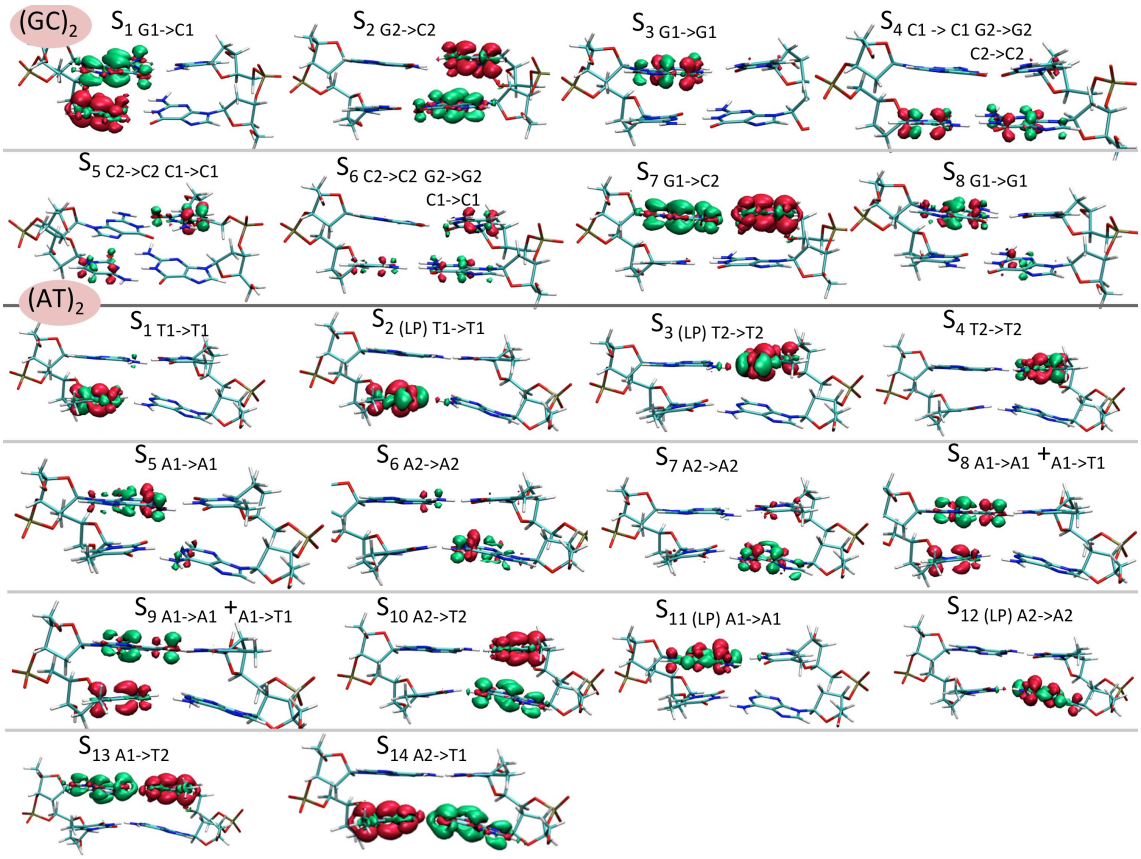
Figure S1. Excited State density difference at the Franck-Condon region for $(GC)_2$ and $(AT)_2$.



Comparison between Ground and Excited state minima

As a further step of our analysis we compare here the key geometry shifts obtained from the ground-state and excited-state calculations.

For GC/GC, the C6-O and C2-NH2 bond of $G^{\bullet+}$ is shorter (Figure S2) than that of neutral G, explaining the former the observed blue-shift of the carbonyl stretch. On the other hand, the C6-O bond for the closed-shell $G(-D1)^-$ (Intra-ET-PT, Figure S3) is significantly longer than that of neutral G, confirming the single-bond character upon deprotonation and consistent with the large red shift of the vibrational frequency. The C2-O and C5-C6 bonds are larger in $C^{\bullet-}$ compared to C. The ground-state approach results in a very similar picture as the excited-state calculation (compare Figure S2b and c), being the discrepancies in these critical

distances <0.01Å, indicating that the vibrational spectra obtained by the ground-state calculation are reliable.

Figure S2. Tetramer units used in the $(GC)_2$ DFT/TD-DFT calculations. (a) Ground state S_0 minimum, (b) Cation and anion S_0 minima and (c) Inter and Intrastrand ET S_1 minima. Representative distances in angstroms.

