Supplementary Data

Synthesis and post-synthetic modification of MIL-101(Cr)-NH_2 *via* a tandem diazotisation process

Dongmei Jiang, Luke L. Keenan, Andrew D. Burrows* and Karen J. Edler

Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK.

E-mail:a.d.burrows@bath.ac.uk

Experimental

Chemicals

Chromium nitrate nonahydrate [$Cr(NO_3)_3{\cdot}9H_2O$, 99%], absolute ethanol (AR) and potassium iodide were bought from Fisher Scientific, whereas 2-aminobenzene-1,4-dicarboxylic acid ($H_2bdc\text{-}NH_2$, 99%), phenol (99%) and HCl (32%) and HBF_4 (48%) were purchased from Sigma-Aldrich Chemical Co.

Safety: Care must be taken with diazonium halides as they are potentially explosive. Although no indications of this were observed in the work reported herein, it is vital to be aware of the potential hazards.

Characterisation

The high resolution powder X-ray diffraction (PXRD) experiment was carried out on Beamline I11 at the Diamond Light Source, UK. A high brightness monochromatic beam of $E = 15$ keV (calibrated $\lambda = 0.825028$ Å) was used to collect the diffraction pattern. The PXRD measurements of the samples were also carried out on a Bruker AXS D8 Advance X-ray diffractometer with Cu Kα radiation ($\lambda = 1.542$ Å). Scanning Electron Microscopy (SEM) measurements were carried on a JEOL JSM6480LV instrument. The transmission electron microscope (TEM) images of the materials were taken on a JEOL IEM1200EXII instrument with an operating voltage of 120 kV. The particle sizes were manually analysed using ImageJ software, with more than 50 particles taken for analysis. The sorption isotherms of N_2 at 77 K and 273 K, and of CO_2 at 273 K were carried out on a BELSORP Mini-II (BEL Japan) instrument. The sample was degassed at 150 °C for 4 h prior to sorption. The specific surface areas of the samples were calculated by the Brunauer-Emmett-Teller method in the P/P_0 range of 0.05-0.1. The total volume was obtained by calculating the data at the relative pressure of 0.99. The selectivities of the materials for CO_2 were calculated from the single gas isotherms by dividing the CO_2 adsorption capacity by that of N_2 at the relative pressure of 1 or 0.1. Infrared spectra of the samples were measured using a PerkinElmer Spectrum 100 spectrometer equipped with an ATR sampling accessory.

Before measurement, the samples were dried under N_2 flowing gas at room temperature for 24 h. UV-visible spectra of the digested samples in basic aqueous solution ($NaOH/H_2O$) were carried out on a Varian 50 Probe UV-visible spectrophotometer. ^1H NMR spectra were recorded on a Bruker AV 300 spectrometer operating at 300 MHz or a Bruker Avance 400 spectrometer operating at 400 MHz. ^{19}F NMR spectra were recorded on a Bruker Avance 400 spectrometer operating at 376 MHz. The second order ^1H NMR spectrum for base-digested MIL-101(Cr)-F was analysed using the NMR simulator at nmrdb.org.[S1]

The samples were digested in $NaOD/D_2O$ for NMR measurements. Mass spectra were recorded on a Bruker microTOF (ESI-TOF) spectrometer.

Synthesis of MIL-101(Cr)-NH_2

In a typical experiment, $H_2bdc\text{-}NH_2$ (0.23 g, 1.26 mmol) and $Cr(NO_3)_3{\cdot}9H_2O$ (0.50 g, 1.25 mmol) were added to water (7 cm^3). The resulting suspension was stirred for 3 h at room temperature then heated under autogeneous pressure at 130 °C for 24 h in a Teflon-lined autoclave. After cooling to room temperature, the solid product was isolated as a green powder by centrifugation and washed five times with ethanol before drying under N_2 flowing gas at room temperature. The resulting solid material was denoted as MIL-101(Cr)-NH_2. The powder X-ray diffraction pattern for MIL-101(Cr)-NH_2 is shown in Figure S1, and both TEM and SEM images of the particles are shown in Figure S2. ^1H NMR ($NaOD/D_2O$): δ 7.24 (dd, J = 8.1, 1.3 Hz, 1H), 7.31 (d, J = 1.3 Hz, 1H), 7.74 (d, J = 8.1 Hz, 1H) (Figure S6a).

