Supporting Information for

Thermodynamics of the interactions of positively charged cellulose nanocrystals with molecules bearing different amounts of carboxylate anions

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S1: grafting of cellulose nanocrystals

In the following figure the reaction scheme for preparation of pyridinium grafted CNCs is shown as previously reported:[1]

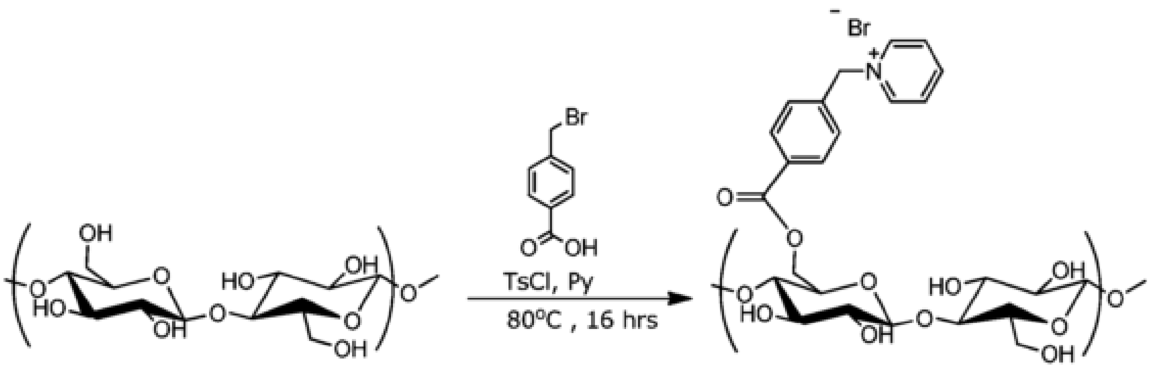

Figure S1. Reaction scheme for preparation of pyridinium grafted CNCs in a single step.

S2. Calorimetric experiments

Adsorption of sodium acetate to py-g-CNCs

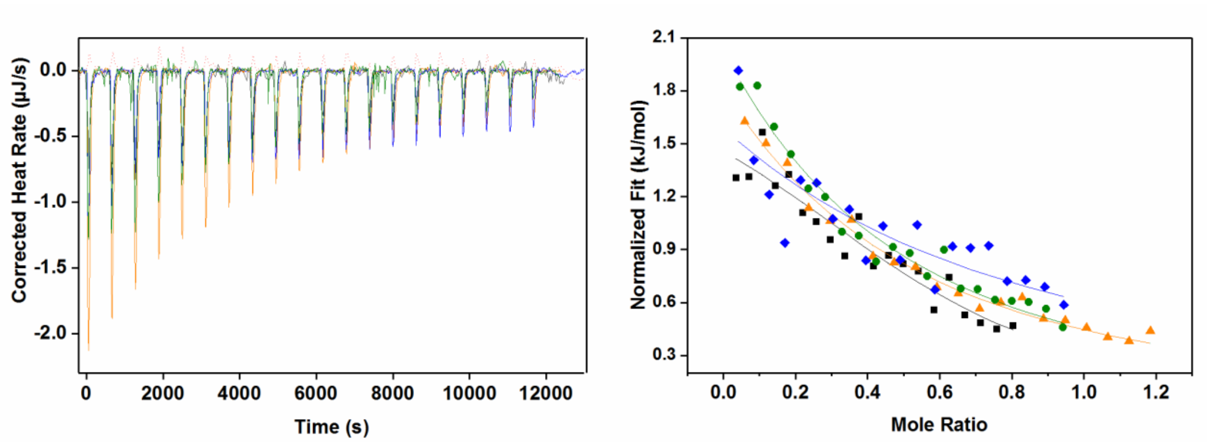

Figure S2. Calorimetric traces (left panel, solid lines) and integral plots (right panel) obtained performing subsequent injection of 10 µl sodium acetate (5.4 mM) to py-g-CNCs DS 0.35 (3.5 mg/ml). Dilution of sodium acetate 5 mM to water is shown in the left panel (dotted line).

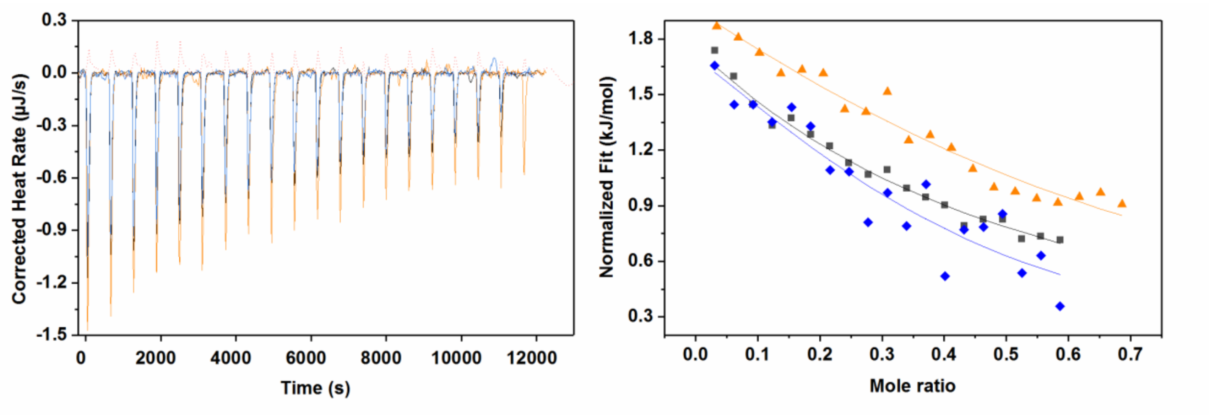

Figure S3. Calorimetric traces (left panel, solid lines) and integral plots (right panel) obtained performing subsequent injection of 10 µl sodium acetate (5.4 mM) to py-g-CNCs DS 0.62 (2.9 mg/ml). Dilution of sodium acetate 5 mM to water is shown in the left panel (red dotted line).

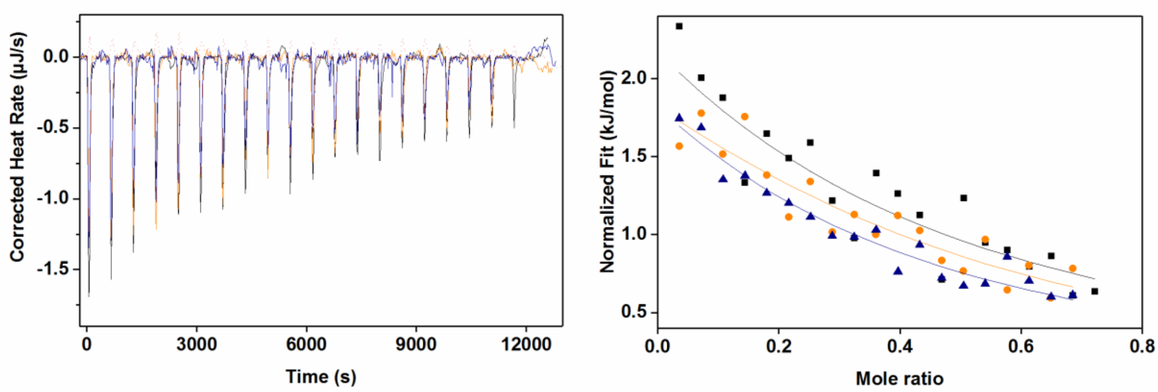

Figure S4. Calorimetric traces (left panel, solid lines) and integral plots (right panel) obtained performing subsequent injection of 10 µl sodium acetate (5.4 mM) to py-g-CNCs DS 0.91(1.9 mg/ml). Dilution of sodium acetate 5 mM to water is shown in the left panel (red dotted line).

DS	ΔH (kJ/mol)	K_a (mM^{-1})	ΔS (J/mol*K)	n	C factor (average)
0.35	8 ± 4	0.9 ± 0.9	82 ± 8	0.3 ± 0.2	0.9
0.62	6 ± 4	0.9 ± 0.6	73 ± 7	0.4 ± 0.2	0.9
0.91	8 ± 4	0.6 ± 0.2	81 ± 9	0.3 ± 0.1	0.4

Table S1. Results obtained from Isothermal titration calorimetry for the adsorption of sodium acetate to py-g-CNCs with different degree of substitution.

