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

Supporting Infomation for: Photophysical Properties of Cytosine Fluorescent Base Analogue Pyrrolocytosine

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1 Pyrrolocytosine Monomer

Energies of the stationary points on the S_1 surface of PC are shown in this section at various levels of theory. Table S1 shows the energies at the NEVPT2 level using an active space of (14,11) as described in the main manuscript. The geometries used are optimized at the ADC(2)/def2-TZVP level. Figure S1 is constructed using these energies. Table S2 shows the energies when a continuum solvation model is used to add the effects of solvation. Comparisons of these two tables show that bulk solvation does not have a big effect. The geometries have not been reoptimized with solvation, so it is possible that the numbers will change when the actual stationary points are found in solution. But the small effect in the energies indicates that reoptimization should not change the current picture qualitatively.

Table S3 shows the energies of stationary points at the ADC(2)/def2-TZVP level. These energies are used to construct Figure 3 in the main manuscript. Table S4 shows the energies when two waters have been added to PC. These energies are also used to construct the bottom figure of Figure 3.

Table S1: Energies of the states in eV along the S_1 PES for gas phase PC at the NEVPT2/cc-pVDZ level

geom	S0	S1	S2
S_0 Min	0	3.76	4.87
S_1 Min1	0.85	3.54	4.33
S_1 Min2	0.88	3.55	4.33
TS	1.21	3.45	5.29
$CI_{S_0-S_1}$	3.14	3.19	6.08

Table S2: Energies of the states in eV along the S_1 PES for aqueous phase PC at the NEVPT2/cc-pVDZ level using the continuum solvation SMD model.

geom	S_0	S_1
S_0 Min	0	3.82
S_1 Min1	0.6	3.53
TS	1.05	3.38
$CI_{S_0-S_1}$	3.11	3.16

Table S3: Energies of the states in eV along the S_1 PES for gas phase PC at the ADC(2)/def2-TZVP level

geom	S_0	S_1	S_2
S_0 Min	0	3.52	4.34
S_1 Min1	0.69	3.04	3.46
S_1 Min2	0.72	3.04	3.46
TS	1.09	3.22	4.68
$CI_{S_0-S_1}$	2.91	3.02	5.3

Table S4: Energies of the states in eV along the S_1 PES for PC with two water molecules at the ADC2 def2-TZVP level

geom	S_0	S_1	S_2
S_0 Min	0	3.66	4.67
S_1 Min1	0.55	3.22	4.15
S_1 Min2	0.54	3.22	4.14
$CI_{S_0-S_1}$	3.66	3.66	5.78

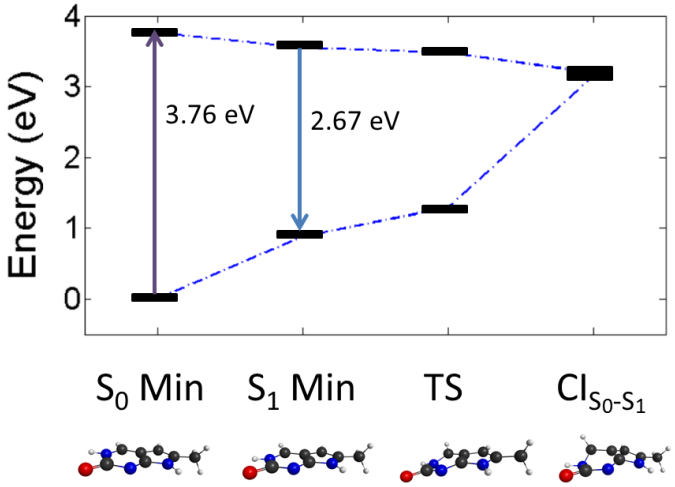

Figure S1: Deactivation pathway for the pyrrolocytosine monomer in vacuo. The geometries were obtained from calculations with ADC(2)/def2-TZVP. All energies are calculated at the NEVPT2/cc-pVDZ level.

2 Pyrrolocytosine Interacting with Guanine

Additional results on the dimers and trimer are included in this section. Table S5 is an extension of Table 1 in the main manuscript. It includes more states for each system. It also includes the excited states of guanine. In addition to CIS(D) and ADC(2) results it also shows CIS(2) results. This is a different configuration interaction singles with second order perturbation theory, which gives improved oscillator strengths,[1] since at the CIS(D) level only the energies are corrected but the oscillator strengths are given at the CIS level. Dunning's basis sets, cc-pVDZ, aug-cc-pVDZ, and the cc-pVDZ basis set with the inclusion of diffuse function on C, N, O atoms (excluding H), written as cc-pVDZ+$Diff$, were employed in all single point calculations of dimers and trimers. Table S6 shows the energies of PC, G, and their hydrogen bonding complex. Tables S7 and S8 show the results on the dimers and trimer using ADC(2)/def-TZVP. These results have been used in Figure 5 of the main document.

Table S5: Excitation energies at different levels of theory in eV with oscillator strengths in parenthesis for BDNA geometries of all systems, PC, G, PCG-Hbonding, 5'-PCG-3',5'-GPC-3',5'-GPCG-3'. The corresponding characters are also included. $*$ corresponds to $\pi\sigma^*$ state.

