Excited-state Relaxation Mechanisms of Janus-type proton in benzimidazole conjugated aminomaleonitrile: Single or Double Proton Transfer?

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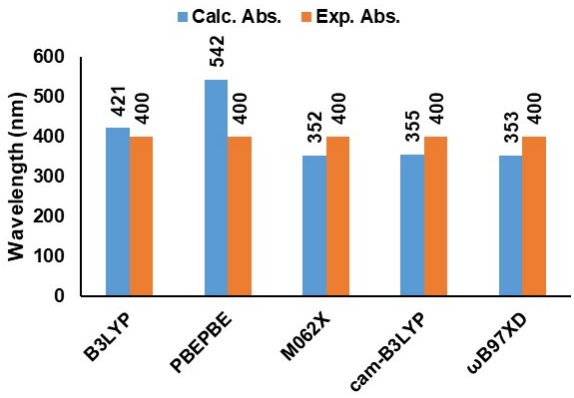

Figure S1. Comparison of experimental and calculated absorption of probe 1 using different functionals.

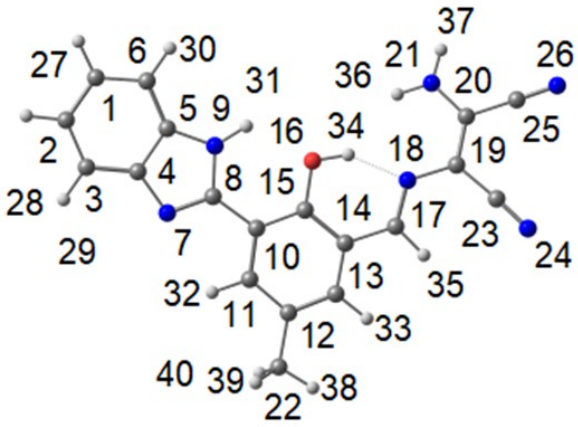

Figure S2. Atomic label of probe 1.

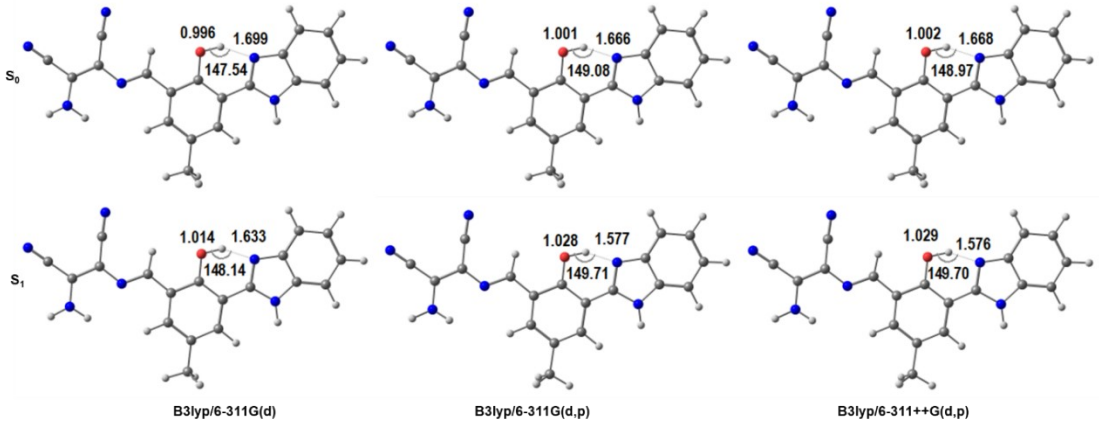

Figure S3. Optimized structure of C3 conformation at the basis sets of B3LYP functional.

