Supporting Information

Chemically Reprogrammable Metal Organic Frameworks (MOFs) based on Diels-Alder Chemistry

Sana Nayab,[a,b] Vanessa Trouillet,[f] Hartmut Gliemann,[e] Silvana Hurrle,[d] Peter G. Weidler,[e] Saadia Rashid Tariq,[b] Anja S. Goldmann,[c,d]* Christopher Barner-Kowollik,[c,d]* Basit Yameen[a]*

[a]Department of Chemistry and Chemical Engineering, SBA School of Science and Engineering Lahore University of Management Sciences, Lahore, Punjab 54792, Pakistan. Email: basit.yameen@lums.edu.pk

[b]Department of Chemistry, Lahore College for Women University, Jail Road, Lahore, Punjab54000, Pakistan

[c]School of Chemistry, Physics and Mechanical Engineering, Queensland University of Technology (QUT), 2 George Street, QLD 4000, Brisbane, Australia. a.goldmann@qut.edu.au, christopher.barnerkowollik@qut.edu.au

[d]Preparative Macromolecular Chemistry, Institut für Technische Chemie und Polymerchemie, Karlsruhe Institute of Technology (KIT), Engesserstrasse 18, 76128 Karlsruhe, Germany. Email: anja.goldmann@kit.edu, christopher.barner-kowollik@kit.edu

[e]Institute for Functional Interfaces (IFG), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

[f]Institute for Applied Materials (IAM), Karlsruhe Institute of Technology (KIT) and Karlsruhe Nano Micro Facility (KNMF), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

Materials

Iron (III) chloride-hexahydrate (98%), 1,4-benzenedicarboxylic acid (BDC, 98%), α-bromoisobutyryl bromide (98%), triethylamine (TEA, 99%), *N*-(4-chlorophenyl)-maleimide (Cl-Mal), *N,N*-dimethylformamide (DMF, 99%), dry dichloromethane (DCM, 99.8%), dry tetrahydrofuran (THF, 99.9%), chloroform (99%) and methanol were purchased from Sigma Aldrich, Germany. 2-aminoterephthalic acid (NH_2-BDC, 99%), were received from Alfa Aesar, Germany. Sodium iodide (NaI) was obtained from Fisher Scientific UK Limited, Triphenyl phosphine (TPP, ≥ 99%) was obtained from Merck Schuchardt OHG, Hohenbrunn Germany. Bis(cyclopentadienyl)nickel ($NiCp_2$, Nickelocene, 99%) was purchased from ABCR GmbH & Co KG, Germany. All chemicals and solvents were used as received without further purification. Br-Mal was prepared according to a literature procedure.[1] Triethylamine (TEA) was dried by refluxing overnight with calcium hydride followed by distillation and was stored under nitrogen.

Synthesis of NH_2-MIL-88B-Fe and ML-MIL-88B-Fe

NH_2-MIL-88B-Fe and ML-MIL-88B-Fe were synthesized as follows: NH_2-BDC (0.67 g) and $FeCl_3.6H_2O$ (1 g) and DMF (80 mL) were placed in a round bottom flask and sonicated to obtain a clear solution. The flask was kept at 140°C for 48 h. The resulting product was separated by centrifugation and washed with fresh DMF and chloroform, then suspended in chloroform overnight, and washed with chloroform, before being dried under vacuum overnight. The mixed linker based MOF (ML-MIL-88B-Fe) was prepared using a similar procedure as above except that 50mol% of NH_2-BDC was replaced with BDC.

Synthesis of Br Functionalized MOFs

The synthesis of Br functionalized MOFs were adapted from the method reported in literature.[2] NH_2-MIL-88B-Fe (0.5g) and ML-MIL-88B-Fe (0.5 g) were taken separately in dry DCM (10 mL). To these solutions, dry TEA (100 μL) and α-bromoisobutyryl bromide (75 μL) were added under inert atmosphere and stirred at ambient temperature for 24 h. The obtained products were washed with DCM and methanol and soaked in methanol for 24 h. The particles were subsequently dried under vacuum at ambient temperature after washing with methanol.

