Supporting Information

"Atomistic Simulations of Chitosan as Possible Carrier System for miRNA Transport"

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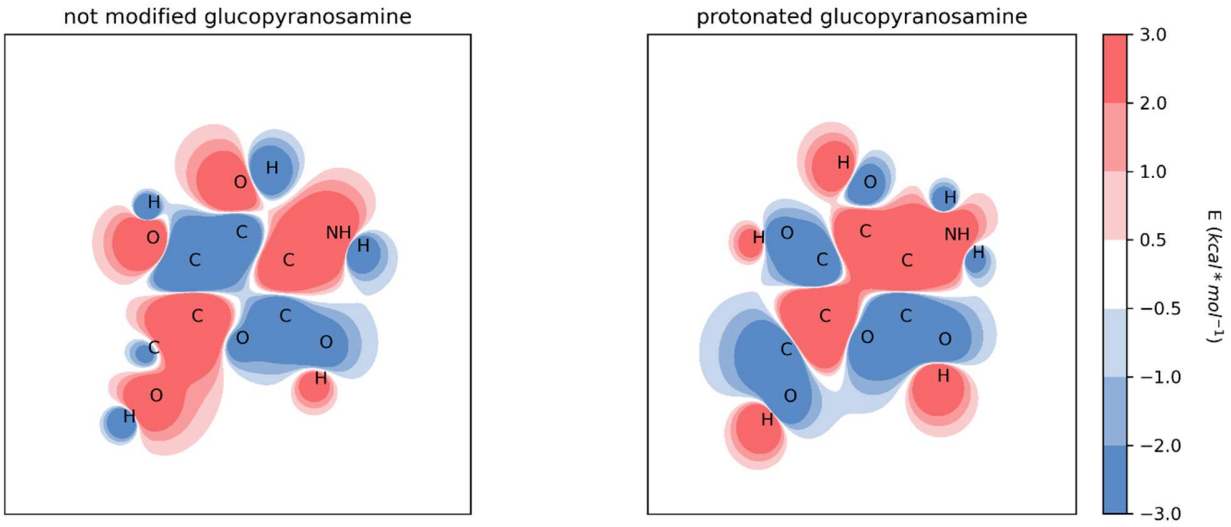
Table S1: Derived resp charges of native and protonated β-D-glucoseamine in comparison to the GLYCAM06[1] force field.

Native residue				Protonated residue			
Atom name	**Glycam charge[1]**	**Our charge**	**Difference**	**Atom name**	**Glycam charge[1]**	**Our charge**	**Difference**
C1	0.422	0.296	0.126	C1	0.458	0.328	0.130
C2	0.374	0.463	-0.089	C2	0.267	0.376	-0.109
C3	0.223	0.132	0.091	C3	0.123	0.175	-0.052
C4	0.279	0.142	0.137	C4	0.326	0.197	0.129
C5	0.247	0.388	-0.141	C5	0.151	0.360	-0.209
C6	0.279	0.220	0.059	C6	0.330	0.201	0.129
O5	-0.528	-0.517	-0.011	O5	-0.407	-0.471	0.064
O3	-0.683	-0.621	-0.062	O3	-0.641	-0.719	0.078
O4	-0.698	-0.690	-0.008	O4	-0.663	-0.693	0.030
O6	-0.680	-0.719	0.039	O6	-0.674	-0.706	0.032
N2	-1.090	-0.956	-0.134	N2	-0.140	-0.052	-0.088
H2A	0.392	0.329	0.063	H1N	0.247	0.220	0.027
H2B	0.392	0.329	0.063	H2N	0.247	0.220	0.027
H3O	0.421	0.353	0.068	H3N	0.247	0.220	0.027
H6O	0.414	0.422	-0.008	H3O	0.448	0.462	-0.014
H6A	0.000	0.000	0	H6O	0.436	0.450	-0.014
H6B	0.000	0.000	0	H61	0.000	0.000	0.000
H1	0.000	0.000	0	H62	0.000	0.000	0.000
H2	0.000	0.000	0	H1	0.000	0.000	0.000
H3	0.000	0.000	0	H2	0.000	0.000	0.000
H4	0.000	0.000	0	H3	0.000	0.000	0.000
H5	0.000	0.000	0	H4	0.000	0.000	0.000
				H5	0.000	0.000	0.000

Figure S1: Difference of the potential surface energy between our parameter set for β-D-glucoseamine in comparison to the GLYCAM06[1] force field.



