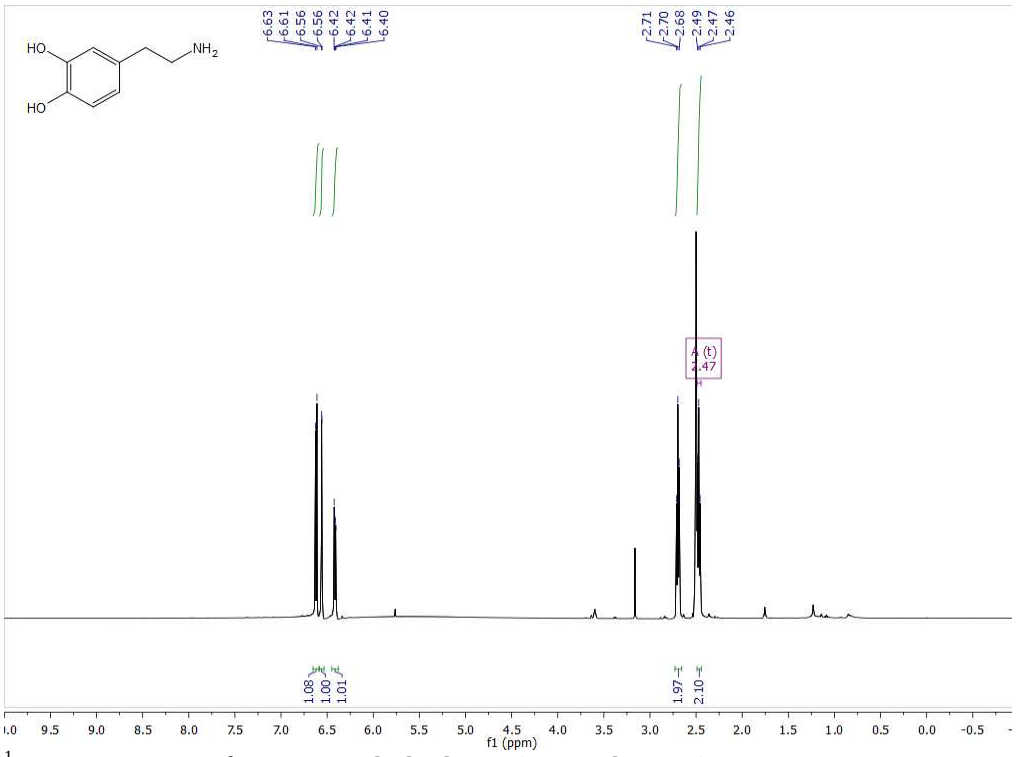

Fig. S3. ^{1}H NMR spectrum of **2**; some residual solvents (THF and MeOH) remain.

