Supporting Information

MS-CASPT2 Study of Hole Transfer in Guanine-Indole complexes using the Generalized Malliken-Hush method: Effective 2-State Treatment

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Table SI1: MS-CASPT2//CASSCF(11,12)/ANO-S energies (in a. u.) of first five states for the calculated $(G\text{-}Ind)^{\cdot+}$ structures.

Structure	D_0	D_1	D_2	D_3	D_4
π1	-903.57210	-903.56789	-903.54484	-903.49627	-903.47618
π2	-903.56825	-903.55269	-903.54295	-903.49268	-903.46303
π3	-903.56295	-903.55533	-903.54593	-903.49254	-903.46429
π4	-903.56698	-903.55449	-903.54750	-903.49088	-903.48853
π5	-903.56878	-903.55229	-903.54937	-903.48736	-903.48243
π6	-903.54761	-903.54603	-903.53764	-903.49175	-903.47752

Table SI2: Comparison between relative site energies and electronic coupling values (eV) obtained proecting the dipole moments along the vector joining the centers of mass of the two molecules (cM), and along the normal vector to the plane of the rings (Zc).

Structure	Projection	ΔG^{3st}_{GS-CT}	ΔG^{3st}_{ES-CT}	$\lvert V^{3st}_{GS-CT} \rvert$	$\lvert V^{3st}_{ES-CT} \rvert$
π1	cM	-0.169	0.3311	0.0666	-0.3006
	Zc	-0.1683	0.3314	0.0665	-0.3007
π2	cM	-0.3448	0.0558	0.2280	-0.1466
	Zc	-0.3436	0.0568	0.2282	-0.1467
π3	cM	-0.0162	0.2798	0.1104	0.1178
	Zc	-0.0197	0.276	0.1108	0.1190
π4	cM	-0.1908	0.2647	0.1407	0.0043
	Zc	-0.1947	0.2626	0.1394	0.0050
π5	cM	-0.1462	0.2297	0.2124	0.0079
	Zc	-0.1482	0.2287	0.2121	0.0082
π6	cM	0.0123	0.244	0.0192	-0.0448
	Zc	0.0158	0.2467	0.0183	-0.0430

Table SI3. Coupling elements (V) and diabatic energy differences ($\Delta\varepsilon$) derived with the 3-state GMH treatment from CASPT2 and CASSCF calculations of the conformations π1 – π6 (in eV).

Structure	method	V^{3st}_{GS-CT}	V^{3st}_{ES-CT}	$\Delta\varepsilon^{3st}_{GS-CT}$	$\Delta\varepsilon^{3st}_{ES-CT}$
π1	CASPT2	0.067	0.301	-0.169	0.331
	CASSCF	0.211	0.312	-0.387	0.147
π2	CASPT2	0.228	0.147	-0.345	0.056
	CASSCF	0.191	0.229	-0.664	-0.186
π3	CASPT2	0.110	0.118	-0.016	0.280
	CASSCF	0.093	0.183	-0.308	0.109
π4	CASPT2	0.141	0.004	-0.191	0.265
	CASSCF	0.205	0.048	-0.515	0.119
π5	CASPT2	0.212	0.008	-0.146	0.230
	CASSCF	0.237	0.140	-0.418	-0.009
π6	π6 CASPT2	0.019	0.045	0.012	0.244
	CASSCF	0.036	0.069	0.030	0.283

Table SI4: Atomic coordinates of π1 structure in Angstroms.

N	0.2668	-2.6360	-0.0040
C	1.6343	-2.7736	0.0020
H	2.1120	-3.7449	-0.0010
N	2.2691	-1.6118	0.0160
C	1.2530	-0.6819	0.0180
C	1.3268	0.7583	0.0090
O	2.2909	1.5139	-0.0030
N	0.0000	1.2919	0.0000
H	-0.0286	2.3041	-0.0980
C	-1.1756	0.5833	0.0060
N	-2.3377	1.3354	-0.0740
H	-2.3545	2.1680	0.5060
H	-3.1558	0.7530	0.0730
N	-1.2429	-0.7256	0.0150
C	0.0000	-1.2919	0.0000
H	-0.4299	-3.3719	-0.0180
C	0.3654	-2.7841	3.3800
C	1.7398	-2.8383	3.3800
C	0.0000	-1.4015	3.3800
H	2.4055	-3.6920	3.3800
N	2.2465	-1.5551	3.3800
C	1.2086	-0.6502	3.3800
C	-1.2261	-0.7088	3.3800
H	3.2293	-1.3174	3.3830
C	1.2268	0.7507	3.3800
C	-1.2137	0.6787	3.3800
H	-2.1677	-1.2547	3.3800
H	2.1609	1.3091	3.3800
C	0.0000	1.4015	3.3800
H	-2.1542	1.2245	3.3800
H	-0.0270	2.4886	3.3800
H	-0.3011	-3.6370	3.3800