Adsorption of sodium oxalate to py-g-CNCs

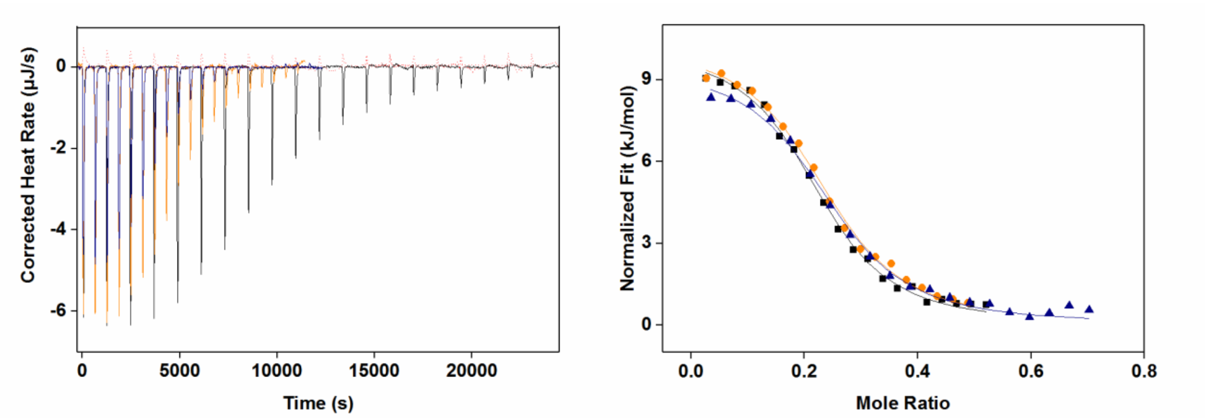

Figure S5. Calorimetric traces (left panel, solid line) and integral plots (right panel) obtained performing subsequent injection of 10 µl sodium oxalate (5 mM) to py-g-CNCs DS 0.35 (4 - 5 mg/ml). Dilution of sodium oxalate 5 mM to water is shown in the left panel (red dotted line).

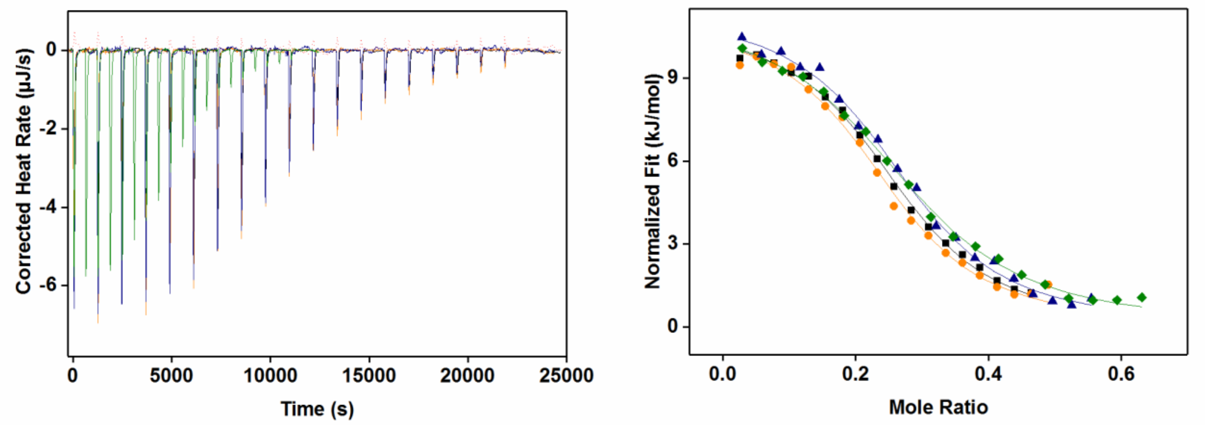

Figure S6. Calorimetric traces (left panel, solid lines) and integral plots (right panel) obtained performing subsequent injection of 10 µl sodium oxalate (5 mM) to py-g-CNCs DS 0.62 (~3 mg/ml). Dilution of sodium oxalate 5 mM to water is shown in the left panel (red dotted line).

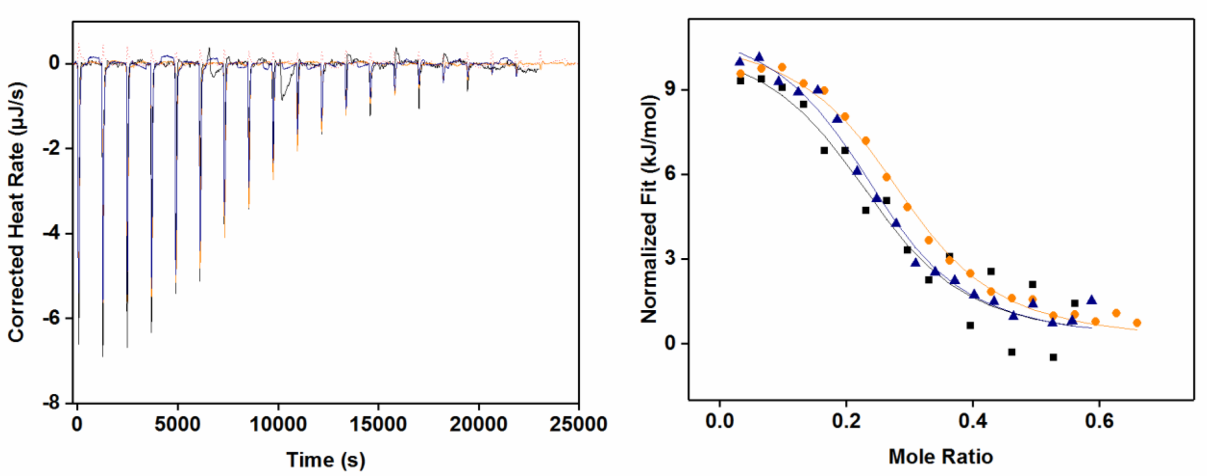

Figure S7. Calorimetric traces (left panel, solid lines) and integral plots (right panel) obtained performing subsequent injection of 10 µl sodium oxalate (5 mM) to py-g-CNCs DS 0.91 (~2 mg/ml). Dilution of sodium oxalate 5 mM to water is shown in the left panel (red dotted line).

DS	ΔH (kJ/mol)	K_a (mM^{-1})	ΔS (J/mol*K)	n	C factor (average)
0.35	10.0 ± 0.5	22 ± 4	116.5 ± 0.3	0.28 ± 0.08	14
0.62	11.2 ± 0.2	17 ± 2	118 ± 1	0.27 ± 0.01	10
0.91	11.1 ± 0.3	20 ± 2	120 ± 1	0.26 ± 0.03	10

Table S2. Results obtained from Isothermal titration calorimetry for the adsorption of sodium oxalate 5 mM to py-g-CNCs with different degree of substitution.

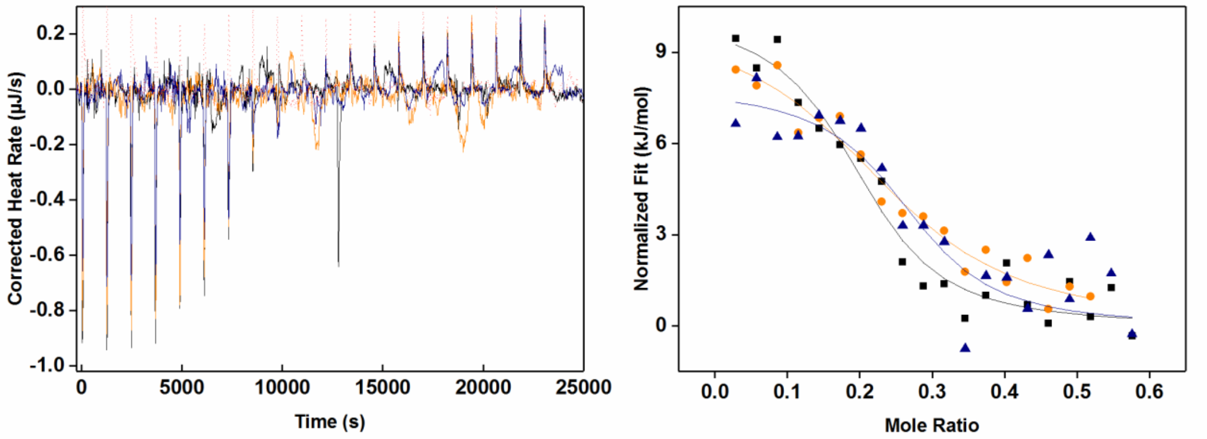

Figure S8. Calorimetric traces (left panel, solid lines) and integral plots (right panel) obtained performing subsequent injection of 10 µl sodium oxalate (1 mM) to py-g-CNCs DS 0.35 (~ 1 mg/ml). Dilution of sodium oxalate 1 mM to water is shown in the left panel (red dotted line).

