Electronic Supplementary Information

Oxidative Ionothermal Synthesis for Micro and Macro Zn-based Materials

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A. TGA experiments details:

Instrument TGA Q500 V20.13 Build 39 Size 1.42700 mg Pan: Platinum Gas1: Nitrogen Gas2: Air Balance Gas: Nitrogen 40.0 ml/min Sample Gas: Nitrogen 60.0 ml/min Method: 1: Equilibrate at 30.00 °C

- 2: Ramp 5.00 °C/min to 650.00 °C
- 3: Isothermal for 1.00 min
- 4: Data storage Off
- 5: Jump to 30.00 °C
- 6: Isothermal for 20.00 min

B. Particle Calcination:

The surface of the metal coupon exposed 44 d to $[C_4C_1im]Cl$ solution at $20 \pm 1^{\circ}C$ was scratched, and the ϵ -Zn(OH)₂ octahedrons, the ZHC crystals and amorphous solids were collected and subsequently calcinated in a TGA instrument. A series of thermal processes can be seen from the TGA thermogram (Figure S1), as a consequence of the superposition of the thermal decomposition of these substances. First, a small mass loss of 1.7% is seen between 80-100°C attributed to removal of the physically adsorbed water molecules onto the surface of the sample, followed by a thermal process attributed to the removal of the hydration water of ZHC¹ simultaneously with the thermal decomposition of ϵ -Zn(OH)₂ (100-300°C) (Eq. S1)². At high temperatures, a massive mass loss is observed in the range of 300-500°C, which is in agreement with the TGA observed for the thermal decomposition of Zh₅(OH)₈Cl₂·H₂O given by Moezzi *et al*³. They explained in detail the different paths for the thermal decomposition of ZHC and attributed this last mass loss to the to the decomposition of an amorphous Zn(OH)₂·ZnCl₂ phase, formed by rearrangement of the crystalline ZHC phase (Eq S2).

$$\begin{split} &\epsilon\text{-Zn}(OH)_2\,(s) \rightarrow \text{ZnO}\,(s) + H_2O\,(g)\,(\text{Eq. S1})^2 \\ &\text{Zn}_5(OH)_8\text{Cl}_2\cdot H_2O_{(Cr)} \,\,^{\otimes}\,\text{Zn}_5(OH)_8\text{Cl}_{2\,(Cr)} + H_2O\,(g)\,(\text{Eq. S2a})^{\,1} \\ &\text{Zn}_5(OH)_8\text{Cl}_{2\,(Cr)} \,\,^{\otimes}\,\text{3}\,\text{ZnO}\,(\text{Cr}) + \text{ZnO}\cdot\text{ZnCl}_2\cdot 2H_2O_{(Cr)} + H_2O\,(g)\,(\text{Eq. S2b})^{\,1} \\ &\text{ZnO}\cdot\text{ZnCl}_2\cdot 2\,H_2O_{(Cr)} \,\,^{\otimes}\,\text{3}\,\text{Zn}(OH)_2\cdot\text{ZnCl}_{2\,(\text{amorphous})} + H_2O(g)\,(\text{Eq. S2c})^{\,1} \\ &\text{Zn}(OH)_2\cdot\text{ZnCl}_{2\,(\text{amorphous})} \rightarrow 2\,\text{ZnO} + 2\text{HCl}(g)\,(\text{Eq. S2d})^{\,1} \end{split}$$

C. 100% Water Case:

In control experiments Zn foils were exposed to demineralized water for a duration of three and six days at room temperature and 70°C. At room temperature for both exposure times, the Zn foils were covered with flat-topped hexagonal nanorods along with the formation of micrometre-scale clusters of a polycrystalline material distributed across the surface (Figure S14). At 6d exposure time, larger nanorods are observed (Figure S16). At 70°C and 3d exposure time, several structures were observed, flat-topped hexagonal nanorods, thicker structures ending with a point and rounded ends, and micro-meter scale polygonal plates (Figure S15). At 6d exposure, the flat-topped hexagonal nanorods are no longer visible, and the entire surface of covered with the

other structures, including the formation of well-defined needles (Figure S17). At 120°C, ZnO flat-topped nanoroads formed along with a thin coarse material (Figure S18), probably as a result of dissolution of ZnO to form Zn^{2+} ions, followed by their subsequent redeposition as ZnO. The structures were analysed by XRD spectra, where peak patterns indicate both the presence of Zn and ZnO at all temperatures and traces of Zinc carbonate hydroxide (ZCAR) $Zn_5(CO_3)_2(OH)_6Cl_2 \cdot H_2O$ (Figure S20).

