Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Molecular interactions of DNA with transfectants: a study based on infrared spectroscopy and quantum chemistry in aid to fluorescence spectroscopy and dynamic light scattering analyses

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Content

1. Cartesian coordinates of the molecular models described in the text.

2. Figure SI.1, reporting the simulated anti-symmetric PO stretching IR signal of all models.

3. Vibrational analysis of the molecular models considered in this work (included text files: dna-ca-gt.txt, model-a.txt, model-b.txt, model-W1.txt, model-W2.txt, model-W3.txt).

1. Cartesian coordinates of the molecular models described in the text

DNA-CA/GT
fully optimized ad B97D/6- 31+G(d,p) level, xyz format

```
125
DNA CA/GT
 H -8.511915 -5.079890 -0.023321
 O -8.120562 -4.196873  0.028353
 C -8.845435 -3.460359  1.035372
 H -8.797757 -3.990179  2.004526
 H -9.906278 -3.344006  0.739654
 C -8.251498 -2.064609  1.221357
 H -8.904034 -1.526014  1.929609
 O -6.927830 -2.173534  1.794888
 C -6.002403 -1.453387  0.936957
 H -5.884332 -0.425827  1.287895
 N -4.682676 -2.079020  1.030542
 C -4.500175 -3.357666  0.583114
 H -5.398125 -3.858540  0.224728
 C -3.270731 -3.958424  0.613361
 H -3.135190 -4.983260  0.272871
 C -2.179097 -3.200133  1.179694
 N -0.954155 -3.741339  1.315488
 H -0.166785 -3.149280  1.664214
 H -0.697582 -4.530586  0.735960
 N -2.361519 -1.945749  1.627390
 C -3.575293 -1.328300  1.560209
 O -3.748576 -0.154657  1.929381
 C -8.115118 -1.221719 -0.079031
 H -8.800704 -1.557041 -0.873107
 C -6.649349 -1.478752 -0.443185
 H -6.568891 -2.474091 -0.898478
 H -6.235354 -0.737888 -1.120386
 O -8.416533  0.137537  0.281569
 P -7.890233  1.447620 -0.658916
 O -8.688338  2.641149 -0.188428
 O -7.736451  1.012660 -2.103932
 O -6.295319  1.578144 -0.110649
 C -5.925048  2.455920  0.958344
 H -5.338799  1.873446  1.685575
 H -6.820439  2.883894  1.439645
 C -5.061290  3.606725  0.427613
 H -4.881684  4.320494  1.247509
 O -3.757524  3.149578 -0.013806
 C -3.712065  3.041261 -1.440700
 H -2.841896  3.619533 -1.778604
 N -3.422655  1.653208 -1.829797
 C -4.296406  0.601091 -2.084478
 H -5.358361  0.771364 -2.232476
 N -3.705780 -0.582072 -2.131315
 C -2.370992 -0.300293 -1.881404
 C -1.229449 -1.125967 -1.759218
 N -1.273649 -2.480245 -1.890924
 H -0.467429 -3.026366 -1.557826
 H -2.192497 -2.900805 -1.818902
 N -0.034507 -0.525459 -1.531420
 C  0.027596  0.823619 -1.413888
 H  1.024633  1.229013 -1.239878
 N -0.990189  1.698070 -1.474231
 C -2.163784  1.078289 -1.702633
 C -5.681422  4.322205 -0.784607
 H -6.777881  4.227956 -0.778299
 C -5.052593  3.586851 -1.986148
 H -5.729050  2.786086 -2.303261
 H -4.884345  4.266818 -2.834007
 O -5.290929  5.718102 -0.725309
 H -5.728907  6.156325 -1.469919
 H  8.457272 -4.917107 -0.304648
 O  8.084107 -4.024744 -0.306328
 C  8.729694 -3.285807 -1.364122
 H  8.603277 -3.811913 -2.328260
 H  9.811127 -3.175719 -1.152314
 C  8.131304 -1.885177 -1.500848
```

