Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Novel Carbon Nitride Composites with Improved Visible Light Absorption Synthesized in $ZnCl_2$-based Salt Melts

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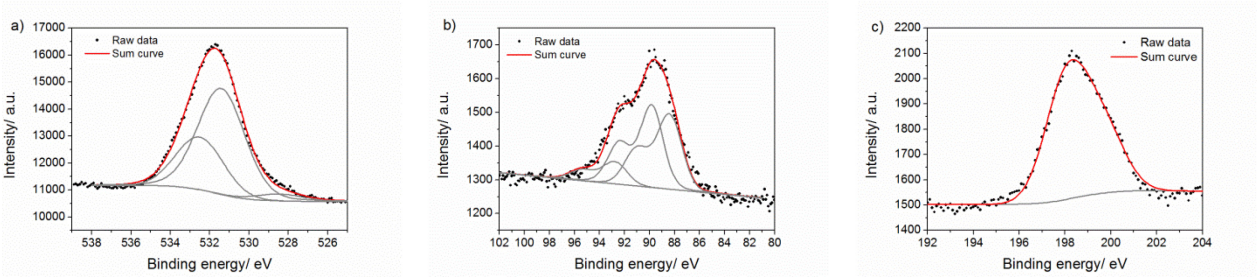


Figure S1. a) O1s, b) Zn3p and c) Cl2p XPS spectra of carbon nitride synthesized in $CsCl/ZnCl_2$.

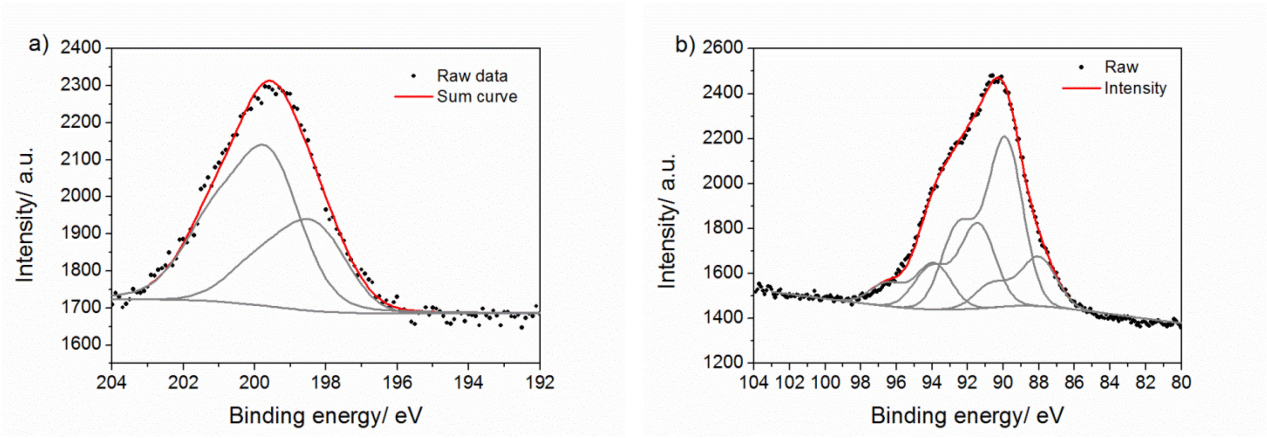
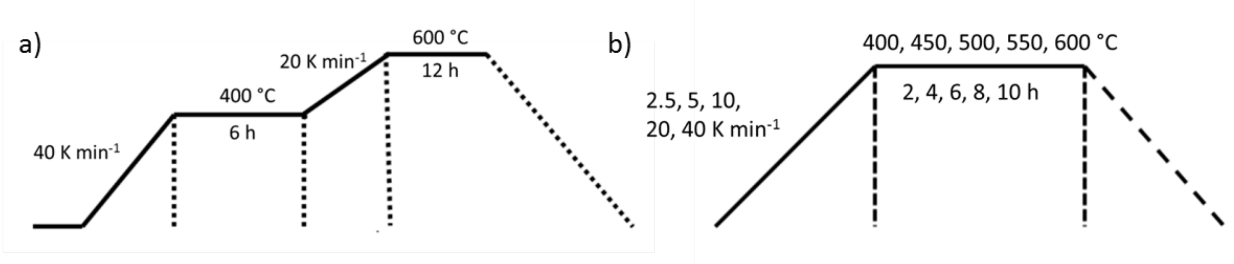


Figure S2. a) Cl2p and b) Zn3p XPS spectra of carbon nitride synthesized in $CsCl/ZnCl_2$ after Ar ion bombardement.