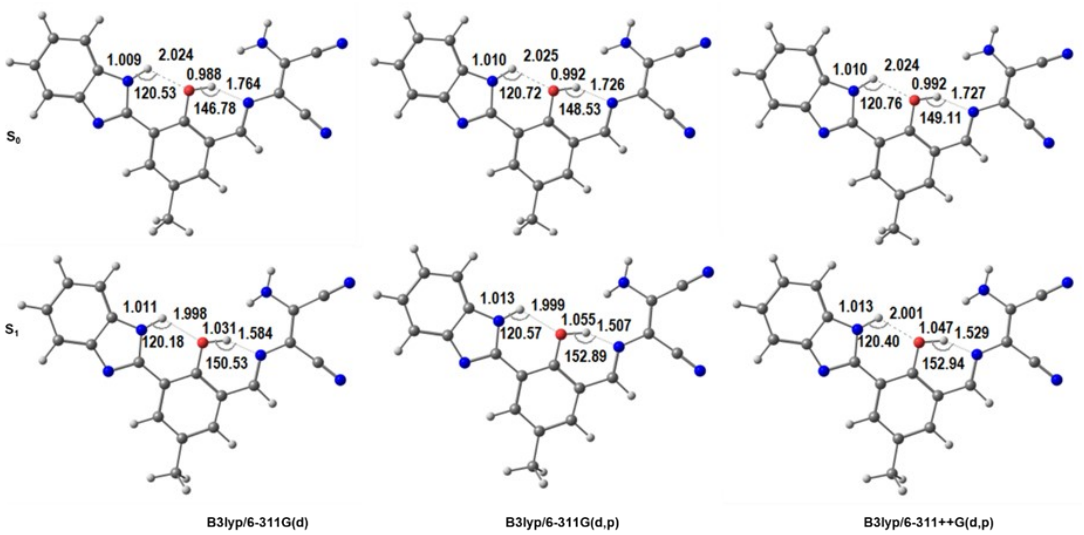

Figure S4. Optimized structure of C4 conformation at the basis sets of B3LYP functional.

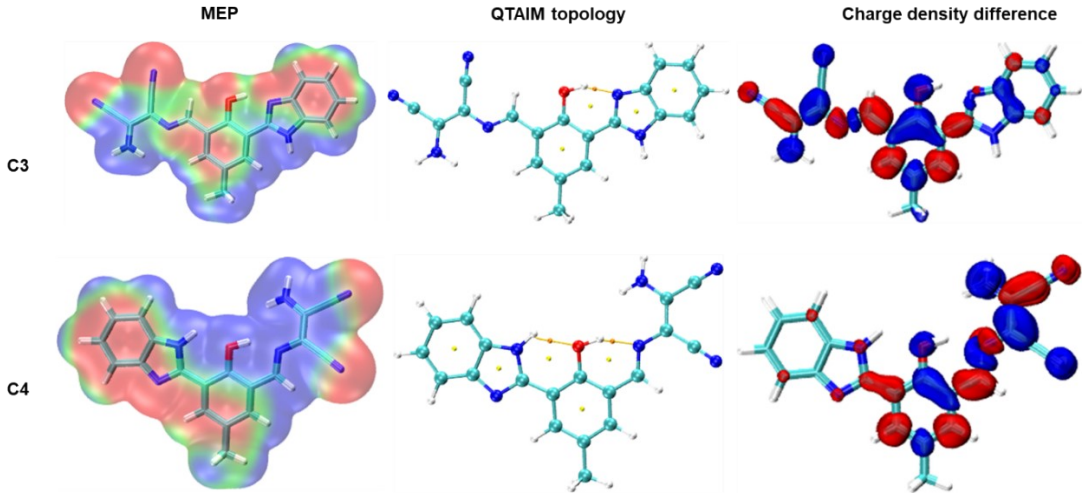

Figure S5. Molecular electrostatic potential maps, QTAIM critical point topologies and charge density difference of C3 and C4.

Table S1. Topology parameters, including electron density (r), Laplacian electron density (V2r), potential energy density [V(r)], total energy density

[H(r)], and hydrogen bonding energy [E^{HB} (kcal mol^{-1})] at the bond critical point of non-covalent interactions (D/HA) for conformers C3 and C4.