H	8.736685	−1.350830	−2.252594
O	6.771512	−1.974130	−1.983492
C	5.894540	−1.316499	−1.030148
H	5.680955	−0.295310	−1.354559
N	4.614236	−2.027622	−1.004149
C	4.579043	−3.357869	−0.648070
H	5.556114	−3.792166	−0.439513
C	3.427704	−4.091270	−0.581363
C	3.407832	−5.540684	−0.170433
H	2.821749	−5.672507	0.753491
H	2.932130	−6.165320	−0.944463
H	4.430706	−5.905944	0.006750
C	2.171406	−3.427607	−0.911001
O	1.057766	−4.006475	−0.933203
N	2.274812	−2.081175	−1.235076
H	1.385636	−1.521869	−1.388313
C	3.433218	−1.319787	−1.322934
O	3.418400	−0.137257	−1.659805
C	8.091410	−1.043677	−0.194691
H	8.840549	−1.372913	0.543082
C	6.661935	−1.317541	0.287888
H	6.630543	−2.310453	0.753412
H	6.293625	−0.578109	0.994053
O	8.358114	0.313123	−0.585230
P	7.879470	1.635338	0.366674
O	8.641240	2.824556	−0.172096
O	7.819053	1.221255	1.823366
O	6.257228	1.743682	−0.091968
C	5.819087	2.595295	−1.155798
H	5.214831	1.989720	−1.849676
H	6.682061	3.037521	−1.681582
C	4.945193	3.729910	−0.605517
H	4.728948	4.433388	−1.426499
O	3.670885	3.247432	−0.124798
C	3.654439	3.174464	1.304428
H	2.791029	3.760557	1.648049
N	3.386427	1.801705	1.748714
C	4.286519	0.759265	1.982952
H	5.355115	0.938293	2.012840
N	3.703510	−0.407398	2.168210
C	2.346515	−0.136735	2.049704
C	1.210623	−1.001828	2.121956
O	1.185877	−2.248763	2.265092
N	−0.001979	−0.284259	1.995787
H	−0.867972	−0.862389	1.965990
C	−0.108593	1.077039	1.770598
N	−1.368730	1.589575	1.716201
H	−2.178568	0.962589	1.728190
H	−1.479800	2.455553	1.202573
N	0.947872	1.881966	1.646693
C	2.123941	1.229245	1.790709
C	5.590591	4.470777	0.578627
H	6.687832	4.394749	0.542299
C	5.005965	3.742808	1.804139
H	5.700196	2.951905	2.106757
H	4.856632	4.427231	2.652604
O	5.178907	5.862200	0.511951
H	5.602138	6.306306	1.262163

Model (a)
optimized ad B97D/6- 31+G(d,p) level including IEFPCM water solvation (see text), xyz format

```
37
 model (a)
 H -6.101318   0.428169   1.206831
 O -5.162114   0.498333   0.986534
 C -4.967914 -0.144150 -0.290766
 H -5.608126   0.329262 -1.057749
 H -5.220767 -1.220238 -0.223918
 C -3.512418 -0.028463 -0.742039
 H -3.412817 -0.616422 -1.670418
 O -3.202315   1.355140 -1.028996
 C -2.040806   1.741033 -0.248328
 H -1.125218   1.579127 -0.841658
 H -2.147408   2.803815   0.009854
 C -2.456355 -0.526792   0.285780
 H -2.877515 -1.240600   1.011132
 C -2.049616   0.791717   0.951499
 H -2.831106   1.081540   1.665496
 H -1.093793   0.740894   1.464087
 O -1.410751 -1.172366 -0.484283
 P   0.138888 -1.380463   0.110677
 O   0.795038 -2.375242 -0.834166
 O   0.101773 -1.594821   1.614981
 O   0.788006   0.147848 -0.117147
 C   1.519882   0.485948 -1.314647
 H   1.086997   1.401659 -1.745841
 H   1.467521 -0.343485 -2.039790
 C   2.993239   0.742132 -0.974430
 H   3.553967   0.877276 -1.913209
 O   3.170890   1.961311 -0.209079
 C   3.351148   1.665480   1.191129
 H   4.280432   2.173114   1.492826
 H   2.508693   2.083495   1.766316
 C   3.623426 -0.375012 -0.125484
 H   3.110385 -1.333941 -0.294022
 C   3.429167   0.129683   1.319308
 H   2.502724 -0.295204   1.720042
 H   4.266261 -0.167416   1.967838
 O   5.023477 -0.476417 -0.491655
 H   5.387214 -1.213852   0.020395
```

