Theoretical Exploration of Structures and Electronic Properties of Double-Electron Oxidized Guanine–Cytosine Base Pairs with Intriguing Radical-Radical Interactions

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Supporting Information

Table S1. The optimized bond lengths (Å) of the Watson-Crick diradical base pair $[GC]^{2+}$ in the ground state

basis set	O6…H4a	H1…N3	H2a…O2
B3LYP/6-311+G*	2.105	1.789	1.610
B3LYP/6-311++G**	2.101	1.774	1.607
B3LYP/aug-cc-pVDZ	2.089	1.752	1.599

Table S2. Natural population charges on each atom and individual base in the corresponding diradical GC base pairs and neutral GC base pair at the (U)B3LYP/6-311++G**

Base Pairs	H_1(G)	H_{2a}	O_6	N_1	N_7	G(G(-H^+))	N_3	O_2	H_{4a}	C(C_p)
$[GC]^{2+}$-1	0.437	0.421	-0.565	-0.597	-0.199	0.973	-0.302	-0.511	0.426	1.027
$[GC]^{2+}$-2	0.450	0.438	-0.377	-0.605	-0.307	1.021	-0.569	-0.649	0.419	0.979
$[GC]^{2+}$-3	0.466	0.457	-0.504	-0.635	-0.369	1.281	-0.638	-0.591	0.445	0.719
$[GC]^{2+}$-4	0.460	0.423	-0.574	-0.622	-0.389	1.017	-0.518	-0.542	0.439	0.983
$[GC]^{2+}$-5	0.443	0.430	-0.493	-0.603	-0.502	1.029	-0.474	-0.437	0.436	0.971
$[G(-H^+)C_p]^{2+}$-3	0.457	0.463	-0.508	-0.647	-0.364	1.025	-0.609	-0.631	0.442	0.975
GC	0.481	0.468	-0.712	-0.666	-0.450	-0.037	-0.663	-0.706	0.485	0.037

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Table S3. Energies (in a.u.) for the close-shell singlet (CS), broken-symmetry (BS) and triplet (OT) states of double-electron oxidized guanine–cytosine base pair at the (U)B3LYP/6-311+G* level

Base Pair	$E_{(CS)}$	$E_{(OS)}$	$E_{(OT)}$
$[GC]^{2+}$-1	-937.1274049		-937.0467357
$[GC]^{2+}$-2	-937.1134499		-937.0607657
$[GC]^{2+}$-3	-937.0986466	-937.1045483	-937.1003219
$[GC]^{2+}$-4	-937.0932329		-937.1043127
$[GC]^{2+}$-5	-937.0789993	-937.0989385	-937.0989430

Table S4. Relative energies (Δ*E* kcal/mol), NPA Charges and dissociation energies (D_e kcal/mol) of the deprotonated structures derived from $[GC]^{2+}$

Base Pair	Δ*E*	NPA G|C		D_e
$[G(N9)C]^+$	0.0	0.852	0.148	63.88
$[GC(N1)]^+$	1.55	0.874	0.126	50.86
$[G(N2b)C]^+$	15.03	0.081	0.919	20.99
$[GC(N4b]^+$	21.70	0.795	0.205	33.39
$[G(N1)C]^+$	23.35	0.772	0.128	42.49
$[GC(N4a)]^+$	26.64	0.924	0.076	34.24
$[G(N2a)C]^+$	31.52	0.771	0.229	29.70

Table S5. Energies (in a.u.) and adiabatic ionization potentials (AIP, eV) of the bases optimized using the (U)B3LYP/6-311+G* method in different states

base	G			C	
Charge/spin	0/1	1/2	2/1	0/1	1/2
E	-542.698	-542.418	-541.941	-395.041	-394.724
AIP	7.64	12.98		8.60	

deprotonated base	[G(N9)]			[C(N4a)]		
Charge/spin	-1/1	0/2	1/1	-1/1	0/2	1/1
E	-542.149.	-542.045	-541.755	-394.465	-394.356	-393.993
AIP	2.85	7.89		2.97	9.89	

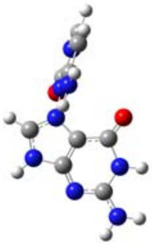
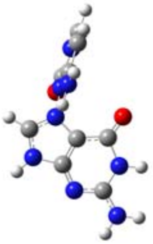
Table S6. Number of electrons outside closed-shell bonding orbitals (BO), occupation number of LUMO and the amounts of the diradical character of the open-shell BS singlet states of the calculated corresponding diradical base pairs using CASSCF(10,10)/6-311+G* //RB3LYP/6-311+G* method

