## **Supplementary Information:**

# Subtle Changes in Hydrogen Bond Orientation Result in Glassification of Carbon Capture Solvents

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1-IPADM-2-BOL M		1-IPADM-2-BOL M		1-IPADM-3-BOL M		1-IPADM-3-BOL G		1-MEIPADM-2- BOL M		1-MEIPADM-2- BOL G		
	X CO2	<u>cP EQ</u>	X CO2	<u>cP EQ</u>	<u>X CO2</u>	<u>cP EQ</u>	<u>X CO2</u>	<u>cP EQ</u>	X CO2	<u>cP EQ</u>	<u>X CO2</u>	<u>cP EQ</u>
	0.03	9.4	0.00	13.0	0.00	7.7	0.00	12.2	0.16	17.9	0.00	13.3
	0.04	9.7	0.00	13.1	0.00	7.8	0.00	12.5	0.17	18.8	0.01	13.8
	0.04	10.2	0.00	13.2	0.01	8.4	0.01	12.9	0.17	19.7	0.01	14.1
	0.05	10.8	0.00	13.0	0.01	8.9	0.01	13.2	0.17	20.7	0.01	14.4
	0.05	11.4	0.00	13.3	0.02	9.3	0.01	13.7	0.18	21.5	0.02	14.9
	0.05	12.0	0.00	13.1	0.02	9.5	0.01	14.0	0.18	22.4	0.02	15.3
	0.06	12.4	0.00	13.4	0.02	9.7	0.01	14.0	0.18	23.4	0.02	15.8
	0.06	13.1	0.00	13.2	0.03	10.7	0.01	14.5	0.19	24.5	0.03	16.2
	0.06	13.8	0.00	13.0	0.05	12.9	0.02	15.3	0.19	25.9	0.03	16.5
	0.07	14.8	0.00	13.4	0.07	17.0	0.02	15.3	0.19	27.4	0.03	17.2
	0.08	16.9	0.00	13.2	0.10	24.5	0.02	15.8	0.22	37.8	0.04	17.6
	0.09	19.2	0.00	12.8	0.13	37.9	0.02	16.1	0.24	54.9	0.04	18.1
	0.10	22.1	0.00	12.7	0.15	60.0	0.02	16.8	0.26	74.4	0.04	18.8
	0.12	25.7	0.00	13.1	0.18	97.2	0.02	17.4	0.29	113.3	0.04	19.3
	0.13	30.2	0.00	12.8	0.21	152.0	0.03	17.9	0.31	160.8	0.05	19.9
	0.15	42.3	0.00	13.3	0.23	239.0	0.03	18.0	0.33	243.9	0.05	20.5
	0.18	57.2	0.00	13.0	0.26	333.0	0.03	18.4	0.35	362.4	0.05	21.2
	0.20	79.3	0.00	12.9			0.03	18.9			0.06	21.8
	0.22	108.8	0.00	12.9			0.03	19.1			0.06	22.4
	0.24	153.1	0.00	12.9			0.03	19.6			0.06	23.1
	0.26	218.6	0.00	12.9			0.04	20.3			0.07	23.8
	0.28	325.1	0.00	13.1			0.04	20.9			0.07	24.6
			0.00	13.2			0.04	21.1			0.07	25.5
			0.01	13.4			0.04	21.8			0.08	26.7
			0.01	13.4			0.04	22.3			0.08	28.4
			0.01	13.0			0.05	22.0			0.08	20.0
			0.01	13.5			0.05	23.0			0.09	29.0
			0.01	13.7			0.05	24.3			0.09	30.5
			0.01	14.1			0.05	24.9			0.09	31.0
			0.01	13.9			0.05	20.0			0.09	32.0 24.1
			0.01	14.1			0.05	20.5			0.10	34.1
			0.01	14.2			0.00	21.5			0.10	36.6
			0.01	14.5			0.00	20.5			0.10	37.5
			0.01	14.0			0.00	29.4			0.11	38.0
			0.01	1.4.7			0.00	00.Z			0.11	00.0

Table S1. Experimental viscosity measurements for metastable (M) and glassy (G) states of water-lean solvents.

