Electronic Supplementary Information for: Photophysical Deactivation Pathways in Adenine Oligonucleotides

Vincent A. Spata and Spiridoula Matsika*
Department of Chemistry
Temple University
Philadelphia, PA 19122

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In this document we present additional data supporting the current work. Initially we provide some monomer adenine calculations to better understand the local minima obtained. ADC(2) and NEVPT2 energies and properties not shown in the main paper are shown in sections 2 and 3. Also presented are linear least motion (LLM) pathways calculated with ADC(2) between the various minima obtained to demonstrate the proposed progression of species is barrierless. Helical conformations of the initial geometries are also presented in order to illustrate decay progression is strongly correlated to the environment. IR spectra at the minima are shown in section 6. The geometrical measurements of the six model minima is also presented along with their xyz coordinates.

1 Monomer Calculations

We optimized 12 different adenine monomer geometries within the QM/MM environment using ADC(2)/def2-SVP. A table of energies and oscillator strengths is provided as Table S1. Our results reveal two types of monomer minima which are similar to our results from the dimer calculations. We will refer to the geometries here as Local 1 and Local 2 to easily compare the monomer geometries to the dimer geometries. We only obtained one geometry of higher energy with the same character as our Local 1 geometry in the dimer studies. This geometry has an energy of 3.65 eV and is bright with high oscillator strength (0.11). The remaining geometries have energies which range from 2.92 to 3.11 eV and illustrate the same character as our Local 2 conformation. These geometries have an average energy of 2.96 eV and an average oscillator strength of 0.07. All monomer geometries illustrate distortion at the C2 carbon atom. As has been suggested by Lu and coworkers, deformation at this carbon is favored over deformation of the C6 carbon as the amino group is involved in hydrogen bonding.[1] These results confirm the local character of these minima.

*Email address: smatsika@temple.edu

Additionally, we ran single point calculations for the same above geometries excluding the QM/MM environment (in the gas phase) in order to determine the effects of the environment. From these calculations, shown in Table S1 as Local GP, we can conclude the energy differences between Local 1 and Local 2 are clearly from geometry differences and not from the QM/MM environment. QM/MM calculations on adenine monomer in $(dA)_{10}$ and also in the duplex $(dA)_{10}(dT)_{10}$ have been undertaken by Lu, Lan, and Thiel.[1] Their results indicate two emissive bands for $(dA)_{10}$ located around 3.0 eV (mostly $\pi\pi^*$) and 3.6 eV (mixed $n/\pi\pi^*$) with oscillator strengths which are about 0.08-0.10. In the duplex $(dA)_{10}(dT)_{10}$ they see three main groups of local minima with energies of 2.6, 2.8, and 3.6 eV respectively.

Minima	S_1-S_0	f
Local 1 QM/MM	3.65	0.11
Local 2 QM/MM	3.06	0.06
Local 1 GP	3.64	0.05
Local 2 GP	3.10	0.04
Ave Local 2 QM/MM	2.96	0.07

Table S1: ADC(2) energies in eV with the accompanying oscillator strengths for QM/MM optimized monomer conformations. Two geometries were chosen to make comparisons between QM/MM and gas-phase values. Also included are the average energy and oscillator strength of 11 additional Local 2 structures obtained from hybrid single points.

2 ADC(2) Energies in the Distribution

Minima	S_1-S_0 Gap/eV	f	S_0/eV	S_1/eV
Local 1	3.68 (0.11)	0.07 (0.01)	-0.08 (0.15)	3.60 (0.05)
Local 2	3.09 (0.14)	0.06 (0.01)	0.06 (0.31)1	3.15 (0.22)
Neutral Excimer	3.01 (na)	0.04 (na)	-0.25 (na)	2.76 (na)
CT Excimer	2.72 (0)	0.04 (0.0)	0.34 (0.07)	3.06 (0.07)
CT Bonded Excimer	2.16 (0.15)	0.04 (0.0)	1.27 (0.23)	3.42 (0.27)
Bonded Excimer	1.22 (0.11)	0.02 (0.0)	1.95 (0.44)	3.17 (0.35)
CI			5.08 (na)	4.47 (na)

Table S2: QM/MM ADC(2)/def2-SVP energies and oscillator strengths for the distribution of minima. Standard deviations are based on the entire data set and presented in parentheses.