Files S2: Prepi files for the C1 terminal chitosan residues (0YB, 0Yn, 0YnP), the central chitosan residues (4YB, 4Yn, 4YnP) and the C4 terminal chitosan residues(rYB, rYn, rYnP) for the acetylated, the native neutral and protonated residues respectively. The residue naming scheme according the figure 1 in the main manuscript.

```
----------0YB.prepi----------
    0    0    2

This is a remark line
tpt.res
0YB   INT  0
CORRECT     OMIT DU   BEG
  0.0000
   1  DUMM  DU    M    0  -1  -2     0.000      .0        .0      .00000
   2  DUMM  DU    M    1   0  -1     1.449      .0        .0      .00000
   3  DUMM  DU    M    2   1   0     1.523   111.21       .0      .00000
   4  O3    oh    M    3   2   1     1.540   111.208  -180.000 -0.631803
   5  H3O   ho    E    4   3   2     0.954   162.052   -99.590  0.377081
   6  C3    c3    M    4   3   2     1.394    64.784   -31.976  0.150957
   7  H3    h1    E    6   4   3     1.087   110.550  -110.635  0.000000
   8  C4    c3    3    6   4   3     1.529   104.910     5.813  0.187756
   9  H4    h1    E    8   6   4     1.088   107.686    56.207  0.000000
  10  O4    oh    S    8   6   4     1.397   109.700   -64.087 -0.700702
  11  H4O   ho    E   10   8   6     0.950   107.530    49.325  0.423393
  12  C5    c3    3    8   6   4     1.522   111.531   175.062  0.430822
  13  C6    c3    3   12   8   6     1.513   113.075  -175.992  0.199034
  14  H6A   h1    E   13  12   8     1.084   108.626   -51.365  0.000000
  15  O6    oh    S   13  12   8     1.402   108.110  -172.244 -0.732769
  16  H6O   ho    E   15  13  12     0.947   109.448  -179.300  0.436268
  17  H6B   h1    E   13  12   8     1.087   108.826    66.916  0.000000
  18  H5    h1    E   12   8   6     1.087   109.684    63.116  0.000000
  19  O5    os    E   12   8   6     1.409   107.696   -56.613 -0.478494
  20  C2    c3    M    6   4   3     1.534   113.616   125.917  0.258114
  21  H2    h1    E   20   6   4     1.085   108.227   -51.080  0.000000
  22  N2    n     B   20   6   4     1.461   116.584    72.387 -0.269827
  23  H1N   hn    E   22  20   6     0.996   112.408   166.186  0.190457
  24  C1A   c     B   22  20   6     1.344   130.905   -21.917  0.291308
  25  O1A   o     E   24  22  20     1.210   125.134     4.255 -0.499628
  26  C2A   c3    3   24  22  20     1.514   115.202  -175.498  0.113987
  27  H1A   hc    E   26  24  22     1.084   108.320   105.738  0.000000
  28  H2A   hc    E   26  24  22     1.081   108.504  -137.421  0.000000
  29  H3A   hc    E   26  24  22     1.084   113.575   -15.312  0.000000
  30  C1    c3    M   20   6   4     1.529   108.729  -167.385  0.254048
  31  H1    h2    E   30  20   6     1.091   109.407   -65.203  0.000000


LOOP
   C1   O5

IMPROPER
  C1A   C2   N2  H1N
  C2A   N2  C1A  O1A
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```
DONE
STOP


----------0Yn.prepi----------
    0    0    2

This is a remark line
tpt.res
0Yn   INT  0
CORRECT     OMIT DU   BEG
  0.0000
   1  DUMM  DU    M    0  -1  -2     0.000      .0        .0      .00000
   2  DUMM  DU    M    1   0  -1     1.449      .0        .0      .00000
   3  DUMM  DU    M    2   1   0     1.523   111.21       .0      .00000
   4  O6    oh    M    3   2   1     1.540   111.208  -180.000 -0.719483
   5  H6O   ho    E    4   3   2     0.946    20.367    92.437  0.422495
   6  C6    c3    M    4   3   2     1.402   122.432   146.861  0.220377
   7  H6A   h1    E    6   4   3     1.084   111.175    44.555  0.000000
   8  H6B   h1    E    6   4   3     1.087   111.168   -76.790  0.000000
   9  C5    c3    M    6   4   3     1.513   108.175   163.853  0.387804
  10  H5    h1    E    9   6   4     1.088   108.135   -49.975  0.000000
  11  C4    c3    3    9   6   4     1.527   112.928  -170.917  0.142092
  12  C3    c3    3   11   9   6     1.520   109.513  -175.614  0.132312
  13  C2    c3    B   12  11   9     1.524   111.332    53.262  0.463151
  14  N2    n3    B   13  12  11     1.453   108.964  -179.090 -0.956336
  15  H2A   hn    E   14  13  12     1.004   110.983    72.784  0.328761
