

# Supplementary materials

## Revisiting the determination of the degree of deacetylation of modified chitosan resins using potentiometric titration

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## 1. Information about the starting materials

**Table S1.** Information on length of polymer chains [expressed by viscosity and molecular weight (MW)] and on the degree of deacetylation (DDA<sub>SM</sub>, %) for the three chitosan starting materials used in this study.

| Commercial name                              | Viscosity (cps) <sup>a</sup> | Calculated MW (KDa) <sup>I</sup> | DDA <sub>SM</sub> (%) <sup>II</sup> |
|--|------------------------------|----------------------------------|-------------------------------------|
| ChitoClear® HQG 10<br>(Product code 43000)   | <20                          | 110-150                          | 75.1 ± 0.2                          |
| ChitoClear® HQG 400<br>(Product code 43020)  | 200-600                      | 250-300                          | 77.5 ± 0.7                          |
| ChitoClear® HQG 1600<br>(Product code 43040) | 1200-2000                    | 340-360                          | 69.5 ± 0.2                          |

I. Data provided by the manufacturer.

II. Determined by potentiometric titration (means and standard deviations of triplicate). See Sections 4 and 5 of this supplementary materials for detailed titration results and determination of DDA.

## 2. Preparation of Naph-Chit resins

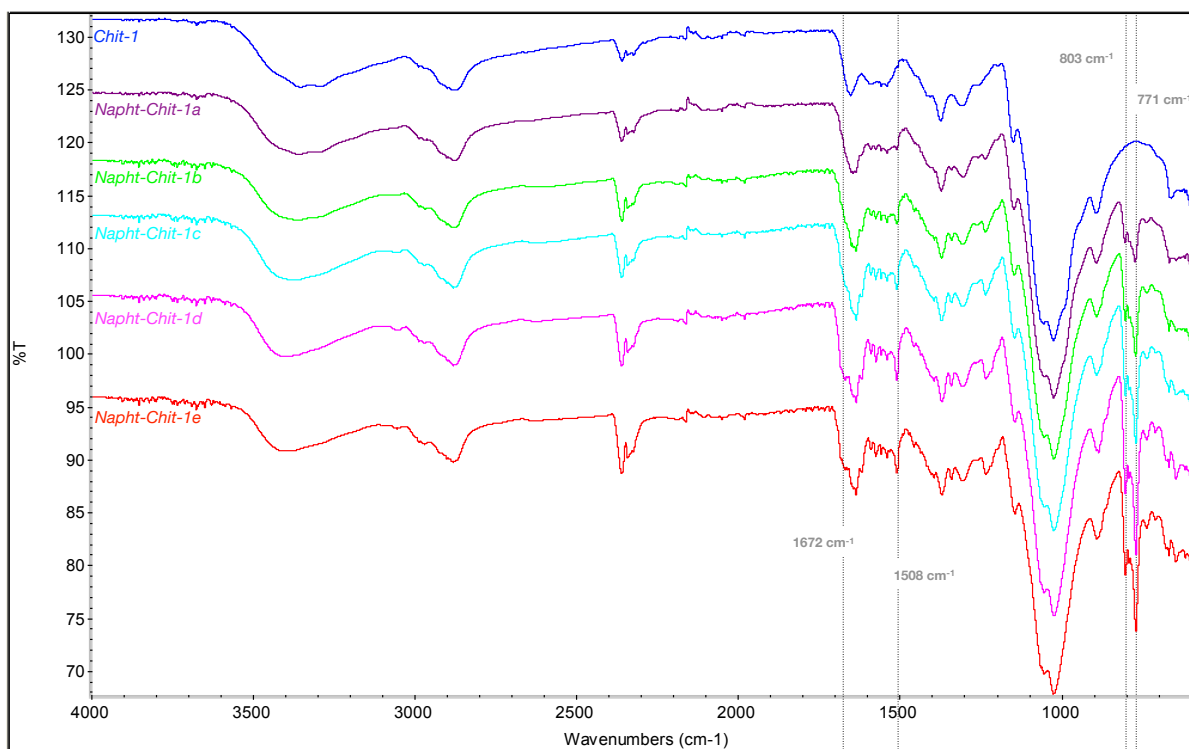
For each reaction, 1 g of lyophilized chitosan was added to 5 mL of distilled water in a conical centrifuge tube. Then, 4 mL of ethanol was added to each tube. Next, a certain volume (calculated to reach the desired Napht:NH<sub>2</sub> ratio and rounded to the closest 0.1 mL, see Table S2) of 1-naphtaldehyde was added, and the volume was topped up to 20 mL with water before the tube cap was tightly screwed. The reaction was stirred for 48 hours at room temperature by using a benchtop laboratory shaker (SHAKER SK-71 Lab. Companion, at 230 rpm). The solution was then centrifuged at 3400 g for 6 minutes. The settled modified chitosan was rinsed 9 times with a volume of 40 mL of [sodium chloride 30 g/L (3x), distilled water (2x), acetone (1x), ethanol (1x), and distilled water (x2)] (with a 5 min agitation followed by centrifugation at 3400 g for 6 minutes). After the ninth rinse, the supernatant water was removed, and the remaining solid was lyophilized.

