

Supplementary Information

“Direct Synthesis of non-breathing MIL-53 (Al)(ht) from a Terephthalate-based Ionic Liquid as Linker Precursor”

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1 Chemicals

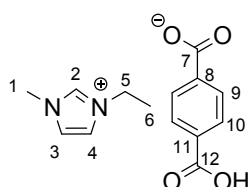
An overview of the chemicals used throughout this work, their purity and respective supplier is given in Table S1. All chemicals were used, if not noted otherwise, without further purification.

Table S1: Listing of used chemicals.

Chemical	Supplier	Purity	CAS Number
Terephthalic acid	Merck KGaA	>98.0 %	100-21-0
Aluminium nitrate nonahydrate	Sigma Aldrich	>98.0 %	7784-27-2
Methanol	Sigma Aldrich	>99.9 %	67-56-1
Ethanol	Sigma Aldrich	>99.8 %	64-17-5
Dimethylformamide	Fluka	>98,0 %	68-12-2
1-ethyl-3-methylimidazolium methylcarbonate solution, 30% in methanol	Proionic GmbH	-	251102-25-7

2 Experimental details on syntheses and analyses

2.1 Synthesis of 1-ethyl-3-methylimidazolium hydrogen terephthalate [EMIM][Hbdc]



Under argon, 5.91 g (35.6 mmol, 1 eq.) of terephthalic acid (H_2bdc) were submitted to a three neck flask and 22.07 g (35.6 mmol, 1 eq.) of a 30 % solution of 1-ethyl-3-methylimidazolium methylcarbonate in methanol was added dropwise.

Strong foaming and gas evolution was observed. After 24 h reflux at 50 °C, methanol was removed and [EMIM][Hbdc] was collected as white precipitate. It was washed with cold ethanol, and dried *in vacuo* for 2 days at 60 °C.

Yield: 9.63 g (34.9 mmol, 98 %).

T_{decomposition}: 279.9 °C

¹H-NMR (DMSO-d₆, 400 MHz): δ [ppm] = 9.24 (s, 1H, **2**), 7.81 (s, 4H, **9/10**), 7.74 (s, 1H, **3**), 7.66 (s, 1H, **4**), 4.14 (q, 2H, J = 7.6 Hz, **5**), 3.80 (s, 3H, **1**), 1.36 (t, 3H, J = 7.2 Hz, **6**).

¹³C-NMR (DMSO-d₆, 100 MHz): δ [ppm] = 168.68 (s, 2C, **7/12**), 138.84 (s, 1C, **2**), 137.10 (s, 2C, **8/11**), 128.95 (s, 4C, **9/10**), 124.07 (s, 1C, **3**), 122.47 (s, 1C, **4**), 44.59 (s, 1C, **5**), 36.16 (s, 1C, **1**), 15.67 (s, 1C, **6**).

2.2 Synthesis of is-MIL-53

415 mg (1.5 mmol) of [EMIM][Hbdc] were suspended in 15 mL of DMF in a 25 mL screw-cap glass bottle. After 1 h stirring at room temperature, 850 mg (2.25 mmol) of Al(NO₃)₃ · 9 H₂O were added and the mixture was stirred for additional 30 min at room temperature for complete dissolution of all components. Thereafter, the stirring bar was removed and the capped bottle was placed in a preheated convection oven at 130 °C for 48 h. After cooling to room temperature, the voluminous white precipitate was separated by centrifugation. Soxhlet extraction was performed for 24 h with ethanol before drying at ambient conditions and subsequently at 130 °C for 24 h.

2.3 Synthesis of MIL-53

The hydrothermal synthesis of conventional MIL-53(Al) was carried out following a literature procedure [S1].

3 Instruments used for this study

The ^{27}Al -MAS-NMR-spectra have been recorded on an Agilent V500WB spectrometer at 130.227 MHz and a spinning frequency of 15 kHz.

Nitrogen physisorption isotherms were measured with a Micromeritics ASAP 2000 with micropore option at -196 °C.

For the measurement of hydrogen sorption isotherms, a Rubotherm IsoSORP magnetic suspension balance with automated gas dosing system was used.

SEM analysis was carried out using a Carl Zeiss ULTRA 55 field emission scanning electron microscope.

All liquid NMR spectra were recorded on a 400 MHz Jeol ECX 400 spectrometer at room temperature using DMSO- d_6 as the solvent.

Thermogravimetric Analysis was performed on a SETSYS Evolution TGA© from SETARAM Instrumentation. Helium was used as carrier gas. The applied heating rate was 10 Kelvin/minute in a range from 30 to 900 °C.