Model (b)
optimized ad B97D/6- 31+G(d,p) level including IEFPCM water solvation (see text), xyz format

```
48
 model (b)
 H  6.261584  0.793375  1.234324
 O  5.379056  0.431612  1.073582
 C  5.205393  0.332836 -0.355423
 H  5.997570 -0.301817 -0.793537
 H  5.249649  1.337155 -0.819927
 C  3.850470 -0.285938 -0.697139
 H  3.742827 -0.245637 -1.794546
 O  3.829221 -1.669633 -0.275495
 C  2.683109 -1.869525  0.589296
 H  1.819583 -2.207952 -0.008165
 H  2.960758 -2.632977  1.332207
 C  2.619966  0.406688 -0.044349
 H  2.826072  1.449704  0.243164
 C  2.392978 -0.488921  1.177732
 H  3.135373 -0.233250  1.944530
 H  1.395721 -0.402514  1.598361
 O  1.551768  0.382049 -1.032362
 P -0.043932  0.487870 -0.615599
 O -0.813462  0.812256 -1.884536
 O -0.215799  1.397687  0.611069
 O -0.382096 -1.042625 -0.073898
 C -0.916340 -2.053741 -0.960053
 H -0.281333 -2.950243 -0.890143
 H -0.940572 -1.678625 -1.996996
 C -2.345698 -2.420181 -0.541975
 H -2.771401 -3.099463 -1.297834
 O -2.377145 -3.135513  0.719365
 C -2.749873 -2.259082  1.791679
 H -3.600969 -2.740553  2.306558
 H -1.906152 -2.160039  2.496384
 C -3.253866 -1.194411 -0.345423
 H -2.909323 -0.347473 -0.957904
 C -3.122719 -0.898265  1.162874
 H -2.336091 -0.150365  1.308638
 H -4.062916 -0.511906  1.582794
 O -4.603010 -1.575619 -0.718264
 H -5.146365 -0.778504 -0.630626
 H -3.141680  2.766404  0.199363
 N -2.233329  2.945452 -0.238524
 H -2.248299  2.552059 -1.188402
 H -1.470435  2.374002  0.259536
 C -1.902813  4.415664 -0.241201
 C -1.826420  4.940248  1.191594
 H -2.676922  4.926922 -0.825506
 H -0.941635  4.510011 -0.760157
 H -1.574975  6.009335  1.171412
 H -2.791156  4.822098  1.707114
 H -1.050008  4.410093  1.761656
```