PC	$\mathbf{S}_1$ $\pi\pi^*$	$\mathbf{S}_2$ $n\pi^*$	$\mathbf{S}_3$ $n\pi^*$
CIS(D)/aug-cc-pVDZ	3.77 (0.255)	4.70* (0.000)	4.96 (0.004)
CIS(D)/cc-pVDZ	3.91 (0.301)	4.97 (0.002)	5.04 (0.001)
CIS(D)/cc-pVDZ/PCM	4.10 (0.287)	5.34 (0.036)	5.48 (0.002)
CIS(2)/cc-pVDZ+$Diff$	3.93 (0.108)	4.99 (0.001)	5.11 (0.000)
ADC(2)/def2-TZVP	3.52 (0.083)	4.34 (0.000)	4.90 (0.001)
ADC(2)/def2-TZVP +2W	3.66 (0.087)	4.67 (0.001)	4.99 (0.001)
NEVPT2(14,11)/cc-pVDZ	3.76 (0.089)	4.87 (0.000)	5.25 (0.003)
NEVPT2(14,11)/cc-pVDZ/water	3.82 (0.093)	5.21 (0.000)	5.31 (0.008)
Experiment[2]	3.74		
G			
CIS(D)/aug-cc-pVDZ	$4.91\pi\sigma^*(0.001)$	$5.11\pi\sigma^*(0.009)$	$5.11\pi\pi^*(0.240)$
CIS(D)/cc-pVDZ	$5.41\pi\pi^*(0.272)$	$5.58n_O\pi^*(0.001)$	$6.08\pi\pi^*(0.545)$
CIS(2)/cc-pVDZ+$Diff$	5.35(0.003)	5.50(0.244)	5.74(0.001)
PCG-Hbonding			
CIS(D)/aug-cc-pVDZ	$3.74\pi\pi_{PC}*(0.261)$	$4.88\pi\sigma_{PC}*(0.001)$	$4.88\pi\sigma_G*(0.001)$
CIS(D)/cc-pVDZ	3.89(0.303)	4.90(0.197)	5.07(0.003)
CIS(D)/cc-pVDZ/water	4.08(0.306)	5.22(0.016)	5.27(0.157)
CIS(2)/cc-pVDZ+$Diff$	3.91(0.112)	5.23(0.000)	5.28(0.023)
5'-PCG-3'			
CIS(D)/aug-cc-pVDZ	3.79(0.200)	4.62(0.004)	4.73(0.001)
	$\pi - \pi\pi^*_{PC}$	$\pi\sigma^*_{PC}$	$\pi\sigma^*_{PC}$
CIS(D)/cc-pVDZ	3.94(0.248)	5.11(0.0002)	5.11(0.030)
	$\pi\pi^*_{PC}$	$n_O\pi^*_{PC}$	$n_N\pi^*_{PC}$
CIS(D)/cc-pVDZ/water	4.08(0.234)	5.31(0.035)	5.32(0.202)
CIS(2)/cc-pVDZ+$Diff$	3.95(0.083)	4.97(0.000)	5.15(0.002)
5'-GPC-3'			
CIS(D)/aug-cc-pVDZ	3.72(0.208)	4.53(0.001)	4.76(0.012)
	$\pi - \pi\pi^*_{PC}$	$\pi\sigma^*_{PC}$	$\pi\sigma^*_G$
CIS(D)/cc-pVDZ	3.88(0.255)	4.95(0.003)	5.21(0.025)
	$\pi\pi^*_{PC}$	$n_N\pi^*_{PC}$	$\pi\pi^* - \pi^*_{PC}$
CIS(D)/cc-pVDZ/water	4.06(0.245)	5.27(0.058)	5.28(0.037)
CIS(2)/cc-pVDZ+$Diff$	3.87(0.085)	4.86(0.000)	5.01(0.001)
5'-GPCG-3'			
CIS(D)/cc-pVDZ	3.90(0.209)	5.12(0.022)	5.20(0.024)
	$\pi\pi^*_{PC}$	$\pi_{Gb}\pi\pi^*_{PC}$	$\pi\pi^* - \pi\pi^*_{PC}$
CIS(D)/cc-pVDZ/water	4.05(0.200)	5.22(0.048)	5.26(0.038)

Table S6: CIS(D)/aug-cc-pVDZ Singlet excited state energies for PC, G monomers and PCG-Hbonded complex. State characters are included.

State	**PC**	**G**	**PCG-Hbonding**
1	3.77 $\pi\pi^*$	4.91 $\pi\sigma^*$	3.74 $\pi_{PC}\pi^*_{PC}$
2	4.70 $\pi\sigma^*$	5.11 $\pi\sigma^*$	4.88 $\pi_{PC}\sigma^*_{PC}$
3	4.91 $n_N\pi^*$	5.11 $\pi\pi^*$	4.88 $\pi_G\sigma^*_G$
4	4.96 $\pi\sigma^*$	5.47 $n_O\pi^*$	4.97 $\pi_{PC}\pi^*_{PC}$
5	5.29 $\pi\sigma^*$	5.74 $\pi\pi^*$	5.18 $\pi_{PC}\pi^*_{PC}$
6	5.34 $\pi\pi^*$	5.81 $\pi\sigma^*$	5.29 $\pi_{PC}\sigma^*_{PC}$
7	5.54 $\pi\pi^*$	5.89 $\pi\sigma^*$	5.30 $n_{PC}\pi^*_{PC}$
8	5.76 $\pi\sigma^*$	6.06 $\pi\sigma^*$	5.34 $\pi_G\pi^*_G$
9	5.77 $\pi\sigma^*$	6.21 $\pi\sigma^*$	5.49
10	5.83$\pi - \pi\pi^*$	6.37 $\pi\pi^*$	5.57 $\pi_{PC} - \pi^*\sigma^*_{PC}$
11	6.00$n_O\pi^*$	6.59 $\pi\sigma^*$	5.58 $\pi_{PC}\sigma^*_{PC}$

Table S7: ADC(2)/def2-TZVP singlet excited state energies for PCG, GPC and PCG-Hbonded complex. State characters are included.