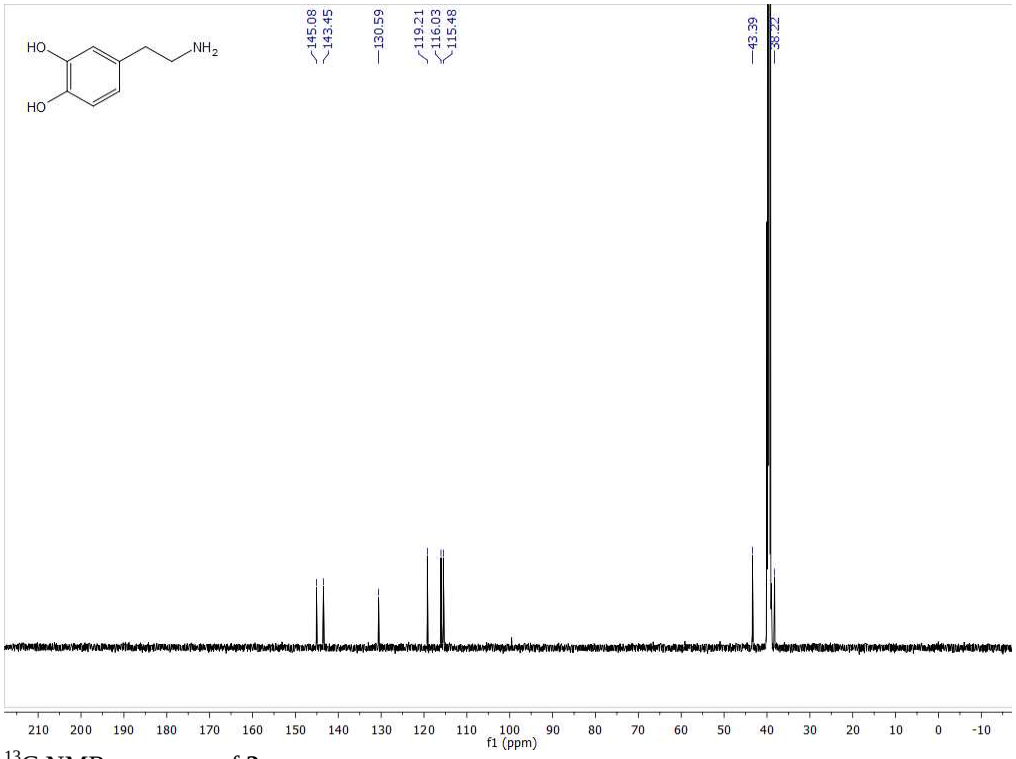

Fig. S4. ^{13}C NMR spectrum of **2**.

Table S1. Elemental analysis of dopamine-modified MIL-101 (Cr) materials.

sample	C(%)[a]	H(%)[a]	N(%)[a]	N/C ratio expected	N/C ratio experimental[c]
MIL-101 (Cr)	36.2	2.8	0.52[b]	0	0.014
$dop_{1/2}$-MIL-101 (Cr)	39.4	3.1	0.94	0.021	0.024
dop_1-MIL-101 (Cr)	39.5	4.0	1.11	0.036	0.028
dop_2-MIL-101 (Cr)	43.1	3.1	2.15	0.058	0.049

[a]All samples subjected to EA were evacuated at 150 °C for 12 h under vacuum. However, %C is much lower and %H is slightly higher than expected, indicating residual H_2O, NH_4F, or terephthalic acid may have remained, as has been observed by others.[S4] [b]The excess N content is attributed to contaminants from the NH_4F wash, which remained even after two additional water washes (see the MIL-101 (Cr) synthesis in section S2 above). While additional washes can potentially remove all N contaminants, we consider this adequate for the next step. [c]Although these numbers have not taken into account the background N content from the aqueous NH_4F wash, there is an increase of N content from the baseline N content for the starting MIL-101 (Cr).

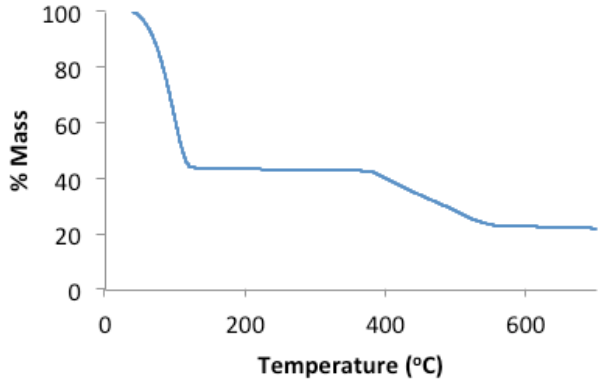

Fig. S5. TGA profile of as-synthesized MIL-101 (Cr) showing two weight-loss steps. The first is attributed to water from the MIL-101 (Cr) synthesis reaction mixture, and the second is due to decomposition of MIL-101 (Cr) at ~ 375 °C.

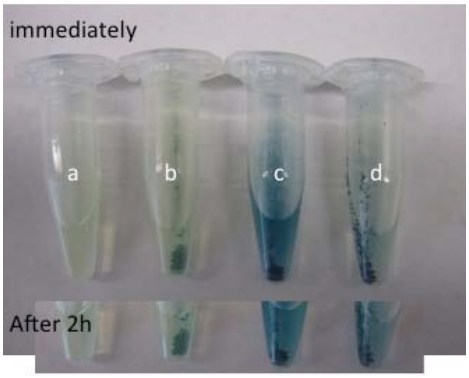

Fig. S6. Prussian-Blue test immediately and after 2 h for: (a) solution of $FeCl_3$ and $K_3[Fe^{III}(CN)_6]$ in water; (b) MIL-101 (Cr) suspended in a solution of $FeCl_3$ and $K_3[Fe^{III}(CN)_6]$ in water; (c) dop-MIL-101 (Cr) suspended in a solution of $FeCl_3$ and $K_3[Fe^{III}(CN)_6]$ in water; (d) V(dop)-MIL-101 (Cr) suspended in a solution of $FeCl_3$ and $K_3[Fe^{III}(CN)_6]$ in water. The blue color in (c) indicates the presence of oxidized catechol while the lack of blue color in (d) indicates no immediately oxidized catechol moieties. The slight light blue color in (d) after 2 h may indicate presence of non-metallated dopamine groups, which reside concealed inside MIL-101 (Cr) framework.

