Electronic Supplementary Material (ESI) for Green Chemistry.

Ionothermal carbonization of sugarcane bagasse in imidazolium tetrachloroferrate ionic liquids: effect of the cation on textural and morphological properties

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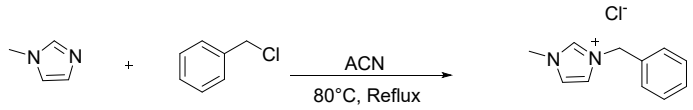
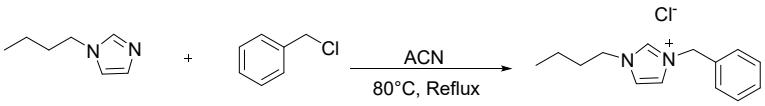
Experimental section

Synthesis of 1-benzyl-3-methylimidazolium chloride [(Bn)mim]Cl and 1-benzyl-3-butylimidazolium chloride [(Bn)bim]Cl

1-benzyl-3-methylimidazolium chloride was obtained by preparing a mixture containing 1-methylimidazole (24.1 g, 0.294 mol) with benzyl chloride (41.0 g, 0.323 mol; which corresponds to a 1:1.1 molar ratio; see reaction (1) below) in 100 mL of acetonitrile under reflux at 80 °C for 3 hours and by stirring for 24 hours at room temperature.
1-benzyl-3-butylimidazolium chloride was obtained by preparing a mixture containing 1-butylimidazole (20.9 g, 0.168 mol) with benzyl chloride (23.4 g, 0.185 mol; which corresponds to a 1:1.1 molar ratio; see reaction (2) below) in 100 mL of acetonitrile under reflux at 80 °C for 3 hours and by stirring for 24 hours at room temperature.



(1)



(2)

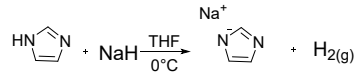
Hexane (3×50mL) was used to eliminate the excess of benzyl chloride. Then, acetonitrile was removed via rotary evaporation. The as-synthesized viscous ILs were freeze-dried overnight.

[(Bn)mim]Cl: (58.2 g, 0.279 mol). Yield: 95%. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 10.64 (s, 1H) ; 7.67-7.29 (m, 7H) ; 5.52 (s, 2H) ; 3.99 (s, 3H). **^{13}C NMR (126 MHz,$CDCl_3$)** δ 137.67; 133.26; 129.35; 129.32; 128.85; 123.8; 121.92; 53.12; 36.53. **Elemental analysis**. wt% theoretical: C (63.309); H (6.278); N (13.422). wt% analytical: C (61.929); H (6.235); N (13.062).

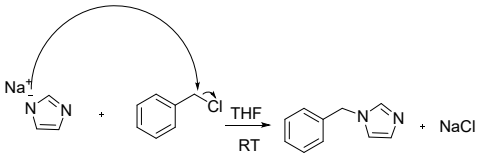
[(Bn)bim]Cl: (36.6 g, 0.146 mol). Yield: 87%. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 10.81 (s, 1H), 7.78-7.05 (m, 7H), 5.54 (s, 2H), 4.22 (t, 2H), 1.81 (t, 2H), 1.35 – 1.20 (m, 2H), 0.85 (t, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 137.15; 133.42 ; 129.24; 128.90; 128.86; 122.34; 122.01; 53.02; 49.74; 32.00; 19.39; 13.35. **Elemental analysis**. wt% theoretical: C (67.054); H (7.636); N (11.170). wt% analytical: C (65.878); H (8.093); N (11.070).

Synthesis of 1,3-(benzyl)imidazolium chloride [(Bn)$_2$im]Cl

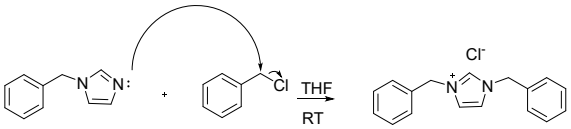
1,3-bis(benzyl)imidazolium chloride was synthesized by suspending sodium hydride (6.6 g, 0.164 mol) in 50 mL of THF in a three-necked flask placed in an ice bath and equipped with a condenser. An equimolar quantity of imidazole (11.3 g, 0.164 mol) dissolved in 100 mL of THF was gradually added to the mixture, which was stirred continuously using a magnetic stirrer. Once the addition was completed, the ice bath was removed (see reaction (3)). Benzyl chloride (42.0 g, 0.328 mol) was added dropwise into the reaction medium in a 2:1 molar ratio relative to the imidazole. Stirring at room temperature was maintained for 12 hours. The sodium chloride was eliminated by filtration on sintered glass topped with celite (reactions (4) and (5)). Washing with hexane (3×50 mL) was carried out to remove traces of benzyl chloride. THF was removed by rotary evaporation. Finally, the ionic liquid was freeze-dried.



(3)



(4)



(5)

[(Bn)$_2$im]Cl: (29.43 g , 0,103 mol). Yield : 63%. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 11.25 (s, 1H); 7.84-6.87 (m, 12H); 5.57 (s, 4H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 138.08; 132.82; 129.57; 129.50; 129.03; 121.59; 53.54. **Elemental analysis.** wt% theoretical: C (71.697); H (6.016); N (9.836). wt% found: C (70.685); H (6.248); N (9.391).

Experimental data

Table S1. Textural properties obtained from nitrogen sorption isotherms at 77 K of ionochars prepared by ionothermal carbonization of bagasse at 240 °C in 1-alkyl-3-methylimidazolium tetrachloroferrate with different aliphatic chain length.

