Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for

Non-linear optical properties of molecules in heterogeneous environment: a quadratic density functional/molecular mechanics response theory

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Supplementary figures

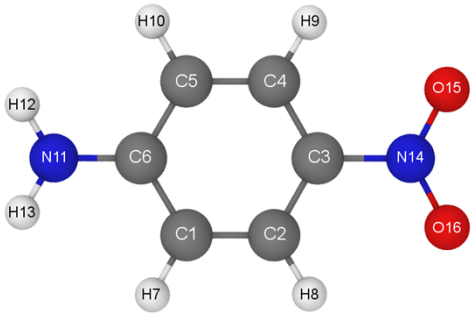

Figure S1. Geometry and atomic numbering of PNA.

Table S1. Comparison between the geometry of PNA optimized by quantum mechanical (QM) calculations at the B3LYP/def-TZVP level of theory and by molecular mechanical (MM) energy minimization using the refined CHARMM general force field.

Bond/Å		QM	MM	Angle/deg			QM	MM	Dihedral/deg				QM	MM
C1	C2	1.381	1.381	C2	C1	C6	120.7	120.7	C6	C1	C2	C3	-0.2	-0.0
C1	C6	1.407	1.406	C2	C1	H7	119.7	119.7	C6	C1	C2	H8	179.8	-179.9
C1	H7	1.084	1.084	C6	C1	H7	119.6	119.6	C3	C2	C1	H7	179.8	179.6
C2	C3	1.392	1.392	C1	C2	C3	119.6	119.6	H7	C1	C2	H8	-0.2	-0.2
C2	H8	1.080	1.081	C1	C2	H8	121.0	121.0	C2	C1	C6	C5	0.3	0.1
C3	C4	1.392	1.392	C3	C2	H8	119.4	119.4	C2	C1	C6	N11	178.0	-179.9
C3	N14	1.462	1.463	C2	C3	C4	120.8	120.9	C5	C6	C1	H7	-179.7	-179.6
C4	C5	1.381	1.381	C2	C3	N14	119.6	119.6	N11	C6	C1	H7	-2.0	0.4
C4	H9	1.080	1.081	C4	C3	N14	119.6	119.6	C1	C2	C3	C4	0.1	-0.0
C5	C6	1.407	1.406	C3	C4	C5	119.6	119.6	C1	C2	C3	N14	179.8	179.9
C5	H10	1.084	1.084	C3	C4	H9	119.4	119.4	C4	C3	C2	H8	-179.9	179.8
C6	N11	1.374	1.375	C5	C4	H9	121.0	121.0	N14	C3	C2	H8	-0.2	-0.3
N11	H12	1.006	1.006	C4	C5	C6	120.7	120.7	C2	C3	C4	C5	-0.1	0.0
N11	H13	1.006	1.006	C4	C5	H10	119.7	119.7	C2	C3	C4	H9	179.9	-179.8
N14	O15	1.229	1.228	C6	C5	H10	119.6	119.6	C5	C4	C3	N14	-179.8	-179.9
N14	O16	1.229	1.228	C1	C6	C5	118.7	118.7	N14	C3	C4	H9	0.2	0.3
				C1	C6	N11	120.7	120.6	C2	C3	N14	O15	-179.9	-179.8
				C5	C6	N11	120.6	120.6	C2	C3	N14	O16	0.2	-0.1
				C6	N11	H12	118.6	118.3	C4	C3	N14	O15	-0.1	0.1
				C6	N11	H13	118.6	118.3	C4	C3	N14	O16	179.9	179.8
				H12	N11	H13	115.1	114.7	C3	C4	C5	C6	0.2	0.0
				C3	N14	O15	118.0	117.9	C3	C4	C5	H10	-179.8	-179.6
				C3	N14	O16	118.0	117.9	C6	C5	C4	H9	-179.8	179.9
				O15	N14	O16	124.1	124.1	H9	C4	C5	H10	0.2	0.2
									C4	C5	C6	C1	-0.3	-0.1
									C4	C5	C6	N11	-178.0	179.9
									C1	C6	C5	H10	179.7	179.6
									N11	C6	C5	H10	2.0	-0.4
									C1	C6	N11	H12	165.0	163.0
									C1	C6	N11	H13	17.2	17.0
									C5	C6	N11	H12	-17.3	-17.0
									C5	C6	N11	H13	-165.1	-163.0
RMSD =		0.001 Å		RMSD =			0.1°		RMSD =				1.0°	

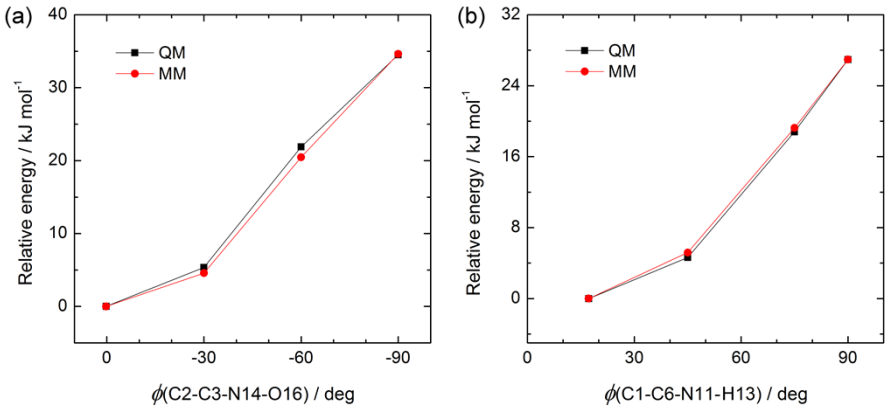

Figure S2. Comparison between the QM and MM rotation energy barriers of (a) the $-NO_2$ group and (b) the $-NH_2$ group of PNA.

Refined CGenFF parameters for PNA (in GROMACS format)

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[ moleculetype ]
;name               nrexcl
pna                 3

[ atoms ]
     1     CG2R61      0    PNA     C1      1      -0.11     12.011   ; qtot -0.11
     2     CG2R61      0    PNA     C2      2     -0.178     12.011   ; qtot -0.288
     3     CG2R61      0    PNA     C3      3       0.32     12.011   ; qtot 0.032
     4     CG2R61      0    PNA     C4      4     -0.178     12.011   ; qtot -0.146
     5     CG2R61      0    PNA     C5      5      -0.11     12.011   ; qtot -0.256
     6     CG2R61      0    PNA     C6      6      0.058     12.011   ; qtot -0.198
     7      HGR61      0    PNA     H7      7      0.115      1.008   ; qtot -0.083
     8      HGR61      0    PNA     H8      8       0.16      1.008   ; qtot 0.077
     9      HGR61      0    PNA     H9      9       0.16      1.008   ; qtot 0.237
    10      HGR61      0    PNA    H10     10      0.115      1.008   ; qtot 0.352
    11      NG2S3      0    PNA    N11     11     -0.834     14.007   ; qtot -0.482
    12       HGP4      0    PNA    H12     12      0.381      1.008   ; qtot -0.101
    13       HGP4      0    PNA    H13     13      0.381      1.008   ; qtot 0.28
    14      NG2O1      0    PNA    N14     14      0.398     14.007   ; qtot 0.678
    15      OG2N1      0    PNA    O15     15     -0.339    15.9994   ; qtot 0.339
    16      OG2N1      0    PNA    O16     16     -0.339    15.9994   ; qtot 0

[ bonds ]
1       2       1          1.342531e-01   2.552240e+05
1       6       1          1.385186e-01   2.552240e+05
1       7       1          1.081963e-01   2.845120e+05
2       3       1          1.326947e-01   2.552240e+05
2       8       1          1.078603e-01   2.845120e+05
3       4       1          1.326947e-01   2.552240e+05
3       14      1          1.377033e-01   1.924640e+05
4       5       1          1.342531e-01   2.552240e+05
4       9       1          1.078603e-01   2.845120e+05
5       6       1          1.385186e-01   2.552240e+05
5       10      1          1.081963e-01   2.845120e+05
6       11      1          1.379528e-01   3.347200e+05
11      12      1          1.006525e-01   4.083584e+05
11      13      1          1.006525e-01   4.083584e+05
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14      16      1          1.221728e-01   4.853440e+05

[ pairs ]
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    1    14     1
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    2     9     1
    2    11     1
    2    15     1
    2    16     1
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    3     7     1
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    4    15     1
    4    16     1
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    5    12     1
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    5    14     1
    6     8     1
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    7     8     1
    7    11     1
    8    14     1
    9    10     1
    9    14     1
   10    11     1

[ angles ]
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3      4      9      5         1.194730e+02   2.510400e+02   2.152500e-01   1.840960e+04
5      4      9      5         1.248960e+02   2.510400e+02   2.152500e-01   1.840960e+04
4      5      6      5         1.204171e+02   3.347200e+02   2.416200e-01   2.928800e+04
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[ dihedrals ]
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```

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