  16  H2B   hn    E   14  13  12     1.002   110.402  -168.808  0.328761
  17  H2    h1    E   13  12  11     1.084   108.536    63.806  0.000000
  18  O3    oh    S   12  11   9     1.399   107.770   175.875 -0.620677
  19  H3O   ho    E   18  12  11     0.951   107.755  -166.558  0.353212
  20  H3    h1    E   12  11   9     1.092   107.614   -66.064  0.000000
  21  H4    h1    E   11   9   6     1.088   108.954   -57.429  0.000000
  22  O4    oh    S   11   9   6     1.399   108.746    63.165 -0.689808
  23  H4O   ho    E   22  11   9     0.950   108.140   172.245  0.427899
  24  O5    os    M    9   6   4     1.409   107.914    69.033 -0.516587
  25  C1    c3    M   24   9   6     1.393   114.889  -174.100  0.296028
  26  H1    h2    E   25  24   9     1.093   108.818    57.852  0.000000


LOOP
   C1   C2

IMPROPER

DONE
STOP
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```
----------0YnP.prepi----------
    0    0    2

This is a remark line
tpt.res
0YnP   INT  0
CORRECT     OMIT DU   BEG
  0.0000
   1  DUMM  DU    M    0  -1  -2     0.000      .0        .0      .00000
   2  DUMM  DU    M    1   0  -1     1.449      .0        .0      .00000
   3  DUMM  DU    M    2   1   0     1.523   111.21       .0      .00000
   4  O6    oh    M    3   2   1     1.540   111.208  -180.000 -0.706121
   5  H6O   ho    E    4   3   2     0.949    21.429    78.009  0.449660
   6  C6    c3    M    4   3   2     1.392   119.908   146.666  0.200899
   7  H6A   h1    E    6   4   3     1.087   111.226    44.073  0.000000
   8  H6B   h1    E    6   4   3     1.087   111.934   -77.616  0.000000
   9  C5    c3    M    6   4   3     1.515   107.066   162.921  0.360334
  10  H5    h1    E    9   6   4     1.087   108.038   -49.114  0.000000
  11  C4    c3    3    9   6   4     1.536   114.215  -170.786  0.197416
  12  C3    c3    3   11   9   6     1.527   109.221  -174.905  0.174844
  13  C2    c3    B   12  11   9     1.514   109.007    53.099  0.375617
  14  N2    n4    3   13  12  11     1.502   109.983  -179.380 -0.052350
  15  H1N   hn    E   14  13  12     1.012   110.195  -176.561  0.219625
  16  H2N   hn    E   14  13  12     1.013   109.370   -56.281  0.219625
  17  H3N   hn    E   14  13  12     1.011   112.633    63.175  0.219625
  18  H2    hx    E   13  12  11     1.080   110.573    64.467  0.000000
  19  O3    oh    S   12  11   9     1.391   113.935   171.896 -0.719303
  20  H3O   ho    E   19  12  11     0.952   109.800    56.136  0.461521
  21  H3    h1    E   12  11   9     1.090   107.190   -65.849  0.000000
  22  H4    h1    E   11   9   6     1.087   109.693   -55.999  0.000000
  23  O4    oh    S   11   9   6     1.396   112.944    68.815 -0.693247
  24  H4O   ho    E   23  11   9     0.948   111.817   -86.120  0.434848
  25  O5    os    M    9   6   4     1.419   107.218    69.137 -0.471455
  26  C1    c3    M   25   9   6     1.376   114.897  -171.431  0.328461
  27  H1    h2    E   26  25   9     1.092   109.965    55.053  0.000000


LOOP
   C1   C2

IMPROPER

DONE
STOP
```

```
----------4YB.prepi----------
    0    0    2

This is a remark line
pet.res
4YB   INT  0
CORRECT     OMIT DU   BEG
  0.0000
   1  DUMM  DU    M    0  -1  -2     0.000      .0        .0      .00000
   2  DUMM  DU    M    1   0  -1     1.449      .0        .0      .00000
   3  DUMM  DU    M    2   1   0     1.523   111.21       .0      .00000
   4  O4    os    M    3   2   1     1.540   111.208  -180.000 -0.654074
   5  C4    c3    M    4   3   2     1.397   109.490    25.942  0.200940
   6  H4    h1    E    5   4   3     1.088   110.490    73.801  0.000000
   7  C5    c3    3    5   4   3     1.522   108.988   -45.249  0.461073
   8  C6    c3    3    7   5   4     1.513   113.075    62.743  0.213009
   9  H6A   h1    E    8   7   5     1.084   108.626   -51.365  0.000000
  10  O6    oh    S    8   7   5     1.402   108.110  -172.244 -0.684007
  11  H6O   ho    E   10   8   7     0.947   109.448  -179.300  0.466902
  12  H6B   h1    E    8   7   5     1.087   108.826    66.916  0.000000
  13  H5    h1    E    7   5   4     1.087   109.684   -58.150  0.000000
