Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Photoreaction channels of the guanine–cytosine base pair explored by long-range corrected TDDFT calculations

Electronic Supplementary Information

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Table S1: TDDFT/DZP and CC2/SV(P) vertical excitation energies (ΔE, eV) and oscillator strengths (f, in parentheses) for low-lying singlet excited states of GC pair and isolated G and C monomers at the ground-state equilibrium geometry optimized with the LC-BLYP/DZP method.

	LC-BLYP/DZP		CAM-B3LYP/DZP		B3LYP/DZP		CC2/SV(P)	
State	ΔE, f	Transition	ΔE, f	Transition	ΔE, f	Transition	ΔE, f	Transition
GC pair								
S_1	5.19 (0.068)	$^1\pi\pi^*$ (G $\rightarrow$ G*)	4.96 (0.015)	$^1\pi\pi^*$ (G $\rightarrow$ C*)	3.35 (0.001)	$^1\pi\pi^*$ (G $\rightarrow$ C*)	5.21 (0.051)	$^1\pi\pi^*$ (G $\rightarrow$ G*)
S_2	5.32 (0.110)	$^1\pi\pi^*$ (C $\rightarrow$ C*)	5.25 (0.070)	$^1\pi\pi^*$ (G $\rightarrow$ G*)	4.66 (0.006)	$^1\pi\pi^*$ (G $\rightarrow$ C*)	5.25 (0.064)	$^1\pi\pi^*$ (C $\rightarrow$ C*)
S_3	5.76 (0.465)	$^1\pi\pi^*$ (G $\rightarrow$ G*)	5.33 (0.095)	$^1\pi\pi^*$ (C $\rightarrow$ C*)	4.78 (0.000)	^{1}nπ^* (G $\rightarrow$ C*)	5.46 (0.019)	$^1\pi\pi^*$ (G $\rightarrow$ C*)
S_4	5.78 (0.001)	^{1}nπ^* (C $\rightarrow$ C*)	5.69 (0.418)	$^1\pi\pi^*$ (G $\rightarrow$ G*)	4.93 (0.087)	$^1\pi\pi^*$ (G $\rightarrow$ G*)	5.70 (0.001)	^{1}nπ^* (C $\rightarrow$ C*)
S_5	5.92 (0.050)	$^1\pi\pi^*$ (G $\rightarrow$ C*)	5.75 (0.001)	^{1}nπ^* (C $\rightarrow$ C*)	4.96 (0.024)	$^1\pi\pi^*$ (C $\rightarrow$ C*)	5.72 (0.216)	$^1\pi\pi^*$ (C $\rightarrow$ C*)
S_6	5.94 (0.000)	^{1}nπ^* (G $\rightarrow$ G*)	5.86 (0.105)	$^1\pi\pi^*$ (C $\rightarrow$ C*)	5.13 (0.036)	$^1\pi\pi^*$ (GC $\rightarrow$ C*)[a]	5.82 (0.448)	$^1\pi\pi^*$ (G $\rightarrow$ G*)
S_7	5.99 (0.068)	$^1\pi\pi^*$ (C $\rightarrow$ C*)	5.99 (0.000)	^{1}nπ^* (G $\rightarrow$ G*)	5.14 (0.000)	^{1}nπ^* (G $\rightarrow$ C*)	5.97 (0.001)	^{1}nπ^* (C $\rightarrow$ C*)
