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Supporting Information for

Influence of 1-methyl-3-octylimidazolium chloride on MIL-53(Al) crystallinity and particle size

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Experimental

Materials

All materials were used as received. $Al(NO_3)_3 \cdot 9H_2O$ (99%), 1,4-benzenedicarboxylic acid (H_2BDC, 99%), *N,N*-dimethylformamide (DMF, 99.8%), dichloromethane (DCM, 99.6%), and sodium hydroxide (NaOH, 97%) were purchased from Thermo Fischer. OmimCl (97%), ethanol (EtOH, 200 proof), acetone (99.5%) and nitric acid (68-70%) were purchased from Fisher Scientific. Disodium maleate (99%) was purchased from TCI chemicals. D_2O (99.9% atom D) was purchased from Cambridge Isotopes Laboratory. Solvothermal growth was conducted in a 23 mL Teflon-lined Parr Acid Digestion Vessel (hereon referred to as the autoclave) purchased from Parr Instrument Company.

Hydrothermal Growth of MIL-53(Al)

Pure MIL-53(Al) was synthesized according to methods previously described in the literature.[1] $Al(NO_3)_3 \cdot 9H_2O$ (1.30 g) and H_2BDC (0.288 g) were mixed in HPLC grade water (5 mL) under vigorous stirring in a 23 mL autoclave, which was sealed and heated in an oven at 200 °C for 24 h, then cooled naturally to room temperature. The white powder was collected by centrifugation in water at 10000 rpm for three 5-minute cycles, then calcined at 400 °C overnight to yield a white or light-yellow powder.

A certain volume fraction of OmimCl (0.05%, 0.10%, 0.15%, 0.20%, 0.50%, 1.0%, 5.0%, and 10%) was dissolved in the synthesis solvent to investigate the effect of OmimCl on MOF crystallization. For MIL-53(Al), two separate experiments were carried out where hydrothermal growth was halted at specific times of 6, 12, and 18 h with or without 0.20% v/v OmimCl. The purification and calcination procedure is identical for all experiments.

XRD of MIL-53(Al) Crystals

XRD patterns of MIL-53(Al) crystals were acquired on a Rigaku MiniFlex 600 X-ray diffractometer using a HyPix-400-MF 2D hybrid pixel array detector using CuKα wavelength (λ = 1.5406 Å) at 40 kV and 15 mA. A scan step of 0.02°/step and a scan rate of 5°/min were used. The average crystallite sizes for MIL-53(Al) were calculated directly on the SmartLab Studio II software based on the three most intense XRD peaks (*i.e.*, the (200), (110), and $(11\bar{1})$ reflections), then the average and standard deviation were recorded.

SEM of MIL-53(Al) Crystals

1 mg/mL suspensions of MIL-53(Al) powder in ethanol were prepared for SEM samples. Glass coverslips were cleaned by sequential sonication in 30% nitric acid, acetone, and ethanol for 15 min and dried under a nitrogen flow. Then, 50 μL of the MIL-53(Al) suspension was spin-coated onto a clean glass coverslip at 5000 rpm for 1 min. Following spin-coating of the MIL-53(Al) suspension, the glass coverslips were dried at 50 °C overnight under vacuum. The glass coverslips were affixed to SEM sample stubs with carbon tape. SEM images of MIL-53(Al) crystals were acquired on a Tescan Vega3 LMU scanning electron microscope on secondary electron variable pressure mode at 15 Pa pressure with an accelerating voltage of 8 kV. Particle size measurements for MIL-53(Al) were performed on 25-40 well-defined, separated particles on average and the standard deviation of the size distribution was taken as the polydispersity. For more precise measurements to determine the particle size during different times of growth, ImageJ software was used to analyze 45-60 particles to generate histograms on the size distribution of the crystals. Pixel count conversions were done based on the SEM scale bar and converted into the length of each crystal on a given SEM image.

ATR-FTIR of MIL-53(Al) Crystals

ATR-FTIR spectra of MIL-53(Al) crystals were recorded on a Nexus 470 FTIR spectrometer attached with a Pike Technologies Horizontal ATR accessory. Approximately 5 mg of MIL-53(Al) powder was sonicated in 1 mL DCM for approximately 30 seconds and the suspension was drop-cast onto a ZnSe trough plate. After evaporation of the solvent under N_2 gas, the spectrum was recorded at 4 cm^{-1} resolution for 16 scans.