**Table S2.** Quantity of 1-naphtaldehyde used for the derivatization of 1g of starting material.

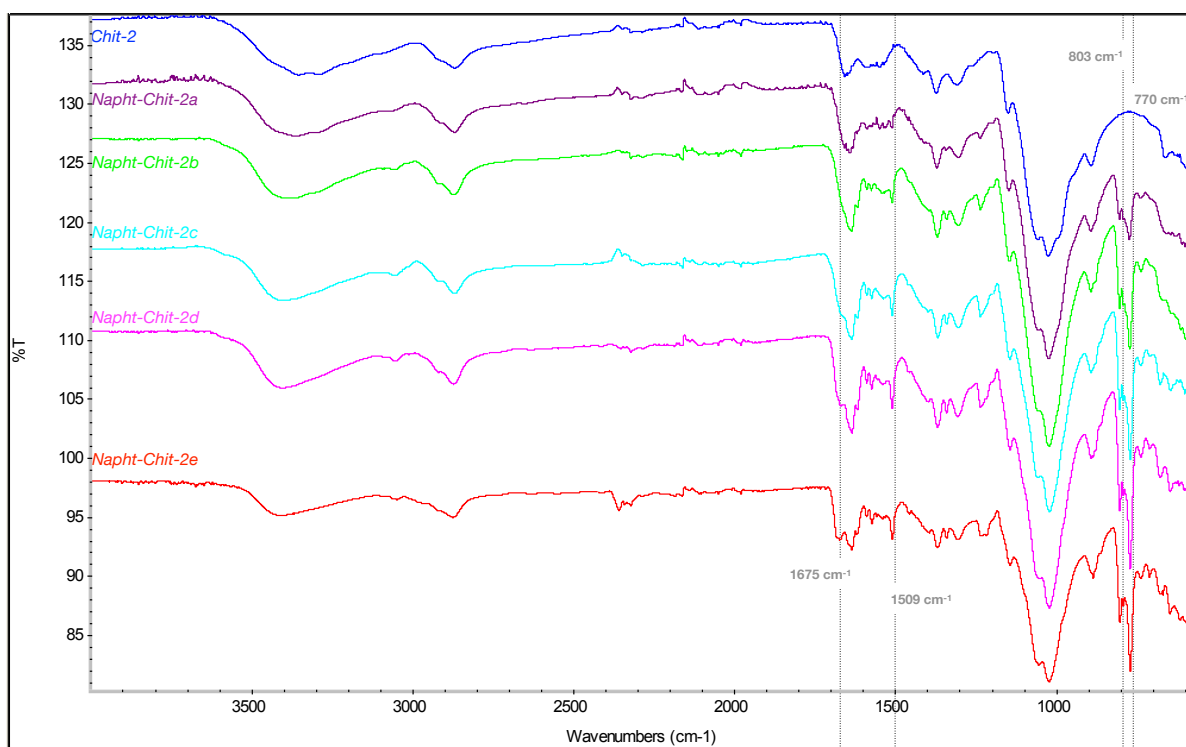
| Chitosan resin prepared | Starting material | Napht:NH <sub>2</sub> ratio | Volume of 1-naphtaldehyde used for the reaction (mL) |
|-------------------------|-------------------|-----------------------------|--|
| <i>Napht-Chit-1a</i>    | <i>Chit-1</i>     | 1:4                         | 0.2  |
| <i>Napht-Chit-1b</i>    |                   | 1:2                         | 0.4  |
| <i>Napht-Chit-1c</i>    |                   | 1:1                         | 0.8  |
| <i>Napht-Chit-1d</i>    |                   | 2:1                         | 1.6  |
| <i>Napht-Chit-1e</i>    |                   | 4:1                         | 3.2  |
| <i>Napht-Chit-2a</i>    | <i>Chit-2</i>     | 1:4                         | 0.2  |
| <i>Napht-Chit-2b</i>    |                   | 1:2                         | 0.4  |
| <i>Napht-Chit-2c</i>    |                   | 1:1                         | 0.8  |
| <i>Napht-Chit-2d</i>    |                   | 2:1                         | 1.6  |
| <i>Napht-Chit-2e</i>    |                   | 4:1                         | 3.2  |
| <i>Napht-Chit-3a</i>    | <i>Chit-3</i>     | 1:4                         | 0.5  |
| <i>Napht-Chit-3b</i>    |                   | 1:2                         | 1.0  |
| <i>Napht-Chit-3c</i>    |                   | 1:1                         | 1.9  |
| <i>Napht-Chit-3d</i>    |                   | 2:1                         | 3.8  |
| <i>Napht-Chit-3e</i>    |                   | 4:1                         | 7.7  |

### 3. FTIR spectra of chitosan resins

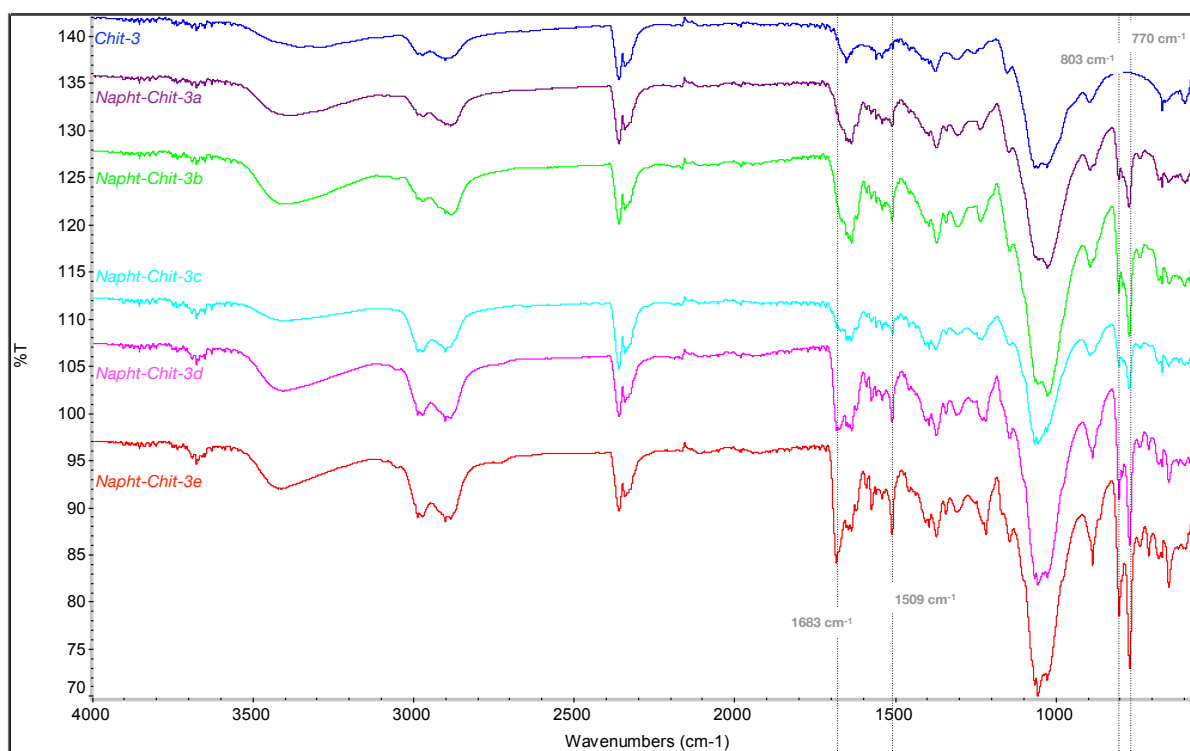
FTIR spectra of the three series of chitosan resins (the starting materials and modified derivatives) are shown in Figures S1–S3. For the three series, four bands were used to confirm the formation of the imine functionalities between 1-naphtaldehyde and chitosan. Those four bands were absent from the IR spectrum of the starting materials. Furthermore, for each series of chitosan resins, those bands become more defined and intense as the level of functionalization increases from *Napht-Chit-Xa* to *Napht-Chit-Xe*. The first two bands around 770 and 800  $\text{cm}^{-1}$  are attributed to the aromatic out-of-plane C-H bending. The third band around 1500  $\text{cm}^{-1}$  is associated with C=C ring stretch. The fourth band around 1675  $\text{cm}^{-1}$  is attributed to the C=N bond of the imine functionality. It is a bit more challenging to observe because unmodified chitosan shows a strong peak around 1645  $\text{cm}^{-1}$  associated with the residual N-acetyl groups (C=O stretching of amide I).