The ADC(2) energies obtained from 60 excited state optimizations are provided in Table S2. The corresponding NEVPT2 energies for only one representative geometry of each case are shown in the main paper.

The energy of the previously found CI[2] embedded in the QM/MM environment is also shown. The energies of S_0 and S_1 are not degenerate anymore since this geometry is not

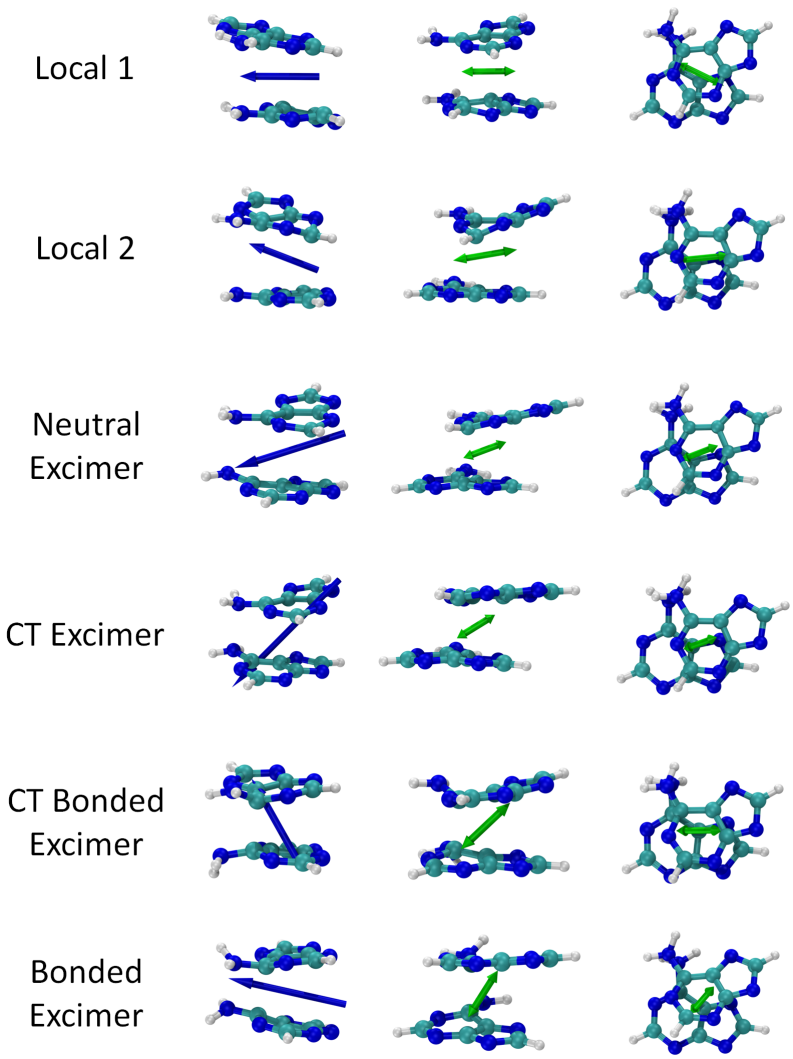

Figure S1: Difference dipole moments and transition moments calculated for 6 model minima with QM/MM CASSCF/def2-SVP.

optimized again. Furthermore, the energy of S_0 is shown here to be higher than the energy of S_1. This is because of the single reference character of the ADC(2) method. Since we are not interested in the exact energies or any properties here we do not attempt to correct or use a different method to describe the CI.