Table S1. Elemental composition (in wt. %) of the product synthesized in $CsCl/ZnCl_2$ analyzed by different characterization methods.

Element	**XPS**	**EA**	**ICP**	**EDX**
C	30	30	-	32
N	50	50	-	50
O	12	-	-	12
Cl	3	-	-	< 1
Zn	5	-	3.5	5
H	-	3	-	-



Scheme S1. Heating programs a) used for the synthesis of products at 1:5 precursor to salts ratio and b) for investigation of the influence of synthesis parameters.

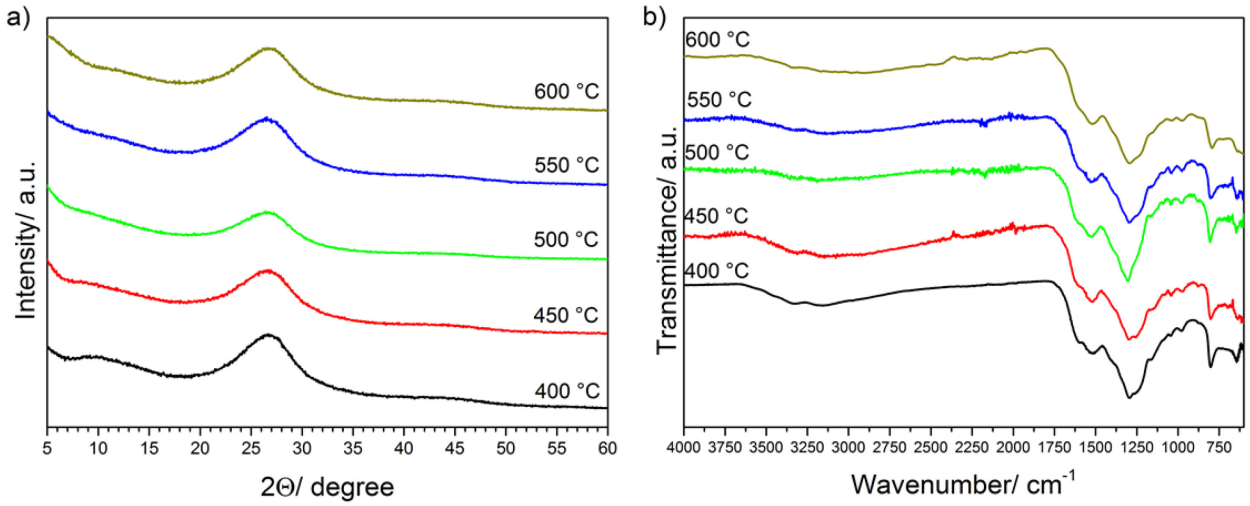


Figure S3. a) Normalized WAXS patterns and b) FTIR spectra of the materials synthesized in NaCl/ $ZnCl_2$ melts at different temperatures (heating rate 10 K min^{-1}; holding time 6 h) after water wash.

Table S2. Composition and BET surface areas of the materials synthesized in NaCl/$ZnCl_2$ melts at different temperatures (heating rate 10 K min^{-1}; holding time 6 h) after water wash.

T, °C	C, wt. %	N, wt. %	H, wt.%	C/N	100-(C+N+H)	Color	S_{BET} m^2/g
400	22.0	33.1	2.33	0.66	42.6	white	434
450	22.9	31.1	2.52	0.74	43.5	white	n/a
500	22.3	28.9	2.49	0.77	46.3	white	n/a
550	23.6	28.6	2.72	0.83	45.1	yellow	554
600	23.8	28.1	2.63	0.85	45.5	dark brown	645

Table S3. Composition and BET surface areas of materials synthesized in $NaCl/ZnCl_2$ melts at different temperatures (heating rate 10 K min^{-1}; holding time 6h) after acid wash.