	PCG			GPC			PCG-Hb		
state	E (eV)	f	char	E (eV)	f	char	E (eV)	f	char
1	3.54	0.064	$\pi_{PC}\pi^*_{PC}$	3.47	0.066	$\pi_{PC}\pi^*_{PC}$	3.51	0.085	$\pi_{PC}\pi^*_{PC}$
2	4.48	0.001	$n_{PC}\pi^*_{PC}$	4.36	0.000	$nN_{PC}\pi^*_{PC}$	4.69	0.005	CT $\pi_G\pi^*_{PC}$
3	4.90	0.009	$\pi_{PC}\pi^*_{PC}$ mix	4.69	0.001	CT $\pi_G\pi^*_{PC}$	4.82	0.034	$\pi_{PC}\pi^*_{PC}$
4	4.99	0.114	$\pi_G\pi^*_G$	4.89	0.003	$n_{PC}\pi^*_{PC}$	4.86	0.000	$n_{PC}\pi^*_{PC}$
5	5.01	0.020	$nN_{PC}\pi^*_{PC}$	4.90	0.012	$n_{PC}\pi^*_{PC}$/pipi*	4.95	0.072	$\pi_G\pi^*_G$
6	5.16	0.005	CT $\pi_G\pi^*_{PC}$	4.99	0.088	$\pi_G\pi^*_G$	5.35	0.000	$n_{PC}\pi^*_{PC}$ mix
7	5.33	0.000	$n_G\pi^*_G$	5.29	0.000	$n_G\pi^*_G$	5.45	0.430	$\pi_G\pi^*_G$
8	5.4	0.221	$\pi_G\pi^*_G$	5.39	0.209	$\pi_G\pi^*_G$	5.58	0.000	$n_G\pi^*_G$
9	5.64	0.419	$\pi_{PC}\pi^*_{PC}$	5.61	0.329	$\pi_{PC}\pi^*_{PC}$	5.67	0.427	$\pi_{PC}\pi^*_{PC}$
10	5.86	0.000	$\pi_{PC}\sigma^*_{PC}$	5.80	0.012	$\pi_{PC}\sigma^*_{PC}$	6.15	0.000	$\pi_{PC}\sigma^*_{PC}$

Table S8: ADC(2)/def2-TZVP singlet excited state energies for GPCG. State characters are included.

state	E (eV)	f	char
1	3.48	0.0503	PC $\pi\pi^*$
2	4.49	0.0008	PC $n\pi^*$
3	4.80	0.0048	PC $\pi\pi^*$
4	4.91	0.0294	part $\pi\pi^*$ 5'G / part CT 5'G to PC
5	4.98	0.0579	mixed
6	4.99	0.0690	mixed
7	5.01	0.0570	PC $n\pi^*$/ 3'G $\pi\pi^*$ some CT from 5'G to PC
8	5.12	0.0094	CT 3'G to PC
9	5.31	0.0003	3'G $n\pi^*$
10	5.31	0.0002	5'G $n\pi^*$
11	5.37	0.0185	5'G $\pi\pi^*$ 3'G $\pi\pi^*$
12	5.41	0.3807	5' $\pi\pi^*$ 3'G $\pi\pi^*$
13	5.57	0.3726	PC $\pi\pi^*$
14	5.62	0.0605	PC Rydberg
15	5.87	0.0397	CT PC to 5'G

Figure S2 shows CIS natural orbitals describing the S1 state in the dimers and trimer studied. Similarly to the ADC(2) results the state is always localized on PC. Figure S3 shows the energies of dimers and trimer at the CIS(D)/cc-pVDZ level of theory. Again, the results depict qualitatively similar behavior as the ADC(2) results. The CT states are more than 1 eV above S1. Figure S4 shows the natural orbitals for the CT states.

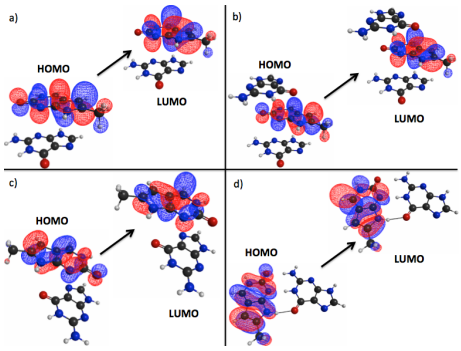

Figure S2: Natural orbitals at the CIS/cc-pVDZ level for the lowest transitions of (a) 5'-GPC-3', (b) 5'-GPCG-3', (c) 5'-PCG-3', (d) PCG-Hbonding. The occupation numbers for the two orbitals shown are 0.9-1, so there are no other relevant contributions besides the pairs shown. Natural orbital calculations were carried out using the GAMESS computational package.[3]

