Supplementary Material (ESI) for Photochemical & Photobiological Sciences

SUPPLEMENTARY INFORMATION FOR:

Experimental and Theoretical Study of the Interaction of Single-Stranded DNA Homopolymers and a Monomethine Cyanine Dye: Nature of Specific Binding

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Computational Details

For each homopolymer we have selected one representative calculation, with the initial and final conditions (2 ns) shown in Figures S1-S4. The blue counterions are Na^+ ions while the cyan counterions are Cl^- ions. For each case the single-stranded model is formed by 10 bases. The solvent is explicitly described by a truncated octahedron containing the solute and ca. 4000 water molecules described by the TIP3P model. The trajectories were run applying periodic boundary conditions. In Figures S1-S4 the explicit solvent has been omitted for clarity.

For each one of these Figures (Figures S1-S4) there is also a movie of the dynamic simulation available as part of the Supporting Information. These movies are based on 1,000 frames, taken from the 1,000,000 frames calculated; as a result of this sampling, some of the motion may appear abrupt in spite of the smooth nature of the actual displacements.

Movie files are named as follows:

For poly(dA) a-dye2_0-2ns.mpg

For poly(dC) c-dye2_0-2ns.mpg

For poly(dG) g-dye2_0-2ns.mpg

For poly(dT) t-dye2_0-2ns.mpg

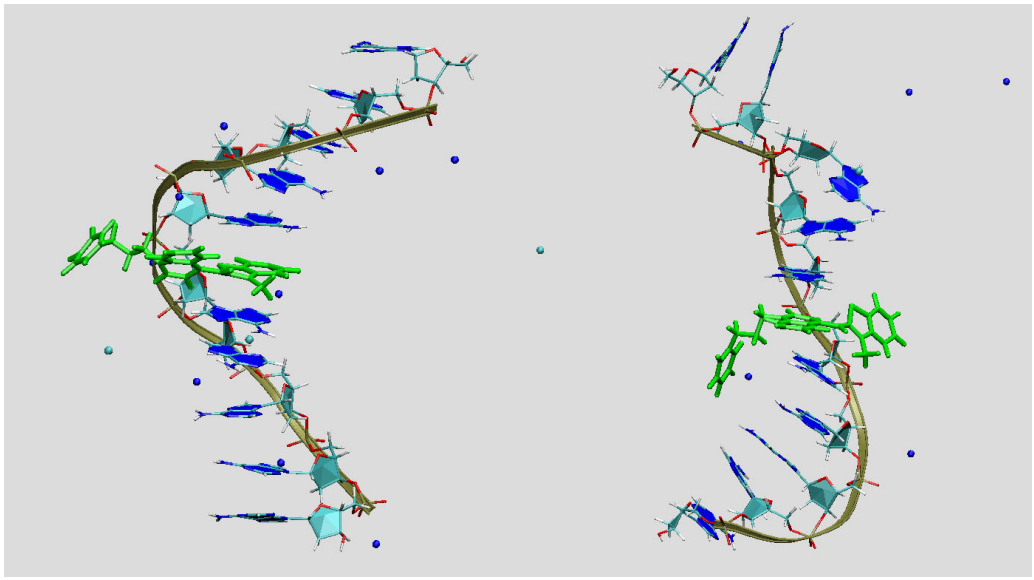

Figure S1. Initial (left) and final result of **1**, in green, with poly(dA). The dye remains associated with poly(dA).