Table SI5: Atomic coordinates of π2 structure in Angstroms.

N	0.2668	-2.6360	-0.0040
C	1.6343	-2.7736	0.0020
H	2.1120	-3.7449	-0.0010
N	2.2691	-1.6118	0.0160
C	1.2530	-0.6819	0.0180
C	1.3268	0.7583	0.0090
O	2.2909	1.5139	-0.0030
N	0.0000	1.2919	0.0000
H	-0.0286	2.3041	-0.0980
C	-1.1756	0.5833	0.0060
N	-2.3377	1.3354	-0.0740
H	-2.3545	2.1680	0.5060
H	-3.1558	0.7530	0.0730
N	-1.2429	-0.7256	0.0150
C	0.0000	-1.2919	0.0000
H	-0.4299	-3.3719	-0.0180
C	2.3654	-2.7841	3.3800
C	3.7398	-2.8383	3.3800
C	2.0000	-1.4015	3.3800
H	4.4055	-3.6920	3.3800
N	4.2465	-1.5551	3.3800
C	3.2086	-0.6502	3.3800
C	0.7739	-0.7088	3.3800
H	5.2293	-1.3174	3.3830
C	3.2268	0.7507	3.3800
C	0.7863	0.6787	3.3800
H	-0.1677	-1.2547	3.3800
H	4.1609	1.3091	3.3800
C	2.0000	1.4015	3.3800
H	-0.1542	1.2245	3.3800
H	1.9730	2.4886	3.3800
H	1.6989	-3.6370	3.3800

Table SI6: Atomic coordinates of π3 structure in Angstroms.

N	0.2668	-2.6360	-0.0040
C	1.6343	-2.7736	0.0020
H	2.1120	-3.7449	-0.0010
N	2.2691	-1.6118	0.0160
C	1.2530	-0.6819	0.0180
C	1.3268	0.7583	0.0090
O	2.2909	1.5139	-0.0030
N	0.0000	1.2919	0.0000
H	-0.0286	2.3041	-0.0980
C	-1.1756	0.5833	0.0060
N	-2.3377	1.3354	-0.0740
H	-2.3545	2.1680	0.5060
H	-3.1558	0.7530	0.0730
N	-1.2429	-0.7256	0.0150
C	0.0000	-1.2919	0.0000
H	-0.4299	-3.3719	-0.0180
C	0.3654	-4.4841	3.3800
C	1.7398	-4.5383	3.3800
C	0.0000	-3.1015	3.3800
H	2.4055	-5.3920	3.3800
N	2.2465	-3.2551	3.3800
C	1.2086	-2.3502	3.3800
C	-1.2261	-2.4088	3.3800
H	3.2293	-3.0174	3.3830
C	1.2268	-0.9493	3.3800
C	-1.2137	-1.0213	3.3800
H	-2.1677	-2.9547	3.3800
H	2.1609	-0.3909	3.3800
C	0.0000	-0.2985	3.3800
H	-2.1542	-0.4755	3.3800
H	-0.0270	0.7886	3.3800
H	-0.3011	-5.3370	3.3800

Table SI7: Atomic coordinates of π4 structure in Angstroms.

