Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supporting Information

Intramolecular charge transfer in aminobenzonitriles and tetrauoro counterparts: fluorescence explained by competition between low lying excited states and radiationless deactivation. Part II: Influence of substitution on luminescence patterns

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Figure 1.- Schematic representation of the orbitals included in the CAS(12,11). R_1=H,CH_3; R_2=H,F.

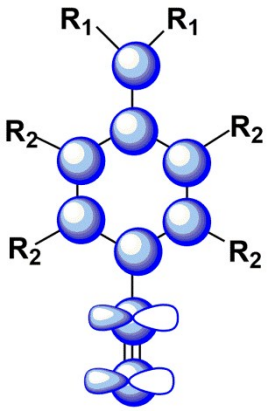
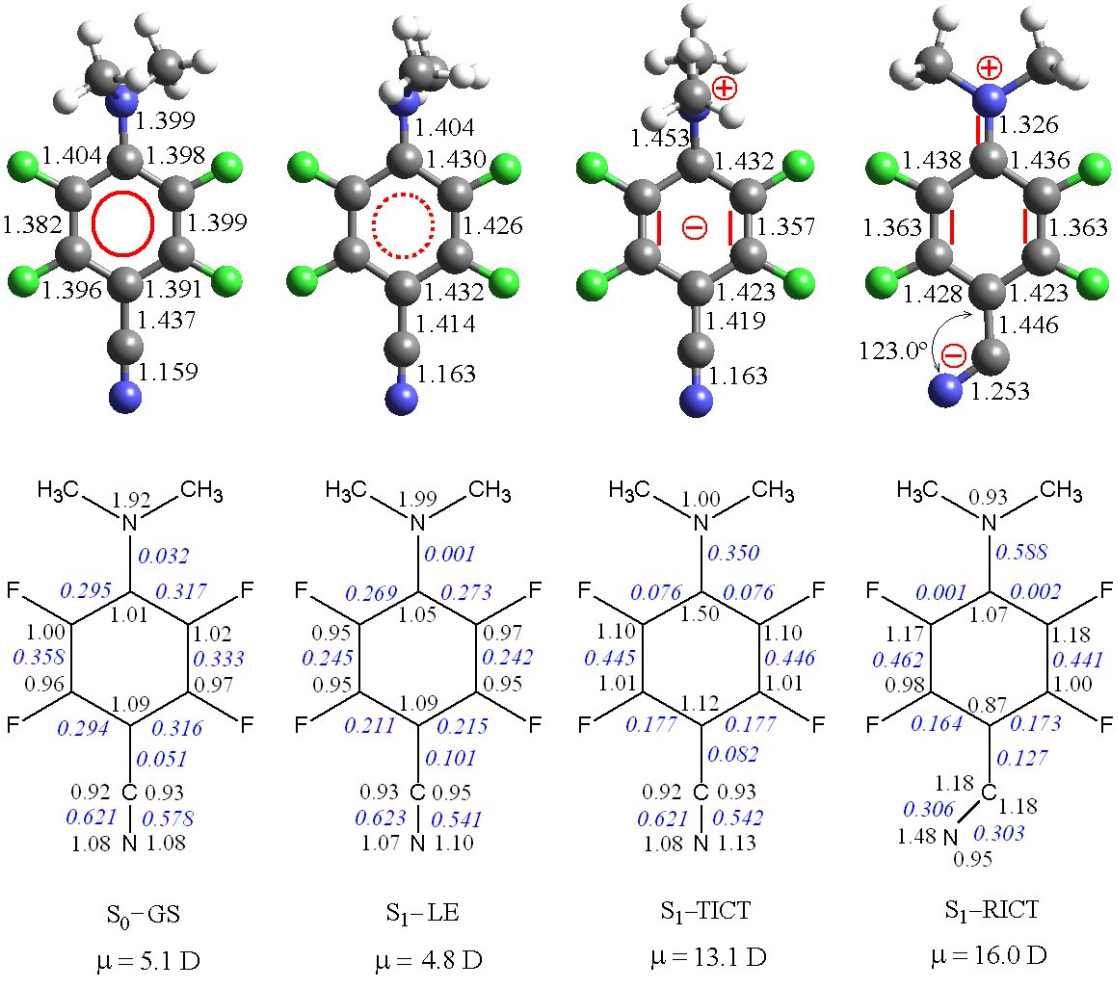


Figure S2.- Geometries and electronic structures (in red) of the ground state, LE, TICT, and RICT minima in DMABN-4F. All bond lengths are in Å.
Values of the second-order exchange density matrix (in italic blue) and the one-electron density matrix (in black) for the same structures.