^{1}H NMR Digestion Analysis of MIL-53(Al) Crystals

^{1}H NMR spectra were acquired on a JEOL JNM-ECZL 400S NMR spectrometer (9.4T magnet, ROYALPROBE 5mm probe) in D_2O. NMR digestion analysis was carried out by weighing ~10 mg of MIL-53(Al) and ~10 mg of the internal standard (disodium maleate) into a 1.5 mL Eppendorf tube and adding 600 μL of 1.0 M NaOH solution in D_2O. Since MIL-53(Al) completely dissolves in basic solutions, the mixture was mixed until clear and then transferred to an NMR tube. Quantitative NMR analysis was performed with a 30 s relaxation delay and 16 scans. Typical data analysis was done directly on the Delta NMR software.

Conductivity Measurements

Conductivity measurements were performed using a PASCO Wireless Conductivity Sensor PS-3210 on solutions of $Al(NO_3)_3$ in HPLC grade water containing various concentrations of OmimCl: 0.10%, 0.50%, and 1.0% v/v. 400 μL of a 1.56 M stock solution of $Al(NO_3)_3$ was added to a 10 mL volumetric flask, along with 60, 300, or 600 μL of 0.730 M OmimCl stock solution, then diluted with HPLC grade water. The final $Al(NO_3)_3$ concentraiton was 62.3 mM, about 10% of the synthesis concentration in order to stay within the detection limit of the conductivity probe. Conductivity measurements were taken over the average of 45 s with 0.5 s

resolution and the probe was cleaned by stirring in HPLC grade water between runs then drying with a Kimwipe.