3 QM/MM CASSCF Physical Properties

We have calculated and analyzed the difference dipole moments and transition moments resulting from QM/MM CASSCF calculations to compare to our ADC(2) results (see Figure S1). The results are very similar between the two methods which supports the validity of

the results since both single reference and multireference methods give similar predictions. There is a slight difference in the difference dipole moments of the excimer species which according to the QM/MM CASSCF wavefunction illustrates slight increases in the amount of CT character as evidenced by the change in the orientation of $\Delta\mu_{10}$ between bases and out-of-plane.

4 Decay Between Species

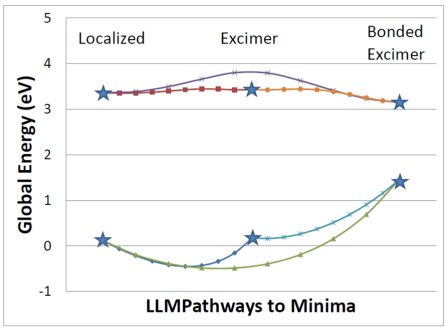

Figure S2: LLM pathways calculated in the gas phase at the ADC(2)/def2-SVP level of theory for three model minima geometries representing our three types of minima.

LLM pathways between the three types of minima were calculated in the gas-phase at the ADC(2)/def2-SVP level to see if there were energy barriers in the progression from one minimum to another. The results reveal there are no or small barriers in progression from Local excitations to Excimers or from Excimers to Bonded Excimers. The progression from Local excitations to Bonded Excimers illustrates that there may be a barrier with a height of about 0.5 eV. Direct decay from the local minima to the bonded excimers seems less likely than stepwise decay through the excimers.

5 Correlation of Decay to Franck-Condon Helical Conformation

Figure S3 shows the rise and twist values for the starting conformations of the different minima obtained from free optimizations on the excited state surfaces. We find the minima we have obtained illustrate correlation to the Franck-Condon helical conformation. Five different types of minima are illustrated. Local 1 and Neutral Excimer minima are formed from starting conformations of large twist, Local 2 conformations are formed within the largest range of helical conformation, CT excimers are formed from geometries just below the average of the MD distribution, and the formation of Bonded Excimers are correlated to Franck-Condon structures which exhibit low rise values.

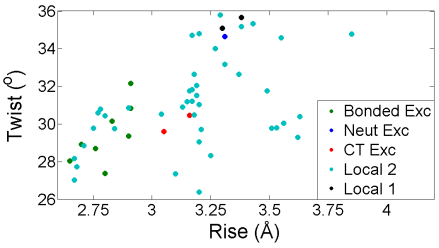

Figure S3: Rise and twist of the starting conformations of 56 excited states optimizations. The minima obtained are color coordinated in the plot to illustrate the initial conformations from the original MD distribution.

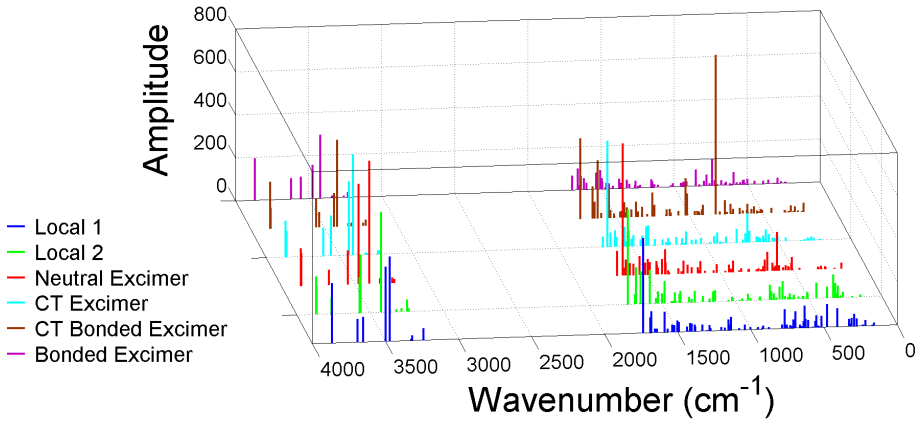

Figure S4: IR spectra obtained at the S_1 minima.

