

Supplementary Information

Hygroscopicity of lithium coordination polymers and their solid solutions.

Monica Lestari, Matteo Lusi,* Aoife O'Leary, Daniel O'Nolan and Michael J. Zaworotko

Department of Chemical Science and Bernal Institute, University of Limerick, Castletroy, Co. Limerick Ireland. matteo.lusi@ul.ie

All reagents were purchased from Sigma Aldrich and used without further purification.

Solid-state synthesis:

$[(\text{PRO})\text{Li}(\text{MBNZ})]_n$ (**1₀**): 12.0 mg LiOH (0.501 mmol), 76.1 mg 2-methoxybenzoic acid (0.500 mmol), 57.6 mg L-proline (0.500 mmol) were placed in a mortar with 2 drops of deionized water (using Pasteur pipette) and were ground for about 10 – 15 minutes.

$\{[(\text{PRO})\text{Li}(\text{MBNZ})_{0.75}(\text{BNZ})_{0.25}]\}_n$ (**1_{0.25}**): 12.0 mg LiOH (0.501 mmol), 57.2 mg 2-methoxybenzoic acid (0.376 mmol), 15.5 mg benzoic acid (0.127 mmol), 57.6 mg L-proline (0.500 mmol) were placed in a mortar with 2 drops of deionized water (using Pasteur pipette) and were ground for about 10 – 15 minutes.

$\{[(\text{PRO})\text{Li}(\text{MBNZ})_{0.50}(\text{BNZ})_{0.50}]\}_n$ (**1_{0.50}**): 12.0 mg LiOH (0.501 mmol), 38.1 mg 2-methoxybenzoic acid (0.250 mmol), 30.6 mg benzoic acid (0.251 mmol), 57.6 mg L-proline (0.500 mmol) were placed in a mortar with 2 drops of deionized water (using Pasteur pipette) and were ground for about 10 – 15 minutes.

$\{[(\text{PRO})\text{Li}(\text{MBNZ})_{0.25}(\text{BNZ})_{0.75}]\}_n$ (**1_{0.75}**): 12.0 mg LiOH (0.501 mmol), 19.0 mg 2-methoxybenzoic acid (0.125 mmol), 45.9 mg benzoic acid (0.376 mmol), 57.6 mg L-proline (0.500 mmol) were placed in a

mortar with 2 drops of deionized water (using Pasteur pipette) and were ground for about 10 – 15 minutes.

$\{[(\text{PRO})\text{Li}(\text{BNZ})]\}_n$ (**1₁**): 12.0 mg LiOH (0.501 mmol), 61.1 mg benzoic acid (0.500 mmol), 57.6 mg L-proline (0.500 mmol) were placed in a mortar with 2 drops of deionized water (using Pasteur pipette) and were ground for about 10 – 15 minutes.

$\{[\text{Li}_2(\text{SUC})]\}_n$ (**2₀**): 73.9 mg Li_2CO_3 (1.00 mmol) and 118.1 mg succinic acid (1.00 mmol) were placed in a mortar with 40 μL of DI and were ground until forming white paste consistency. 30 μL of DI were added into the mortar and were ground for about 10 - 15 minutes until the powder dried.

$\{[\text{Li}_2(\text{SUC})_{0.8}(\text{MAL})_{0.2}]\}_n$ (**2_{0.2}**): 73.9 mg Li_2CO_3 (1.00 mmol), 26.8 mg L(-) malic acid (0.20 mmol), and 94.5 mg succinic acid (0.80 mmol) were placed in a mortar with 40 μL of DI and were ground until forming white paste consistency. 30 μL of DI were added into the mortar and were ground for about 10 - 15 minutes until the powder dried.

$\{[\text{Li}_2(\text{SUC})_{0.6}(\text{MAL})_{0.4}]\}_n$ (**2_{0.4}**): 73.9 mg Li_2CO_3 (1.00 mmol), 53.6 mg L(-) malic acid (0.40 mmol), and 70.9 mg succinic acid (0.60 mmol) were placed in a mortar with 40 μL of DI and were ground until forming white paste consistency. 30 μL of DI were added into the mortar and were ground for about 10 - 15 minutes until the powder dried.

$\{[\text{Li}_2(\text{SUC})_{0.5}(\text{MAL})_{0.5}]\}_n$ (**2_{0.5}**): 73.9 mg Li_2CO_3 (1.00 mmol), 67.1 mg L(-) malic acid (0.50 mmol), and 59.1 mg succinic acid (0.50 mmol) were placed in a mortar with 40 μL of DI and were ground until forming white paste consistency. 30 μL of DI were added into the mortar and were ground for about 10 - 15 minutes until the powder dried.

$\{[\text{Li}_2(\text{SUC})_{0.4}(\text{MAL})_{0.6}]\}_n$ (**2_{0.6}**): 73.9 mg Li_2CO_3 (1.00 mmol), 80.5 mg L(-) malic acid (0.60 mmol), and 47.2 mg succinic acid (0.40 mmol) were placed in a mortar with 40 μL of DI and were ground until forming white paste consistency. 30 μL of DI were added into the mortar and were ground for about 10 - 15 minutes until the powder dried.