N	0.2668	-2.6360	-0.0040
C	1.6343	-2.7736	0.0020
H	2.1120	-3.7449	-0.0010
N	2.2691	-1.6118	0.0160
C	1.2530	-0.6819	0.0180
C	1.3268	0.7583	0.0090
O	2.2909	1.5139	-0.0030
N	0.0000	1.2919	0.0000
H	-0.0286	2.3041	-0.0980
C	-1.1756	0.5833	0.0060
N	-2.3377	1.3354	-0.0740
H	-2.3545	2.1680	0.5060
H	-3.1558	0.7530	0.0730
N	-1.2429	-0.7256	0.0150
C	0.0000	-1.2919	0.0000
H	-0.4299	-3.3719	-0.0180
C	0.3654	-4.4841	3.3800
C	1.7398	-4.5383	3.3800
C	0.0000	-3.1015	3.3800
H	2.4055	-5.3920	3.3800
N	2.2465	-3.2551	3.3800
C	1.2086	-2.3502	3.3800
C	-1.2261	-2.4088	3.3800
H	3.2293	-3.0174	3.3830
C	1.2268	-0.9493	3.3800
C	-1.2137	-1.0213	3.3800
H	-2.1677	-2.9547	3.3800
H	2.1609	-0.3909	3.3800
C	0.0000	-0.2985	3.3800
H	-2.1542	-0.4755	3.3800
H	-0.0270	0.7886	3.3800
H	-0.3011	-5.3370	3.3800

Table SI8: Atomic coordinates of π5 structure in Angstroms.

N	0.2668	-2.6360	-0.0040
C	1.6343	-2.7736	0.0020
H	2.1120	-3.7449	-0.0010
N	2.2691	-1.6118	0.0160
C	1.2530	-0.6819	0.0180
C	1.3268	0.7583	0.0090
O	2.2909	1.5139	-0.0030
N	0.0000	1.2919	0.0000
H	-0.0286	2.3041	-0.0980
C	-1.1756	0.5833	0.0060
N	-2.3377	1.3354	-0.0740
H	-2.3545	2.1680	0.5060
H	-3.1558	0.7530	0.0730
N	-1.2429	-0.7256	0.0150
C	0.0000	-1.2919	0.0000
H	-0.4299	-3.3719	-0.0180
C	2.4912	1.2956	3.3800
C	2.0721	2.6056	3.3800
C	1.3170	0.4793	3.3800
H	2.6466	3.5232	3.3800
N	0.6930	2.6429	3.3800
C	0.1976	1.3581	3.3800
C	1.0854	-0.9097	3.3800
H	0.1335	3.4851	3.3830
C	-1.1250	0.8961	3.3800
C	-0.2227	-1.3726	3.3800
H	1.9204	-1.6078	3.3800
H	-1.9692	1.5828	3.3800
C	-1.3170	-0.4793	3.3800
H	-0.4139	-2.4431	3.3800
H	-2.3293	-0.8765	3.3800
H	3.5206	0.9610	3.3800

Table SI9: Atomic coordinates of π6 structure in Angstroms.

N	0.2668	-2.6360	-0.0040
C	1.6343	-2.7736	0.0020
H	2.1120	-3.7449	-0.0010
N	2.2691	-1.6118	0.0160
C	1.2530	-0.6819	0.0180
C	1.3268	0.7583	0.0090
O	2.2909	1.5139	-0.0030
N	0.0000	1.2919	0.0000
H	-0.0286	2.3041	-0.0980
C	-1.1756	0.5833	0.0060
N	-2.3377	1.3354	-0.0740
H	-2.3545	2.1680	0.5060
H	-3.1558	0.7530	0.0730
N	-1.2429	-0.7256	0.0150
C	0.0000	-1.2919	0.0000
H	-0.4299	-3.3719	-0.0180
C	-1.8653	2.2620	-3.1909
C	-1.0145	3.3122	-2.9354
C	-1.0583	1.0873	-3.3088
H	-1.2273	4.3624	-2.7814
N	0.2832	2.8464	-2.8888
C	0.2932	1.4878	-3.1133
C	-1.3308	-0.2712	-3.5602
H	1.1007	3.4168	-2.7192
C	1.3629	0.5843	-3.1612
C	-0.2749	-1.1703	-3.6087
H	-2.3539	-0.6091	-3.7140
H	2.3906	0.9085	-3.0093
C	1.0583	-0.7473	-3.4112
H	-0.4730	-2.2218	-3.8021
H	1.8618	-1.4788	-3.4559
H	-2.9418	2.3282	-3.2826