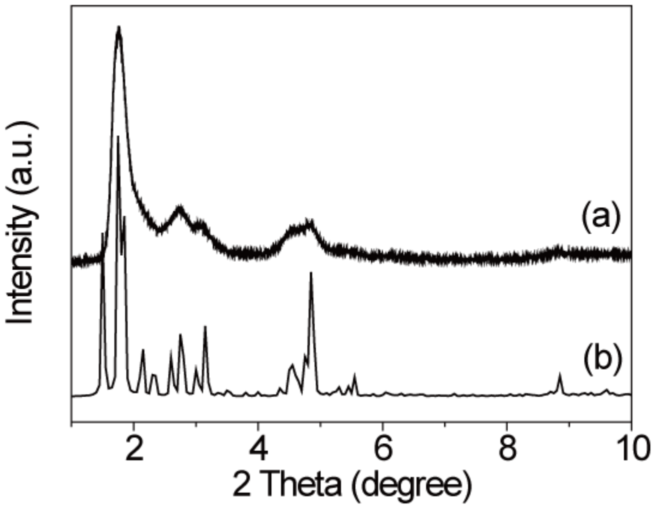

Figure S1. (a) High resolution PXRD pattern of MIL-101(Cr)-NH_2, (b) the simulated PXRD pattern calculated from the MIL-101(Cr) crystal structure.

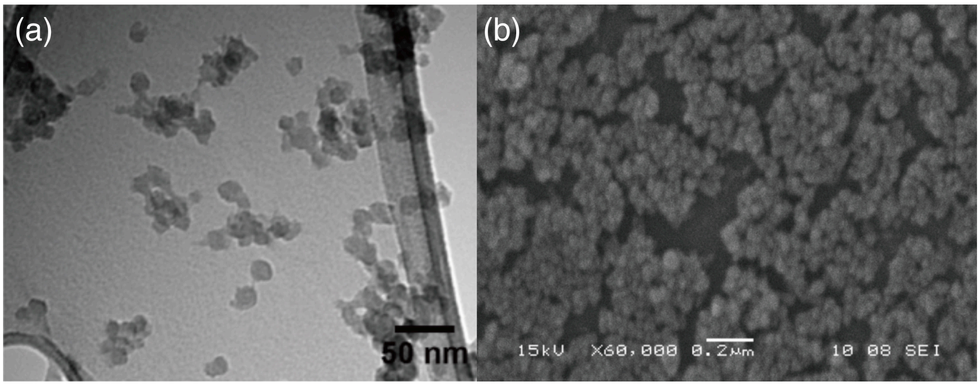

Figure S2 (a) TEM image and (b) SEM image of MIL-101(Cr)-NH_2.

Synthesis of iodo-functionalised MIL-101(Cr) (MIL-101(Cr)-I)

The synthesis was modified from a procedure reported by Vinod and co-workers.[S2] MIL-101(Cr)-NH_2 (0.075 g, 0.26 mmol NH_2 eq.) was suspended in 1:1 mixture of water and 32% conc. HCl (6 cm^3). The suspension was cooled to below 5 °C in an ice bath, diazotised by addition of an aqueous solution of $NaNO_2$ (0.045 g) in water (1.6 cm^3), and further stirred for 3 h at 0-5 °C. KI (0.260 g) in H_2O (9 cm^3) was slowly added into the solution and the reaction mixture was stirred at room temperature for 72 h. After this time, $NaHSO_3$ were added until the dark colour of the solution dissipated. The solid product was separated, soaked with 3 × 5 cm^3 water over 72 h, with fresh water added every 24 h, and triturated in a 10 cm^3 mixture of CH_2Cl_2:H_2O (1:1). The solid sample obtained was separated by centrifugation and washed with ethanol before drying under a flow of N_2 at room temperature (> 97% conversion). The resulting product was denoted as MIL-101(Cr)-I. ESI (negative ion): *m/z* 290.9161 (calc. 290.9154 for $[Hbdc\text{-}I]^-$, $C_8H_4IO_4^-$). The powder X-ray diffraction pattern for MIL-101(Cr)-I is shown in Figure S3b. ^1H NMR (NaOD/D_2O): δ 7.35 (d, $J = 8.0$ Hz, 1H), 7.87 (d, $J = 8.0$ Hz, 1H), 8.34 (s, 1H) (Figure S6b).