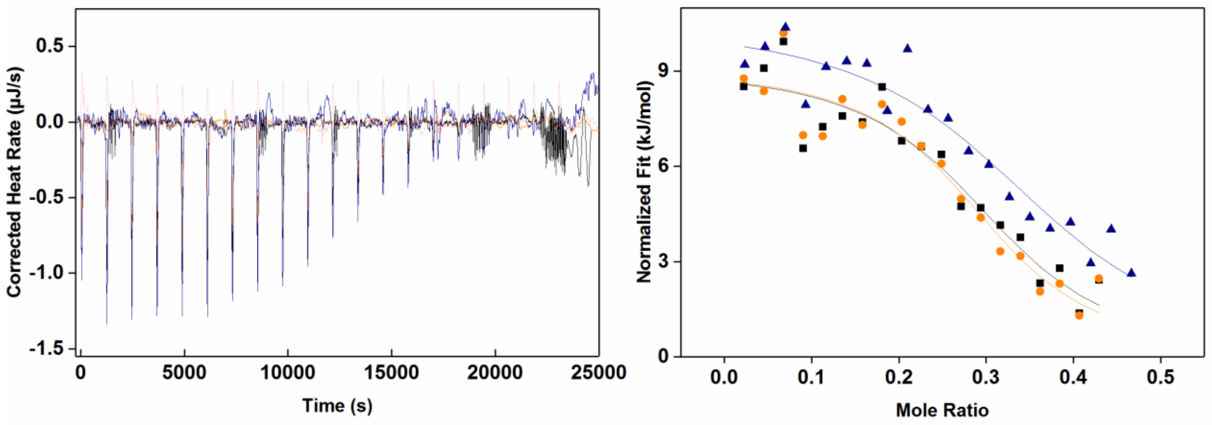

Figure S9. Calorimetric traces (left panel, solid lines) and integral plots (right panel) obtained performing subsequent injection of 10 µl sodium oxalate (1 mM) to py-g-CNCs DS 0.62 (~ 0.8 mg/ml). Dilution of sodium oxalate 1 mM to water is shown in the left panel (red dotted line).

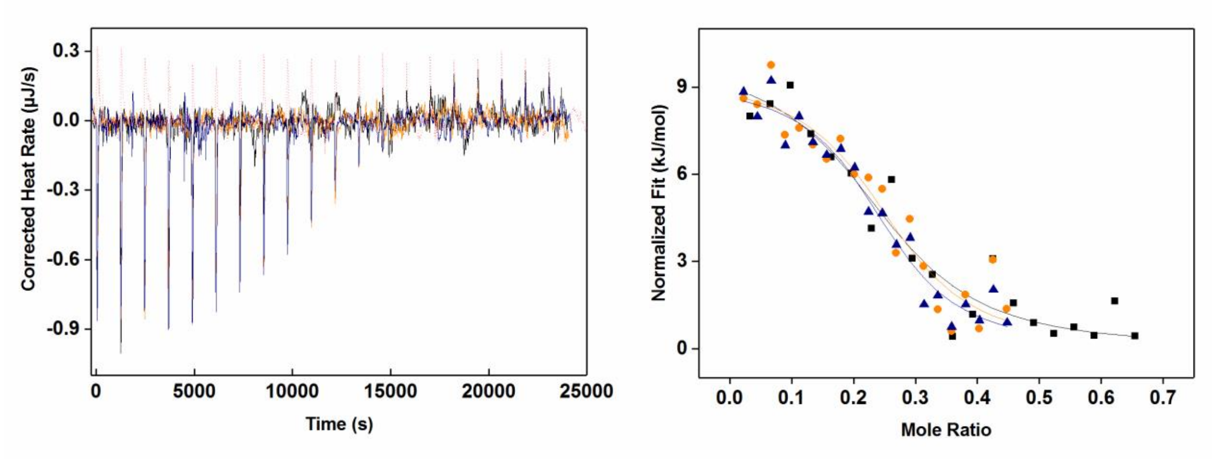

Figure S10. Calorimetric traces (left panel, solid lines) and integral plots (right panel) obtained performing subsequent injection of 10 µl sodium oxalate (1 mM) to py-g-CNCs DS 0.91 (~ 0.4 – 0.6 mg/ml). Dilution of sodium oxalate 1 mM to water is shown in the left panel (red dotted line).

DS	ΔH (kJ/mol)	K_a (mM^{-1})	ΔS (J/mol*K)	n	C factor (average)
0.35	9 ± 1	110 ± 40	127 ± 4	0.24 ± 0.03	12
0.62	9.6 ± 0.7	80 ± 20	127 ± 1	0.33 ± 0.03	17
0.91	9.5 ± 0.4	90 ± 10	126 ± 1	0.26 ± 0.01	12

Table S3. Results obtained from Isothermal titration calorimetry for the adsorption of sodium oxalate 1 mM to py-g-CNCs with different degree of substitution.

Adsorption of sodium sulfate to py-g-CNCs

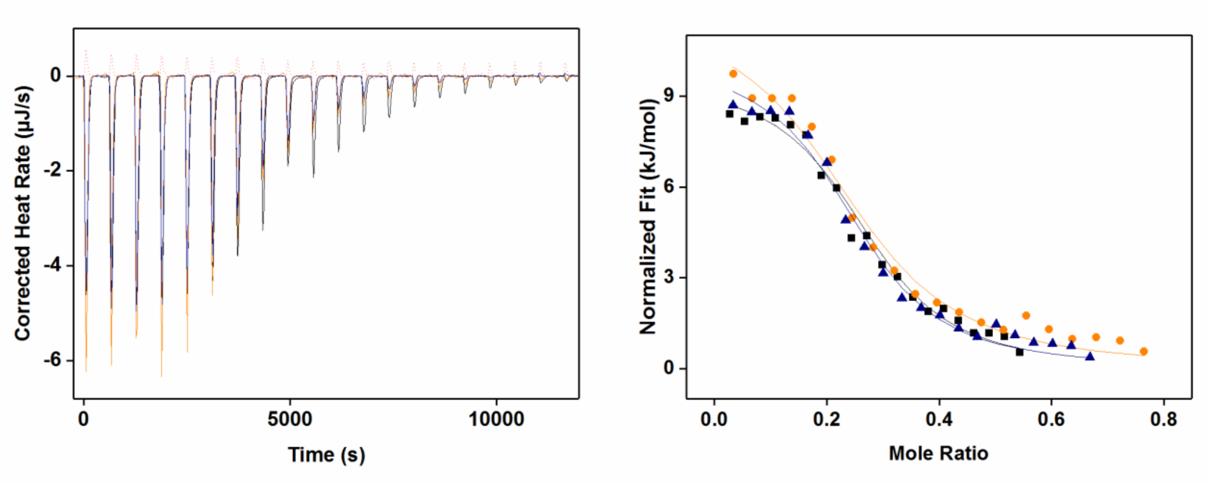

Figure S11. Calorimetric traces (left panel, solid lines) and integral plots (right panel) obtained performing subsequent injection of 10 µl sodium sulfate (5 mM) to py-g-CNCs DS 0.35 (4 - 5 mg/ml). Dilution of sodium sulfate 5 mM to water is shown in the left panel (red dotted line).