0.02	14.7		0.06	31.3		0.11	40.5
0.02	14.7		0.06	32.4		0.12	41.6
0.02	14.8		0.07	33.6		0.12	42.8
0.02	14.9		0.07	34.6		0.12	43.9
0.02	15.1		0.07	39.0		0.12	46.7
0.02	15.3		0.08	44.5		0.13	48.8
0.02	15.5		0.09	51.5		0.13	49.8
0.02	15.6		0.10	59.9		0.13	51.4
0.02	15.7		0.11	70.1		0.14	53.3
0.02	15.8		0.11	80.3		0.14	55.3
0.02	16.5		0.12	93.5		0.14	57.1
0.02	16.4		0.13	110.1		0.14	59.2
0.02	16.5		0.14	129.1		0.15	62.0
0.03	16.7		0.14	150.2		0.15	64.2
0.03	17.2		0.15	177.3		0.15	65.9
0.03	17.4		0.16	209.0		0.16	68.7
0.03	17.3		0.17	243.7		0.16	71.5
0.03	17.6		0.17	280.3		0.16	74.5
0.03	18.0		0.18	317.8		0.16	77.4
0.03	18.1	 	0.18	358.5	 	0.17	80.7
0.03	18.4		0.19	413.9		0.17	82.5
0.03	18.5	 	0.20	461.3	 	0.17	86.7
0.03	18.6		0.20	521.0		0.18	91.0
0.03	18.8		0.21	583.7		0.18	92.2
0.03	19.2		0.22	621.9		0.18	95.3
0.03	19.3		0.22	744.4		0.18	100.8
0.04	19.3		0.23	834.8		0.19	104.8
0.04	19.3		0.23	911.8		0.19	109.2
0.04	19.2		0.24	979.8		0.19	113.5
0.04	19.3		0.25	987.2		0.20	120.0
0.04	19.5					0.20	124.0
0.04	19.7					0.20	127.2
0.04	20.1					0.20	132.0
0.04	20.0					0.21	135.4
0.04	20.2					0.21	141.0
0.05	23.Z					0.21	145.7
0.06	25.4					0.21	150.2
0.05	20.Ŏ					0.22	104.9
0.07	20.7					0.22	166 5
0.08	31.0 35.0					0.22	170.0
0.08	30.Z					0.22	172.3
0.09	12 0					0.23	18/ 6
0.09	42.0					0.23	104.0
0.10	40.1					0.23	192.2
0.11	-+3.1					0.23	206.1
0.11	59.7					0.24	210.1
0.12	65.2					0.24	218.4
0.12	71.0					0.24	223.3
0.13	77.4					0.25	231 7
0.14	84.5					0.25	158.7
0.15	92.5					0.25	241.5
0.15	101.3					0.25	252.7
0.16	111.8					0.26	260.3

0.16	123.2				0.26	265.5
0.17	135.3				0.26	278.6
0.18	148.1				0.26	289.0
0.18	163.5				0.27	301.2
0.19	179.5				0.27	313.0
0.19	199.1				0.27	330.3
0.20	218.9				0.27	339.0
0.20	248.4				0.28	344.3
0.21	269.5				0.28	359.5
0.22	291.8				0.28	369.2
0.22	313.9				0.28	383.1
0.23	338.1				0.28	391.6
0.23	362.3				0.29	406.3
0.24	391.5				0.29	422.8
0.24	437.1				0.29	432.2
0.25	484.1				0.29	450.9
0.25	534.2				0.29	453.4
0.26	583.7				0.30	460.3
0.26	536.9				0.30	470.4
0.27	532.2				0.30	478.3
0.27	547.4				0.30	490.2
0.28	586.8				0.30	511.8
0.28	634.3				0.30	522.3
0.29	684.9				0.31	493.2
0.29	730.9				0.31	519.3
0.29	785.9				0.32	569.3
0.30	843.3				0.33	638.0
0.30	905.3				0.33	687.2
0.31	979.4				0.34	735.1
0.31	1055.2				0.34	790.0
0.32	1129.7					
0.32	1210.1					
0.33	1290.9					
0.33	1369.4					
0.33	1399.8					



Figure S1. Temperature dependent neutron diffraction.