Base Pair	Total occupancy outside BO	Occupation number of LUMO	Diradical percentage
$[GC]^{2+}$-3	0.347	0.122	12.2
$[GC]^{2+}$-5	1.206	0.970	97.0
$[GC(N4a)]^{+}$	1.237	0.998	99.8
$[GC(N4b)]^{+}$	1.220	0.991	99.1

[a] Notes: used RB3LYP/6-311+G* as its initial guess in accord with the optimized geometry

Table S7. $R_{N\text{-}H\ldots O}$ (the H-bond length of $(G^{\bullet+})$N-H…O$(C^{\bullet+})$, as an indicator of $G^{+}\ldots G^{+}$ separation); spin-squared values for the open-shell BS singlet($\langle S^2\rangle$); the occupation number of LUMO and the amounts of the diradical character of the open-shell BS singlet states of the $[GC]^{2+}$-3 diradical base pair using the CASSCF(10,10)/6-311+G*//RB3LYP/6-311+G* method

$R_{N\text{-}H\ldots O}$(Å)	$\langle S^2\rangle$	Occupation number of LUMO	Diradical percentage
2.001	0.690	0.988	98.8
2.101	0.702	0.992	99.2
2.201	0.727	0.994	99.4
2.301	0.790	0.996	99.6
2.401	0.732	0.998	99.8
2.501	0.849	0.998	99.8
2.601	0.851	1.000	100.0
2.701	0.888	1.001	100.1
2.801	0.945	1.001	100.1
2.901	0.897	1.001	100.2

Geometries	CS	OS	OT
			
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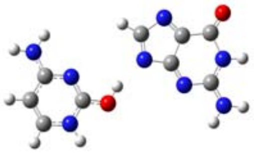	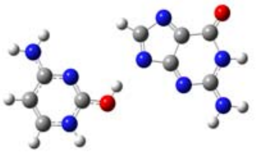		
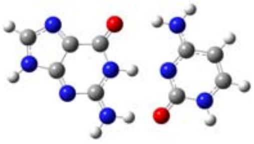	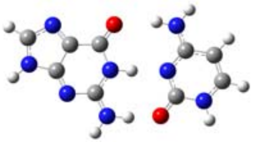	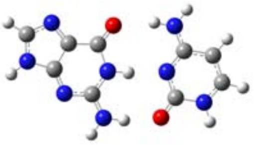	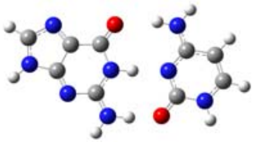
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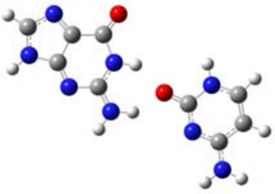	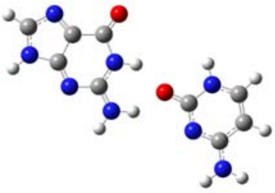		
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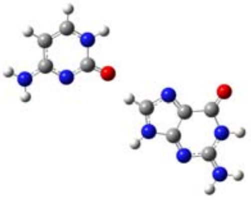	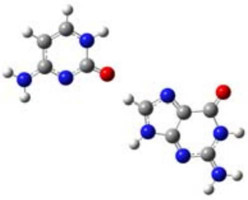		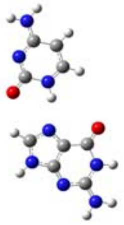
	-937.0789	-937.0989386	-937.098943

Figure S1 The optimized structures of double-electron oxidized guanine–cytosine base pairs. The closed-shell singlet (CS), open-shell singlet (OS), and open-shell triplet (OT) states of every structure are given, and the numbers under the figures are the corresponding energies (in a.u.).