6 IR spectroscopy

A very attractive way to distinguish experimentally between the minima we have predicted is by using an IR probe in a time resolved experiment. The IR spectra obtained at the six representative minima are shown in Figure S4. It is seen there that the spectra have differences that could be used as a signature.

The differences evidenced in the normal modes between species are relevant to differences in the geometry. The Local 1 minimum spectrum exhibits modes characteristic of motions around C2' in the 3' ring while the Local 2 spectrum has different modes which describe motions around C2 in the 5' ring. The excimers and bonded excimers illustrate differences in spectra based on modes present which are characteristic of motion of the amino groups and heavy atom modes in the rings. In addition, the neutral and CT excimers exhibit frequencies which are characteristic of modes around C2 in the 5' ring. The signature of the CT bonded excimer is a massively large peak at 818 cm^{-1} which is due to pyramidalization at the C6 carbon. The bonded excimer spectrum illustrates peaks of much smaller amplitudes compared to the other minima.

7 Geometries

In this section we present images illustrating the bond lengths and bond length changes of 6 model minima compared to gas-phase MP2/cc-PVDZ optimized adenine. Changes between ADC(2) minimum geometries and the MP2 ground state minima are color coded for easier analysis. Blue values illustrate increased bond lengths. Red values indicate a decrease in bond length. Bold values are changes in the bond lengths greater than 0.03 Å while underlined bolded values are changes in bond lengths greater than 0.05 Å. At the end of the section we include the xyz coordinates of the 6 model minima.

7.1 Geometry Measurements

The figures provided below illustrate the geometry measurements and changes of the minima presented in this study (see Figures S6 to S11).

The Localized minima illustrate pyramidalization of the C2 carbon with accompanying deformation in the 6-membered rings and shortening of the C6N10 bond with the amino Nitrogen. For Local 1 the excited state character is localized on the 3' adenine and for Local 2 the excited state is local to the 5' adenine.

The Excimers exhibit distortion in both 5' and 3' rings including a symmetric stretch in both rings of the C6N10 bond with the amino Nitrogen. In the Excimer geometries there is increased deformation near C2 in the 5' ring which may illustrate a progression from a 5' Local 2 geometry to Neutral or CT excimers is likely.

The Bonded Excimers illustrate symmetric changes in bond lengths between the 5' and 3' rings although for the two different types of bonded excimers the changes are different. Both Bonded Excimer structures illustrate a simultaneous symmetric pyramidalization around the C6 carbons. In the CT Bonded Excimer geometry the 5' C6N10 bond shortens and 3' C6N10 bond stretches. The Bonded Excimer geometry illustrates stretching of C6N10 bonds in both rings.

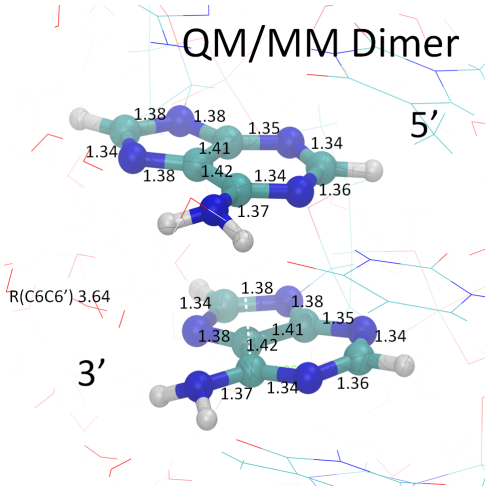

Figure S5: Geometry measurements of the "QM/MM dimer" which is optimized originally in the gas-phase with MP2/cc-PVDZ.