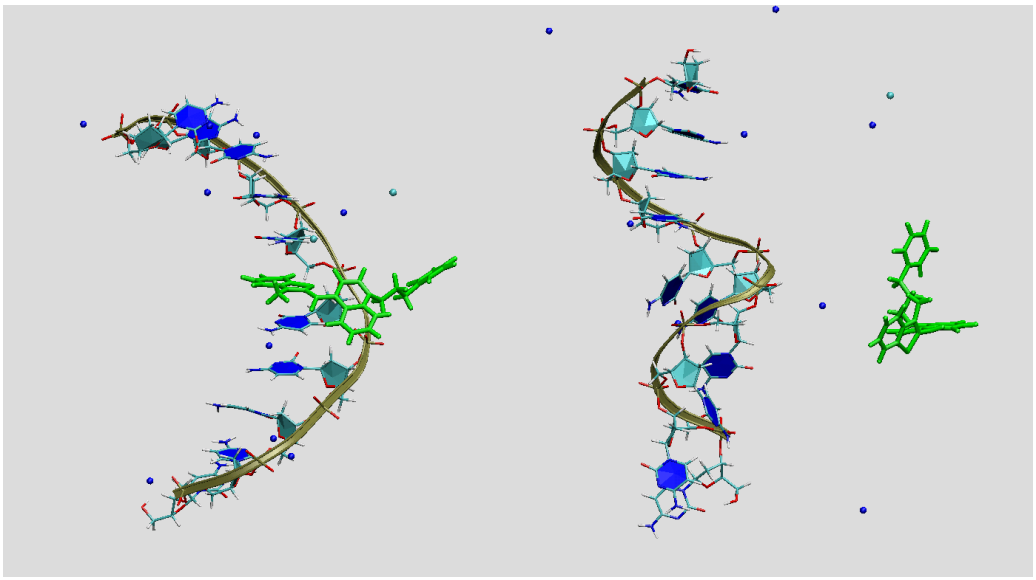

Figure S2. Initial (left) and final result of **1**, in green, with poly(dC). The dye leaves the single strand.

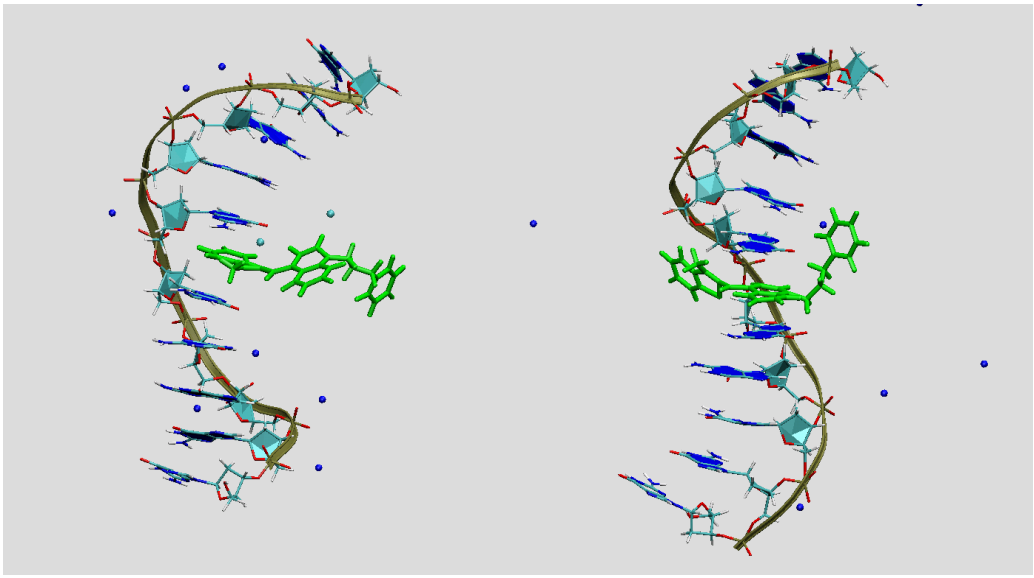

Figure S3. Initial (left) and final result of **1**, in green, with poly(dG). The dye remains strongly associated with poly(dG) which preserves its structure over the 2 ns.

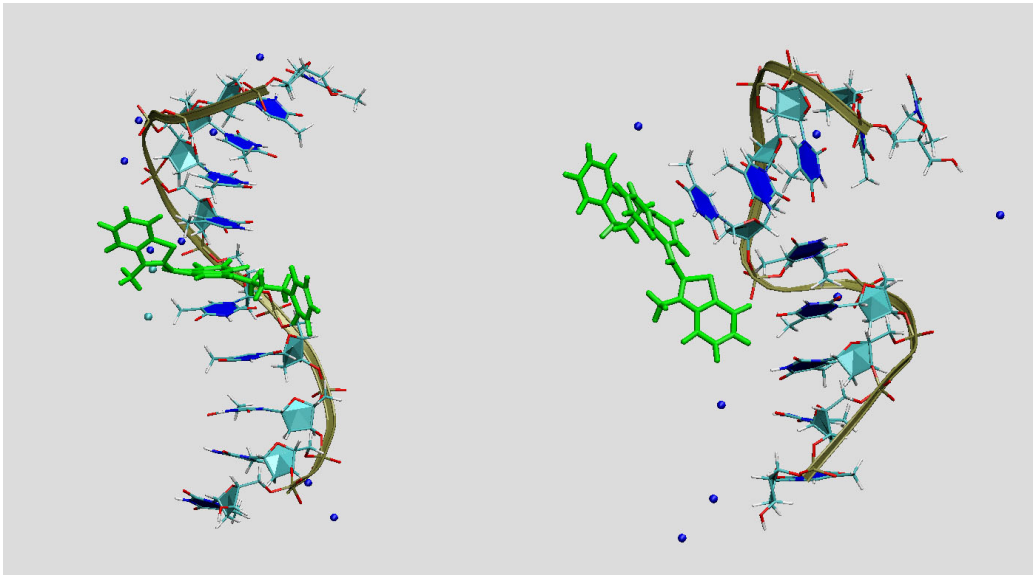

Figure S4. Initial (left) and final result of **1**, in green, with poly(dT). The dye leaves the single strand. Notice how poly(dT) has changed compared to the canonical structure.

In several cases the calculations were extended for an additional 2 ns, by taking the final condition in the original calculation (such as in Figures S1-S4, right) and using it as the starting point for a new dynamic simulation. While the detailed orientations vary slightly, the overall conclusions were unaffected, i.e., **1** associates readily with poly(dA) and

poly(dG), and the preferred form of association is with the quinoline ring between the bases in a stacked arrangement. For the two bases that show strong association close-ups of the initial and final arrangement are shown in Figures S5 and S6.

In the cases of poly(dC) and poly(dT) the calculations (2 ns or extended to 4 ns) predict very loose binding that in most simulations leads to dye-DNA separation even in this short time scale.

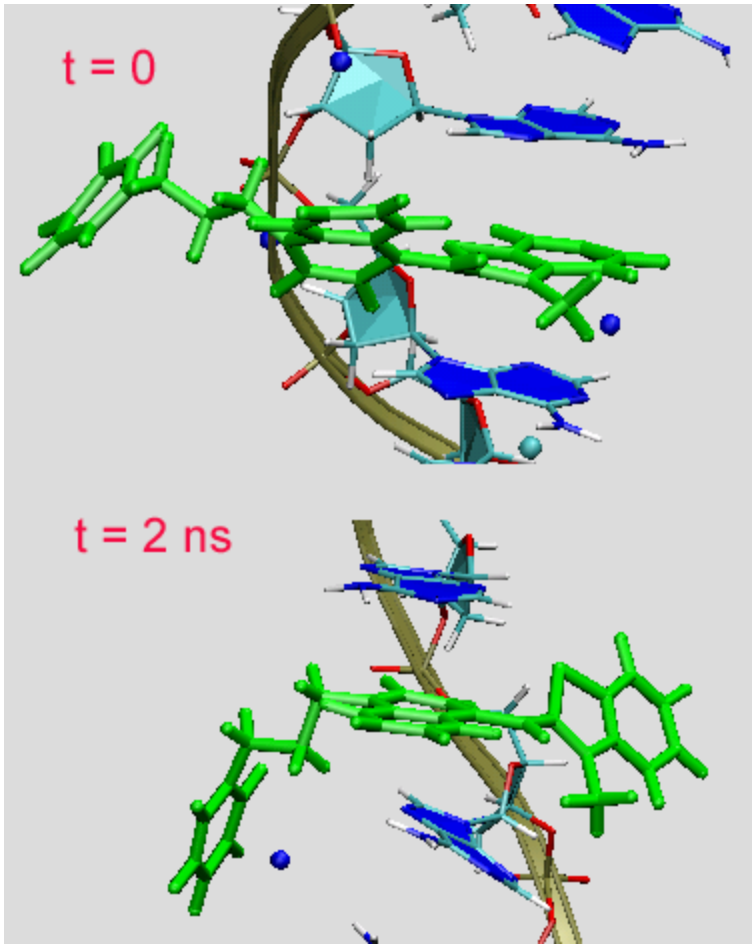

Figure S5. Close-up of the initial (top) and final result of **1**, in green, with poly(dA). The intercalated moiety shifts from the benzothiazole to the quinoline.

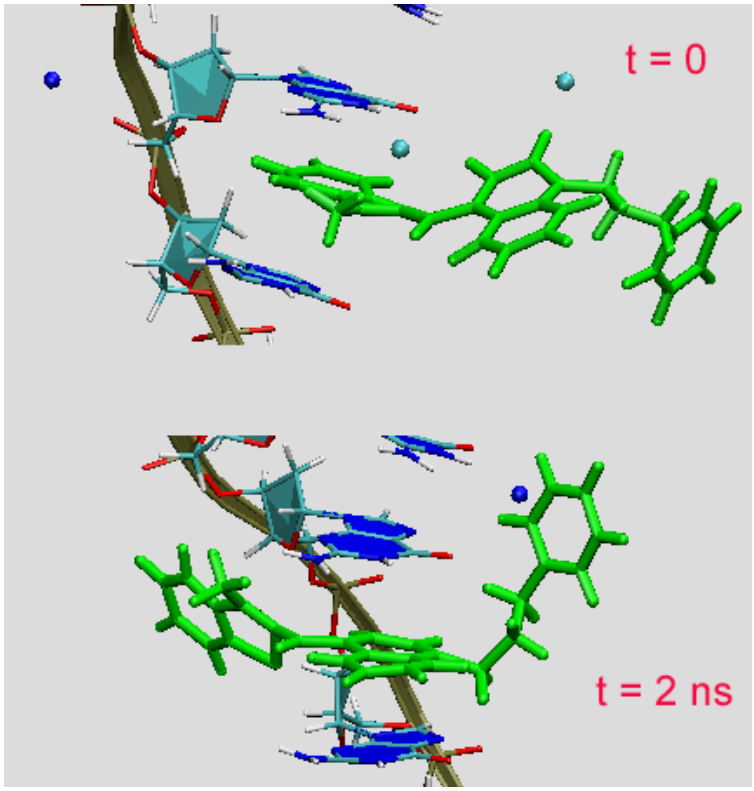

Figure S6. Close-up of the initial (top) and final result of **1**, in green, with poly(dG). The intercalated moiety shifts from the benzothiazole to the quinoline.

Appendix 1

Structures and energies of all stationary points located in the course of the study, in the form of Gaussian input files, followed by Energies. These structures are presented in the same order as in Figure 7.

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B3LYP structures
================
#n b3lyp/6-31g*

conformation 1

2,1
  6          5.589043   -1.115014    0.007386
  6          5.316640   -0.182564    1.019088
  6          6.290707    0.199223    1.939856
  6          7.549956   -0.388409    1.838063
  6          7.823302   -1.331730    0.836551
  6          6.852651   -1.707344   -0.088317
  7          4.481228   -1.329805   -0.828016
```

6	3.352293	-0.653503	-0.482697
16	3.649685	0.371687	0.913694
1	6.074294	0.925761	2.716209
1	8.325639	-0.114070	2.545517
1	8.808831	-1.782214	0.779346
1	7.079143	-2.447043	-0.847781
6	4.556680	-2.207103	-2.000230
1	5.571923	-2.177282	-2.396068
1	4.301069	-3.238196	-1.734632
1	3.877371	-1.841609	-2.770486
6	2.099199	-0.917096	-1.077536
1	2.048152	-1.890229	-1.557614
6	1.398713	3.461295	-0.585921
6	1.625294	2.124544	-0.855287
6	0.613567	1.150377	-0.712690
6	-0.702094	1.603410	-0.388279
6	-0.915263	2.963029	-0.084084
6	0.126192	3.873616	-0.166555
1	2.195317	4.186749	-0.713358
1	2.595894	1.814846	-1.220599
6	0.861213	-0.263117	-0.981608
7	-1.773696	0.699104	-0.423723
1	-1.896790	3.326668	0.190456
1	-0.061679	4.918285	0.060918
6	-1.555874	-0.562308	-0.898682
6	-0.315041	-1.040950	-1.200067
1	-2.422080	-1.200652	-0.997352
1	-0.230267	-2.071374	-1.527025
6	-3.116303	1.177390	-0.045496
1	-3.407106	1.976808	-0.738756
1	-3.034075	1.626189	0.951158
6	-4.219075	0.109077	-0.018298
1	-3.939271	-0.720055	0.641931
1	-4.390683	-0.302312	-1.019508
6	-5.523389	0.747873	0.489322
1	-5.828063	1.588460	-0.139170
1	-5.414904	1.122185	1.510070
7	-6.659055	-0.220051	0.499047
6	-7.434669	-0.355894	-0.606097
6	-8.485743	-1.256292	-0.627488
6	-8.746223	-2.029770	0.506940
6	-7.938386	-1.877520	1.636994
6	-6.899153	-0.963589	1.608328
1	-7.190401	0.280150	-1.448991
1	-9.093886	-1.338045	-1.521584
1	-9.570599	-2.736057	0.512468
1	-8.112056	-2.452504	2.539837
1	-6.245489	-0.791965	2.455587

SCF Done: E(RB+HF-LYP) = -1567.78075241

#n b3lyp/6-31g*

conformation 2

2,1

6	-6.643978	-1.401338	1.256269
7	-6.244698	-0.957884	0.037613
6	-6.556782	-1.650057	-1.086959
6	-7.287640	-2.823498	-1.016326
6	-7.707103	-3.293392	0.231190
6	-7.377009	-2.568948	1.379714
6	-5.446643	0.298687	-0.065862
6	-3.931939	0.036247	0.000778
6	-3.193308	1.378317	-0.101979
7	-1.721040	1.310852	-0.048295
6	-0.989523	2.509068	-0.121651
6	0.437364	2.472369	-0.072911
6	1.147999	1.196509	0.066823
6	0.311688	0.044194	0.115481
6	-1.049934	0.134599	0.065780
6	-1.658994	3.742485	-0.250284
6	-0.946795	4.926625	-0.340807
6	0.453462	4.909476	-0.317908
6	1.118998	3.704990	-0.190194
6	2.545354	1.156117	0.179026
6	3.421270	0.056082	0.121170
7	4.744218	0.150518	0.433519
6	5.502418	-1.006760	0.192707
6	4.716866	-2.067551	-0.281647
16	3.042199	-1.559053	-0.455411
6	5.265482	-3.316828	-0.565037
6	6.634672	-3.485866	-0.372949
6	7.428571	-2.426047	0.089228
6	6.878952	-1.179358	0.375504
6	5.337616	1.367503	0.996943
1	4.647490	-4.130822	-0.929609
1	7.090341	-4.446649	-0.588776
1	8.494968	-2.574709	0.224090
1	7.515725	-0.371642	0.717418
1	6.251611	1.102109	1.525414
1	5.573305	2.089060	0.208006
1	4.647678	1.811603	1.716022
1	3.049236	2.102370	0.310576
1	1.014335	5.833815	-0.408084
1	2.201368	3.717661	-0.202922
1	-2.739173	3.790076	-0.283406
1	-1.481850	5.865765	-0.439799
1	-1.649908	-0.761540	0.136037
1	0.727399	-0.942320	0.265757
1	-3.472447	1.867805	-1.042865
1	-3.526898	2.029806	0.714476
1	-3.695256	-0.468679	0.944482
1	-3.645905	-0.631987	-0.819597
1	-5.728306	0.777529	-1.006862
1	-5.775001	0.950855	0.746973
1	-6.213918	-1.228106	-2.024563

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  1         -7.529847   -3.351483   -1.932003
  1         -8.288342   -4.207135    0.306694
  1         -7.690084   -2.894924    2.365433
  1         -6.367471   -0.789761    2.107242

 SCF Done:  E(RB+HF-LYP) =  -1567.78722272

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#n b3lyp/6-31g*

conformation 3

2,1
  6         -7.092128   -0.487084    1.531177
  7         -6.738499    0.024424    0.325233
  6         -7.451991   -0.275069   -0.789409
  6         -8.554819   -1.108926   -0.721609
  6         -8.932569   -1.643460    0.513082
  6         -8.186843   -1.325429    1.651465
  6         -5.545320    0.914744    0.222172
  6         -4.251234    0.125125   -0.039760
  6         -3.080811    1.111266   -0.170271
  7         -1.751829    0.502893   -0.359304
  6         -0.630122    1.343156   -0.439919
  6          0.670836    0.777154   -0.612060
  6          0.849014   -0.675654   -0.636231
  6         -0.368081   -1.423390   -0.723633
  6         -1.586289   -0.838415   -0.566366
  6         -0.779468    2.744044   -0.396868
  6          0.311634    3.577918   -0.585264
  6          1.578555    3.038722   -0.842233
  6          1.742946    1.664986   -0.851514
  6          2.047826   -1.397045   -0.671230
  6          3.390458   -1.076102   -0.345176
  7          3.867157   -0.305734    0.663484
  6          5.270389   -0.239142    0.740975
  6          5.898092   -1.048792   -0.218831
 16          4.696224   -1.826447   -1.237068
  6          7.287676   -1.147647   -0.286514
  6          8.038383   -0.411700    0.627094
  6          7.413539    0.403789    1.583447
  6          6.026672    0.502167    1.654210
  6          3.027373    0.235652    1.734697
  1          7.769181   -1.776734   -1.027895
  1          9.121512   -0.468978    0.595170
  1          8.020397    0.972023    2.280828
  1          5.556671    1.144136    2.391140
  1          3.531993    0.067065    2.687986
  1          2.850701    1.304861    1.592912
  1          2.075473   -0.294329    1.733698
  1          1.947132   -2.412438   -1.048217
  1          2.421207    3.691337   -1.045963
  1          2.717203    1.253533   -1.085533
  1         -1.750339    3.195939   -0.241792
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  1          0.169604    4.653845   -0.561885
  1         -2.482166   -1.442052   -0.575297
  1         -0.329257   -2.499272   -0.852302
  1         -3.275357    1.785661   -1.014051
  1         -3.036654    1.729309    0.734380
  1         -4.079570   -0.575124    0.786007
  1         -4.371818   -0.461431   -0.957541
  1         -5.748657    1.626442   -0.581762
  1         -5.488215    1.479595    1.155792
  1         -7.116372    0.179191   -1.714438
  1         -9.111009   -1.324607   -1.627176
  1         -9.798905   -2.293300    0.588136
  1         -8.451201   -1.713059    2.629084
  1         -6.481259   -0.194749    2.377329

 SCF Done:  E(RB+HF-LYP) =  -1567.77622330

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#n b3lyp/6-31g*

conformation 4

2,1
  6         -6.467360   -1.739670    0.999190
  7         -6.065709   -1.082004   -0.117523
  6         -6.335605   -1.582156   -1.349781
  6         -7.024676   -2.773717   -1.495092
  6         -7.445657   -3.463305   -0.354758
  6         -7.159333   -2.935054    0.906895
  6         -5.315474    0.201818    0.008896
  6         -3.791865   -0.009358    0.052034
  6         -3.110070    1.359684    0.192951
  7         -1.636597    1.354421    0.159422
  6         -0.961896    2.588766    0.136227
  6          0.461153    2.611805    0.048840
  6          1.226033    1.364888   -0.026053
  6          0.453209    0.170289    0.096416
  6         -0.909482    0.202506    0.162430
  6         -1.678384    3.799317    0.210701
  6         -1.011398    5.014442    0.204927
  6          0.387299    5.054192    0.143248
  6          1.099617    3.870966    0.074184
  6          2.598534    1.373712   -0.299449
  6          3.524420    0.304857   -0.249808
  7          3.612831   -0.703950    0.654749
  6          4.669875   -1.605379    0.425488
  6          5.460695   -1.236218   -0.673680
 16          4.814132    0.212318   -1.429575
  6          6.580101   -1.981378   -1.043259
  6          6.889332   -3.111337   -0.289605
  6          6.097502   -3.485486    0.806755
  6          4.981047   -2.741153    1.178824
  6          2.891069   -0.714901    1.931224
  1          7.191603   -1.690310   -1.890969
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  1          7.754751   -3.709107   -0.556467
  1          6.357044   -4.371380    1.377169
  1          4.373375   -3.044726    2.024351
  1          2.092716   -1.462522    1.931105
  1          3.601822   -0.946672    2.727210
  1          2.466780    0.272850    2.105615
  1          3.007805    2.274226   -0.743009
  1          0.910193    6.004563    0.164194
  1          2.182187    3.913970    0.067732
  1         -2.757697    3.806340    0.285741
  1         -1.582314    5.935627    0.265551
  1         -1.470114   -0.721397    0.188319
  1          0.927259   -0.800263    0.026348
  1         -3.451301    2.003760   -0.625411
  1         -3.433243    1.828948    1.130874
  1         -3.544280   -0.663752    0.895640
  1         -3.468701   -0.509347   -0.868356
  1         -5.607476    0.824619   -0.840106
  1         -5.676297    0.692249    0.916251
  1         -5.994386   -0.995202   -2.194607
  1         -7.234142   -3.145223   -2.492099
  1         -7.994812   -4.395064   -0.448187
  1         -7.475672   -3.434420    1.815991
  1         -6.227003   -1.272888    1.947322

 SCF Done:  E(RB+HF-LYP) =  -1567.77932600

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