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Selectivity of hosts for guests by LAG: differences between solution and mechanochemistry

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Electronic Supplementary Information

Experimental details

Instrument details

Single-crystal X-ray diffraction was carried out using a Bruker SMART Apex III X-ray diffractometer with a MoKα radiation source (λ = 0.71073 Å). This was acquired from a 0.5 mm MonoCap collimator and a fine-focus sealed tube. Sample temperature was maintained using an Oxford Cryosystems Cryostream 700+. Data collection and reduction were carried out using the Bruker software package SAINT[1] from within the APEXII suite. Finally, X-Seed was utilised as the graphical interface[2] to solve (SHELXS[3]) and refine (SHELXL[4]) the crystal structures.

^{1}H NMR was performed with a 300 MHz, 400 MHz or a 600 MHz Agilent spectrometer. Samples – between 10-30 mg – were all dissolved in deuterated dimethyl sulfoxide (DMSO-d6).

PXRD analyses were performed on a Bruker D2 phaser X-ray diffractometer. The diffractometer, which operated at 10 mA current and 30 kV voltage, produced radiation from a Cu source that has a wavelength of 1.54183 Å. The crystal sample was removed and dried on filter paper, after which it was gently ground with a mortar and pestle. It was then carefully compressed on a zero-background holder with a microslide. The scans comprised of approximately 2260 steps of 0.500 seconds, with step size 0.0161 °, at angles from 2θ = 4 – 40 °.

Experimental details

Chemicals were purchased from Sigma-Aldrich (South Africa) and used as received.

Synthesis of the solvates of **1**

Crystals of **1·DMA** were obtained by combining pamoic acid (53 mg, 0.14 mmol) with 1,10-phenanthroline hydrate (27 mg, 0.15 mmol) in 6 ml DMA at 80 °C in a glass vial, and stirring until the components dissolved. The vial was capped and left on a shelf to allow crystallisation to occur. Clear, yellow crystals formed within a week. δ_H (300 MHz, DMSO-d_6) 1.95 (3H, s), 2.78 (3H, s), 2.93 (3H, s), 4.80 (2H, s), 7.21 (2H, J = 7.9 Hz, J = 6.9 Hz, J = 0.8 Hz, ddd), 7.36 (2H, J = 8.3 Hz, J = 6.8 Hz, J = 1.4 Hz, ddd), 7.85 (4H, m), 8.04 (2H, s), 8.13 (2H, J = 8.8 Hz, d), 8.46 (2H, s), 8.58 (2H, J = 8.1 Hz, J = 1.7 Hz, dd), 9.13 (2H, J = 4.4 Hz, J = 1.75, dd).

Similarly, crystals of **1·DMF** were obtained by combining pamoic acid (53 mg, 0.14 mmol) with 1,10-phenanthroline hydrate (27 mg, 0.15 mmol) in 3 ml DMF at 80 °C, followed by crystallisation. Clear, yellow crystals formed within 1 to 2 days. δ_H (300 MHz, DMSO-d_6) 2.72 (3H, s), 2.88 (3H, s), 4.79 (2H, s), 7.21 (2H, J = 7.9 Hz, J = 6.9 Hz, J = 0.8 Hz, ddd), 7.36 (2H, J = 8.3 Hz, J = 6.8 Hz, J = 1.4 Hz, ddd), 7.84 (4H, m), 7.95 (1H, s), 8.05 (2H, s), 8.13 (2H, J = 8.8 Hz, d), 8.46 (2H, s), 8.59 (2H, J = 8.1 Hz, J = 1.7 Hz, dd), 9.14 (2H, J = 4.4 Hz, J = 1.8 Hz, dd).

The DMSO solvate, **1·DMSO**, was obtained by combining pamoic acid (53 mg, 0.14 mmol) with 1,10-phenanthroline hydrate (27 mg, 0.15 mmol) in 4 ml DMF at 65 °C, followed by crystallisation. Clear, yellow crystals formed within a week. δ_H (300 MHz, DMSO-d_6) 2.54 (6H, s), 4.79 (2H, s), 7.21 (2H, J = 7.9 Hz, J = 6.8 Hz, J = 0.8 Hz, ddd), 7.37 (2H, J = 8.3 Hz, J = 6.8 Hz, J = 1.4 Hz, ddd), 7.86 (4H, m), 8.05 (2H, s), 8.13 (2H, J = 8.1 Hz, d), 8.46 (2H, s), 8.58 (2H, J = 8.2 Hz, J = 1.8 Hz, dd), 9.14 (2H, J = 4.4 Hz, J = 1.8 Hz, dd).