Ionochar	SSA_{BET} ($m^2\ g^{-1}$)	$SSA_{micropore}$ ($m^2\ g^{-1}$)	$SSA_{external}$ ($m^2\ g^{-1}$)	V_{total} ($cm^3\ g^{-1}$)	$V_{micropore}$ ($cm^3\ g^{-1}$)	$V_{external}$ ($cm^3\ g^{-1}$)
C_2m-Bg	**734**	**467**	**267**	**0.83**	**0.20**	**0.63**
C_4m-Bg	**628**	**495**	**133**	**0.46**	**0.21**	**0.25**
C_6m-Bg	**518**	**396**	**122**	**0.31**	**0.17**	**0.14**
C_8m-Bg	**173**	**123**	**50**	**0.12**	**0.05**	**0.07**

Table S2. Mass yields, elemental composition† and carbon yields of ionochars prepared by ionothermal carbonization of bagasse at 240 °C in 1-alkyl-3-methylimidazolium tetrachloroferrate with different aliphatic chain length.

Ionochar	Yield (wt%)	C[a] (wt%)	H[a] (wt%)	N[a] (wt%)	O[a] (wt%)	Fe[b] (wt%)	Cl[b] (wt%)	Corrected Yield (wt%)	Carbon Yield (wt%)
C_2m-Bg	**53.0**	**67.4**	**4.1**	**0.2**	**25.3**	**2.3**	**1.7**	**50.8**	**78.1**
C_4m-Bg	**54.8**	**69.0**	**4.7**	**0.4**	**20.9**	**1.2**	**2.4**	**52.2**	**81.9**
C_6m-Bg	**55.9**	**65.4**	**4.3**	**0.3**	**23.6**	**3.9**	**2.7**	**51.7**	**79.2**
C_8m-Bg	**57.0**	**66.0**	**4.6**	**0.5**	**23.0**	**3.3**	**2**	**52.6**	**80.3**

[a]Combustional elemental analysis. [b]SEM-EDX. †The total elemental composition may exceed 100 wt% because SEM-EDX is not quantitative and may overestimate some elements.

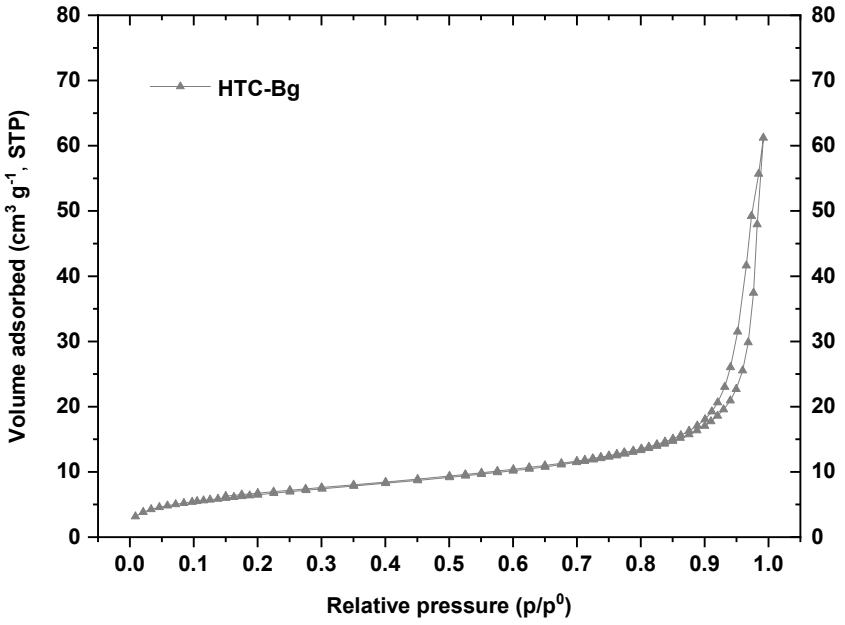


Figure S1. Nitrogen sorption isotherm at 77 K of **HTC-Bg**.

Table S3. Textural properties obtained from nitrogen sorption isotherms at 77 K of **HTC-Bg**.

Hydrochar	SSA_{BET} ($m^2\ g^{-1}$)	$SSA_{micropore}$ ($m^2\ g^{-1}$)	$SSA_{external}$ ($m^2\ g^{-1}$)	V_{total} ($cm^3\ g^{-1}$)	$V_{micropore}$ ($cm^3\ g^{-1}$)	$V_{external}$ ($cm^3\ g^{-1}$)
HTC-Bg	**24**	**7**	**17**	**0.09**	**0.00**	**0.09**

