

Electronic Supplementary Information (ESI)

Mobility and phase transitions of the [EMIm⁺][FSI⁻] ionic liquid confined in micro- and mesoporous carbons

Paula Ratajczak^{a*}, Christopher Bachetzky^{b*}, Zhuanpei Wang^{a*}, Agnieszka Chojnacka^a, Natalia Fulik^b, Emmanuel Pamet a^a, SEM Pourhosseini^a, Eike Brunner^b, Francois Beguin^{a†}

^a Poznan University of Technology, Institute of Chemistry and Technical Electrochemistry, Berdychowo 4, 60-965 Poznan, Poland

^b TU Dresden, Faculty of Chemistry and Food Chemistry, 01062 Dresden, Germany

* co-first authorship.

† corresponding author: francois.beguin@put.poznan.pl

1. Deconvolution of the DSC thermograms of IL@STC-20-1 and IL@STC-12-1

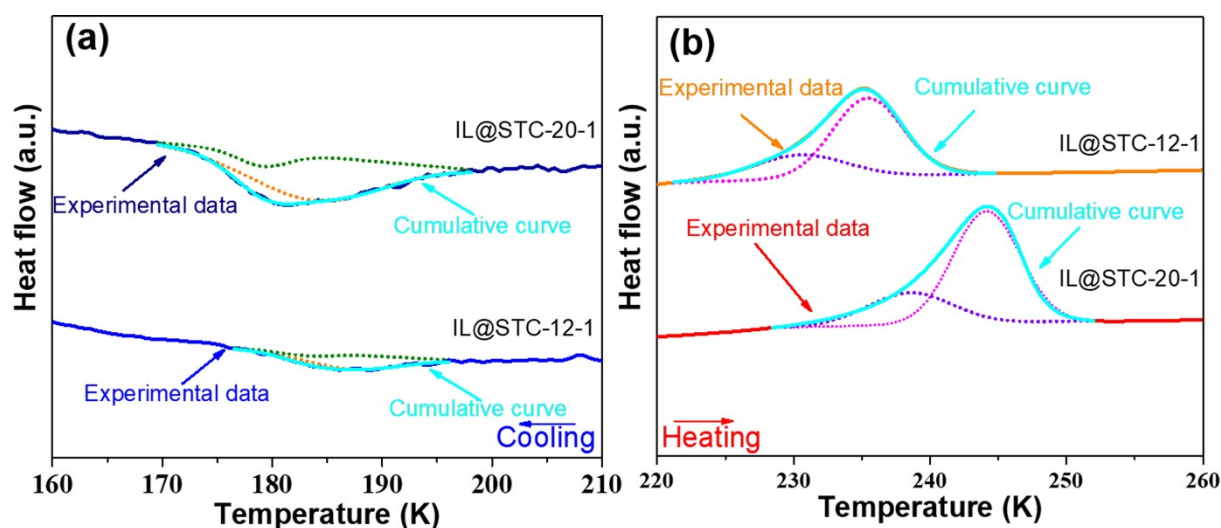
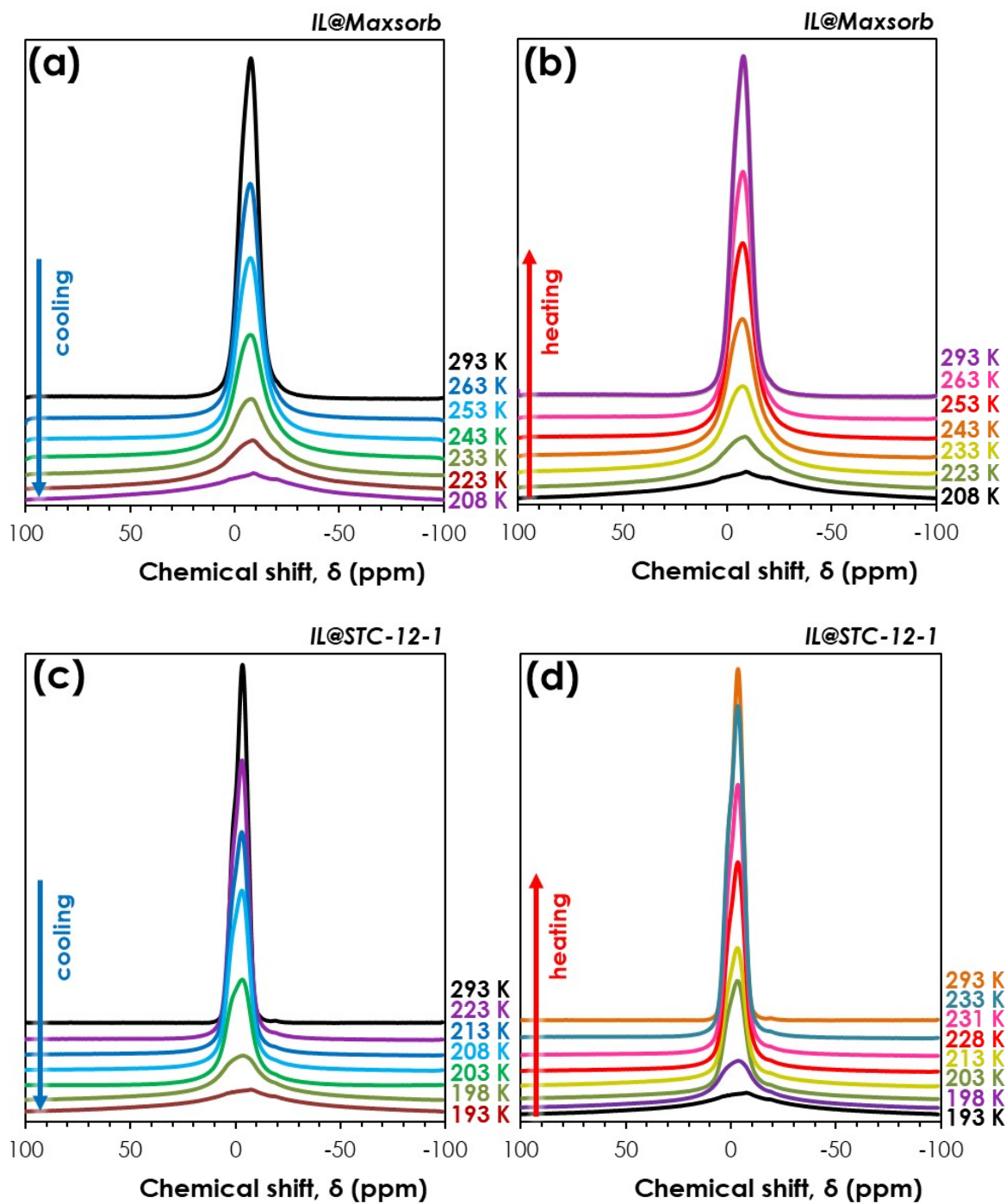


Figure S1. DSC thermograms and their fitting by using two Gaussian curves for [EMIm⁺][FSI⁻] confined in the STC-20-1 and STC-12-1 carbons (IL@STC-20-1 and IL@STC-12-1, respectively) upon (a) cooling and (b) heating at a rate of 10 K min⁻¹.