**Figure S1.** FTIR spectra of *Chit-1* and derivatives. From top to bottom: *Chit-1* (blue trace), *Napht-Chit-1a* (plum trace), *Napht-Chit-1b* (green trace), *Napht-Chit-1c* (turquoise trace), *Napht-Chit-1d* (pink trace), *Napht-Chit-1e* (red trace).



**Figure S2.** FTIR spectra of *Chit-2* and derivatives. From top to bottom: *Chit-2* (blue trace), *Napht-Chit-2a* (plum trace), *Napht-Chit-2b* (green trace), *Napht-Chit-2c* (turquoise trace), *Napht-Chit-2d* (pink trace), *Napht-Chit-2e* (red trace).



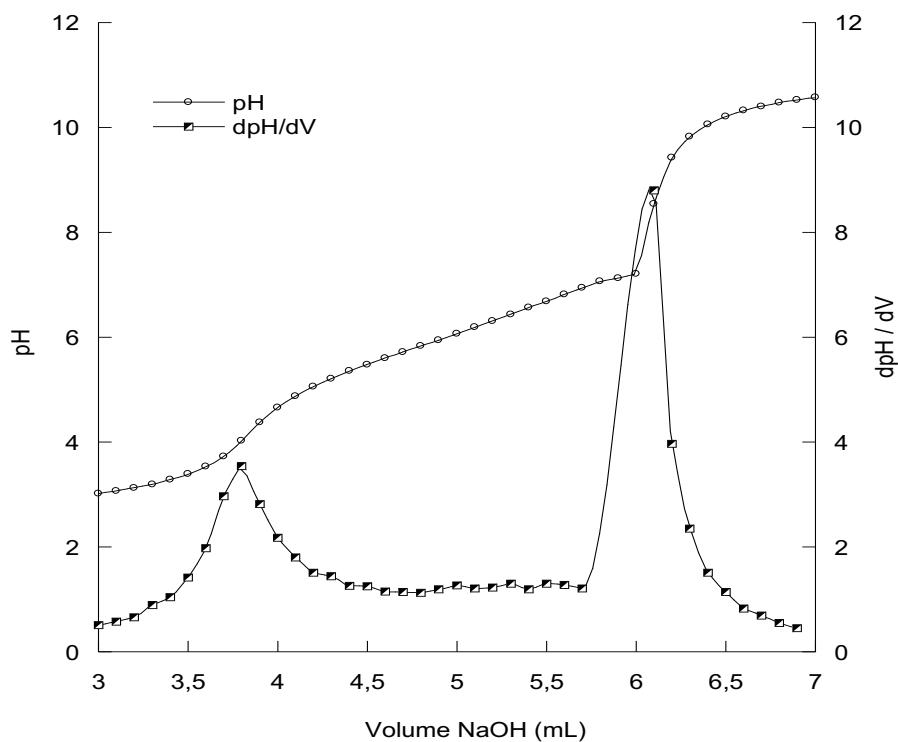
**Figure S3.** FTIR spectra of *Chit-3* and derivatives. From top to bottom: *Chit-3* (blue trace), *Napht-Chit-3a* (plum trace), *Napht-Chit-3b* (green trace), *Napht-Chit-3c* (turquoise trace), *Napht-Chit-3d* (pink trace), *Napht-Chit-3e* (red trace).

#### 4. Potentiometric titration of the chitosan resins.

##### a. General principle

pH metric titration for unmodified and modified chitosan was made using an automatic titrator (848 Titrino plus, Metrohm). In brief, the chitosan resin is initially dissolved in HCl to protonate all the amine functionalities. Then, this solution is titrated with NaOH. The volume of sodium hydroxide used corresponds both to the volume necessary to neutralize the excess HCl acid used for dissolving the chitosan ( $V_1$ ) and to neutralize the total acidity of the medium ( $V_2$ ). The difference between  $V_2$  and  $V_1$  gives the quantity of NaOH necessary for the neutralization of the ammonium functions of the chitosan resins.

Figure S4 presents a titration curve for ChitoClear® HQG 400 (Table S3, Entry 19). Total titration time = 20 minutes. Another example of titration curve is presented in the manuscript (Figure 2).