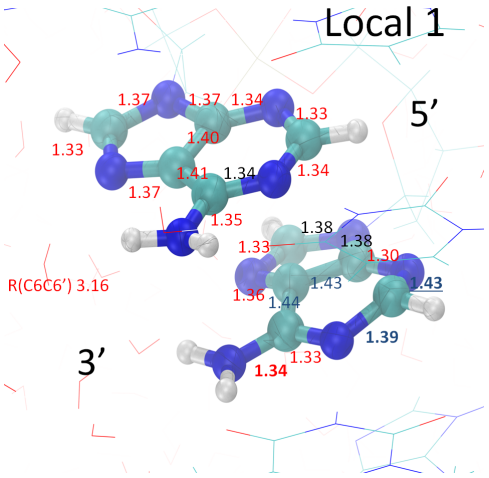

Figure S6: Geometry measurements of the Local 1 minimum model geometry.

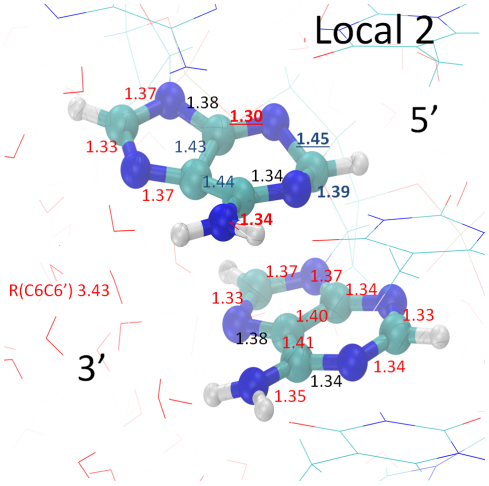

Figure S7: Geometry measurements of the Local 2 minimum model geometry.

7.2 XYZ Coordinates

Provided below in Tables S3 to S8 are the XYZ coordinates for the 6 model minima utilized for calculations and analysis in the study. The geometries presented include the coordinates of the link atom Hydrogens which are unoptimized but are included to ensure the charge of the molecule is 0 in the QM region.

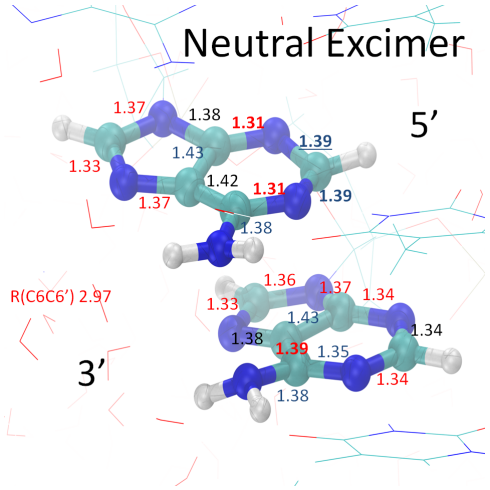

Figure S8: Geometry measurements of the Neutral Excimer minimum model geometry.

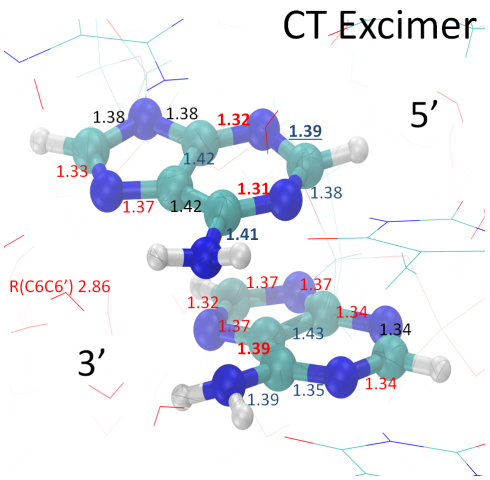

Figure S9: Geometry measurements of the CT Excimer minimum model geometry.

