

Supporting Information

Visible-light-mediated guest trapping in a photosensitizing porous coordination network: metal-free C-C bond-forming modification of metal-organic frameworks for aqueous-phase herbicide adsorption

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Experimental Section

Chemicals

Chromium nitrate nonahydrate [$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 99.95%], terephthalic acid, tin(II) chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$), hydrofluoric acid (HF), fluoroboric acid (HBF_4 , 48%), N-bromo succinimide (NBS) and sodium nitrite (NaNO_2) were purchased from Sigma-Aldrich Chemical Co., Ltd. Concentrated nitric acid (conc. HNO_3), concentrated sulfuric acid (conc. H_2SO_4), N,N-dimethyl formamide (DMF), trifluoroacetic acid (TFA), methanol (CH_3OH) and ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) were obtained from Sinopharm Chemical Reagent Co., Ltd. All other chemicals in this study were of analytical grade and utilized without further purification.

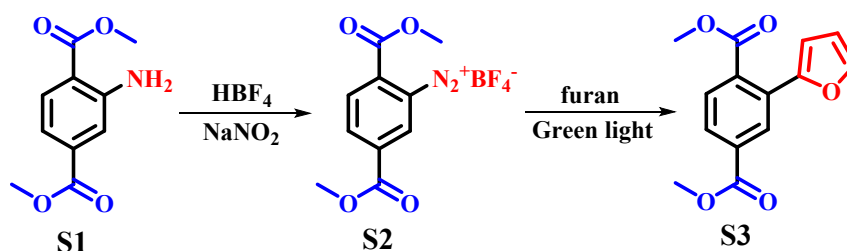
Characterization

Powder X-ray diffraction (PXRD) data were obtained at ambient temperature on a Brüker AXS D8 Advance X-ray diffractometer at 40 kV, 40 mA for Cu $K\alpha$ ($\lambda = 1.5418 \text{ \AA}$), with a scan speed of 1 s per step and a 2θ range of 5-50 °. Analyses of the morphology of the samples were conducted by using a Hitachi SU8010 scanning electron microscope (SEM). Transmission electron microscope (TEM) images of the materials were taken on a Hitachi H7650 instrument. Brunauer–Emmett–Teller (BET) surface areas were measured by using a Micromeritics ASAP 2020 analyzer at 77 K. The samples were outgassed at 100 °C for 24 h under vacuum prior to measurement. All infrared experiments were performed on a Brüker Alpha FT-IR spectrometer using 1 mg of the solid sample at 4 cm^{-1} resolution. Before measurement, the samples were dried under vacuum at 100 °C for 24 h. Thermogravimetric analysis (TGA) data were obtained using a PerkinElmer TGA 7 system running from 27 °C to 600 °C with a scan rate of 10 °C·min⁻¹. Mass spectra were recorded on an Esquire-LC-00075 mass spectrometer. High performance liquid chromatography (HPLC) analysis [Column: InertSustain^R C18;

Column temperature: 40 °C; Mobile phase: TFA (1%) -MeOH; Gradient: MeOH reached 20% after the injection and then reached 80% at 15 min; Flow rate: 1 mL·min⁻¹; Detection wavelength: 254 nm] was performed on a Shimadzu LC-20A instrument. ¹H NMR spectra were recorded on a Bruker DPX-500 spectrometer at 500 MHz with tetramethyl silane (TMS) as internal standard.

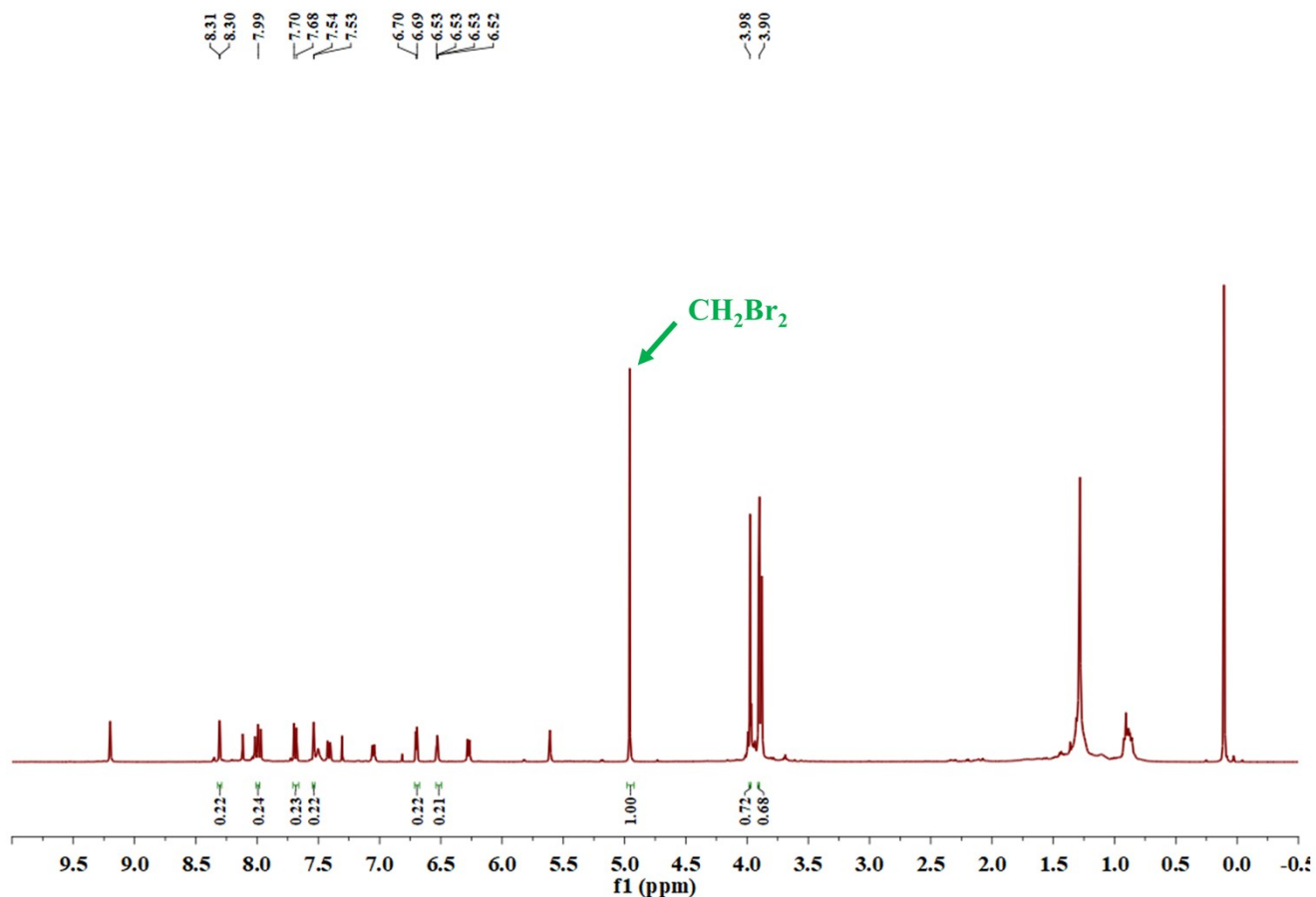
The samples were digested in 10 wt.% sodium hydroxide (NaOH) aqueous solution at 70 °C for MS and HPLC measurements. To obtain ¹H NMR spectra, the materials were first fully digested by NaOH (10 wt.%) at 70 °C for 15 min. The insoluble solid was removed by filtration, and the pH of filtrate was adjusted to 3 by using HCl (6 N). Then, the filtrate was extracted with ethyl acetate. The organic phases were combined and dried in vacuo to afford the corresponding organic ligands.

Synthesis of dimethyl 2-(furan-2-yl) terephthalate (organic linker) as a model reaction

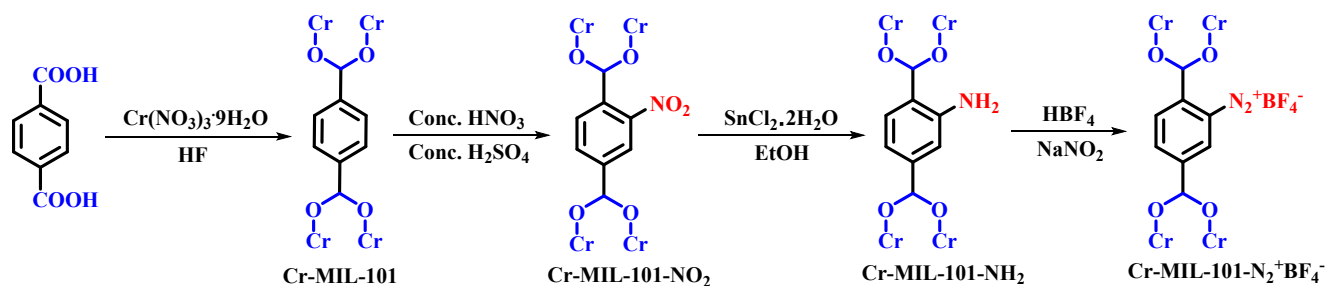


A solution of sodium nitrite (431 mg, 6.25 mmol) in water (2.5 mL) was added dropwise over a period of 10 min to an ice-cooled solution of dimethyl 2-aminoterephthalate (**S1**, 1045 mg, 2.5 mmol) in 20% HBF₄ aqueous solution (7.5 mL). After stirring for a further 1 h at 0 °C, the white precipitation (**S2**) was filtered, washed by methanol and diethyl ether, and then dried under vacuum.

S2 (77 mg, 0.25mmol) was soaked in water (2.5 mL) and reacted with furan (10 eq.). After the reaction was irradiated under 7 W green LED at room temperature for 6 h, the aqueous phase was extracted with ethyl acetate (5 mL×3). The combined organic phases were dried over anhydrous Na₂SO₄ and then concentrated under reduced pressure to afford the product **S3** (NMR yield, 48%). The ¹H NMR analysis was performed by using dibromomethane (CH₂Br₂) as the internal standard (100 mg).



Preparation of Cr-MIL-101-N₂⁺BF₄⁻



Cr-MIL-101 was initially synthesized starting from Cr(NO₃)₃·9H₂O and terephthalic acid via hydrothermal reaction according to the literature.^{S1} Cr-MIL-101-NO₂ was obtained by nitration of Cr-MIL-101 using a mixture solution of conc. HNO₃ and conc. H₂SO₄.^{S2} Subsequently, the nitro groups were reduced to amino groups using tin(II) chloride dihydrate.^{S2} Afterwards, Cr-MIL-101-NH₂ (100

mg) was suspended in 1:1 mixture of water and 48% HBF₄ (2 mL) and diazotized by addition of an aqueous solution of NaNO₂ (50 mg) in water (0.5 mL) and further stirred for 2 h at 0-5 °C.^{S3} The solid sample obtained was separated by centrifugation and denoted as Cr-MIL-101-N₂⁺BF₄⁻.

General Procedures for Synthesis of Cr-MIL-101-C1~C4

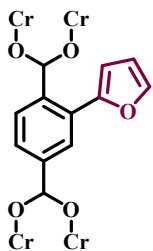
Cr-MIL-101-N₂⁺BF₄⁻ (100 mg, 0.25mmol, according to the ligand) was soaked in water (2.5 mL) and reacted with an appropriate five-membered heterocyclic compound (10 eq.). After the sample was irradiated under 7 W green LED at room temperature for 6 h, the resulting solid was isolated by filtration. The suspension of the obtained solid in ethanol (50 mL) was heated at 60 °C for 1 h, and then filtered to collect the solid (repeating three times). Finally, the resulting solid material was dried under vacuum at 70 °C for 8 h to give title postmodified MOFs.

General Procedure for Synthesis of Cr-MIL-101-C5

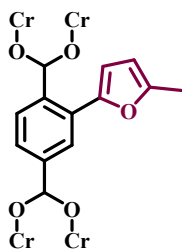
In a typical experiment, Cr-MIL-101-C1 (100 mg, 0.25 mmol, according to the ligand) and NBS (1.1 eq.) were added to DMF (1 mL). After the resulting suspension was stirred for 12 h at room temperature, the solid product was isolated by filtration and washed three times with ethanol. The resulting solid material was dried under vacuum at 70 °C for 8 h and denoted as Cr-MIL-101-C5.

Competition experiment

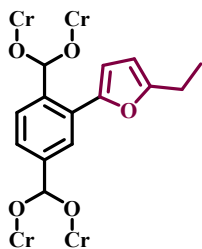
In order to investigate that whether the π - π interaction participated, a competition experiment was performed. Atrazine is a herbicide, which has been affirmed that π - π stacking is responsible for driving atrazine adsorption (*ACS Appl. Mater. Interfaces*, 2019,11(6): 6097-6103). In a typical adsorption experiment, 3 mg Cr-MIL-101-C1 was added to 40 mL of a fixed pH (7.0) solution of diuron (30 ppm) and atrazine (30 ppm). The removal percentage of diuron decreased by 62%, which indicated that furan-based linkers may offer sites for π - π interactions.