Crystals of **1·THF** were obtained by combining pamoic acid (53 mg, 0.14 mmol) with 1,10-phenanthroline hydrate (27 mg, 0.15 mmol) in 8 ml THF and 0.5 ml water at 65 °C, and stirring until the components dissolved. The vial was capped and left on a shelf for crystallisation to occur. Clear, yellow crystals formed within a week. δ_H (300 MHz, DMSO-d_6) 1.74 (4H*, m), 3.59 (4H*, m), 4.79 (2H, s), 7.21 (2H, J = 7.9 Hz, J = 6.8 Hz, J = 0.8 Hz, ddd), 7.37 (2H, J = 8.3 Hz, J = 6.8 Hz, J = 1.4 Hz, ddd), 7.86 (4H, m), 8.04 (2H, s), 8.13 (2H, J = 8.1 Hz, d), 8.46 (2H, s), 8.58 (2H, J = 8.2 Hz, J = 1.7 Hz, dd), 9.13 (2H, J = 4.3 Hz, J = 1.7 Hz, dd).

* These peaks represent the eight hydrogen atoms of THF, however the integrals do not add up to this total as the THF solvate is not fully occupied by solvent molecules.

Single crystal data

Table S1 Selected crystallographic parameters for the isostructural solvates of **1**

	1·DMA	**1·DMSO**	**1·DMF***	**1·THF**
Chemical formula	$C_{39}H_{32}N_2O_7$	$C_{39}H_{33}N3O_7S$	$C_{38}H_{31}N_3O_7$	$C_{39}H_{32}N_2O_7$
Formula weight /g mol^{-1}	655.68	646.69	641.66	640.66
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a /Å	11.035(2)	10.5540(2)	10.699(2)	10.653(3)
b /Å	11.907(2)	11.3682(2)	11.630(2)	11.153(3)
c /Å	13.273(3)	13.7388(2)	13.421(2)	13.566(4)
α /°	81.380(2)	84.165(1)	82.162(5)	85.062(4)
β /°	70.064(2)	74.550(1)	72.106(5)	74.512(3)
γ /°	71.719(2)	72.852(1)	72.058(5)	72.396(3)
Calculated density /g cm^{-3}	1.400	1.415	1.411	1.437
Volume /Å^3	1555.0(5)	1517.71(5)	1510.4(5)	1480.6(7)
Z	2	2	2	2
Temperature /K	101(2)	100(2)	105(2)	108(2)
Independent reflections	8339	7684	7485	7068
R_{int}	0.0637	0.0311	0.0974	0.0289
R_1 [I > 2σ(I)]	0.0496	0.0459	0.0503	0.0681

* Although the structure of the DMF solvate has been published previously (QEZJEJ[5]), data were recollected at 100 K for comparative purposes.

Powder X-ray diffraction

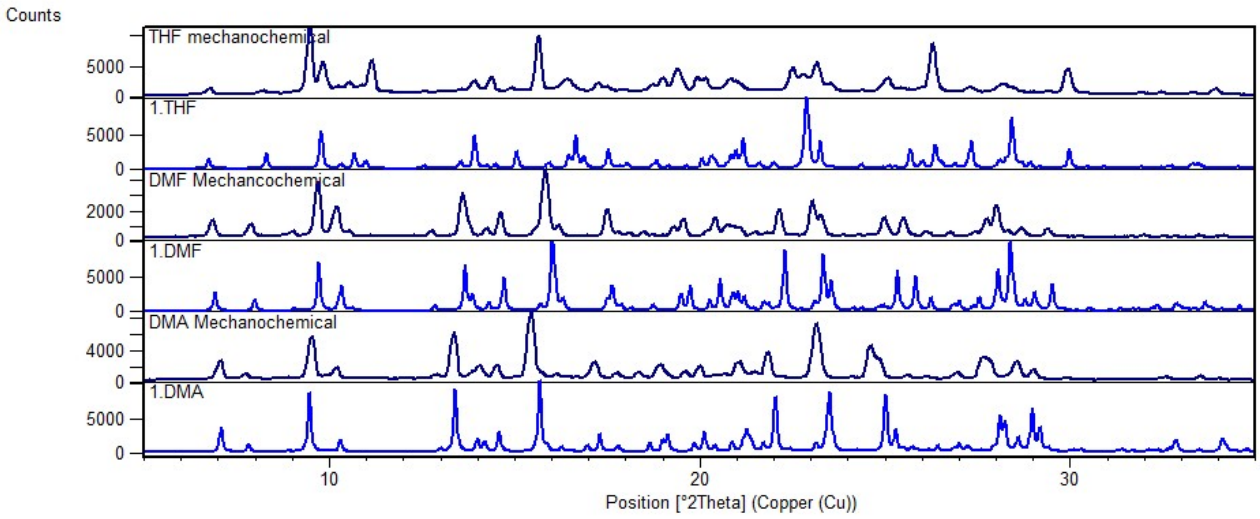

Figure S1: PXRD patterns of **1·solvent** synthesized mechanochemically.