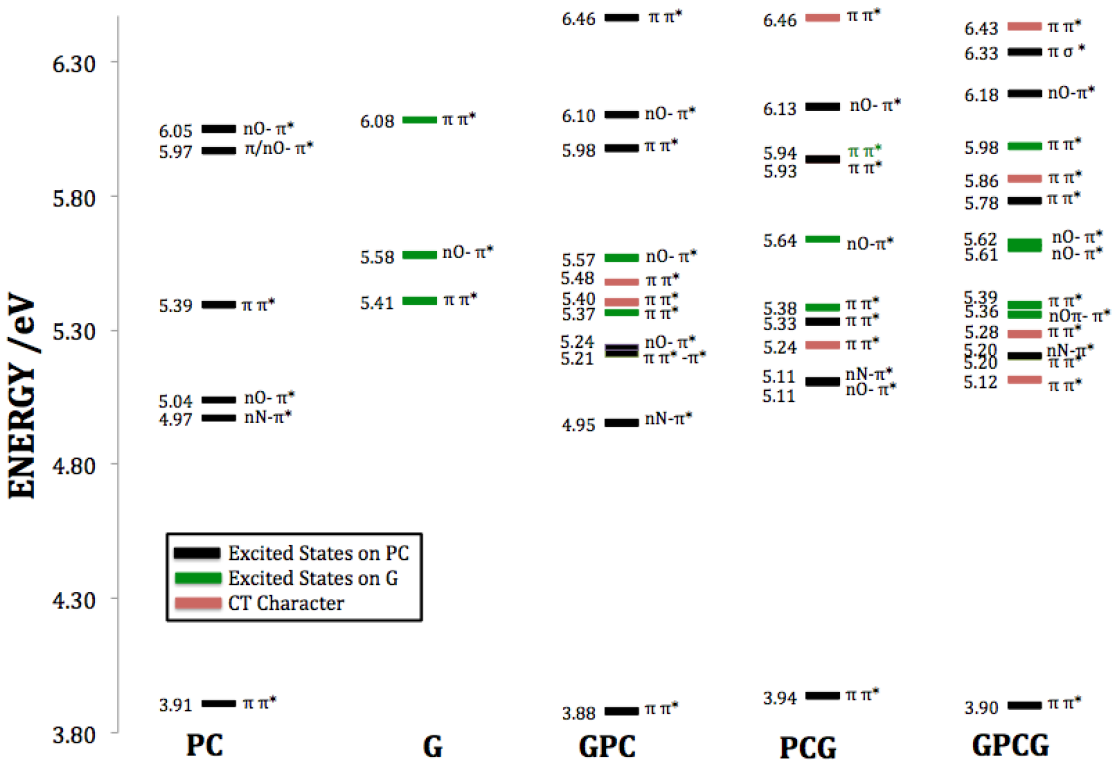

Figure S3: Excited states of G, PC, the dimers and the trimer formed between them calculated at the CIS(D)/cc-pVDZ level of theory.

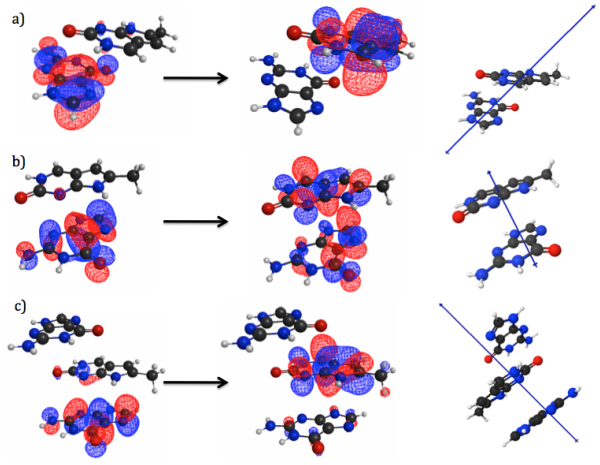

Figure S4: CIS/cc-pVDZ natural orbitals (left) and difference of the dipole moment of the CT state minus the dipole moment of the ground state ($\Delta\mu$) describing the first CT state in (a) 5'-PCG-3': S_0 - S_4 transition, $\Delta\mu$=19.68 Debye (b) 5'-GPC-3': S_0-S_6 transition, $\Delta\mu$=7.62 Debye (c) 5'-GPCG-3', S_0-S_2 transition, $\Delta\mu$=16.65 Debye. Occupation numbers are 0.9-1, except for 5'-GPC-3' where the occupation numbers are 1.2 and 0.8.

3 Redox Properties

In the main manuscript we present the IPs and EAs of PC, 2AP, and G. Table S9 shows the values of adiabatic (A) and vertical (V) IP and EA for all the methods used here. Optimizations for the ground state equilibrium geometries for the cations and anions of 2AP, PC, and G, were performed at the MP2 level with several Dunning correlation basis sets[4] and the DFT/B3LYP level with Pople basis sets. The continuum solvation in EA is calculated using the IEFPCM method as implemented in Gaussian 03.[5]

Table S9: Vertical (V) and adiabatic (A) electron affinities and ionization potentials for PC, 2AP, and G computed at different levels of theory. Dipole moments (D) in Debye for each system at different levels are also shown.