The formation of ZnO nanoparticles by wet-oxidation of etched zinc foils in water had been reported 4,5 without the formation of Zn(OH)₂, which is in agreement with our experiments. Interestedly, the ZnO structures observed in each of those works and in ours are similar but not identical, suggesting that other factors are driving the crystal morphology of these materials in water.

D. Solvent structure water-rich case

The aggregation behaviour of $[C_4C_1im]Cl$ in water had been studied by others with different techniques⁶. For this system, it has been found an aggregation number (n) of 8, a degree of ionization of aggregates (α) of 0.7698, a

standard free energy of aggregation (ΔG_m^0) of -12.41 ± 0.27 kJ mol⁻¹, and an equilibrium constant (K) for the equilibrium between monomers and monodisperse aggregates of 1.0050⁶. The experimental value for the Critical Aggregation Concentration (CAC) for the [C₄C₁im]Cl-water system depends on the experimental technique used for its determination: 948 mmol/L (refractive index), 800 mmol/L (fluorescence) and 935 mmol/L (NMR)⁶. However, another study on the aggregation of [C₄C₁im]Cl in water though surface tension measurement was not conclusive as no discontinuities were observed in the plot of surface tension against concentration⁷. CAC determination though electrical conductivity measurements has not been reported. Therefore, in section E, we provide a determination of the CAC from electrical conductivities measurements form literature.

The $[C_4C_1im]Cl$ total concentration in the water rich case is 1.03 mol/L, which lies just above the CAC, which means that the individual ionic liquid molecules are in equilibrium with its aggregated form. According the values given above, $[C_4C_1im]Cl$ monomer concentration at equilibrium is 115.0 mmol/L while the aggregate ($[C_4C_1im]Cl$)₈ is 115.6 mmol/L.

E. Electrical conductivity

Experimental values of the specific conductivity κ as a function of IL concentration are shown in Figure S2. Two data sets from literature have been taken for diluted [C₄C₁im]Cl and one data set for concentrated [C₄C₁im Cl. The electrical conductivities κ have been converted to molar conductivities (Λ) (κ /c) and plotted according to Kohlraush's empirical law (Figure S3) (Eq S3).

$$\Lambda = \Lambda_0 - KC^{1/2}$$
(Eq S3)

In Eq S3, Λ_0 is the molar conductivity at infinite dilution, K is an empirical constant that depends on the type of the electrolyte and C is the solute concentration in mol/L. The linear portions in represent regimes of approximately constant association. The break points between these portions occur when the nature of the charge carriers changes^{8,9}.

From Figure S2, it can be seen that the specific conductivity deviate from linearity at concentrations higher than 0.29 mmol/L. However, due to the number of data points, it is not possible to accurately determine the CAC from these conductivity data sets.

From Figure S3, it can be seen that at high IL concentrations, the values of molar conductivity follow a linear trend, that doesn't extrapolate to the molar conductivity at infinite dilution. At concentrations lower that 1 mol/L, the molar conductivity values start to diverge from this line and approaches the Kohlraush's empirical law. The two experimental conditions selected for this study. *i.e.* water-rich case and IL-rich case, lie within the extremes of a linear portion of the Kohlraush's plot, suggesting that the nature of the charge carriers is the same for both cases.

F. Thermodynamic aspects of ZnO formation

The mechanisms for the ZnO formation in solution and over the metal surface can be supported from thermodynamic calculations. The change in the standard-state free energy for reaction S4 is negative ($\Delta G^0 = -79.3$ kJ/mol < 0) and it is favoured by both enthalpy ($\Delta H^0 = -70.3$ kJ/mol < 0) and entropy ($\Delta S^0 = 30.3$ J/mol.K> 0) changes, thus metallic zinc will react with water to from Zn(OH)₂ spontaneously. Once formed, it can dehydrate to form ZnO (Eq S5)

 $Zn_{(s)}^{0} + 2 H_2O_{(I)} \rightarrow H_{2(g)} + Zn(OH)_{2(s)}$ (Eq. S4)

$Zn(OH)_2(s) \rightarrow ZnO(s) + H_2O(I)$ (Eq. S5)