Figure S2. The simulated neutron diffraction using structures of glassy (left), metastable (middle), transition from metastable to glassy states (right) at 40 °C.



Figure S3. The simulated neutron diffraction of different boxes used in the classical molecular simulations. Note that 1x1x1 signifies an 8x8x8 nm cell, 2x2x2 a 16x16x16 nm and 8x1x1 a 64x8x8. The smoother low Q signifies the cell effect that point to the poorer long-range structure sampling in the smaller cell.

## Larmor Experiment

#### Larmor Experimental Setup:

SANS measurements: Measurements were carried out at the Larmor beamline of the ISIS pulsed neutron source at the Rutherford Appleton Laboratory, Didcot, UK, using a sample changer and 1 mm and 2 mm path length quartz cuvette cells, for hydrogeneous and deuterated samples, respectively. Typical data collection times on Larmor were 15 min. Measurements on Larmor were carried out in event mode and data sets were sliced into two-minute intervals in order to observe any time dependence in the SANS signal. In SANS, intensity as a function of the scattering vector Q is collected with  $Q = (4\pi/\lambda)\sin(\theta)$ . Here, 2 $\theta$  is the scattering angle, and  $\lambda$  is the neutron wavelength range of 0.9 - 12.5 Å used simultaneously by time of flight. The Q range for this experiment was 0.006 - 0.6 Å<sup>-1</sup>. The instrument was in the 4 m sample-detector configuration, with A1=20mm<sup>2</sup>, S1=14mm<sup>2</sup>, and a sample aperture of 6mm (horizontal) by 8mm (vertical). Data reduction was performed using Mantid[1] and scattering simulations fitted using SasView v3.0.[2]

#### **UEP Model**

The UEP model allows extracting information from multiple structural regimes and was fit to I(Q) SANS curves for the data that exhibited the temperature-dependent changes. The solid lines in **Error! Reference source not found.** A are a subset of the model fits to the data. In the UEP model:

$$I(Q) = \sum_{i=1}^{N} \left[ G_i \ e^{-Q^2 R_{g,i}^2/3} + \frac{B_i e^{-Q^2 R_{g,i+1}^2/3} \left( erf(QR_{g,i}/\sqrt{6}) \right)^{3P_i}}{Q^{P_i}} \right] + \text{bgd}$$

where i = 1 refers to the largest structure to be fit with the model,  $G_i$  is a constant related to the structure's composition and concentration,  $R_g$  is the radius of gyration of the structure,  $B_i$  is specific to the type of power-law scattering and is defined by the regime in which the exponent  $P_i$  falls, and bgd is a constant to account for a background signal. A scattering exponent  $P_i > 4$  corresponds to a diffuse interface. Values of  $3 < P_i < 4$  correspond to surface fractal scattering, where  $P_i = 3$  corresponds to rough surfaces, and  $P_i = 4$  corresponds to smooth surfaces. Values of  $2 < P_i < 3$  correspond to mass fractal scattering, where  $P_i = 2$  corresponds to an open, loosely connected structure and  $P_i = 3$  corresponds to a more highly connected compact structure.  $P_i \approx 5/3$  corresponds to scattering from a swollen chain-like structure. The scattering exponent directly gives the fractal dimension, d, as follows: for surface fractals,  $d_s = 6 - P_i$ , and for mass fractals,  $d_m = P_i$ .

#### Low Temperature Larmor measurements

Figure. S4 shows the observed temperature-dependent changes in intensity for measurements collected over the range of -5 °C to 40 °C (prefix L<sub>n</sub> indicates the order in which measurements were performed).