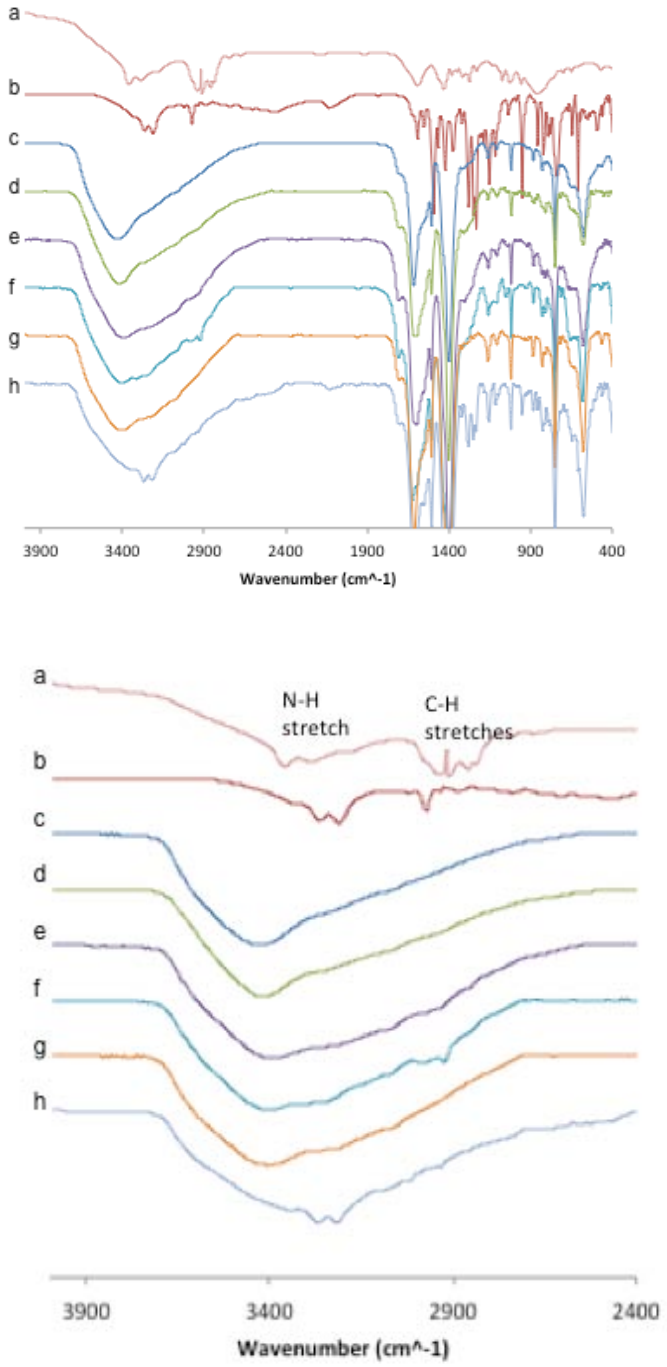

Fig. S7. The FTIR spectra of: a) 2-(methythio)ethylamine; b) free-base dopamine; c) MIL-101 (Cr); d) dop-MIL-101 (Cr); e) $(TBDMS)_2$dop-MIL-101 (Cr); f) $(MeSCH_2CH_2NH_2)$-$(TBDMS)_2$dop-MIL-101 (Cr); g) MIL-101 (Cr) mixed with ~ 13 % dopamine/Cr site; h) MIL-101 (Cr) mixed with ~66 % dopamine/Cr site. Except for spectrum a, which was obtained as a liquid film over a polyethylene insert, all spectra were obtained as KBr pellets. Top panel: full spectra. Bottom panel: Expanded region from 2000 to 4000 cm^{-1}. As discussed in footnote *b* of Table S1, MIL-101 (Cr) is likely to be contaminated with the NH_4F used in our purification. In addition, it has OH and H_2O moieties that are inherently coordinated to Cr sites. All three of these species can contribute to the broad peak at 3300-3700 cm^{-1} observed in the spectrum for unmodified MIL-101 (spectrum c). This broad peak would partially overlap over any