  14  O5    os    E    7   5   4     1.409   107.696  -177.879 -0.446653
  15  C3    c3    M    5   4   3     1.529   109.700  -167.625  0.161557
  16  O3    oh    S   15   5   4     1.394   104.910   -64.087 -0.589760
  17  H3O   ho    E   16  15   5     0.954   107.405   168.439  0.403558
  18  H3    h1    E   15   5   4     1.087   108.221    53.952  0.000000
  19  C2    c3    M   15   5   4     1.534   109.939   173.393  0.276238
  20  H2    h1    E   19  15   5     1.085   108.227    66.135  0.000000
  21  N2    n     B   19  15   5     1.461   116.584  -170.398 -0.251872
  22  H1N   hn    E   21  19  15     0.996   112.408   166.186  0.203831
  23  C1A   c     B   21  19  15     1.344   130.905   -21.917  0.311762
  24  O1A   o     E   23  21  19     1.210   125.134     4.255 -0.466380
  25  C2A   c3    3   23  21  19     1.514   115.202  -175.498  0.121990
  26  H1A   hc    E   25  23  21     1.084   108.320   105.738  0.000000
  27  H2A   hc    E   25  23  21     1.081   108.504  -137.421  0.000000
  28  H3A   hc    E   25  23  21     1.084   113.575   -15.312  0.000000
  29  C1    c3    M   19  15   5     1.529   108.729   -50.170  0.271886
  30  H1    h2    E   29  19  15     1.091   109.407   -65.203  0.000000


LOOP
   C1   O5

IMPROPER
  C1A   C2   N2  H1N
  C2A   N2  C1A  O1A

DONE
STOP
```

```
----------4Yn.prepi----------
    0    0    2

This is a remark line
pet.res
4Yn   INT  0
CORRECT     OMIT DU   BEG
  0.0000
   1  DUMM  DU    M    0  -1  -2     0.000      .0        .0      .00000
   2  DUMM  DU    M    1   0  -1     1.449      .0        .0      .00000
   3  DUMM  DU    M    2   1   0     1.523   111.21       .0      .00000
   4  O4    os    M    3   2   1     1.540   111.208  -180.000 -0.646232
   5  C4    c3    M    4   3   2     1.399   112.442    23.571  0.151640
   6  C3    c3    3    5   4   3     1.520   110.813  -158.683  0.141202
   7  C2    c3    B    6   5   4     1.524   111.332   173.226  0.494272
   8  N2    n3    B    7   6   5     1.453   108.964  -179.090 -0.895923
   9  H2A   hn    E    8   7   6     1.004   110.983    72.784  0.350851
  10  H2B   hn    E    8   7   6     1.002   110.402  -168.808  0.350851
  11  H2    h1    E    7   6   5     1.084   108.536    63.806  0.000000
  12  O3    oh    S    6   5   4     1.399   107.770   -64.160 -0.581469
  13  H3O   ho    E   12   6   5     0.951   107.755  -166.558  0.376946
  14  H3    h1    E    6   5   4     1.092   107.614    53.901  0.000000
  15  H4    h1    E    5   4   3     1.088   110.576    81.327  0.000000
  16  C5    c3    M    5   4   3     1.527   108.746   -38.262  0.413862
  17  C6    c3    3   16   5   4     1.513   112.928    63.165  0.235185
  18  O6    oh    S   17  16   5     1.402   108.175  -170.917 -0.674033
  19  H6O   ho    E   18  17  16     0.946   109.382  -178.685  0.450884
  20  H6A   h1    E   17  16   5     1.084   108.716   -50.078  0.000000
  21  H6B   h1    E   17  16   5     1.087   108.767    68.222  0.000000
  22  H5    h1    E   16   5   4     1.088   109.194   -57.173  0.000000
  23  O5    os    M   16   5   4     1.409   108.603  -177.181 -0.483954
  24  C1    c3    M   23  16   5     1.393   114.889    63.162  0.315919
  25  H1    h2    E   24  23  16     1.093   108.818    57.852  0.000000


LOOP
   C1   C2

IMPROPER

DONE
STOP
```

```
----------4YnP.prepi----------
    0    0    2

This is a remark line
pet.res
4YnP   INT  0
CORRECT     OMIT DU   BEG
  0.0000
   1  DUMM  DU    M    0  -1  -2     0.000      .0        .0      .00000
   2  DUMM  DU    M    1   0  -1     1.449      .0        .0      .00000
   3  DUMM  DU    M    2   1   0     1.523   111.21       .0      .00000
   4  O4    os    M    3   2   1     1.540   111.208  -180.000 -0.643533
   5  C4    c3    M    4   3   2     1.396   106.816    25.051  0.212516
   6  C3    c3    3    5   4   3     1.527   104.872  -159.296  0.188218
   7  C2    c3    B    6   5   4     1.514   109.007   174.414  0.404348
   8  N2    n4    3    7   6   5     1.502   109.983  -179.380 -0.048596
   9  H1N   hn    E    8   7   6     1.012   110.195  -176.561  0.236424