Conformation	State	Interaction	ρ	∇2ρ	H(r)	E^{HB}
C3	S_0	O_{16}–H_{34}···N_7	0.05249	0.11419	-0.01095	-10.97
	S_1	O_{16}–H_{34}···N_7	0.06592	0.10863	-0.02001	-13.96
C4	S_0	O_{16}–H_{34}···N_{18}	0.04618	0.10892	-0.00732	-9.56
	S_1	O_{16}–H_{34}···N_{18}	0.08186	0.08505	-0.03224	-17.52
PC3	S_0	O_{16}–H_{34}···N_{18}	0.04472	0.11226	-0.00640	-9.23
	S_1	O_{16}–H_{34}···N_{18}	0.07886	0.09484	-0.02984	-16.85
PC4	S_0	O_{16}–H_{34}···N_7	0.05706	0.11396	-0.01389	-11.99
	S_1	O_{16}–H_{34}···N_7	0.06738	0.10762	-0.02108	-14.29

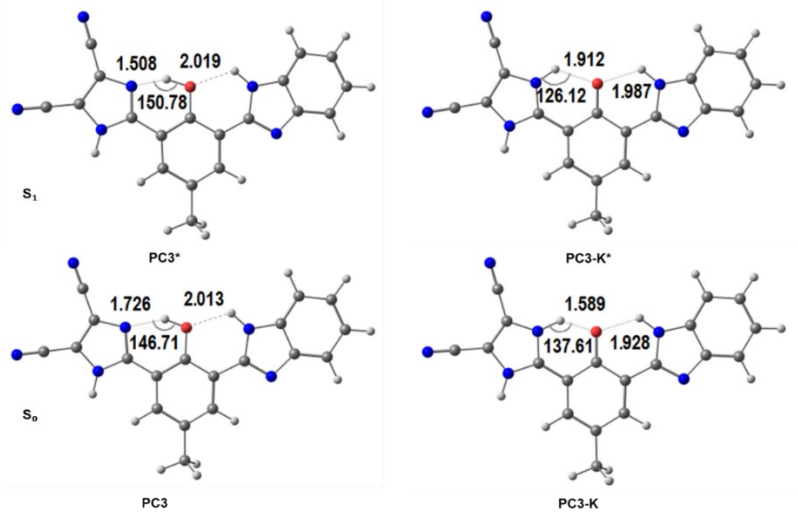

Figure S6. Optimized structure of PC3 conformation in different configurations.

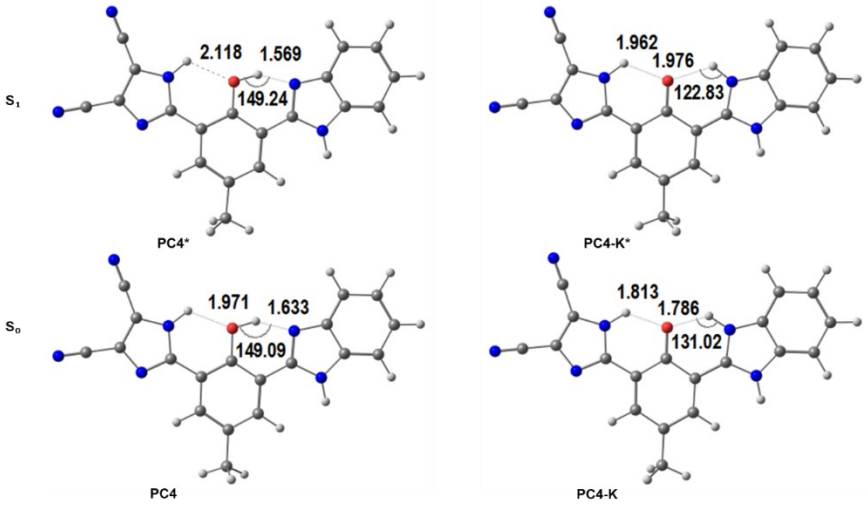

Figure S7. Optimized structure of PC4 conformation in different configurations.