2. NMR spectra of [EMIm⁺][FSI] confined in the micro- and mesoporous carbons



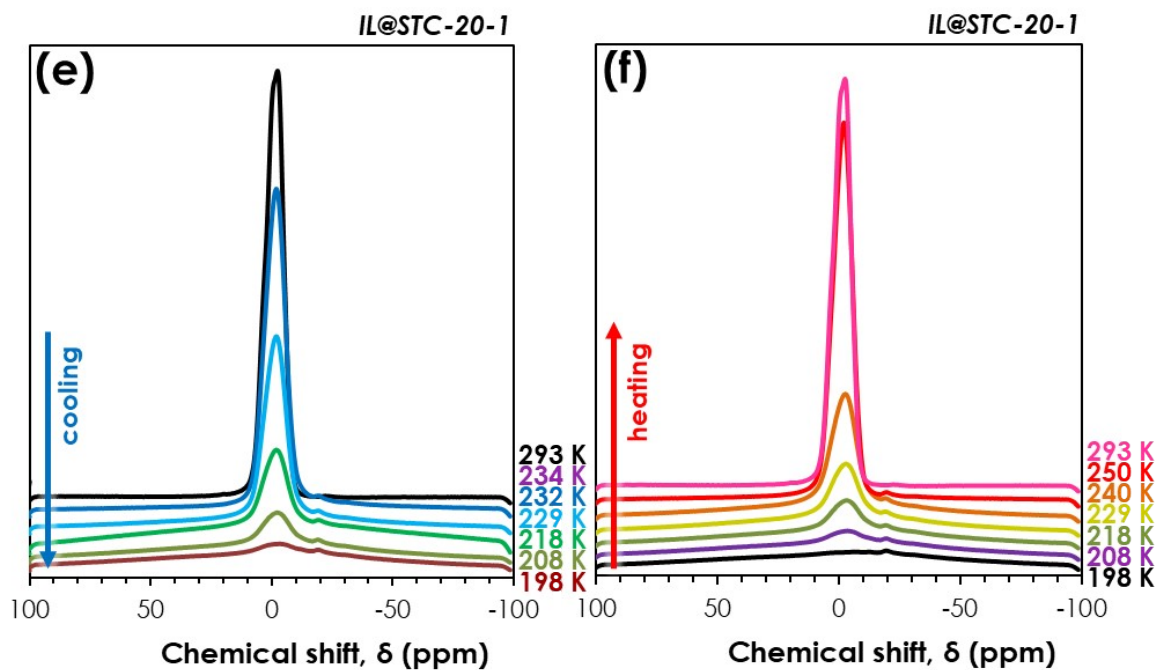


Figure S2. Static ^1H NMR spectra of $[\text{EMIm}^+][\text{FSI}^-]$ confined in (a, b) Maxsorb, (c, d) STC-12-1 and (e, f) STC-20-1 under (a, c, e) cooling and (b, d, f) heating. In order to allow a quantitative comparison between the spectra, the detected intensities were normalized by multiplication with the factor $T/293\text{ K}$ (which accounts for the temperature-dependence of the magnetization) [1].