S_0–GS
$\mu = 5.1$ D

S_1–LE
$\mu = 4.8$ D

S_1–TICT
$\mu = 13.1$ D

S_1–RICT
$\mu = 16.0$ D

Figure S3. Geometry of the lowest energy excited state minima of ABN, DMABN, ABN-4F and DMBN-4F optimized at the CASSCF(12,11)/6-31G* level. Bond distances in Å.

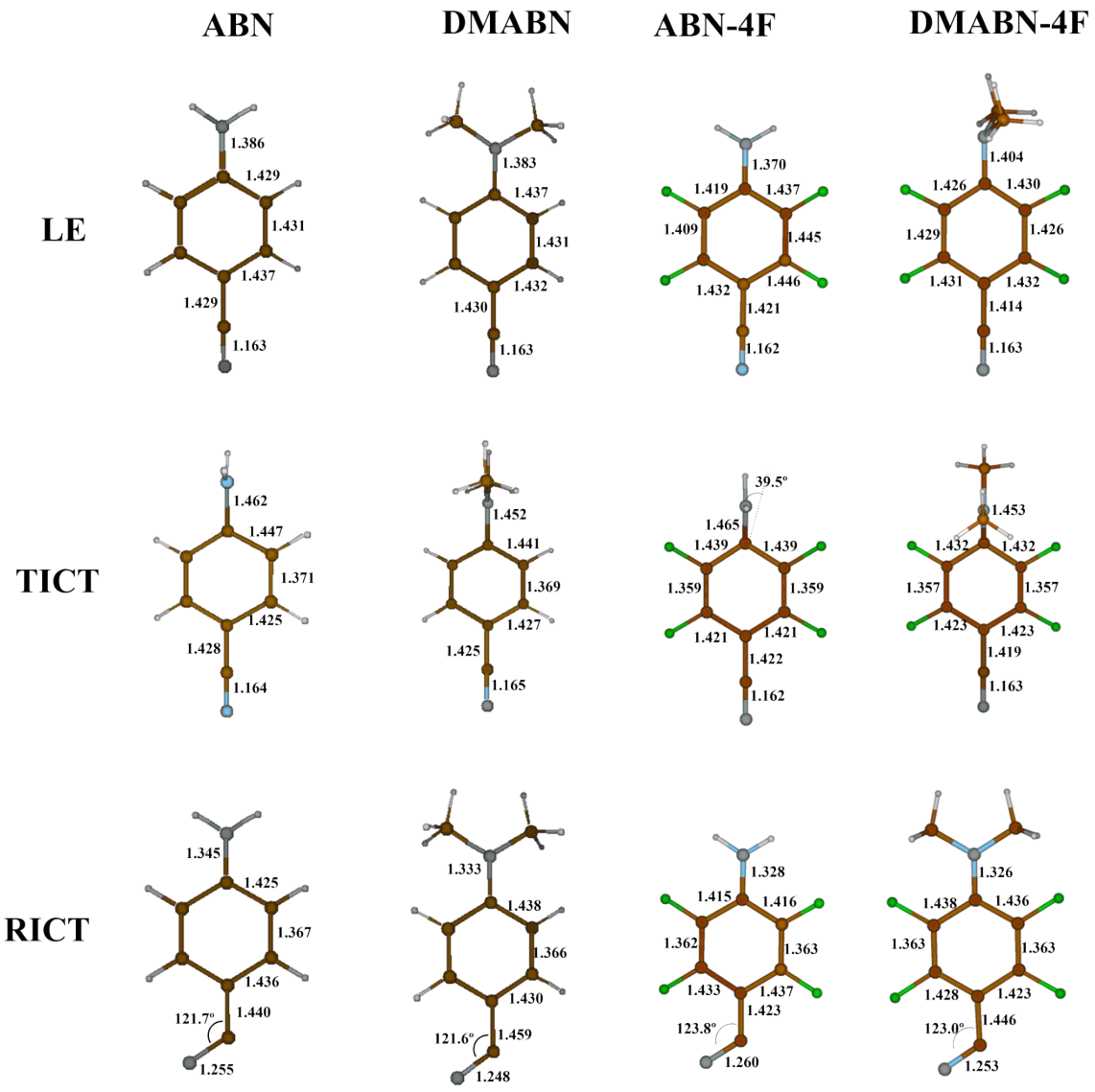


Figure S4.- Geometry of the S_3/S_2 ICT(Q)/ICT(CN) conical intersection for ABN-4F optimized at CASSCF(12,11)/6-31G(d) level.