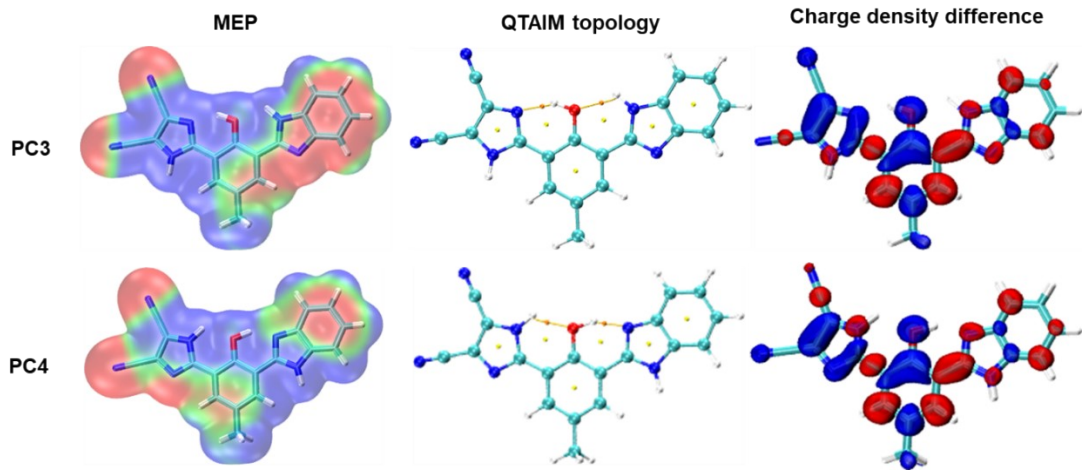

Figure S8. Molecular electrostatic potential maps, QTAIM critical point topologies and charge density difference of PC3 and PC4.

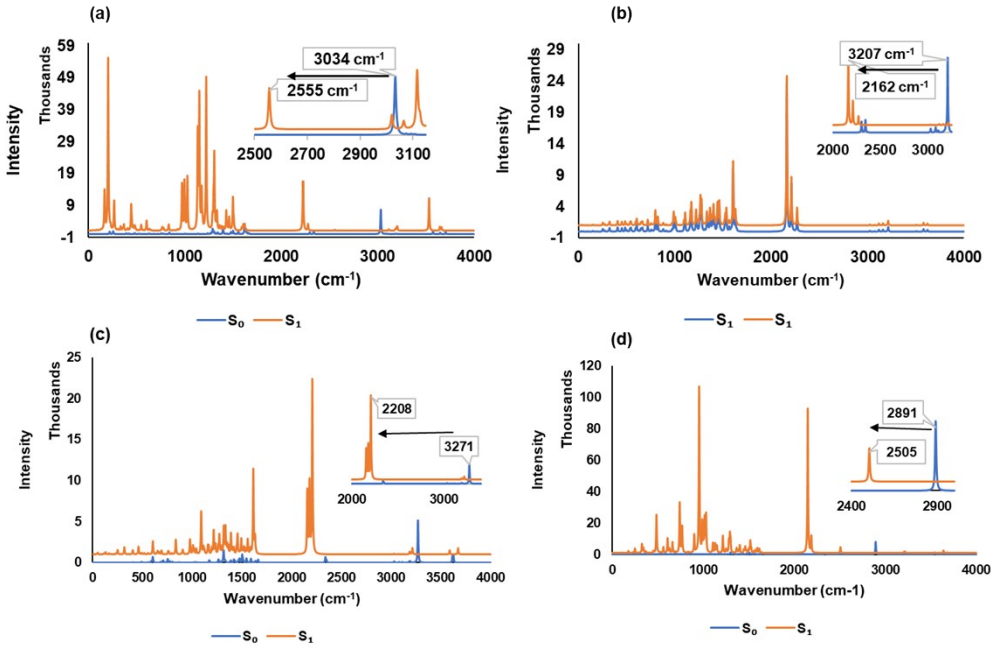

Figure S9. FTIR spectra of (a) C3, (b) C4 , (c) PC3 and (d) PC4 configuration at S_0 and S_1 states.