Synthesis of Cp Terminated MOFs

The synthesis of Cp terminated MOFs was performed at ambient temperature in a glovebox under N_2 (g) atmosphere using a previously reported method.[3,4] Br-MIL-88B-Fe (0.5 g) and Br-ML-MIL-88B-Fe (0.5 g) were taken separately in dry THF (20 mL), to which NaI (0.069 g), TPP (0.040 g) and $NiCp_2$

(0.058 g) were added. The reaction mixtures were stirred at ambient temperature for 24 h. The particles were washed with THF and methanol and soaked in methanol for 24 h. After 24 h, the particles were washed with methanol and dried under vacuum at ambient temperature.

Conjugation of Br-Mal to Cp Terminated MOFs via Diels-Alder Ligation

Diels-Alder ligation was employed utilizing the reported procedure.[5] Cp-MIL-88B-Fe (0.2 g) and Cp-ML-MIL-88B-Fe (0.2 g) were placed in separate flasks to which chloroform (3 mL) and Br-Mal (0.1 g) were added under inert atmosphere (N_2). The solutions were stirred at ambient temperature for 24 h. The products were washed with chloroform and methanol and dried under vacuum at ambient temperature.

Retro Diels-Alder Reactions

The retro Diels-Alder reactions were performed by heating the MOFs (obtained after DA conjugation) at 150 °C under vacuum for 24 h.

Conjugation of Cl-Mal to Cp Terminated MOFs via Diels-Alder Ligation

The second Diels-Alder cycloaddition reactions were performed to support the hypothesis that the MOFs after rDA retained their activity and could be reused in a second DA conjugation. MOFs (obtained after rDA) (0.1 g) and Cl-Mal (0.05 g) were added to chloroform (1.5 mL) under inert atmosphere (N_2) in separate flasks. The solutions were stirred at ambient temperature for 24 h. The products were washed with chloroform and methanol and dried under vacuum at ambient temperature.

Characterization

X-ray Diffraction (XRD)

Each sample was characterized by using a Bruker D8 Advance equipped with a Si-strip detector (PSD Lynxeye©; position sensitive detector) with Cu $K_{\alpha1,2}$ radiation ($\lambda = 0.15418$ nm) in θ–θ geometry, and a variable slit on primary circle. Scans were run with a step width of 0.024° in the 3-40 2θ range. Lattice parameters were determined using the Bruker program TOPAS 5.0[6] and applying the Pawley[7] fit routine with space group $P6_3/mmc$ (#194).

X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy measurements were performed using a K-Alpha+ XPS spectrometer (ThermoFisher Scientific, East Grinstead, UK). All samples were analyzed using a microfocused, monochromated Al Kα X-ray source (400 µm spot size). The kinetic energy of the electrons was measured by a 180° hemispherical energy analyzer operated in the constant analyzer energy mode (CAE) at 50 eV pass energy for elemental spectra. Data acquisition and processing using the Thermo Avantage software is described elsewhere.[8] The spectra were fitted with one or more Voigt profiles (BE uncertainty: ±0.2eV). The analyzer transmission function, Scofield sensitivity factors[9] and effective attenuation lengths (EALs) for photoelectrons were applied for quantification. EALs were calculated using the standard TPP-2M formalism.[10] All spectra were referenced to the C 1s peak of hydrocarbon at 285.0 eV binding energy controlled by means of the well-known photoelectron peaks of metallic Cu, Ag, and Au, respectively.

Thermogravimetric Analysis (TGA)

Thermogravimetric measurements were carried out on a TGA Q50 V6.2 Build 187 thermogravimetric analyzer. Samples were heated at 10 °C min^{-1} from ambient temperature to 700 °C under nitrogen flow.