  10  H2N   hn    E    8   7   6     1.013   109.370   -56.281  0.236424
  11  H3N   hn    E    8   7   6     1.011   112.633    63.175  0.236424
  12  H2    hx    E    7   6   5     1.080   110.573    64.467  0.000000
  13  O3    oh    S    6   5   4     1.391   113.935   -66.789 -0.667721
  14  H3O   ho    E   13   6   5     0.952   109.800    56.136  0.496823
  15  H3    h1    E    6   5   4     1.090   107.190    55.467  0.000000
  16  H4    h1    E    5   4   3     1.087   111.323    83.463  0.000000
  17  C5    c3    M    5   4   3     1.536   112.944   -40.459  0.387896
  18  C6    c3    3   17   5   4     1.515   114.215    68.815  0.216266
  19  O6    oh    S   18  17   5     1.392   107.066  -170.786 -0.655484
  20  H6O   ho    E   19  18  17     0.949   110.419  -175.787  0.484055
  21  H61   h1    E   18  17   5     1.087   108.888   -50.434  0.000000
  22  H62   h1    E   18  17   5     1.087   109.059    67.918  0.000000
  23  H5    h1    E   17   5   4     1.087   109.166   -52.234  0.000000
  24  O5    os    M   17   5   4     1.419   108.371  -171.755 -0.437646
  25  C1    c3    M   24  17   5     1.376   114.897    64.832  0.353585
  26  H1    h2    E   25  24  17     1.092   109.965    55.053  0.000000


LOOP
   C1   C2

IMPROPER

DONE
STOP
```

```
----------rYB.prepi----------
    0    0    2

This is a remark line
hpt.res
rYB   INT  0
CORRECT     OMIT DU   BEG
  0.0000
   1  DUMM  DU    M    0  -1  -2     0.000      .0        .0      .00000
   2  DUMM  DU    M    1   0  -1     1.449      .0        .0      .00000
   3  DUMM  DU    M    2   1   0     1.523   111.21       .0      .00000
   4  O4    os    M    3   2   1     1.540   111.208  -180.000 -0.641637
   5  C4    c3    M    4   3   2     1.397   109.490    25.942  0.204456
   6  H4    h1    E    5   4   3     1.088   110.490    73.801  0.000000
   7  C5    c3    3    5   4   3     1.522   108.988   -45.249  0.469142
   8  C6    c3    3    7   5   4     1.513   113.075    62.743  0.216737
   9  H6A   h1    E    8   7   5     1.084   108.626   -51.365  0.000000
  10  O6    oh    S    8   7   5     1.402   108.110  -172.244 -0.671000
  11  H6O   ho    E   10   8   7     0.947   109.448  -179.300  0.475073
  12  H6B   h1    E    8   7   5     1.087   108.826    66.916  0.000000
  13  H5    h1    E    7   5   4     1.087   109.684   -58.150  0.000000
  14  O5    os    S    7   5   4     1.409   107.696  -177.879 -0.438160
  15  C1    c3    3   14   7   5     1.384   113.825    63.520  0.276644
  16  O1    oh    S   15  14   7     1.381   108.557   176.675 -0.596614
  17  H1O   ho    E   16  15  14     0.950   108.802   -51.206  0.483678
  18  H1    h2    E   15  14   7     1.091   109.347    56.230  0.000000
  19  C2    c3    B   15  14   7     1.529   111.260   -64.734  0.281072
  20  H2    h1    E   19  15  14     1.085   107.349   -61.143  0.000000
  21  N2    n     B   19  15  14     1.461   106.421  -177.937 -0.247082
  22  H1N   hn    E   21  19  15     0.996   112.408    44.734  0.207398
  23  C1A   c     B   21  19  15     1.344   130.905  -143.370  0.317218
  24  O1A   o     E   23  21  19     1.210   125.134     4.255 -0.457512
  25  C2A   c3    3   23  21  19     1.514   115.202  -175.498  0.124125
  26  H1A   hc    E   25  23  21     1.084   108.320   105.738  0.000000
  27  H2A   hc    E   25  23  21     1.081   108.504  -137.421  0.000000
  28  H3A   hc    E   25  23  21     1.084   113.575   -15.312  0.000000
  29  C3    c3    M    5   4   3     1.529   109.700  -167.625  0.164385
  30  H3    h1    E   29   5   4     1.087   108.221    53.952  0.000000
  31  O3    oh    M   29   5   4     1.394   104.910   -64.087 -0.578546
  32  H3O   ho    E   31  29   5     0.954   107.405   168.439  0.410621


LOOP
   C3   C2

IMPROPER
  C1A   C2   N2  H1N
  C2A   N2  C1A  O1A

DONE
STOP
```

```
----------rYn.prepi----------
    0    0    2

This is a remark line
hpt.res
rYn   INT  0
CORRECT     OMIT DU   BEG
  0.0000
   1  DUMM  DU    M    0  -1  -2     0.000      .0        .0      .00000
   2  DUMM  DU    M    1   0  -1     1.449      .0        .0      .00000