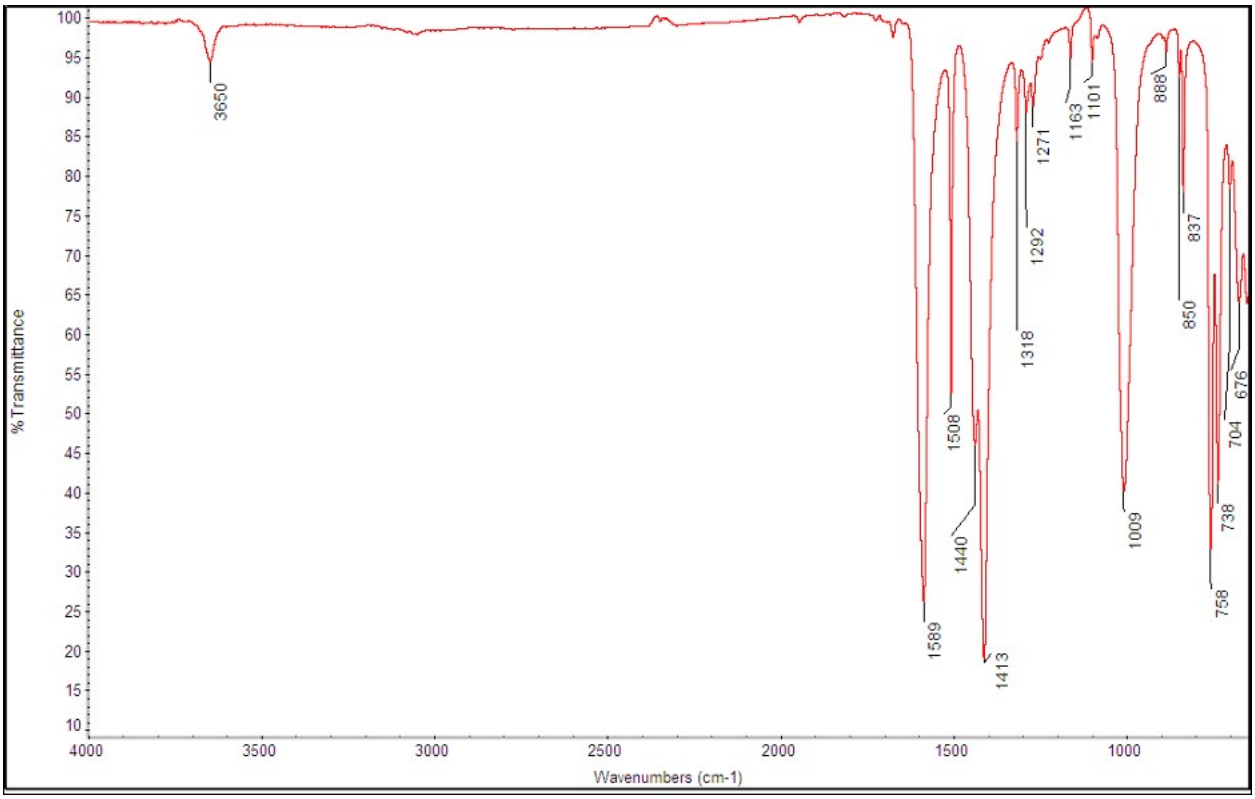

Figure S1. ATR- FTIR spectrum of pure MIL-53(Al).

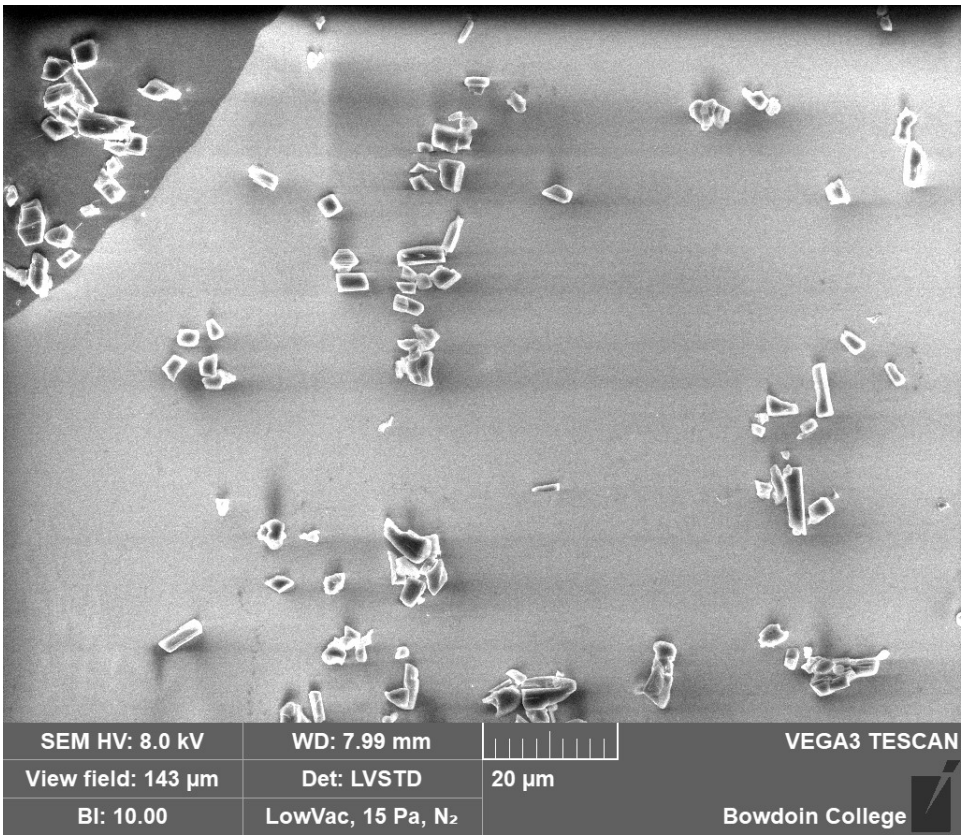

Figure S2. SEM image of sample **2** (synthesized with 0.05% v/v IL; synthesis time: 24 h).