Differential Scanning Calorimetry (DSC)

DSC analysis were performed using DSC Q100 V8.2 Build 268 instrument over a temperature range from ambient temperature to 150 °C with heating rate of 10 °C min^{-1}.

Scanning Electron Microscopy (SEM)

Morphological analysis was carried out using FEI Nova NanoSEM 450 Scanning Electron Microscope.

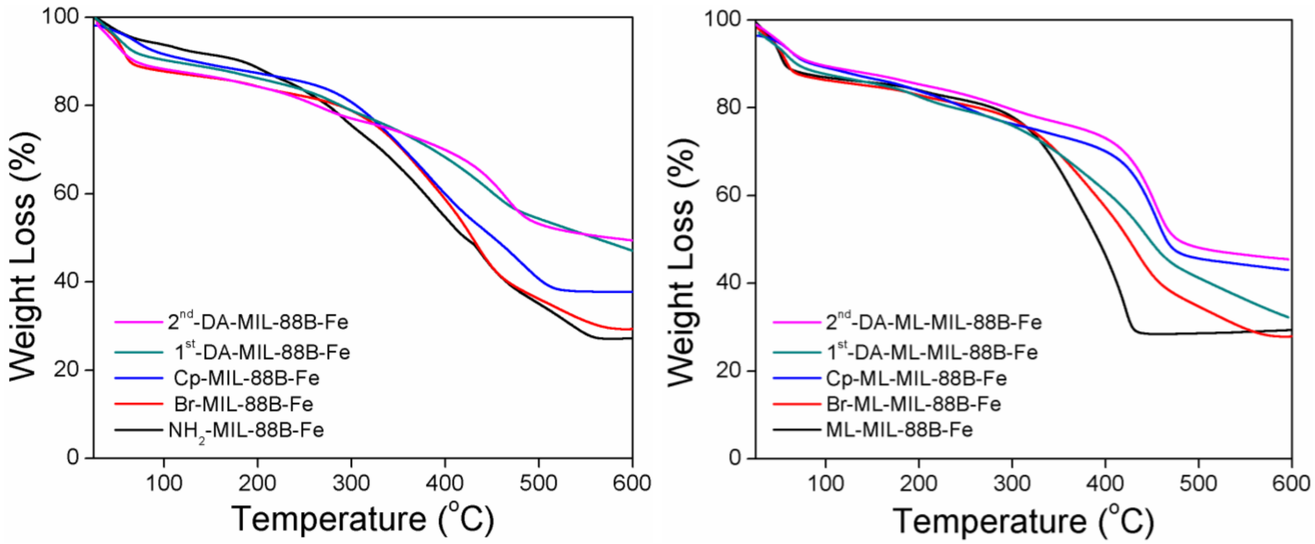

Figure S1. TGA thermograms of NH_2-MIL-88B-Fe (left) and ML-MIL-88B-Fe (right).