   3  DUMM  DU    M    2   1   0     1.523   111.21       .0      .00000
   4  O4    os    M    3   2   1     1.540   111.208  -180.000 -0.630841
   5  C4    c3    M    4   3   2     1.399   112.442    23.571  0.155013
   6  C3    c3    3    5   4   3     1.520   110.813  -158.683  0.144343
   7  C2    c3    3    6   5   4     1.524   111.332   173.226  0.505265
   8  C1    c3    3    7   6   5     1.523   109.029   -52.122  0.322945
   9  O5    os    E    8   7   6     1.393   110.133    54.879 -0.472428
  10  O1    oh    S    8   7   6     1.377   108.629   173.575 -0.639188
  11  H1O   ho    E   10   8   7     0.949   108.729  -170.356  0.488045
  12  H1    h2    E    8   7   6     1.093   110.254   -65.219  0.000000
  13  N2    n3    B    7   6   5     1.453   108.964  -179.090 -0.874585
  14  H2A   hn    E   13   7   6     1.004   110.983    72.784  0.358654
  15  H2B   hn    E   13   7   6     1.002   110.402  -168.808  0.358654
  16  H2    h1    E    7   6   5     1.084   108.536    63.806  0.000000
  17  O3    oh    S    6   5   4     1.399   107.770   -64.160 -0.567620
  18  H3O   ho    E   17   6   5     0.951   107.755  -166.558  0.385329
  19  H3    h1    E    6   5   4     1.092   107.614    53.901  0.000000
  20  H4    h1    E    5   4   3     1.088   110.576    81.327  0.000000
  21  C5    c3    M    5   4   3     1.527   108.746   -38.262  0.423067
  22  H5    h1    E   21   5   4     1.088   109.194   -57.173  0.000000
  23  C6    c3    M   21   5   4     1.513   112.928    63.165  0.240415
  24  H6A   h1    E   23  21   5     1.084   108.716   -50.078  0.000000
  25  H6B   h1    E   23  21   5     1.087   108.767    68.222  0.000000
  26  O6    oh    M   23  21   5     1.402   108.175  -170.917 -0.657979
  27  H6O   ho    E   26  23  21     0.946   109.382  -178.685  0.460911


LOOP
   C5   O5

IMPROPER

DONE
STOP
```

```
----------rYnP.prepi----------
    0    0    2

This is a remark line
hpt.res
rYnP   INT  0
CORRECT     OMIT DU   BEG
  0.0000
   1  DUMM  DU    M    0  -1  -2     0.000      .0        .0      .00000
   2  DUMM  DU    M    1   0  -1     1.449      .0        .0      .00000
   3  DUMM  DU    M    2   1   0     1.523   111.21       .0      .00000
   4  O4    os    M    3   2   1     1.540   111.208  -180.000 -0.629014
   5  C4    c3    M    4   3   2     1.396   106.816    25.051  0.216927
   6  C3    c3    3    5   4   3     1.527   104.872  -159.296  0.192124
   7  C2    c3    3    6   5   4     1.514   109.007   174.414  0.412739
   8  C1    c3    3    7   6   5     1.521   110.877   -55.532  0.360923
   9  O5    os    E    8   7   6     1.376   106.740    59.375 -0.427772
  10  O1    oh    S    8   7   6     1.370   106.554   178.441 -0.663383
  11  H1O   ho    E   10   8   7     0.952   110.731  -170.612  0.536381
  12  H1    h2    E    8   7   6     1.092   111.043   -60.477  0.000000
  13  N2    n4    3    7   6   5     1.502   109.983  -179.380 -0.047500
  14  H1N   hn    E   13   7   6     1.012   110.195  -176.561  0.241331
  15  H2N   hn    E   13   7   6     1.013   109.370   -56.281  0.241331
  16  H3N   hn    E   13   7   6     1.011   112.633    63.175  0.241331
  17  H2    hx    E    7   6   5     1.080   110.573    64.467  0.000000
  18  O3    oh    S    6   5   4     1.391   113.935   -66.789 -0.652655
  19  H3O   ho    E   18   6   5     0.952   109.800    56.136  0.507133
  20  H3    h1    E    6   5   4     1.090   107.190    55.467  0.000000
  21  H4    h1    E    5   4   3     1.087   111.323    83.463  0.000000
  22  C5    c3    M    5   4   3     1.536   112.944   -40.459  0.395946
  23  H5    h1    E   22   5   4     1.087   109.166   -52.234  0.000000
  24  C6    c3    M   22   5   4     1.515   114.215    68.815  0.220754
  25  H6A   h1    E   24  22   5     1.087   108.888   -50.434  0.000000
  26  H6B   h1    E   24  22   5     1.087   109.059    67.918  0.000000
  27  O6    oh    M   24  22   5     1.392   107.066  -170.786 -0.640695
  28  H6O   ho    E   27  24  22     0.949   110.419  -175.787  0.494100


LOOP
   C5   O5

IMPROPER

DONE
STOP
```