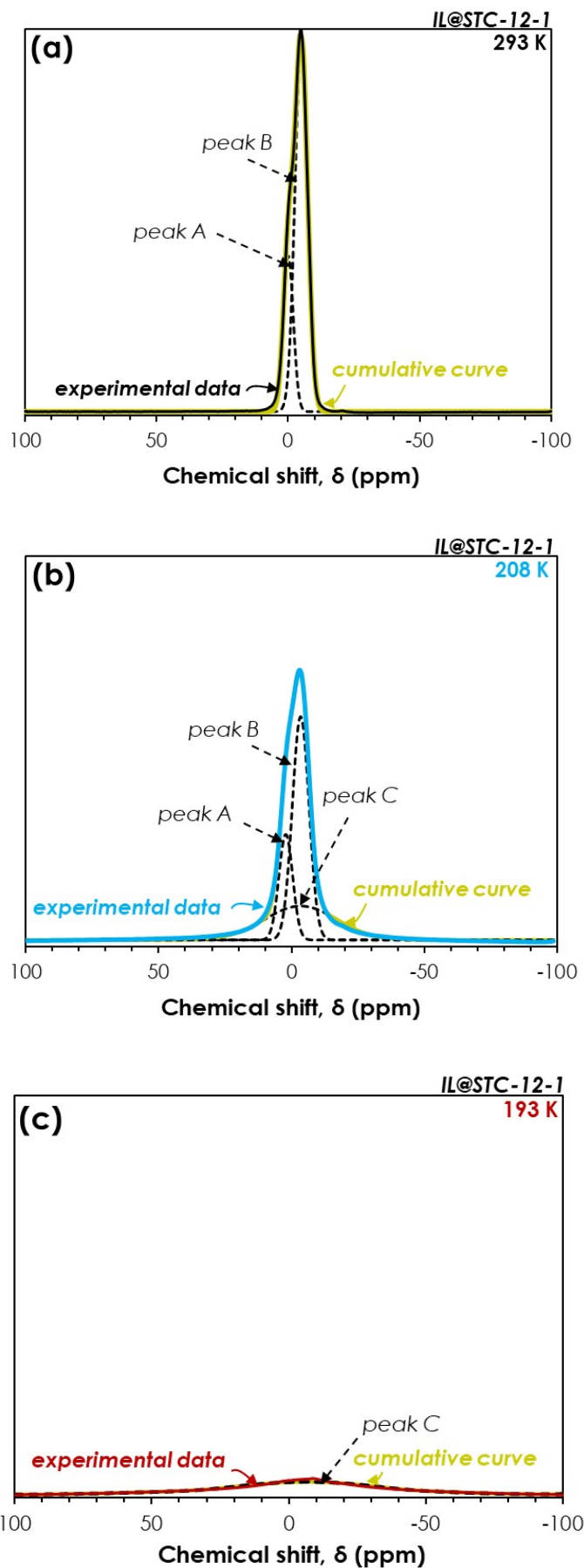


Figure S3. Deconvolution of the static ^1H NMR spectra of IL@STC-12-1 recorded at (a) 293 K, (b) 208 K and (c) 193 K under cooling (data from **Figure S2c**).

3. Surface functionality of the carbon materials

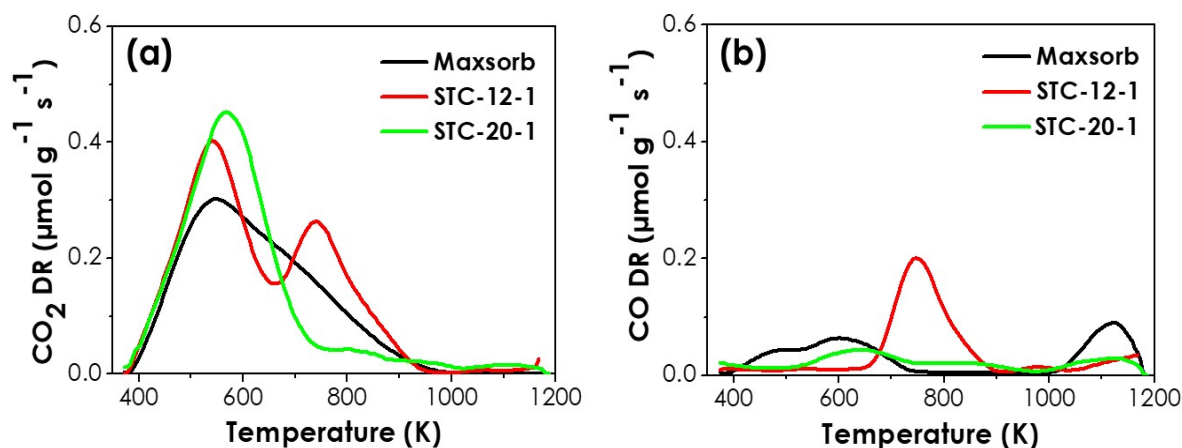


Figure S4. TPD analysis of the Maxsorb, STC-12-1, and STC-20-1 carbons: (a) CO₂ and (b) CO desorption.

Table S1. TPD data of the Maxsorb, STC-12-1, and STC-20-1 carbons (mass loss at 1223 K, amount of desorbed CO, CO₂, H₂O, and total amount of evolved oxygen (O)).