T, °C	C, wt. %	N, wt. %	H, wt.%	C/N	100-(C+N+H)	Color	S_{BET} m^2/g
400	28.5	48.0	3.10	0.59	20.4	white	n/a
450	29.0	48.7	3.11	0.60	19.2	white	n/a
500	29.4	49.0	3.13	0.60	18.5	white	n/a
550	29.5	48.6	3.14	0.61	18.8	yellow	144
600	29.8	48.7	3.10	0.61	18.4	brown	115

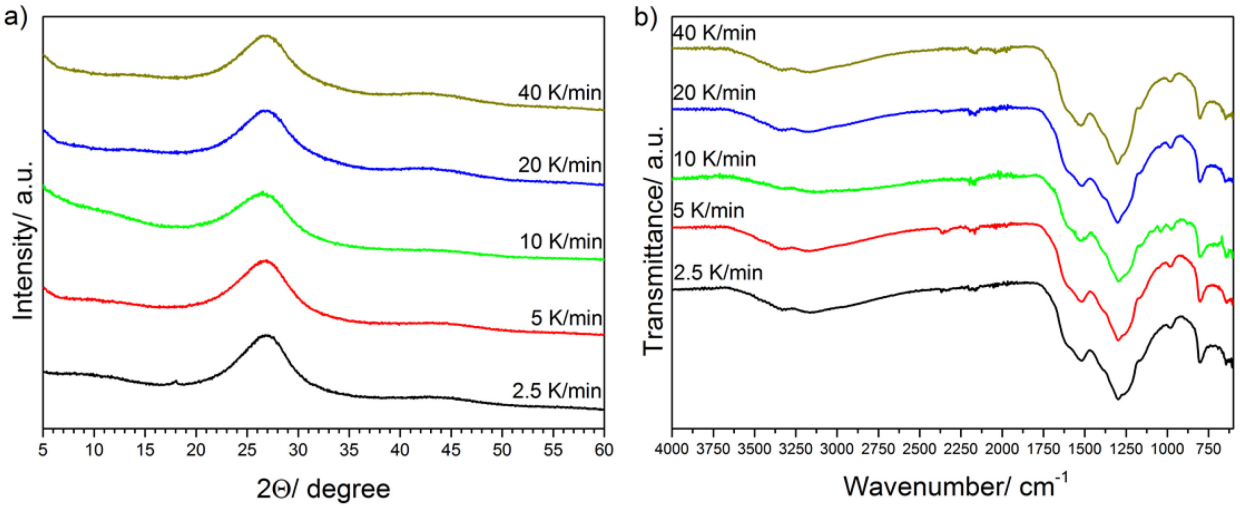


Figure S4. a) Normalized WAXS patterns and b) FTIR spectra of the materials synthesized in NaCl/ $ZnCl_2$ melt using different heating rates (temperature 550 °C; holding time 6h) after acid wash.

Table S4. Composition of the products synthesized in $NaCl/ZnCl_2$ melts using different heating rates (temperature 550 °C; holding time 6h) after acid wash.

Heating rate, K min^{-1}	C, wt. %	N, wt. %	H, wt.%	C/N	100-(C+N+H)	Color
2.5	28.8	50.9	3.03	0.57	17.3	yellow
5	29.0	50.4	3.02	0.58	17.6	yellow
10	29.5	48.6	3.14	0.61	18.8	yellow
20	29.4	50.8	3.06	0.58	16.7	yellow
40	28.8	49.8	3.11	0.58	18.3	yellow