Synthesis of fluoro-functionalised MIL-101(Cr) (MIL-101(Cr)-F)

MIL-101(Cr)-NH_2 (0.075 g, 0.261 mmol NH_2 eq.) was suspended in 1:1 mixture of water and 48% conc. HBF_4 (6 cm^3). The suspension was cooled to below 5 °C in an ice bath, diazotised by addition of an aqueous solution of $NaNO_2$ (0.045 g) in water (1.6 cm^3), and further stirred for 2 h at 0-5 °C. This mixture was washed, by centrifuge, with deionised water and the dried sample heated at 100 °C for 18 h. The solid product was washed with 3 × 5 cm^3 MeOH over 72 h, with fresh MeOH added every 24 h. The solid sample obtained was separated by centrifugation before drying under a flow of N_2 at room temperature (> 95% conversion). The resulting sample was denoted as MIL-101(Cr)-F. ESI (negative ion): *m/z* 183.0113 (calc. 183.0099 for $[Hbdc\text{-}F]^-$, $C_8H_4FO_4^-$). The powder X-ray diffraction pattern for MIL-101(Cr)-F is shown in Figure S3c. ^1H NMR (NaOD/D_2O, 400 MHz): δ 7.43 (m, $J_{HH} = 1.2$ Hz, J_{HF} 10.9 Hz, 1H), 7.46 (m, $J_{HH} = 8.0$ Hz, $J_{HF} = 6.8$ Hz, 1H), 7.51 (m, $J_{HH} = 8.0$ Hz, $J_{HH} =$

1.2 Hz, 1H) (Figure S7). ^{19}F NMR (NaOD/D_2O, 376 MHz): δ –116.4 (dd, J_{FH} 6.8, 10.9 Hz).

Synthesis of azo dye-functionalised MIL-101(Cr) (MIL-101(Cr)-azo)

MIL-101(Cr)-NH_2 (0.075 g, 0.261 mmol NH_2 eq.) was suspended in 1:1 mixture of water and 32% conc. HCl (6 cm^3). The suspension was cooled to below 5 °C in an ice bath, diazotised by addition of an aqueous solution of $NaNO_2$ (0.045 g) in water (1.6 cm^3), and further stirred for 3 h at 0-5 °C. An aqueous solution of phenol (0.087 g, 0.92 mmol) and Na_2CO_3 (1.0 g) was added to the reaction mixture, the pH of which was adjusted to 7 by addition of further Na_2CO_3 (0.9 g). The resultant dark red mixture was stirred for 72 h at room temperature, after which the solid product was separated and washed with water and EtOH. The resulting solid material was dried under a flow of N_2 at room temperature and denoted MIL-101(Cr)-azo. The powder X-ray diffraction pattern for MIL-101(Cr)-azo is shown in Figure S3d. ^{1}H NMR (NaOD/D_2O, 400 MHz): δ 6.74 (d, *J* = 8.9 Hz, 2H, P1), 7.54 (d, *J* = 7.9 Hz, 1H, P5), 7.81 (d, *J* = 8.9 Hz, 2H, P2), 7.90 (dd, *J* = 1.6, 7.9 Hz, 1H, P4), 7.99 (d, *J* = 1.6 Hz, 1H, P3) (see Figure S8 for proton identities).

Characterisation of MIL-101(Cr)-$N_2^+BF_4^-$

A sample of MIL-101(Cr)-$N_2^+BF_4^-$, the intermediate in the synthesis of MIL-101(Cr)-F, was isolated and digested in NaOD/D_2O. ^{1}H NMR (NaOD/D_2O, 300 MHz): 7.29 (s, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H).