additional amine N-H stretches that come from dopamine and thioamine modifications and make it difficult to ascertain their existence. Although the doubly modified ($MeSCH_2CH_2NH_2$)-$(TBDMS)_2$dop-MIL-101 (Cr) sample (spectrum f) exhibited new stretches in the N-H stretching region that are somewhat distinguishable above this broad background, much less noticeable stretches were observed for dop-MIL-101 (Cr) (spectrum d) and $(TBDMS)_2$dop-MIL-101 (spectrum e), potentially due to the lower amine loadings for these samples. Finally, the FTIR spectra for the two physical mixtures of MIL-101 grounded with dopamine (spectra g and h) demonstrate that at low amine loadings (13 % dopamine/Cr) the N-H or C-H stretches from the amine ligands are barely noticeable, while comparable "quantitative" loading to that in a fully modified MIL-101 (66 % dopamine/Cr) only afford slightly more noticeable signals.

Table S2. Si/Cr ratio for several attempts to graft $(TBDMS)_2$dopamine onto MIL-101 (Cr).

$(TBDMS)_2$dopamine used (# equiv)	Expected Si/Cr ratio (%)	Observed Si/Cr ratio (%)
0.5	33	10.2 ± 1.2
1	67	10.1 ± 1.3
2	133	10.5 ± 2.0

Table S3. S/Cr ratio for ($MeSCH_2CH_2NH_2$)-$(TBDMS)_2$dop-MIL-101 (Cr) and ($MeSCH_2CH_2NH_2$)-dop-MIL-101 (Cr).

Sample	Expected S/Cr ratio (%)	Observed S/Cr ratio (%)
($MeSCH_2CH_2NH_2$)-$(TBDMS)_2$dop-MIL-101 (Cr)	62[a]	61 ± 5
($MeSCH_2CH_2NH_2$)-dop-MIL-101 (Cr)	≤ 54[b]	55 ± 2

[a]The maximum possible % modification is 67% ligand/Cr. The expected S/Cr ratio of 62% is determined based on the Si/Cr ratio of 10% (thus 5% dopamine) for the $(TBDMS)_2$dop-MIL-101 (Cr) sample, leaving a possible 62% of the Cr sites still available to support amine grafting. [b]Based on a 13% V/Cr metal loading for our V(dop)-MIL-101 (Cr) sample, we expected 54% or less of the Cr sites to be available for additional amine grafting.

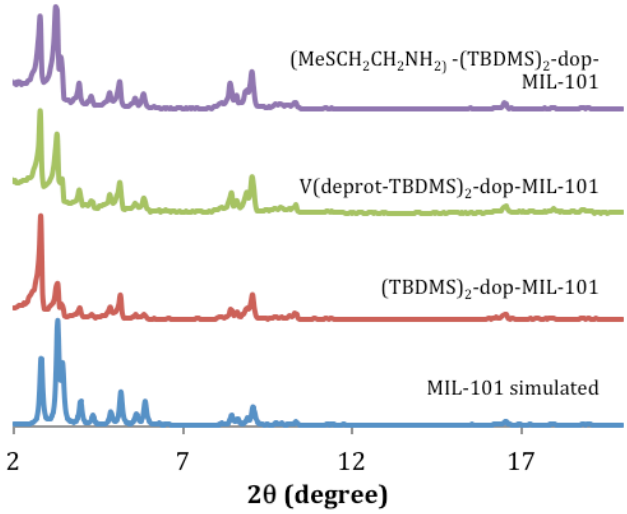

Fig. S8. Experimental PXRD patterns for: $(MeSCH_2CH_2NH_2)$-$(TBDMS)_2$dop-MIL-101 (top), V(deprot-$TBDMS)_2dop_x$-MIL-101 (top-middle), and $(TBDMS)_2dop_x$-MIL-101 (bottom-middle). The simulated PXRD pattern for MIL-101 (Cr) is shown at the bottom.