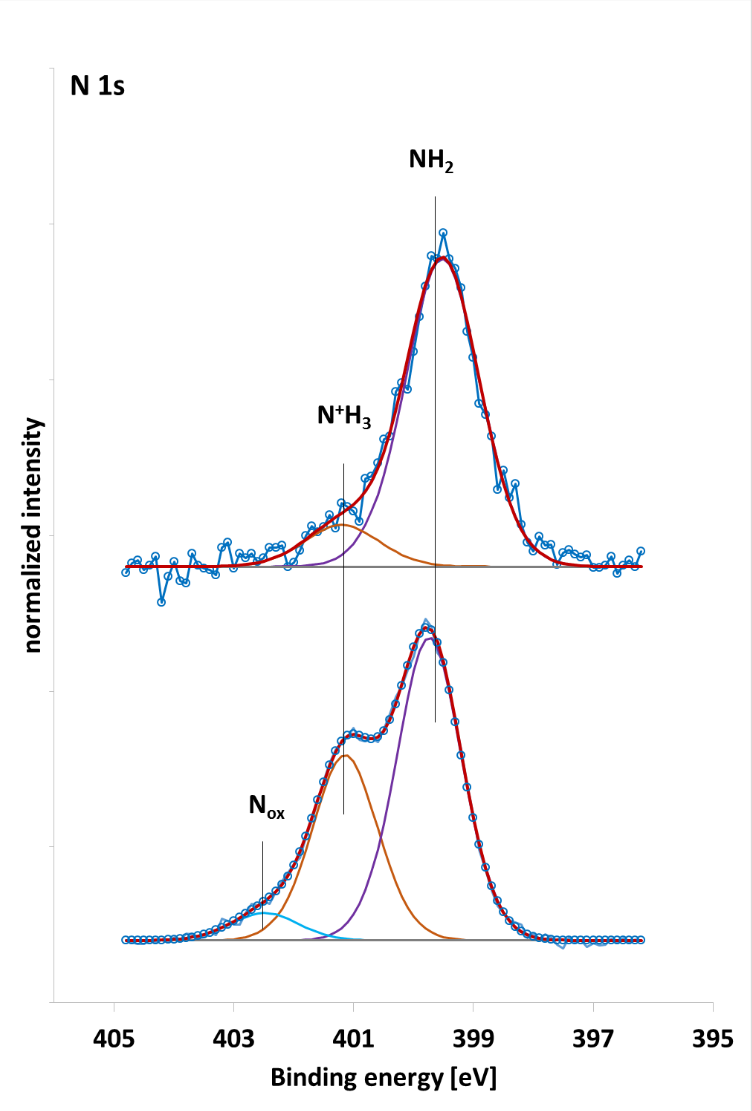

Figure S2. N 1s XPS spectra of NH$_2$-MIL-88B-Fe (bottom) and ML-MIL-88B-Fe (top).

We monitored the progress of the PSM reactions by following the appearance of specific XPS signals associated with our hetero atom markers (Br and Cl). The bar charts depicted in Figure S3 provides information on the concentration of bound bromine and chlorine in the different samples, generated as a result of different PSM reactions. The data provided in these charts helps in better appreciating the quantitative increase and decrease of Br and Cl contents, and validate the success of PSM reactions within both MOF platforms. While monitoring the change in the Br signal, we focused on the relevant C-Br component (i.e., covalently bound bromine) using the Br $3d_{3/2}$ signal at 70.1 eV, since the other signal at 68.0 eV corresponds to the captured Br^- and does not contribute towards the effectiveness of the reactions.

The data provided in the bar charts in Fig. S3 suggest that the mixed linker approach is more effective than the one using only an amino group linker. This is supported by our observation that only for the mixed linker MOF platform the PSM reactions resulted in the functionalization followed by the complete substitution of the covalently bound bromine (Fig. S3 right). The XPS data suggest a yield of 100 % for the transformation of bromo groups of Br-ML-MIL-88B-Fe to the Cp groups resulting in the formation of Cp-ML-MIL-88B-Fe. The 1st DA PSM reaction on Cp-ML-MIL-88B-Fe employing a Br group bearing maleimide molecule resulted in the appearance of Br signal that again completely disappeared during the rDA PSM reaction, indicating a 100% yield of the rDA reaction and suggesting a complete recovery of the Cp groups ready for a second DA reaction. While considering these estimations, we caution the reader to reflect upon the sampling depth of XPS analysis, which is close to 10 nm from the sample surface.

In case of the MOF platform synthesized by using only the amino group bearing linker, the transformation of Br into Cp groups indicate a conversion degree of close to 80% (Fig. S3, left). The XPS data also reveal (Fig. S3, left) a complete replacement of Br by Cl during the 2nd DA reaction, where a Cl functionalized maleimide molecule was employed.