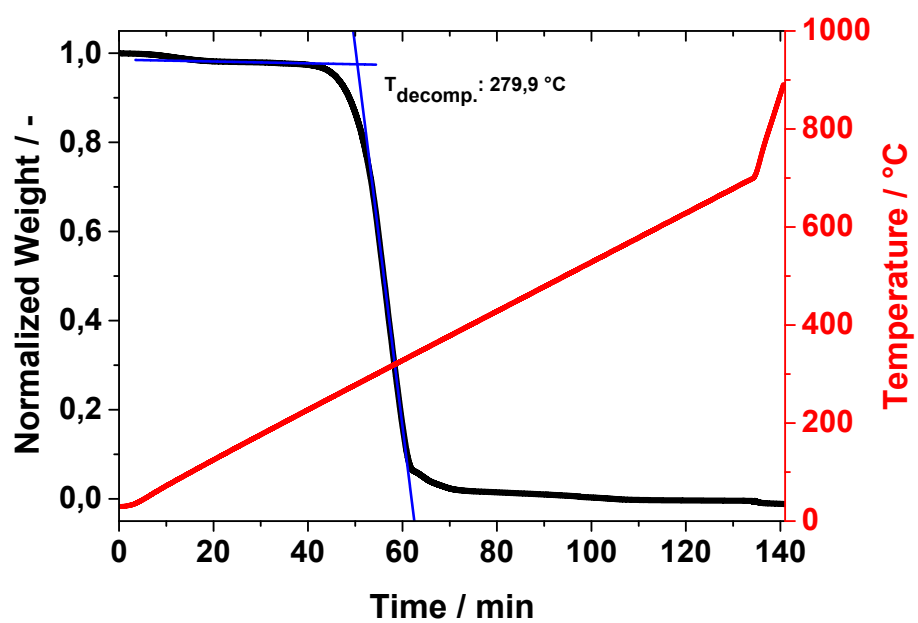


Figure S1: Thermogram of [EMIM][Hbdc].

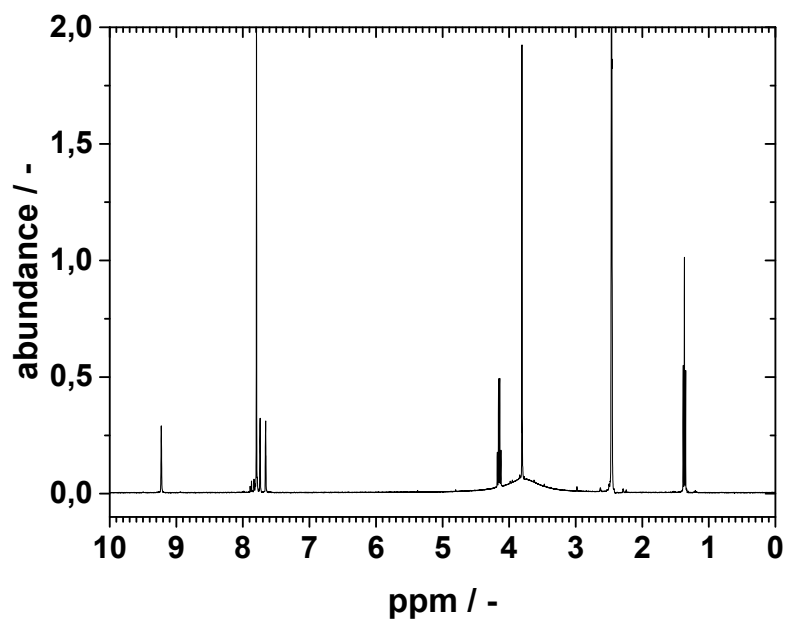


Figure S2: ^1H -NMR spectrum of [EMIM][Hbdc].

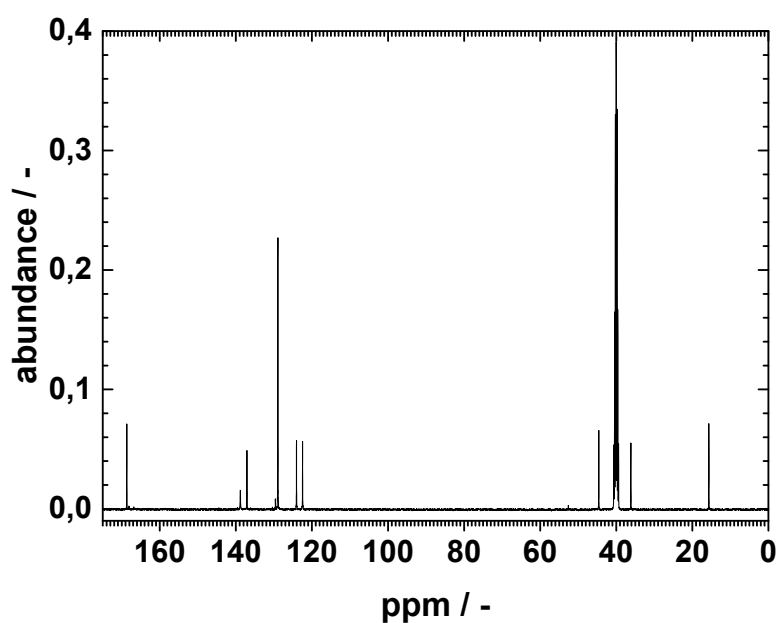


Figure S3: ^{13}C -NMR spectrum of [EMIM][Hbdc].