Cr-MIL-101-C1:

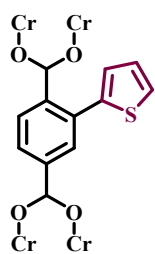
IR (KBr pellet): ν 3385, 1696, 1566, 1501, 1410, 1305, 1271, 1132, 1045, 1018, 931, 829, 802, 771, 748, 588 cm^{-1} . ^1H NMR (500 MHz, $\text{CD}_3\text{OD}-d_4$) δ 8.23 (s, 1H), 7.92 (d, $J = 8.0$ Hz, 1H), 7.61 (d, $J = 8.0$ Hz, 1H), 7.54 (s, 1H), 6.70 (d, $J = 3.3$ Hz, 1H), 6.57 – 6.36 (m, 1H). ^{13}C NMR (101 MHz, $\text{CD}_3\text{OD}-d_4$) δ 170.93, 167.13, 151.21, 143.05, 133.27, 129.30, 128.45, 128.39, 128.18, 128.03, 111.39, 108.38. ESI-MS: m/z $[\text{M}-\text{H}]^-$ 231. HRMS: $\text{C}_{12}\text{H}_8\text{O}_5\text{Na}$ for $[\text{M}+\text{Na}]^+$, calculated 255.0269, found 255.0265.

Cr-MIL-101-C2:

IR (KBr pellet): ν 3404, 2958, 2924, 2856, 1622, 1568, 1495, 1411, 1304, 1276, 1166, 1090, 832, 771, 748, 667, 586 cm^{-1} . ^1H NMR (500 MHz, $\text{CD}_3\text{OD}-d_4$) δ 8.22 (d, $J = 1.2$ Hz, 1H), 7.89 (dd, $J = 8.0, 1.3$ Hz, 1H), 7.57 (d, $J = 8.0$ Hz, 1H), 6.61 (d, $J = 3.2$ Hz, 1H), 6.08 (d, $J = 2.5$ Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $\text{CD}_3\text{OD}-d_4$) δ 171.30, 167.41, 153.03, 149.33, 134.44, 132.28, 128.97, 128.17, 127.49, 127.38, 109.45, 107.56, 12.04. ESI-MS: m/z $[\text{M}-\text{H}]^-$ 245. HRMS: $\text{C}_{13}\text{H}_{10}\text{O}_5\text{Na}$ for $[\text{M}+\text{Na}]^+$, calculated 269.0426, found 269.0427.

Cr-MIL-101-C3:

IR (KBr pellet): ν 3384, 2974, 1699, 1616, 1564, 1500, 1410, 1307, 1270, 1136, 1046, 829, 802, 771, 749, 726, 587 cm^{-1} . ^1H NMR (500 MHz, $\text{CD}_3\text{OD}-d_4$) δ 8.21 (d, $J = 0.8$ Hz, 1H), 7.89 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.56 (d, $J = 8.0$ Hz, 1H), 6.62 (d, $J = 3.2$ Hz, 1H), 6.09 (d, $J = 3.1$ Hz, 1H), 2.66 (q, $J = 7.5$ Hz, 2H), 1.23 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (101 MHz, $\text{CD}_3\text{OD}-d_4$) δ 171.43, 167.31, 158.62, 149.31, 134.46, 132.28, 128.99, 128.16, 127.46, 127.41, 109.10, 106.08, 20.91, 11.37. ESI-MS: m/z $[\text{M}-\text{H}]^-$ 259. HRMS: $\text{C}_{14}\text{H}_{12}\text{O}_5\text{Na}$ for $[\text{M}+\text{Na}]^+$, calculated 283.0582, found 283.0581.

Cr-MIL-101-C4:

IR (KBr pellet): ν 3385, 2958, 2924, 1620, 1568, 1504, 1405, 1265, 1136, 838, 770, 749,

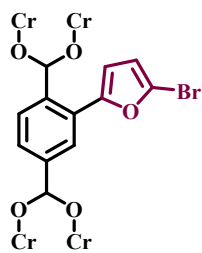
582 cm^{-1} . ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 7.99 (d, $J = 1.4$ Hz, 1H), 7.97 (dd, $J = 7.9$,

1.6 Hz, 1H), 7.73 (d, $J = 8.0$ Hz, 1H), 7.65 (dd, $J = 5.1, 0.9$ Hz, 1H), 7.21 (dd, $J = 3.6, 1.2$

Hz, 1H), 7.14 (dd, $J = 5.1, 3.6$ Hz, 1H). ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 176.22,

174.61, 139.63, 137.47, 135.96, 134.05, 133.67, 133.12, 132.52, 132.09, 124.58, 122.83. ESI-MS: m/z

$[\text{M-H}]^-$ 247. HRMS: $\text{C}_{12}\text{H}_8\text{O}_4\text{SNa}$ for $[\text{M}+\text{Na}]^+$, calculated 271.0041, found 271.0036.

Cr-MIL-101-C5:

IR (KBr pellet): ν 3381, 2958, 2925, 2852, 1624, 1566, 1498, 1481, 1412, 1304, 1274,

1167, 1131, 1019, 945, 926, 830, 802, 771, 748, 667, 589 cm^{-1} . ^1H NMR (500 MHz,

$\text{DMSO-}d_6$) δ 8.12 (d, $J = 1.5$ Hz, 1H), 7.96 (dd, $J = 8.0, 1.7$ Hz, 1H), 7.72 (d, $J = 8.0$

Hz, 1H), 6.91 (d, $J = 3.5$ Hz, 1H), 6.73 (d, $J = 3.5$ Hz, 1H). ^{13}C NMR (101 MHz,

$\text{DMSO-}d_6$) δ 174.38, 171.43, 158.25, 139.87, 137.84, 134.67, 134.25, 134.07, 133.12, 127.59, 119.19,

116.74. ESI-MS: m/z $[\text{M-H}]^-$ 309. HRMS: $\text{C}_{12}\text{H}_7\text{O}_5\text{BrNa}$ for $[\text{M}+\text{Na}]^+$, calculated 332.9375, found

332.9372.

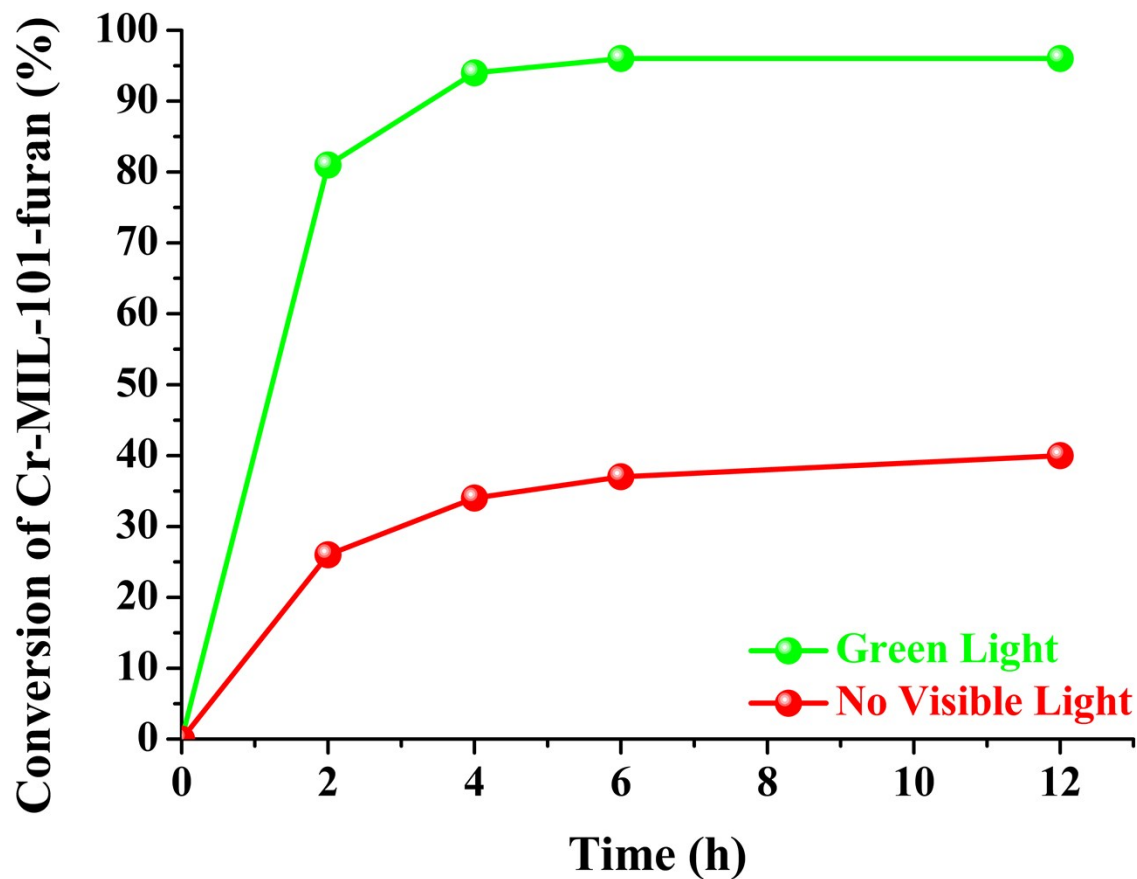


Fig. S1 Effect of contact time on conversion of Cr-MIL-101-furan (**Cr-MIL-101-C1**). Reactions were performed with Cr-MIL-101-N₂⁺BF₄⁻ (0.25 mmol) and furan (10 eq.) in water (2.5 mL) at room temperature. (a) The reaction was irradiated using green LED (7W). (b) The reaction was irradiated without visible light.

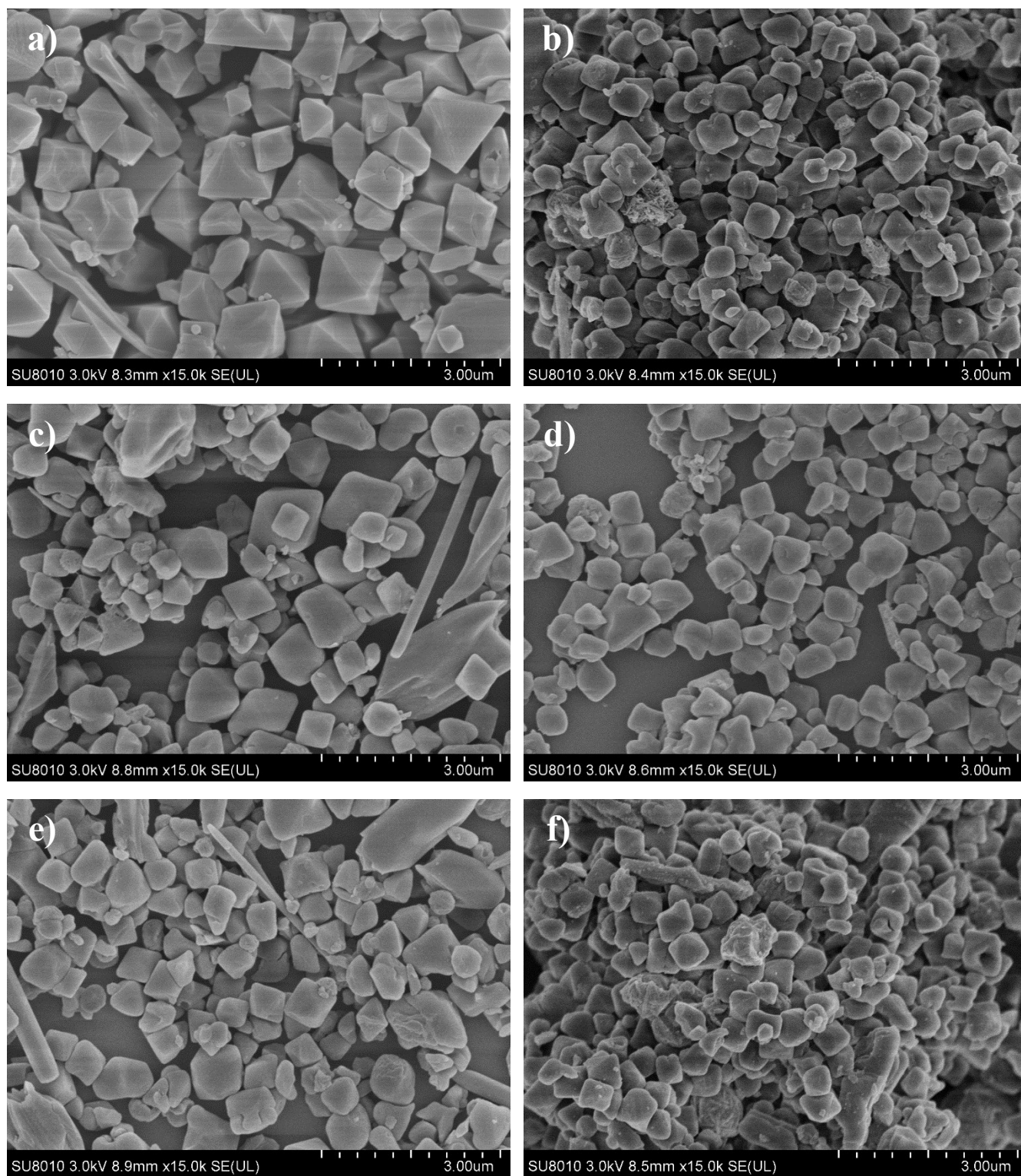


Fig. S2 SEM images of (a) Cr-MIL-101, (b) Cr-MIL-101-C1, (c) Cr-MIL-101-C2, (d) Cr-MIL-101-C3, (e) Cr-MIL-101-C4 and (f) Cr-MIL-101-C5.