The change in the standard-state free energy for reaction S5 is small in magnitude and its value will strongly depend on the data set used for the thermodynamic calculations. When CRC data is used (Table S4), we obtain a value of $\Delta G^0 = -4.1$ kJ/mol, which is consistent with the values found in literature¹⁰, however, other authors had reported a value of $\Delta G^0 = -1.13$ kJ/mol¹¹. In any case, reaction S5 is not favoured by the change in enthalpy ($\Delta H^0 > 0$) but it is favoured by the change in entropy ($\Delta S^0 > 0$) due to an increase in the number of molecules, one being liquid. This indicates that Zn(OH)₂ does spontaneously convert to ZnO at room temperature under standard conditions, and explain why Zn(OH)₂ is not observed at high temperatures.

G. Crystallographic information

The diffraction patterns of the as prepared samples are given in Figure S20 to Figure S24. Detected species were matched to the following references compounds using HighScore suite, PANalytical's commercial powder diffraction analysis software:

- Zinc (Zn): Reference code 00-004-0831.
- Zinc carbonate hydroxide (Zn₅(CO₃)₂(OH)₆Cl₂·H₂O): (ZCAR). Reference code 00-019-1458.
- Zinc chloride hydroxide monohydrate (Zn₅(OH)₈Cl₂·H₂O): ZHC or Simonkolleite Reference code 00-007-0155.
- Zinc hydroxide (ε- Zn(OH)₂): (Wülfingite). Reference code 00-038-0385
- Zinc oxide (ZnO): Zincite "Würtzite structure". Reference code 00-036-1451



Figure S1. Thermogram for the calcination of ϵ -Zn(OH)₂ and ZHC into ZnO.



Figure S2. Specific conductivity (κ) over IL molar concentration. Experiment data: (**◊**) This work (water-rich case 1.02 mol/L^{1/2}., IL-rich case 2.17 mol/L^{1/2}, residual water Case 2.48 mol/L^{1/2}). Data from literature included (error bars not shown): (\Box) 30 °C¹⁶ (**0**) 25 °C¹⁷ (**▲**) 25 °C¹⁸ (**0**) 25 °C¹⁹. Line represent the linear regression of the data for diluted solutions. Insert shows a detail in the diluted region.



Figure S3. Molar electrical conductivity (Λ_m) over the square root of the IL molar concentration. Experiment data: (\diamond) This work (water-rich case 1.02 mol/L^{1/2}., IL-rich case 2.17 mol/L^{1/2}, residual water Case 2.48 mol/L^{1/2}). Data from literature included (error bars not shown): (\Box) 30 °C¹⁶ (\bullet) 25 °C¹⁷ (\blacktriangle) 25 °C²⁰ (\bullet) 25 °C²¹. Lines represent the linear regression of the data for concentrated solutions. Insert shows a detail in the diluted region.



Figure S4. Magnified zinc surface exposed to $[C_4C_1 \text{im}]Cl$ solution (IL-1, X_{H2O} =0.98 and 20 ± 1°C) for 18 d showing a ZnO structure.



Figure S5. Magnified zinc surfaces exposed to $[C_4C_1im]Cl$ solution (IL-1, X_{H20} =0.98 at 20 ± 1°C) for 18 d showing ZHC.



Figure S6. Magnified zinc surface exposed to $[C_4C_1im]Cl$ solution (IL-1, $X_{H2O}=0.98$ and $20 \pm 1^{\circ}C$) for 44 d. (A) ZHC tablets. (B): ϵ - Zn(OH)₂ octahedrons and amourphous solid containing chlorides.



Figure S7. . Magnified zinc surface exposed to $[C_4C_1im]Cl$ solution (IL-2, X_{H2O} =0.98 and 20 ± 1°C) for 46 d. ϵ -Zn(OH)₂ octahedrons.



Figure S8. Magnified zinc surface exposed to $[C_4C_1 \text{im}]Cl$ solution (IL-1, X_{H2O} =0.98 solution and 70 ± 1°C) for 15 d showing ZnO structures.



Figure S9. Magnified zinc surface exposed to $[C_4C_1im]Cl$ solution (IL-2, $X_{H2O}=0.98$ at 120 ± 1°C) for 1 d. (A) ZnO structures. (B) Detail of ZnO hexagonal nanorods.