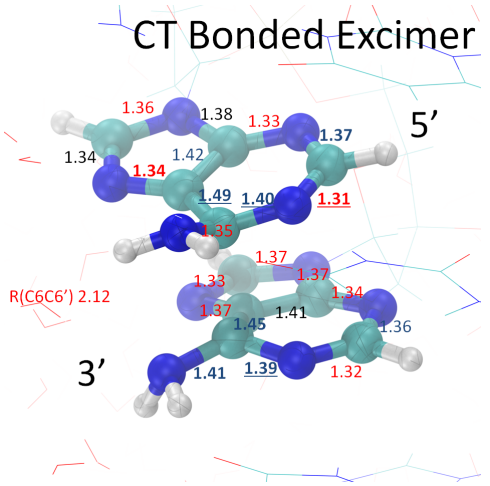

Figure S10: Geometry measurements of the CT Bonded Excimer minimum model geometry.

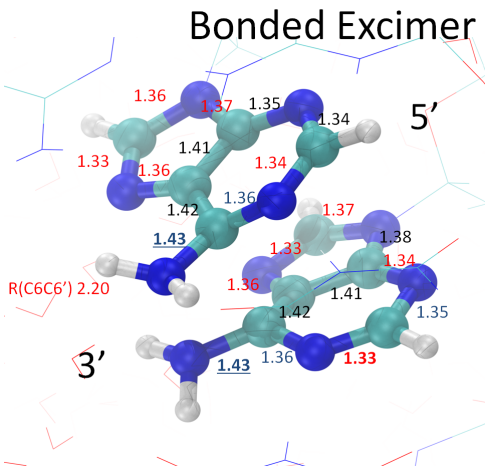

Figure S11: Geometry measurements of the CT Bonded Excimer minimum model geometry.

Atom	X	Y	Z
N	38.2360107	25.8400072	55.3640155
C	36.9890104	26.2550074	55.7430156
H	36.1890102	25.5470072	55.9470157
N	36.8840103	27.5740077	55.8140157
C	38.1360107	28.0300079	55.4800156
C	38.6410108	29.3330082	55.2660155
N	37.9280106	30.4560085	55.4860156
H	38.3260108	31.3300088	55.1350155
H	36.9170104	30.3830085	55.5750156
N	39.9250112	29.4340083	54.9070154
C	40.6760114	28.3360079	54.7390154
H	41.7190117	28.5180080	54.4680153
N	40.2900113	27.0640076	54.8340154
C	39.0030109	26.9640076	55.1950155
N	42.0890118	26.7320075	57.8060162
C	40.8510115	26.2900074	58.2150163
H	40.6570114	25.2540071	58.4800164
N	39.9590112	27.2750077	58.2670163
C	40.5900114	28.3660080	57.7660162
C	40.3180113	29.7700084	57.9060162
N	39.1170110	30.2020085	58.3260164
H	38.9260109	31.2090088	58.2770163
H	38.3560108	29.5440083	58.4670164
N	41.2250116	30.6810086	57.5760162
C	42.3670119	30.2590085	56.9110160
H	43.1280121	31.0210087	56.7280159
N	42.8800120	28.9520081	57.2030160
C	41.9640118	28.0720079	57.4840161
H	38.5376225	24.8955392	55.2336977
H	42.8654356	26.1498577	57.5646862

Table S3: XYZ coordinates of the Local 1 model minimum geometry.