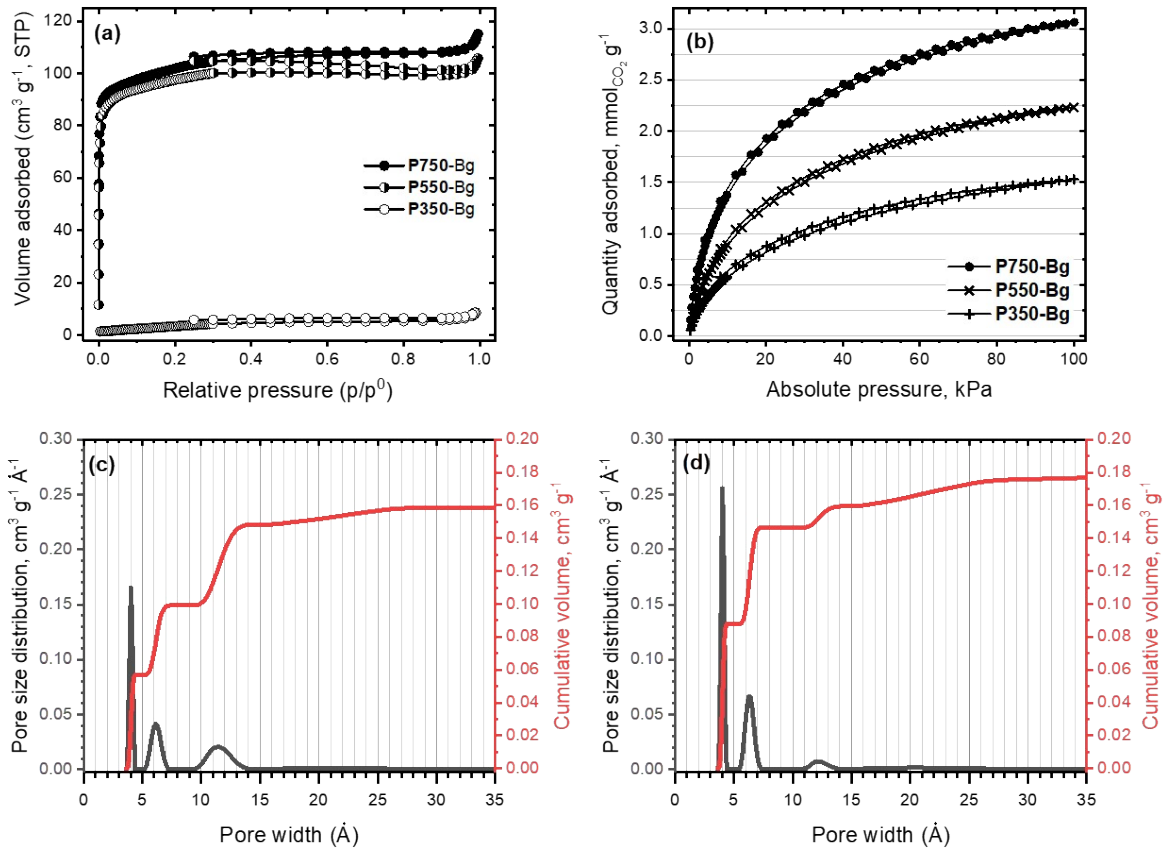


Figure S2. (a) Nitrogen sorption isotherms at 77 K and **(b)** carbon dioxide sorption isotherms at 273 K of **P350-Bg**, **P550-Bg** and **P750-Bg**. Pore size distributions calculated using 2D-NLDFT models for carbons with heterogeneous surfaces (SAIEUS software) for (c) **P550-Bg** and (d) **P750-Bg**. Both nitrogen sorption isotherms at 77 K and carbon dioxide sorption isotherms at 273 K were combined [J. Jagiello *et al. Carbon 91*, **2015**, 330-337; http://dx.doi.org/10.1016/j.carbon.2015.05.004].

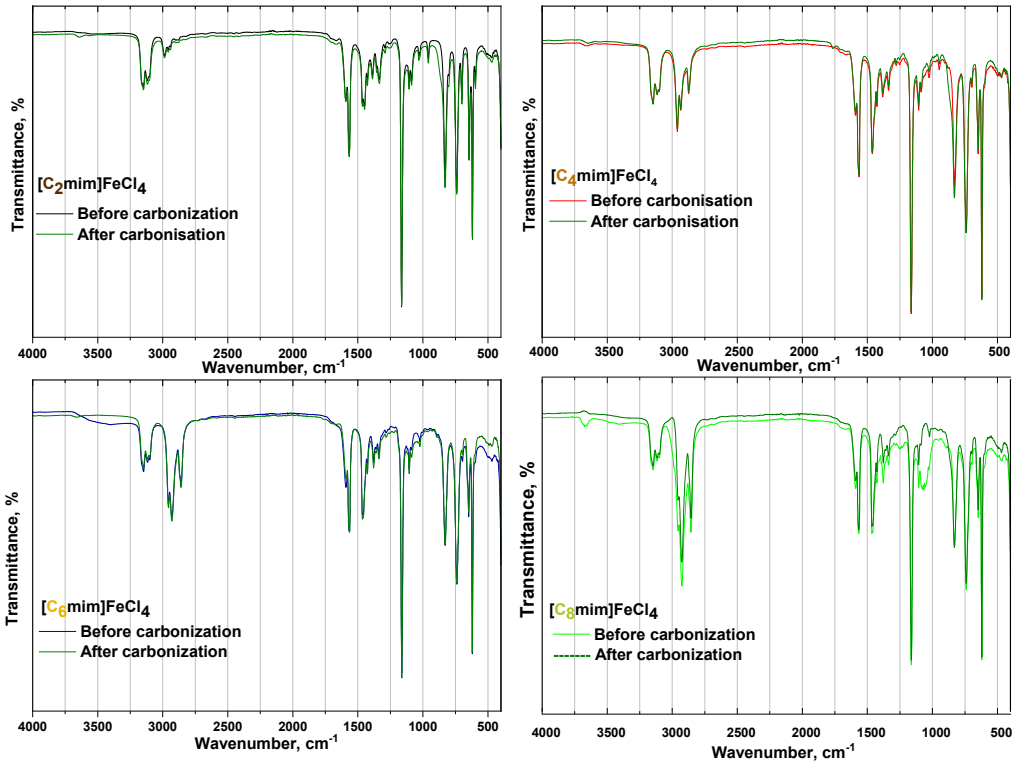


Figure S3. FTIR spectrum of the four 1-alkyl-3-methylimidazolium tetrachloroferrate ILs with various alkyl chain lengths before and after ITC of bagasse at 240 °C for 20h.

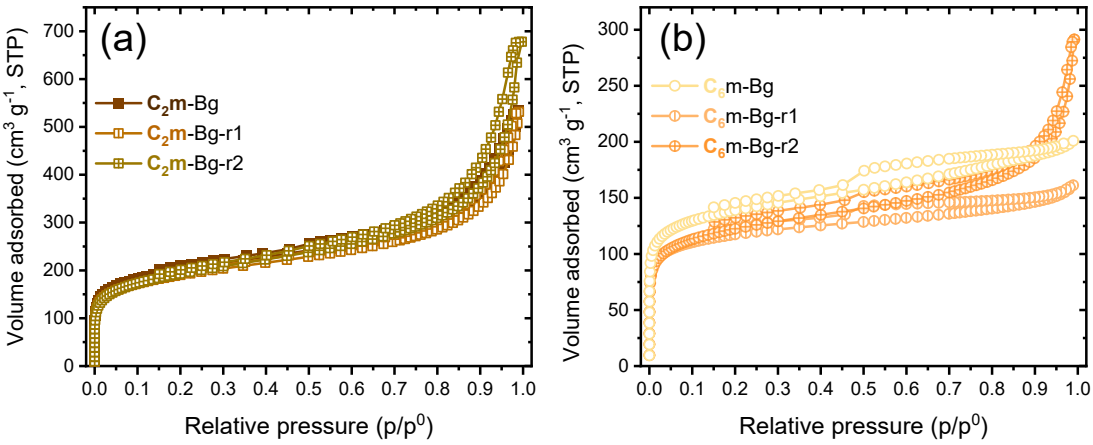


Figure S4. Nitrogen sorption isotherms at 77 K of (a) C_2m-Bg, C_2m-Bg-r1, C_2m-Bg-r2 and (b) C_6m-Bg, C_6m-Bg-r1, C_6m-Bg-r2.