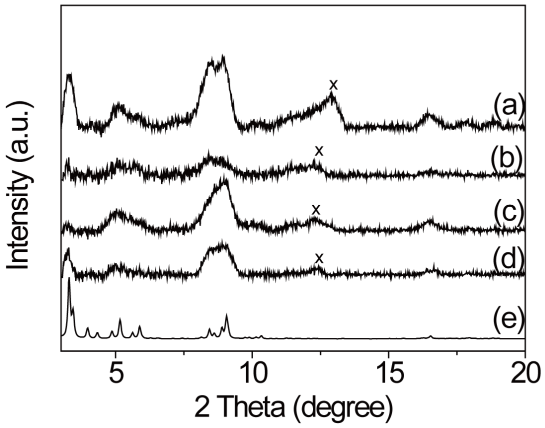

Figure S3 PXRD patterns of (a) MIL-101(Cr)-NH_2, (b) MIL-101(Cr)-I, (c) MIL-101(Cr)-F, (d) MIL-101(Cr)-azo and (e) the simulated PXRD pattern derived from the crystal structure of MIL-101(Cr) (λ = 1.542 Å).

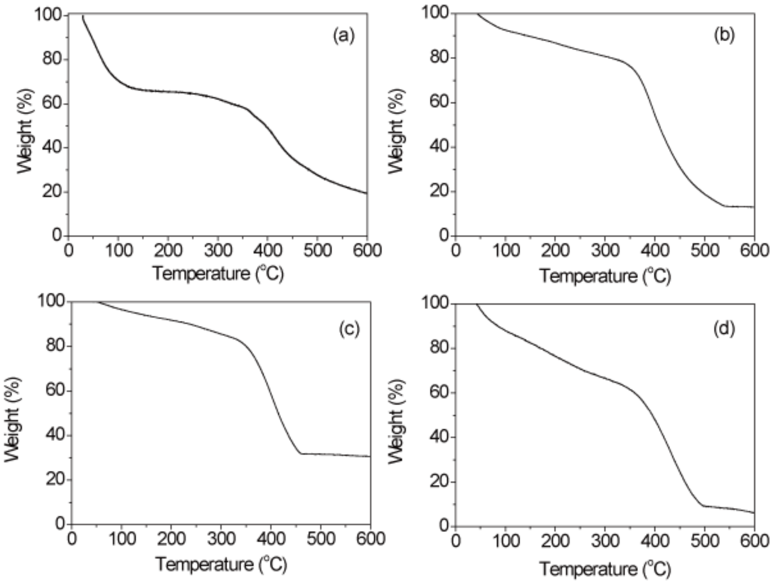

Figure S4 TG curves for (a) MIL-101(Cr)-NH_2, (b) MIL-101(Cr)-I, (c) MIL-101(Cr)-F, and (d) MIL-101(Cr)-azo.

Synthesis of $H_2bdc\text{-}N{=}N\text{-}C_6H_4OH$ [S3]

In a 50 cm^3 round-bottomed flask, H_2bdc-NH_2 (1.00 g, 5.52 mmol) was suspended in 32% conc. HCl (5 cm^3) at below 5 °C in an ice bath. An aqueous solution of $NaNO_2$ (0.74 g, 10.7 mmol) in water (10 cm^3), was slowly added over 30 min and the mixture was stirred for a further 1 h. An alkaline solution of phenol (1.00 g, 10.6 mmol) and NaOH (1.0 g) in water (10 cm^3) was added, during which a solid precipitate formed in the acidic reaction mixture. After stirring this reaction mixture solution overnight, the pH of the resulting reaction mixture was adjusted to pH 10 by addition of NaOH and the solid product dissolved in the reaction solution. The resultant dark red solution was again stirred overnight and then acidified with conc. HCl. The precipitate was separated by filtration, washed with 3 × 50 cm^3 water and dried at 100 °C. The crude solid was recrystallised from ethanol. Yield 1.499 g (95 %). ^{1}H NMR analysis showed a 2:1 *para*:*ortho* ratio of H_2bdc-N=N-C_6H_4OH isomers. The UV-visible spectrum (Figure S5) of the product dissolved in ethanol gave a strong adsorption peak at 354 nm deriving from the -N=N- group in the compound.[S3] ESI-MS (negative ion): *m/z* 285.0522 (calc. 285.0517 for [Hbdc-N=N-C_6H_4OH]$^-$, $C_{14}H_9N_2O_5^-$).