Electron Affinity							
		PC		2AP		G	
		A	V	A	V	A	V
B3LYP/	6-311++G(2df,p)	0.15	-0.02	-0.32	-0.46	-0.06*	-0.08
	6-311+G(2df,p)	0.15	-0.02	-0.32	-0.46	-0.36*	-0.39
	6-311G(2df,p)	-0.62	-0.34	-0.74	-0.91	-0.79	-1.68
	6-311+G(2df,p) /PCM/water	2.11	1.85	1.81	1.66	1.21	0.95
MP2/	aug-cc-pVDZ	-0.07	/	/	/	-1.57	/
	cc-pVDZ	-0.73	/	-1.21	/	-2.92	/
Ionization Potential							
		A	V	A	V	A	V
B3LYP/	6-31++G(d,p)	7.41	7.54	7.83	7.97	7.63	7.87
MP2	aug-cc-pVDZ	7.84	/	/	/	7.84	/
	cc-pVDZ	7.48	/	7.99	/	7.79	/

*Dipole-Bounds

Unlike IPs, the determination of EAs is much more difficult so we discuss them in more detail here. In nucleobases in particular the situation is even worse since there are two states associated with the negative ion, the non-valence and the valence state. The non-valence is also known as the dipole-bound (DB) state, where the extra electron occupies a diffuse orbital around the molecule that faces the dipole moment.[6] Meanwhile, in the valence state, the captured electron occupies a π orbital centered on the molecular frame. EAs are very sensitive to the addition of diffuse functions in the basis set. A series of previous studies, which were done to estimate the ionization potentials and electron affinities of DNA/ RNA natural nucleobases and fluorescent analogues, found that adding diffuse functions allows the extra electron to move away from the molecular framework to continuum or dipole-bound states.[6–13] These studies also showed that the EAs for G, A, C, T, U, I computed with the B3LYP functionals and the 6-311++G(d,p) basis set, which includes an extra diffuse component on hydrogen atoms while excluding the angular momentum polarization on heavy atoms, are strongly influenced by the dipole-bound state characterization.

Figure S5 shows the EA calculated for PC, 2AP and G in this work using a series of

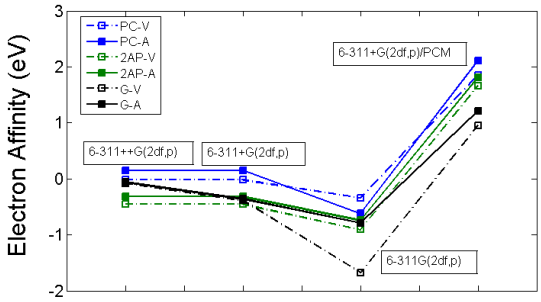

Figure S5: Adiabatic (A) and Vertical (V) electron affinities of PC, 2AP, G monomers computed at the DFT/B3LYP level with different basis sets. Solvation effects were modeled using IEFPCM.

basis sets and the B3LYP method. The last point on the graph includes solvation effects using the IEFPCM model. The graph makes it clear that there is a strong dependence of EA on the basis set and the values vary a lot. It is also obvious that, regardless of the basis set used, PC always has the highest EA compared to 2AP and G. EAs for 2AP and G in the gas phase are always negative indicating that they are unstable anions, while the EA of PC is positive when diffuse functions are included. Even though several experimental and theoretical studies were conducted to approximate the EAs and IPs of 2AP,[9,14] no studies have been done for pyrrolocytosine. The singly occupied molecular orbitals (SOMO) for 2AP and PC displayed in Figure S6 confirm that the anionic state predicted is a valence state and not dipole-bound. In guanine on the other hand the lowest state is dipole-bound when diffuse functions are included in the calculations. Overall, the expansion of the diffuse basis causes the EA to approach zero as we have seen for all three monomers. This may result in redox potentials that do not correspond to the valence states. This problem can be eliminated with the presence of aqueous medium since the diffuse states are destabilized in polar solvents. The presence of water markedly increases the adiabatic and vertical electron affinities for all systems as shown in Figure S5, where the AEA for PC, 2AP, and G are 2.11, 1.81, 1.21 eV. The calculated EAs in the presence of water are dominated by valence-state character. Hence, they are the most reliable results. They reveal that PC has the most stable anion.

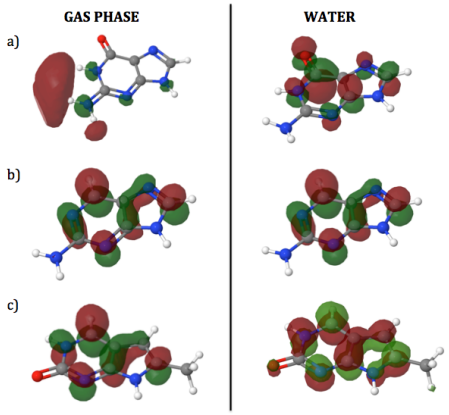

Figure S6: B3LYP/6-311++G (2df,p) singly occupied molecular orbitals of (a) G, (b) 2AP, (c) PC anions in gas phase and water environment.