Figure S10. Magnified zinc surface exposed to $[C_4C_1im]Cl$ solution (IL-1, $X_{H20}=0.75$ at 20 ± 1°C). (A) 18 d exposure showing ZnO hexagonal flat-topped nanorods. (B) 26 d exposure showing ZnO hexagonal flat-topped nanorods.



Figure S11. Magnified zinc surface exposed to $[C_4C_1 \text{im}]Cl$ solution (IL-1, X_{H2O} =0.75 at 120 ± 1°C) for 16 h. Surface is covered with ZnO nanorods with micrometer-scale ZnO crystals.



Figure S12. Magnified zinc surface exposed to $[C_4C_1im]Cl$ solution (IL-1, $X_{H2O}=0.75$ and $20 \pm 1^{\circ}C$) for 26 d. Detail of the Cl containing material.



Figure S13. Magnified zinc surface exposed to dry [C₄C₁im]Cl. (A) IL-1, X_{H20} =0.04 at 70 ± 1°C for 14 d. (B) IL-2, X_{H20} =0.04 at 120 ± 1°C for 12 d.



Figure S14. Micrometer-scale ZnO polycrystalline material. Zinc exposed to demineralized water for 3 days at 20°C.



Figure S15. Zinc exposed to demineralized water for 3 days at 70°C. (A) Flattopped hexagonal nanorods and flowers ending with a point and rounded end. (B) Example of micro-meter scale polygonal plates and other ZnO rods.



Figure S16. Example of polycrystalline material. Zinc exposed to demineralized water for 6 days at 20°C. (A) Overall surface. (B) Detail of flattopped hexagonal nanorods.



Figure S17. ZnO Nanorods formed in demineralized water after 6 d exposure at 70°C.



Figure S18. ZnO structures formed in demineralized water after 4.6 d exposure at 120°C.



Figure S19. Summary of the must representative structures. [A] ZnO flat-topped hexagonal rods. [B] ε-Zn(OH)2 octahedrons. [C] ZHC plates. [D] ZnO short rods (round and sharp ended). [E] ZnO needles. [F] ZnO polycrystalline structure. [G] ZnO thick crystals. [H] ZnO 3D needle flower. [I] ZnO 3D thick crystal flower.



Figure S20. XRD pattern of zinc coupons (as prepared) exposed to water. [A] unexposed metal. [B] 20 °C and 3 days. [C] 20 °C and 6 days. [D] 70 °C and 3days. [E] 70 °C and 6 days. [D] 120 °C and 2.6 days. [E] 120 °C and 4.6 days.



Figure S21. XRD pattern of zinc coupons (as prepared) exposed to $[C_4C_1\text{im}]Cl$ solutions with a water content of 98 mol%. [A] unexposed metal. [B] 120 °C and 16 hours (IL-2). [C] 70 °C and 3.5 days (IL-1) [D] 20 °C and 18 days (IL-1). [E] 20 °C and 44 days (IL-1).



Figure S22. XRD pattern of zinc coupons (as prepared) exposed to $[C_4C_1im]Cl$ (IL-2) at 20°C and 98%mol. [A] unexposed metal. [B] 6 days. [C] 12 days. [D] 46 days.



Figure S23. XRD pattern of zinc coupons (as prepared) exposed to $[C_4C_1im]Cl$ solutions with a water content of 75 mol%. [A] unexposed metal. [B] 20 °C and 18 days (IL-1). [C] 20 °C and 26 days (IL-1). [D] 70 °C and 5 days (IL-1). [E] 70 °C and 6 days (IL-2). [F] 120 °C and 16 hours (IL-2).



Figure S24. XRD pattern of zinc coupons (as prepared) exposed to dried $[C_4C_1im]Cl$. [A] unexposed metal. [B] 70 °C and 14 days. [C] 120 °C and 12 days. [D] 120 °C and 16 days.

TABLES

		Water	Temn	Exposure	Species detected by XRD					
Solvent	IL	Content [mol%]	[°C]	Time [days]	Zn	ZnO	ε-Zn(OH) ₂	ZHC	ZCAR	
	1	75	20	18	Х	(Traces)				
	1	75	20	26	Х	Х				
	1	75	70	5	Х	Х				
	2	75	120	5.8	Х	Х				
	2	75	120	16h	Х	Х				
	2	98	20	14	Х	Х		Х	(Traces)	
	1	98	20	18	Х	Х		Х		
[C ₄ C ₁ im]Cl	1	98	20	44	Х	Х	х	Х		
	2	98	20	48	Х	Х	х	Х		
	1	98	70	3.5	Х	Х				
	1	98	70	15	Х	Х		(Traces)		
	2	98	120	16h	Х	Х				
	1	Residual	70	14	Х					
	2	Residual	120	12	Х					
	2	Residual	120	16	Х					
	-	-	20	3	Х	Х			Х	
	-	-	20	6	Х	Х			Х	
Matar	-	-	70	3	Х	Х			(Traces)	
Water	-	-	70	6	Х	Х			(Traces)	
	-	-	120	2.6	Х	Х				
	-	-	120	4.6	Х	Х				