^{1}H NMR (NaOD/D_2O, 400 MHz): *para* isomer δ 6.74 (d, J = 8.9 Hz, 2H, P1), 7.54 (d, J = 7.9 Hz, 1H, P5), 7.81 (d, J = 8.9 Hz, 2H, P2), 7.90 (dd, J = 1.6, 7.9 Hz, 1H, P4), 7.99 (d, J = 1.6 Hz, 1H, P3); *ortho* isomer δ 6.62 (ddd, J = 1.5, 7.4, 7.6 Hz, 1H, O3), 6.77 (dd, J = 1.5, 7.8 Hz, 1H, O1), 7.10 (dd, J = 1.5, 7.4 Hz, 1H, O4), 7.19 (ddd, J = 1.5, 7.6, 7.8 Hz, 1H, O2), 7.50 (d, J = 7.7 Hz, 1H, O7), 7.77 (dd, J = 1.8, 7.7 Hz, 1H, O6), 7.84 (d, J = 1.8 Hz, 1H, O5) (see Figure S8 for proton identities).

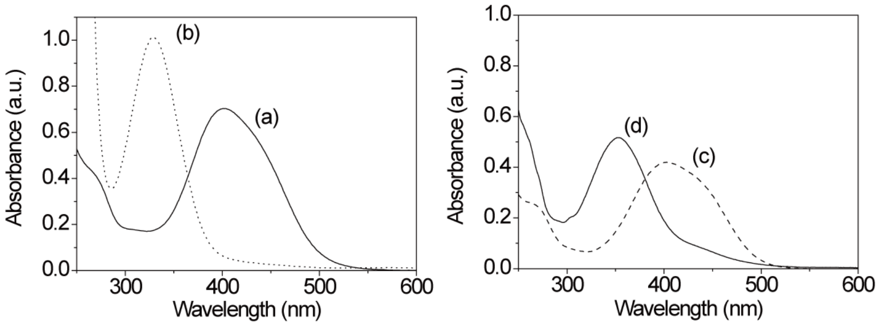

Figure S5 UV-visible spectra of (a) MIL-101(Cr)-azo digested in water at pH 10, (b) MIL-101(Cr)-NH_2 digested in water at pH 10, (c) H_2bdc-N=N-C_6H_4OH dissolved in water with pH 10, and (d) H_2bdc-N=N-C_6H_4OH dissolved in ethanol.

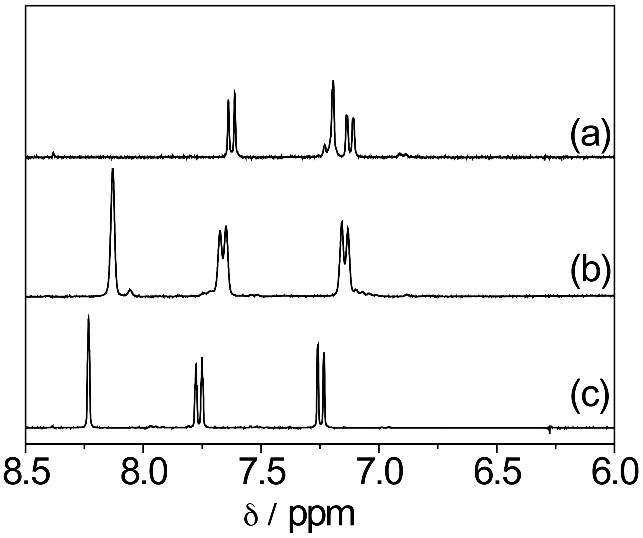

Figure S6 ^1H NMR spectra of the samples digested in the basic aqueous solution (NaOD/D_2O): (a) MIL-101(Cr)-NH_2, (b) MIL-101(Cr)-I, (c) H_2bdc-I.