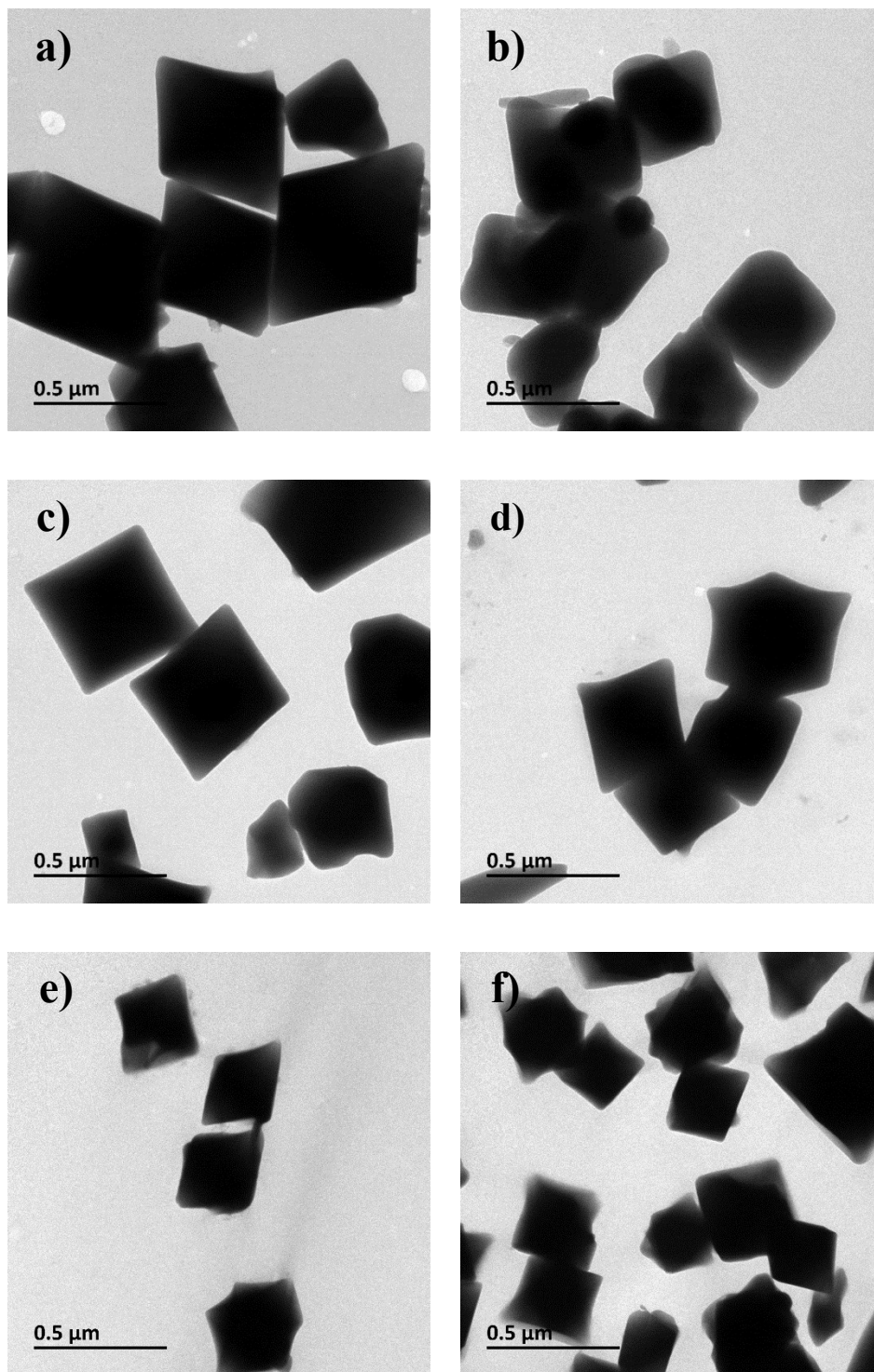


Fig. S3 TEM images of (a) Cr-MIL-101, (b) Cr-MIL-101-C1, (c) Cr-MIL-101-C2, (d) Cr-MIL-101-C3, (e) Cr-MIL-101-C4 and (f) Cr-MIL-101-C5.

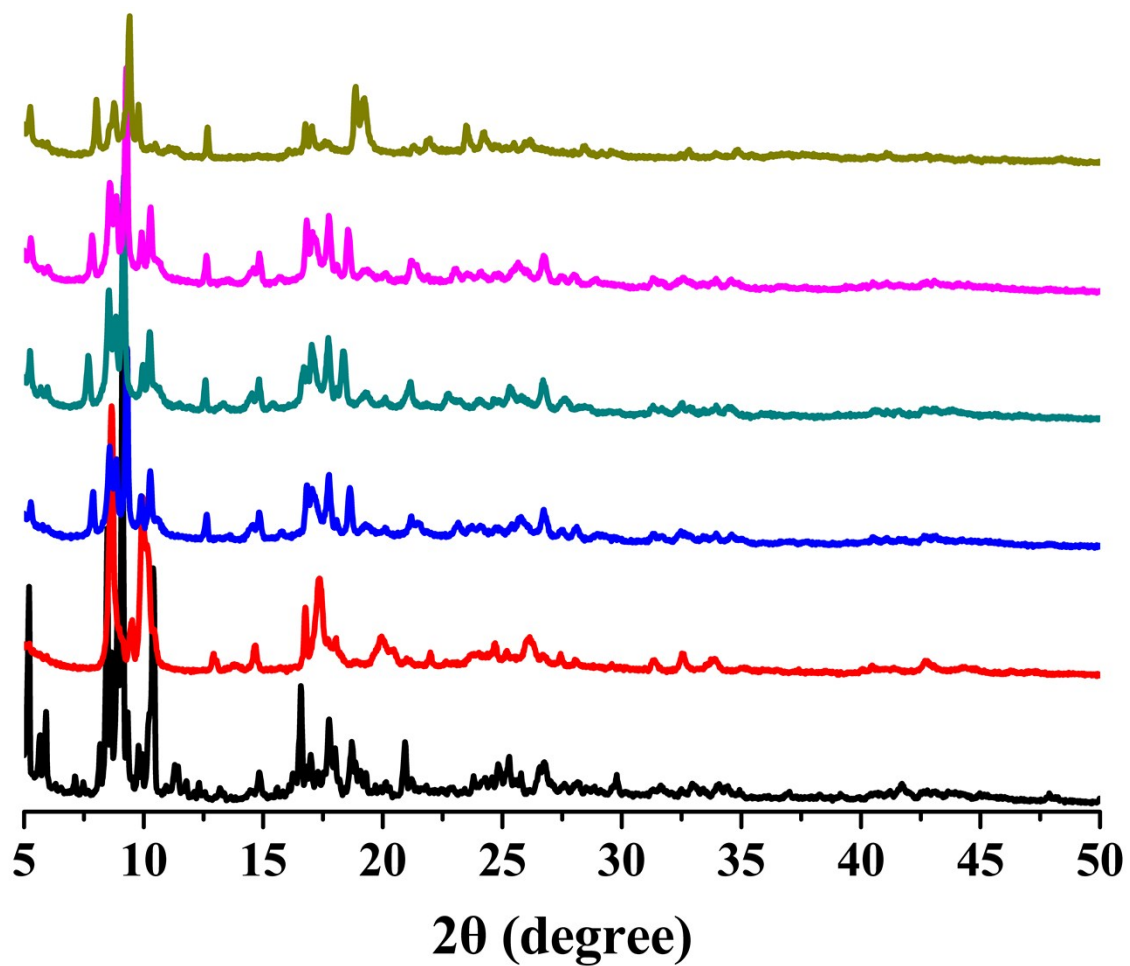


Fig. S4 PXRD patterns of Cr-MIL-101 (black), Cr-MIL-101-C1 (red), Cr-MIL-101-C2 (blue), Cr-MIL-101-C3 (dark cyan), Cr-MIL-101-C4 (magenta) and Cr-MIL-101-C5 (dark yellow).

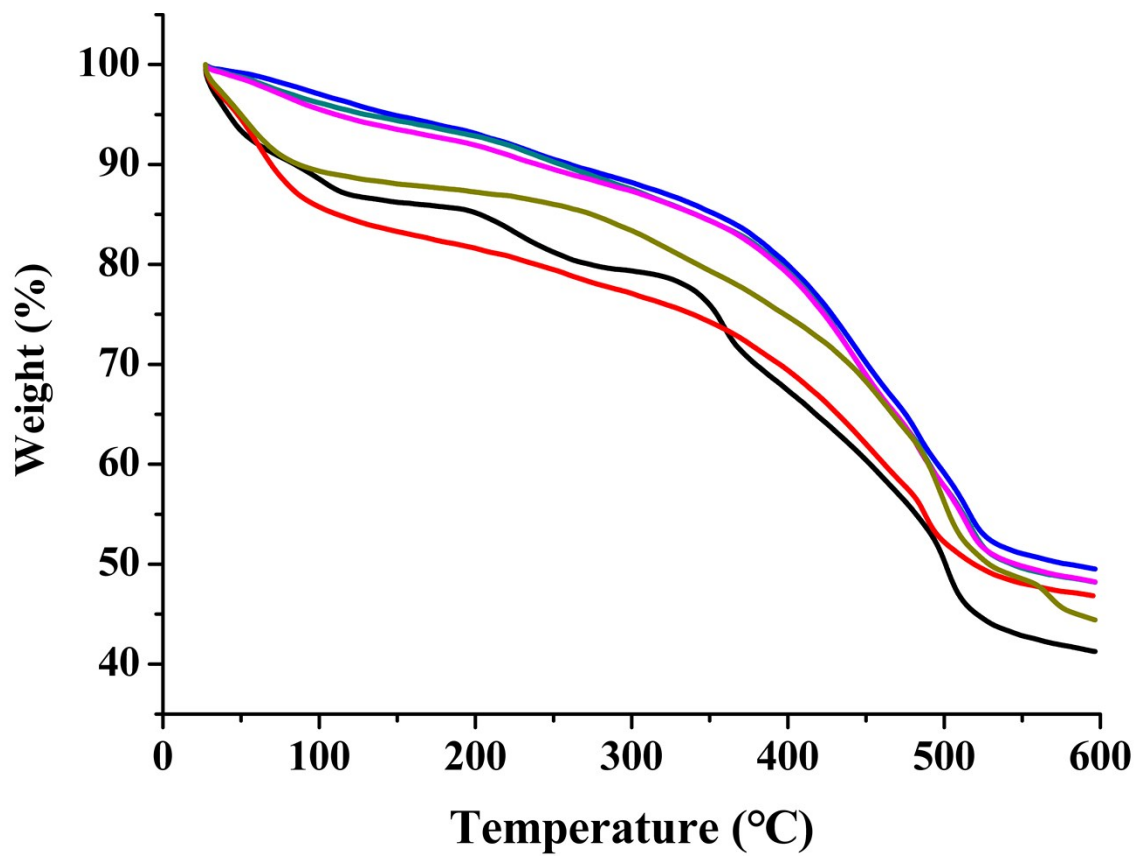


Fig. S5 TGA plots of Cr-MIL-101 (black), Cr-MIL-101-C1 (red), Cr-MIL-101-C2 (blue), Cr-MIL-101-C3 (dark cyan), Cr-MIL-101-C4 (magenta) and Cr-MIL-101-C5 (dark yellow).

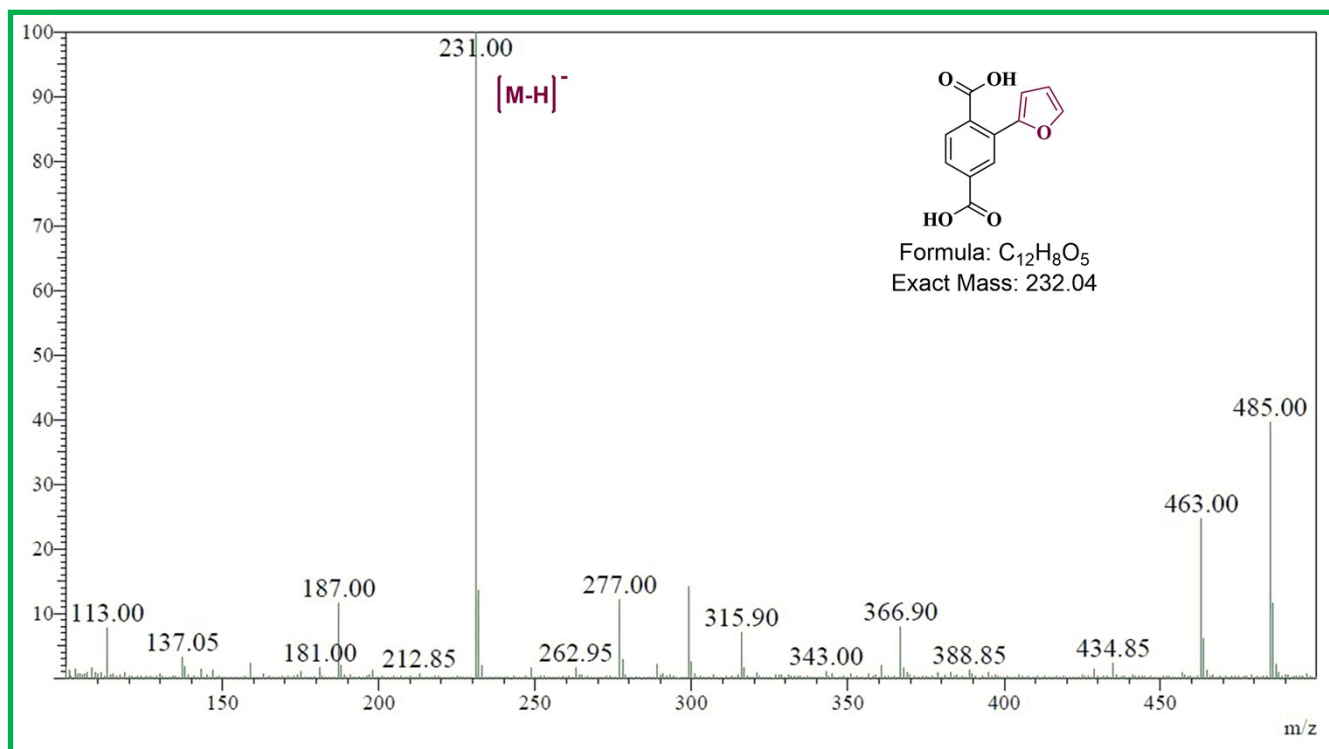


Fig. S6a ESI-MS (negative mode) of Cr-MIL-101-C1.