Carbon	Mass loss (wt. %)	CO (μmol g ⁻¹)	CO ₂ (μmol g ⁻¹)	H ₂ O (μmol g ⁻¹)	O (wt. %)
Maxsorb	3.0	319	87	248	1.6
STC-12-1	3.4	441	135	519	2.5
STC-20-1	2.0	292	53	328	1.5

Figure S4 shows the temperature programmed desorption (TPD) rates of CO₂ and CO for the three carbons; the quantitative data as mass loss and amount of desorbed CO, CO₂, H₂O, and oxygen are reported in Table S1. The CO₂ desorption observed for Maxsorb between 400 and 950 K (**Figure S4a**) reveals the presence of carboxylic functionalities (evolving up to around 800 K) and lactones (evolving between 700 and 950 K) [2]. Besides, the MS thermograms in **Figure S4b** indicate that Maxsorb contains a small amount of carbonyl groups, namely aldehydes/ketones and quinones, desorbed as CO up to about 750 K and above 1000 K, respectively [2, 3]. On the other hand, the surface of the STC-12-1 carbon is characterized by the presence of carboxylic functionalities (evolving as CO₂ up to around 700 K; **Figure S4a**) and anhydrides (releasing CO₂ as well as CO between 600 and 950 K; **Figure S2a** and **b**, respectively) [3]. In the case of the STC-20-1 carbon, the CO₂ desorption (**Figure S2a**) is related to the decomposition of carboxylic functionalities (evolving up to around 750 K) as well

as a very small amount of lactones (evolving between 700 and 1000 K), whereas CO evolution (Figure 2b) indicates the presence of a small number of aldehydes/ketones (evolving between 500 and 800 K) [2, 3]. The slightly higher (by 1 wt.%) surface oxygen content in STC-12-1 than in STC-20-1 (**Table S1**) is probably related to a higher density of siloxane and silanol (charged and uncharged, viz. SiO⁻ and SiOH, respectively) groups on the surface of the silica template of STC-12-1, due to the smaller diameter of the SiO₂ particles (12 nm) [4]. Indeed, during the final thermal treatment of the carbon/silica composite at 1173 K, oxygenated functionalities can be created on the carbon surface by carboreduction of the SiO⁻ and SiOH surface species of silica [5]. Overall, the low mass loss and low amount of evolved oxygen confirm that the three carbons are surface clean materials with a negligible amount of surface oxygenated functionalities.

4. Volume of a monolayer of [EMIm⁺]/[FSI⁻] confined in mesoporous carbons

The cumulative DFT surface area of the STC-12-1 and STC-20-1 carbons vs. their pore size is presented in **Figure S5**. The surface area due to mesopores (S_{meso} for pores between ca. 5 and 15 nm) was estimated by subtracting the surface area due to micropores (S_{micro} for pores below 2 nm) from the total surface area ($S_{\text{DFT}} = S_{\text{micro}} + S_{\text{meso}}$; the cumulative surface area values due to micropores and mesopores are reported in **Table S2**).