**Figure S4.** Potentiometric determination of DDA in starting material ChitoClear® HQG 400 (Table S3, Entry 19).

b. Titration results : complete raw values

**Table S3** Titration results for all the chitosan resins involved in this study ([NaOH] = 0.10 mol/L)

| Entry | Chitosan resin <sup>1</sup> | Mass used for titration (mg) | V <sub>1</sub> (mL) | V <sub>2</sub> (mL) |
|-------|-----------------------------|------------------------------|---------------------|---------------------|
| 1     | <i>Chit-1</i>               | 50.269                       | 3.866               | 6.066               |
| 2     |                             | 50.555                       | 3.875               | 6.092               |
| 3     |                             | 49.557                       | 3.925               | 6.084               |
| 4     | <i>Napht-Chit-1a</i>        | 50.050                       | 4.288               | 6.164               |
| 5     |                             | 50.579                       | 4.260               | 6.180               |
| 6     |                             | 50.200                       | 4.250               | 6.160               |
| 7     | <i>Napht-Chit-1b</i>        | 50.917                       | 4.467               | 6.212               |
| 8     |                             | 50.956                       | 4.414               | 6.157               |
| 9     |                             | 50.150                       | 4.479               | 6.224               |
| 10    | <i>Napht-Chit-1c</i>        | 50.144                       | 4.547               | 6.151               |
| 11    |                             | 50.665                       | 4.591               | 6.235               |
| 12    |                             | 50.285                       | 4.589               | 6.171               |
| 13    | <i>Napht-Chit-1d</i>        | 50.800                       | 4.478               | 6.085               |
| 14    |                             | 50.127                       | 4.673               | 6.252               |
| 15    |                             | 50.311                       | 4.580               | 6.158               |
| 16    | <i>Napht-Chit-1e</i>        | 50.864                       | 4.668               | 6.205               |
| 17    |                             | 50.192                       | 4.661               | 6.158               |
| 18    |                             | 50.503                       | 4.687               | 6.224               |
|       |                             |                              |                     |                     |
| 19    | <i>Chit-2</i>               | 49.656                       | 3.844               | 6.073               |
| 20    |                             | 50.18                        | 3.878               | 6.175               |
| 21    |                             | 49.774                       | 3.819               | 6.086               |
| 22    | <i>Napht-Chit-2a</i>        | 50.35                        | 4.242               | 6.259               |
| 23    |                             | 50.233                       | 4.246               | 6.219               |
| 24    |                             | 50.2                         | 4.228               | 6.165               |
| 25    | <i>Napht-Chit-2b</i>        | 50.269                       | 4.382               | 6.140               |
| 26    |                             | 50.072                       | 4.16                | 5.840               |
| 27    |                             | 49.75                        | 4.397               | 6.177               |
| 28    | <i>Napht-Chit-2c</i>        | 50.856                       | 4.575               | 6.173               |
| 29    |                             | 50.415                       | 4.653               | 6.256               |
| 30    |                             | 50.399                       | 4.653               | 6.192               |
| 31    | <i>Napht-Chit-2d</i>        | 50.495                       | 4.742               | 6.159               |
| 32    |                             | 50.976                       | 4.763               | 6.171               |
| 33    | <i>Napht-Chit-2e</i>        | 50.399                       | 4.852               | 6.180               |
| 34    |                             | 50.28                        | 4.836               | 6.170               |

**Table S3 (continued)** Titration results for all the chitosan resins involved in this study ([NaOH] = 0.10 mol/L)

| Entry | Chitosan resin <sup>I</sup> | Mass used for titration (mg) | V <sub>1</sub> (mL) | V <sub>2</sub> (mL) |
|-------|-----------------------------|------------------------------|---------------------|---------------------|
| 35    | <i>Chit-3</i>               | 50.243                       | 4.049               | 6.051               |
| 36    |                             | 50.162                       | 4.062               | 6.062               |
| 37    |                             | 50.076                       | 4.046               | 6.053               |
| 38    | <i>Napht-Chit-3a</i>        | 50.312                       | 4.666               | 6.148               |
| 39    |                             | 50.163                       | 4.660               | 6.152               |
| 40    |                             | 50.524                       | 4.735               | 6.178               |
| 41    | <i>Napht-Chit-3b</i>        | 50.282                       | 4.769               | 6.114               |
| 42    |                             | 50.449                       | 4.813               | 6.154               |
| 43    |                             | 50.623                       | 4.803               | 6.157               |
| 44    | <i>Napht-Chit-3c</i>        | 50.635                       | 4.840               | 6.157               |
| 45    |                             | 50.012                       | 4.920               | 6.159               |
| 46    |                             | 50.072                       | 4.934               | 6.163               |
| 47    | <i>Napht-Chit-3d</i>        | 50.431                       | 3.4.956             | 6.155               |
| 48    |                             | 50.077                       | 4.960               | 6.159               |
| 49    |                             | 50.788                       | 4.962               | 6.150               |
| 50    | <i>Napht-Chit-3e</i>        | 50.894                       | 5.045               | 6.151               |
| 51    |                             | 50.681                       | 5.075               | 6.152               |
| 52    |                             | 50.067                       | 5.066               | 6.157               |

I. See Table 1 of the manuscript for details on those samples.

## 5. Determination of DDA from potentiometric titration: example

### a. Using Equation (1): example

Let us use the first titration of *Napht-Chit-1a* as our example (Table S3, Entry 4). The experimental data of this titration are the following:

$$V_1 = 4.288 \text{ mL}$$

$$V_2 = 6.164 \text{ mL}$$

$$\Delta V = 1.876 \text{ mL}$$

$$m = 50.050 \text{ mg}$$

$$[\text{NaOH}] = 0.10 \text{ mol/L}$$

In the manuscript, we defined Equation (1) as:

$$DDA (\%) = 100 \frac{(161.16 \text{ g/mol} \cdot \Delta V \cdot [\text{NaOH}])}{m} \quad (\text{S1})$$

for which  $[\text{NaOH}]$  is the concentration (0.1 mol/L) of the sodium hydroxide solution used for titration,  $\Delta V$  is the volume of HCl required to neutralize the ammonium functionalities ( $V_2 - V_1$ , L), 161.16 (g/mol) is the molecular weight of the D-glucosamine monomer, and  $m$  is the mass (g) of the sample in the dry state before titration.

Applying Equation (S1) to our example gives:

$$DDA (\%) = 100 \frac{(161.16 \text{ g/mol} \cdot 1.876 \cdot 10^{-3} \text{ L} \cdot 0.10 \text{ mol/L})}{50.05 \cdot 10^{-3} \text{ g}}$$

$$DDA (\%) = 60.41$$

Titration was performed in triplicate for each chitosan resin.

The values were reported in the manuscript (Table 2) as means  $\pm$  standard deviations.

For example, for *Napht-Chit-1a*, the three titrations gave the following *DDA* values.