Atom	X	Y	Z
N	37.4110105	25.7740072	54.8880154
C	36.1370101	26.1990073	55.1620155
H	35.2890099	25.5170072	55.1430155
N	36.0770101	27.4930077	55.4490156
C	37.3810105	27.9190078	55.4580156
C	37.9580106	29.2170082	55.2180155
N	37.1990104	30.3160085	55.1840155
H	37.6380106	31.2230088	54.9830154
H	36.2070102	30.2790085	55.4360156
N	39.2660110	29.3660082	54.9890154
C	40.0680112	28.2470079	55.1920155
H	41.1290115	28.3780080	54.9760154
N	39.5190111	26.9730076	54.7800154
C	38.2560107	26.8480075	55.0830155
N	40.9790115	26.9950076	57.9500163
C	39.7170111	26.6620075	58.3540164
H	39.4170111	25.6220072	58.4930164
N	38.9370109	27.7170078	58.5460164
C	39.7380111	28.7900081	58.2310163
C	39.4820111	30.1750085	58.1370163
N	38.2660107	30.7170086	58.3450164
H	38.1790107	31.7320089	58.3360164
H	37.5420105	30.1660085	58.7820165
N	40.5040114	30.9710087	57.7800162
C	41.6950117	30.4390085	57.4760161
H	42.4790119	31.1510087	57.2020160
N	42.0360118	29.1510082	57.4650161
C	41.0130115	28.3640080	57.8290162
H	37.7081928	24.8327059	54.7279942
H	41.6855673	26.3514653	57.6557297

Table S4: XYZ coordinates of the Local 2 model minimum geometry.

Atom	X	Y	Z
N	37.4660105	25.8020072	54.8100154
C	36.1780101	26.2270074	55.0300154
H	35.3370099	25.5400072	54.9930154
N	36.0990101	27.5300077	55.2740155
C	37.4010105	27.9670078	55.2510155
C	38.0200107	29.2440082	55.2250155
N	37.3190105	30.4140085	55.4630156
H	37.7550106	31.3020088	55.1820155
H	36.2970102	30.3850085	55.5640156
N	39.3190110	29.3680082	55.0650154
C	40.1140113	28.2340079	54.9750154
H	41.1410115	28.4100080	54.6480153
N	39.5930111	26.9630076	54.7690154
C	38.2900107	26.8990075	54.9330154
N	40.7690114	27.0120076	57.6280162
C	39.4780111	26.6710075	57.8870162
H	39.1690110	25.6350072	58.0000163
N	38.6710108	27.7230078	58.0300163
C	39.4860111	28.8060081	57.7970162
C	39.2660110	30.1780085	57.7570162
N	38.0060107	30.7430086	57.7690162
H	37.9790107	31.7600089	57.9040162
H	37.2590105	30.2120085	58.2090163
N	40.3230113	31.0100087	57.6070162
C	41.5430117	30.4800085	57.4610161
H	42.3690119	31.1920087	57.3960161
N	41.8740117	29.1850082	57.3930161
C	40.8100114	28.3780080	57.4800161
H	37.7724247	24.8613089	54.6645189
H	41.4851929	26.3643538	57.3680141

Table S5: XYZ coordinates of the Neutral Excimer model minimum geometry.

Atom	X	Y	Z
N	39.0510110	25.7460072	54.5410153
C	37.7720106	25.9560073	55.0080154
H	37.0700104	25.1390071	55.1620155
N	37.5180105	27.2430076	55.2170155
C	38.6850109	27.8880078	54.9190154
C	39.0640110	29.2540082	54.8020154
N	38.2040107	30.2990085	55.1840155
H	38.4310108	31.2190088	54.7810154
H	37.2070104	30.0820084	55.2500155
N	40.2870113	29.5730083	54.4560153
C	41.2290116	28.5870080	54.2530152
H	42.1850118	28.9220081	53.8420151
N	40.9290115	27.2330076	54.1480152
C	39.6810111	26.9690076	54.4840153
N	42.2770119	27.3740077	56.9840160
C	41.0680115	26.8450075	57.3380161
H	40.9360115	25.7780072	57.5090161
N	40.1170113	27.7560078	57.4820161
C	40.7360114	28.9430081	57.1910160
C	40.3080113	30.2670085	57.1660160
N	38.9820109	30.6450086	57.3070161
H	38.8080109	31.6460089	57.4560161
H	38.3400108	29.9950084	57.7810162
N	41.2050116	31.2480088	56.9400160
C	42.4840119	30.9180087	56.7310159
H	43.1800121	31.7530089	56.6080159
N	43.0120121	29.6900083	56.6740159
C	42.1000118	28.7260081	56.8240159
H	39.4950166	24.8714302	54.3462170
H	43.1022665	26.8359443	56.8125083