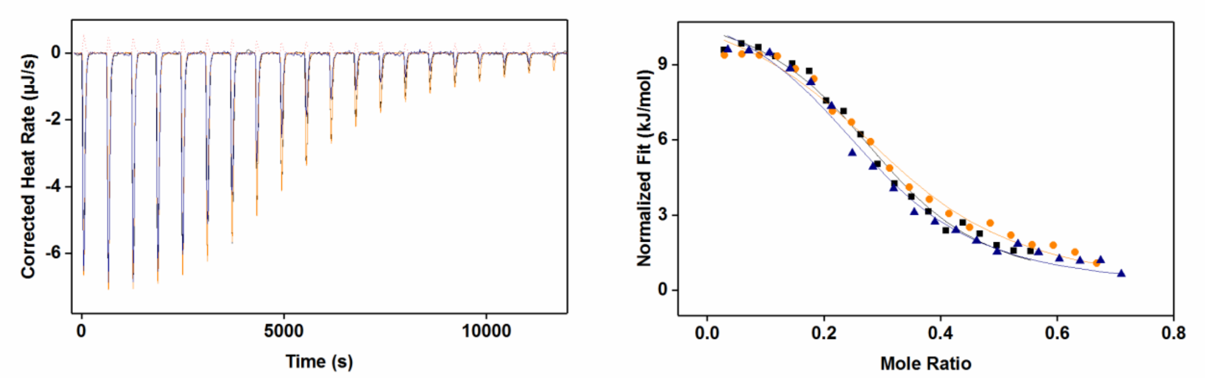

Figure S12. Calorimetric traces (left panel, solid lines) and integral plots (right panel) obtained performing subsequent injection of 10 µl sodium sulfate (5 mM) to py-g-CNCs DS 0.62 (2 - 3 mg/ml). Dilution of sodium sulfate 5 mM to water is shown in the left panel (red dotted line).

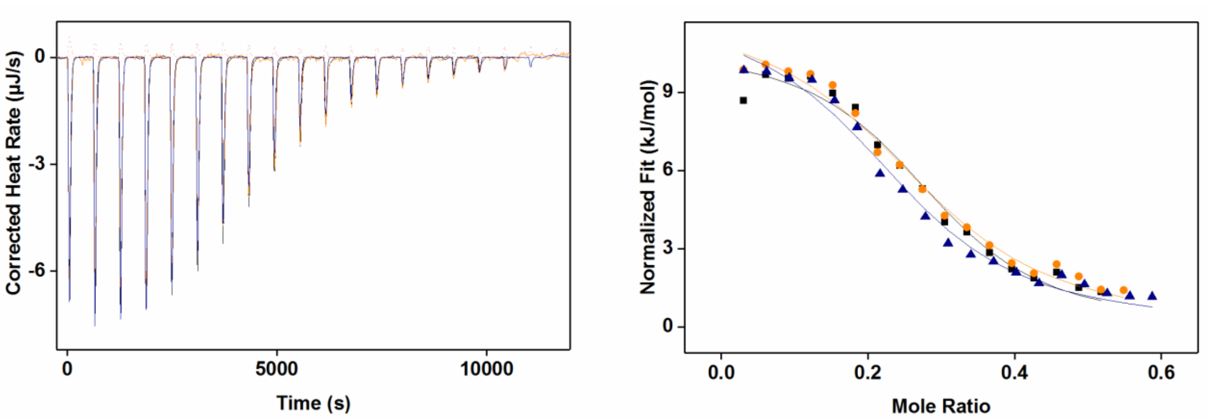

Figure S13. Calorimetric traces (left panel, solid lines) and integral plots (right panel) obtained performing subsequent injection of 10 µl sodium sulfate (5 mM) to py-g-CNCs DS

0.91 (2 mg/ml). Dilution of sodium sulfate 5 mM to water is shown in the left panel (red dotted line).

DS	ΔH (kJ/mol)	K_a (mM^{-1})	ΔS (J/mol*K)	n	C factor (average)
0.35	10 ± 1	17 ± 4	116 ± 2	0.27 ± 0.02	9
0.62	11.7 ± 0.3	12 ± 2	117 ± 2	0.31 ± 0.02	7
0.91	11.6 ± 0.8	16 ± 4	119 ± 1	0.28 ± 0.02	9

Table S4. Results obtained from Isothermal titration calorimetry for the adsorption of sodium sulfate 5 mM to py-g-CNCs with different degree of substitution.

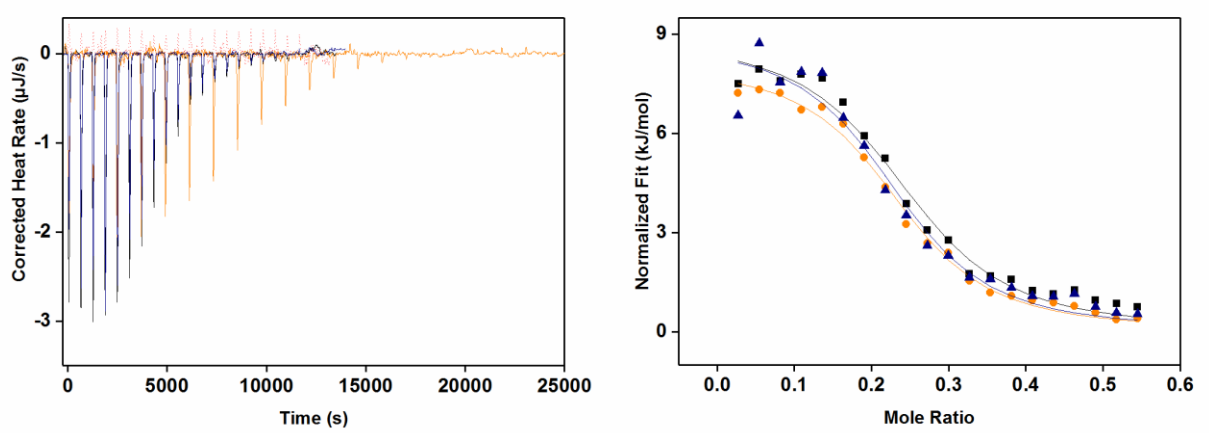

Figure S14. Calorimetric traces (left panel, solid lines) and integral plots (right panel) obtained performing subsequent injection of 10 µl sodium sulfate (2.5 mM) to py-g-CNCs DS 0.35 (~ 2.5 mg/ml). Dilution of sodium sulfate 2.5 mM to water is shown in the left panel (red dotted line).

DS	ΔH (kJ/mol)	K_a (mM^{-1})	ΔS (J/mol*K)	n	C factor (average)
0.35	8.6 ± 0.4	49 ± 4	119 ± 1	0.24 ± 0.01	13

Table S5. Results obtained from Isothermal titration calorimetry for the adsorption of sodium sulfate 2.5 mM to py-g-CNCs (DS = 0.35).

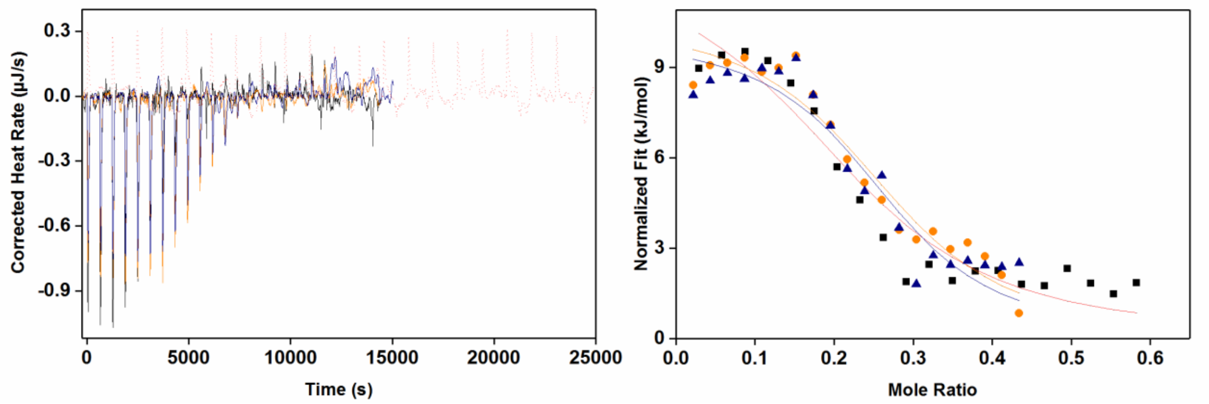

Figure S15. Calorimetric traces (left panel, solid lines) and integral plots (right panel) obtained performing subsequent injection of 10 µl sodium sulfate (1 mM) to py-g-CNCs DS 0.35 (~ 1 mg/ml). Dilution of sodium sulfate 1 mM to water is shown in the left panel (red dotted line).