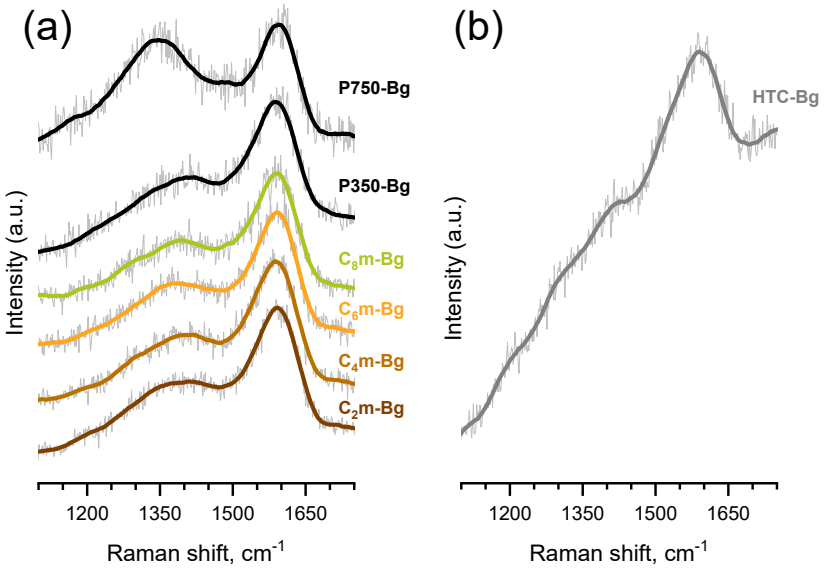


Figure S5. Raman spectra obtained by irradiation with a 532 nm wavelength laser of (a) the two pyrochars **P750-Bg** and **P350-Bg** and the four ionochars of the **C_xm-Bg** series; (b) the hydrochar **HTC-Bg**.

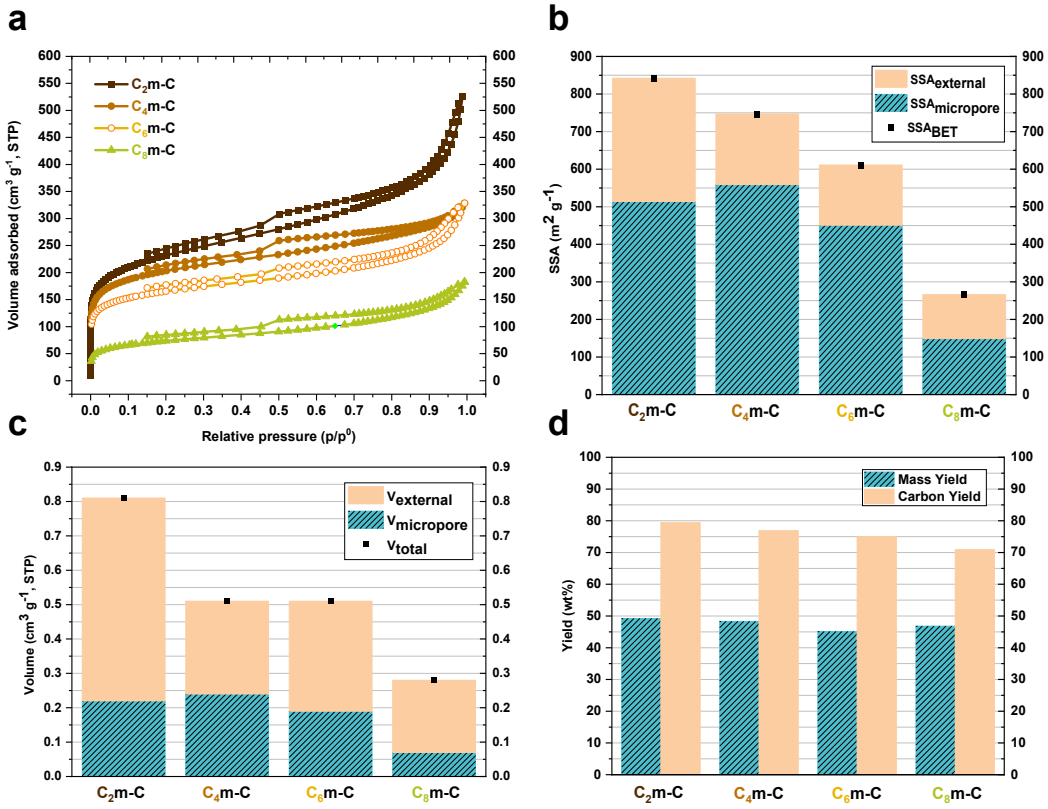


Figure S6. (a) Nitrogen sorption isotherms at 77 K, (b) specific surface areas, (c) pore volumes and (d) mass and carbon yields of **C_2m-C**, **C_4m-C**, **C_6m-C** and **C_8m-C**.

Table S4. Textural properties obtained from nitrogen sorption isotherms at 77 K of ionochars prepared by ionothermal carbonization of cellulose at 240 °C in 1-alkyl-3-methylimidazolium tetrachloroferrate with different aliphatic chain length.