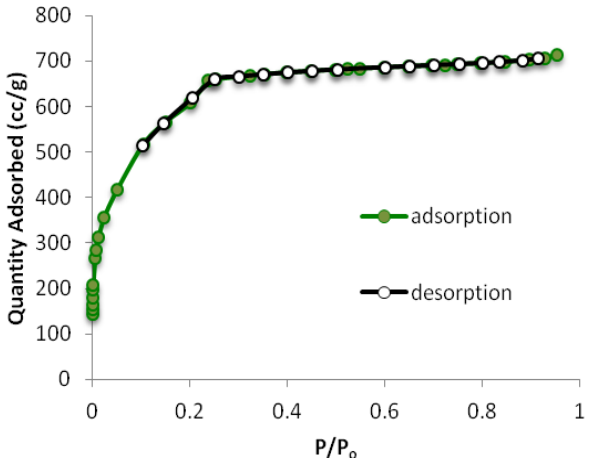

Fig. S9. Representative nitrogen isotherm at 77K for $(TBDMS)_2$dop-MIL-101 (Cr) (BET SA = 2200 ± 200 m^2/g). Closed symbols = adsorption; open symbols = desorption.

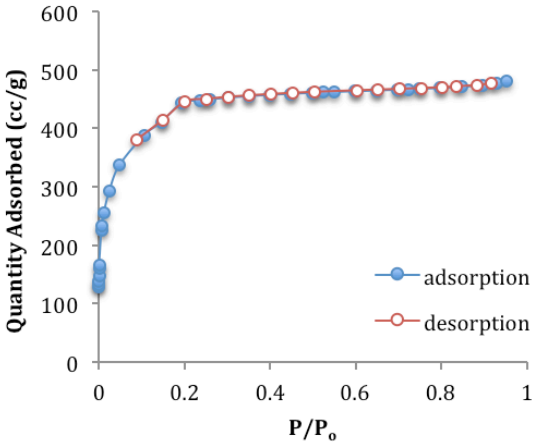

Fig. S10. Nitrogen isotherm at 77K for $(MeSCH_2CH_2NH_2)$-$(TBDMS)_2$dop-MIL-101 (Cr) (BET SA = 1600 m^2/g). Closed symbols = adsorption; open symbols = desorption.

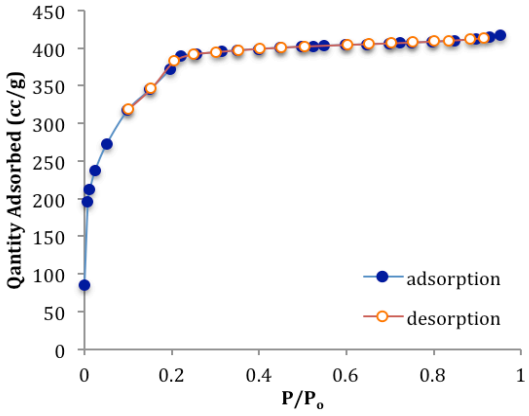

Fig. S11. Nitrogen isotherm at 77K for V(deprot-TBDMS)$_2$dop-MIL-101 (Cr) (BET SA = 1350 m^2/g). Closed symbols = adsorption; open symbols = desorption.

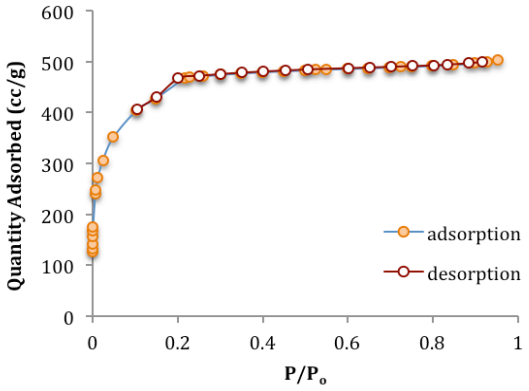

Fig. S12. Nitrogen isotherm at 77K for $(MeSCH_2CH_2NH_2)$-dop-MIL-101 (Cr) (BET SA = 1650 m^2/g). Closed symbols = adsorption; open symbols = desorption.