Measurements were first collected from 10 to 0 °C (L<sub>1</sub>–L<sub>3</sub>), to 30 °C (L<sub>4</sub>–L<sub>7</sub>), then to -5°C (L<sub>8</sub>–L<sub>11</sub>) and finally to 40 °C (L<sub>12</sub>) to confirm that the intensity in fact varied reversibly with temperature. Figure S6 shows the calculated scattering invariant,  $Z = \int_0^{\infty} Q^2 I(Q) dQ$ , of each curve as a metric of the relative changes in low-Q intensity. For a two-phase system, Z is proportional to the volume fraction,  $\phi$ , as follows:  $Z = 2\pi^2 (\Delta \rho)^2 \phi (1 - \phi)$ . Here  $\Delta \rho$  is the scattering length density contrast. After the experiment, we were able to confirm from temperature log files that in some cases, especially on the first measurement after reversing the direction of temperature change, thermocouples near the samples showed a higher than expected lag in reaching the target temperature despite having been allowed ~15–20 minutes to equilibrate. This caused some discrepancies in the measured temperature-dependent intensity between samples measured at the same temperature a different points of the temperature cycling.



Figure S4. Low-temperature SANS results showing large scale aggregation. (A) SANS data collected over the range of temperatures from -5 °C to 40 °C. The L value indicates the order in which the temperature-dependent data was collected. The increase in intensity at low-Q generally correlates with low temperature and decreases at high temperature.



Figure S5. Scattering invariant,  $Z = \int_0^\infty Q^2 I(Q) dQ$  for Larmor low temperature data.

## WAXS

Wide angle x-ray scattering (WAXS) of CO<sub>2</sub>-free and CO<sub>2</sub>-bound (0%, 25%, and 50% by mole CO<sub>2</sub>) 1-IPADM-2-BOL were carried out over a Q-range of  $0.1 - 2.6 \text{ Å}^{-1}$ . The broad signals in the data show several overlapping length scales, primarily within the Q range of  $0.6-2 \text{ Å}^{-1}$  (Fig. S7A)

Peak positions  $Q_1-Q_4$ , from low to high Q, were transformed into correlation distances  $d_1-d_4$  via the expression  $d_n=2\pi/Q_n$ . **Error! Reference source not found.** shows the temperature dependence of correlations  $d_2-d_4$ . The peaks near 1.5, 1.3 and 0.96 Å<sup>-1</sup> corresponding to correlations of 4.1, 4.8 and 6.6 Å for 50%-CO<sub>2</sub> at 0 °C, respectively, are primarily due to the solvation shell of the zwitterion. For the 0%-CO<sub>2</sub> liquid, these values are generally larger, at 4.2, 5.3, and 6.8 Å. These values reflect the asymmetry of the molecule, in which 4.1 Å is the closest contact of 1<sup>st</sup> nearest neighbors along one axis, and 6.6 Å is the close contact separation along the molecules along the "long" axis. The 25% and 50% data also show a broad "hump" at about Q = 0.36, or 17.4 Å, that becomes more pronounced for the 50% loaded sample, which is completely absent in the 0% data. These features demonstrate intermediate range order, in which regions of CO<sub>2</sub>-rich and CO<sub>2</sub>-free alternate with a periodicity of 17.4 Å. This periodicity increases to 18.6 Å at 60 °C, perhaps as the originally tightly bound CO<sub>2</sub>-containing polar phase relaxes as CO<sub>2</sub> becomes unbound, and the nonpolar nature of the liquid begins to determine the short and intermediate-range order of the liquid.