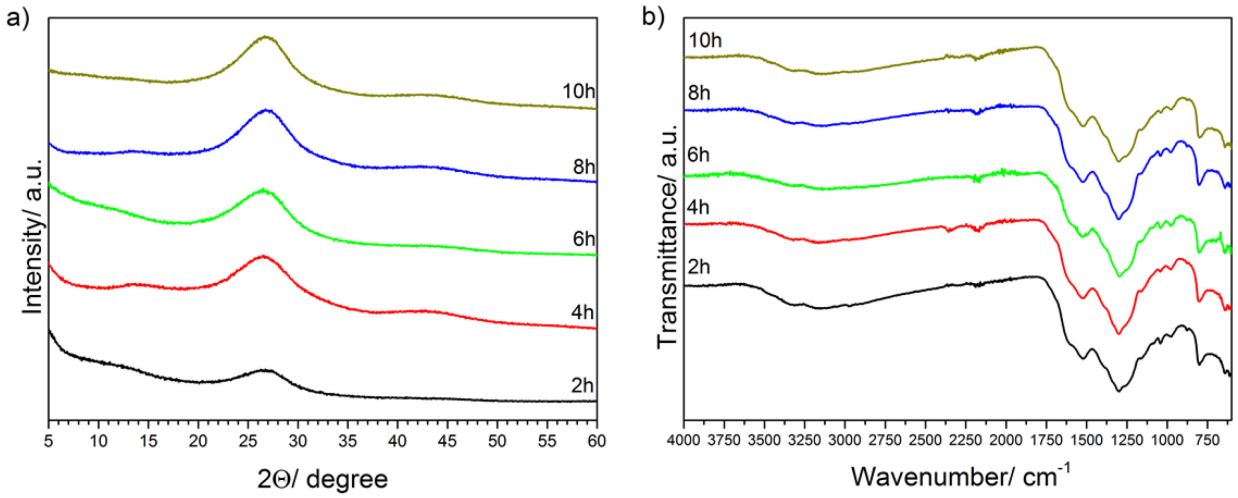


Figure S5. a) WAXS patterns and b) FTIR spectra of the materials synthesized in NaCl/ $ZnCl_2$ melts using different holding times (temperature 550 °C; heating rate 10 K min^{-1}) after acid wash.

Table S5. Composition and BET surface areas of the materials synthesized in NaCl/$ZnCl_2$ melts using different holding times after acid wash.

Holding time, h	**C, wt. %**	**N, wt. %**	**H, wt.%**	**C/N**	**100-(C+N+H)**	**Color**	**S_{BET} m^2/g**
2	29.5	50.1	3.12	0.59	17.3	yellow	204
4	30.2	50.5	3.06	0.60	16.2	yellow	n/a
6	29.5	48.6	3.14	0.61	18.8	yellow	144
8	30.1	50.8	3.13	0.59	15.9	yellow	n/a
10	29.5	50.9	3.06	0.58	16.5	yellow	50

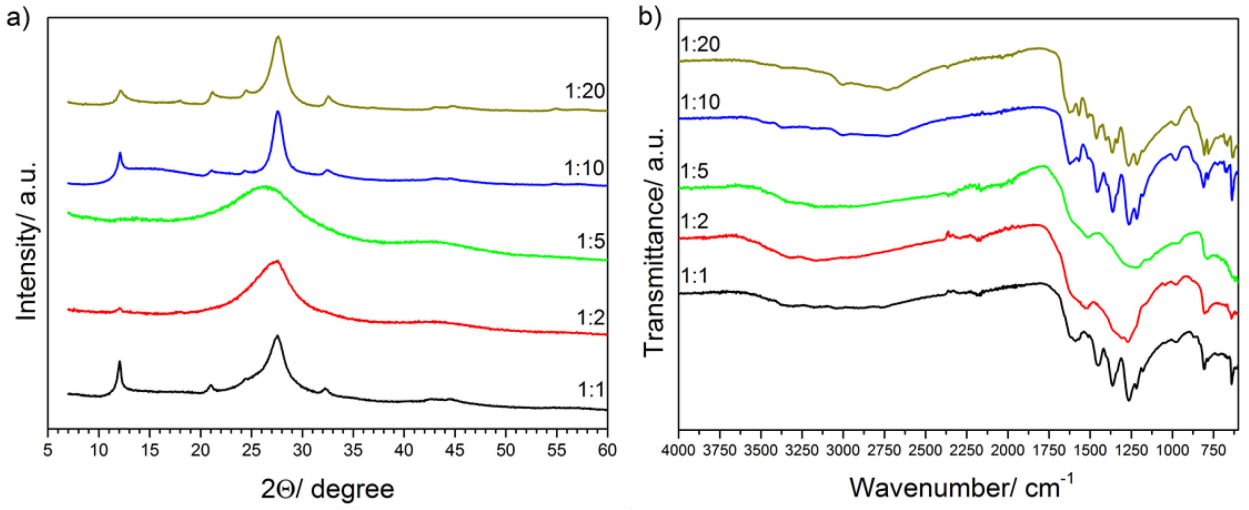


Figure S6. a) Normalized WAXS patterns and b) FTIR spectra of the materials synthesized in NaCl/ $ZnCl_2$ melt using different precursor to salt ratios, after acid wash.