4 Cartesian Coordinates

Atom	X	Y	Z
C	3.40566000	-0.18160000	-0.02642000
H	2.00421000	-0.41535000	1.58918000
C	1.79796000	0.19210000	-1.55989000
C	3.21486000	0.08067000	-1.35826000
C	0.93783000	0.43390000	-2.60124000
H	1.23233000	0.61311000	-3.62717000
N	-0.38626000	0.44897000	-2.31965000
O	-2.21802000	0.28756000	-0.96847000
H	-1.06290000	0.62242000	-3.05039000
C	4.66138000	-0.39281000	0.74564000
H	5.51980000	-0.31158000	0.08291000
H	4.67935000	-1.38041000	1.20847000
H	4.76881000	0.35071000	1.53654000
H	3.99495000	0.17998000	-2.09503000
N	2.16505000	-0.23817000	0.61039000
C	1.15620000	-0.01571000	-0.28835000
N	-0.12703000	-0.00524000	0.00637000
C	-0.99216000	0.23746000	-1.03839000

Table S10: S_0 Minimum for PC optimized with MP2/6-31G(d,p).

Atom	X	Y	Z
C	3.39270783	-0.17756111	-0.01590388
H	2.04013573	-0.23718302	1.60701971
C	1.81948062	0.52451623	-1.48595074
C	3.16918706	0.13083096	-1.35725289
C	0.84300697	0.63282890	-2.58822902
H	0.66837293	1.56532541	-3.12425088
N	-0.11019765	-0.28839310	-2.45918237
O	-2.07711208	0.25665225	-1.23147887
H	-0.84636076	-0.19540821	-3.14077353
C	4.66808864	-0.47446479	0.70681043
H	5.47959138	-0.59777905	-0.00896781
H	4.59124110	-1.39602868	1.28834833
H	4.94128947	0.33395848	1.38975511
H	3.91465597	0.09914952	-2.13470806
N	2.19421120	-0.07521975	0.63523478
C	1.22470756	0.34706727	-0.23466731
N	-0.09921217	0.22572963	-0.00998353
C	-0.91952582	0.12108656	-1.02985082

Table S11: Conical intersection between S_1 and S_0 for PC monomer optimized with CASSCF/cc-pVDZ.

Atom	X	Y	Z
C	3.37595900	-0.21244700	0.01256000
H	2.01544700	-0.25580200	1.61895000
C	1.83575200	0.46709500	-1.48350300
C	3.15009500	0.09501800	-1.35863100
C	0.88186900	0.60297400	-2.61422900
H	0.75134200	1.49919200	-3.20429300
N	-0.16642000	-0.23001800	-2.42336300
O	-2.10093300	0.31448600	-1.20639400
H	-0.88297700	-0.10434100	-3.14049700
C	4.64240500	-0.51866600	0.72548700
H	5.46036000	-0.64172900	0.01671900
H	4.56192000	-1.44140900	1.30427600
H	4.91732300	0.28375900	1.41493000
H	3.91662300	0.04701100	-2.12136000
N	2.18998800	-0.10193100	0.63495500
C	1.21758800	0.31499800	-0.25064000
N	-0.10966300	0.23384900	-0.00116700
C	-0.90466800	0.15397100	-1.07755800

Table S12: Conical intersection between S_1 and S_0 for PC monomer optimized with ADC(2)/def2-TZVP.

Atom	X	Y	Z
C	3.39505800	-0.19002890	0.02233550
H	1.99604960	-0.39605800	1.59492040
C	1.79474480	0.14725890	-1.54508420
C	3.17642400	0.05361280	-1.34629580
C	0.93029800	0.41187230	-2.68347940
H	1.19558070	0.33256640	-3.72931460
N	-0.39477360	0.48476990	-2.32745600
O	-2.18814790	0.27994550	-0.98512760
H	-1.11717960	0.66052100	-3.01539480
C	4.66602380	-0.38471980	0.76457790
H	5.50739590	-0.28725980	0.08031470
H	4.72058390	-1.37538920	1.22243490
H	4.79078690	0.35771780	1.55625610
H	3.96210260	0.14791780	-2.08178520
N	2.18038390	-0.23247400	0.61457390
C	1.18987610	-0.03443790	-0.32133510
N	-0.15623460	-0.03803860	0.00026430
C	-0.91469120	0.22832490	-1.03828650

Table S13: S_1 minimum 1 for PC monomer optimized with ADC(2)/def2-TZVP.

Atom	X	Y	Z
C	3.39497610	-0.19014580	0.02207170
H	1.99534980	-0.41227930	1.59206230
C	1.79934690	0.22874500	-1.52992880
C	3.17907470	0.09619240	-1.33833340
C	0.93352560	0.47567630	-2.67151580
H	1.22011240	0.91377820	-3.61850650
N	-0.39822030	0.38589220	-2.34482170
O	-2.18729200	0.28703550	-0.98514130
H	-1.12169760	0.52590930	-3.03981640
C	4.66417850	-0.41424380	0.75898050
H	5.50369980	-0.34440120	0.06909510
H	4.69401020	-1.40262480	1.22359450
H	4.81413480	0.32967910	1.54510030
H	3.96444700	0.18571800	-2.07479660
N	2.18013350	-0.23223150	0.61470980
C	1.19328740	0.02416710	-0.31042600
N	-0.15144320	0.05528690	0.01670690
C	-0.91307730	0.23420840	-1.03744820

Table S14: S_1 minimum 2 for PC monomer optimized with ADC(2)/def2-TZVP.