Ionochar	SSA_{BET} ($m^2\ g^{-1}$)	$SSA_{micropore}$ ($m^2\ g^{-1}$)	$SSA_{external}$ ($m^2\ g^{-1}$)	V_{total} ($cm^3\ g^{-1}$)	$V_{micropore}$ ($cm^3\ g^{-1}$)	$V_{external}$ ($cm^3\ g^{-1}$)
C_2m-C	842	514	328	0.81	0.22	0.59
C_4m-C	747	559	188	0.51	0.24	0.27
C_6m-C	611	451	160	0.51	0.19	0.32
C_8m-C	266	149	117	0.28	0.07	0.21

Table S5. Mass yields, elemental composition† and carbon yields of ionochars prepared by ionothermal carbonization of cellulose at 240 °C in 1-alkyl-3-methylimidazolium tetrachloroferrate with different aliphatic chain length.

Ionochar	Yield (wt%)	C[a] (wt%)	H[a] (wt%)	N[a] (wt%)	O[a] (wt%)	Fe[b] (wt%)	Cl[b] (wt%)	Corrected Yield (wt%)	Carbon Yield (wt%)
C_2m-C	50.1	72.9	4.0	0.1	21.7	0.0	1.9	49.0	79.4
C_4m-C	49.3	72.1	4.5	0.2	22.4	0.5	1.5	47.9	76.9
C_6m-C	46.5	74.3	4.2	0.1	20.0	0.5	2.5	44.9	75.0
C_8m-C	52.8	67.6	4.7	1.2	13.8	3.6	7.6	42.6	70.9

[a]Combustional elemental analysis. [b]SEM-EDX. †The total elemental composition may exceed 100 wt% because SEM-EDX is not quantitative and may overestimate some elements.

Table S6. Mass yields, elemental composition† and carbon yields of ionochars **(Bn)m-Bg**, **(Bn)b-Bg** and **$(Bn)_2$-Bg** before and after soxhlet extraction (**-S**).

Ionochar	Yield (wt%)	C[a] (wt%)	H[a] (wt%)	N[a] (wt%)	O[a] (wt%)	Fe[b] (wt%)	Cl[b] (wt%)	Corrected Yield (wt%)	Carbon Yield (wt%)
(Bn)m-Bg	74.5	70.0	4.3	0.7	18.0	4.7	2.9	66.5	110.3
(Bn)m-Bg-S	69.9	70.7	4.3	0.6	20.9	2.5	0.3	66.1	105.2
(Bn)b-Bg	78.6	72.0	4.5	0.4	16.0	3.3	3.4	72.0	121.6
(Bn)b-Bg-S	66.8	72.8	5.9	0.1	23.4	1.5	0.4	66.1	107.6
$(Bn)_2$-Bg	213.5	71.5	4.8	2.5	5.4	10.8	9.0	127.6	256.2
$(Bn)_2$-Bg-S	140.8	78.1	4.7	1.6	6.9	3.3	2.4	114.4	208.1

[a]Combustional elemental analysis. [b]SEM-EDX. †The total elemental composition may exceed 100 wt% because SEM-EDX is not quantitative and may overestimate some elements.

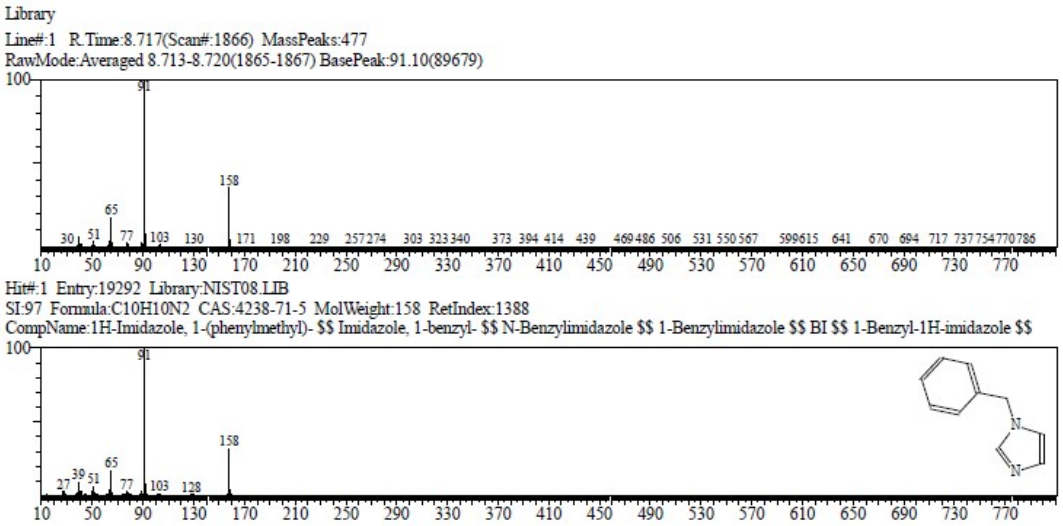


Figure S7. GC-MS of [$(Bn)_2$im]$FeCl_4$ recovered after ionothermal carbonization of bagasse at 240 °C for 20h, filtration and separation from the ionochar **$(Bn)_2$-Bg**.