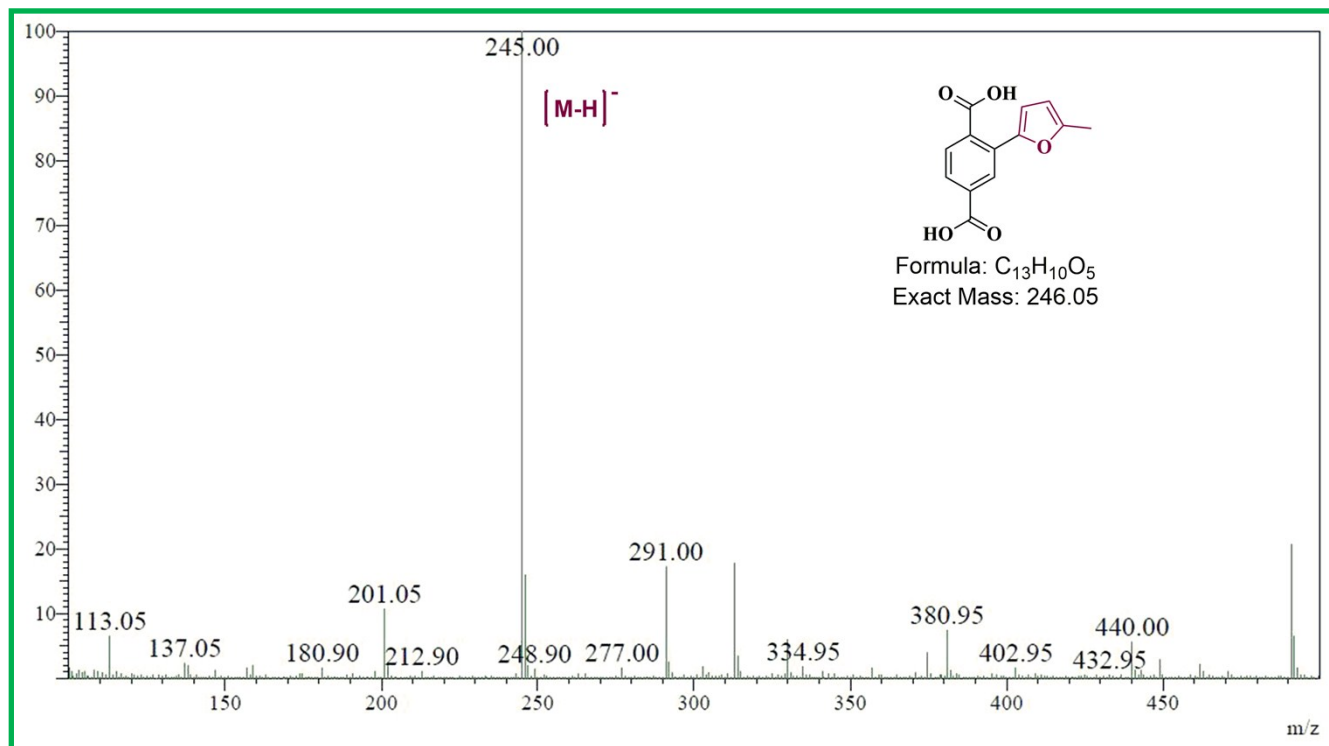


Fig. S6b ESI-MS (negative mode) of Cr-MIL-101-C2.

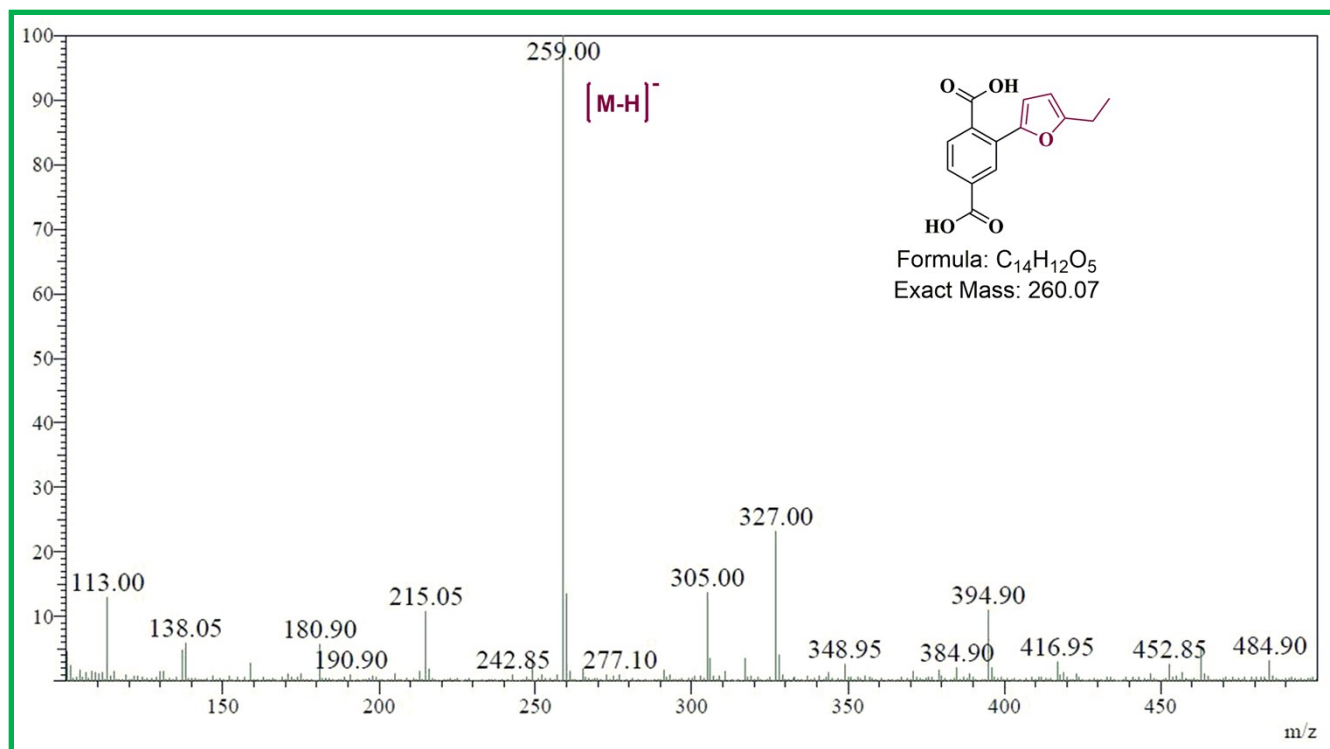


Fig. S6c ESI-MS (negative mode) of Cr-MIL-101-C3.

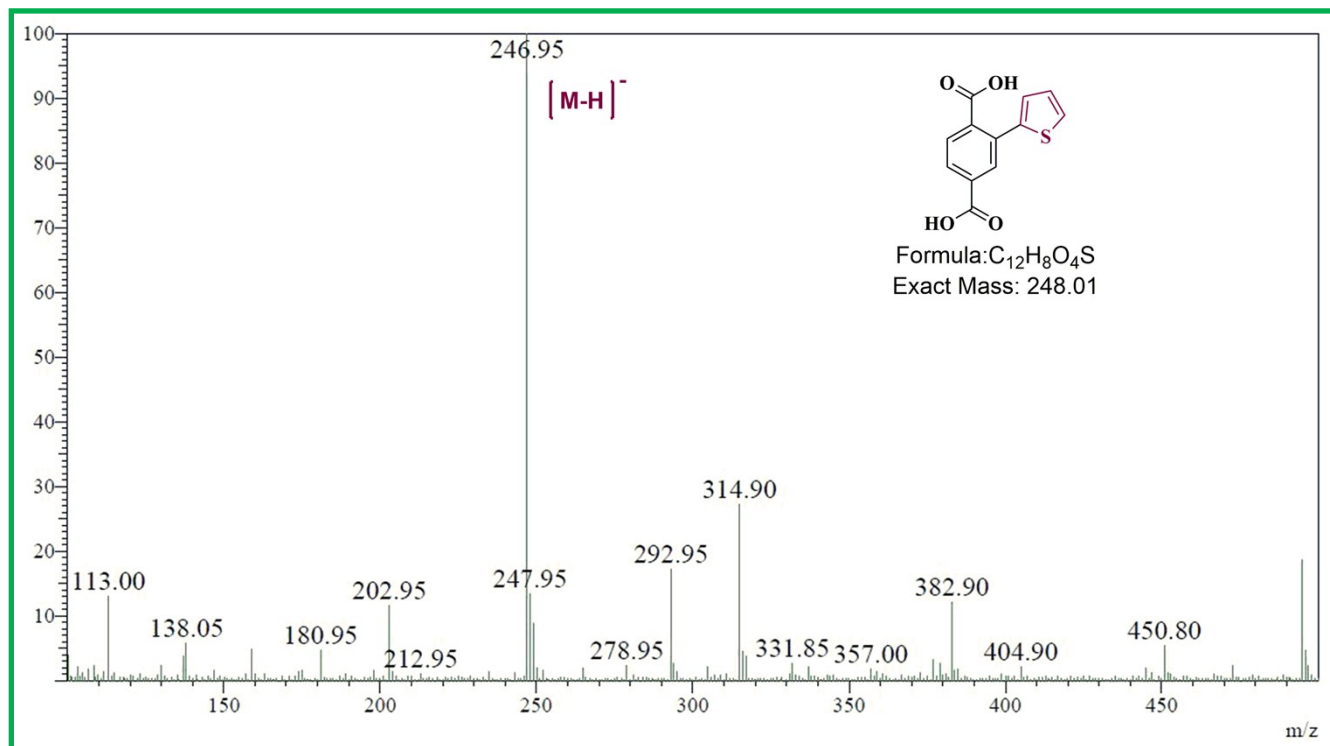


Fig. S6d ESI-MS (negative mode) of Cr-MIL-101-C4.

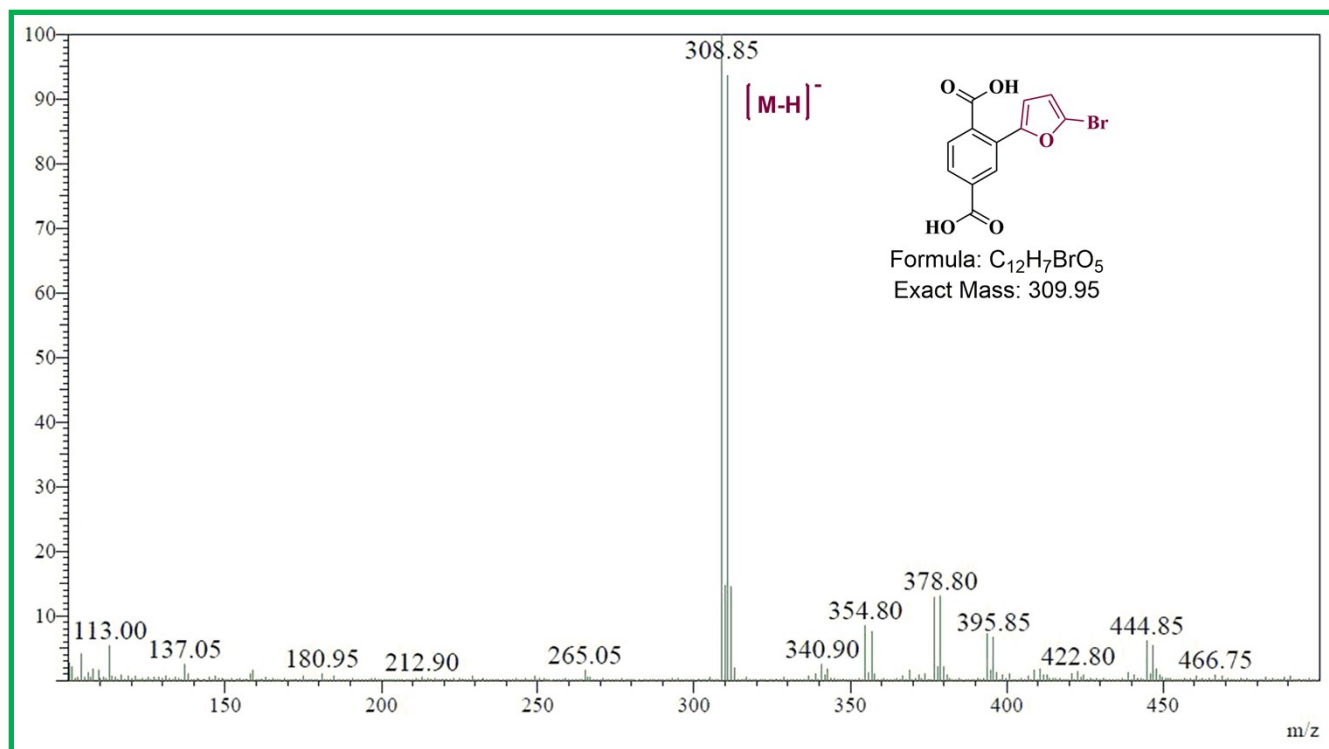


Fig. S6e ESI-MS (negative mode) of Cr-MIL-101-C5.