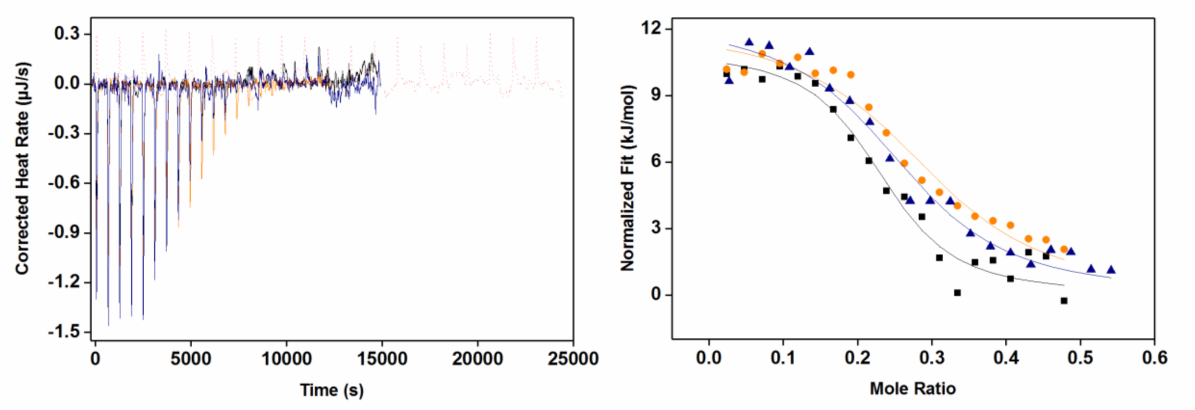

Figure S16. Calorimetric traces (left panel, solid lines) and integral plots (right panel) obtained performing subsequent injection of 10 µl sodium sulfate (1 mM) to py-g-CNCs DS 0.62 (~ 0.7 mg/ml). Dilution of sodium sulfate 1 mM to water is shown in the left panel (red dotted line).

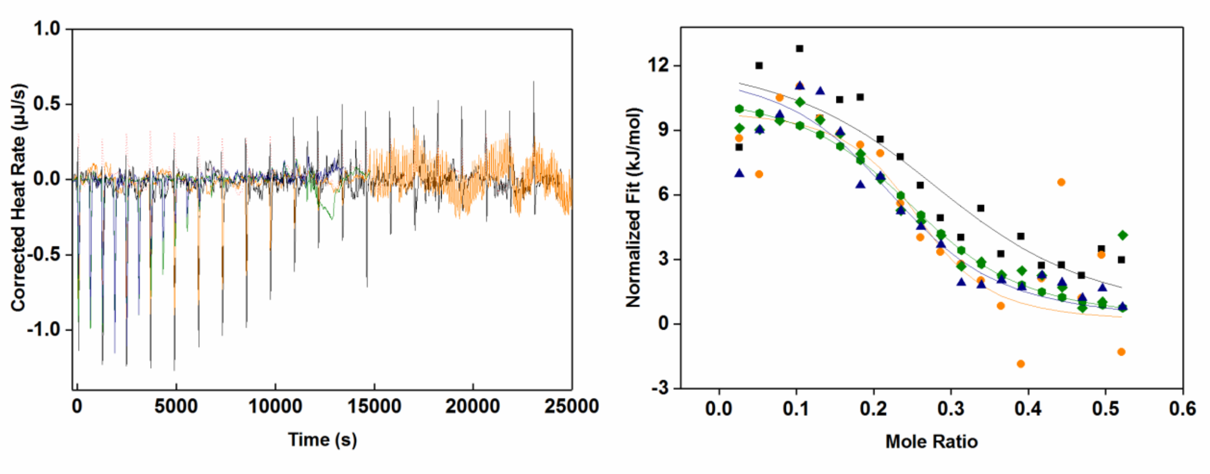

Figure S17. Calorimetric traces (left panel, solid lines) and integral plots (right panel) obtained performing subsequent injection of 10 µl sodium sulfate (1 mM) to py-g-CNCs DS 0.91 (~ 0.5 mg/ml). Dilution of sodium sulfate 1 mM to water is shown in the left panel (red dotted line).

DS	ΔH (kJ/mol)	K_a (mM^{-1})	ΔS (J/mol*K)	n	C factor (average)
0.35	11 ± 1	60 ± 20	129 ± 1	0.26 ± 0.02	10
0.62	11.9 ± 0.5	100 ± 30	135 ± 1	0.27 ± 0.03	14

0.91	12.0 ± 0.7	90 ± 20	133 ± 2	0.28 ± 0.04	10

Table S6. Results obtained from Isothermal titration calorimetry for the adsorption of sodium sulfate 1 mM to py-g-CNCs with different degree of substitution.

Adsorption of sodium glutarate to py-g-CNCs

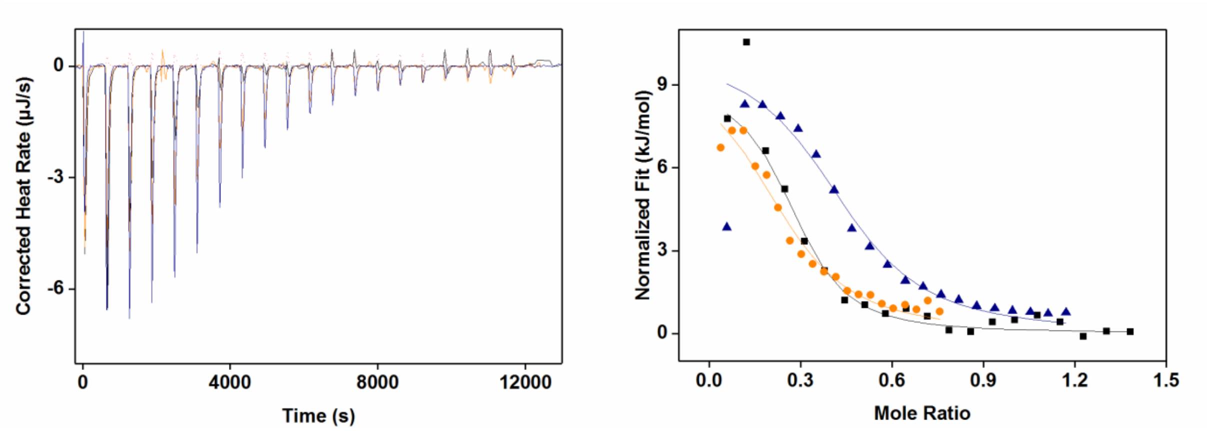

Figure S18. Calorimetric traces (left panel, solid lines) and integral plots (right panel) obtained performing subsequent injection of 10 µl sodium glutarate (5.5 mM) to py-g-CNCs DS 0.35 (3 - 4 mg/ml). Dilution of sodium glutarate 5.5 mM to water is shown in the left panel (red dotted line).

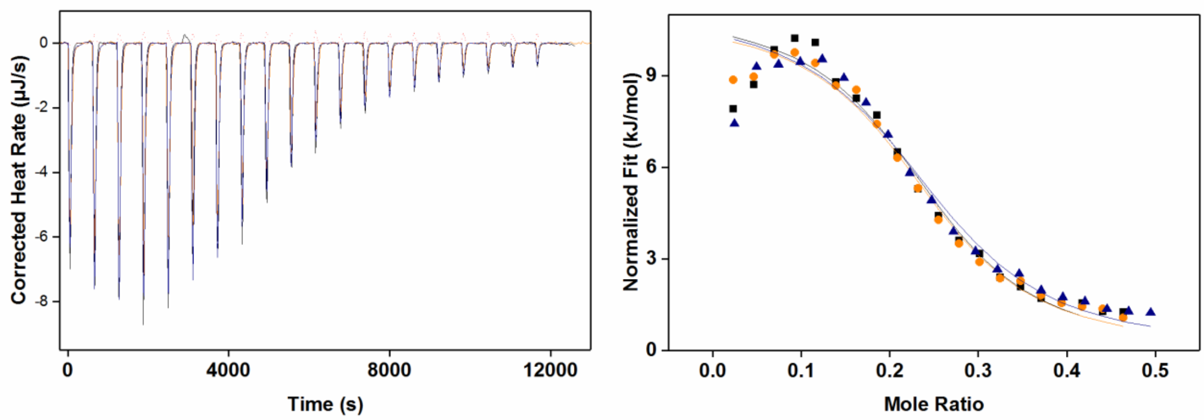

Figure S19. Calorimetric traces (left panel, solid lines) and integral plots (right panel) obtained performing subsequent injection of 10 µl sodium glutarate (5.5 mM) to py-g-CNCs DS 0.62 (4 mg/ml). Dilution of sodium glutarate 5.5 mM to water is shown in the left panel (red dotted line).