Figure S3: (left) development of the free energy profiles along the puckering angle Θ. The global minimum at Θ=10° describes the $^4C_1$ conformation, a local minimum at 170° represents the $^1C_4$ conformation. A second local minima at Θ= 90° is clearly visible. **(right)** The energy barriers between $^4C_1$ and the secondary minimum as well as the $^1C_4$ conformation are converged to values of 33 kJ and 75 kJ respectively within the simulation time.

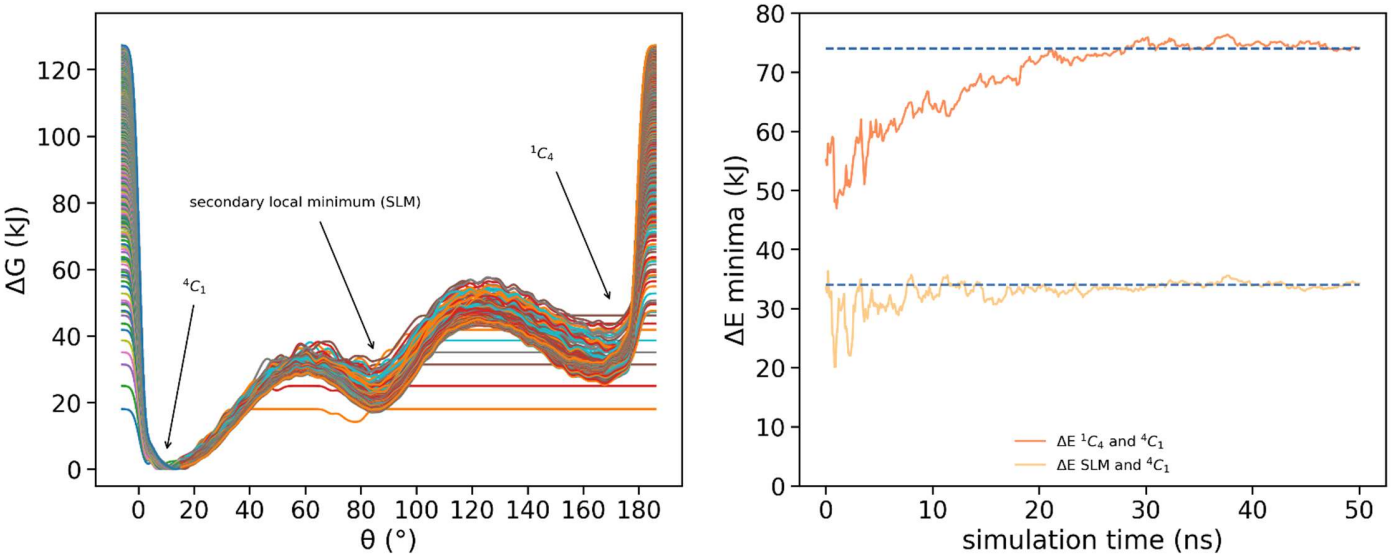

Table S4: Chitosan replica exchange simulations are performed with PLUMED v 2.4.3 [2] with 24 replicas from 300 to 500 K for 100 ns. The propability (%/100) and round table times (RTT) (ns) are listed for the 24 chitosan replicas

Replica	1	2	3	4	5	6	7	8	9	10	11	12
Probability	0.38	0.38	0.39	0.40	0.40	0.41	0.41	0.42	0.42	0.43	0.43	0.44
RTT (ns)	1.1	1.3	1.1	1.1	1.1	1.2	1.4	1.0	1.2	1.1	1.2	1.3

Replica	13	14	15	16	17	18	19	20	21	22	23	24
Probability	0.44	0.44	0.45	0.46	0.46	0.46	0.47	0.47	0.47	0.48	0.48	
RTT (ns)	1.1	1.1	1.5	1.0	1.6	1.3	1.4	1.2	1.3	1.9	1.2	1.2

Figure S4: exchange map of the replica exchange simulation of chitosan with 24 replicas from 300 to 500 K for 100 ns.