60.41 (Table S3, Entry 4)

61.18 (Table S3, Entry 5)

61.32 (Table S3, Entry 6)

$$\mu = 60.97 \quad \sigma = 0.49$$

Thus for this sample, the definitive value *DDA* (%) as calculated with Equation (1) is:

$$DDA (\%) = 61.0 \pm 0.5$$

Complete detailed results can be found in Table S4.

b. Using Equation (2): example

Let us use again the first titration of *Napht-Chit-1a* as our example (Table S3, Entry 4). The experimental data of this titration are the following:

$$V_1 = 4.288 \text{ mL}$$

$$V_2 = 6.164 \text{ mL.}$$

$$\Delta V = 1.876 \text{ mL.}$$

$$m = 50.050 \text{ mg}$$

$$[\text{NaOH}] = 0.10 \text{ mol/L}$$

In the manuscript, we defined Equation (S2) as:

$$DDA (\%) = 100 \frac{(203.19 \text{ g/mol} \cdot \Delta V \cdot [\text{NaOH}])}{m + (42.03 \text{ g/mol} \cdot \Delta V \cdot [\text{NaOH}])} \quad (\text{S2})$$

for which  $[\text{NaOH}]$  is the concentration (0.1 mol/L) of the sodium hydroxide solution used for titration,  $\Delta V$  is the volume of HCl required to neutralize the ammonium functionalities (L), 203.19 (g/mol) is the molecular weight of the N-acetyl-glucosamine monomer, 42.033 (g/mol) is the difference between the molecular weight of N-acetyl-glucosamine monomer and that of D-glucosamine monomer, and  $m$  is the mass (g) of the sample in the dry state before titration.

Applying Equation (S2) to our example gives:

$$DDA (\%) = 100 \frac{(203.19 \text{ g/mol} \cdot 1.876 \cdot 10^{-3} \text{ L} \cdot 0.10 \text{ mol/L})}{50.05 \cdot 10^{-3} \text{ g} + (42.03 \text{ g/mol} \cdot 1.876 \cdot 10^{-3} \text{ L} \cdot 0.10 \text{ mol/L})}$$

$$DDA (\%) = 65.80$$

Titration was performed in triplicate for each chitosan resin.

The values were reported in the manuscript (Table 2) as means  $\pm$  standard deviations.

For example, for *Napht-Chit-1a*, the three titrations gave the following *DDA* values.

65.80 (Table S3, Entry 4)

66.52 (Table S3, Entry 5)

66.65 (Table S3, Entry 6)

$$\mu = 66.32 \quad \sigma = 0.46$$

Thus for this sample, the definitive value *DDA* (%) as calculated with Equation (S1)

is:

$$DDA (\%) = 66.3 \pm 0.5$$

Complete detailed results can be found in Table S4.

c. Calculating  $\Delta DDA$  [Equation (2)-Equation (1)] : example

Let us use *Napht-Chit-1a* again as our example.

As detailed in the two precedent sections (5a and 5b), the  $DDA$  values (means of triplicate  $\pm$  standard deviation) are as follows:

$$DDA_{\text{Calculated with Equation (1)}} (\%) = 61.0 \pm 0.5$$

$$DDA_{\text{Calculated with Equation (2)}} (\%) = 66.3 \pm 0.5$$

Consequently,

$$\begin{aligned} \Delta DDA [\text{Equation (2)} - \text{Equation (1)}] (\%) &= DDA_{\text{Calculated with Equation (2)}} \\ &\quad - DDA_{\text{Calculated with Equation (1)}} (\%) \\ &= 66.3 - 61.0 = 5.3 \end{aligned}$$

The uncertainty associated with this value corresponds to the sum of the uncertainties on  $DDA_{\text{Calculated with Equation (1)}}$  and  $DDA_{\text{Calculated with Equation (2)}}$

Thus, for this sample, the definitive value for  $\Delta DDA$  [Equation (S2) – Equation (S1)] is:

$$5 \pm 1$$

d. Using Equation (17): example

Let us use again the first titration of *Napht-Chit-1a* as our example (Table S3, Entry 4). The experimental data of this titration are the following:

$$V_1 = 4.288 \text{ mL}$$

$$V_2 = 6.164 \text{ mL}$$

$$\Delta V = 1.876 \text{ mL}$$

$$m = 50.050 \text{ mg}$$

$$[NaOH] = 0.10 \text{ mol/L}$$

In the manuscript, we defined Equation (17) as:

$$DDA (\%) = 100 \frac{(\Delta V \cdot [NaOH])((203.19 \text{ g/mol} \cdot DA) + (299.33 \text{ g/mol} \cdot DDA_{SM}))}{m_{chit} + (138.17 \text{ g/mol} \cdot \Delta V \cdot [NaOH])} \quad (S17)$$

for which  $\Delta V$  is the difference between the two inflexion points (mL),  $[NaOH]$  is the concentration of the sodium hydroxide solution used for titration (mol /L),  $DDA_{SM} (\%)$  is the degree of acetylation of the chitosan starting material (*Chit-1*, *Chit-2*, or *Chit-3*) used for modification as determined by Equation (S2) (see Table 2),  $DA$  is the degree of acetylation (%) of the resin ( $DA = 100\% - DDA_{SM}$ ), 203.19 g/mol is the molecular weight of the N-acetylglucosamine monomer, 299.33 g/mol is the molecular weight of the modified monomer (*N-Napht-glucosamine*),  $m_{chit}$  is the mass of the chitosan sample used in the titration (g), and 138.17 g/mol is the difference between the molar mass of the modified monomer and the D-glucosamine monomer (299.33 g/mol – 161.16 g/mol).

For *Napht-Chit-1a*, we also know that:

$$\begin{aligned} DDA_{SM} &= 75.1\% \pm 0.2\% & [DDA \text{ for } Chit-1 \text{ calculated with Equation (2)}] \\ DA &= 24.9\% \pm 0.2\% & [100\% - 75.1\% = 24.9\%] \end{aligned}$$

Applying Equation (S17) to our example gives:

$$DDA (\%) = 100 \frac{(1.876 \cdot 10^{-3} \text{ L} \cdot 0.1 \text{ mol/L})((203.19 \text{ g/mol} \cdot 24.9\%) + (299.33 \text{ g/mol} \cdot 75.1\%))}{50.050 \cdot 10^{-3} \text{ g} + (138.17 \text{ g/mol} \cdot 1.876 \cdot 10^{-3} \text{ L} \cdot 0.1 \text{ mol/L})}$$

$$DDA (\%) = 68.00$$

Uncertainties in the  $DDA$  values obtained from Equation (S17) were calculated considering the uncertainties on  $DDA_{SM}$  and  $DA$  using the upper-lower bound method of uncertainty propagation.