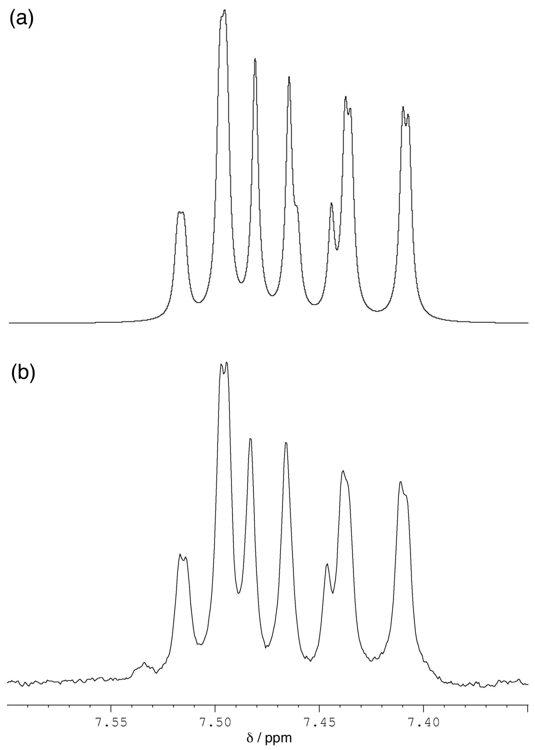

Figure S7 (a) Simulated and (b) experimental ^{1}H NMR spectra of MIL-101(Cr)-F digested in basic aqueous solution (NaOD/D_2O).

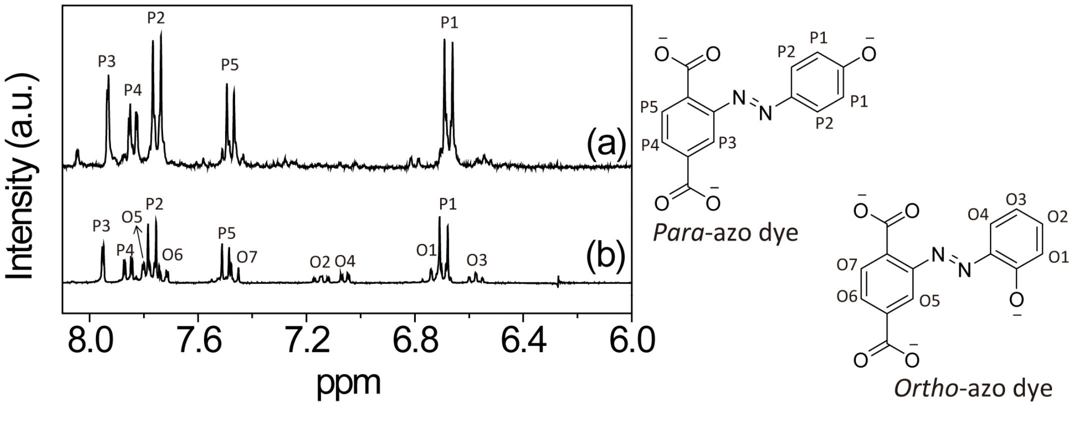

Figure S8 ^{1}H NMR spectra of the samples digested in basic aqueous solution (NaOD/D_2O): (a) MIL-101(Cr)-azo synthesised at pH 7, and (b) H_2bdc-N=N-C_6H_4OH.