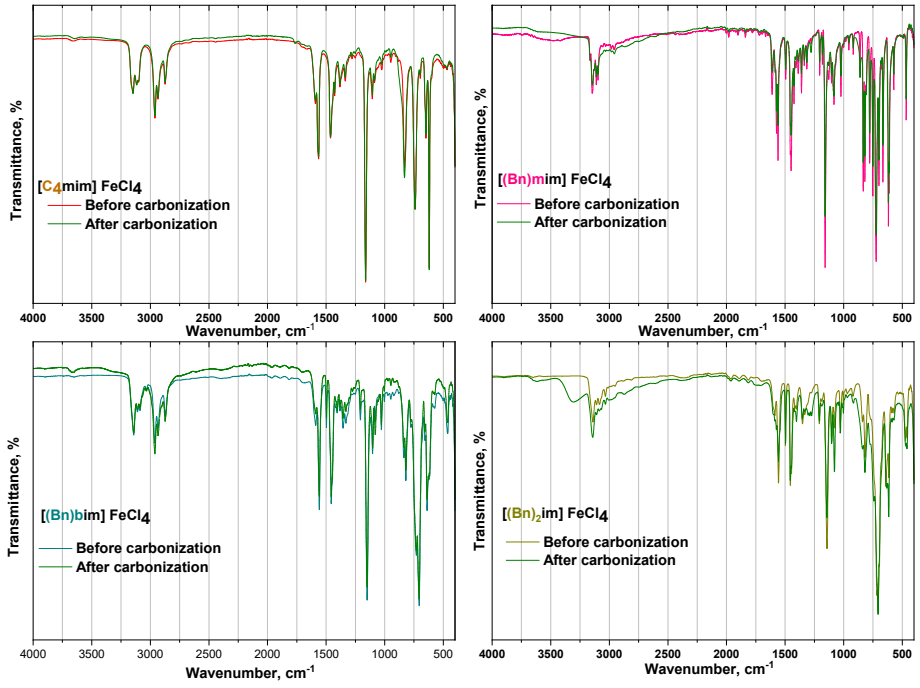


Figure S8. FTIR spectrum of the three benzyl-containing imidazolium tetrachloroferrate ILs before and after ITC of bagasse at 240 °C for 20h and comparison with [C_4mim] $FeCl_4$.

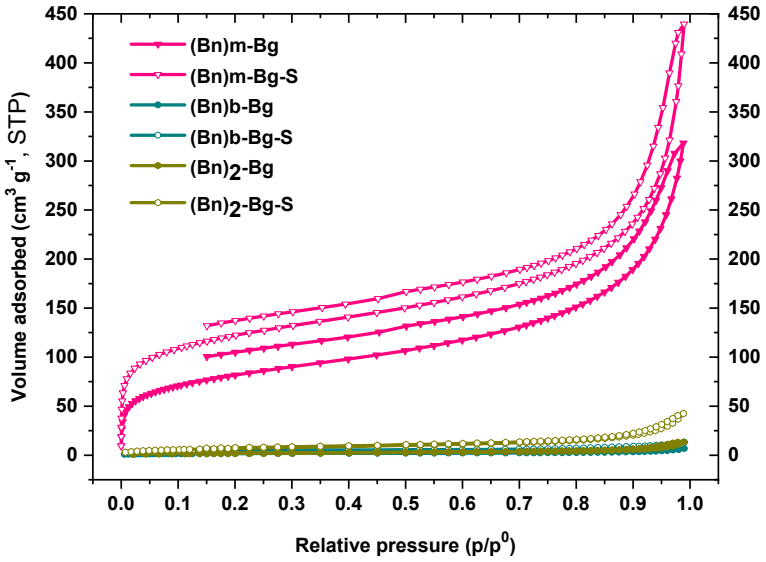


Figure S9. Nitrogen sorption isotherms at 77 K of **(Bn)m-Bg**, **(Bn)b-Bg** and **$(Bn)_2$-Bg** before and after soxhlet extraction (**-S**).

Table S7. Textural properties obtained from nitrogen sorption isotherms at 77 K of ionochars **(Bn)m-Bg**, **(Bn)b-Bg** and **$(Bn)_2$-Bg** before and after soxhlet extraction (**-S**).

Ionochar	SSA_{BET} ($m^2\ g^{-1}$)	$SSA_{micropore}$ ($m^2\ g^{-1}$)	$SSA_{external}$ ($m^2\ g^{-1}$)	V_{total} ($cm^3\ g^{-1}$)	$V_{micropore}$ ($cm^3\ g^{-1}$)	$V_{external}$ ($cm^3\ g^{-1}$)
(Bn)m-Bg	294	118	176	0.49	0.05	0.44
(Bn)m-Bg-S	433	241	192	0.68	0.11	0.57
(Bn)b-Bg	6	4	2	0.00	0.00	0.00
(Bn)b-Bg-S	14	6	8	0.02	0.00	0.02
$(Bn)_2$-Bg	7	1	6	0.02	0.00	0.02
$(Bn)_2$-Bg-S	25	4	21	0.07	0.00	0.07