To determine the minimum and maximum values, we also kept in mind that, by definition:

$$DA + DDA_{SM} = 100\%$$

For our example above, this gives us:

$$\begin{aligned} DDA_{Max} (\%) \\ = 100 \frac{(1.876 \cdot 10^{-3} \text{ L} \cdot 0.1 \text{ mol/L})((203.19 \text{ g/mol} \cdot (24.9\% - 0.2\%)) + (299.33 \text{ g/mol} \cdot (75.1\% + 0.2\%)))}{50.050 \cdot 10^{-3} \text{ g} + (138.17 \text{ g/mol} \cdot 1.876 \cdot 10^{-3} \text{ L} \cdot 0.1 \text{ mol/L})} \end{aligned}$$

$$DDA_{Max} (\%) = 100 \frac{(1.876 \cdot 10^{-3} \text{ L} \cdot 0.1 \text{ mol/L})((203.19 \text{ g/mol} \cdot 24.7\%) + (299.33 \text{ g/mol} \cdot 75.3\%))}{50.050 \cdot 10^{-3} \text{ g} + (138.17 \text{ g/mol} \cdot 1.876 \cdot 10^{-3} \text{ L} \cdot 0.1 \text{ mol/L})}$$

$$DDA_{Max} (\%) = 68.05$$

$$\begin{aligned} DDA_{Min} (\%) \\ = 100 \frac{(1.876 \cdot 10^{-3} \text{ L} \cdot 0.1 \text{ mol/L})((203.19 \text{ g/mol} \cdot (24.9\% + 0.2\%)) + (299.33 \text{ g/mol} \cdot (75.1\% - 0.2\%)))}{50.050 \cdot 10^{-3} \text{ g} + (138.17 \text{ g/mol} \cdot 1.876 \cdot 10^{-3} \text{ L} \cdot 0.1 \text{ mol/L})} \end{aligned}$$

$$DDA_{Max} (\%) = 100 \frac{(1.876 \cdot 10^{-3} \text{ L} \cdot 0.1 \text{ mol/L})((203.19 \text{ g/mol} \cdot 25.1\%) + (299.33 \text{ g/mol} \cdot 74.9\%))}{50.050 \cdot 10^{-3} \text{ g} + (138.17 \text{ g/mol} \cdot 1.876 \cdot 10^{-3} \text{ L} \cdot 0.1 \text{ mol/L})}$$

$$DDA_{Max} (\%) = 67.95$$

Thus for this sample, the definitive value for  $DDA$  calculated with Equation (S17) is:

$$DDA (\%) = 68.00 \pm 0.05$$

To calculate the *DDA* for the whole triplicate, we calculated the mean. Uncertainties were obtained by considering the maximum and minimum values for each term and calculating the standard deviation.

For example, for *Napht-Chit-1a* (Table S4, Entry 4,5 and 6)

*DDA* (%) = 68.00 ± 0.05 (Table S4, Entry 4)

*DDA* (%) = 68.57 ± 0.05 (Table S4, Entry 5)

*DDA* (%) = 68.68 ± 0.05 (Table S4, Entry 6)

$$\mu = \frac{68.00 + 68.57 + 68.68}{3} = 68.42$$

$$\sigma = \sqrt{\frac{(\mu - 68.00)^2 + (\mu - 67.95)^2 + (\mu - 68.05)^2 + (\mu - 68.57)^2 + (\mu - 68.52)^2 + (\mu - 68.62)^2 + (\mu - 68.68)^2 + (\mu - 68.63)^2 + (\mu - 68.73)^2}{9}} = 0.3$$

Thus, for *Napht-Chit-1a* the final value of *DDA* calculated with Equation (S17) and reported in Table 4 of the manuscript is :

*DDA* (%) = 68.4 ± 0.3

*e. Calculating ΔDDA [Equation (S17)-Equation (S2)] : example*

Let us use *Napht-Chit-1a* again as our example.

As detailed in the preceding sections (5b and 5d), the *DDA* values (means of triplicate ± standard deviation) are as follows:

$$DDA_{\text{Calculated with Equation (S2)}} (\%) = 66.3 \pm 0.5$$

$$DDA_{\text{Calculated with Equation (S17)}} (\%) = 68.4 \pm 0.3$$

Consequently,

$$\begin{aligned} \Delta DDA [\text{Equation (S17)} - \text{Equation (S2)}] (\%) &= DDA_{\text{Calculated with Equation (S17)}} \\ &- DDA_{\text{Calculated with Equation (S2)}} (\%) \\ &= 68.4 - 66.3 = 2.1 \end{aligned}$$

The uncertainty associated with this value corresponds to the sum of the uncertainties on  $DDA_{\text{Calculated with Equation (S17)}}$  and  $DDA_{\text{Calculated with Equation (S2)}}$

Thus, for this sample, the definitive value for  $\Delta DDA$  [Equation (S17)-Equation (S2)] as indicated in Table 4 of the manuscript is:

$$2.1 \pm 0.8$$

f. Complete results

**Table S4** Determination of DDA values for all the chitosan resins involved in this study as determined by potentiometric titration after calculation with Equation (S1), Equation (S2) and Equation (S17): complete detailed results.