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Table St. Summa	y of the crystannic	e phases deletted	i on the metal su		iguies 520 (0 524).

Table S2. Summary of the must representative structures. [A] ZnO flat-topped hexagonal rods. [B] ε -Zn(OH)₂ octahedrons. [C] ZHC plates. [D] ZnO short rods (round and sharp ended). [E] ZnO needles. [F] ZnO polycrystalline structure. [G] ZnO thick crystals. [H] ZnO 3D needle flower. [I] ZnO 3D thick crystal flower. Refer to Figure S19.

		Water	Temp	Exposure										
Solvent	IL	Content		Time	[A]	[B]	[C]	[D]	[E]	[F]	[G]	[H]	[I]	Others
		[mol%]	[°C]	[days]										
	1	Residual	70	14										
	2	Residual	120	12										
	2	Residual	120	16										
	2	75	120	5.8	Х								Х	
	1	75	20	18/26	Х									
	2	75	120	1	Х									(3)
	2	75	120	16h	Х						Х		х	
	2	98	20	6		Х								(1,5)
[C₁C₄im]Cl	2	98	20	14										(1,5)
	2	98	20	16		х								(1,5)
	1	98	20	18	х									
	1	98	20	44		х	Х	х					х	(1,2)
	2	98	20	48			Х							(1,5)
	1	98	70	3.5	х						Х	Х		
	1	98	70	15			Х	х	х		Х	Х	х	
	2	98	120	1	х						Х		х	(4)
	2	98	120	16h	х									
	-	-	20	2	Х					Х				(2)
Water	-	-	20	2	х					х			х	(2)
	-	-	70	6	х			х	х		Х	Х		
	-	-	70	6					х		х	х		
	-	-	120	2.6										(6)
	-	-	120	4.6	х						х		х	(3)

1. Amorphous.

2. Cotton Like.

3. Coarse material

4. Agglomerate of small crystals

5. Flakes

6. Small crystal without well-defined shape

Table S3. pH measurements for IL-1 solutions.								
Solvent	Water Content [mol%]	Temp [°C]	Exposure Time [days]	рН				
	Residual	70	14	-				
	75	20	18	7.15				
	75	20	26	7.49				
[C ₄ C ₄ im]Cl	75	70	5	7.28				
	98	20	18	7.98				
	98	20	44	8.07				
	98	70	4	7.57				
	98	70	15	7.71				
	-	20	3	6.7				
W/ster	-	20	6	6.73				
water	-	70	3	6.91				
	-	70	6	6.81				

Table S4. List of standard enthalpy (ΔH^0), standard free energy (ΔG^0) and standard entropy (ΔS^0) used for thermodynamic calculations²².

	ΔH ⁰	ΔG ⁰	ΔS ⁰
	kJ/mol	kJ/mol	J/mol.K
Zn(OH) ₂ (s)	-641.9	-553.5	81.2
ZnO (s)	-350.5	-320.5	43.7
∎Zn (s)	-	-	41.6
H ₂ O (I)	-285.8	-237.1	70.0
H_2 (g)	-	-	130.68

