**MAS NMR Investigation of Molecular Order in an Ionic Liquid Crystal**

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In the following, the names of all raw data files from the measurements are presented.

1. **Raw files from SAXS experiments.** Measurements were performed by Steven Huband.

 **Figures 2a and S6:** Variable temperature SAXS (recorded on 31/07/18). List of temperatures: **Temps.xls** , parameters: **Parameters.xls**, and raw data file for each temperature, formatted as three columns: *q* (Å-1), intensity (cm-1) and uncertainty (cm-1): **T\_####C.xye**

1. **Raw files from polarising optical microscopy.** Images taken by Chi Long Chanand Mohit K. Devgan.

**Figure 3:** Polarising optical micrograph (×) of CAGE oct: **4X\_heating\_4x\_2degmin15\_t2.tif** (recorded on 15/09/19).

**Figure S7:** Polarising optical micrographs (×20) of CAGE oct upon heating the sample (recorded on 15/09/19). Images taken from videos: **20x\_slow\_heating\_part1\_(from\_18C).avi** and **20x\_slow\_heating part2\_(from\_21C\_to 25).avi**

1. **Raw files from MAS NMR experiments.** Measurements were performed by Sarah K. Mann.

**Figure 4a:** 1H (500 MHz) one-pulse MAS (5 kHz) NMR spectrum (T = 273 K): **190130\_3.2mm\_HXY\_CAGE-oct\_1H1DVT/8**

**Figure 4b:** 1H (500 MHz) one-pulse MAS (5 kHz) variable temperature NMR spectra:

T = 268 K: **190130\_3.2mm\_HXY\_CAGE-oct\_1H1DVT/7**

T = 273 K: **190130\_3.2mm\_HXY\_CAGE-oct\_1H1DVT/8**

T = 278 K: **190130\_3.2mm\_HXY\_CAGE-oct\_1H1DVT/9**

T = 283 K: **190130\_3.2mm\_HXY\_CAGE-oct\_1H1DVT/10**

T = 288 K: **190130\_3.2mm\_HXY\_CAGE-oct\_1H1DVT/11**

T = 293 K: **190130\_3.2mm\_HXY\_CAGE-oct\_1H1DVT/12**

T = 298 K: **190130\_3.2mm\_HXY\_CAGE-oct\_1H1DVT/12**

T = 303 K: **190130\_3.2mm\_HXY\_CAGE-oct\_1H1DVT/14**

T = 308 K: **190130\_3.2mm\_HXY\_CAGE-oct\_1H1DVT/15**

T = 313 K: **190130\_3.2mm\_HXY\_CAGE-oct\_1H1DVT/16**

T = 318 K: **190130\_3.2mm\_HXY\_CAGE-oct\_1H1DVT/17**

T = 323 K: **190130\_3.2mm\_HXY\_CAGE-oct\_1H1DVT/18**

**Figures 5 and S8:** 1H13C (500 MHz) HETCOR MAS (5 kHz) NMR spectrum, recorded with a CP contact time of 2.5 ms at 273 K: **180926\_3.2mm\_HX\_CAGE-oct\_CPbu\_HETCOR/8**

**Figure 6:** 1H13C (500 MHz) CP MAS (5 kHz) NMR build-up curves, recorded at 273 K: **180926\_3.2mm\_HX\_CAGE-oct\_CPbu\_HETCOR/5**

**Figures 8 and S11:** 1HDQ 1H SQ (500 MHz) MAS (5 kHz) NMR spectrum, recorded with POST-C7 recoupling for DQ = 1.2 ms at 273 K: **181019\_3.2m\_HX\_CAGE-oct\_DQC7/100**

**Figures 9 and S12:** 1HDQ MAS NMR (500 MHz, 5 kHz) build-up curves, recorded with POST-C7 recoupling at 273 K: **181019\_3.2m\_HX\_CAGE-oct\_DQC7/8**

**Figure S10:** *T*2-recDIPSHIFT profiles (500 MHz, 5 kHz), recorded with 8 rotor periods of recoupling at 273 K:

1H13C CP: **190323\_3.2mm\_HXY\_CAGE-oct\_CPDIPSHIFT/10**

DP: **181129\_3.2mm\_HXY\_CAGE-oct\_DPDIPSHIFT/10**

**Figure S13:** 1HDQ MAS NMR (500 MHz, 5 kHz) build-up curves, recorded with DQ pre-selection at 273 K: **181019\_3.2m\_HX\_CAGE-oct\_DQC7/3**

**Figure S14:** *T*2-recDIPSHIFT profiles (500 MHz, 5 kHz), recorded with 8 rotor periods of recoupling at variable temperatures:

243 K: **190920\_3.2mm\_HXY\_CAGE-oct\_DIPSHIFT\_-30/10**

253 K: **190815\_3.2mm\_HXY\_CAGE-oct\_DIPSHIFT\_-20/10**

257 K: **190323\_3.2mm\_HXY\_CAGE-oct\_CPDIPSHIFT/10**

1. **Raw files from solution NMR experiments.** Measurements were performed by David Pugh.

**Figure S1:**

Solution phase 1H NMR spectrum in (CD3)2SO (recorded on 11/09/17): **HNMR**

Solution phase 13C NMR spectrum in (CD3)2SO (recorded on 11/09/17): **CNMR**

1. **Raw files from IR (ATR).** Measurements were performed by David Pugh.

**Figure S2:** IR spectrum (recorded on 17/10/19): **IR**

1. **Raw files from MS.** Measurements were performed by Lisa Haigh.

**Figure S3:** Negative ion mass spectrum (recorded on 4/10/19): **MS-negative**

**Figure S4:** positive ion mass spectrum (recorded on 4/10/19): **MS-positive**

1. **Calculations.** Calculations were performed by Sarah K. Mann:

Initial CIF file: **CIQBEJ.cif**

CIF file after geometry optimisation of an isolated molecule: **CIQBEJ\_SM-out.cif**