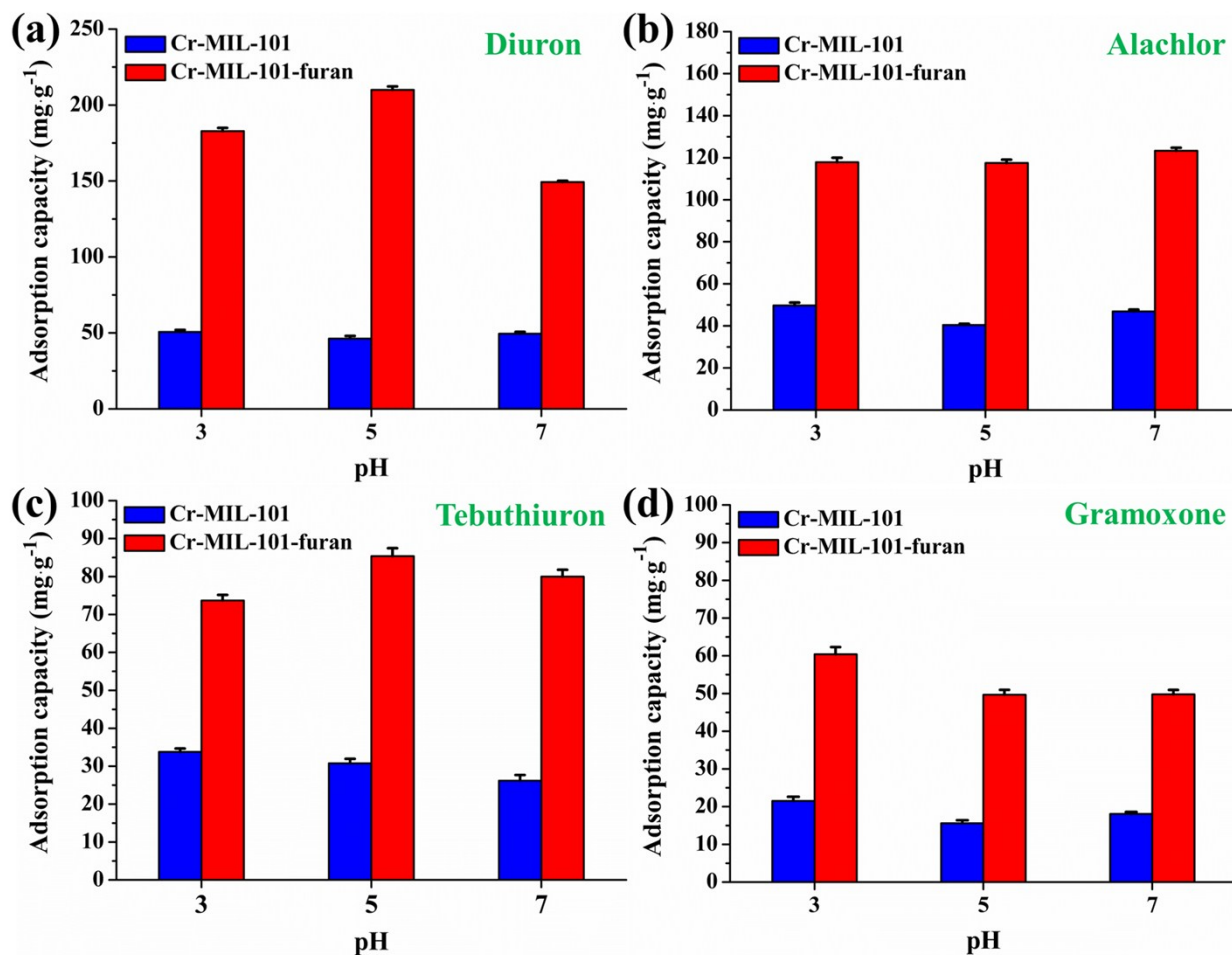


Fig. S7 Effect of pH on adsorption capacity of (a) diuron, (b) alachlor, (c) tebuthiuron and (d) gramoxone onto Cr-MIL-101 and Cr-MIL-101-furan (Cr-MIL-101-C1). The effect of ambient pH value was investigated by mixing adsorbents (Cr-MIL-101 and Cr-MIL-101, 3 mg) with 40 mL herbicides solution with concentration of 30 ppm in the pH range of 3-7 at 30 °C for 24 h. HCl and NaOH solution of 0.1 M were utilized to adjust the pH value of herbicide solution. The mixture was shaken in a temperature-controllable orbital shaker at 200 rpm. MOFs were dried at 100 °C for 24 h before adsorption. All experiments were repeated three times.

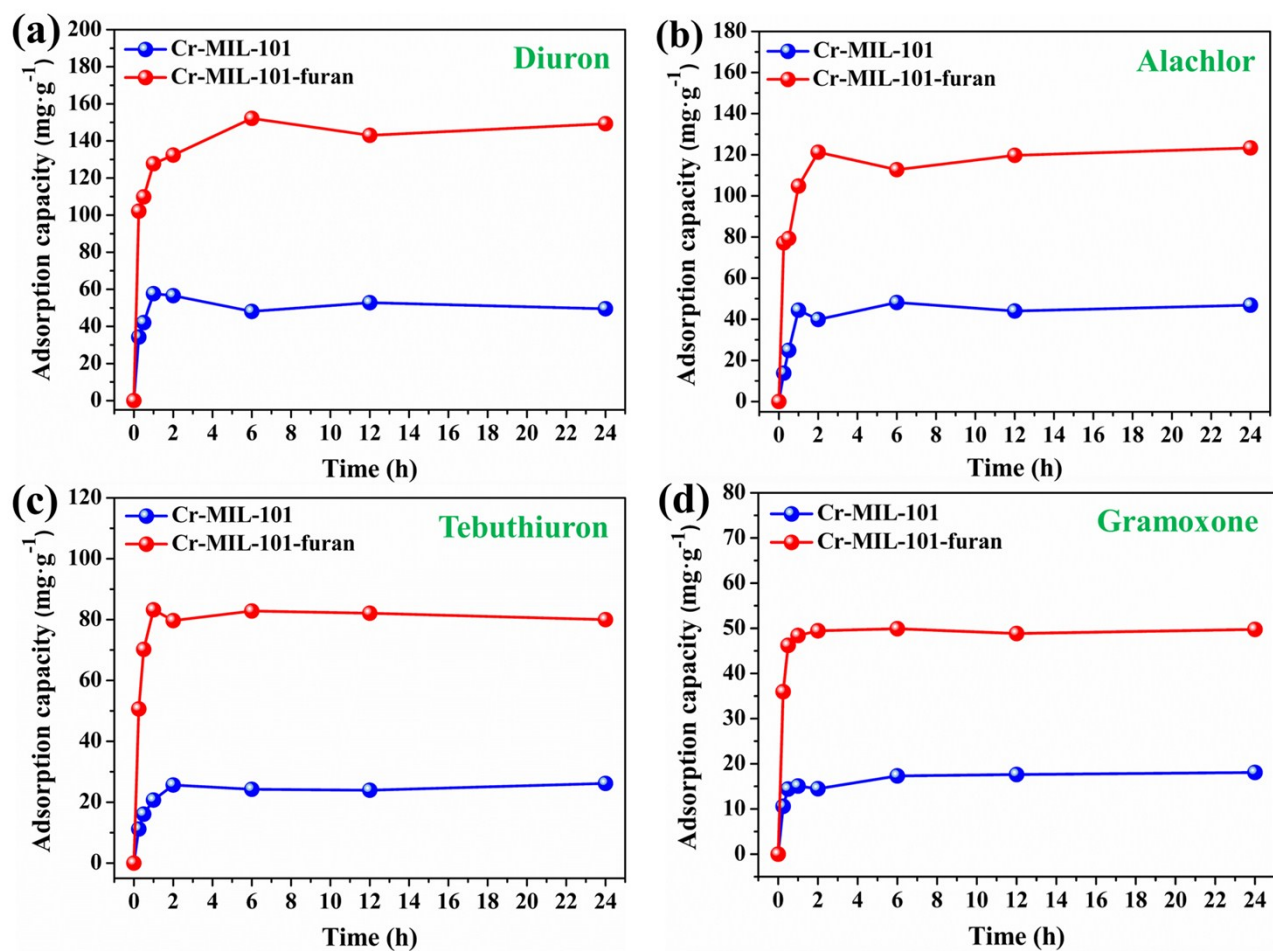


Fig. S8 Effect of contact time on adsorption capacity of (a) diuron, (b) alachlor, (c) tebuthiuron and (d) gramoxone onto Cr-MIL-101 and Cr-MIL-101-furan (**Cr-MIL-101-C1**). In the kinetic adsorption experiment, 3 mg Cr-MIL-101 (Cr-MIL-101-furan) was added to 40 mL of a fixed pH (7.0) solution of the corresponding herbicide (30 ppm). The herbicide solution and the adsorbent were mixed thoroughly in a thermostatic shaker (200 rpm) at 30 °C. MOFs were dried at 100 °C for 24 h before adsorption. All experiments were repeated three times.

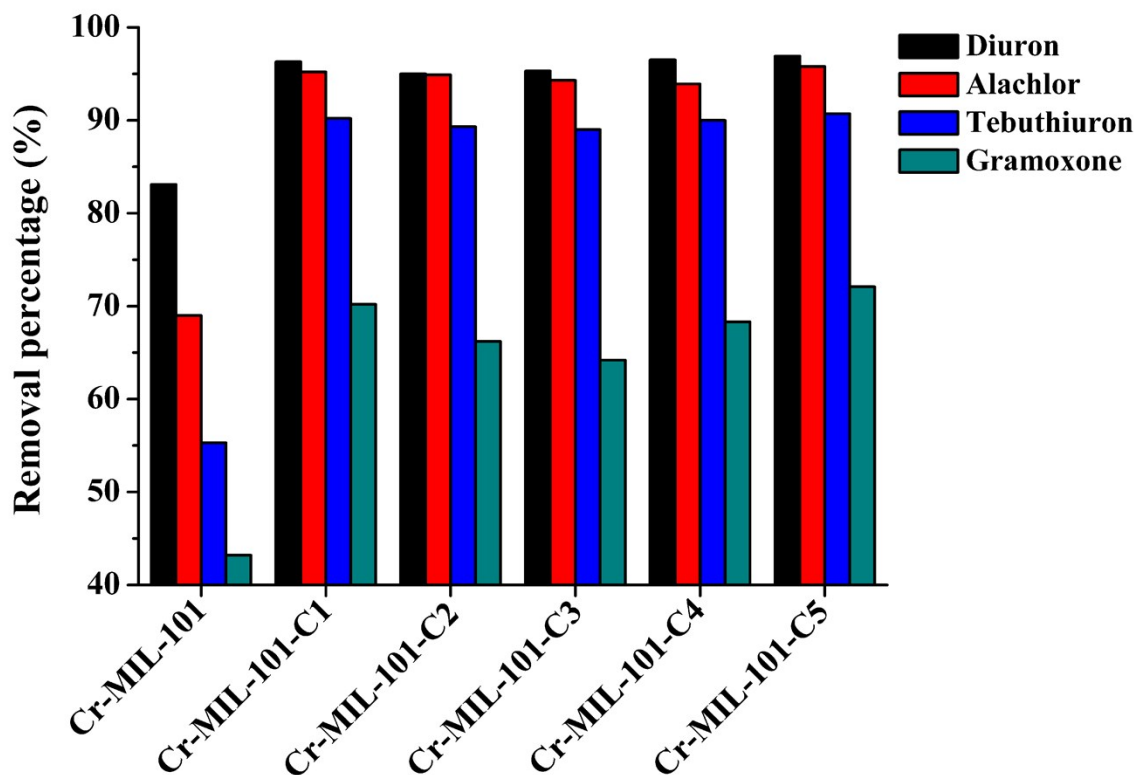


Fig. S9 Removal percentage of adsorbed herbicides from aqueous solution of four herbicides (30 ppm) over Cr-MIL-101 and its functionalized derivatives. In the adsorption experiment, 30 mg MOFs was added to 40 mL of a fixed pH (7.0) solution of the corresponding herbicide (30 ppm). The herbicide solution and the adsorbent were mixed thoroughly in a thermostatic shaker (200 rpm) at 25 °C for 6 h. All of obtained MOFs were dried at 100 °C for 24 h before adsorption. All experiments were repeated three times.