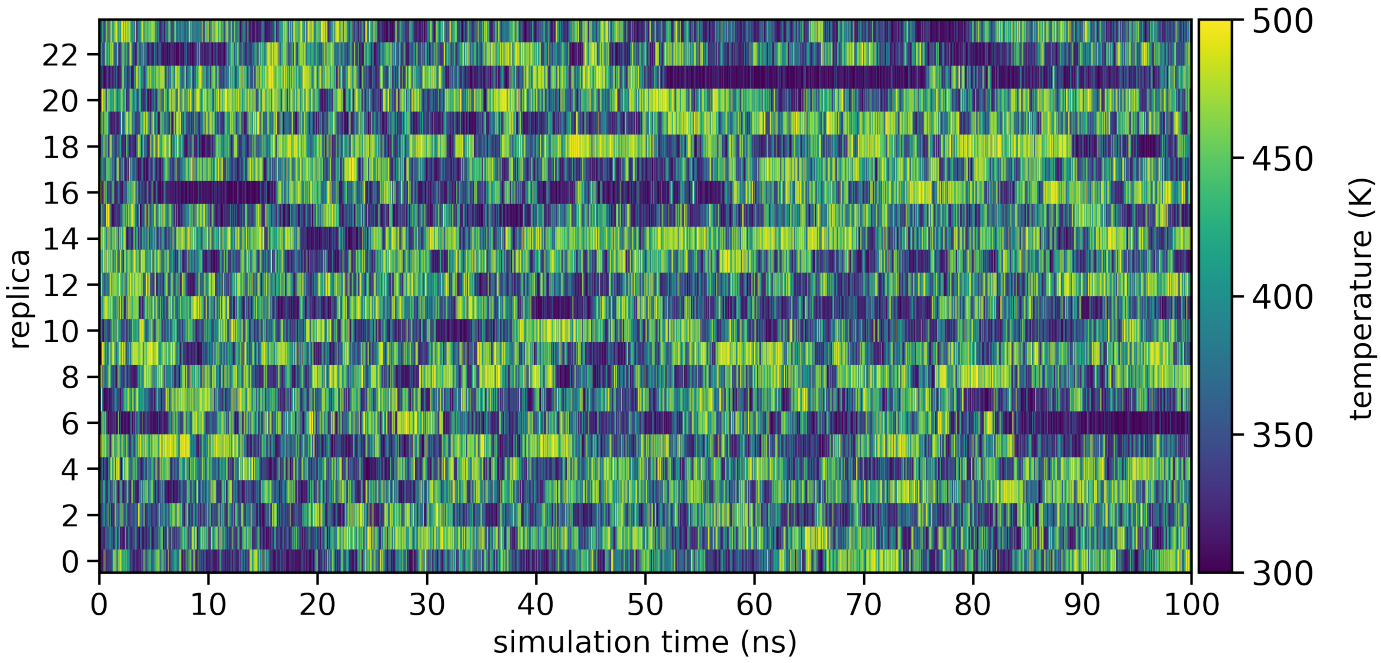

Table S5: Chitin replica exchange simulations are performed with PLUMED v 2.4.3 [2] with 24 replicas from 300 to 500 K for 100 ns. The propability (%/100) and round table times (RTT) (ns) are listed for the 24 chitin replicas

Replica	1	2	3	4	5	6	7	8	9	10	11	12
Probability	0.49	0.49	0.49	0.50	0.51	0.50	0.52	0.52	0.51	0.52	0.52	0.53
RTT (ns)	6.9	5.9	8.0	12.5	5.7	5.6	11.2	12.6	14.3	6.1	15.4	9.1

Replica	13	14	15	16	17	18	19	20	21	22	23	24
Probability	0.53	0.54	0.54	0.54	0.53	0.54	0.53	0.53	0.53	0.51	0.53	
RTT (ns)	6.3	11.2	6.5	28.7	12.5	6.7	6.9	11.5	8.0	10.0	8.4	33.5

Figure S5: exchange map of the replica exchange simulation of chitin with 24 replicas from 300 to 500 K for 100 ns.