Figure S6. (A) A multi-Lorentzian peak model was used to fit correlations in both CO<sub>2</sub>-loaded and CO<sub>2</sub>-free liquid. (B) The change in d-spacing, calculated as  $d = 2\pi/Q$ , plotted as the fractional change compared to the spacing at 0 °C. All d-spacings increase with increasing temperature, but the CO<sub>2</sub>-bound  $d_1 = 17.4$  Å correlation experiences a sharper increase between 40 and 60 °C, which corresponds to the temperature range over which CO<sub>2</sub> becomes unbound from the liquid. (C)(i-iii) Short range inter- and intra-molecular dimensions are shorter for the CO<sub>2</sub>-bound material compared to the CO<sub>2</sub>-free liquid over the measured temperature range. The rate of change of  $d_n$  is lower from 30–60°C compared to 0–30°C in the CO<sub>2</sub>-bound liquid. Correlations  $d_2$ ,  $d_3$ , and  $d_4$  for the CO<sub>2</sub>-bound and CO<sub>2</sub>-free liquid begin to approach each other at high temperature as CO<sub>2</sub> continues to become unbound from the CO<sub>2</sub>-loaded liquid.



Figure S7. The simulated neutron diffraction data for structures with different deuteration levels at different temperatures.



Figure S8. Calculated XRD for both the metastable and glassy states in the molecular simulations.



Figure S9. Comparison of glassy and metastable runs at 40 °C (yellow) to 42 °C (orange).



Figure S10. (A)  $^{1}H - ^{13}C$  gHSQC NMR to validate resonance assignments of unreacted 1-IPADM-2-BOL. The  $^{1}H - ^{1}C$ <sup>13</sup>C gradient heteronuclear single quantum correlation (gHSQC) NMR spectrum was acquired on an Agilent spectrometer with a 5mm OneProbe 2-channel autotuning probe at a magnetic field strength of 9.4 T at a temperature of 40°C. Acquisition utilized the two dimensional heteronuclear single-quantum 1-bond J-correlation with gradient coherence selection pulse sequence (vendor supplied pulse sequence, gHSQC) and consisted of 128 complex points along the indirect dimension, 8 transients, a delay of 1 second between transients, and 32 dummy scans before data collection. The acquisition time was 150 ms with 962 complex points. The one-bond coupling constant was 146 Hz with a transfer delay of 3.425 ms, and multiplicity editing was performed such that CH<sub>2</sub> resonances (blue) are of opposite phase relative to CH<sub>3</sub> and CH resonances (red) utilizing the phase sensitive, hypercomplex mode in the indirect detection. The spectrum was processed in Mestrenova (version 14.01-23559, released 2019-06-07, Mestrelab Research S.L.) where 77 and 20 Hz of Gaussian line broadening was applied in the F1 and F2 dimension, respectively. The spectrum is shown after baseline correcting in both the F1 and F2 dimensions with spline functions. The <sup>1</sup>H projection of the HSQC scan is a one dimensional <sup>1</sup>H NMR spectrum acquired at 9.4 T at a temperature of 40°C on the aforementioned instrument by a single pulse, direct excitation pulse sequence utilizing a 3.3  $\mu$ s excitation pulse corresponding to a  $\pi/4$  excitation pulse length, an acquisition time of 2.566 seconds with 16384 complex points, a delay between experiments of 1 s, and 16 transients. The  ${}^{1}$ H projection was processed in Mestrenova. The <sup>13</sup>C projection of the HSQC scan is a one dimensional <sup>13</sup>C NMR spectrum acquired at 40°C on the aforementioned instrument by a single pulse, direct excitation pulse sequence utilizing a 3.3  $\mu$ s excitation pulse corresponding to a  $\pi/4$  excitation pulse length, an acquisition time of 1.3 seconds with 32768 complex points, a delay between experiments of 1 s, and 512 transients. 36.5 kHz proton decoupling was applied. The <sup>13</sup>C projection was processed in Mestrenova where 0.5 Hz of exponential line broadening was applied. (B) <sup>1</sup>H assignments and (C) <sup>13</sup>C NMR assignments for unreacted 1-IPADM-2-BOL. The unassigned peaks

(\*) in this spectrum are likely small amounts of zwitterionic species from advantageous  $CO_2$  based on the emergence of similar peaks during in situ <sup>13</sup>C NMR during  $CO_2$  capture by aqueous amines.[3]