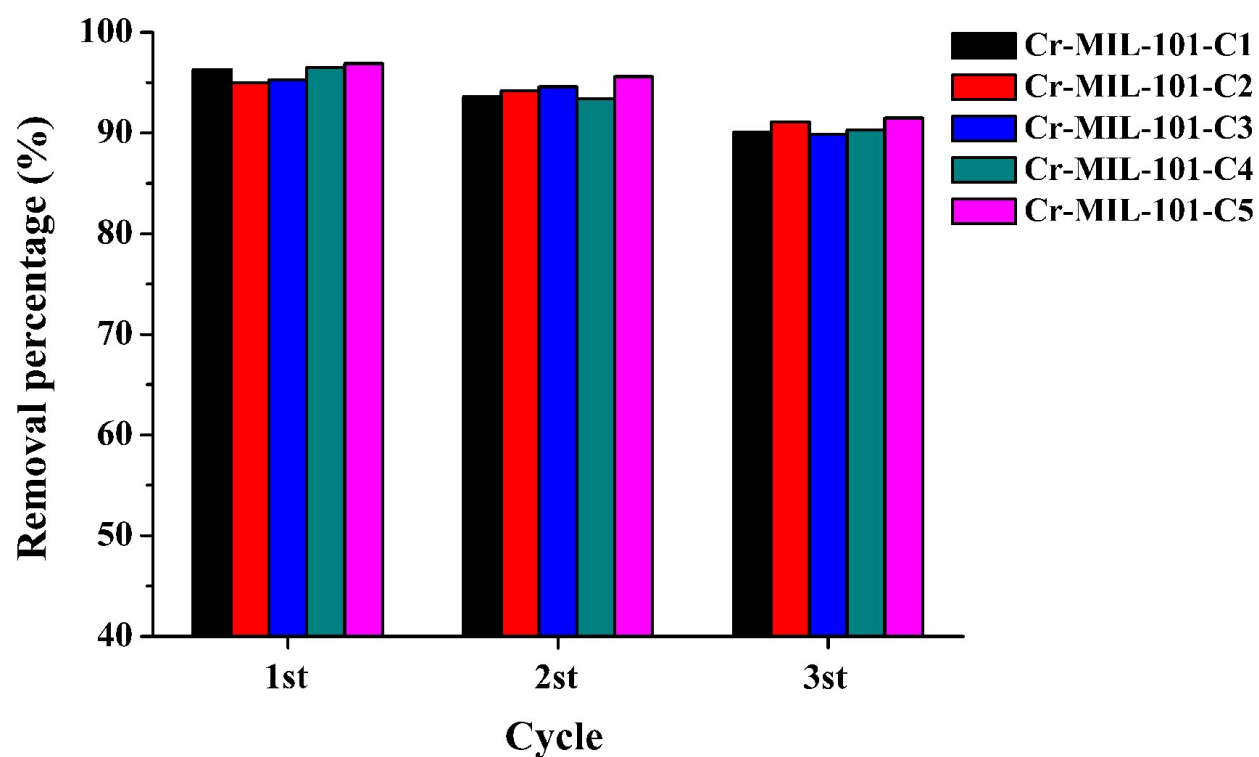


Fig. S10 Through three cycles of diuron adsorption and regeneration with acetone, furan/thiophene-derived Cr-MIL-101s (30 mg) show only a slight decrease in diuron uptake. In a typical experiment, after the MOF samples (Cr-MIL-101-C1~C5) were loaded with diuron, then treated the MOF with acetone at room temperature to remove the diuron for the next cycle test.

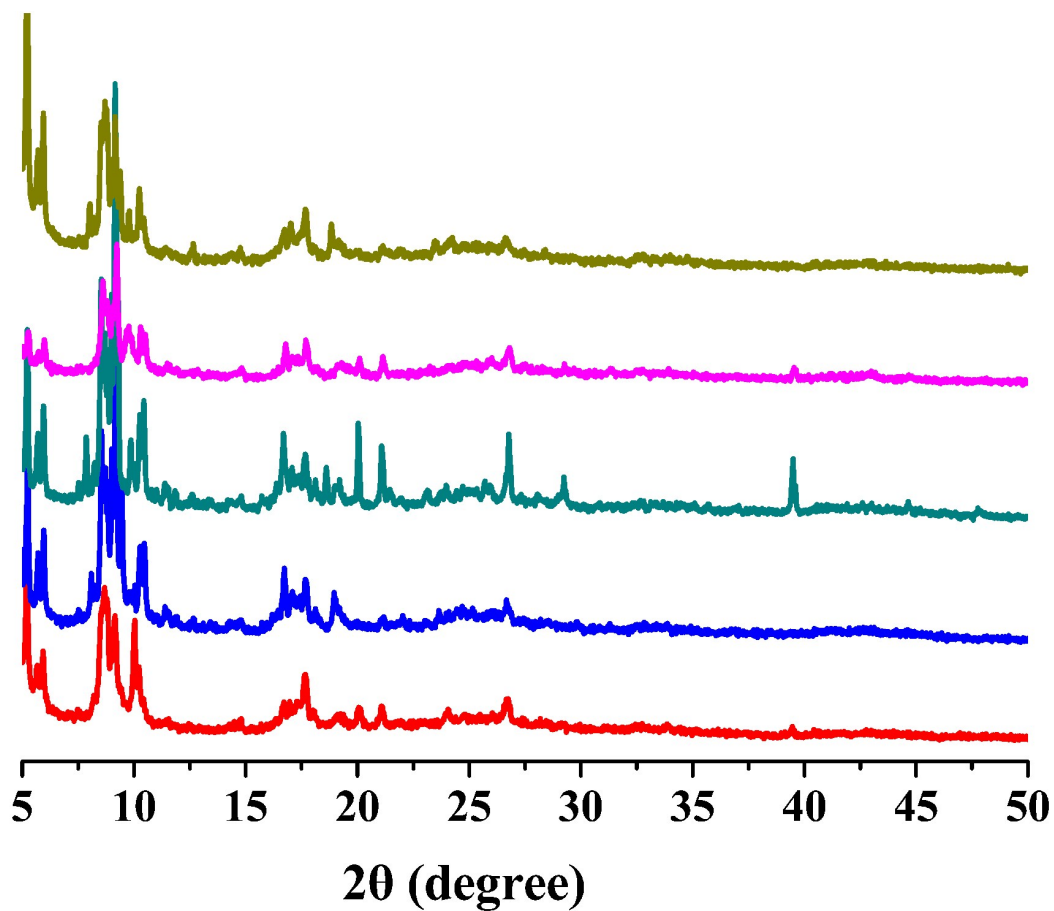


Fig. S11 Through three cycles of diuron adsorption and regeneration with acetone, furan/thiophene-derived Cr-MIL-101s retains its bulk structural integrity as demonstrated by PXRD. Cr-MIL-101-C1 (red), Cr-MIL-101-C2 (blue), Cr-MIL-101-C3 (dark cyan), Cr-MIL-101-C4 (magenta) and Cr-MIL-101-C5 (dark yellow).

For validating if the adsorption was caused by π - π or hydrogen bonding interactions, X-ray photoelectron spectroscopy (XPS) was applied to investigate the adsorption mechanism of diuron to Cr-MIL-101-C1. As shown in the following figure, the verify (0.2 eV) indicated that the O-C groups (furan) in Cr-MIL-101-C1 may present hydrogen bonding affinity toward diuron molecules.

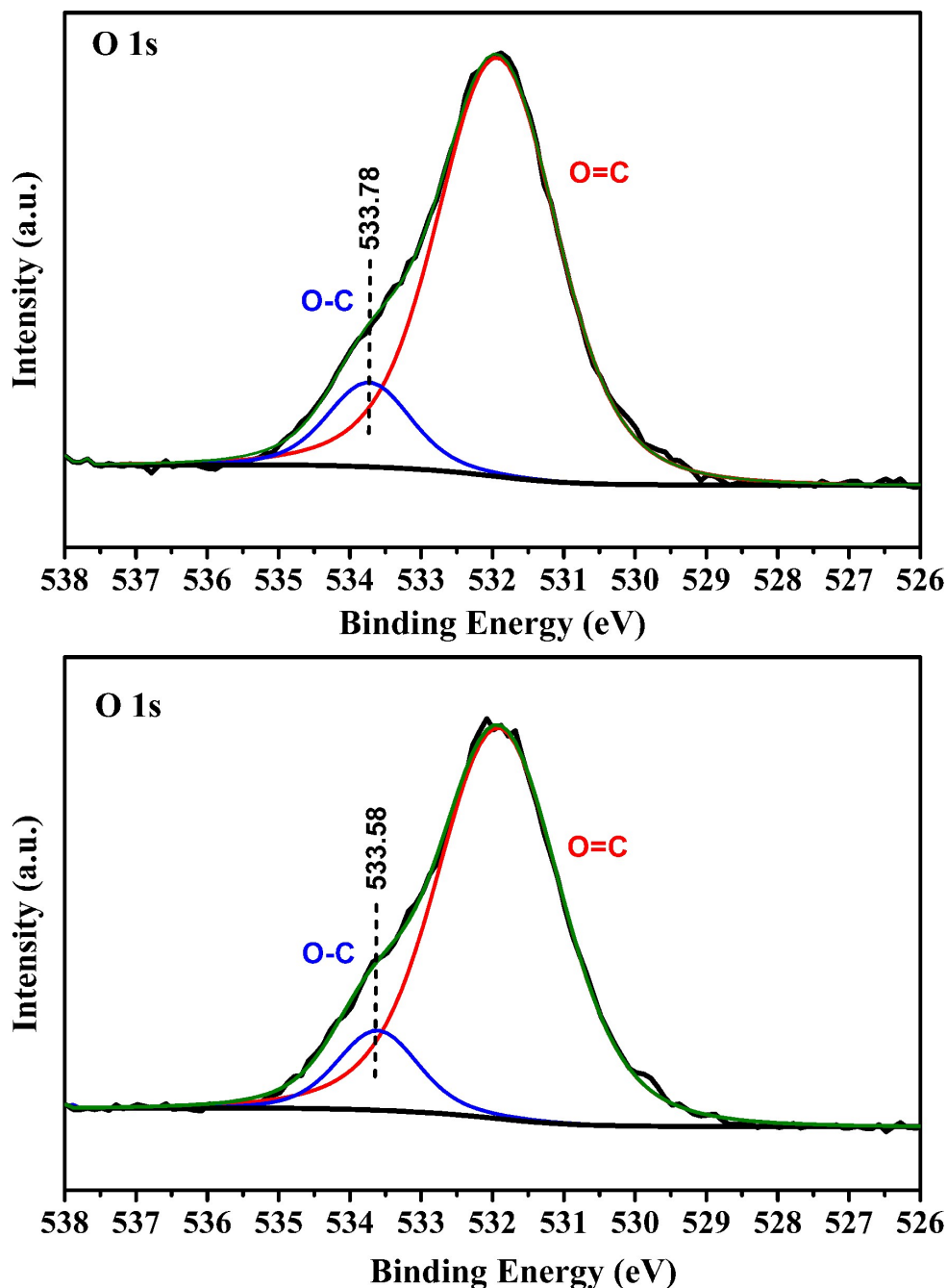


Fig. S12 XPS spectra of Cr-MIL-101-C1 (up) and after diuron adsorption to Cr-MIL-101-C1 (down).