S_8	6.35 (0.002)	^{1}nπ^* (G $\rightarrow$ G*)	6.26 (0.001)	$^1\pi\pi^*$ (G $\rightarrow$ C*)	5.33 (0.000)	$^1\pi\sigma^*$ (G $\rightarrow$ C*)	6.05 (0.000)	^{1}nπ^* (G $\rightarrow$ G*)
S_9	6.47 (0.000)	^{1}nπ^* (C $\rightarrow$ C*)	6.38 (0.002)	^{1}nπ^* (G $\rightarrow$ G*)	5.34 (0.247)	$^1\pi\pi^*$ (G $\rightarrow$ G*)	6.60 (0.000)	^{1}nπ^* (G $\rightarrow$ G*)
S_{10}	6.56 (0.000)	^{1}nπ^* (G $\rightarrow$ G*)	6.53 (0.000)	^{1}nπ^* (C $\rightarrow$ C*)	5.41 (0.102)	$^1\pi\pi^*$ (C $\rightarrow$ C*)	6.61 (0.002)	^{1}nπ^* (G $\rightarrow$ G*)
G monomer								
S_1	5.32 (0.149)	$^1\pi\pi^*$ (G $\rightarrow$ G*)	5.32 (0.149)	$^1\pi\pi^*$ (G $\rightarrow$ G*)	5.09 (0.121)	$^1\pi\pi^*$ (G $\rightarrow$ G*)	5.44 (0.195)	$^1\pi\pi^*$ (G $\rightarrow$ G*)
S_2	5.57 (0.000)	^{1}nπ^* (G $\rightarrow$ G*)	5.63 (0.000)	^{1}nπ^* (G $\rightarrow$ G*)	5.36 (0.001)	$^1\pi\sigma^*$ (G $\rightarrow$ G*)	5.80 (0.001)	^{1}nπ^* (G $\rightarrow$ G*)
S_3	5.89 (0.332)	$^1\pi\pi^*$ (G $\rightarrow$ G*)	5.79 (0.308)	$^1\pi\pi^*$ (G $\rightarrow$ G*)	5.39 (0.234)	$^1\pi\pi^*$ (G $\rightarrow$ G*)	6.03 (0.309)	$^1\pi\pi^*$ (G $\rightarrow$ G*)
S_4	6.43 (0.004)	^{1}nπ^* (G $\rightarrow$ G*)	6.20 (0.001)	$^1\pi\sigma^*$ (G $\rightarrow$ G*)	5.41 (0.000)	^{1}nπ^* (G $\rightarrow$ G*)	6.58 (0.000)	^{1}nπ^* (G $\rightarrow$ G*)
C monomer								
S_1	5.09 (0.063)	$^1\pi\pi^*$ (C $\rightarrow$ C*)	5.08 (0.058)	$^1\pi\pi^*$ (C $\rightarrow$ C*)	4.75 (0.033)	$^1\pi\pi^*$ (C $\rightarrow$ C*)	5.05 (0.049)	$^1\pi\pi^*$ (C $\rightarrow$ C*)
S_2	5.30 (0.001)	^{1}nπ^* (C $\rightarrow$ C*)	5.35 (0.001)	^{1}nπ^* (C $\rightarrow$ C*)	4.81 (0.000)	^{1}nπ^* (C $\rightarrow$ C*)	5.23 (0.000)	^{1}nπ^* (C $\rightarrow$ C*)
S_3	5.96 (0.000)	^{1}nπ^* (C $\rightarrow$ C*)	5.97 (0.000)	^{1}nπ^* (C $\rightarrow$ C*)	5.21 (0.001)	^{1}nπ^* (C $\rightarrow$ C*)	5.59 (0.002)	^{1}nπ^* (C $\rightarrow$ C*)
S_4	6.15 (0.136)	$^1\pi\pi^*$ (C $\rightarrow$ C*)	6.07 (0.117)	$^1\pi\pi^*$ (C $\rightarrow$ C*)	5.57 (0.080)	$^1\pi\pi^*$ (C $\rightarrow$ C*)	5.98 (0.169)	$^1\pi\pi^*$ (C $\rightarrow$ C*)