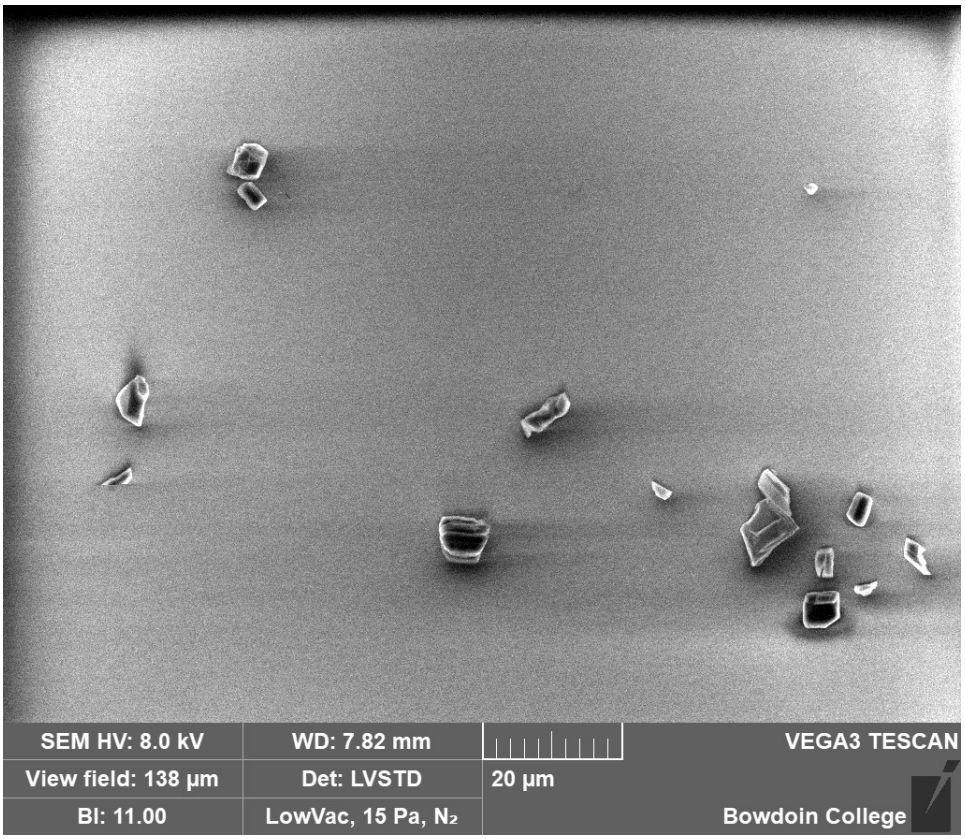

Figure S3. SEM image of sample **3** (synthesized with 0.10% v/v IL; synthesis time: 24 h).

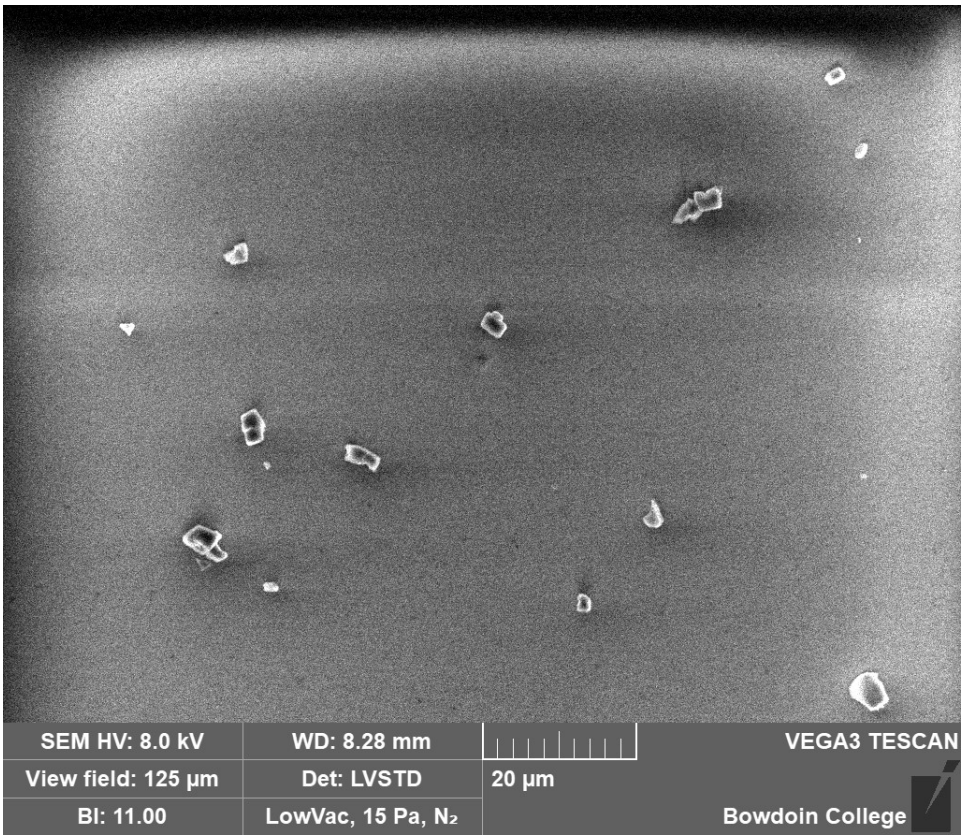

Figure S4. SEM image of sample **7** (synthesized with 5.0% v/v IL; synthesis time: 24 h).