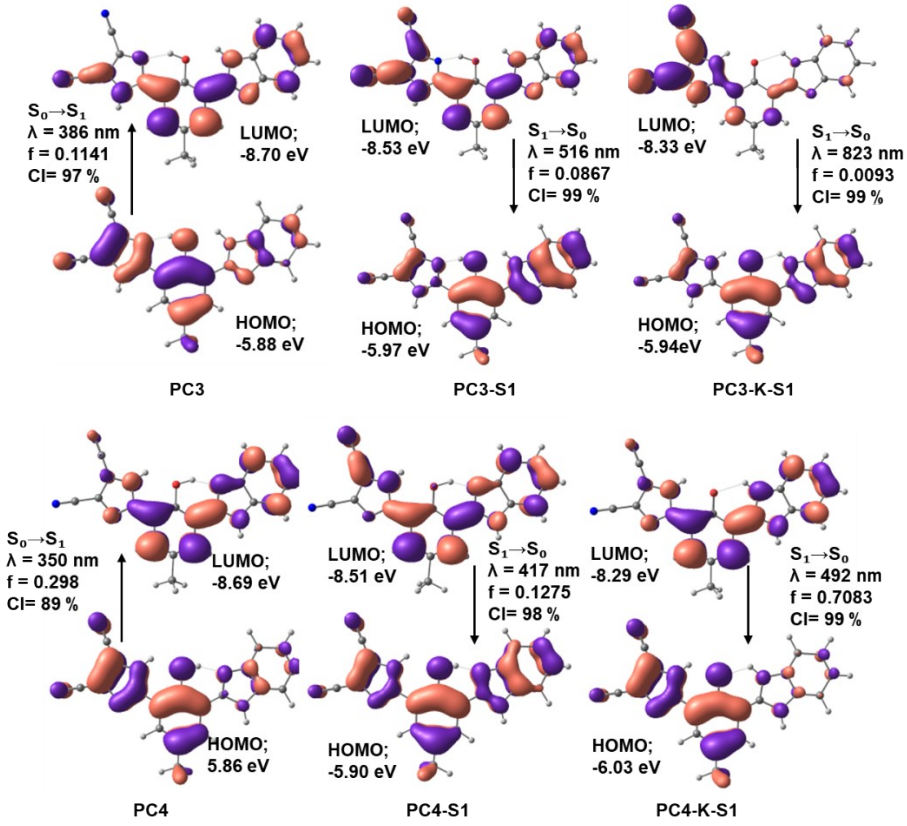

Figure S10 Calculated excitation and vertical emission spectra of PC3 and PC4 conformations.

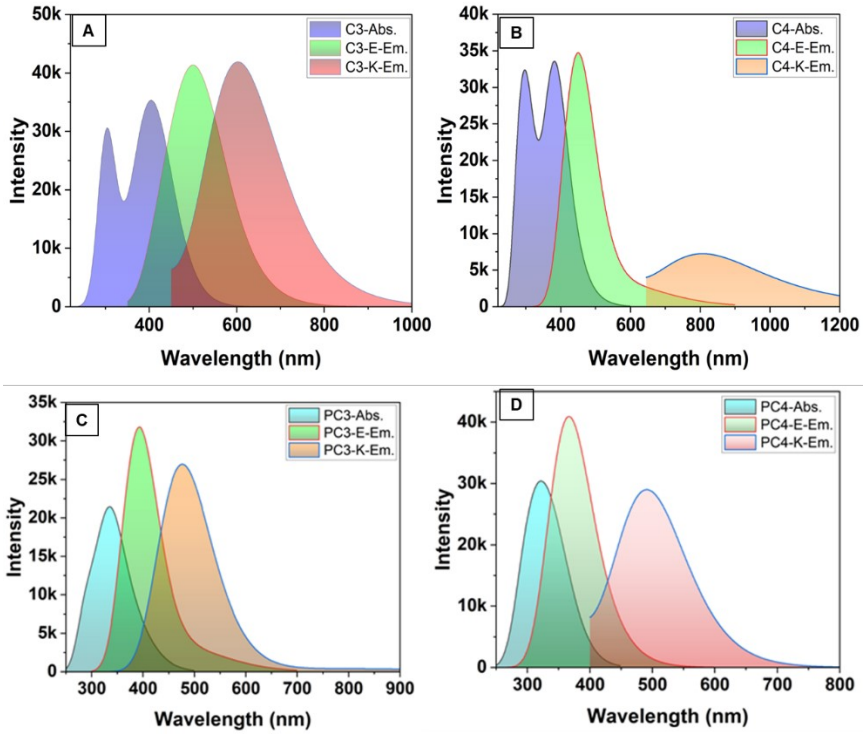

Figure S11. Calculated vertical absorption and emission spectra of (A) C3, (B) C4, (C) PC3 and (D) PC4 conformations.