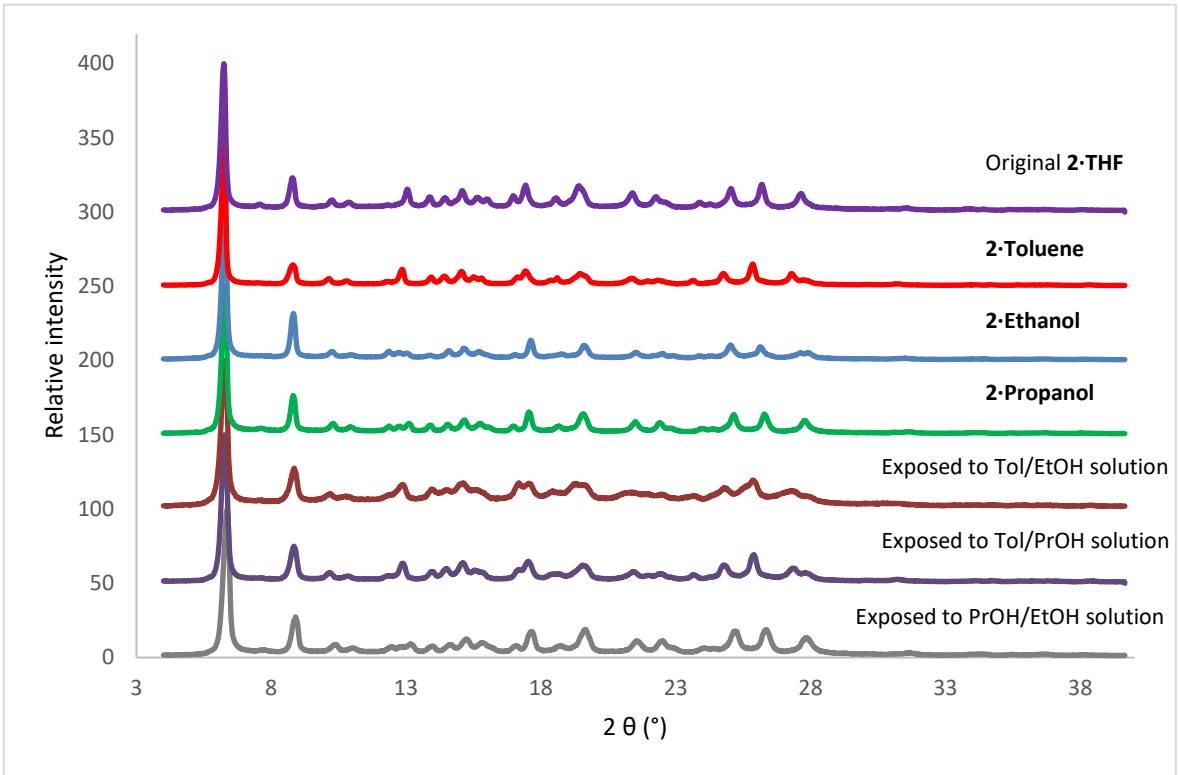

Figure S2: PXRD patterns of **2·THF** after exchanged occurred with toluene, ethanol and 1-propanol. Crystals of **2·THF** were also immersed in mixtures of these solvents, and both these sets display a similar pattern to the original **2·THF**, implying that the framework was retained after exchange.

Results of selectivity experiments

Selectivity from solution with 1

Values given on bold are from experiments carried out at room temperature. For the other experiments crystallisation was done in the refrigerator.