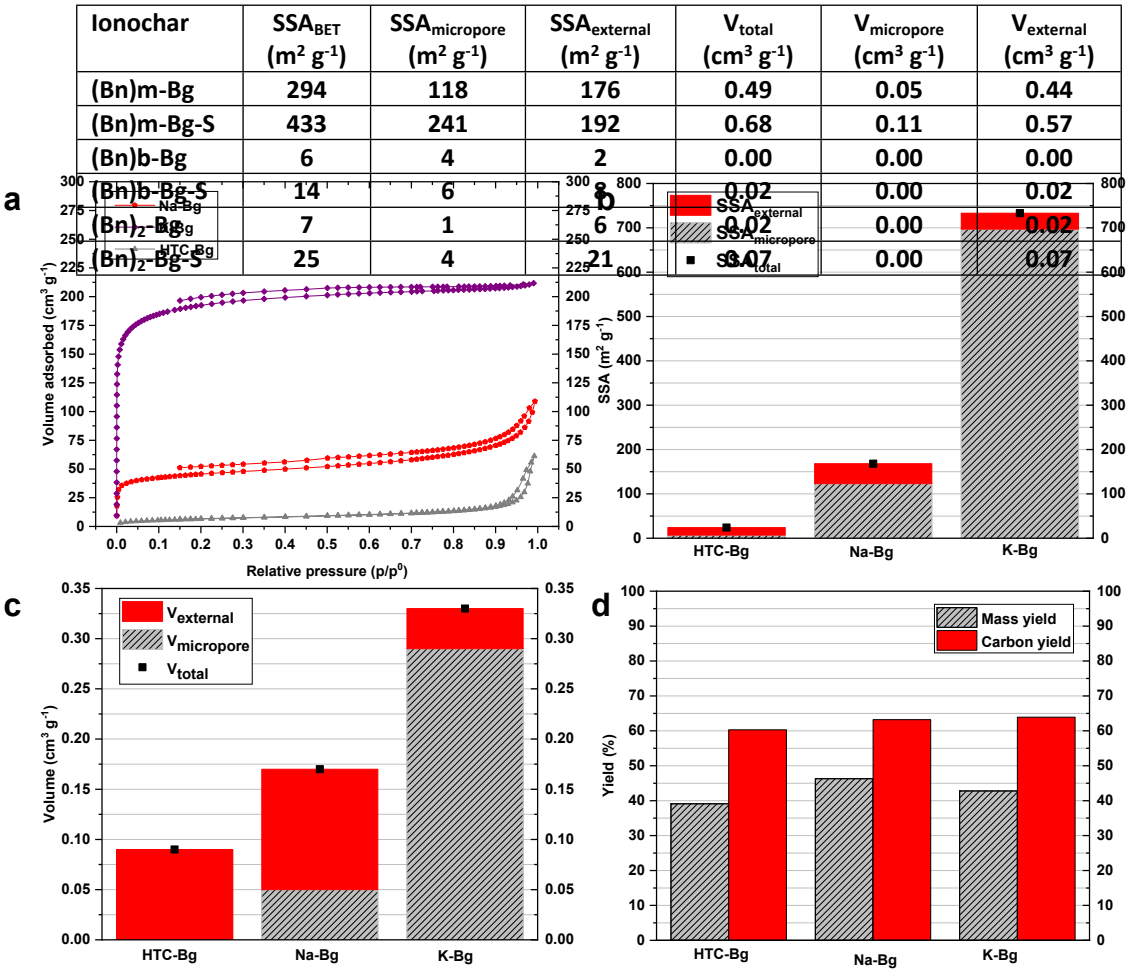


Figure S10. (a) Nitrogen sorption isotherms at 77 K, (b) BET-equivalent specific surface areas (SSA), (c) pore volumes and (d) mass and carbon yields of of **HTC-Bg**, **Na-Bg** and **K-Bg**.

Table S8. Textural properties obtained from nitrogen sorption isotherms at 77 K of **HTC-Bg**, **Na-Bg** and **K-Bg**.

Char	SSA_{BET} ($m^2\ g^{-1}$)	$SSA_{micropore}$ ($m^2\ g^{-1}$)	$SSA_{external}$ ($m^2\ g^{-1}$)	V_{total} ($cm^3\ g^{-1}$)	$V_{micropore}$ ($cm^3\ g^{-1}$)	$V_{external}$ ($cm^3\ g^{-1}$)
HTC-Bg	**24**	**7**	**17**	**0.09**	**0.00**	**0.09**
Na-Bg	**168**	**123**	**45**	**0.17**	**0.05**	**0.12**
K-Bg	**733**	**697**	**36**	**0.33**	**0.29**	**0.04**

Table S9. Mass yields, elemental composition† and carbon yields of **HTC-Bg**, **Na-Bg** and **K-Bg**.

Char	Yield (wt%)	C[a] (wt%)	H[a] (wt%)	N[a] (wt%)	O[a] (wt%)	Fe[b] (wt%)	Cl[b] (wt%)	Corrected Yield (wt%)	Carbon Yield (wt%)
HTC-Bg	**39.1**	**70.4**	**5.3**	**0.16**	**24.3**	**0.0**	**0.0**	**39.1**	**60.3**
Na-Bg	**51.4**	**56.1**	**2.9**	**0.21**	**32.2**	**6.1**	**3.9**	**46.2**	**63.2**
K-Bg	**43.7**	**66.7**	**3.3**	**0.03**	**33.7**	**1.3**	**0.7**	**42.9**	**63.9**

[a]Combustional elementary analysis. [b]SEM-EDX. †The total elemental composition may exceed 100 wt% because SEM-EDX is not quantitative and may overestimate some elements.

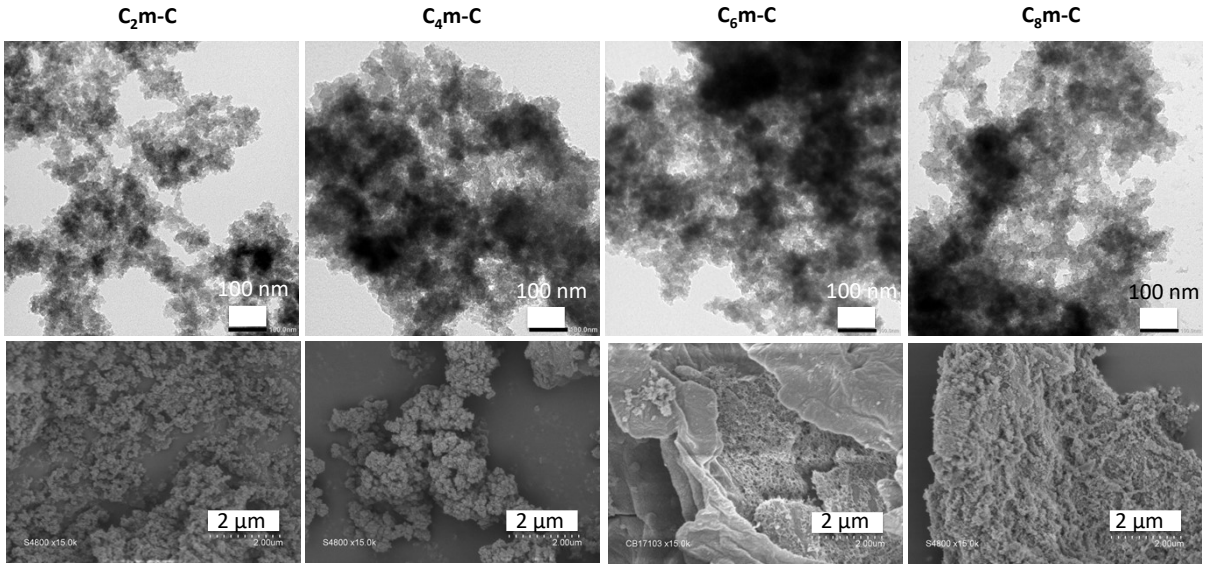


Figure S11. TEM (at the top) and SEM (at the bottom) micrographs of **C_2m-C**, **C_4m-C**, **C_6m-C** and **C_8m-C** ionochars.