Table S6: XYZ coordinates of the CT Excimer model minimum geometry.

Atom	X	Y	Z
N	40.4300113	29.8800084	53.1020149
C	39.2310110	29.9760084	53.7370151
H	38.6360108	29.1020082	53.9970151
N	38.8620109	31.2450088	53.9660151
C	39.8780112	31.9870090	53.4980150
C	40.0590112	33.4670094	53.3930150
N	38.9280109	34.1960096	53.2430149
H	39.0390110	35.1720099	52.9410149
H	38.1520107	33.9910095	53.8840151
N	41.0940115	33.8220095	52.5220147
C	41.9340118	32.9400092	52.0500146
H	42.7490120	33.3330094	51.4340144
N	41.9150118	31.5720089	52.1740146
C	40.8710115	31.1680087	52.8920148
N	43.2600121	31.4000088	55.0020154
C	42.2690119	30.7330086	55.6720156
H	42.3460119	29.6800083	55.9230157
N	41.2260116	31.5150088	55.9340157
C	41.5580117	32.7360092	55.4060155
C	40.8600115	33.9960095	55.2830155
N	39.7050111	34.2730096	56.0450157
H	39.6460111	35.2950099	56.1450157
H	39.7810112	33.8590095	56.9820160
N	41.6650117	35.0800098	54.9730154
C	42.8830120	34.8900098	54.5070153
H	43.4530122	35.7830100	54.2320152
N	43.5600122	33.7200095	54.3540152
C	42.8520120	32.6960092	54.8450154
H	40.8565593	29.0362578	52.7762631
H	44.1022602	31.0294196	54.6105385

Table S7: XYZ coordinates of the CT Bonded Excimer model minimum geometry.

Atom	X	Y	Z
N	40.9410115	29.6720083	52.5440147
C	39.6580111	29.7260083	53.0040149
H	39.0690110	28.8350081	53.1950149
N	39.2240110	30.9740087	53.1550149
C	40.2750113	31.7500089	52.7650148
C	40.4780114	33.1540093	52.7450148
N	39.3480110	34.0310095	52.8270148
H	39.5690111	35.0070098	52.5850148
H	38.4310108	33.6990095	52.5000147
N	41.5760117	33.6080094	52.0910146
C	42.5530119	32.7480092	51.7880145
H	43.4480122	33.2010093	51.3550144
N	42.5580119	31.4100088	51.9110146
C	41.3810116	30.9650087	52.3920147
N	43.4050122	31.2830088	55.2230155
C	42.3220119	30.5360086	55.5960156
H	42.3990119	29.4810083	55.8530157
N	41.1970116	31.2490088	55.6170156
C	41.5710117	32.5060091	55.2510155
C	40.8630115	33.6690094	54.8440154
N	39.4490111	33.8690095	54.9780154
H	39.1530110	34.7360097	55.4320155
H	38.8430109	33.0550093	55.1340155
N	41.5570117	34.8370098	54.7640154
C	42.8870120	34.7740098	54.6730153
H	43.4100122	35.7250100	54.5550153
N	43.6630122	33.6710094	54.7140153
C	42.9600121	32.5680091	55.0080154
H	41.4432536	28.8456957	52.2891958
H	44.3289339	30.9352819	55.0635569

Table S8: XYZ coordinates of the Bonded Excimer model minimum geometry.

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