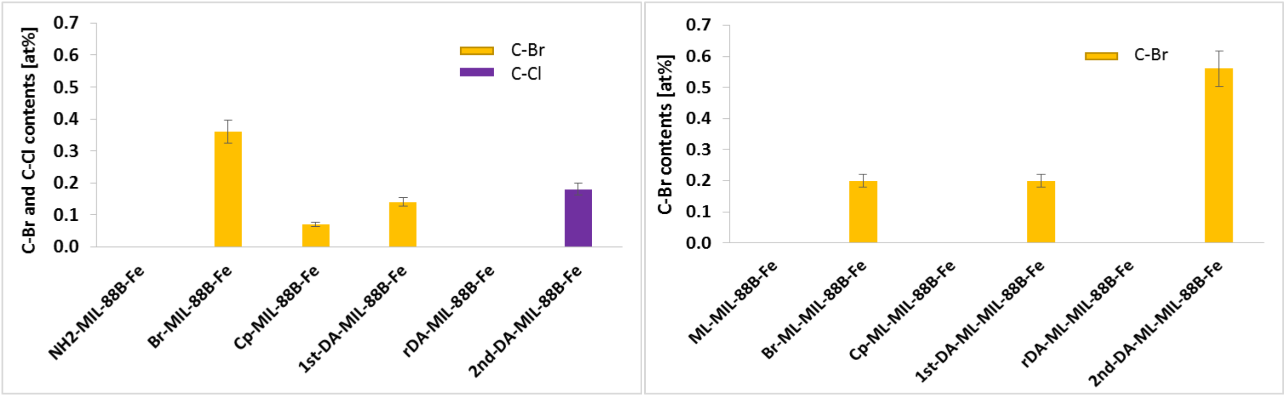

Figure S3. Variation in the concentration of the covalently bound Br and Cl during the PSM reactions, estimated based on XPS data obtained on the MOF synthesized from an amine group bearing linker (left) and the MOF synthesized from the mixed linker approach (right). Only the relevant C-Br component (covalently bound bromine) with Br 3d$_{3/2}$ at 70.1 eV is depicted since the other signal at 68.0 eV refers to the presence of captured Br$^-$ and does not contribute towards the effectiveness of the reactions.

Table S1. Calculated cell parameters of NH_2-MIL-88B-Fe and ML-MIL-88B-Fe; before modification and after incorporating of the variable functional groups.

MOFs	**a [Å]**	**c [Å]**	**Space Groups**	**V [$Å^3$]**
NH_2-MIL-88B-Fe	10.8688 ±0.0026	19.1469 ±0.0080	$P6_3/mmc$	1958.7524
Br-MIL-88B-Fe	11.0117 ±0.0021	19.1575 ±0.0066	$P6_3/mmc$	2011.7323
Cp-MIL-88B-Fe	11.0911 ±0.0016	19.3640 ± 0.0040	$P6_3/mmc$	2062.8241
1st-DA-MIL-88B-Fe	10.9888 ±0.01620	19.1029 ±0.0233	$P6_3/mmc$	1997.6747
2nd-DA-MIL-88B-Fe	11.0499 ±0.0031	19.1113 ±0.0058	$P6_3/mmc$	2020.8501
ML-MIL-88B-Fe	10.4478 ±0.0012	19.1470 ±0.0034	$P6_3/mmc$	1809.9573
Br-ML-MIL-88B-Fe	10.7465 ±0.0008	19.2164 ±0.0027	$P6_3/mmc$	1921.8691
Cp-ML-MIL-88B-Fe	11.0108 ±0.0022	19.1392 ±0.0059	$P6_3/mmc$	2009.4495
1st-DA-ML-MIL-88B-Fe	10.9733 ±0.0033	19.0878 ±0.0081	$P6_3/mmc$	1990.4509
2nd-DA-ML-MIL-88B-Fe	10.9910 ±0.0074	19.1208 ±0.0193	$P6_3/mmc$	2000.3071

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