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	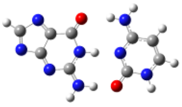		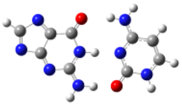
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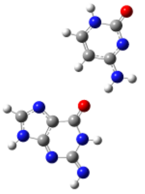			
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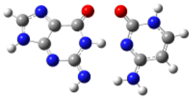	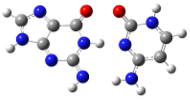		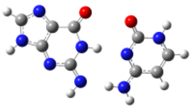
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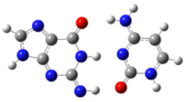	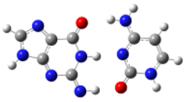		
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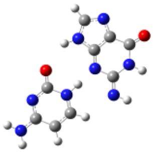	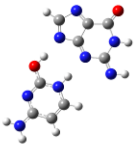		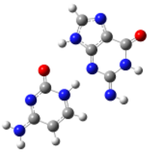
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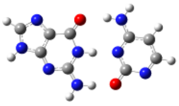	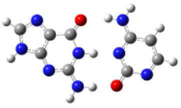	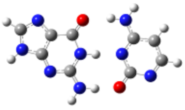	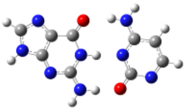
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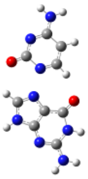			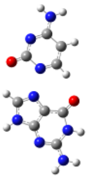
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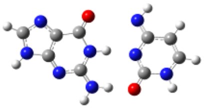	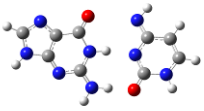	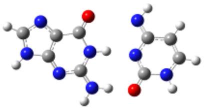	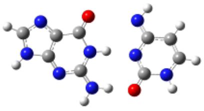
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	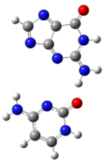		
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	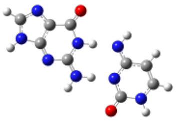		
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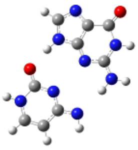	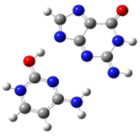	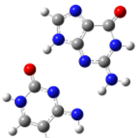	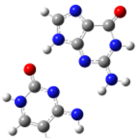
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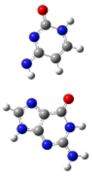	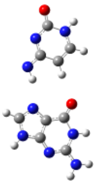	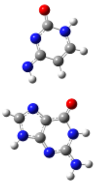	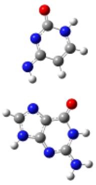
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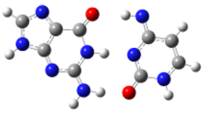			
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Figure S2 The optimized deprotonated structures of the double-electron oxidized guanine–cytosine base pairs. The closed-shell singlet (CS), open-shell singlet (OS) and open-shell triplet (OT) states of every structure are given, and the numbers under the figures are the corresponding energies (in a.u.).

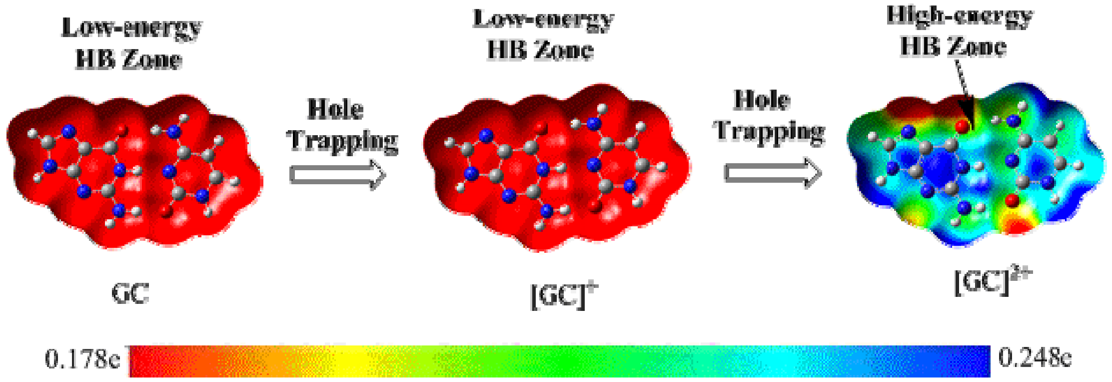

Figure S3. Variation of electrostatic potential (ESP) surfaces of GC unit upon hole trapping (molecular total electron density = 4×10^{-4} au).

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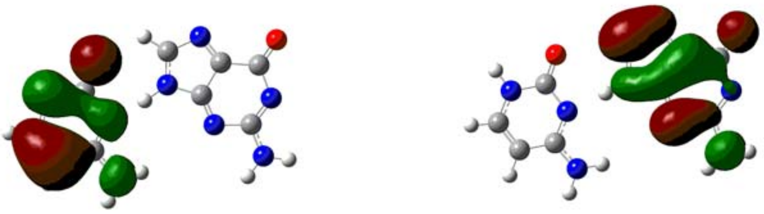

[G(N1)C]$^+$ HOMO [G(N1)C]$^+$ LUMO

Figure S3. Plots of the frontier orbitals for representative deprotonated structures of [G(N9)C]$^+$ and [G(N1)C]$^+$.