Table S6. Composition and BET surface areas of materials synthesized in $NaCl/ZnCl_2$ melts using different precursor to salt ratios, after acid wash

Precursor:salt weight ratio	**C, wt. %**	**N, wt. %**	**H, wt.%**	**C/N**	**100-(C+N+H)**	**Color**	**S_{BET} m^2/g**
1:1	30.5	47.6	3.36	0.64	18.5	brown	72
1:2	30.0	46.3	3.43	0.65	15.3	orange	62
1:5	29.6	49.1	3.04	0.60	18.3	brown	193
1:10	31.3	50.5	2.89	0.62	15.3	beige	78
1:20	30.2	50.1	2.49	0.60	17.2	light brown	105

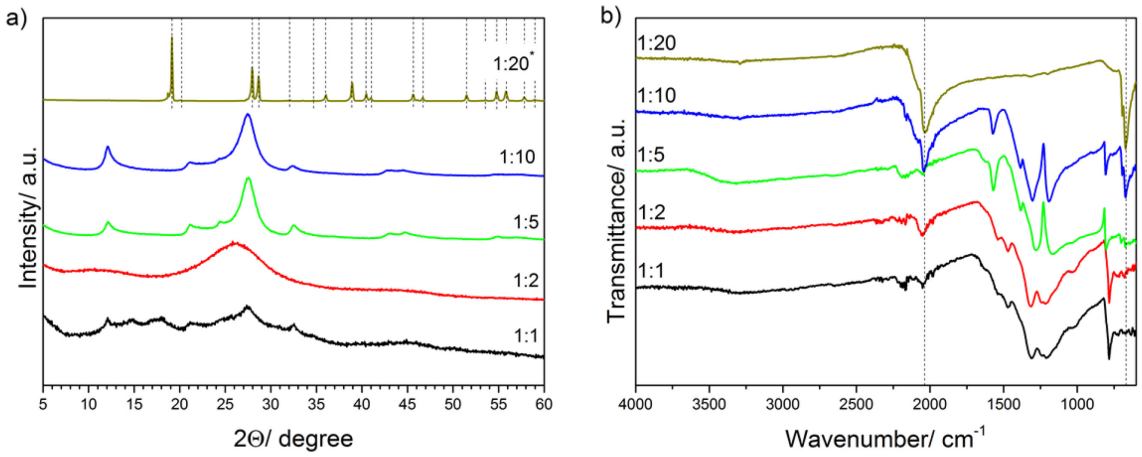


Figure S7. a) Normalized WAXS patterns of the materials synthesized in pure $ZnCl_2$ melt using different precursor to salt ratios, after acid wash (* sample after EtOH wash because Zn(CN)2 is not stable under acidic conditions) and b) FTIR spectra of EtOH washed products; --- $ZnCN_2$

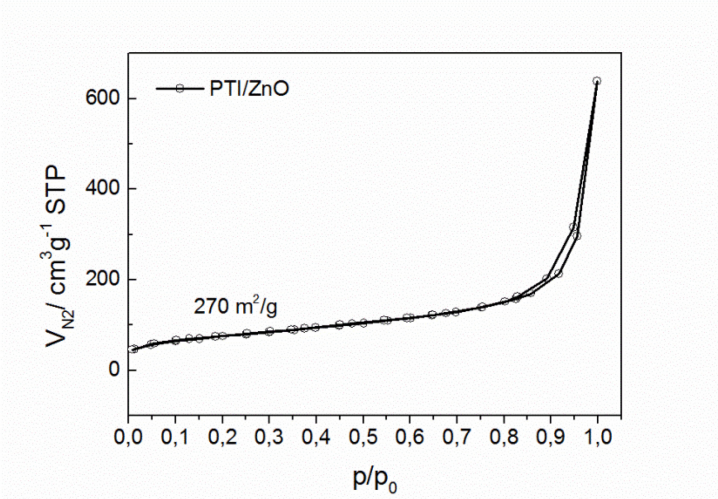


Figure S8: N_2 sorption isotherm of PTI/ZnO with corresponding value of specific surface area according to BET model.