Model W_1
optimized ad B97D/6- 31+G(d,p) level including IEFPCM water solvation (see text), xyz format

```
51
 model W1
 H   6.387654   1.591513   1.303265
 O   5.577390   1.112799   1.079966
 C   5.244563   1.438541  -0.285711
 H   6.080817   1.169986  -0.957164
 H   5.036269   2.521713  -0.384374
 C   4.000555   0.675472  -0.739163
 H   3.747795   1.038364  -1.750071
 O   4.298282  -0.738435  -0.810538
 C   3.331667  -1.453607  -0.000864
 H   2.479585  -1.767389  -0.627507
 H   3.842790  -2.331868   0.422538
 C   2.754094   0.831347   0.178454
 H   2.792030   1.746531   0.790004
 C   2.860631  -0.433855   1.035825
 H   3.632278  -0.277267   1.800375
 H   1.927353  -0.710528   1.516845
 O   1.595510   0.884191  -0.700613
 P   0.076917   0.499815  -0.185878
 O  -0.856115   1.004261  -1.287436
 O  -0.126502   0.935023   1.262155
 O   0.096446  -1.156684  -0.168777
 C  -0.334175  -1.931637  -1.313697
 H   0.464113  -2.638333  -1.587761
 H  -0.562015  -1.260923  -2.159183
 C  -1.601740  -2.720937  -0.963877
 H  -1.982824  -3.200692  -1.879613
 O  -1.334343  -3.788977  -0.019709
 C  -1.727514  -3.406334   1.305405
 H  -2.397940  -4.203651   1.674319
 H  -0.835245  -3.351677   1.952818
 C  -2.694748  -1.856656  -0.312520
 H  -2.599632  -0.804401  -0.620528
 C  -2.430893  -2.035300   1.196883
 H  -1.789675  -1.217443   1.542339
 H  -3.366061  -2.022695   1.775568
 O  -3.982527  -2.389653  -0.715080
 H  -4.652503  -1.804268  -0.331936
 H  -3.981903   1.893832  -0.899767
 N  -3.123695   2.266529  -0.484510
 H  -2.281511   1.757643  -0.887794
 H  -3.113890   2.046181   0.544803
 C  -3.010470   3.750006  -0.710668
 C  -4.188400   4.493272  -0.082049
 H  -2.959526   3.908221  -1.794605
 H  -2.055448   4.053367  -0.265164
 H  -4.072405   5.571988  -0.255629
 H  -5.140526   4.172124  -0.530047
 H  -4.228567   4.317811   1.002851
 O  -2.547853   1.653240   2.173266
 H  -1.637345   1.334305   1.902406
 H  -3.005292   0.876637   2.528777
```

Model W_2
optimized ad B97D/6- 31+G(d,p) level including IEFPCM water solvation (see text), xyz format

```
54
 model W2
 H -4.987075   3.105536   1.428909
 O -4.076097   2.897498   1.179121
 C -4.109975   2.327677 -0.146064
 H -4.580727   3.034535 -0.853902
 H -4.685441   1.381514 -0.144751
 C -2.697574   2.020382 -0.642213
 H -2.799461   1.504501 -1.612268
 O -1.974707   3.257187 -0.843746
 C -0.742244   3.199007 -0.082799
 H  0.070838   2.809894 -0.718937
 H -0.513625   4.222536   0.251840
 C -1.836034   1.140541   0.308381
 H -2.449076   0.538745   0.997605
 C -1.028555   2.211698   1.048464
 H -1.670446   2.673498   1.809523
 H -0.129485   1.826961   1.520242
 O -1.052221   0.260055 -0.543164
 P  0.361122 -0.439440 -0.027668
 O  0.665676 -1.528969 -1.051590
 O  0.275376 -0.762685   1.460631
 O  1.450017   0.799302 -0.163405
 C  2.235146   0.989619 -1.365068
 H  2.104123   2.025045 -1.715159
 H  1.916262   0.276374 -2.143628
 C  3.719323   0.748425 -1.063101
 H  4.281204   0.775234 -2.010486
 O  4.279512   1.788891 -0.222100
 C  4.375321   1.346081   1.138648
 H  5.423085   1.512902   1.447922
 H  3.706925   1.954855   1.771828
 C  3.980550 -0.571559 -0.317904
 H  3.191311 -1.307641 -0.533399
 C  3.973623 -0.145298   1.164694
 H  2.966429 -0.291254   1.569226
 H  4.684851 -0.737011   1.759341
 O  5.273648 -1.073914 -0.742223
 H  5.395793 -1.925264 -0.296573
 H -3.040986 -3.267314 -1.967998
 N -2.941714 -3.491796 -0.973209
 H -1.905228 -3.748324 -0.776614
 H -3.533253 -4.306902 -0.784801
 C -3.344298 -2.315507 -0.114882
 C -4.783395 -1.889141 -0.392444
 H -2.626284 -1.519579 -0.340306
 H -3.203975 -2.636721   0.923826
 H -5.042711 -1.049091   0.266173
 H -4.902899 -1.559683 -1.435150
 H -5.486607 -2.711326 -0.194036
 O -0.201238 -3.298888   2.253726
 H -0.008571 -2.347859   2.009692
 H  0.605129 -3.623809   2.681288
 H  0.062077 -3.107682 -0.723396
 O -0.367326 -3.957046 -0.419944
 H -0.299464 -3.891507   0.568780
```