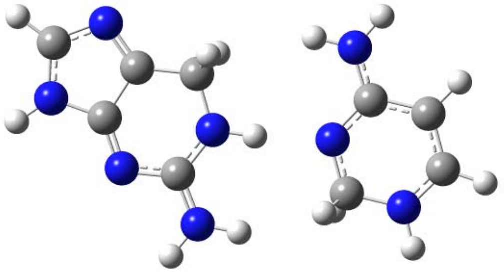

Figure S4. The geometry of the [GG]$^{2+}$-3 diradical on replacing the two oxygen atoms by four hydrogen atoms.

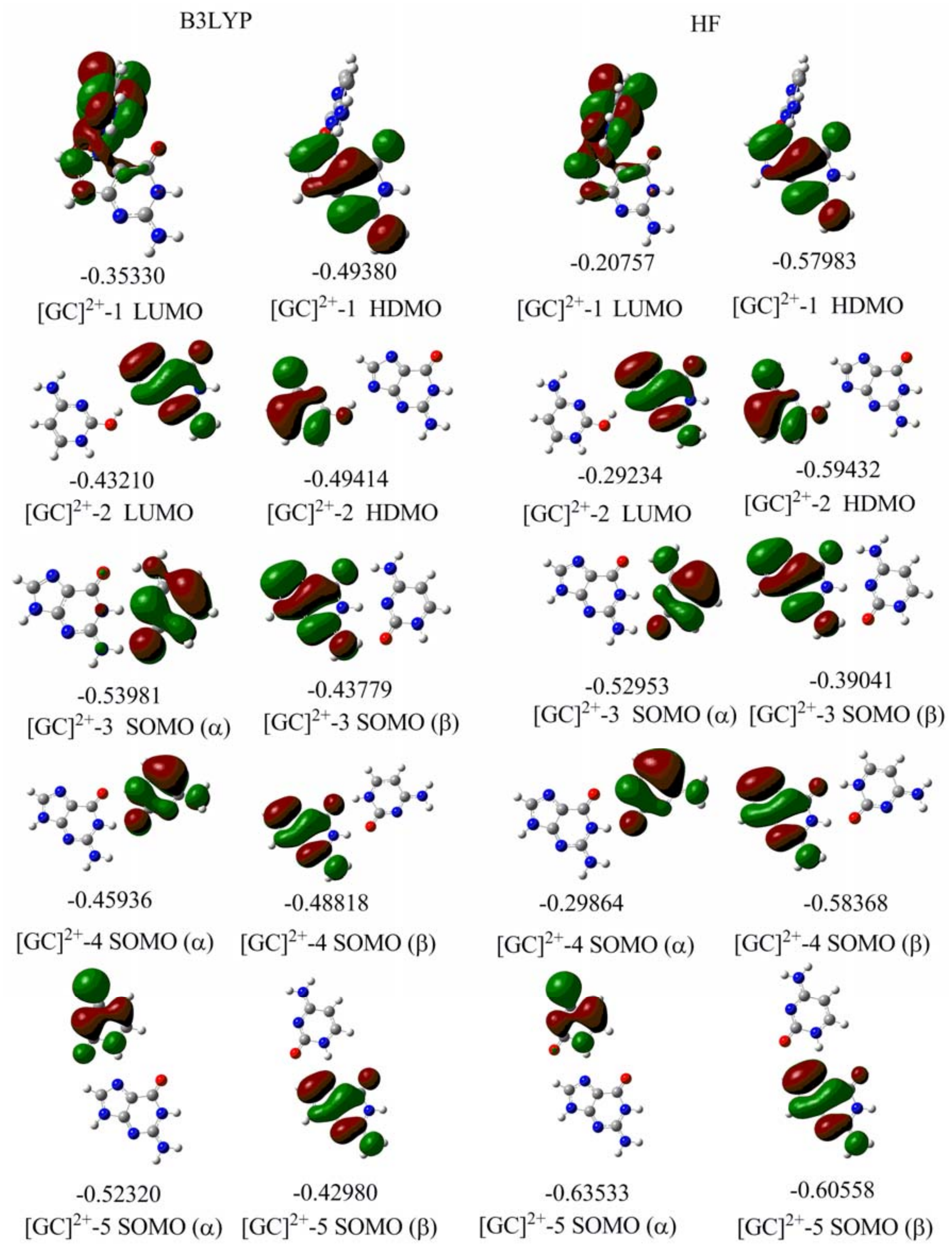

Figure S5. Comparison of orbital characters with the corresponding energies between the B3LYP and Hartree-Fock methods for the $[GC]^{2+}$-n dication complexes (the DFT Kohn-Sham orbital versus Hartree-Fock molecular orbital).