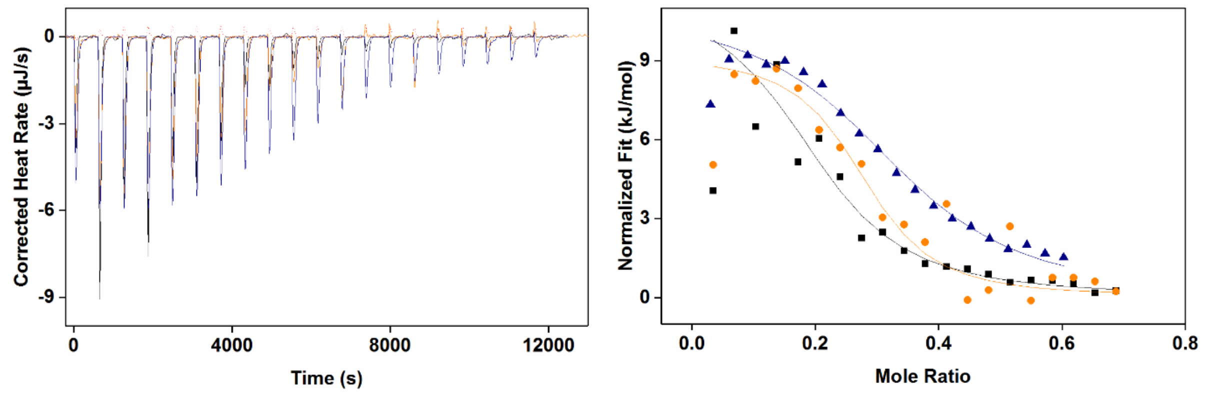

Figure S20. Calorimetric traces (left panel, solid lines) and integral plots (right panel) obtained performing subsequent injection of 10 µl sodium glutarate (5.5 mM) to py-g-CNCs DS 0.91 (2 -3 mg/ml). Dilution of sodium glutarate 5.5 mM to water is shown in the left panel (red dotted line).

DS	ΔH (kJ/mol)	K_a (mM^{-1})	ΔS (J/mol*K)	n	C factor (average)
0.35	9.7 ± 0.6	18 ± 10	113 ± 5	0.28 ± 0.01	7
0.62	11.1 ± 0.1	18 ± 2	118 ± 1	0.25 ± 0.01	13
0.91	11 ± 1	22 ± 15	117 ± 3	0.28 ± 0.07	13

Table S7. Results obtained from Isothermal titration calorimetry for the adsorption of sodium glutarate 5.5 mM to py-g-CNCs with different degree of substitution.

Adsorption of trisodium citrate to py-g-CNCs

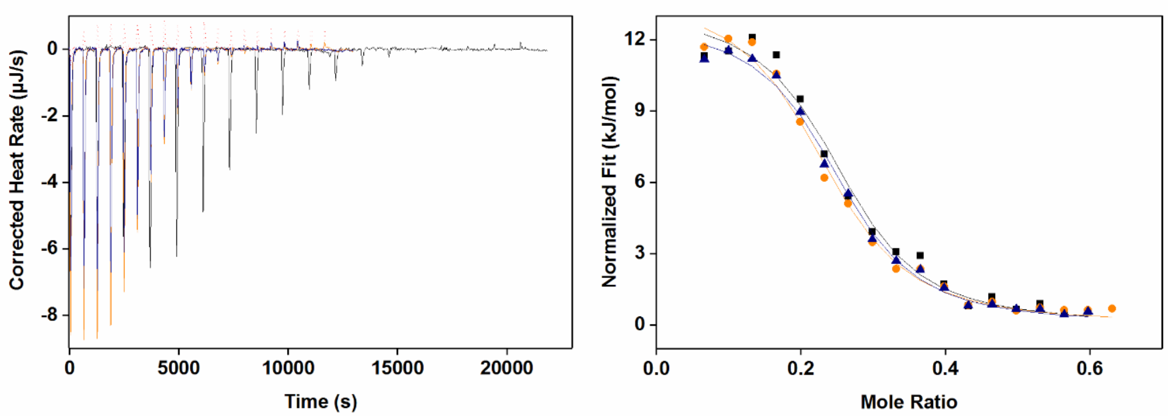

Figure S21. Calorimetric traces (left panel, solid lines) and integral plots (right panel) obtained performing subsequent injection of 10 µl sodium citrate (5 mM) to py-g-CNCs DS 0.35 (4 mg/ml). Dilution of sodium citrate 5 mM to water is shown in the left panel (red dotted line).

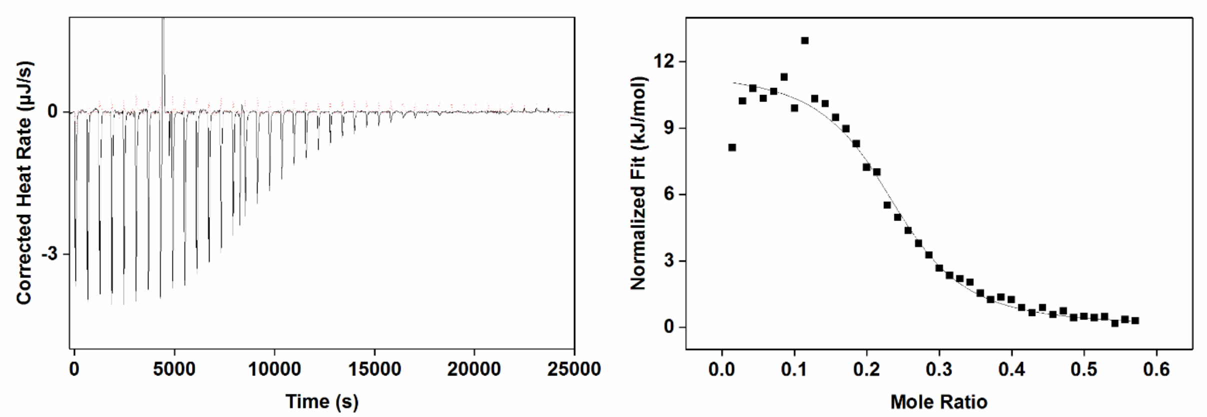

Figure S22. Calorimetric traces (left panel, solid lines) and integral plots (right panel) obtained performing subsequent injection of 5 µl sodium citrate (5 mM) to py-g-CNCs DS 0.35 (4.7 mg/ml). Dilution of sodium citrate 5 mM to water is shown in the left panel (red dotted line). The 8th injection had a temporary external effect and not considered in the fit.

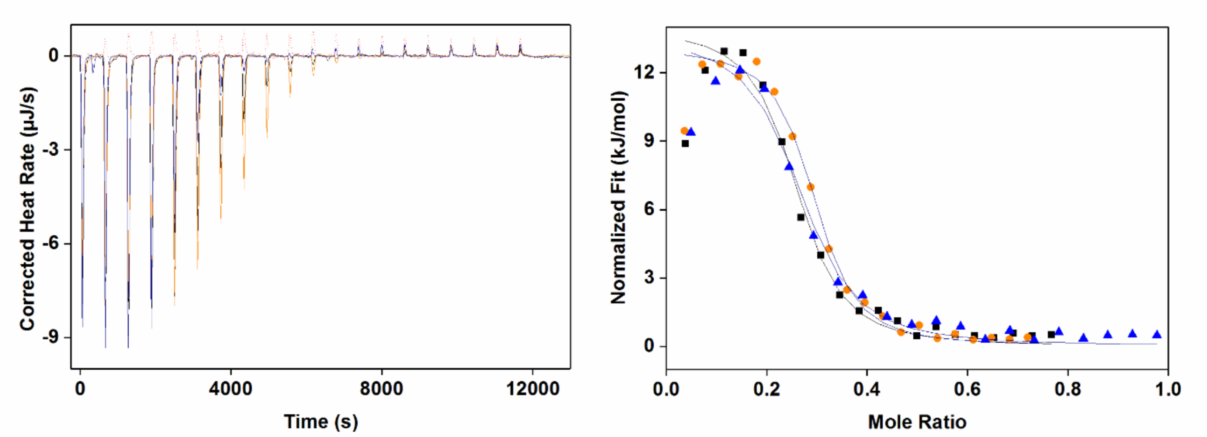

Figure S23. Calorimetric traces (left panel, solid lines) and integral plots (right panel) obtained performing subsequent injection of 10 µl sodium citrate (5 mM) to py-g-CNCs DS 0.62 (~ 2 mg/ml). Dilution of sodium citrate 5 mM to water is shown in the left panel (red dotted line).