Atom	X	Y	Z
C	3.41232900	-0.18992990	0.03106000
H	2.00518940	-0.33073990	1.65072950
C	1.80758950	0.29972990	-1.50778960
C	3.18277910	0.09820000	-1.35583960
C	0.91242970	0.48050990	-2.69523920
H	1.11768970	1.11210970	-3.56137900
N	-0.35365990	0.14149000	-2.39738930
O	-2.16089940	0.25962990	-1.02091970
H	-1.08681970	0.28211990	-3.08559910
C	4.68196870	-0.45629990	0.75586980
H	5.50775850	-0.45939990	0.04785000
H	4.64354870	-1.42028960	1.26413960
H	4.85865860	0.32612990	1.49402960
H	3.96546890	0.11753000	-2.11580940
N	2.17304940	-0.19830990	0.64453980
C	1.17638970	0.10772000	-0.29099990
N	-0.13124000	0.15542000	0.04094000
C	-0.96025970	0.18039990	-1.05193970

Table S15: S_1 second order saddle point for PC monomer optimized with ADC(2)/def2-TZVP.

Atom	X	Y	Z
C	3.38261935	-0.12710146	-1.30215277
C	1.98666536	0.12796598	-1.50717226
C	1.35062207	0.13225264	-0.22272274
N	2.33748284	-0.10961618	0.69354658
C	3.56491783	-0.26784414	0.05077551
N	0.07601919	0.32290336	0.06595869
C	-0.75320265	0.54877333	-0.99898268
N	-0.17141558	0.56714762	-2.28778277
C	1.13441448	0.36395547	-2.56081006
O	-1.97980465	0.73874369	-0.88794008
C	4.80062006	-0.54224292	0.83553330
O	-3.85105012	0.68457769	-2.87037058
H	2.17253733	-0.16356459	1.68621756
H	1.42140774	0.40025614	-3.60390350
H	-0.80497636	0.74899422	-3.08302203
H	5.65071459	-0.63343162	0.16341375
H	4.71219204	-1.47055783	1.40162252
H	5.00847336	0.26320475	1.54128338
H	4.15621571	-0.19949949	-2.04889030
H	-3.24476594	0.76217508	-2.10015133
H	-4.26896435	-0.17472047	-2.75904093
O	-1.77445570	0.97064063	-4.55473758
H	-1.83669919	1.89450581	-4.81910558
H	-2.63392140	0.79733030	-4.10493711

Table S16: S_0 minimum for PC monomer with two explicit waters optimized with MP2/6-31G(d,p).

Atom	X	Y	Z
C	3.18064630	0.07673420	-1.31786090
C	3.44173150	-0.20924110	0.05479650
N	2.28043170	-0.05283240	0.70998180
H	2.12875170	-0.21775290	1.69708680
C	1.29972470	0.38202080	-0.15930800
C	1.87956420	0.49866340	-1.41529100
H	3.90100780	-0.01284300	-2.11446570
C	4.71716030	-0.53589480	0.73530920
H	5.02551120	0.26158990	1.41530300
H	4.63146570	-1.45668560	1.31667470
H	5.50819450	-0.67449710	0.00079520
C	0.89824670	0.59808450	-2.53415960
H	0.74062440	1.50813430	-3.13456080
N	-0.10195290	-0.29416830	-2.26792740
C	-0.75228780	-0.00738120	-0.96926270
N	-0.01384540	0.25761440	0.10027100
H	-0.80555240	-0.24809160	-3.02233140
O	-1.70715870	0.32838110	-4.12651970
H	-1.50534100	1.11482360	-4.68246840
H	-2.50459200	0.53228780	-3.57491440
O	-1.97133010	-0.08199890	-0.93175040
H	-3.03218530	0.59146440	-1.77062680
O	-3.63982400	0.89569500	-2.49961810
H	-4.43131360	0.35069740	-2.34363520

Table S17: Conical intersection between S_1 and S_0 for PC monomer with two explicit waters optimized with ADC(2)/def2-TZVP.

Atom	X	Y	Z
C	3.50783240	-0.24311140	0.10889410
H	2.10836230	-0.14105730	1.68138460
C	1.94369710	0.08454210	-1.50499920
C	3.30400810	-0.12188660	-1.28846600
C	1.10365380	0.33968280	-2.66823090
H	1.36087310	0.15432140	-3.70268670
N	-0.20616070	0.56592530	-2.34649070
O	-1.97857780	0.75235350	-0.95106370
H	-0.87907590	0.74247940	-3.10700030
C	4.75290540	-0.52840750	0.86384930
H	5.62058740	-0.31722720	0.24046640
H	4.80972770	-1.57655250	1.16997400
H	4.82569180	0.08664550	1.76274340
H	4.09522580	-0.17406350	-2.02271140
N	2.30374060	-0.10155550	0.68991900
C	1.32477760	0.09423710	-0.27188590
N	0.01065150	0.31726700	0.04242280
C	-0.73516220	0.54430000	-1.03382810
O	-4.00796060	0.80646210	-2.83930530
H	-3.37567300	0.81862010	-2.09193810
H	-4.62308690	0.09183150	-2.64859060
O	-1.93457360	0.90106860	-4.57445580
H	-1.97828340	1.72385920	-5.07200990
H	-2.80500950	0.82321050	-4.12565320

Table S18: S_1 minimum 1 for PC monomer with two explicit waters optimized with ADC(2)/def2-TZVP.