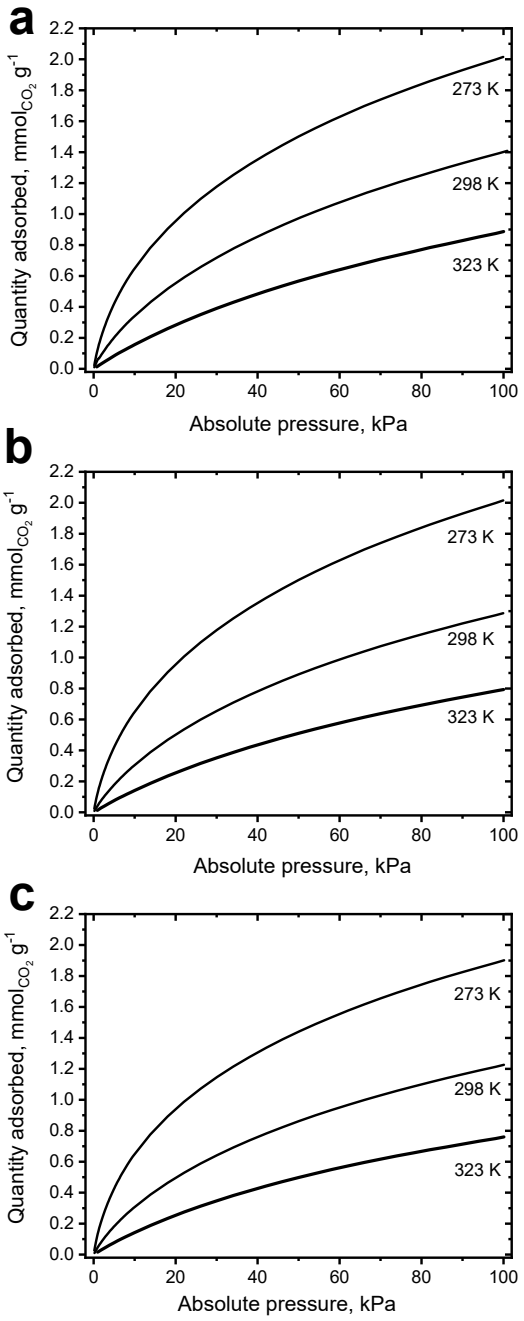


Figure S12. Carbon dioxide sorption isotherms at 273, 298 and 323 K of (a) **C_2m-Bg**, (b) **C_4m-Bg** and (c) **C_6m-Bg**.

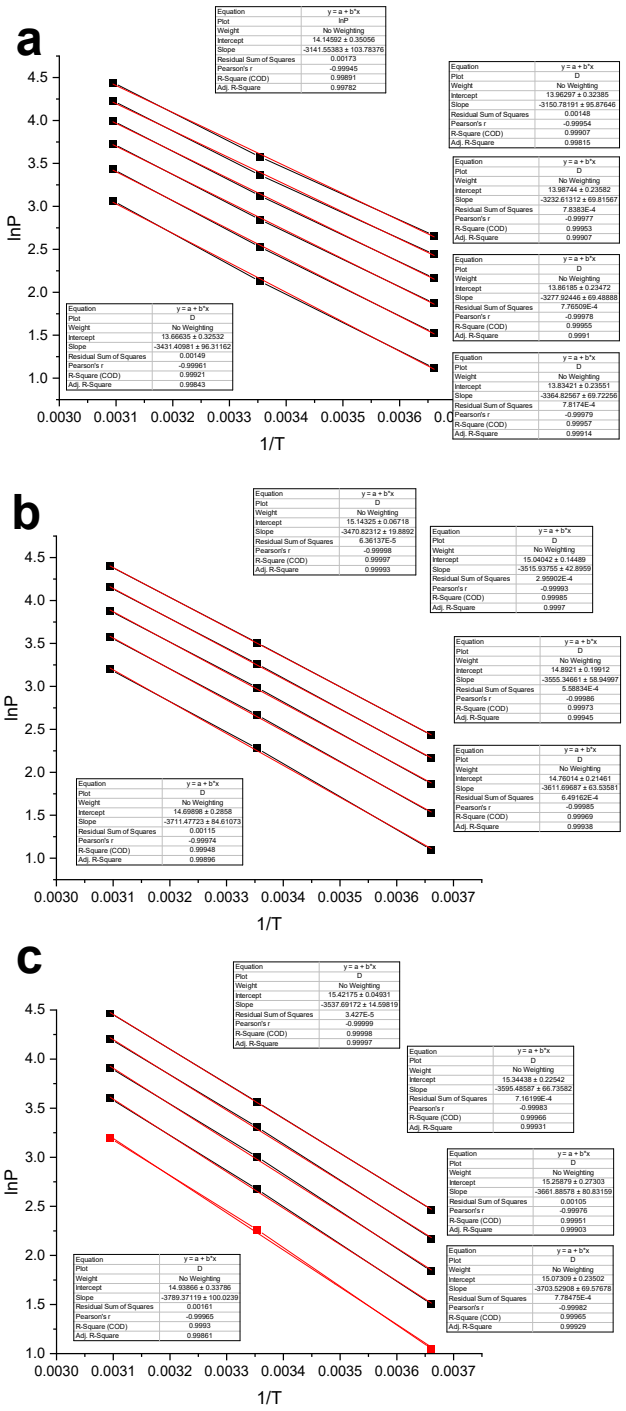


Figure S13. Application of the Clausius-Clapeyron equation to CO_2 adsorption isotherms; ln p = f (1/T) at different recovery rates, *i.e.*, mmol of CO_2 adsorbed per gram of ionochar of (a) **C_2m-Bg**, (b) **C_4m-Bg** and (c) **C_6m-Bg**.