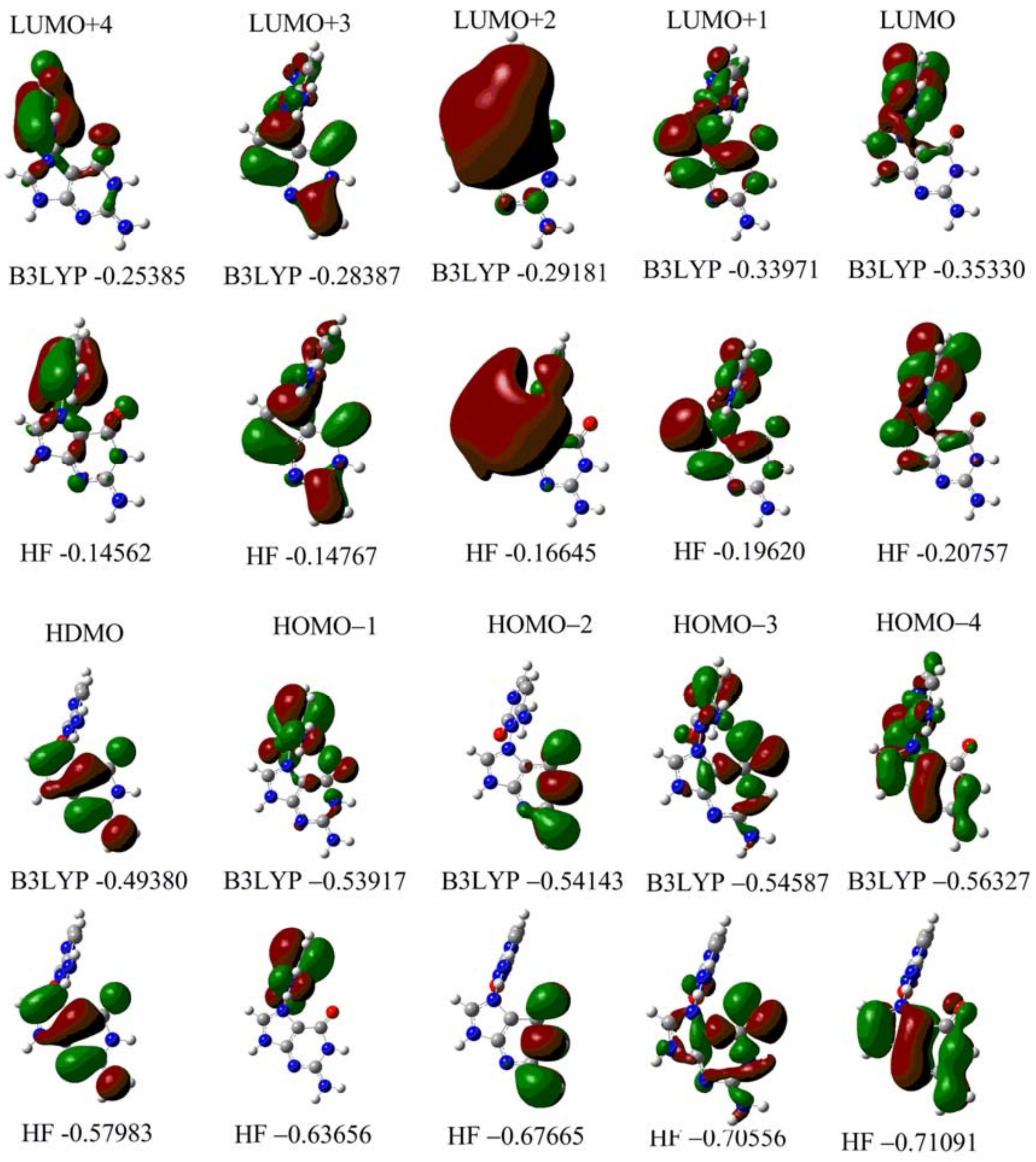

Figure S6. Comparison of the B3LYP Kohn-Sham orbitals with their energy levels with those the corresponding Hartree-Fock orbitals for $[GC]^{2+}$-1 as an example.

Simple Analyses: To verify the equivalency of DFT and Hartree-Fock methods in producing the molecular orbitals of the species considered here, we calculate the Kohn-Sham orbitals and Hartree-Fock molecular orbitals with their corresponding energies, and the results are displayed in Figure S5 and S6 for comparisons. These results indicate that the Kohn-Sham orbital characters calculated from DFT method are quite similar to those calculated by Hartree-Fock method, but the orbital energies are slightly different from each other. The differences should be attributed to such a fact that the Hartree-Fock method does not include the electron correlation effect.