| Entry | Chitosan resin | DDA <sub>SM</sub> (%) | DA (%)     | m (mg) | V <sub>1</sub> (mL) | V <sub>2</sub> (mL) | DDA (%) calculated with Equation (S1) |            | DDA (%) calculated with Equation (S2) |            | DDA (%) calculated with Equation (S17) |            |
|-------|----------------|-----------------------|------------|--------|---------------------|---------------------|---------------------------------------|------------|---------------------------------------|------------|--|------------|
|       |                |                       |            |        |                     |                     | triplicate                            | mean       | triplicate                            | mean       | triplicate                             | mean       |
| 1     | Chit-1         | n/a                   | n/a        | 50.269 | 3.866               | 6.066               | 70.53                                 | 70.5 ± 0.2 | 75.11                                 | 75.1 ± 0.2 | n/a                                    | n/a        |
| 2     |                |                       |            | 50.555 | 3.875               | 6.092               | 70.67                                 |            | 75.24                                 |            | n/a                                    |            |
| 3     |                |                       |            | 49.557 | 3.925               | 6.084               | 70.21                                 |            | 74.82                                 |            | n/a                                    |            |
| 4     | Napht-Chit-1a  | 75.1 ± 0.2            | 75.1 ± 0.2 | 50.050 | 4.288               | 6.164               | 60.41                                 | 61.0 ± 0.5 | 65.80                                 | 66.3 ± 0.5 | 68.00 ± 0.05                           | 68.4 ± 0.3 |
| 5     |                |                       |            | 50.579 | 4.260               | 6.180               | 61.18                                 |            | 66.52                                 |            | 68.57 ± 0.05                           |            |
| 6     |                |                       |            | 50.200 | 4.250               | 6.160               | 61.32                                 |            | 66.65                                 |            | 68.68 ± 0.05                           |            |
| 7     | Napht-Chit-1b  | 75.1 ± 0.2            | 75.1 ± 0.2 | 50.917 | 4.467               | 6.212               | 55.23                                 | 55.5 ± 0.5 | 60.87                                 | 61.1 ± 0.5 | 64.05 ± 0.04                           | 64.2 ± 0.3 |
| 8     |                |                       |            | 50.956 | 4.414               | 6.157               | 55.13                                 |            | 60.77                                 |            | 63.97 ± 0.04                           |            |
| 9     |                |                       |            | 50.150 | 4.479               | 6.224               | 56.08                                 |            | 61.68                                 |            | 64.71 ± 0.04                           |            |
| 10    | Napht-Chit-1c  | 75.1 ± 0.2            | 75.1 ± 0.2 | 50.144 | 4.547               | 6.151               | 51.55                                 | 51.5 ± 0.8 | 57.29                                 | 57.3 ± 0.8 | 61.09 ± 0.04                           | 61.1 ± 0.6 |
| 11    |                |                       |            | 50.665 | 4.591               | 6.235               | 52.29                                 |            | 58.02                                 |            | 61.70 ± 0.04                           |            |
| 12    |                |                       |            | 50.285 | 4.589               | 6.171               | 50.70                                 |            | 56.46                                 |            | 60.39 ± 0.04                           |            |
| 13    | Napht-Chit-1d  | 75.1 ± 0.2            | 75.1 ± 0.2 | 50.800 | 4.478               | 6.085               | 50.98                                 | 50.8 ± 0.2 | 56.73                                 | 56.5 ± 0.2 | 60.62 ± 0.04                           | 60.4 ± 0.2 |
| 14    |                |                       |            | 50.127 | 4.673               | 6.252               | 50.77                                 |            | 56.52                                 |            | 60.44 ± 0.04                           |            |
| 15    |                |                       |            | 50.311 | 4.580               | 6.158               | 50.55                                 |            | 56.31                                 |            | 60.26 ± 0.04                           |            |
| 16    | Napht-Chit-1e  | 75.1 ± 0.2            | 75.1 ± 0.2 | 50.864 | 4.668               | 6.205               | 48.70                                 | 48.6 ± 0.5 | 54.48                                 | 54.4 ± 0.5 | 58.71 ± 0.04                           | 58.6 ± 0.4 |
| 17    |                |                       |            | 50.192 | 4.661               | 6.158               | 48.07                                 |            | 53.85                                 |            | 58.17 ± 0.04                           |            |
| 18    |                |                       |            | 50.503 | 4.687               | 6.224               | 49.05                                 |            | 54.83                                 |            | 59.00 ± 0.04                           |            |

**Table S4 (continued)** Determination of *DDA* values for all the chitosan resins involved in this study as determined by potentiometric titration after calculations (S1), Equation (S2) and Equation (S17): complete detailed results. with Equation

| Entry | Chitosan resin       | <i>DDA</i> <sub>SM</sub> (%) | <i>DA</i> (%) | m (g)  | <i>V</i> <sub>1</sub> (mL) | <i>V</i> <sub>2</sub> (mL) | <i>DDA</i> (%) calculated with Equation (S1) |            | <i>DDA</i> (%) calculated with Equation (S2) |            | <i>DDA</i> (%) calculated with Equation (S17) |            |
|-------|----------------------|------------------------------|---------------|--------|----------------------------|----------------------------|--|------------|--|------------|---|------------|
|       |                      |                              |               |        |                            |                            | triplicate                                   | mean       | triplicate                                   | mean       | triplicate                                    | mean       |
| 19    | <i>Chit-2</i>        | n/a                          | n/a           | 49.656 | 3.844                      | 6.073                      | 72.34  | 73.2 ± 0.7 | 76.73  | 77.5 ± 0.7 | n/a   | n/a        |
| 20    |                      |                              |               | 50.18  | 3.878                      | 6.175                      | 73.77  |            | 79.00  |            | n/a   |            |
| 21    |                      |                              |               | 49.774 | 3.819                      | 6.086                      | 73.40  |            | 77.67  |            | n/a   |            |
| 22    | <i>Napht-Chit-2a</i> | 77.5 ± 0.7                   | 22.5 ± 0.7    | 50.35  | 4.242                      | 6.259                      | 64.56  | 63 ± 1     | 69.67  | 68 ± 1     | 71.6 ± 0.2                                    | 70.7 ± 0.8 |
| 23    |                      |                              |               | 50.233 | 4.246                      | 6.219                      | 63.30  |            | 68.50  |            | 70.7 ± 0.2                                    |            |
| 24    |                      |                              |               | 50.2   | 4.228                      | 6.165                      | 62.02  |            | 67.31  |            | 69.8 ± 0.2                                    |            |
| 25    | <i>Napht-Chit-2b</i> | 77.5 ± 0.7                   | 22.5 ± 0.7    | 50.269 | 4.382                      | 6.140                      | 56.36  | 56 ± 2     | 61.95  | 62 ± 2     | 65.5 ± 0.2                                    | 65 ± 1     |
| 26    |                      |                              |               | 50.072 | 4.16                       | 5.840                      | 53.94  |            | 59.62  |            | 63.6 ± 0.1                                    |            |
| 27    |                      |                              |               | 49.75  | 4.397                      | 6.177                      | 57.66  |            | 63.20  |            | 66.5 ± 0.2                                    |            |
| 28    | <i>Napht-Chit-2c</i> | 77.5 ± 0.7                   | 22.5 ± 0.7    | 50.856 | 4.575                      | 6.173                      | 50.64  | 50 ± 1     | 56.40  | 56 ± 1     | 60.8 ± 0.1                                    | 60.6 ± 0.8 |
| 29    |                      |                              |               | 50.415 | 4.653                      | 6.256                      | 51.24  |            | 56.99  |            | 61.3 ± 0.1                                    |            |
| 30    |                      |                              |               | 50.399 | 4.653                      | 6.192                      | 49.21  |            | 54.99  |            | 59.6 ± 0.1                                    |            |
| 31    | <i>Napht-Chit-2d</i> | 77.5 ± 0.7                   | 22.5 ± 0.7    | 50.495 | 4.742                      | 6.159                      | 45.22  | 44.9 ± 0.5 | 51.00  | 50.6 ± 0.5 | 56.1 ± 0.1                                    | 55.8 ± 0.4 |
| 32    |                      |                              |               | 50.976 | 4.763                      | 6.171                      | 44.51  |            | 50.28  |            | 55.5 ± 0.1                                    |            |
| 33    | <i>Napht-Chit-2e</i> | 77.5 ± 0.7                   | 22.5 ± 0.7    | 50.399 | 4.852                      | 6.180                      | 42.46  | 42.6 ± 0.2 | 48.20  | 48.4 ± 0.2 | 53.6 ± 0.1                                    | 53.8 ± 0.2 |
| 34    |                      |                              |               | 50.28  | 4.836                      | 6.170                      | 42.76  |            | 48.50  |            | 53.9 ± 0.1                                    |            |