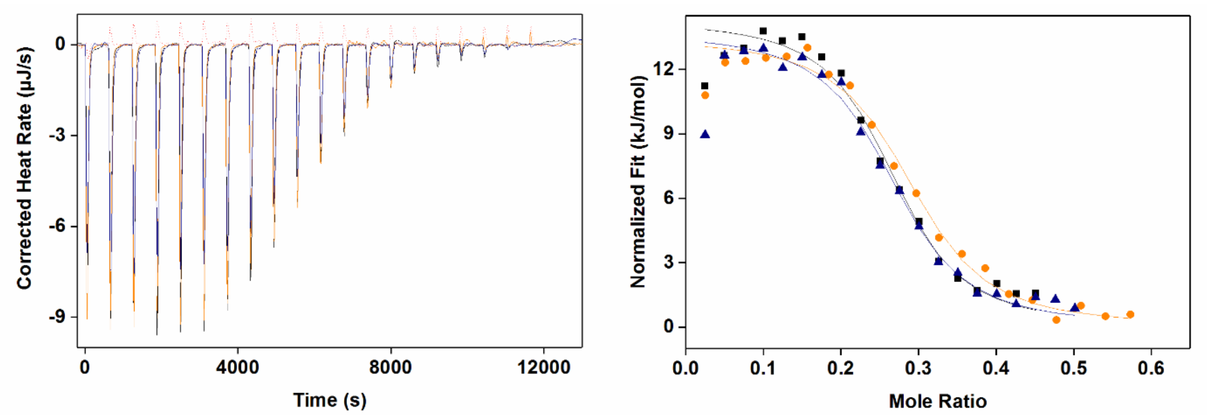

Figure S24. Calorimetric traces (left panel, solid lines) and integral plots (right panel) obtained performing subsequent injection of 10 µl sodium citrate (5 mM) to py-g-CNCs DS

0.91 (2.6 mg/ml). Dilution of sodium citrate 5 mM to water is shown in the left panel (red dotted line).

DS	ΔH (kJ/mol)	K_a (mM^{-1})	ΔS (J/mol*K)	n	C factor (average)
0.35	12.9 ± 0.9	38 ± 3	131 ± 3	0.24 ± 0.01	18
0.62	13.6 ± 0.4	72 ± 16	138 ± 1	0.26 ± 0.02	32
0.91	13.8 ± 0.4	45 ± 7	135 ± 3	0.27 ± 0.01	31

Table S8. Results obtained from Isothermal titration calorimetry for the adsorption of trisodium citrate 5 mM to py-g-CNCs with different degree of substitution.

Adsorption of Ethylenediaminetetraacetic (EDTA) tetrasodium salt to py-g-CNCs

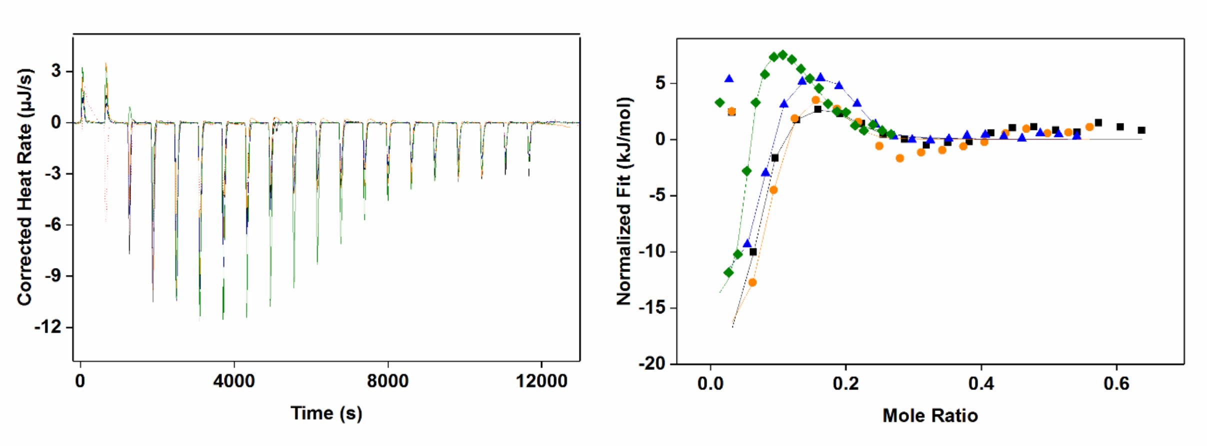

Figure S25. Calorimetric traces (left panel, solid lines) and integral plots (right panel) obtained performing subsequent injection of 10 µl EDTA tetrasodium salt (5 mM) to py-g-CNCs DS 0.35 (4 - 5 mg/ml). Dilution of EDTA tetrasodium salt 5 mM to water is shown in the left panel (red dotted line).

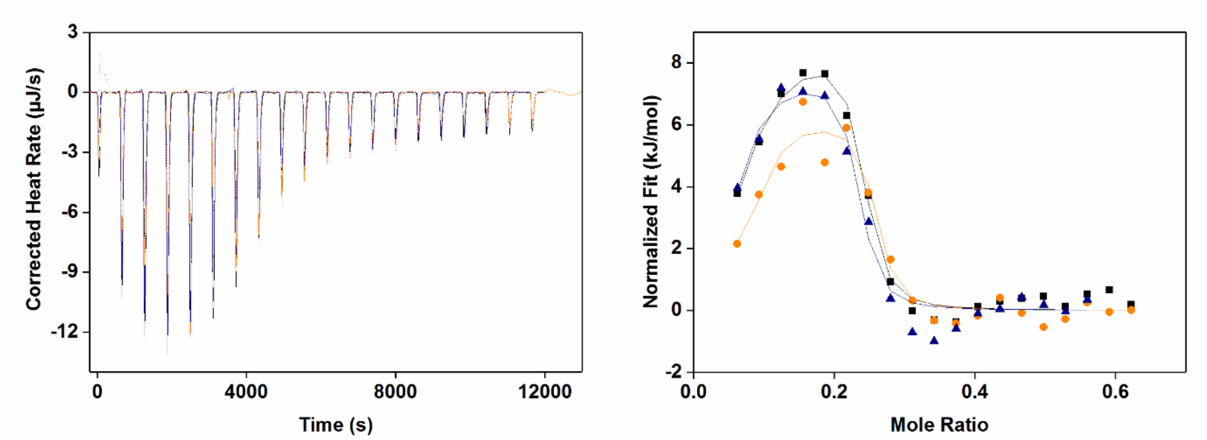

Figure S26. Calorimetric traces (left panel, solid lines) and integral plots (right panel) obtained performing subsequent injection of 10 µl EDTA tetrasodium salt (5 mM) to py-g-CNCs DS 0.62 (3.7 mg/ml). Dilution of EDTA tetrasodium salt 5 mM to water is shown in the left panel (red dotted line).