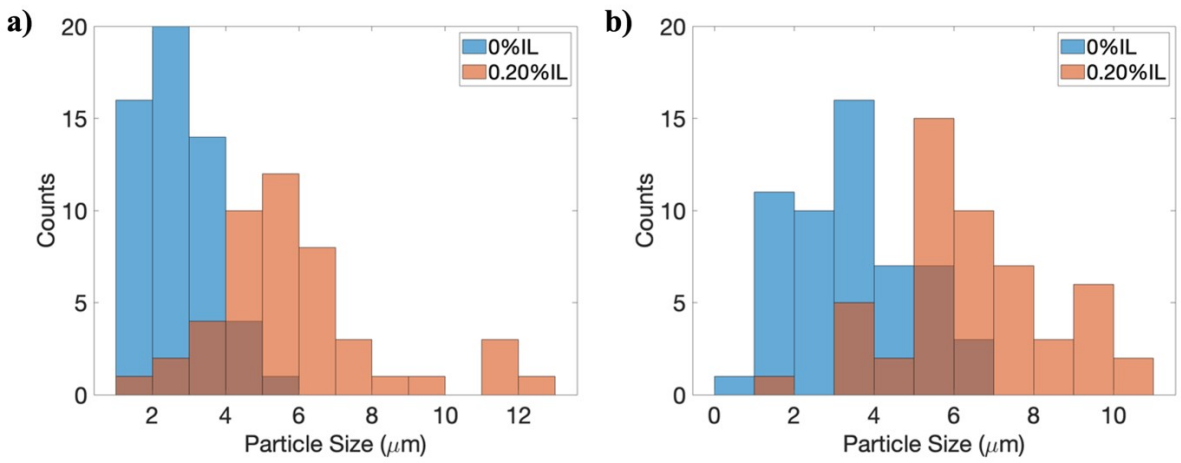

Figure S5. Histograms on the size distribution of MIL-53(Al) crystals grown in the absence (blue) or the presence (orange) of 0.20% v/v IL at synthesis times of 6 hours (a, left) and 24 hours (b, right).