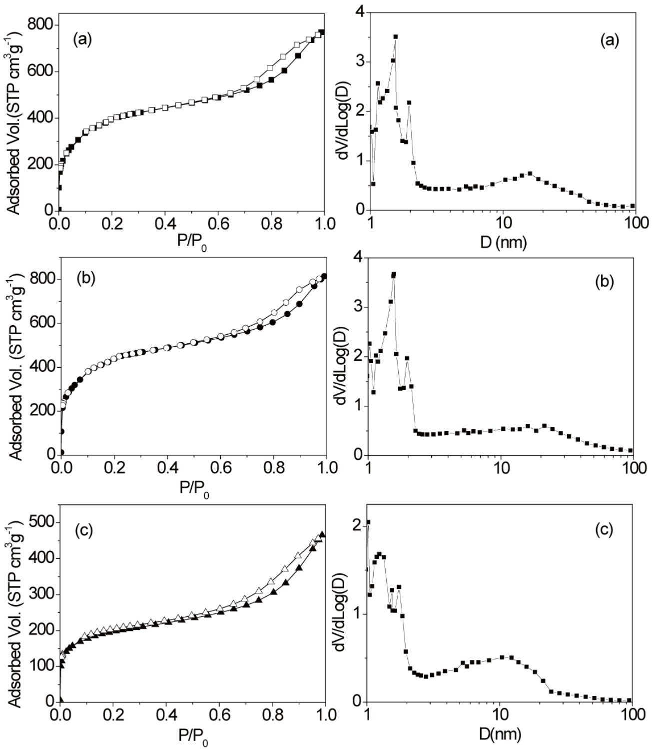

Figure S9 N_2 adsorption-desorption isotherms (left) and pore size distributions (right) for (a) MIL-101(Cr)-I, (b) MIL-101(Cr)-F, and (c) MIL-101(Cr)-azo.

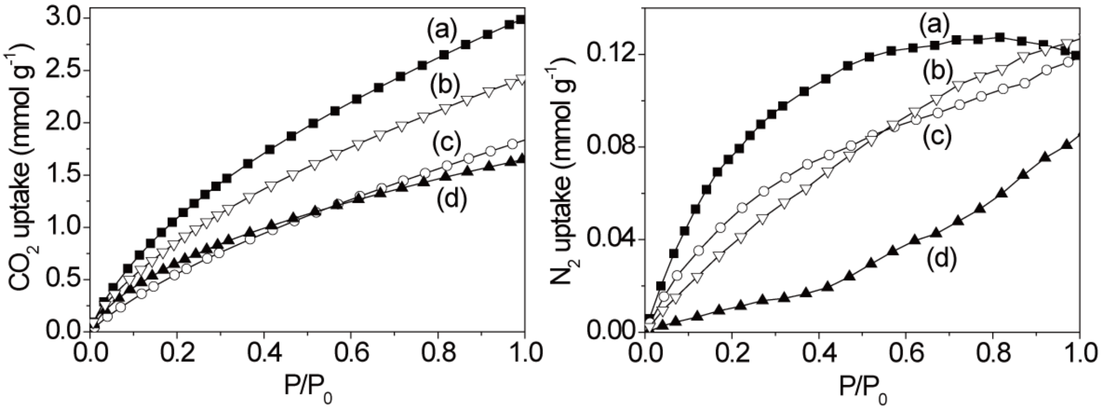

Figure S10 CO_2 (left) and N_2 (right) sorption for (a) MIL-101(Cr)-NH_2, (b) MIL-101(Cr)-F, (c) MIL-101(Cr)-I and (d) MIL-101(Cr)-azo.

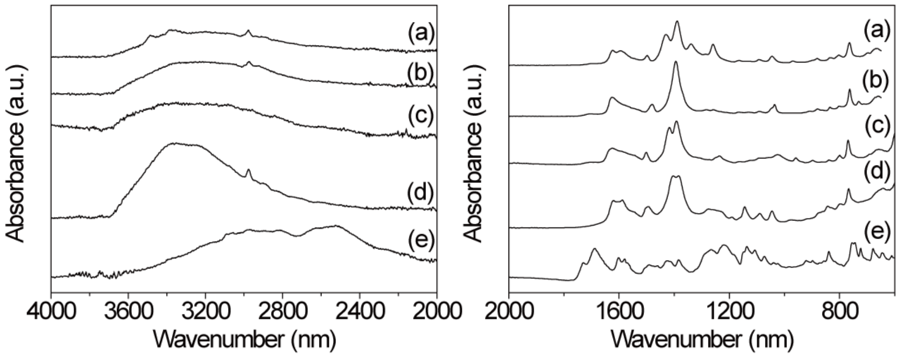

Figure S11 ATR-IR spectra of (a) MIL-101(Cr)-NH_2, (b) MIL-101(Cr)-I, (c) MIL-101(Cr)-F, (d) MIL-101(Cr)-azo, and (e) H_2bdc-N=N-C_6H_4OH.

References

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[S2] A. Kommreddy, M. S. Bowsher, M. R. Gunna, K. Botha and T. K. Vinod, *Tetrahedron Lett.*, 2008, **49**, 4378.

[S3] J. N. Ospenson, *Acta Chem. Scand.* 1950, **4**, 1351.