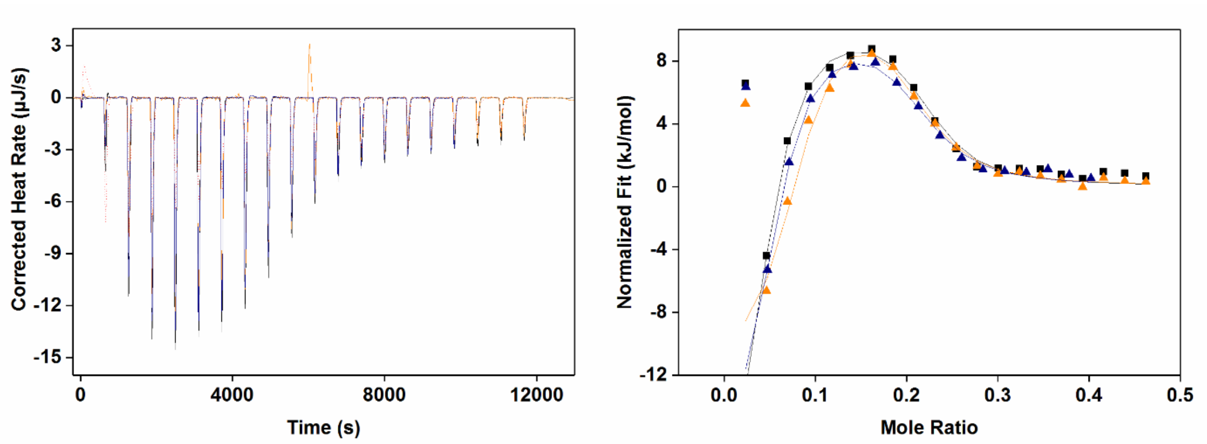

Figure S27. Calorimetric traces (left panel, solid lines) and integral plots (right panel) obtained performing subsequent injection of 10 µl EDTA tetrasodium salt (5 mM) to py-g-CNCs DS 0.91 (3.7 mg/ml). Dilution of EDTA tetrasodium salt 5 mM to water is shown in the left panel (red dotted line).

DS	ΔH_1 (kJ/mol)	K_{a1} (μM^{-1})	ΔS_1 (J/mol*K)	n_1	ΔH_2 (kJ/mol)	K_{a2} (mM^{-1})	ΔS_2 (J/mol*K)	n_2
0.35	-18 ± 5	7 ± 5	72 ± 20	0.07 ± 0.01	5 ± 1	260 ± 50	121 ± 6	0.13 ± 0.02
0.62	-3.8 ± 0.5	4 ± 2	113 ± 3	0.05 ± 0.02	8.3 ± 0.6	424 ± 70	136 ± 2	0.18 ± 0.01
0.91	-17 ± 4	0.9 ± 0.1	56 ± 14	0.05 ± 0.01	12 ± 1	58 ± 6	131 ± 3	0.15 ± 0.02

Table S9. Results obtained from Isothermal titration calorimetry for the adsorption of EDTA tetrasodium salt 5 mM to py-g-CNCs with different degree of substitution.

Adsorption of oxalic acid to py-g-CNCs

The investigation of the adsorption of oxalic acid to py-g-CNCs was less detailed, since the calorimetric trace yield a low exothermic enthalpy which was very close to the heat of dilution. This small difference made this process very difficult to detect and the results less reliable. From such results we expect no adsorption or very little adsorption with stoichiometric number lower than 0.1 and very low association constant.

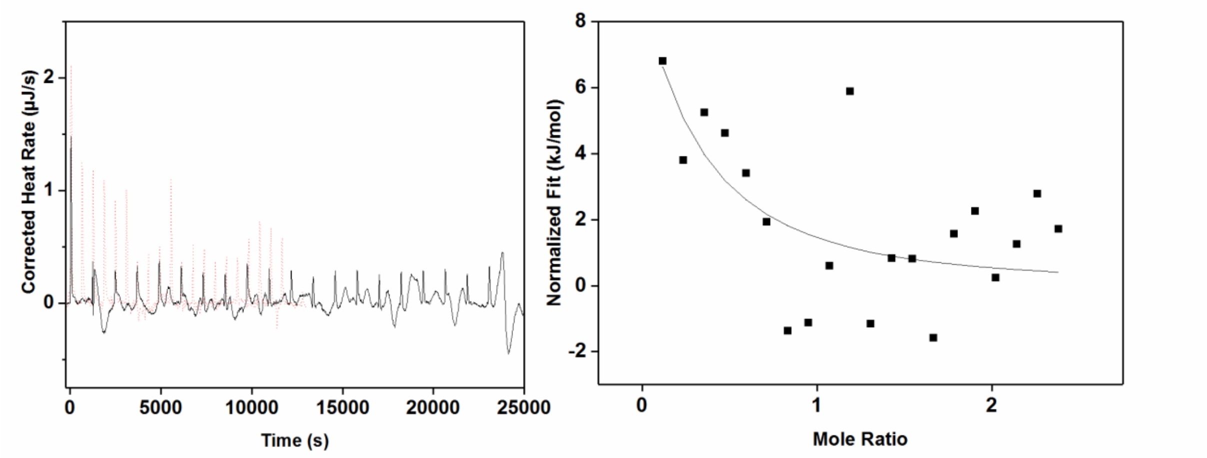

Figure S28. Results obtained from Isothermal titration calorimetry for the adsorption of oxalic acid 1 mM toto py-g-CNCs (DS 0.91, 0.2 mg/ml)

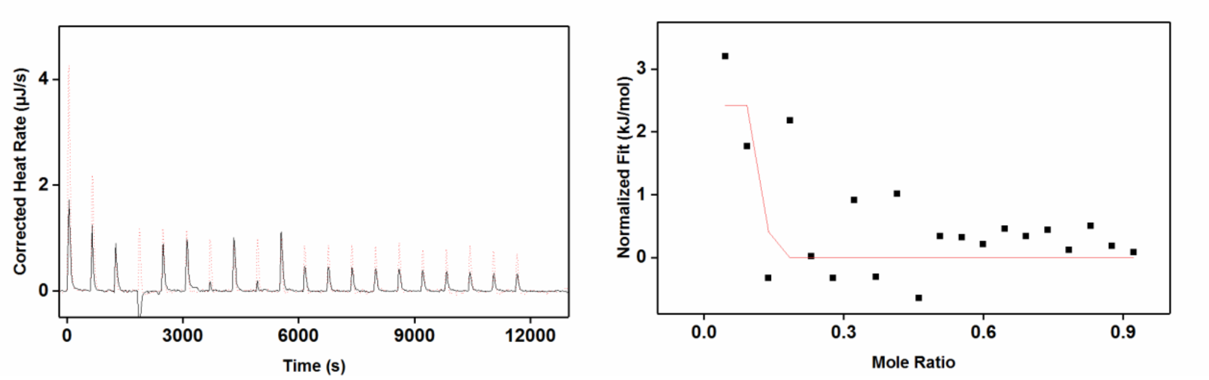

Figure S29. Results obtained from Isothermal titration calorimetry for the adsorption of oxalic acid 5 mM toto py-g-CNCs (DS 0.35, 2.9 mg/ml)

S3. List of pK_b of the salts used in this work[2]

The value of pK_b was determined from literature values of pk_a of the conjugated acid, using the following formula: $pK_b = 14 – pK_a$

We decide to report the pK_b values instead of the more common pKa for simplicity, considering that all salts used behave as bases in water.

Sodium Acetate: 9.24

Sodium sulfate: pK_{b1} 12.01; pK_{b2} > 14

Disodium oxalate: pK_{b1} 10.19; pK_{b2} 12.75

Disodium glutarate[3]: pK_{b1} 8.58; pK_{b2} 9.68 (https://pubchem.ncbi.nlm.nih.gov/compound/glutaric_acid#section=Decomposition)

Trisodium Citrate: pK_{b1} 7.6; pK_{b2} 9.24; pK_{b3} 10.87

Tetrasodium EDTA[4]: pK_{b1} 3.7; pK_{b2} 7.8; pK_{b3} 11.3; pK_{b4} 12.0

References

1. Jasmani, L.; Eyley, S.; Wallbridge, R.; Thielemans, W. A Facile One-Pot Route to Cationic Cellulose Nanocrystals. *Nanoscale* **2013**, *5* (21), 10207–10211.

2. Lide, D. R. Dissociation Constants of Organic Acids and Bases. In *CRC Handbook of Chemistry and Physics*; 2008; pp. 8-42 – 8-46

3. https://pubchem.ncbi.nlm.nih.gov/compound/glutaric_acid#section=Decomposition

4. Dawson, R. M. C., et al., Data for Biochemical Research, 3rd ed., Oxford University Press (New York, NY: 1986), p. 404.