REFERENCES

- 1. Moezzi, A., Cortie, M. & McDonagh, A. Transformation of zinc hydroxide chloride monohydrate to crystalline zinc oxide. *Dalt. Trans.* **45**, 7385–7390 (2016).
- 2. Ghotbi, M. Y. Synthesis and characterization of nano-sized ε-Zn(OH)2 and its decomposed product, nano-zinc oxide. *J. Alloys Compd.* **491**, 420–422 (2010).
- 3. Moezzi, A., Cortie, M. & McDonagh, A. Transformation of zinc hydroxide chloride monohydrate to crystalline zinc oxide. *Dalt. Trans.* **45**, 7385–7390 (2016).
- 4. Tan, W. K. *et al.* Formation of highly crystallized ZnO nanostructures by hot-water treatment of etched Zn foils. *Mater. Lett.* **91**, 111–114 (2013).
- 5. Balela, M. D. L., Pelicano, C. M. O. & Lockman, Z. In situ mixed potential study of the growth of zinc oxide hierarchical nanostructures by wet oxidation of zinc foil. *J. Mater. Sci.* **52**, 2319–2328 (2017).
- 6. Singh, T. & Kumar, A. Aggregation behavior of ionic liquids in aqueous solutions: Effect of alkyl chain length, cations, and anions. *J. Phys. Chem. B* **111**, 7843–7851 (2007).
- 7. Jungnickel, C. *et al.* Micelle formation of imidazolium ionic liquids in aqueous solution. *Colloids Surfaces A Physicochem. Eng. Asp.* **316**, 278–284 (2008).
- 8. Bowers, J., Butts, C. P., Martin, P. J., Vergara-Gutierrez, M. C. & Heenan, R. K. Aggregation Behavior of Aqueous Solutions of Ionic Liquids. *Langmuir* **20**, 2191–2198 (2004).
- 9. Hanibah, H., Hashim, N. Z. N. & Shamsudin, I. J. Molar conductivity behavior of ionic liquid compare to inorganic salt in electrolyte solution at ambien temperature. *AIP Conf. Proc.* **1877**, (2017).
- 10. Demoisson, F., Piolet, R. & Bernard, F. Hydrothermal synthesis of ZnO crystals from Zn(OH)2 metastable phases at room to supercritical conditions. *Cryst. Growth Des.* **14**, 5388–5396 (2014).
- 11. Nicholas, N. J., Franks, G. V. & Ducker, W. A. The mechanism for hydrothermal growth of zinc oxide. *CrystEngComm* **14**, 1232–1240 (2012).
- 12. Li, Y., Zou, Y. & Hou, Y. Synthesis and characterization of simonkolleite nanodisks and their conversion into ZnO nanostructures. *Cryst. Res. Technol.* **46**, 305–308 (2011).

- 13. Tanaka, H., Fujioka, A., Futoyu, A., Kandori, K. & Ishikawa, T. Synthesis and characterization of layered zinc hydroxychlorides. *J. Solid State Chem.* **180**, 2061–2066 (2007).
- 14. Cousy, S., Gorodylova, N., Svoboda, L. & Zelenka, J. Influence of synthesis conditions over simonkolleite/ZnO precipitation. *Chem. Pap.* **71**, 2325–2334 (2017).
- 15. Kowalik, P. *et al.* Structure and morphology transformation of ZnO by carbonation and thermal treatment. *Mater. Res. Bull.* **65**, 149–156 (2015).
- 16. Liu, W., Cheng, L., Zhang, Y., Wang, H. & Yu, M. The physical properties of aqueous solution of room-temperature ionic liquids based on imidazolium: Database and evaluation. *J. Mol. Liq.* **140**, 68–72 (2008).
- 17. Shekaari, H. & Mousavi, S. S. Conductometric studies of aqueous ionic liquids, 1-alkyl-3methylimidazolium halide, solutions at T = 298.15-328.15 K. *Fluid Phase Equilib.* **286**, 120–126 (2009).
- 18. Yang, Q. *et al.* The effect of molecular solvents on the viscosity, conductivity and ionicity of mixtures containing chloride anion-based ionic liquid. *J. Ind. Eng. Chem.* **19**, 1708–1714 (2013).
- 19. Chen, Y. J., Xuan, X. P., Zhang, H. H. & Zhuo, K. L. Conductivities of 1-alkyl-3-methylimidazolium chloride ionic liquids in monosaccharide+water solutions at 298.15K. *Fluid Phase Equilib.* **316**, 164–171 (2012).
- 20. Yang, Q. *et al.* The effect of molecular solvents on the viscosity, conductivity and ionicity of mixtures containing chloride anion-based ionic liquid. *J. Ind. Eng. Chem.* **19**, 1708–1714 (2013).
- Chen, Y. J., Xuan, X. P., Zhang, H. H. & Zhuo, K. L. Conductivities of 1-alkyl-3-methylimidazolium chloride ionic liquids in monosaccharide+water solutions at 298.15K. *Fluid Phase Equilib.* **316**, 164–171 (2012).
- 22. CRC Handbook of Chemistry and Physics, 99th Edition. (CRC Press, 2018).