Model W_3
optimized ad B97D/6- 31+G(d,p) level including IEFPCM water solvation (see text), xyz format

```
57
 model W3
 H -5.271528   2.690209   1.451552
 O -4.338463   2.571567   1.226010
 C -4.271333   2.234462 -0.175351
 H -4.744849   3.028029 -0.782249
 H -4.790827   1.275394 -0.366926
 C -2.819962   2.084045 -0.629629
 H -2.842010   1.736376 -1.676605
 O -2.159892   3.370296 -0.577617
 C -0.966913   3.242659   0.235955
 H -0.101176   3.006808 -0.405961
 H -0.814962   4.204125   0.750110
 C -1.959382   1.097653   0.210866
 H -2.571510   0.358739   0.751529
 C -1.253892   2.064774   1.166943
 H -1.959549   2.359125   1.954280
 H -0.359684   1.648927   1.621239
 O -1.077727   0.404914 -0.722164
 P   0.359414 -0.297271 -0.228143
 O   0.760912 -1.202794 -1.383294
 O   0.195494 -0.836239   1.187634
 O   1.360711   1.006831 -0.109103
 C   2.194454   1.428743 -1.215227
 H   2.022383   2.501142 -1.394643
 H   1.957534   0.843852 -2.119844
 C   3.672524   1.211089 -0.868706
 H   4.279941   1.425516 -1.762592
 O   4.128029   2.118994   0.166615
 C   4.178959   1.456318   1.437506
 H   5.198112   1.618111   1.833031
 H   3.445018   1.915809   2.121956
 C   3.970419 -0.202348 -0.340153
 H   3.236883 -0.928010 -0.722896
 C   3.862749 -0.035270   1.189662
 H   2.846118 -0.295980   1.502523
 H   4.575237 -0.684733   1.718939
 O   5.310346 -0.562688 -0.763545
 H   5.458080 -1.470584 -0.459866
 H -2.512945 -2.778957 -1.194549
 N -2.298749 -3.518713 -0.480035
 H -1.274128 -3.779973 -0.597448
 H -2.885097 -4.336600 -0.667143
 C -2.540883 -2.977935   0.907451
 C -3.974112 -2.468690   1.055650
 H -1.802737 -2.179947   1.053469
 H -2.322640 -3.791284   1.609871
 H -4.116294 -2.079390   2.073388
 H -4.178475 -1.655994   0.343561
 H -4.702841 -3.276065   0.889629
 O   1.198587 -3.261575   1.852643
 H   0.880262 -2.334148   1.667230
 H   2.161567 -3.190354   1.932693
 H   0.598615 -2.957829 -1.082272
 O   0.421002 -3.877661 -0.754527
 H   0.756224 -3.840524   0.175797
 H -2.053069 -0.697179 -1.800710
 O -2.607606 -1.365572 -2.269554
 H -3.498557 -0.986135 -2.309293
```