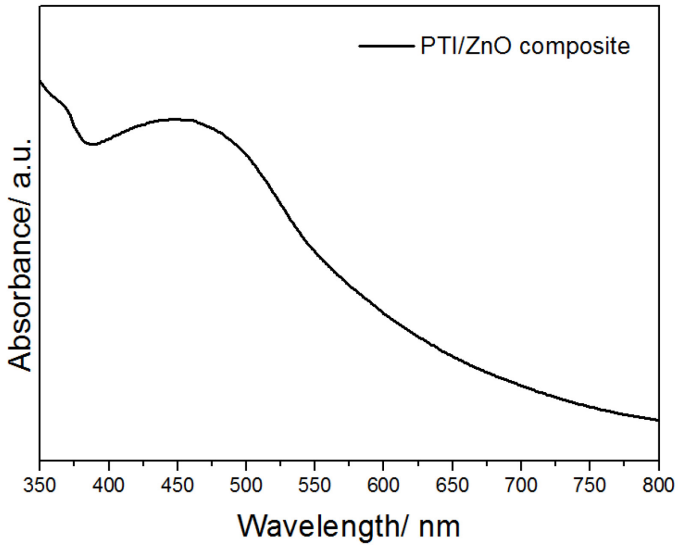


Figure S9. Visible light diffuse reflectance spectra of PTI/ZnO composite.

Table S7. Composition and BET surface areas of materials synthesized in $NaCl/ZnCl_2$ melts at different temperatures (heating rate 10 K min^{-1}; holding time 6h) after water wash.

T, °C	C, wt. %	N, wt. %	H, wt.%	C/N	100-(C+N+H)	Color	S_{BET} m^2/g
400	22.0	33.1	2.33	0.66	42.6	white	434
450	22.9	31.1	2.52	0.74	43.5	white	n/a
500	22.3	28.9	2.49	0.77	46.3	white	n/a
550	23.6	28.6	2.72	0.83	45.1	yellow	554
600	23.8	28.1	2.63	0.85	45.5	dark brown	645

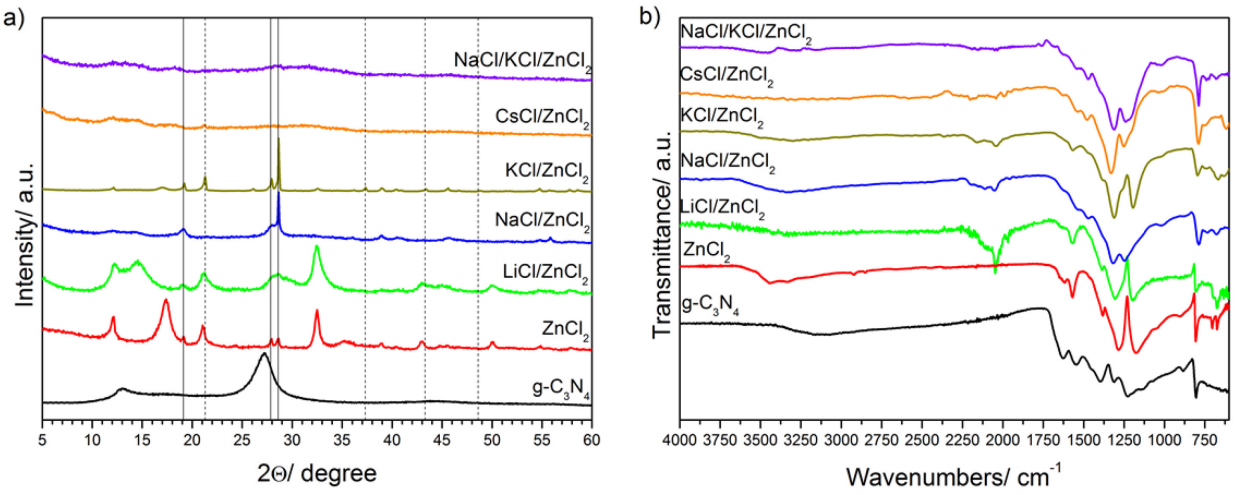


Figure S10. a) WAXS patterns and b) FTIR spectra of materials synthesized in salt melts containing $ZnCl_2$ and g-C_3N_4 after water wash; — $ZnCN_2$ --- $Zn(CN)_2$