[a] π orbital is delocalized on the G and C moieties.

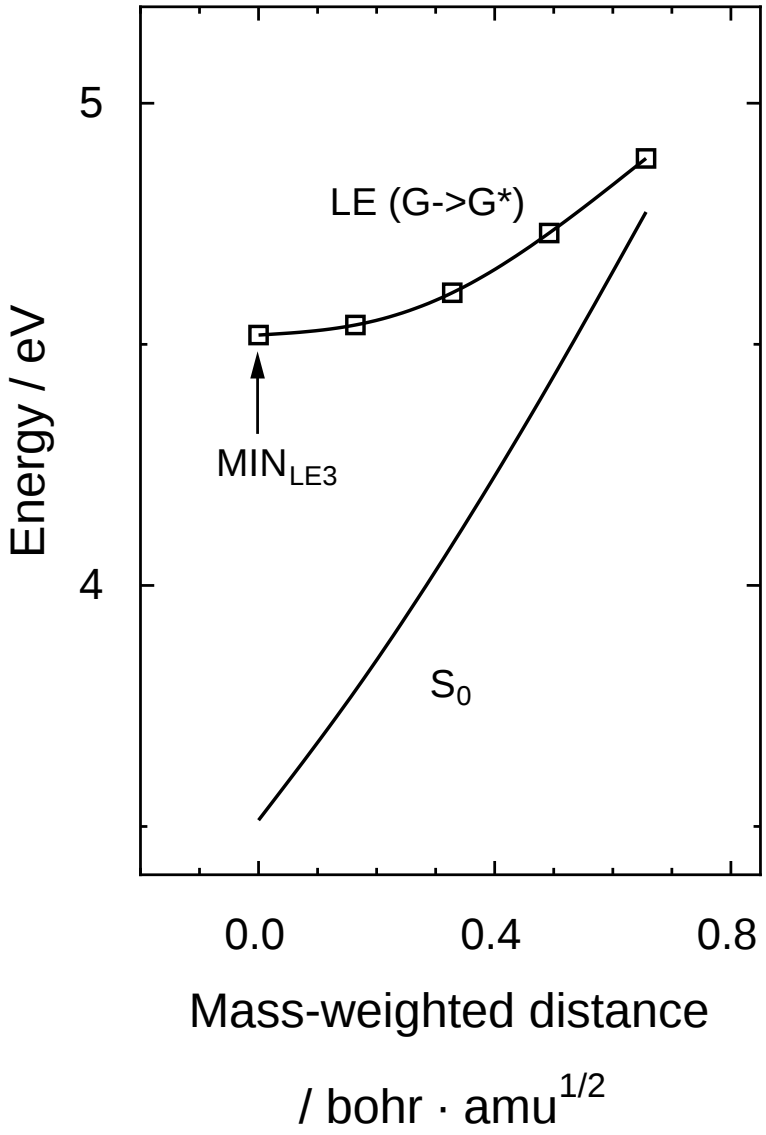

Figure S1: (TD-)LC-BLYP/DZP potential energy curves of the LE ($G \rightarrow G^*$) and S_0 states starting with MIN_{LE3}, along the vector of gradient difference between these states calculated at the minimum structure. Energies are relative to the ground-state energy of the FC geometry.

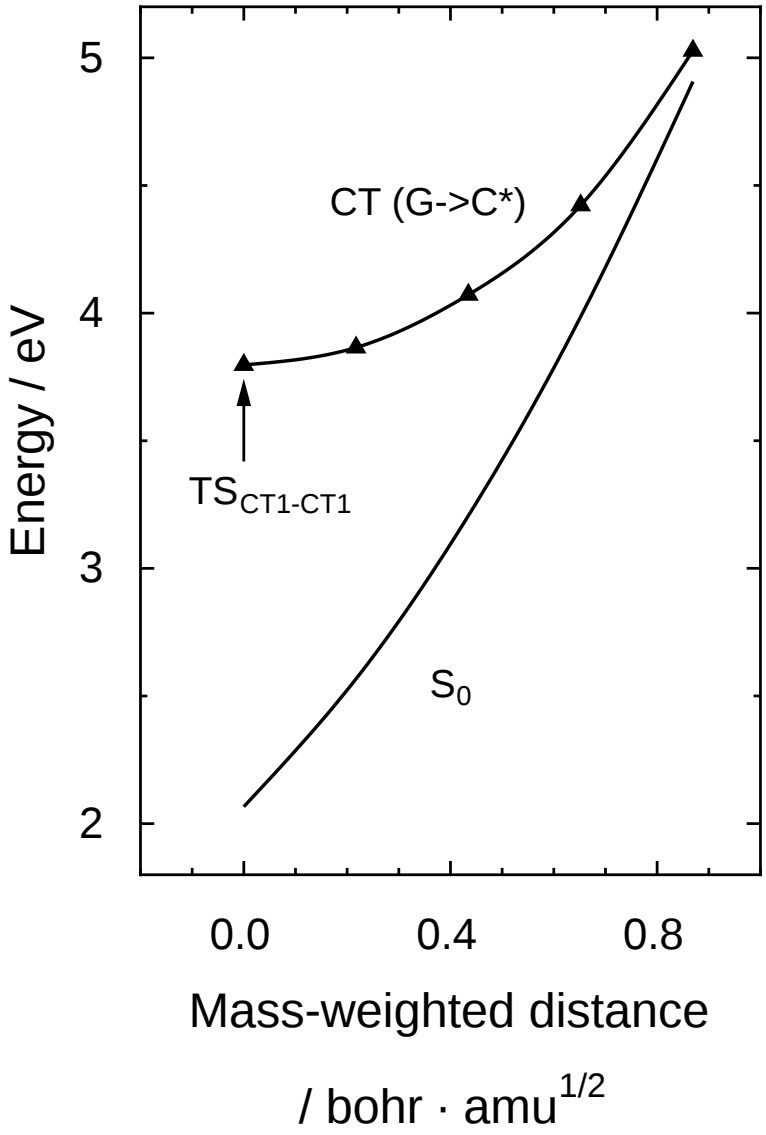

Figure S2: (TD-)LC-BLYP/DZP potential energy curves of the CT (G $\rightarrow$ C*) and S_0 states starting with $TS_{CT1\text{-}CT1}$, along the vector of gradient difference between these states calculated at the transition-state structure. Energies are relative to the ground-state energy of the FC geometry.