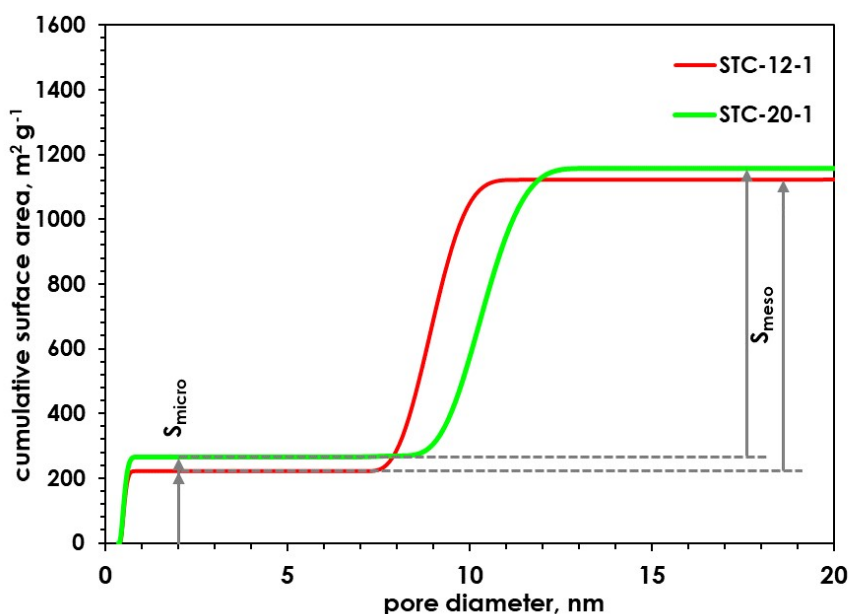


Figure S5. Cumulative DFT surface area vs. pore diameter of the STC-12-1 and STC-20-1 carbons; the vertical arrows represent the respective values of surface area due to micro- and mesopores (S_{micro} and S_{meso} , respectively); note that, similarly to the pore size distribution shown in **Figure 1a** of the manuscript, the curves of the two carbons are totally flat between ca. 1 and 7 nm.

Table S2. Cumulative surface area due to micro- and mesopores (S_{micro} and S_{meso} , respectively) for the STC-12-1 and STC-20-1 carbons.

Carbon	S_{DFT} ($\text{m}^2 \text{g}^{-1}$)	S_{micro} ($\text{m}^2 \text{g}^{-1}$)	S_{meso} ($\text{m}^2 \text{g}^{-1}$)
STC-12-1	1130	223	907
STC-20-1	1167	265	902

The volume V_x occupied by a single IL molecule can be estimated by applying the **Equation (S1)**:

$$V_x = \frac{M}{\rho N_A} \quad [\text{cm}^3] \quad (\text{S1}),$$

where M is the molecular mass of $[\text{EMIm}^+][\text{FSI}^-]$ equal to 291 g mol^{-1} , ρ – density of $[\text{EMIm}^+][\text{FSI}^-]$ of 1.44 g cm^{-3} , and N_A – the Avogadro number, giving $V_x = 336 \times 10^{-24} \text{ cm}^3$. Since the ions in direct contact with the mesopore walls may be randomly oriented, the average volume of one molecule can be represented by a cube of side $a_x = (336 \times 10^{-24})^{1/3} = 6.95 \times 10^{-8} \text{ [cm]}$; hence, the thickness of an IL monolayer is $d_{\text{mono}} = 6.95 \times 10^{-8} \text{ [cm]}$.

Henceforward, the volume occupied by the IL in direct contact with the walls, V_{mono} , can be calculated by applying the **Equation (S2)**:

$$V_{\text{mono}} = S_{\text{meso}} \times d_{\text{mono}} \times 10^4 \quad [\text{cm}^3 \text{g}^{-1}] \quad (\text{S2}),$$

giving $V_{\text{mono}} = 0.63 \text{ cm}^3 \text{g}^{-1}$, for the two carbons. Then, by subtracting V_{mono} from V_{meso} (see **Table 1**), $V_{\text{meso}} - V_{\text{mono}}$ values of 1.43 and $1.74 \text{ cm}^3 \text{g}^{-1}$ in IL@STC-12-1 and IL@STC-20-1, respectively, are obtained to represent the molecules located close to the mesopore center. Finally, the ratio of the volumes of $[\text{EMIm}^+][\text{FSI}^-]$ in contact with the mesopore walls and located close to the mesopores center, viz. $V_{\text{mono}} : (V_{\text{meso}} - V_{\text{mono}})$, is 0.44 and 0.36 for IL@STC-12-1 and IL@STC-20-1, respectively.

References:

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