DMA/DMF	
Z_{DMA}	X_{DMA}
0.0842	0.1
0.064	0.1
0.1757	0.2
0.1909	0.2
0.1374	0.2
0.1535	0.2
0.1058	**0.2**
0.1153	**0.2**
0.296	0.3
0.3266	0.3
0.5275	0.4
0.5306	0.4
0.5208	0.4
0.5427	0.4
0.4449	**0.4**
0.4497	**0.4**
0.6832	0.5
0.6929	0.5
0.8084	0.6
0.8117	0.6
0.8048	0.6
0.8154	0.6
0.8819	0.7
0.8841	0.7
0.9279	0.8
0.9238	0.8
0.9349	0.8
0.93	0.8
0.9632	0.9
0.9682	0.9

DMA/DMSO	
Z_{DMA}	X_{DMA}
0.04124	0.2
0.04841	0.2
0.05303	**0.2**
0.00748	**0.2**
0.8541	0.5
0.7672	0.5
0.8094	**0.5**
0.8291	**0.5**
0.9669	0.8
0.9765	0.8

DMSO/DMF	
Z_{DMF}	X_{DMF}
0.1189	0.2
0.1211	0.2
0.1105	**0.2**
0.1119	**0.2**
0.3701	0.5
0.3879	0.5
0.403	**0.5**
0.4388	**0.5**
0.7962	0.8
0.7877	0.8
0.8075	**0.8**
0.8227	**0.8**

Selectivity by mechanochemistry with 1

DMA/DMF	
Z_{DMA}	X_{DMA}
0.2453	0.2
0.2132	0.2
0.2171	0.2
0.1566	0.2
0.213	0.2
0.4869	0.4
0.5053	0.4
0.4858	0.4
0.748	0.6
0.725	0.6
0.7424	0.6
0.909	0.8
0.9241	0.8
0.9179	0.8

DMA/DMSO	
Z_{DMA}	X_{DMA}
0.02899	0.2
0.05128	0.2
0.5312	0.5
0.5149	0.5
0.7919	0.8
0.8744	0.8

DMSO/DMF	
Z_{DMF}	X_{DMF}
0.0797	0.2
0.1086	0.2
0.1055	0.2
0.3513	0.5
0.3479	0.5
0.3616	0.5
0.6094	0.7
0.4931	0.7
0.8197	0.8
0.8105	0.8
0.7057	0.8
0.6929	0.8
0.8223	0.9
0.8356	0.9

Selectivity from solution with 2

These values have been normalized to give a total of 100% to enable comparison, even when the guest occupancy was not 100 %. In all cases, either no THF was evident in the NMR, or only trace amounts of THF were observed, *i.e.* exchange was complete.

Toluene/EtOH	
$Z_{toluene}$	$X_{toluene}$
0.9261	0.2
0.9556	0.2
0.9496	0.4
0.9649	0.4
0.9601	0.4
0.9583	0.5
0.9681	0.5
0.9610	0.5
0.9673	0.6
0.9754	0.6
0.9680	0.6
0.9720	0.8
0.9773	0.8
0.9742	0.8

Toluene/PrOH	
$Z_{toluene}$	$X_{toluene}$
0.5139	0.2
0.719	0.2
0.7183	0.2
0.6421	0.4
0.8400	0.4
0.8583	0.4
0.8777	0.5
0.9707	0.5
0.8608	0.5
0.8858	0.6
0.9061	0.6
0.9326	0.6
0.9107	0.8
0.9330	0.8
0.9292	0.8

PrOH/EtOH	
Z_{PrOH}	X_{PrOH}
0.3772	0.2
0.5429	0.4
0.7262	0.5
0.8169	0.6
0.9415	0.8

Selectivity by mechanochemistry with 2

Toluene/EtOH	
$Z_{toluene}$	$X_{toluene}$
0.6353	0.2
0.709	0.2
0.7453	0.2
0.7901	0.4
0.952	0.4
0.9655	0.4
0.8333	0.5
0.974	0.5
0.9708	0.5
0.9479	0.6
0.9551	0.6
0.9774	0.6
0.9412	0.8
0.9924	0.8
0.9754	0.8

Toluene/PrOH	
$Z_{toluene}$	$X_{toluene}$
0.0418	0.2
0.1289	0.2
0.0663	0.2
0.4265	0.4
0.5286	0.4
0.5245	0.4
0.4341	0.5
0.6267	0.5
0.7458	0.5
0.6486	0.6
0.754	0.6
0.8083	0.6
0.8174	0.8
0.8495	0.8
0.9048	0.8

PrOH/EtOH	
Z_{PrOH}	X_{PrOH}
0.77	0.2
0.7548	0.2
0.957	0.4
0.9511	0.4
0.9724	0.4
0.9507	0.5
0.8978	0.5
0.9825	0.6
0.9461	0.6
0.9874	0.6
0.9785	0.8
0.9742	0.8
1	0.8

References

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