Figure S11. <sup>13</sup>C DOSY spectra at 14.1 T of 1-IPADM-2-BOL loaded with approximately 0.2 moles CO<sub>2</sub> per mole of 1-IPADM-2-BOL at (A) 40 and (B) 60°C. Semi-transparent lines overlay the diffusion values acquired from simulation

described in this work, and previously published simulations.[4] Note that the scale of the diffusion axis is different in the two graphs. Notably, in addition to the presence of multiple resonances in the 160 ppm region, there are also many additional peaks in the spectra between 70 and 20 ppm beyond what was found in  ${}^{1}\text{H} - {}^{13}\text{C}$  gHSQC NMR on unreacted IPADM-2-BOL. The additional peaks between 70 and 20 ppm are assigned to zwitterionic species, as similar complexities emerged during in situ  ${}^{13}\text{C}$  NMR studies of CO<sub>2</sub> capture by aqueous amines.[3]



Figure S12. (A) Single pulse <sup>1</sup>H NMR of 1-IPADM-2-BOL at a loading of 0.2 natural abundance CO<sub>2</sub> per mole 1-IPADM-2-BOL and L = 0 at 40°C, where the methyl resonances analyzed via PFG NMR are marked. The single pulse <sup>1</sup>H spectra were acquired with a short tip angle (1  $\mu$ s duration, equivalent to a  $\pi$ /40 tip angle), with one transient

on a relaxed sample, and an acquisition time of 734 ms. (B) <sup>1</sup>H pulsed field gradient NMR results, showing diffusion coefficients of the methyl resonances ca. 1.2 and 1.4 ppm of 1-IPADM-2-BOL. Based on the increased abundance of the resonance at 1.4 ppm following CO<sub>2</sub> sorption, the resonance at 1.4 ppm is assigned to a methyl resonance of a zwitterionic form of 1-IPADM-2-BOL and the diffusion coefficient of this resonance is smaller than the resonance at 1.2 ppm, assigned to unreacted 1-IPADM-2-BOL. Also shown are PFG NMR experiments of unreacted 1-IPADM-2-BOL and comparison with previously published diffusion coefficients calculated through molecular dynamics simulations.[4] (C) Nearly equivalent <sup>1</sup>H pulsed field gradient NMR results acquired with a 200 and a 250 ms diffusion delay indicates that the acquired diffusion coefficients are independent of the diffusion delay parameter over these conditions.



Figure S13. The partial radial distribution function of zwitterion-zwitterion ( $g_{Z-Z}$ ), zwitterion-neutral ( $g_{Z-N}$ ), and neutral-neutral ( $g_{N-N}$ ) in different systems.



Figure S14. The average percentage of zwitterionic neighbors of zwitterions in the systems.



Figure S15. Vector parameters defined and angles measured in this work.



Figure S16. (a) The normalized angle distribution of the angles between the vector parameter 1 and the 3-N plane in zwitterions. The other two subplots show the normalized angle distribution of vector 1 (upper) and 3-N plane (lower), respectively, between zwitterion and their zwitterion neighbors at the neighbor cutoff of (b) 0.65 nm and (c) 1.1 nm.



Figure S17. Visual examples of zwitterion molecular configurations or zwitterion neighbor pairs with different pairing angles.



Figure S18. The amount of external hydrogen bonds in the metastable and glassy states.

<sup>13</sup>C NMR (CDCl<sub>3</sub>): 1-aminopropan-1,1,2,3,3,3-d<sub>6</sub>-2-ol.



<sup>13</sup>C NMR (CDCl<sub>3</sub>): 1-((1,3-dimethylimidazolidin-2-ylidene)amino)propan-1,1,2,3,3,3-d<sub>6</sub>-2-ol



Figure S19. <sup>13</sup>C Spectra for 1-aminopropan-1,1,2,3,3,3-d<sub>6</sub>-2-ol and 1-((1,3-dimethylimidazolidin-2-ylidene)amino)propan-1,1,2,3,3,3-d<sub>6</sub>-2-ol.

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