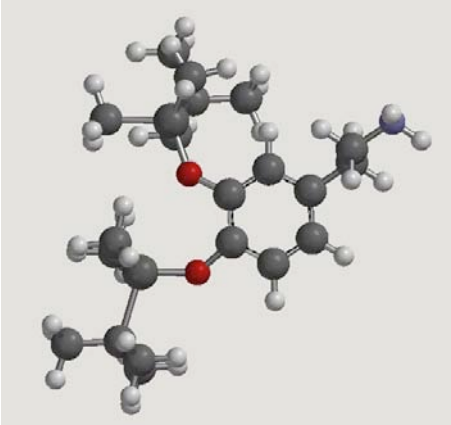

Fig. S13. Spartan modeling of $(TBDMS)_2$dopamine (**1**). Dimensions are estimated to be 12 × 12 Angstroms.

S4. Catalytic Reactions

Catalytic oxidation of thioanisole. In a 10 mL microwave vial, catalyst (either V(dop)-MIL-101 (Cr) (16.6 mg, 2.5 μmol V), $VO(acac)_2$ (0.66 mg, 2.5 μmol V), or control MIL-101 (Cr) (11.97 mg, 0 mmol V, 0.05 mmol Cr)), thioanisole (31.1 mg, 0.25 mmol), and naphthalene (25.6 mg, 0.2 mmol, as an internal standard) were mixed in anhydrous DCM (3 mL). *Tert*-butyl hydroperoxide (0.043 mL of a 5-6 M solution in nonane; a 6 M solution is assumed for TON calculation) was added dropwise and the reaction vial was left on a shaker (Thermolyne Maxi-mix III type 65800, set at speed 400) and analyzed over time (8 h) by gas chromatography by removing aliquots from the reaction mixture (~ 0.02 mL) using a syringe. Each aliquot is diluted with DCM to 1 mL in a GC vial before being analyzed.

Catalyst recycling. Before each recycling experiment, the used V(dop)-MIL-101 (Cr)catalyst was shaken up in anhydrous DCM (~ 3 mL) and let stand undisturbed for 1 h. The DCM was then gently removed via a syringe to leave the settled catalyst behind. This process was repeated a total of three times to remove all substrates. Then a new aliquot of substrates and oxidant (as shown above) could then be added to repeat the sulfoxidation.

Presoaking catalyst in oxidant. In a 10 mL microwave vial was placed V(dop)-MIL-101 (16.6 mg, 2.5 μmol V) and the vial was capped. Anhydrous DCM (1 mL) was added via a syringe, followed by *tert*-butyl hydroperoxide (0.043 mL of a 5-6 M solution in nonane; a 6 M solution is assumed for TON calculation). The vial was left on a shaker ((Thermolyne Maxi-mix III type 65800, set at speed 400) for 8 h. A solution of thioanisole (31.1 mg, 0.25 mmol) and naphthalene (25.6 mg, 0.2 mmol, as an internal standard) in anhydrous DCM (2 mL) was added. Sulfoxidation was analyzed over time (8 h) by gas chromatography by removing aliquots from the reaction mixture (~ 0.02 mL) using a syringe. Each aliquot is diluted with DCM to 1 mL in a GC vial before being analyzed.

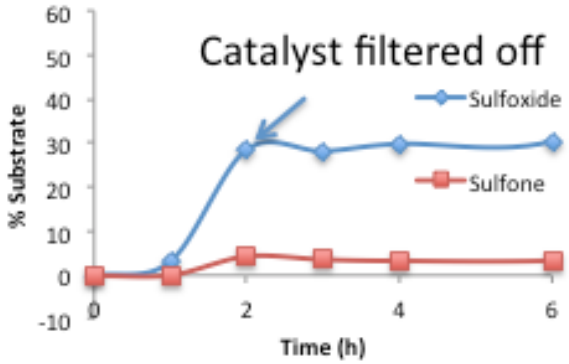

Fig. S14. Product formation profiles in the oxidation of thioanisole to sulfoxide and sulfone using V(dop)-MIL-101 (V/Cr = 15%) that was filtered off at time = 2h.

Author contributions. J.T.H. conceived the initial experiment. H.G.T.N. and M.H.W. carried out all the experiments and measurements. O.K.F., J.T.H., and S.T.N. supervised the project and provided guidance with control experiments. H.G.T.N. wrote the initial drafts of the paper. H.G.T.N, J.T.H., and S.T.N. finalized the manuscript.

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