Atom	X	Y	Z
C	3.50742100	-0.22923000	0.11139700
H	2.09993320	-0.18998060	1.68003130
C	1.94731450	0.13575710	-1.49832910
C	3.30850110	-0.06563630	-1.28212830
C	1.10935490	0.41608530	-2.65721090
H	1.37393960	0.26721670	-3.69566530
N	-0.20534670	0.61267530	-2.33523960
O	-1.98658060	0.73042860	-0.94377470
H	-0.87725730	0.80258850	-3.09342700
C	4.75329510	-0.51932370	0.86326790
H	5.61814470	-0.34550270	0.22480720
H	4.79049680	-1.55886520	1.19982970
H	4.84971550	0.12025700	1.74288000
H	4.10337920	-0.08801780	-2.01393220
N	2.29953590	-0.11689320	0.69133190
C	1.32311790	0.10055710	-0.26840980
N	0.00448810	0.29559480	0.04609330
C	-0.73955080	0.54384150	-1.02663320
O	-4.00587750	0.78463110	-2.84345930
H	-3.37876950	0.79133260	-2.09171190
H	-4.60615600	0.05180920	-2.67597700
O	-1.92628800	0.98663600	-4.56220940
H	-1.98736870	1.82590570	-5.02947570
H	-2.79700640	0.87133840	-4.12224920

Table S19: S_1 minimum 2 for PC monomer with two explicit waters optimized with ADC(2)/def2-TZVP.

Atom	X	Y	Z
H	-4.02091	3.05935	0.00000
N	-1.91252	1.75563	0.00000
N	-3.38223	-0.10997	0.00002
C	-2.42064	-1.17000	0.00003
C	-0.95127	0.78095	0.00001
H	-4.32662	-0.44259	0.00003
O	-2.79757	-2.33140	0.00004
C	-1.09212	-0.60642	0.00002
N	0.39737	0.99579	0.00000
N	0.12760	-1.22891	0.00002
C	0.99562	-0.23878	0.00001
H	0.84795	1.89528	0.00000
H	2.07402	-0.35035	0.00002
C	-3.11602	1.24175	0.00001
N	-4.19607	2.06848	0.00000
H	-5.13699	1.74524	0.00001
O	-7.14928	1.09509	0.00000
C	-7.21092	-0.13224	0.00000
N	-6.14085	-1.00047	0.00003
N	-8.51028	-0.73651	-0.00003
C	-6.43085	-2.28482	0.00003
H	-9.25928	-0.05761	-0.00004
C	-8.78660	-2.06179	-0.00002
C	-7.72004	-2.92501	0.00001
H	-9.82850	-2.35474	-0.00004
N	-5.50828	-3.29668	0.00006
C	-6.14679	-4.53770	0.00005
H	-4.51332	-3.13748	0.00008
C	-7.50382	-4.34414	0.00001
C	-5.35124	-5.79652	0.00008
H	-8.24764	-5.12386	0.00001
H	-6.01910	-6.65481	0.00007
H	-4.71275	-5.86048	0.88219
H	-4.71271	-5.86049	-0.88201

Table S20: Hydrogen bonded dimer

Atom	X	Y	Z
N	-0.665990	3.040760	2.305940
C	-2.038680	3.151420	2.344230
C	0.178730	3.275490	1.174710
H	-0.154160	2.772100	3.123470
N	-2.778830	3.496290	1.321620
C	-0.634710	3.656090	0.045080
N	-2.632120	2.877670	3.537080
O	1.387500	3.139700	1.281260
C	-2.017400	3.733300	0.208940
N	-0.268380	3.973870	-1.235550
H	-2.130140	2.610220	4.353350
H	-3.634410	2.953300	3.583950
C	-1.407150	4.239810	-1.840760
N	-2.494260	4.109740	-1.014120
H	-1.511760	4.532960	-2.879280
H	-3.461860	4.258490	-1.245910
C	3.405660	-0.181600	-0.026420
H	2.004210	-0.415350	1.589180
C	1.797960	0.192100	-1.559890
C	3.214860	0.080670	-1.358260
C	0.937830	0.433900	-2.601240
H	1.232330	0.613110	-3.627170
N	-0.386260	0.448970	-2.319650
O	-2.218020	0.287560	-0.968470
H	-1.062900	0.622420	-3.050390
C	4.661380	-0.392810	0.745640
H	5.519800	-0.311580	0.082910
H	4.679350	-1.380410	1.208470
H	4.768810	0.350710	1.536540
H	3.994950	0.179980	-2.095030
N	2.165050	-0.238170	0.610390
C	1.156200	-0.015710	-0.288350
N	-0.127030	-0.005240	0.006370
C	-0.992160	0.237460	-1.038390
N	-1.280520	-3.595550	1.032070
C	-1.741250	-3.431040	-0.255820
C	0.084440	-3.732310	1.440110
H	-1.920850	-3.630220	1.801010
N	-0.971110	-3.375780	-1.312380
C	0.936460	-3.671760	0.276930
N	-3.088890	-3.322200	-0.404280
O	0.353200	-3.872680	2.622890
C	0.350060	-3.502030	-0.976850
N	2.299750	-3.756400	0.179640
H	-3.731020	-3.355740	0.354890
H	-3.443750	-3.201470	-1.338090
C	2.539440	-3.640350	-1.109890
N	1.397110	-3.484530	-1.853420
H	3.521120	-3.661200	-1.569540
H	1.325000	-3.376860	-2.851070

Table S21: Cartesian coordinates of the trimer GPCG. The π-stacked dimers were extracted

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