**Table S4 (continued)** Determination of DDA values for all the chitosan resins involved in this study, as determined by potentiometric titration after calculations with Equation (S1), Equation (S2) and Equation (S17): complete detailed results.

| Entry | Chitosan resin | DDA <sub>SM</sub> (%) | DA (%)     | m (g)  | V <sub>1</sub> (mL) | V <sub>2</sub> (mL) | DDA (%) calculated with Equation (S1) |            | DDA (%) calculated with Equation (S2) |            | DDA (%) calculated with Equation (S17) |            |
|-------|----------------|-----------------------|------------|--------|---------------------|---------------------|---------------------------------------|------------|---------------------------------------|------------|--|------------|
|       |                |                       |            |        |                     |                     | triplicate                            | mean       | triplicate                            | mean       | triplicate                             | mean       |
| 35    | Chit-3         | n/a                   | n/a        | 50.243 | 4.049               | 6.051               | 64.22                                 | 64.4 ± 0.2 | 69.35                                 | 69.5 ± 0.2 | n/a                                    | n/a        |
| 36    |                |                       |            | 50.162 | 4.062               | 6.062               | 64.26                                 |            | 69.39                                 |            | n/a                                    |            |
| 37    |                |                       |            | 50.076 | 4.046               | 6.053               | 64.59                                 |            | 69.7                                  |            | n/a                                    |            |
| 38    | Napht-Chit-3a  | 69.5 ± 0.2            | 30.5 ± 0.2 | 50.312 | 4.666               | 6.148               | 47.47                                 | 47 ± 1     | 53.26                                 | 53 ± 1     | 56.53 ± 0.04                           | 56.2 ± 0.7 |
| 39    |                |                       |            | 50.163 | 4.660               | 6.152               | 47.93                                 |            | 53.72                                 |            | 56.92 ± 0.04                           |            |
| 40    |                |                       |            | 50.524 | 4.735               | 6.178               | 46.03                                 |            | 51.81                                 |            | 55.29 ± 0.04                           |            |
| 41    | Napht-Chit-3b  | 69.5 ± 0.2            | 30.5 ± 0.2 | 50.282 | 4.769               | 6.114               | 43.11                                 | 43.0 ± 0.2 | 48.86                                 | 48.8 ± 0.2 | 52.73 ± 0.04                           | 52.6 ± 0.1 |
| 42    |                |                       |            | 50.449 | 4.813               | 6.154               | 42.84                                 |            | 48.58                                 |            | 52.49 ± 0.04                           |            |
| 43    |                |                       |            | 50.623 | 4.803               | 6.157               | 43.1                                  |            | 48.85                                 |            | 52.73 ± 0.04                           |            |
| 44    | Napht-Chit-3c  | 69.5 ± 0.2            | 30.5 ± 0.2 | 50.635 | 4.840               | 6.157               | 41.92                                 | 40 ± 1     | 47.64                                 | 46 ± 1     | 51.66 ± 0.04                           | 50 ± 1     |
| 45    |                |                       |            | 50.012 | 4.920               | 6.159               | 39.93                                 |            | 45.59                                 |            | 49.83 ± 0.03                           |            |
| 46    |                |                       |            | 50.072 | 4.934               | 6.163               | 39.56                                 |            | 45.21                                 |            | 49.49 ± 0.03                           |            |
| 47    | Napht-Chit-3d  | 69.5 ± 0.2            | 30.5 ± 0.2 | 50.431 | 3.4956              | 6.155               | 38.32                                 | 38.2 ± 0.5 | 43.92                                 | 43.8 ± 0.5 | 48.32 ± 0.03                           | 48.2 ± 0.4 |
| 48    |                |                       |            | 50.077 | 4.960               | 6.159               | 38.59                                 |            | 44.2                                  |            | 48.58 ± 0.03                           |            |
| 49    |                |                       |            | 50.788 | 4.962               | 6.150               | 37.7                                  |            | 43.27                                 |            | 47.73 ± 0.03                           |            |
| 50    | Napht-Chit-3e  | 69.5 ± 0.2            | 30.5 ± 0.2 | 50.894 | 5.045               | 6.151               | 35.02                                 | 34.8 ± 0.5 | 40.46                                 | 40.2 ± 0.5 | 45.13 ± 0.03                           | 44.9 ± 0.4 |
| 51    |                |                       |            | 50.681 | 5.075               | 6.152               | 34.25                                 |            | 39.64                                 |            | 44.35 ± 0.03                           |            |
| 52    |                |                       |            | 50.067 | 5.066               | 6.157               | 35.12                                 |            | 40.56                                 |            | 45.22 ± 0.03                           |            |