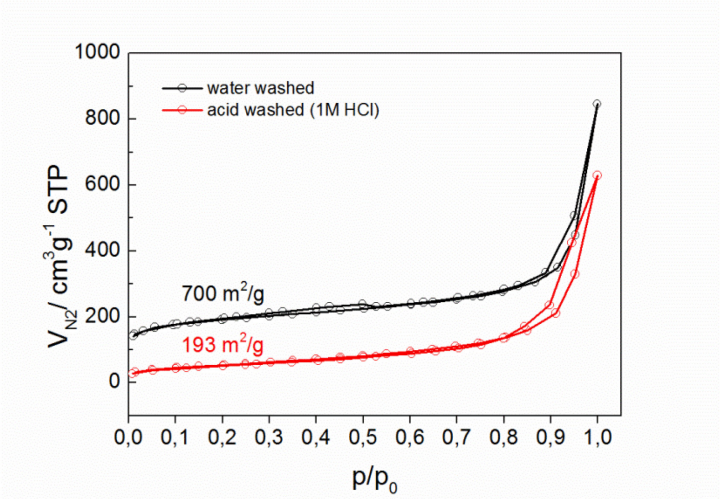


Figure S11. N_2 Sorption isotherms of $NaCl/ZnCl_2$-C_3N_4 after water wash and acid treatment with the corresponding values of the specific surface area according to the BET model.

Additional gas adsorption data and gas selectivity calculations:

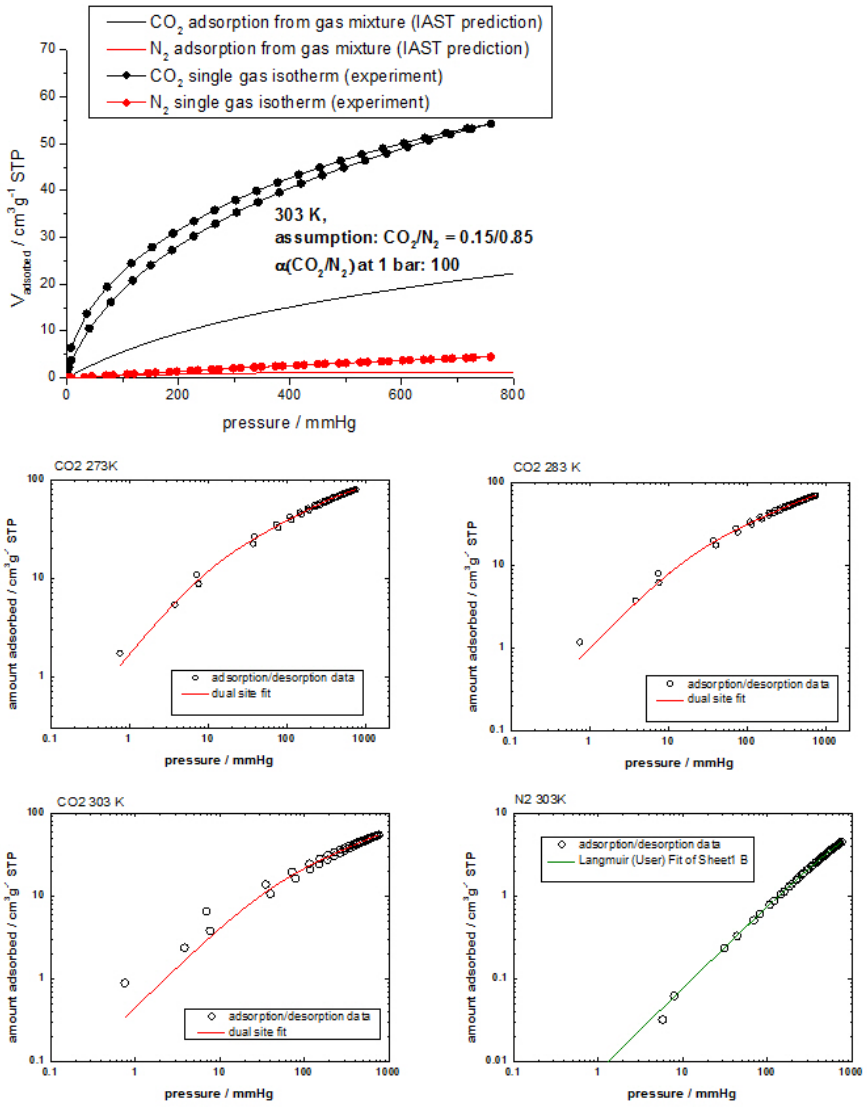


Figure S12. *Upper graph:* CO_2 and N_2 single gas adsorption/desorption experimental isotherms at 303 K on NaCl/ZnCl2-C_3N_4 (water washed only) and predictions of gas uptake of CO_2 and N_2 at 303 K for a gas mixture of 0.15/0.85 (v/v) CO_2/N_2 (common flue gas assumption) according to the IAST model; *middle panel:* dual-site Langmuir fit of CO_2 adsorption/desorption on NaCl/ZnCl2-C_3N_4 (water washed only) at 273K (left-hand side) and at 283K (right-hand side). *Lower panel*: dual-site Langmuir fit of CO_2 adsorption/desorption on NaCl/ZnCl2-C_3N_4 (water washed only) at 303K (left-hand side) and Langmuir fit of N2 adsorption/desorption on NaCl/ZnCl2-C_3N_4 (water washed only) at 303K (right-hand side). See Table x for fit parameters. Isotherm fitting was conducted using the OriginPro 8.5® non-linear curve fitting tool.

CO_2 adsorption/desorption isotherms were fitted using a dual-site Langmuir approach to account for heterogeneity:

$$V_{ads} = \frac{q\ a p}{1 + a p} + \frac{u\ b\ p}{1 + b\ p} \qquad \text{(eq S1)}$$

(*p:* pressure; *a, b*: Langmuir adsorption coefficients of site 1 and 2, respectively; *q, u*: Langmuir maximum capacity of site 1 and 2, respectively)

N_2 adsorption/desorption isotherms were fitted using a single-site Langmuir approach:

$$V_{ads} = \frac{q\ a p}{1 + a p} \qquad \text{(eq S2)}$$

(*p:* pressure; *a:* Langmuir adsorption coefficient; *q:* Langmuir maximum capacity)

Table S8. fit parameters of adsorption/desorption isotherms shown in Figure S12

NaCl/$ZnCl_2$-C_3N_4	**q**	**a**	**u**	**b**	**R^2**
CO_2 273K	25.07394	0.06227	83.65919	0.00245	0.9974
CO_2 283K	25.07394	0.03479	83.65919	0.00154	0.9972
CO_2 303K	25.07394	0.01543	83.65919	7.84678E-4	0.9917
N_2 273K	25.55613	6.77356E-4	-	-	0.9999
N_2 303K	19.61415	3.89961E-4	-	-	0.9999

The IAST calculations were performed using common protocols following the theory of Myers (1965). Calculation of the adsorbed fraction of CO_2 (x_CO2) was performed using the fit parameters given in Table S8 using MatLab®. The used script is available at: http://www.mpikg.mpg.de/144866/xDownloads or from the authors.

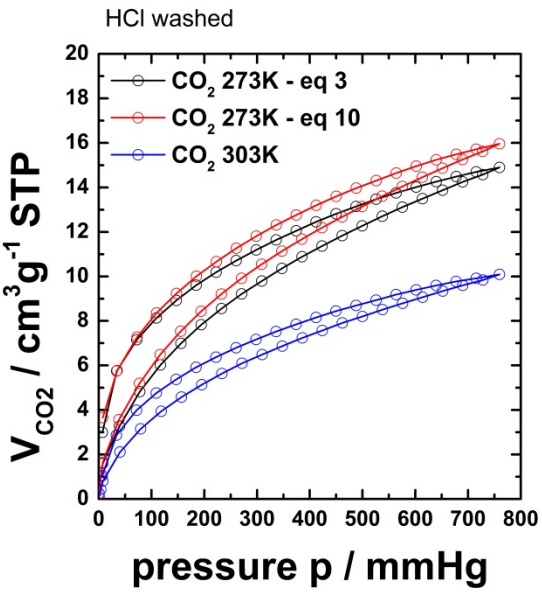


Figure S13. Measurement of CO_2 adsorption/desorption on NaCl/$ZnCl_2$-C_3N_4 at two different kinetic setting. A slightly higher uptake is observed at longer equilibration setting, but the magnitude of the hysteresis is unchanged. This indicates that the hysteresis is not due to kinetic effect singularily, but probably due to additional (weak) chemical interactions.