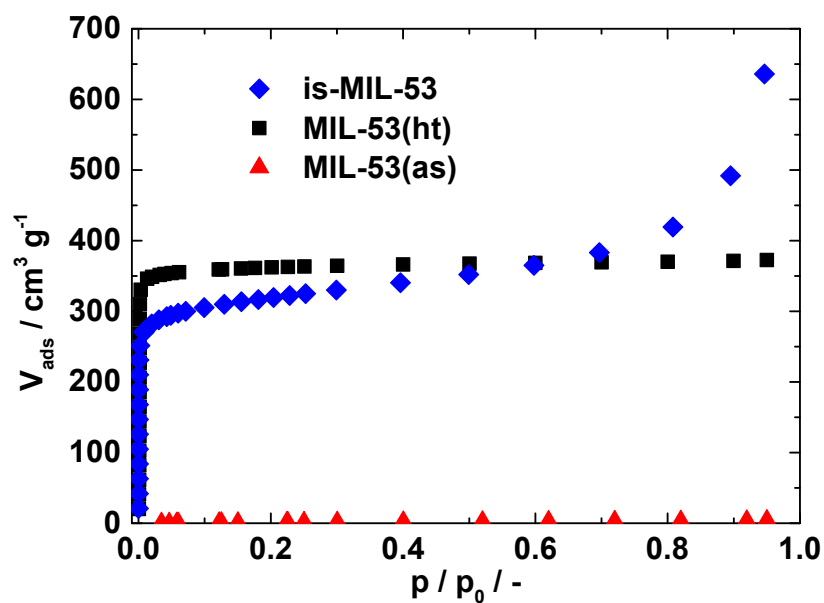


Figure S4: Nitrogen sorption isotherms of hydrothermally synthesized MIL-53(Al) before (as) and after (ht) calcination compared to as-synthesized [EMIM][Hbdc] derived is-MIL-53(Al).

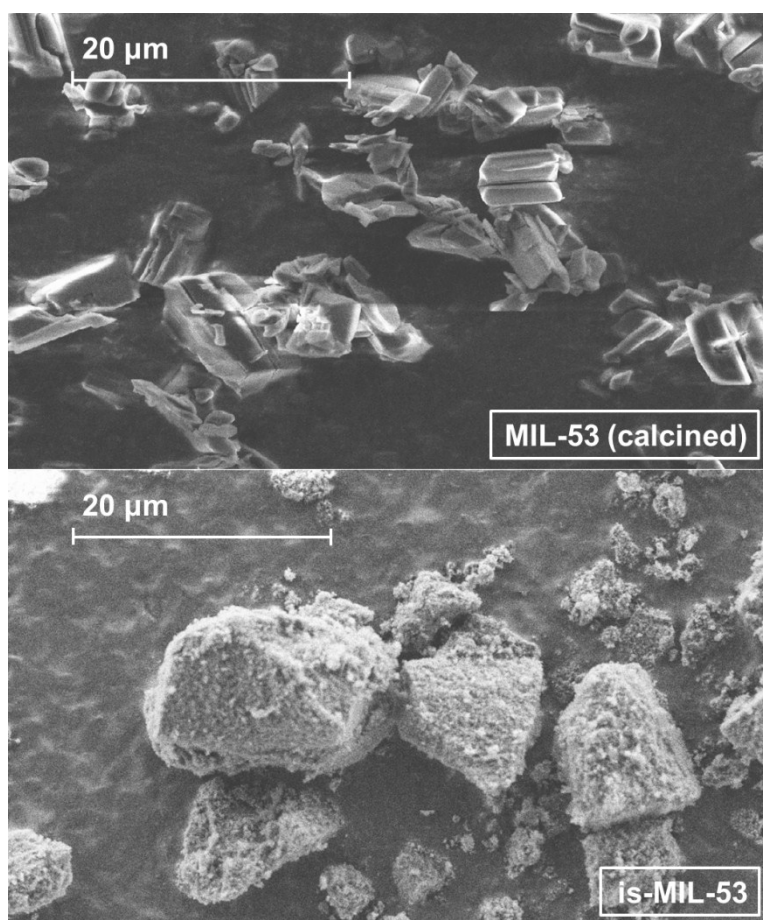


Figure S5: SEM-pictures of hydrothermally synthesized MIL-53 after calcination and as synthesized is-MIL-53.

Table S2: Elemental Analysis.

MOF	C [%]	H [%]	N [%]
MIL-53(Al) calc.	46.17	2.42	0
is-MIL-53	32.45	2.39	0.12
MIL-53(Al) / γ -AlO(OH) calc.	35.84	2.26	0