2. Simulated anti-symmetric PO stretching signal of (W_3) model

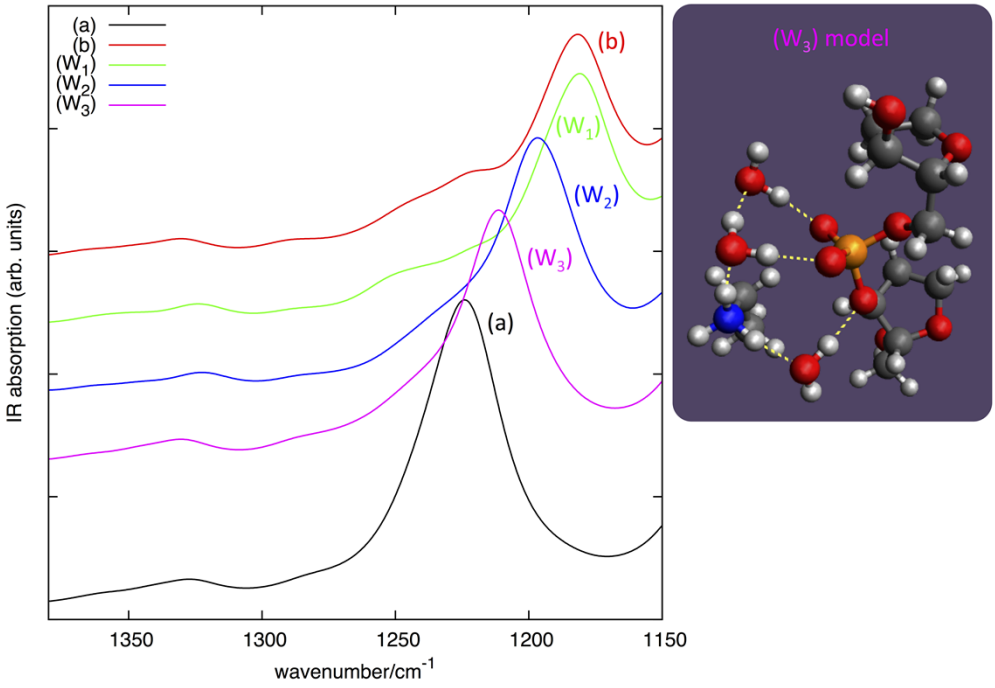

Figure SI.1. Left: simulated IR spectrum of model W_3, from DFT B97D/6-31+G(d,p) calculations including IEFPCM water solvation. The position of the anti-symmetric PO stretching mode varies monotonically with the content of water molecules shielding the direct NH_3^+:PO_4^- interaction (which is represented by model (b)). Right: ball and stick representation of the structure of model W_3, which compared with model W_2 includes one additional water molecule hydrogen-bonded to the phosphodiester oxygen of the PO4$^-$ group.

3. Vibrational analysis of the molecular models considered in this work

Vibrational analysis is included as output of a custom code developed in our laboratory, which provides the contributions from internal coordinates to each normal mode ($\mathbf{L}_R$ matrix). This is carried out based on the Hessian in Cartesian coordinates computed by Gaussian ($\mathbf{F}_X$) and following Wilson's definition of internal coordinates (*i.e.*, $\mathbf{R} = \mathbf{B}\ \mathbf{X}$) so that $\mathbf{L}_R = \mathbf{B}\ \mathbf{L}_X$, where the *k*-th column of $\mathbf{L}_X$ satisfies the secular equation $\mathbf{M}^{-1}\mathbf{F}_X\ (\mathbf{L}_X)_k = \omega^2_k\ (\mathbf{L}_X)_k$. The data contained in the $\mathbf{L}_R$ matrix, limited to the PO stretching coordinates, has been used to plot Figure 6.

Since the full output is cumbersome, we prefer not listing it here. We provide the individual files for each model to help the analysis by the interested reader, as listed below:

1. dna-ca-gt.txt
2. model-a.txt
3. model-b.txt
4. model-W1.txt
5. model-W2.txt
6. model-W3.txt