$\{[\text{Li}_2(\text{SUC})_{0.2}(\text{MAL})_{0.8}]\}_n$ (**2_{0.8}**): 73.9 mg Li_2CO_3 (1.00 mmol), 107.3 mg L(-) malic acid (0.80 mmol), and 23.6 mg succinic acid (0.20 mmol) were placed in a mortar with 40 μL of DI and were ground until forming white paste consistency. 30 μL of DI were added into the mortar and were ground for about 10 - 15 minutes until the powder dried.

$\{[\text{Li}_2(\text{MAL})]\}_n$ (**2₁**): 73.9 mg Li_2CO_3 (1.00 mmol) and 134.1 mg L(-) malic acid (1.00 mmol) were placed in a mortar with 40 μL of DI and were ground until forming white paste consistency. 30 μL of DI were added into the mortar and were ground for about 10 - 15 minutes until the powder dried.

Powder X-ray diffraction (PXRD) measurements for the mechanochemically made samples were performed on the PANalytical Empyrean at ambient temperature equipped with a sealed tube X-ray generator with a Cu anode ($K\alpha_{1,2} = 1.540598$), and Pix-Cell detector on zero background discs.

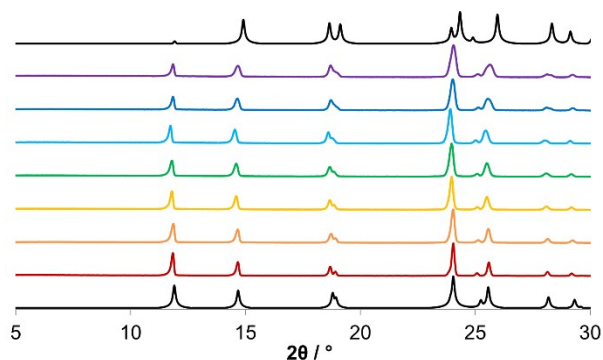


Figure S1. PXRD patterns for the 2_x series obtained by grinding. From top to bottom: calculated for 2_1 (CCDC refcode REXBED), measured for $2_{1.0}$, $2_{0.8}$, $2_{0.6}$, $2_{0.5}$, $2_{0.4}$, $2_{0.2}$, 2_0 and calculated for 2_0 (CCDC refcode LISUCC01).

Thermal and sorption analysis:

Thermogravimetric analysis (TGA) was performed in Perkin Elmer TGA 4000 with typical sample size of 4.8 – 5.6 mg under the ramp rate of 20.00 °C/min from 35 °C to 400 °C and nitrogen gas flow of 20 ml/min. Dynamic vapour sorption (DVS) measurements were performed on DVS Intrinsic (Surface Measurement System). The method stage type used was step dm/dt with an equilibrium criterion of 0.002 %/min. The dm/dt window was set to 5 minutes, with minimum dm/dt stability duration of 10 minutes and maximum dm/dt stage time of 360 minutes, and total flow rate was set to 200 sccm. The temperature was set to be constant (isotherm) at 25 °C. The relative humidity (RH) was set to increase by 10% from 0% to 90% and back to 0%.

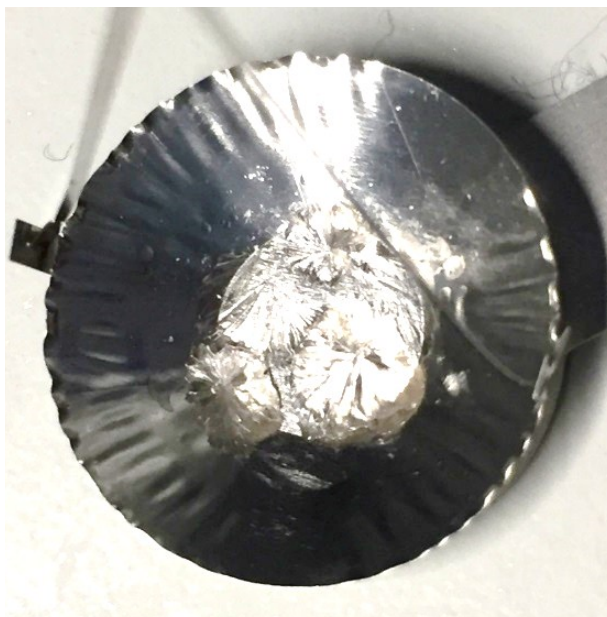


Figure S2. Crystals of **1₀** obtained at the end of the DVS cycle.

Single crystal synthesis and structure determination:

The mechanochemical product was dissolved in a minimum amount of water, sonicated at 40 °C for 15 minutes and recrystallized by slow solvent evaporation. Colourless single crystals appeared within a week. Single crystal data were collected at ambient temperature using Bruker D8 Quest with sealed tube Mo anode and a Photon detector. The data were integrated and corrected for absorption with the Bruker Apex Suite of programs. The structure solution was obtained by direct methods and refined against all F^2 with the SHELX software interfaced through X-Seed. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated positions refined using idealized geometries (riding model) and assigned fixed isotropic displacement parameters.