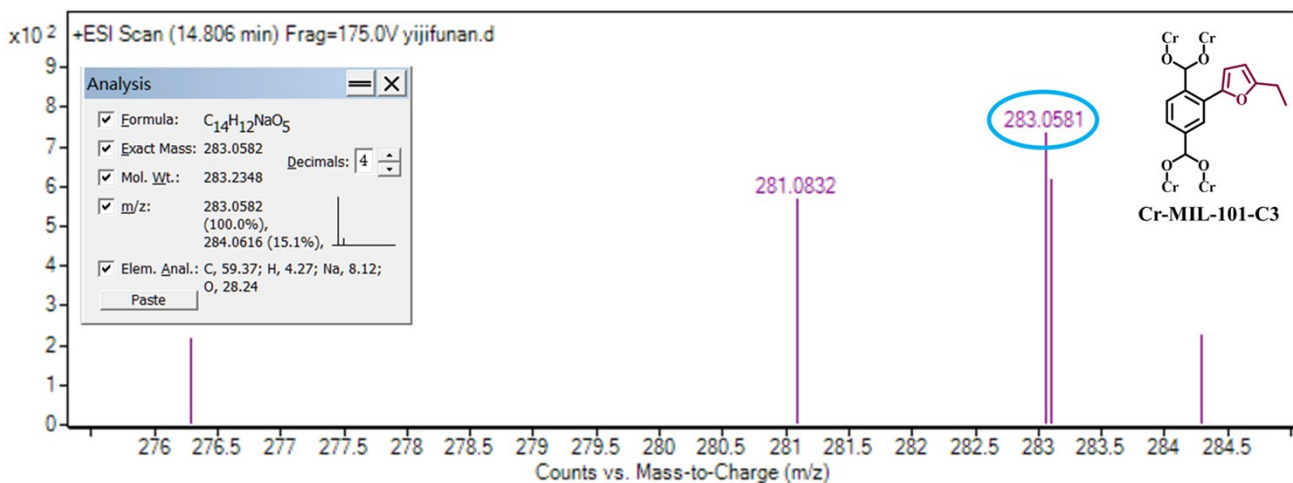
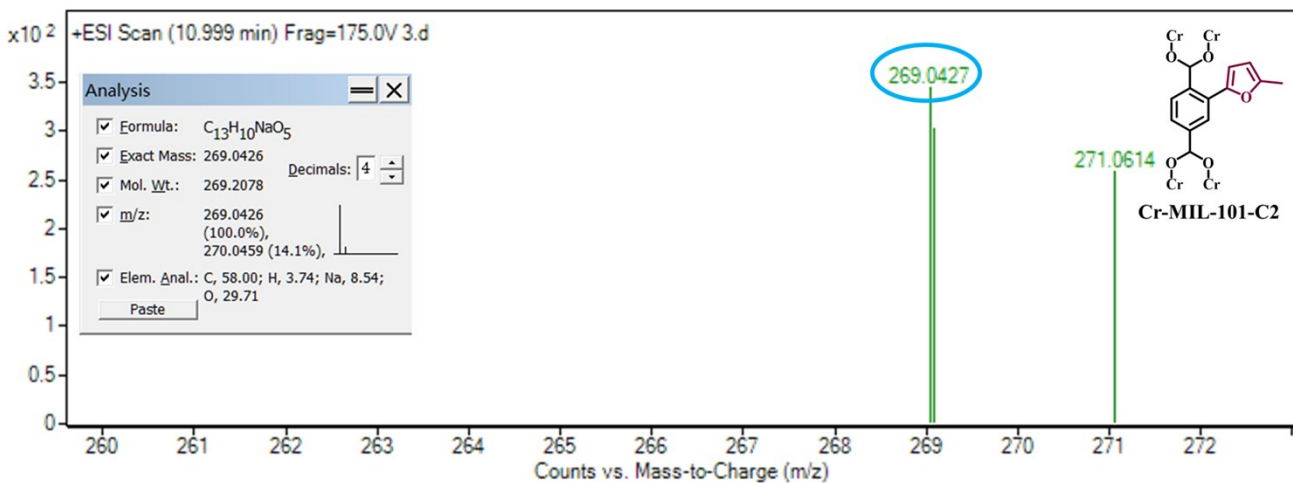
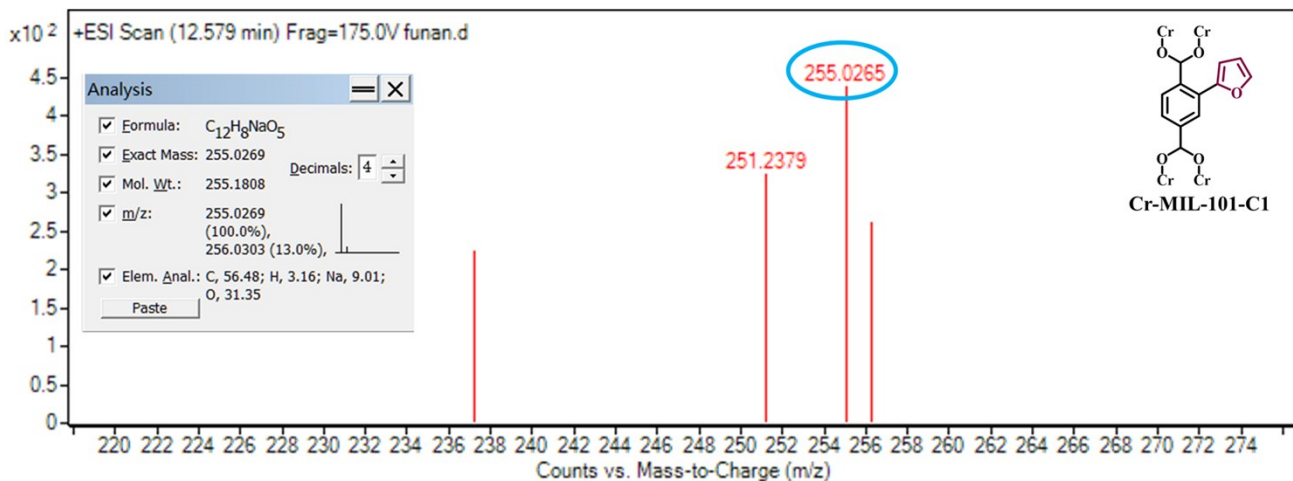
Table S1 Textural parameters of Cr-MIL-101 and Cr-MIL-101-C1~C5.

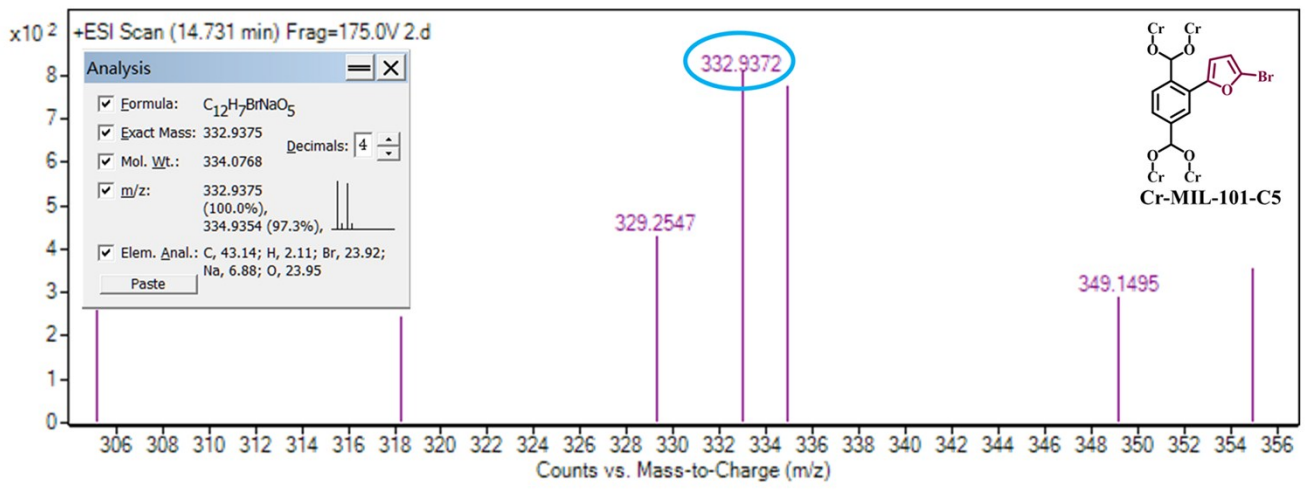
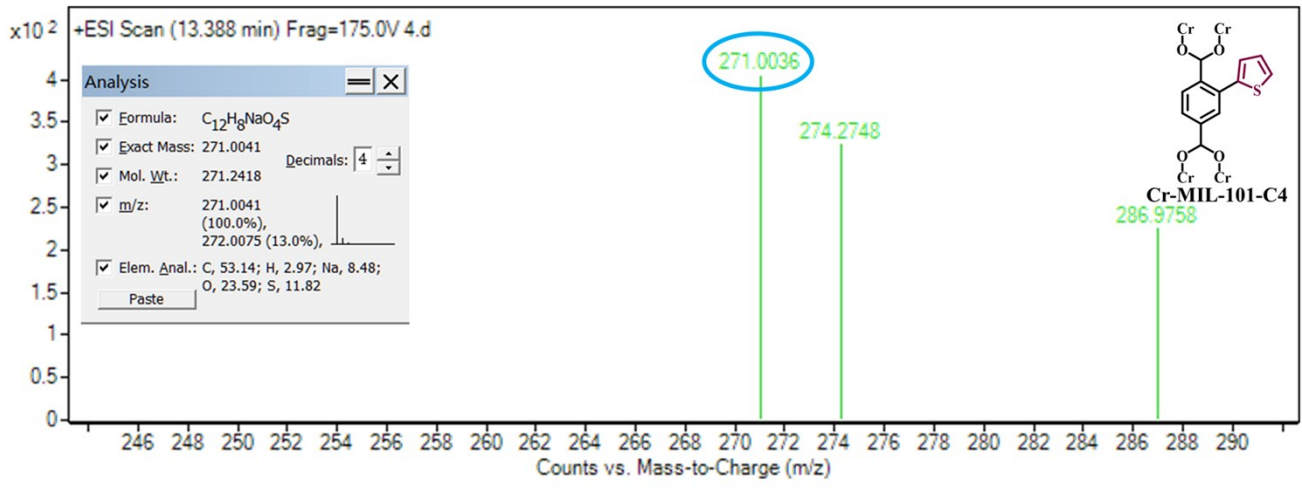
Sample	BET surface area (m ² ·g ⁻¹)	Pore volume (mL·g ⁻¹)
Cr-MIL-101	2274.0	1.219
Cr-MIL-101-C1	951.3	0.554
Cr-MIL-101-C2	502.6	0.302
Cr-MIL-101-C3	490.6	0.282
Cr-MIL-101-C4	492.4	0.285
Cr-MIL-101-C5	543.2	0.319

Reference:

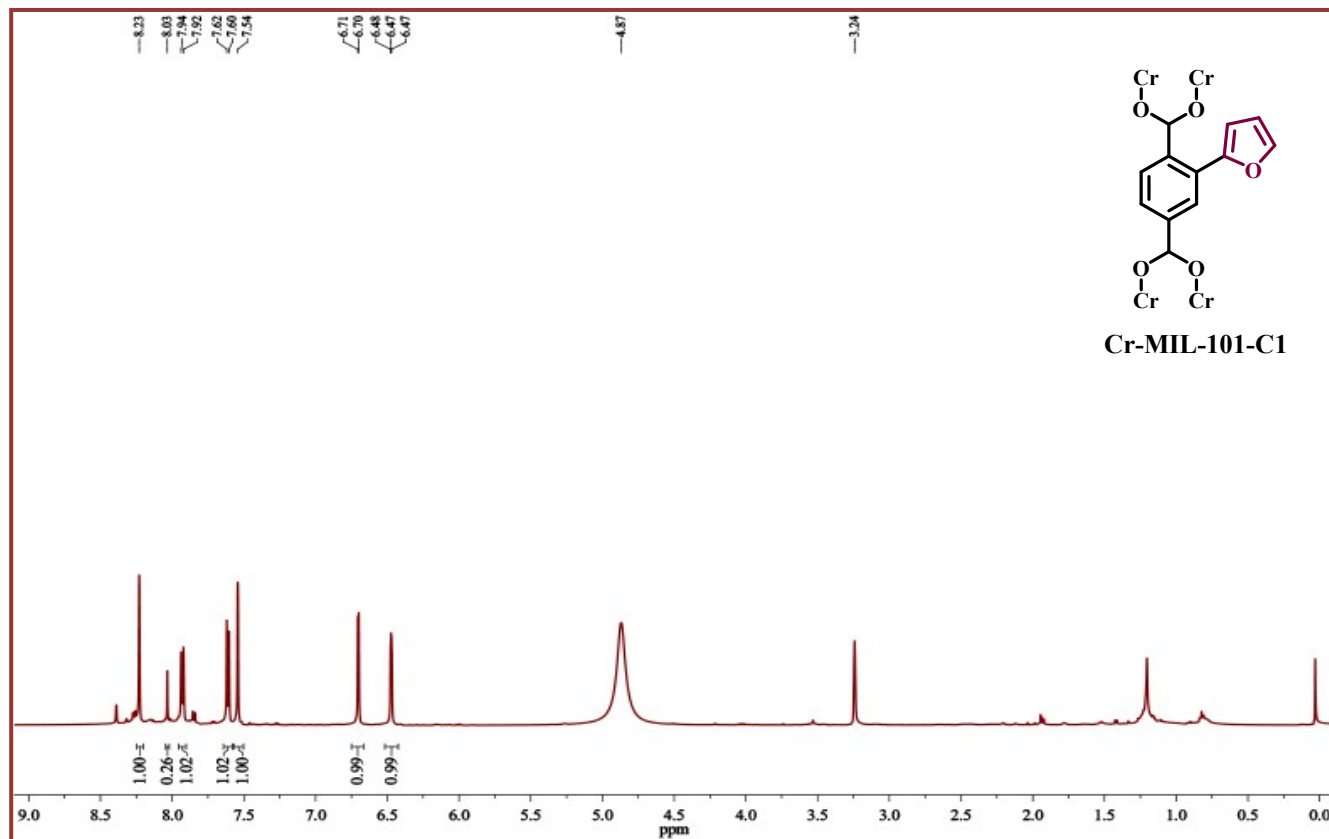
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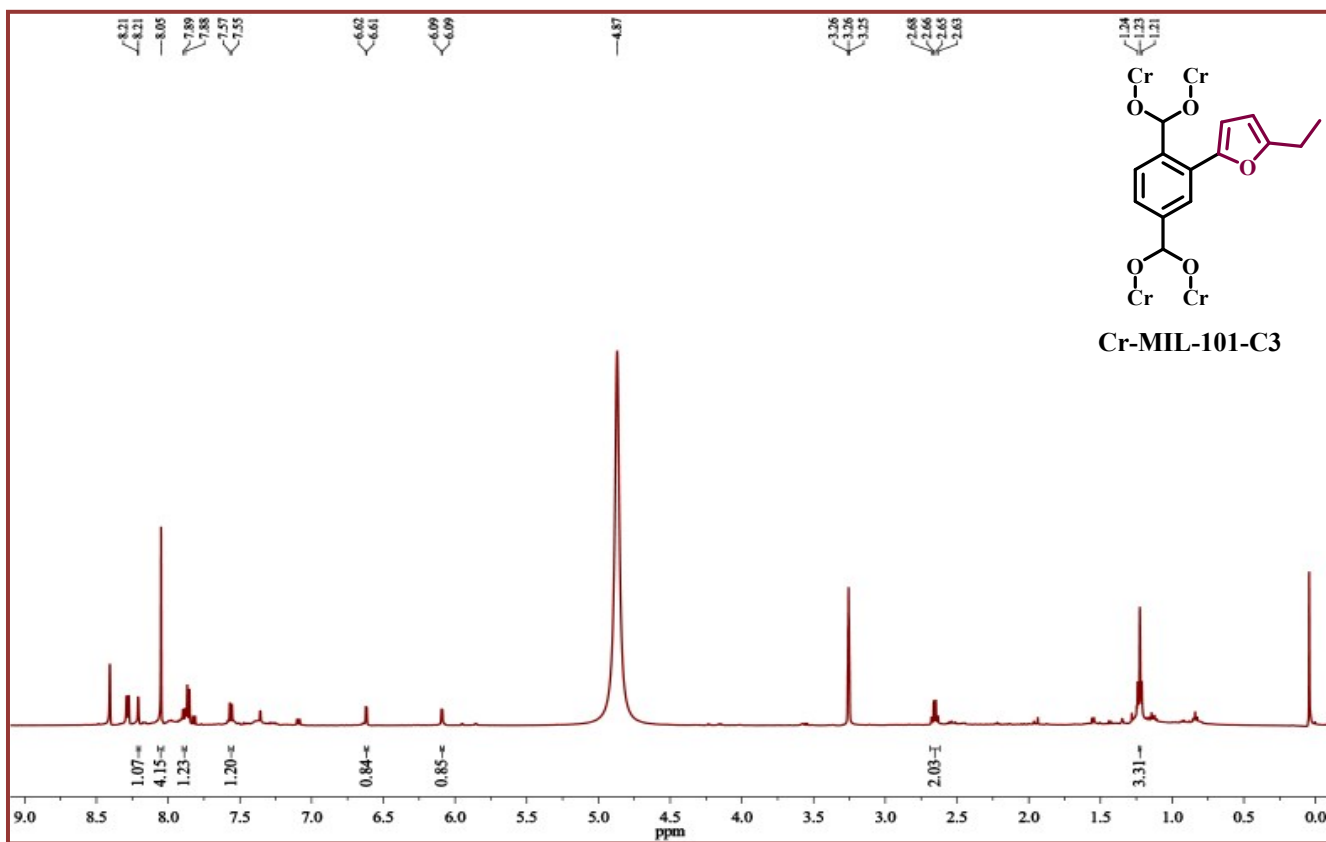
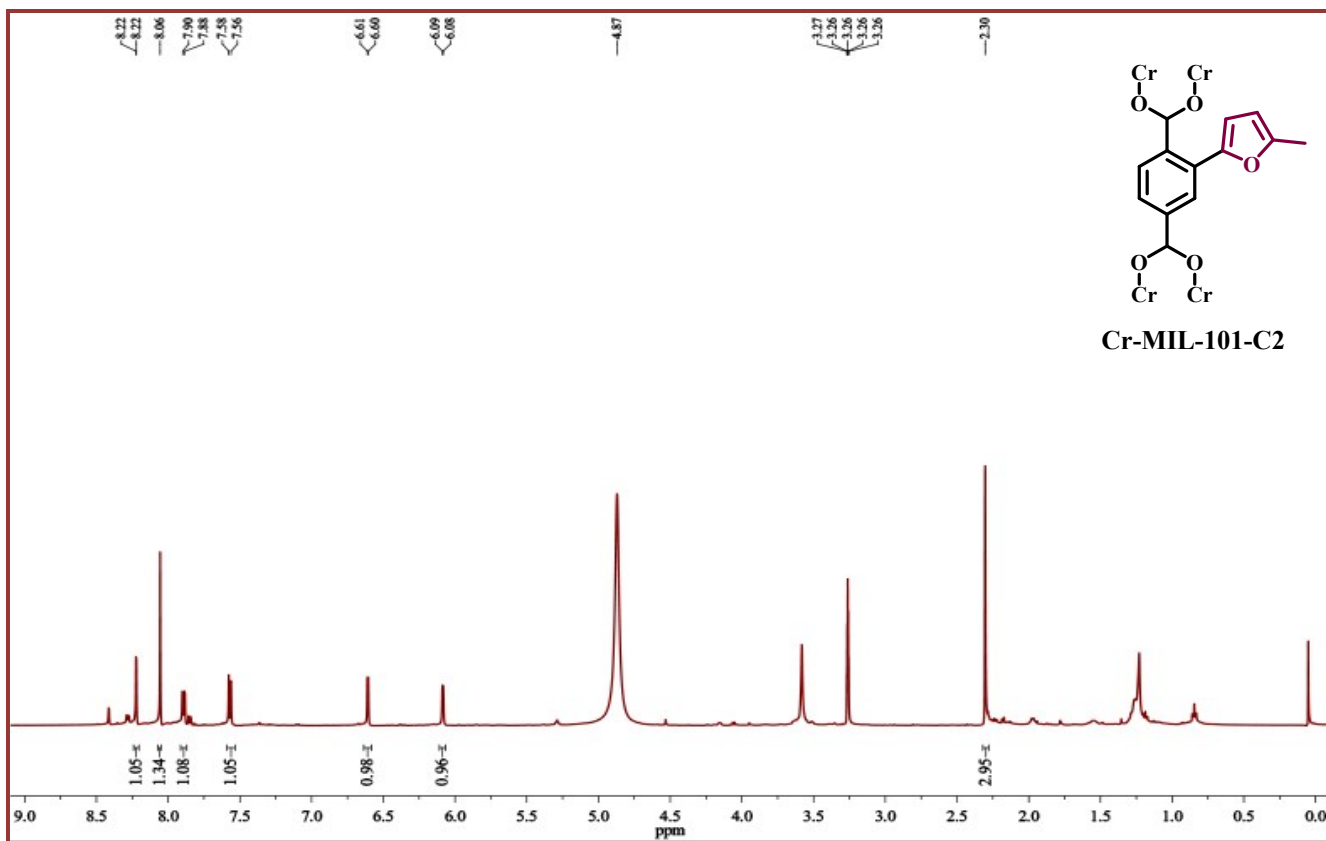
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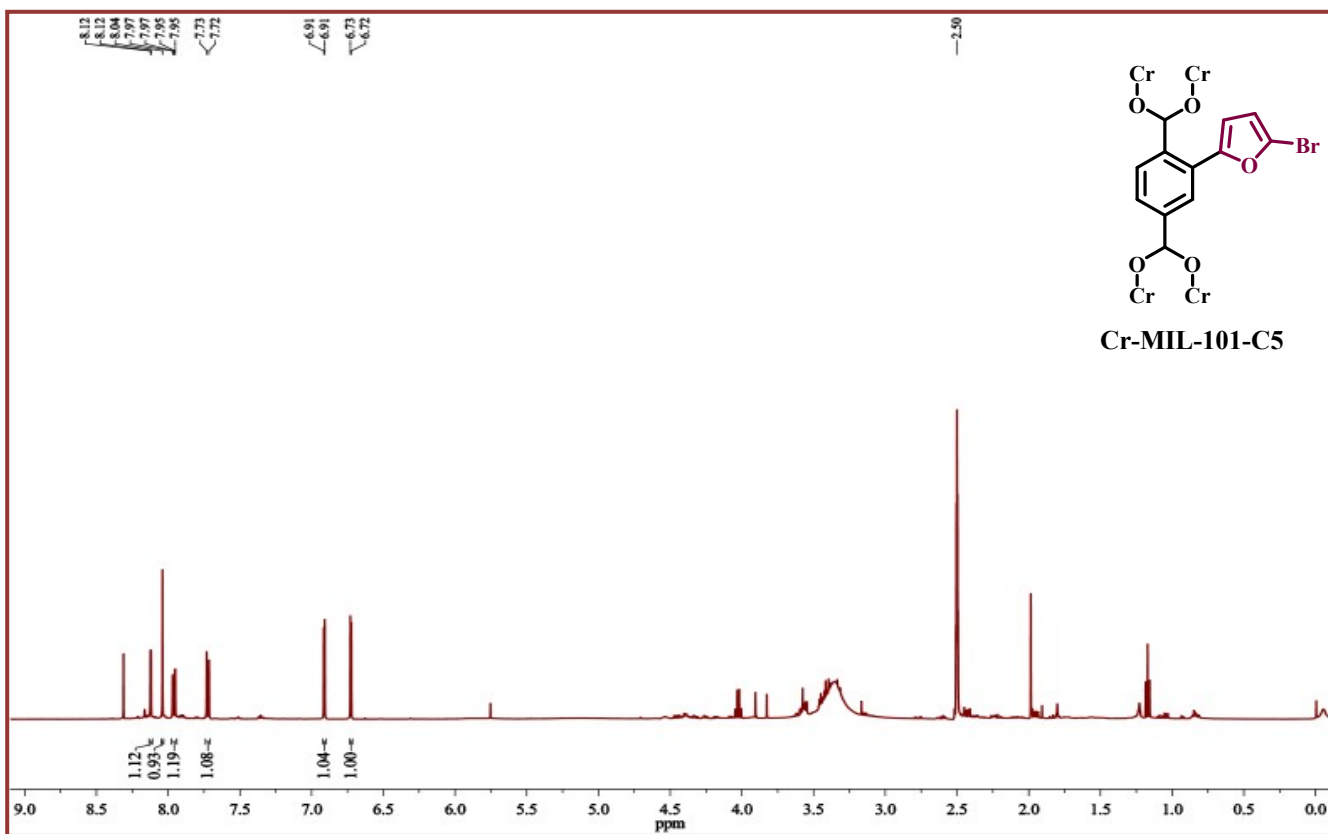
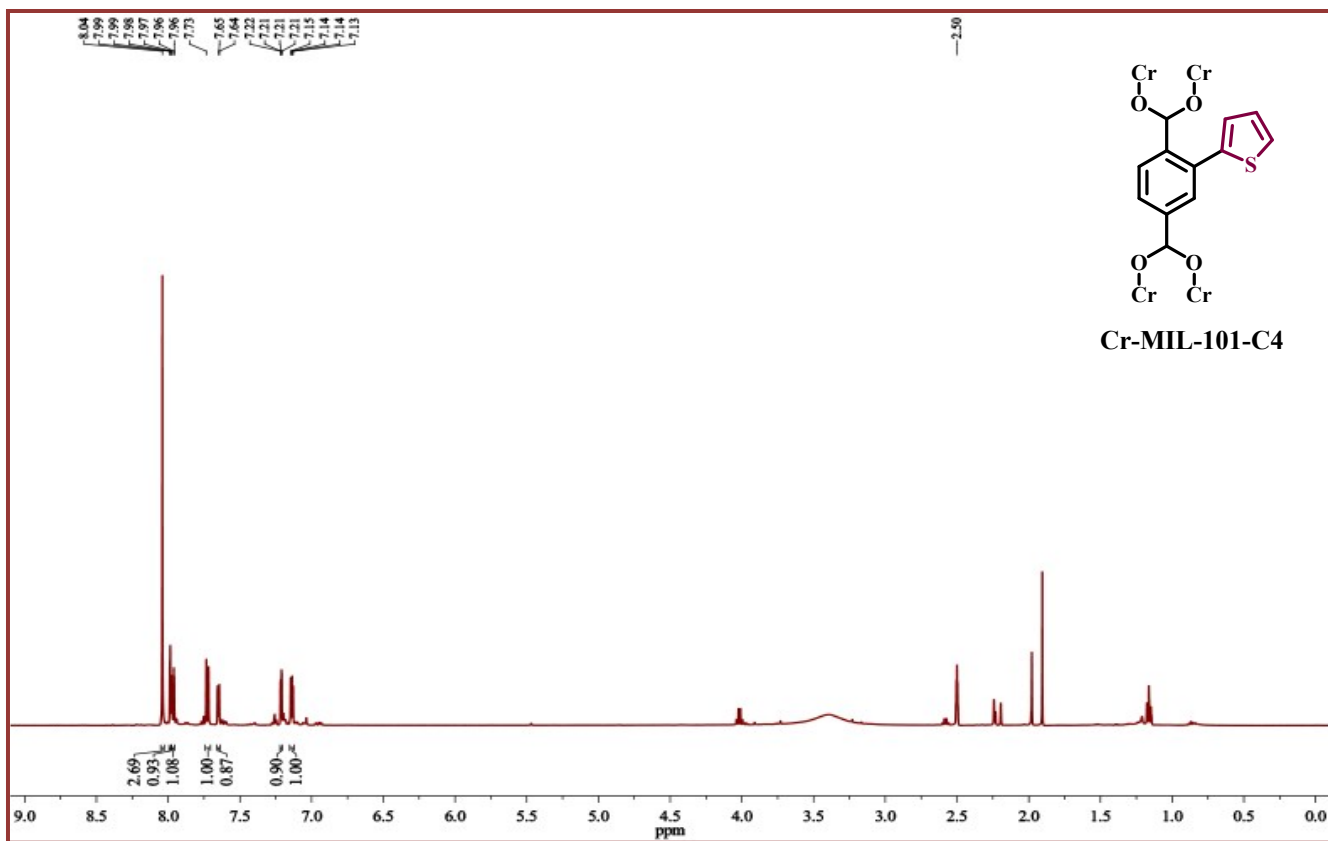




¹H NMR Spectra:







¹³C NMR Spectra:

