Electronic Supplementary Material (ESI) for Photochemical & Photobiological Science
This journal is © The Royal Society of Chemistry and Owner Societies 2013

Supporting information for: Exciplexes and conical intersections lead to fluorescence quenching in π-stacked dimers of 2-aminopurine with natural purine nucleobases

JingXin Liang, Quynh L. Nguyen, and Spiridoula Matsika*

Department of Chemistry, Temple University, Philadelphia, PA 19122 USA

E-mail: smatsika@temple.edu

In this file additional information is given about linear interpolation paths, vertical excitation energies with oscillator strengths, redox potentials, attachment/detachment densities and dipole moments to characterize excited states and geometries.

Linear Interpolation paths

Figures S1 and S2 provide LIIC paths for 5′-A2AP-3′, 5′-G2AP-3′, 5′-2APA-3′ and 5′-2APG-3′, using RI-CIS(D)/aug-cc-pVDZ.

*To whom correspondence should be addressed

This journal is © The Royal Society of Chemistry and Owner Societies 2013

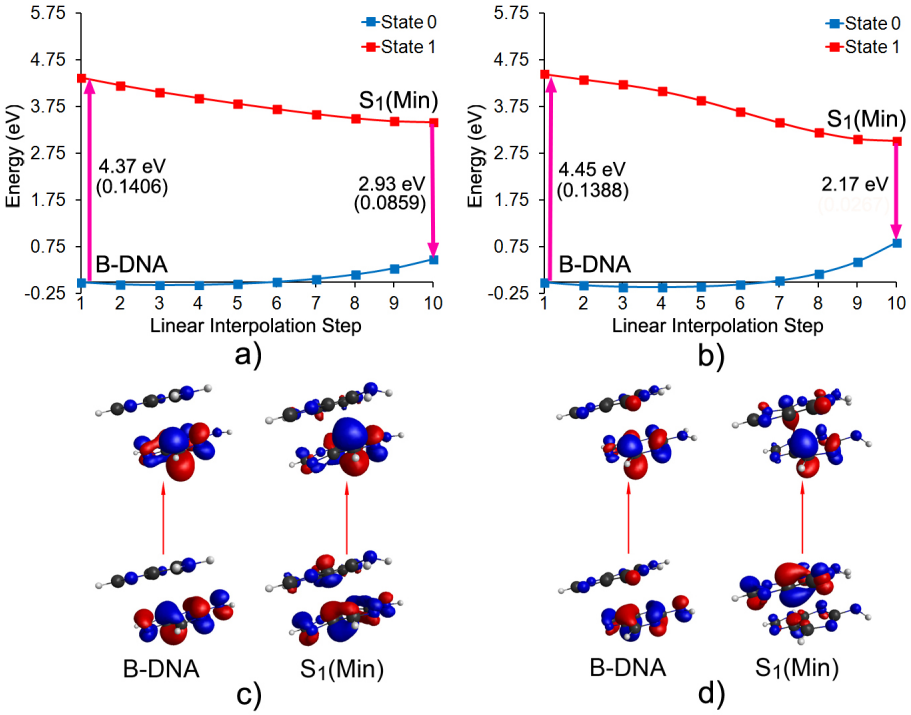

Figure S1: Energies of the S_0 and S_1 states along the LIIC path connecting B-DNA to S_1(Min) for a) 5′-A2AP-3′ and b) 5′-G2AP-3′. The vertical excitation energies at B-DNA and vertical emission energies at S_1(Min) along with oscillator strengths are also shown. Natural orbitals describing the S_1 state at the FC region and at the S_1 optimized minima for (c) 5′-A2AP-3′ and (d) 5′-G2AP-3′.

This journal is © The Royal Society of Chemistry and Owner Societies 2013

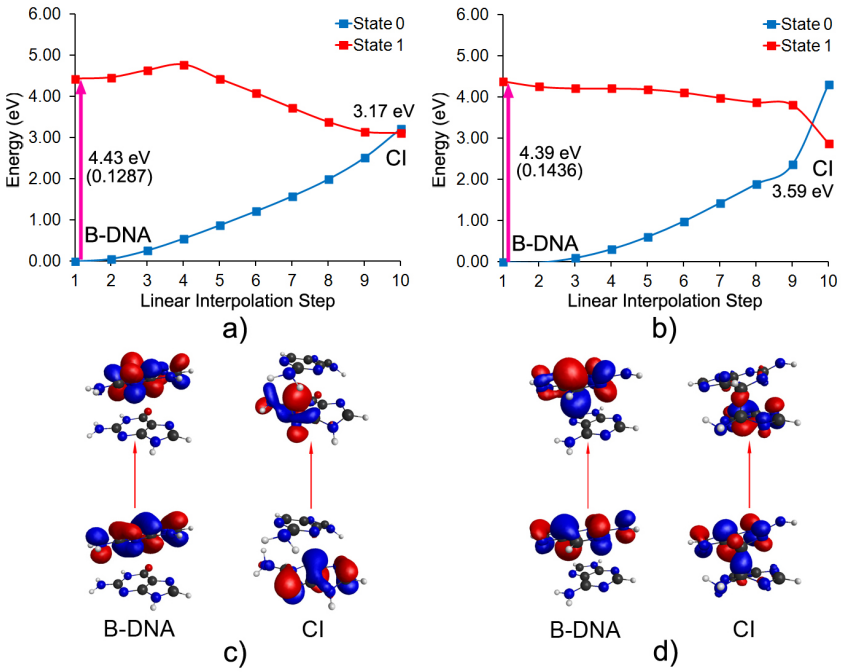

Figure S2: Energies of the S_0 and S_1 states along the LIIC path connecting B-DNA and CI for (a) 5′-2APG-3′ and (b) 5′-2APA-3′. The vertical excitation energies and oscillator strengths along with the energies at the CI are also shown. The energies of S_0 and S_1 are not necessarily equal here since a different method has been used for the CI optimization. The average of the S_0 and S_1 energies is used as the CI energy in this case. Natural orbitals describing the S_1 state of (c) 5′-2APG-3′ and (d) 5′-2APA-3′ at the FC region and at the S_1-S_0 CI are also shown.

This journal is © The Royal Society of Chemistry and Owner Societies 2013

Characterization of the charge-transfer at the CI

Attachment and detachment densities were calculated for the three bonded exciplex structures using CIS/cc-pVDZ and the QChem computational package.

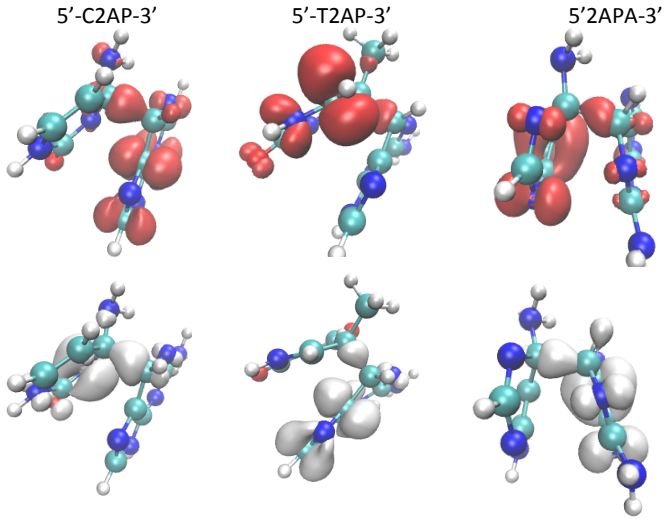

Figure S3: Attachment (top) and detachment (bottom) densities characterizing the S_0 -> S_1 transitions at the CIs for 5′-C2AP-3′, 5′-T2AP-3′ and 5′-2APA-3′ calculated using CIS/cc-pVDZ. In all structures 2AP is on the right side of the structure and the natural base on the left side.

This journal is © The Royal Society of Chemistry and Owner Societies 2013

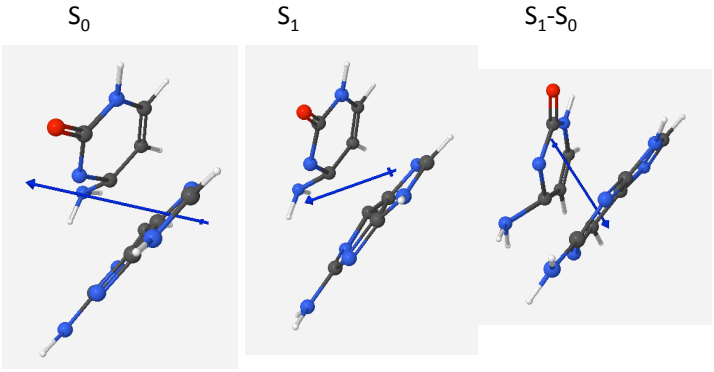

Figure S4: Dipole moment of the ground state S_0, dipole moment of the first excited state S_1 and difference of the dipole moments of S_1 minus S_0 for 5′-C2AP-3′ at geometry 9 of the LIIC path calculated using CIS/cc-pVDZ.

This journal is © The Royal Society of Chemistry and Owner Societies 2013

Vertical excitation energies

Tables S1 and S2 present vertical excitation energies for monomers and dimers in this study.

Table S1: The first ten vertical excitation energies (E in eV) of the monomers and dimers in B-DNA geometries studied in this work calculated at the RI-CIS(D)/aug-cc-pVDZ level of theory. The characters of the excited state transitions are assigned using natural orbitals obtained at the CIS/aug-cc-pVDZ level of theory. Oscillator strengths (f) are given at the CIS/aug-cc-pVDZ level.

		2AP	A	G	5′-A2AP-3′	5′-2APA-3′	5′-G2AP-3′	5′-2APG-3′
S_1	E	4.45	5.36	4.90	4.37	4.39	4.45	4.43
	f	0.3141	0.0002	0.0001	0.2036	0.1984	0.1902	0.1994
	Transition	$\pi\pi^*$	$n_N\pi^*$	$\pi\sigma^*$	$\pi_{2AP}\pi^*_{2AP}$	$\pi_{2AP}\pi^*_{2AP}$	$\pi_{2AP}\pi^*_{2AP}$	$\pi_{2AP}\pi^*_{2AP}$
S_2	E	4.77	5.40	5.08	4.89	4.84	4.74	4.75
	f	0.0057	0.0369	0.2388	0.0165	0.0077	0.0043	0.0076
	Transition	$n_N\pi^*$	$\pi\pi^*$	$\pi\pi^*$	$n_{N2AP}\pi^*_{2AP}$	$n_{N2AP}\pi^*_{2AP}$	$\pi_G\sigma^*_G$	$n_{N2AP}\pi^*_{2AP}$
S_3	E	5.20	5.40	5.11	5.06	4.99	4.74	4.85
	f	0.0003	0.4221	0.0088	0.0013	0.0003	0.0167	0.0012
	Transition	$\pi\sigma^*$	$\pi\pi^*$	$\pi\sigma^*$	$\pi_{2AP}\sigma^*_{2AP}$	$\pi_{2AP}\sigma^*_{2AP}$	$n_{N2AP}\pi^*_{2AP}$	$\pi_G\sigma^*_G$
S_4	E	5.41	5.49	5.43	5.22	5.22	4.86	4.89
	f	0.0103	0.0077	0.0002	0.0371	0.0282	0.0384	0.0028
	Transition	$\pi\sigma^*$	$\pi\sigma^*$	$n_O\pi^*$	$\pi_{2AP}\sigma^*_{2AP}$	$\pi_{2AP}\sigma^*_{2AP}$	$\pi_G\sigma^*_G$	$\pi_{2AP}\sigma^*_{2AP}$
S_5	E	5.73	5.72	5.71	5.28	5.26	4.98	4.94
	f	0.1507	0.0010	0.3817	0.2486	0.0411	0.1777	0.0232
	Transition	$\pi\pi^*$	$\pi\sigma^*$	$\pi\pi^*$	$\pi_A\pi^*_A$	$\pi_A\sigma^*_A$	$\pi_G\pi^*_G$	$\pi_G\sigma^*_G$
S_6	E	5.84	6.24	5.81	5.29	5.27	5.00	5.04
	f	0.0003	0.0024	0.0001	0.0350	0.0006	0.0017	0.0764
	Transition	$\pi\sigma^*$	$\pi\sigma^*$	$\pi\sigma^*$	$\pi_A\pi^*_A$	$n_{NA}\pi^*_A$	$\pi_{2AP}\sigma^*_{2AP}$	$\pi_{2AP,G}\pi^*_G$
S_7	E	6.17	6.41	5.88	5.33	5.31	5.10	5.06
	f	0.0011	0.0004	0.0018	0.0280	0.3198	0.0222	0.0728
	Transition	$\pi\sigma^*$	$\pi\sigma^*$	$\pi\sigma^*$	$\pi_A\sigma^*_A$	$\pi_A\pi^*_A$	$\pi_{2AP}\sigma^*_{2AP}$	$\pi_{G,2AP}\pi^*_G$
S_8	E	6.37	6.59	6.07	5.40	5.32	5.42	5.37
	f	0.0003	0.0036	0.0008	0.0026	0.0137	0.0371	0.0002
	Transition	$\pi\sigma^*$	$\pi\sigma^*$	$\pi\sigma^*$	$n_{NA}\pi^*_A$	$\pi_A\pi^*_A$	$\pi_G\sigma^*_G$	$n_{OG}\pi^*_G$
S_9	E	6.47	6.60	6.21	5.44	5.43	5.43	5.40
	f	0.0159	0.0148	0.1491	0.0947	0.0036	0.0133	0.2144
	Transition	$\pi\sigma^*$	$\pi\sigma^*$	$\pi\pi^*$	$\pi_{2AP}\pi^*_{2AP}$	$\pi_{2AP}\sigma^*_{2AP}$	$\pi_G\pi^*_{2AP}$	$\pi_G\pi^*_G$
S_{10}	E	6.62	6.88	6.58	5.46	5.62	5.46	5.52
	f	0.0001	0.0044	0.0050	0.0116	0.0207	0.0736	0.0765
	Transition	$\pi\sigma^*$	$\pi\sigma^*$	$\pi\sigma^*$	$\pi_{2AP}\sigma^*_{2AP}$	$\pi_A\sigma^*_A$	$\pi_G\sigma^*_G$	$\pi_{2AP}\pi^*_{2AP}$

This journal is © The Royal Society of Chemistry and Owner Societies 2013

Table S2: Vertical excitation energies (E in eV) and oscillator strengths (f) of the monomers and dimers in B-DNA geometries studied in this work calculated at the CIS(2′)/cc-pVDZ+Diff level of theory.

		2AP	A	G	5′-A2AP-3′	5′-2APA-3′	5′-G2AP-3′	5′-2APG-3′
S_1	E	4.79	5.71	5.34	4.71	4.72	4.81	4.76
	f	0.1992	0.0013	0.0025	0.1406	0.1436	0.1388	0.1287
S_2	E	5.07	5.71	5.47	5.00	5.02	5.04	5.12
	f	0.0039	0.3605	0.2418	0.0055	0.0056	0.0050	0.0043
S_3	E	5.70	5.77	5.71	5.58	5.50	5.18	5.31
	f	0.0032	0.0290	0.0001	0.0002	0.0255	0.0267	0.0031
S_4	E	6.01	5.97	5.77	5.64	5.57	5.36	5.38
	f	0.0123	0.0113	0.0073	0.1243	0.1800	0.1141	0.1532
S_5	E	6.01	6.31	5.97	5.66	5.62	5.50	5.45
	f	0.1423	0.0012	0.4299	0.1331	0.0242	0.0164	0.0074
S_6	E	6.55	6.38	6.44	5.67	5.70	5.53	5.56
	f	0.0034	0.0040	0.0001	0.0030	0.0331	0.0063	0.0128
S_7	E	6.56	6.82	6.5	5.79	5.80	5.67	5.65
	f	0.0014	0.0034	0.0014	0.0518	0.0189	0.0001	0.0003

This journal is © The Royal Society of Chemistry and Owner Societies 2013

Redox potentials

The vertical ionization potentials of the monomers 2AP, C, T, and A were calculated at their equilibrium positions and at the CI geometries using B3LYP/6-31++G(d,p). The electron affinities of the same bases at the same geometries were calculated using B3LYP/6-311++G(2df,p). These results are further used to calculate redox potentials using the fitted expressions by Crespo-Hernandez et al. (J. Phys. Chem B, 111, 5386-53-95, 2007). The expressions

$$E^o_{ox} = -2.59 + 0.56 \times IP \quad (1)$$

$$E^o_{red} = -2.09 + 0.81 \times EA \quad (2)$$

taken from Crespo-Hernandez et al. were used to obtain the oxidation E^o_{ox} and reduction E^o_{red} potentials. These authors fitted the IPs vs. oxidation potentials and the EAs vs. reduction potentials of several bases and other organic molecules and obtained a linear expression which can be used for other similar molecules to obtain the redox properties after the IP and EA have been calculated. The redox potential for 2AP in its excited state is obtained by

$$E^{o*}_{ox} = E^o_{ox} - E_{00} \quad (3)$$

$$E^{o*}_{red} = E^o_{red} + E_{00}, \quad (4)$$

where $E_{00} = 3.7$ eV is the excitation energy of 2AP (see J. Phys. Chem. B, 114, 10573-10580, (2010)). Finally, the free energy for oxidation of the natural nucleobase (T, C, A) ΔG^o_{NBO} and the free energy for reduction of the natural nucleobases ΔG^o_{NBR} can be calculated using the Rehn-Weller equations (Isr. J. Chem., 8, 259-271, 1970)

$$\Delta G^o_{NBO} = E^{o,base}_{ox} - E^{o,2AP}_{red} \quad (5)$$

$$\Delta G^o_{NBR} = E^{o,2AP}_{ox} - E^{o,base}_{red} \quad (6)$$

This journal is © The Royal Society of Chemistry and Owner Societies 2013

For the equilibrium geometries the redox potentials of excited 2AP are used while for the conical intersections the values of the ground state at that geometry. At the conical intersection the energies between the ground and excited states are very close, so E_{00} theoretically should be 0. This is not exactly true, because the conical intersection is for the dimer and not for the monomer. The results are given in Table S3. The values for the redox potentials of the natural bases at their equilibrium positions are the same as those reported by Crespo-Hernandez et al. since we used identical methods. The values of the redox potentials for excited 2AP are similar to the values reported by Narayanan et al.(J. Phys. Chem. B, 114, 10573-10580, (2010)) By comparing the values of ΔG^o_{NBO} and ΔG^o_{NBR} in each dimer one can see that initially using BDNA structures 2AP* will reduce C and T and it will oxidize A. At the CIs the values predict that 2AP will reduce all three bases.

Table S3: IPs, EAs, redox potentials for the monomer bases 2AP, A, T, C at their equilibrium position and at the CIs. ΔG^o_{NBO} and ΔG^o_{NBR} are also shown. All values are given in eV. The properties of 2AP in B-DNA are the same since we use the equilibrium structure of 2AP. At the CI however 2AP has a different geometry on each dimer, and thus different properties.

		EA	IP	E^o_{red}	E^o_{ox}	E^{o*}_{red}	E^{o*}_{ox}	ΔG^o_{NBO}	ΔG^o_{NBR}
BDNA									
2APA	2AP	-0.46	7.97	-2.46	1.87	1.24	-1.83	0.79	0.87
	A	-0.76	8.26	-2.71	2.04				
C2AP	2AP	-0.46	7.97	-2.46	1.87	1.24	-1.83	1.04	0.73
	C	-0.58	8.69	-2.56	2.28				
T2AP	2AP	-0.46	7.97	-2.46	1.87	1.24	-1.83	1.22	0.49
	T	-0.29	9.01	-2.32	2.46				
CI									
2APA	2AP	0.74	7.76	-1.50	1.76			3.46	3.26
	A	0.73	8.13	-1.50	1.96				
C2AP	2AP	0.41	7.74	-1.76	1.74			3.88	3.10
	C	0.91	8.42	-1.36	2.12				
T2AP	2AP	0.77	7.74	-1.47	1.74			3.74	3.35
	T	0.60	8.67	-1.61	2.26				

This journal is © The Royal Society of Chemistry and Owner Societies 2013

Geometries

Tables S4, S5, S6 present bond lengths for various structures in this work. Tables S7-S18 are cartesian coordinates. The Cartesian coordinates for the geometries of the dimers in the following important geometries are provided: B-DNA, fluorescence maxima, S_1(Min), and conical intersections. The S_0 and S_1 energies in Hartree are also given at the RI-CIS(D)/aug-cc-pVDZ and CIS(2')/cc-pVDZ+Diff levels.

This journal is © The Royal Society of Chemistry and Owner Societies 2013

Table S4: Bond lengths of 2AP, adenine and guanine in B-DNA, the $\pi\pi^*$ minimum of monomer 2AP and S_1 minima of 5′-A2AP-3′ and 5′-G2AP-3′. "△ Bond" for 2AP denotes the difference in bond lengths between the 2AP $\pi\pi^*$ and S_1(Min) geometries. "△ Bond" for adenine and guanine denotes the difference between the initial B-DNA and final S_1(Min) geometries. "Average △" denotes the average deviations with the absolute deviations given in parentheses.

Bond	B-DNA	2AP $\pi\pi^*$	5′-G2AP-3′ S_1(Min)	△ Bond	5′-A2AP-3′ S_1(Min)	△ Bond
N^1C^2 (2AP)	1.363	1.352	1.324	-0.028	1.359	0.007
C^2N^3 (2AP)	1.347	1.388	1.382	-0.006	1.388	0.000
N^3C^4 (2AP)	1.335	1.364	1.362	-0.002	1.356	0.008
C^4C^5 (2AP)	1.407	1.428	1.412	-0.016	1.421	0.007
C^5C^6 (2AP)	1.397	1.465	1.448	-0.017	1.486	-0.021
C^6N^1 (2AP)	1.333	1.397	1.401	0.004	1.388	0.009
C^5N^7 (2AP)	1.386	1.361	1.379	0.018	1.356	0.005
N^7C^8 (2AP)	1.320	1.357	1.350	-0.007	1.363	-0.006
C^8N^9 (2AP)	1.379	1.361	1.375	0.014	1.362	-0.001
N^9C^4 (2AP)	1.375	1.388	1.384	-0.004	1.384	0.004
C^2N^{10} (2AP)	1.362	1.358	1.425	0.067	1.351	0.007
Average △				0.002 (0.017)		0.000 (0.007)
N^1C^2 (A)	1.352				1.368	-0.016
C^2N^3 (A)	1.339				1.342	-0.003
N^3C^4 (A)	1.344				1.347	-0.003
C^4C^5 (A)	1.398				1.418	-0.020
C^5C^6 (A)	1.410				1.418	-0.008
C^6N^1 (A)	1.342				1.341	0.001
C^5N^7 (A)	1.381				1.382	-0.001
N^7C^8 (A)	1.326				1.330	-0.004
C^8N^9 (A)	1.373				1.381	-0.008
N^9C^4 (A)	1.377				1.379	-0.002
C^6N^{10} (A)	1.352				1.374	-0.022
Average △						-0.008 (0.008)
N^1C^2 (G)	1.374		1.368	0.006		
C^2N^3 (G)	1.314		1.362	-0.048		
N^3C^4 (G)	1.365		1.321	0.044		
C^4C^5 (G)	1.393		1.470	-0.077		
C^5C^6 (G)	1.439		1.462	-0.023		
C^6N^1 (G)	1.432		1.427	0.005		
C^5N^7 (G)	1.379		1.357	0.022		
N^7C^8 (G)	1.323		1.338	-0.015		
C^8N^9 (G)	1.376		1.379	-0.003		
N^9C^4 (G)	1.369		1.383	-0.014		
C^6O^{11} (G)	1.225		1.217	0.008		
C^2N^{10} (G)	1.363		1.369	-0.006		
Average △				-0.008 (0.023)		

This journal is © The Royal Society of Chemistry and Owner Societies 2013

Table S5: Bond lengths of 2AP and guanine in 5′-2APG-3′. "△ Bond" denotes the difference in bond lengths between B-DNA and CI structure. "Average △" denotes the average deviations with the absolute deviations given in parentheses.

Bond	5′-2APG-3′ B-DNA	5′-2APG-3′ CI	△ Bond
N^1C^2 (2AP)	1.363	1.367	-0.004
C^2N^3 (2AP)	1.347	1.348	-0.001
N^3C^4 (2AP)	1.335	1.341	-0.006
C^4C^5 (2AP)	1.407	1.416	-0.009
C^5C^6 (2AP)	1.397	1.407	-0.010
C^6N^1 (2AP)	1.333	1.341	-0.008
C^5N^7 (2AP)	1.386	1.386	0.000
N^7C^8 (2AP)	1.320	1.328	-0.008
C^8N^9 (2AP)	1.379	1.382	-0.003
N^9C^4 (2AP)	1.375	1.374	0.001
C^2N^{10} (2AP)	1.362	1.392	-0.030
Average △			-0.007 (0.007)
N^1C^2 (G)	1.374	1.435	-0.061
C^2N^3 (G)	1.314	1.505	-0.191
N^3C^4 (G)	1.365	1.300	0.065
C^4C^5 (G)	1.393	1.461	-0.068
C^5C^6 (G)	1.439	1.488	-0.049
C^6N^1 (G)	1.432	1.429	0.003
C^5N^7 (G)	1.379	1.367	0.012
N^7C^8 (G)	1.323	1.340	-0.017
C^8N^9 (G)	1.376	1.369	0.007
N^9C^4 (G)	1.369	1.399	-0.030
C^6O^{11} (G)	1.225	1.223	0.002
C^2N^{10} (G)	1.363	1.404	-0.041
Average △			-0.031 (0.046)

This journal is © The Royal Society of Chemistry and Owner Societies 2013

Table S6: Bond lengths of 2AP and adenine in 5′-2APA-3′. "△ Bond" denotes the difference in bond lengths between B-DNA and CI structure. "Average △" denotes the average deviations with the absolute deviations given in parentheses.

Bond	5′-2APA-3′ B-DNA	5′-2APA-3′ CI	△ Bond
N^1C^2 (2AP)	1.363	1.337	0.026
C^2N^3 (2AP)	1.347	1.402	0.055
N^3C^4 (2AP)	1.335	1.337	0.002
C^4C^5 (2AP)	1.407	1.431	0.024
C^5C^6 (2AP)	1.397	1.512	0.115
C^6N^1 (2AP)	1.333	1.439	0.106
C^5N^7 (2AP)	1.386	1.362	0.024
N^7C^8 (2AP)	1.320	1.346	0.026
C^8N^9 (2AP)	1.379	1.379	0.000
N^9C^4 (2AP)	1.375	1.386	0.011
C^2N^{10} (2AP)	1.362	1.359	0.003
Average △			-0.026 (0.036)
N^1C^2 (A)	1.352	1.305	0.047
C^2N^3 (A)	1.339	1.437	-0.098
N^3C^4 (A)	1.344	1.336	0.008
C^4C^5 (A)	1.398	1.428	-0.030
C^5C^6 (A)	1.410	1.499	-0.089
C^6N^1 (A)	1.342	1.448	-0.106
C^5N^7 (A)	1.381	1.382	-0.001
N^7C^8 (A)	1.326	1.340	-0.014
C^8N^9 (A)	1.373	1.382	-0.009
N^9C^4 (A)	1.377	1.388	-0.011
C^6N^{10} (A)	1.352	1.441	-0.089
Average △			-0.036 (0.046)

This journal is © The Royal Society of Chemistry and Owner Societies 2013

Table S7: 5′-A2AP-3′ Absorption Geometry. RI-CIS(D): $E(S_0)$ = -932.26543, $E(S_1)$ = -932.10482. CIS(2'): $E(S_0)$ = -932.08203, $E(S_1)$ = -931.90889

N	-2.235410	-2.428800	-1.147460
H	-1.936320	-3.387320	-1.144750
H	-2.833920	-2.078970	-1.873030
C	-1.818650	-1.609030	-0.156410
C	-2.201300	-0.253130	-0.103030
N	-2.997640	0.513690	-0.930750
C	-2.975440	1.706480	-0.352960
H	-3.491680	2.579010	-0.718040
N	-2.215320	1.747120	0.790080
C	-1.700440	0.483680	0.974530
N	-0.899020	0.039230	1.957040
C	-0.614460	-1.257610	1.785530
H	0.029180	-1.703930	2.533770
H	-2.056090	2.542020	1.388790
N	-1.018370	-2.096190	0.804900
C	1.038340	-0.207850	-1.658960
C	1.281310	0.989900	-0.982040
C	2.114430	0.887140	0.146890
H	2.680210	-3.315580	-0.256860
N	2.684440	-0.221090	0.625360
C	2.368800	-1.298510	-0.118500
N	1.579810	-1.347960	-1.229210
C	1.441120	2.960130	-0.201950
N	2.202920	2.170290	0.633270
N	2.894150	-2.492300	0.273670
H	0.412100	-0.254310	-2.542600
N	0.867100	2.296270	-1.187840
H	1.345610	4.021720	-0.034080
H	2.725670	2.461920	1.442480
H	3.484370	-2.533720	1.082330

This journal is © The Royal Society of Chemistry and Owner Societies 2013

Table S8: 5′-A2AP-3′ Fluorescence Maximum. RI-CIS(D): $E(S_0)$ = -932.25246, $E(S_1)$ = -932.11631. CIS(2'): $E(S_0)$ = -932.06906, $E(S_1)$ = -931.92361

N	-2.235410	-2.428800	-1.147460
H	-1.936320	-3.387320	-1.144750
H	-2.833920	-2.078970	-1.873030
C	-1.818650	-1.609030	-0.156410
C	-2.201300	-0.253130	-0.103030
N	-2.997640	0.513690	-0.930750
C	-2.975440	1.706480	-0.352960
H	-3.491680	2.579010	-0.718040
N	-2.215320	1.747120	0.790080
C	-1.700440	0.483680	0.974530
N	-0.899020	0.039230	1.957040
C	-0.614460	-1.257610	1.785530
H	0.029180	-1.703930	2.533770
H	-2.056090	2.542020	1.388790
N	-1.018370	-2.096190	0.804900
C	0.988340	-0.237850	-1.738960
C	1.281281	0.984137	-0.984958
C	2.126086	0.878574	0.161024
H	2.686938	-3.309148	-0.247644
N	2.723732	-0.233216	0.677554
C	2.349409	-1.288056	-0.142815
N	1.578977	-1.404409	-1.248078
C	1.463559	2.963096	-0.170915
N	2.212343	2.175110	0.648123
N	2.889568	-2.461541	0.275812
H	0.358934	-0.286642	-2.628359
N	0.879362	2.269262	-1.180532
H	1.357896	4.036648	-0.013969
H	2.739888	2.466523	1.464846
H	3.482703	-2.460080	1.100977

This journal is © The Royal Society of Chemistry and Owner Societies 2013

Table S9: 5′-A2AP-3′ S_1(Min). RI-CIS(D): E(S_0) = -932.24744, E(S_1) = -932.13971. CIS(2'): E(S_0) = -932.05645, E(S_1) = -931.94073

N	-0.660627	-1.986004	1.054660
C	-0.354499	-1.093603	2.045883
N	-0.666547	0.207792	2.142909
C	-1.322882	0.619449	1.040712
C	-1.712410	-0.171638	-0.070283
C	-1.364290	-1.544238	0.001541
N	-2.413392	0.562560	-1.008561
C	-2.425050	1.785676	-0.486849
N	-1.813983	1.874183	0.748962
N	-1.754539	-2.433159	-0.970868
H	-1.112480	-3.220616	-1.044241
H	-1.913382	-1.974962	-1.867225
H	0.202656	-1.515963	2.889114
H	-1.666378	2.716072	1.296060
H	-2.871822	2.659338	-0.962069
N	1.233669	-1.419376	-1.484503
C	1.872886	-1.406572	-0.285512
N	2.062000	-0.431602	0.683458
C	1.522078	0.713593	0.197315
C	0.791883	0.907576	-1.006680
C	0.482207	-0.300459	-1.815186
N	0.505583	2.217579	-1.209444
C	1.007088	2.842591	-0.107224
N	1.616747	1.978043	0.751092
N	2.508756	-2.557845	0.021897
H	2.382494	-3.360706	-0.586820
H	2.915949	-2.650516	0.947380
H	2.049162	2.195105	1.644295
H	0.944349	3.914338	0.083543
H	0.110276	-0.214336	-2.843185

This journal is © The Royal Society of Chemistry and Owner Societies 2013

Table S10: 5′-2APA-3′ Absorption Geometry. RI-CIS(D): $E(S_0)$ = -932.26666, $E(S_1)$ = -932.10537. CIS(2'): $E(S_0)$ = -932.08291, $E(S_1)$ = -931.90959

N	-1.392810	2.110650	0.528180
C	-1.047250	1.918920	-0.776590
N	-1.202030	0.805950	-1.518970
C	-1.768640	-0.176390	-0.814710
C	-2.176470	-0.125790	0.530750
C	-1.955250	1.091890	1.178960
N	-2.727040	-1.330560	0.938120
C	-2.649590	-2.085250	-0.141990
N	-2.083870	-1.449700	-1.227270
N	-0.477270	2.993200	-1.389770
H	-0.346580	3.838700	-0.867210
H	-0.197040	2.926610	-2.349480
H	-1.926640	-1.830360	-2.145690
H	-2.987210	-3.108040	-0.206500
H	-2.227540	1.251130	2.216100
N	1.594540	1.088350	1.665610
C	2.178820	1.659960	0.588640
N	2.496820	1.110210	-0.589860
C	2.152440	-0.188190	-0.616700
C	1.545050	-0.920610	0.407750
C	1.267410	-0.211570	1.594310
N	1.328560	-2.236100	0.047350
C	1.803910	-2.294000	-1.188680
N	2.309190	-1.098520	-1.637550
N	0.682120	-0.804920	2.658860
H	0.504540	-0.260100	3.483410
H	0.431850	-1.775970	2.620430
H	2.420850	2.709690	0.701920
H	2.719000	-0.909340	-2.538630
H	1.808680	-3.176040	-1.807610

This journal is © The Royal Society of Chemistry and Owner Societies 2013

Table S11: 5′-2APA-3′ Fluorescence Maximum. RI-CIS(D): $E(S_0)$ = -932.25359, $E(S_1)$ = -932.11695. CIS(2'): $E(S_0)$ = -932.06989, $E(S_1)$ = -931.92428

C	-1.975250	1.121890	1.268960
C	-2.178642	-0.127829	0.531111
C	-1.763083	-0.175790	-0.833853
H	-0.349434	3.826549	-0.871991
N	-1.182658	0.806372	-1.581197
C	-1.062487	1.906911	-0.744426
N	-1.382784	2.158965	0.544988
C	-2.641507	-2.099352	-0.183746
N	-2.081481	-1.461512	-1.247679
N	-0.491186	2.959817	-1.384030
H	-2.249837	1.282484	2.312211
N	-2.717199	-1.314891	0.921202
H	-2.986179	-3.132217	-0.235732
H	-1.920590	-1.841555	-2.175011
H	-0.220008	2.852093	-2.357460
N	0.682120	-0.804920	2.658860
H	0.504540	-0.260100	3.483410
H	0.431850	-1.775970	2.620430
C	1.267410	-0.211570	1.594310
C	1.545050	-0.920610	0.407750
N	1.328560	-2.236100	0.047350
C	1.803910	-2.294000	-1.188680
H	1.808680	-3.176040	-1.807610
N	2.309190	-1.098520	-1.637550
C	2.152440	-0.188190	-0.616700
N	2.496820	1.110210	-0.589860
C	2.178820	1.659960	0.588640
H	2.420850	2.709690	0.701920
H	2.719000	-0.909340	-2.538630
N	1.594540	1.088350	1.665610

This journal is © The Royal Society of Chemistry and Owner Societies 2013

Table S12: 5′-2APA-3′ Conical Intersection. RI-CIS(D): E(S_0) = -932.10794, E(S_1) = -932.16119. CIS(2'): E(S_0) = -931.97304, E(S_1) = -931.91440

N	-0.578083	1.912954	0.401467
C	-0.751092	1.838378	-0.921960
N	-1.139905	0.789457	-1.767452
C	-1.458609	-0.248213	-0.986758
C	-1.438317	-0.352359	0.440628
C	-0.738048	0.739286	1.217902
N	-1.929901	-1.544039	0.880144
C	-2.230270	-2.209063	-0.251072
N	-1.955583	-1.478671	-1.388017
N	-0.657471	3.013163	-1.599349
H	-0.215907	3.786663	-1.108646
H	-0.590939	2.953973	-2.609153
H	-2.168697	-1.745894	-2.347015
H	-2.650543	-3.215491	-0.293266
H	-1.260023	1.005508	2.159301
N	1.563715	1.105656	1.933383
C	2.055681	1.672269	0.865606
N	2.059153	1.231922	-0.502500
C	1.646804	-0.037778	-0.553209
C	1.036360	-0.791100	0.494545
C	0.637620	0.019668	1.690933
N	0.904368	-2.126426	0.164420
C	1.416293	-2.182329	-1.072359
N	1.835227	-0.962831	-1.570452
N	0.456253	-0.790744	2.868791
H	0.142957	-0.167438	3.618577
H	-0.329934	-1.422381	2.687388
H	2.602576	2.619591	1.011442
H	2.305136	-0.793100	-2.455798
H	1.509729	-3.096817	-1.664346

This journal is © The Royal Society of Chemistry and Owner Societies 2013

Table S13: 5′-G2AP-3′ Absorption Geometry. RI-CIS(D): $E(S_0)$ = -1007.34979, $E(S_1)$ = -1007.18632. CIS(2'): $E(S_0)$ = -1007.14934, $E(S_1)$ = -1006.97263

N	-2.392090	1.448970	0.940990
C	-1.764340	0.234470	0.864520
N	0.415520	-2.113160	2.255150
N	-0.900190	-0.272480	1.791110
N	-0.828740	-2.102610	0.283780
H	0.691300	-1.652890	3.101870
C	-0.459860	-1.459380	1.440740
H	-2.289120	2.112510	1.692640
H	0.784800	-3.019280	2.040400
C	-1.728060	-1.619850	-0.720230
N	-3.086650	0.520800	-0.986820
C	-3.169500	1.571600	-0.187930
H	-0.453220	-3.018010	0.070750
O	-1.963240	-2.309500	-1.705470
C	-2.209180	-0.319270	-0.334090
H	-3.770520	2.447860	-0.368540
C	0.982140	0.356490	-1.836450
C	1.107050	1.409700	-0.927060
C	1.953920	1.163740	0.169060
H	2.939950	-2.790250	-1.071810
N	2.636530	0.044420	0.420440
C	2.426670	-0.885290	-0.531090
N	1.639250	-0.786840	-1.639640
C	1.071650	3.185880	0.239070
N	1.915210	2.323350	0.907090
N	3.072940	-2.074860	-0.382200
H	0.357860	0.428030	-2.719800
N	0.561200	2.682180	-0.869050
H	0.870190	4.175990	0.617680
H	2.411180	2.495320	1.765900
H	3.669770	-2.220360	0.409400

This journal is © The Royal Society of Chemistry and Owner Societies 2013

Table S14: 5′-G2AP-3′ Fluorescence Maximum. RI-CIS(D): E(S_0) = -1007.33735, E(S_1) = -1007.19798. CIS(2'): E(S_0) = -1007.13692, E(S_1) = -1006.98760

N	-2.392090	1.448970	0.940990
C	-1.764340	0.234470	0.864520
N	0.415520	-2.113160	2.255150
N	-0.900190	-0.272480	1.791110
N	-0.828740	-2.102610	0.283780
H	0.691300	-1.652890	3.101870
C	-0.459860	-1.459380	1.440740
H	-2.289120	2.112510	1.692640
H	0.784800	-3.019280	2.040400
C	-1.728060	-1.619850	-0.720230
N	-3.086650	0.520800	-0.986820
C	-3.169500	1.571600	-0.187930
H	-0.453220	-3.018010	0.070750
O	-1.963240	-2.309500	-1.705470
C	-2.209180	-0.319270	-0.334090
H	-3.770520	2.447860	-0.368540
C	0.932140	0.336490	-1.916450
C	1.106287	1.403448	-0.927077
C	1.967310	1.153591	0.183926
H	2.945953	-2.785871	-1.057639
N	2.678949	0.026304	0.471769
C	2.406336	-0.872611	-0.549723
N	1.642133	-0.839652	-1.664899
C	1.094180	3.184368	0.273067
N	1.925986	2.326404	0.924542
N	3.066190	-2.045947	-0.370939
H	0.303254	0.405730	-2.804859
N	0.574574	2.654259	-0.863160
H	0.881667	4.187546	0.642909
H	2.428334	2.497932	1.789694
H	3.663234	-2.151928	0.444546

This journal is © The Royal Society of Chemistry and Owner Societies 2013

Table S15: 5′-G2AP-3′ S_1(Min). RI-CIS(D): $E(S_0)$ = -1007.31864, $E(S_1)$ = -1007.23900. CIS(2'): $E(S_0)$ = -1007.10885, $E(S_1)$ = -1007.02212

N	-1.942091	1.448970	0.900990
C	-1.266136	0.245789	0.812489
N	0.618091	-2.326954	2.244834
N	-0.678970	-0.413590	1.795567
N	-0.527084	-2.212983	0.217437
H	1.008425	-1.699208	2.948493
C	-0.146306	-1.594805	1.377001
H	-1.673967	2.195928	1.541561
H	1.381434	-2.784126	1.728439
C	-1.316085	-1.648683	-0.829600
N	-2.430728	0.621734	-1.176269
C	-2.510870	1.660799	-0.337046
H	-0.100421	-3.110079	-0.015636
O	-1.672250	-2.321195	-1.778860
C	-1.623497	-0.252926	-0.523724
H	-3.026248	2.592456	-0.571303
C	0.549597	0.197393	-1.792794
C	0.652543	1.310262	-0.872776
C	1.359253	1.055655	0.323386
H	2.830919	-2.684265	-0.939727
N	1.951618	-0.107759	0.709911
C	1.969607	-0.972382	-0.368308
N	1.400747	-0.891482	-1.561861
C	0.545287	3.121011	0.284318
N	1.260528	2.229774	1.048631
N	2.613014	-2.206479	-0.061989
H	0.124883	0.304458	-2.797431
N	0.153058	2.595296	-0.895905
H	0.374871	4.151304	0.600583
H	1.717260	2.412625	1.936851
H	3.479758	-2.022251	0.449590

This journal is © The Royal Society of Chemistry and Owner Societies 2013

Table S16: 5′-2APG-3′ Absorption Geometry. RI-CIS(D): $E(S_0)$ = -1007.34972, $E(S_1)$ = -1007.18689. CIS(2'): $E(S_0)$ = -1007.14943, $E(S_1)$ = -1006.97433

C	1.410050	-1.863170	1.108010
C	2.182430	-0.818210	0.594820
C	1.925340	-0.479540	-0.746200
H	-1.101730	-3.434740	-1.245860
N	1.033080	-1.047730	-1.560490
C	0.360000	-2.036400	-0.941380
N	0.502170	-2.470250	0.343210
C	3.506540	0.780380	0.139680
N	2.791170	0.553750	-1.017350
N	-0.581320	-2.692940	-1.674730
H	1.517930	-2.213080	2.128350
N	3.176620	-0.019170	1.136710
H	4.260560	1.550620	0.189000
H	2.875640	1.040700	-1.894200
H	-0.741800	-2.428830	-2.627890
N	-1.230660	2.251070	-1.575950
C	-1.555690	1.310840	-0.635080
N	-3.440490	-1.476690	0.299910
N	-2.474220	0.313990	-0.792940
N	-1.827020	-0.225060	1.424510
H	-3.985190	-1.635980	-0.526380
C	-2.566740	-0.431080	0.284890
H	-1.632870	2.317160	-2.497770
H	-3.554190	-2.078750	1.092470
C	-0.852970	0.800920	1.644700
N	0.047730	2.711230	0.216900
C	-0.269500	3.062720	-1.018050
H	-1.945080	-0.835750	2.222930
O	-0.268310	0.860870	2.719970
C	-0.753400	1.615950	0.462370
H	0.157580	3.889760	-1.561460

This journal is © The Royal Society of Chemistry and Owner Societies 2013

Table S17: 5′-2APG-3′ Fluorescence Maximum. RI-CIS(D): $E(S_0)$ = -1007.33678, $E(S_1)$ = -1007.19840. CIS(2'): $E(S_0)$ = -1007.13652, $E(S_1)$ = -1006.98908

C	1.400050	-1.913170	1.188010
C	2.177872	-0.823654	0.591745
C	1.916282	-0.479730	-0.768918
H	-1.099868	-3.425529	-1.262563
N	1.015421	-1.035922	-1.628662
C	0.370963	-2.037520	-0.916422
N	0.462825	-2.515084	0.345403
C	3.502641	0.793738	0.100622
N	2.791603	0.563229	-1.036793
N	-0.559776	-2.670183	-1.676390
H	1.507180	-2.267685	2.213878
N	3.154407	-0.035259	1.117242
H	4.267024	1.568167	0.166123
H	2.874788	1.053477	-1.921667
H	-0.691586	-2.370391	-2.638398
N	-1.230660	2.251070	-1.575950
C	-1.555690	1.310840	-0.635080
N	-3.440490	-1.476690	0.299910
N	-2.474220	0.313990	-0.792940
N	-1.827020	-0.225060	1.424510
H	-3.985190	-1.635980	-0.526380
C	-2.566740	-0.431080	0.284890
H	-1.632870	2.317160	-2.497770
H	-3.554190	-2.078750	1.092470
C	-0.852970	0.800920	1.644700
N	0.047730	2.711230	0.216900
C	-0.269500	3.062720	-1.018050
H	-1.945080	-0.835750	2.222930
O	-0.268310	0.860870	2.719970
C	-0.753400	1.615950	0.462370
H	0.157580	3.889760	-1.561460

This journal is © The Royal Society of Chemistry and Owner Societies 2013

Table S18: 5′-2APG-3′ Conical Intersection. RI-CIS(D): $E(S_0)$ = -1007.23119, $E(S_1)$ = -1007.23550. CIS(2'): $E(S_0)$ = -1007.03232, $E(S_1)$ = -1007.02900

C	1.256160	-2.471330	1.084740
C	1.939690	-1.250440	0.941330
C	1.651180	-0.531330	-0.244200
H	-1.331960	-3.211680	-1.527550
N	0.834360	-0.913870	-1.237170
C	0.223900	-2.081570	-0.951350
N	0.393100	-2.881280	0.144060
C	2.972420	0.597330	1.108780
N	2.347840	0.647150	-0.123430
N	-0.645660	-2.572410	-1.920650
H	1.384490	-3.111190	1.966880
N	2.785750	-0.535960	1.774620
H	3.566480	1.436610	1.471930
H	2.131770	1.486920	-0.660550
H	-1.076830	-1.822640	-2.457140
N	-1.973280	1.419030	-2.145750
C	-1.988250	0.693890	-0.948940
N	-2.434510	-2.009120	0.993430
N	-2.892600	-0.070250	-0.411550
N	-1.800350	0.261550	1.706140
H	-3.137230	-2.337680	0.328610
C	-2.053650	-0.697610	0.669470
H	-2.641500	1.330860	-2.906280
H	-1.632200	-2.649900	1.004600
C	-0.708770	1.045100	1.219280
N	-0.098750	2.068430	-1.030680
C	-0.813610	2.146810	-2.161160
H	-1.616250	-0.130900	2.635030
O	0.136660	1.590600	1.914490
C	-0.796140	1.180660	-0.259700
H	-0.521390	2.739170	-3.030160