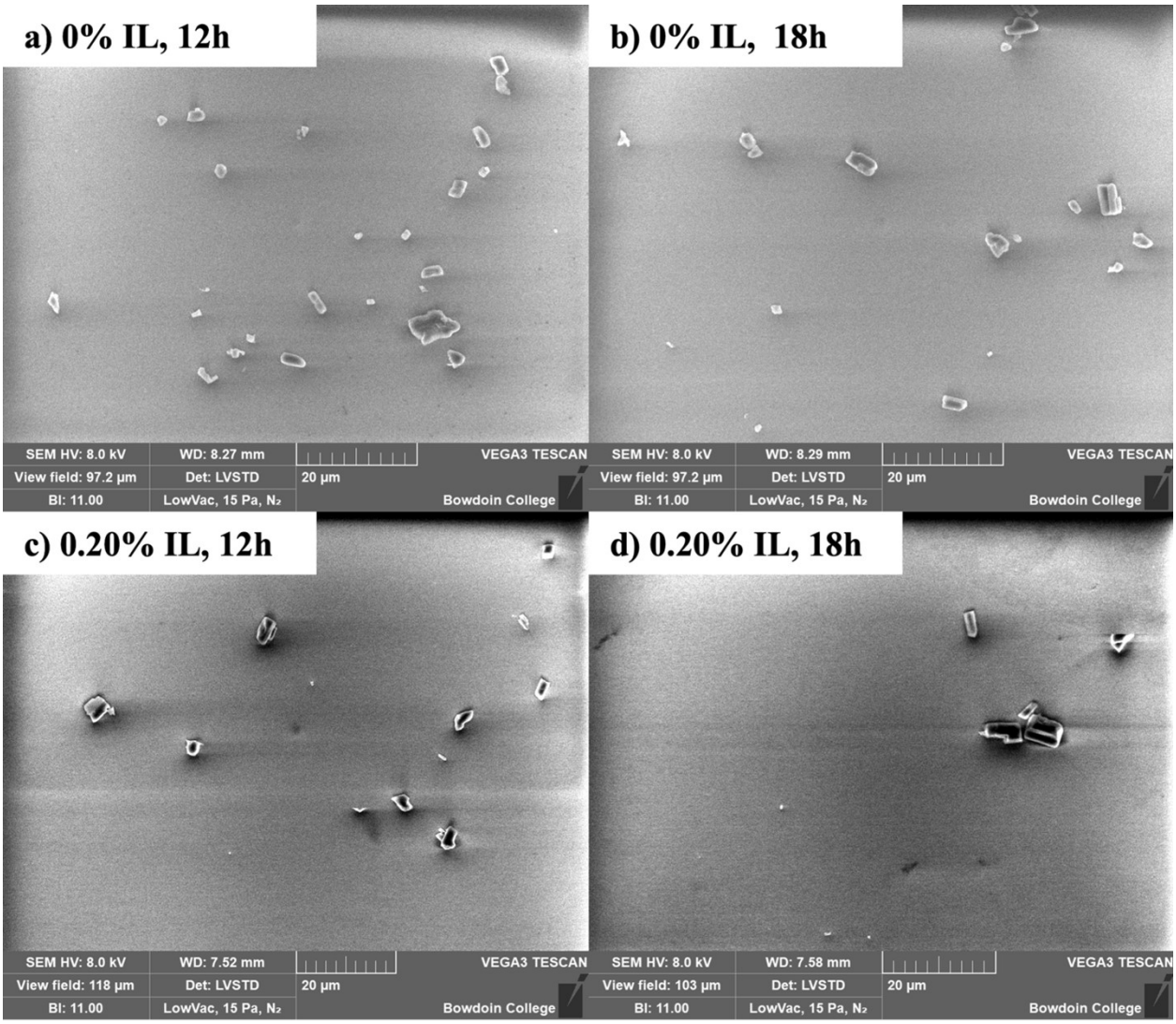

Figure S6. SEM images of MIL-53(Al) grown in the absence (a, b) or the presence (c, d) of 0.20% v/v IL at synthesis times of 12 h (a, c) and 18 h (b, d).

Table S1. Relative intensities of the 220 and $11\bar{1}$ peaks with respect to the 110 peak as well as the average crystallite size for MOFs synthesized with various IL loadings. Average crystallite size is calculated by the SmartLab Studio II software.

OmimCl concentration (% v/v)	Relative Intensity of 220 peak to 110 peak	Relative Intensity of $11\bar{1}$ peak to 110 peak	Average Crystallite Size (nm)
0.00	22.66	30.48	34.4 ± 1.8
0.05	20.57	27.51	35.7 ± 2.2
0.10	21.26	24.63	34.5 ± 1.0
0.20	17.60	21.91	35.0 ± 1.6
0.50	14.97	22.47	35.5 ± 1.5
1.0	9.66	27.14	36.9 ± 2.2
5.0	12.16	37.64	39.0 ± 2.9
10	19.04	37.84	39.3 ± 2.2
Literature[2]	41.31	55.30	42.6

Table S2. Linker weight of MOFs determined through NMR digestion analysis, compared with the calculated value

OmimCl concentration (% v/v)	Linker weight (%)
0.00	74.2
0.05	72.8
0.10	72.8
0.20	74.2
0.50	72.2
1.0	67.8
5.0	52.1
10	43.4
Calculated	72.6

Table S3. Conductivities of $Al(NO_3)_3$ solutions (62.3mM) containing various concentrations of OmimCl

OmimCl concentration (% v/v)	Conductivity (μS/cm)	Change
(control) 0.00	15085	0.00%
0.10	15932	5.6%
0.50	15140	0.36%
1.0	18146	17%

References

1. Loiseau, T.; Serre, C.; Huguenard, C.; Fink, G.; Taulelle, F.; Henry, M.; Bataille, T.; Férey, G. A Rationale for the Large Breathing of the Porous Aluminum Terephthalate (MIL-53) Upon Hydration. *Chem. – Eur. J.* **2004**, *10* (6), 1373–1382.

2. A. Taheri, E. G. Babakhani and J. Towfighi, *Adsorption Science & Technology*, 2018, **36**, 247–269.