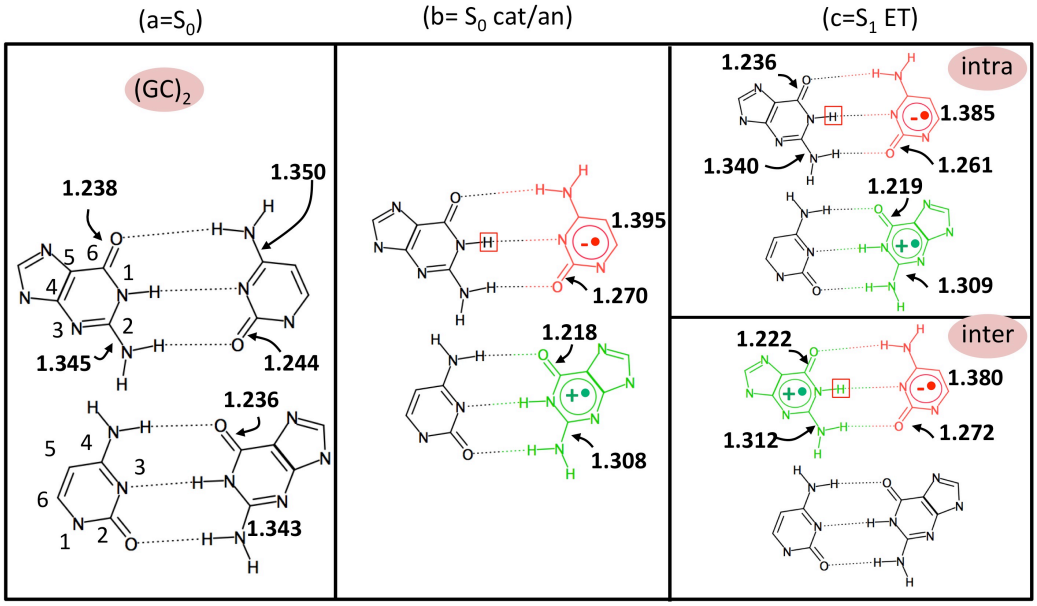
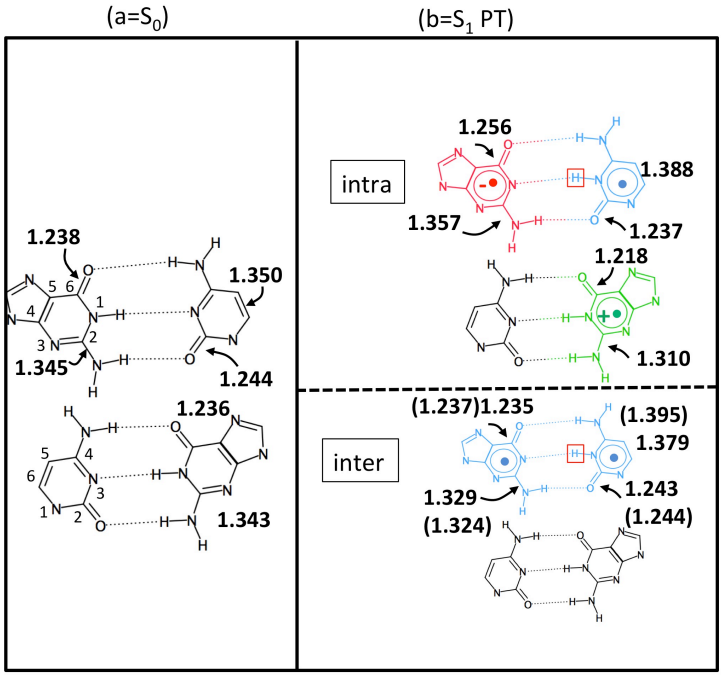


Figure S3. Tetramer units used in the $(GC)_2$ DFT/TD-DFT calculations. (a) Ground state S_0 minimum and (b) Inter and Intrastrand ET-PT S_1 minima. Representative distances in angstroms (in parenthesis for the PT S_0 minima) .



For AT/AT, Figure S4 show that the $T^{\bullet-}$ radical anion shows C4-O bond significantly elongated respect to neutral T and experience dramatic red shifts; whereas $A^{\bullet+}$ radical cation presents shorter C6-NH_2 distances compared to A. These key bond lengths are very similar for both ground and excited state calculations. However, the C5-C6 distance is much larger in the ground state $T^{\bullet-}$ minimum than in the S_1 ET one.

Figure S4. Tetramer units used in the $(AT)_2$ DFT/TD-DFT calculations. (a) Ground state S_0 minimum, (b) Cation and anion S_0 minima and (c) Intrastrand ET S_1 minima. Representative distances in angstroms.