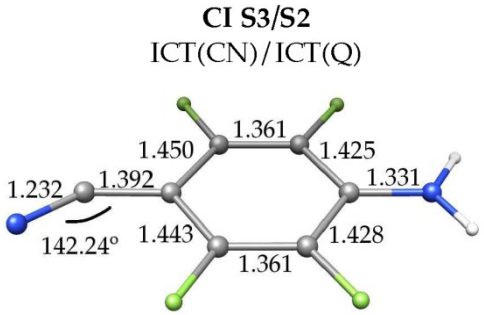


Figure S5.- MS-CASPT2 profiles of the LE and ICT states of ABN-4F along the LIIC path from LE to TICT minima.

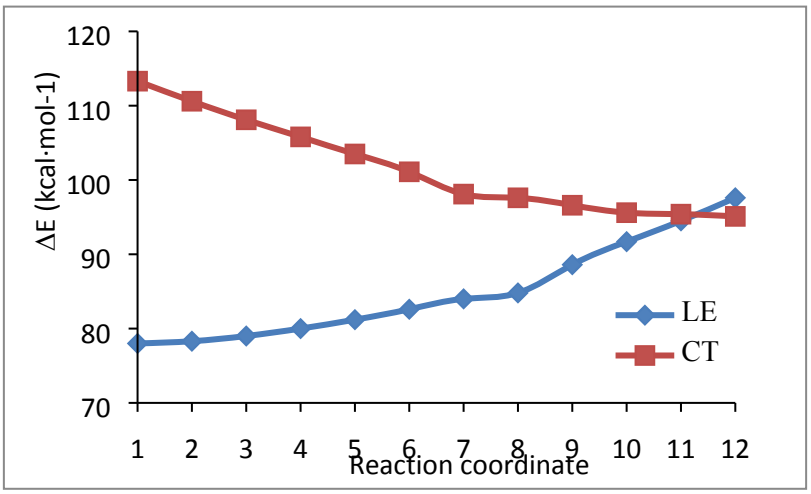


Figure S6.- Geometry of the ICT(Q)/LE (S_2/S_1) conical intersection and vectors of the branching space for DMABN-4F: a) derivative coupling; b) gradient difference.

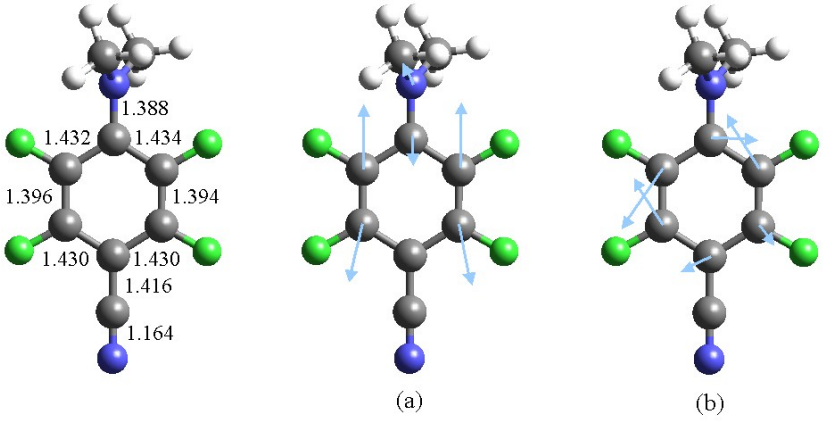


Figure S7.- MS-CASPT2 profiles of the LE and ICT states of DMABN-4F along the LIIC path from FC to the LE minimum

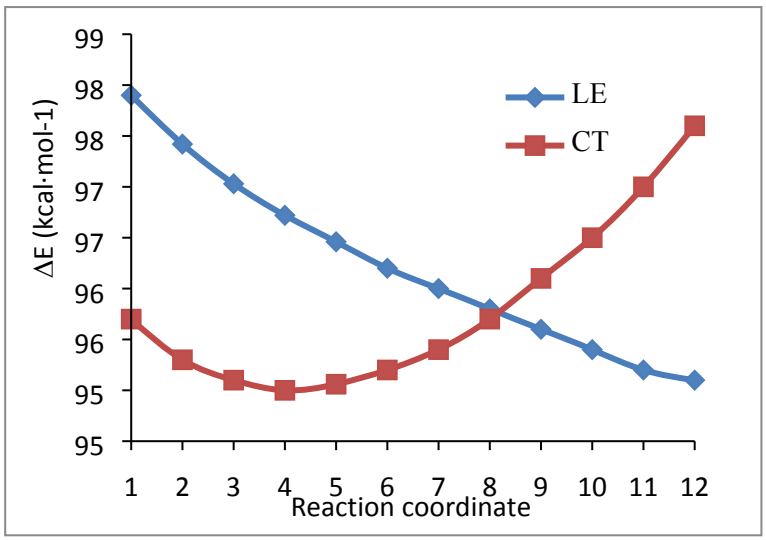


Fig S8.- Geometries of the S_1/S_0 conical intersections located for ABN-4F at CASSCF level.

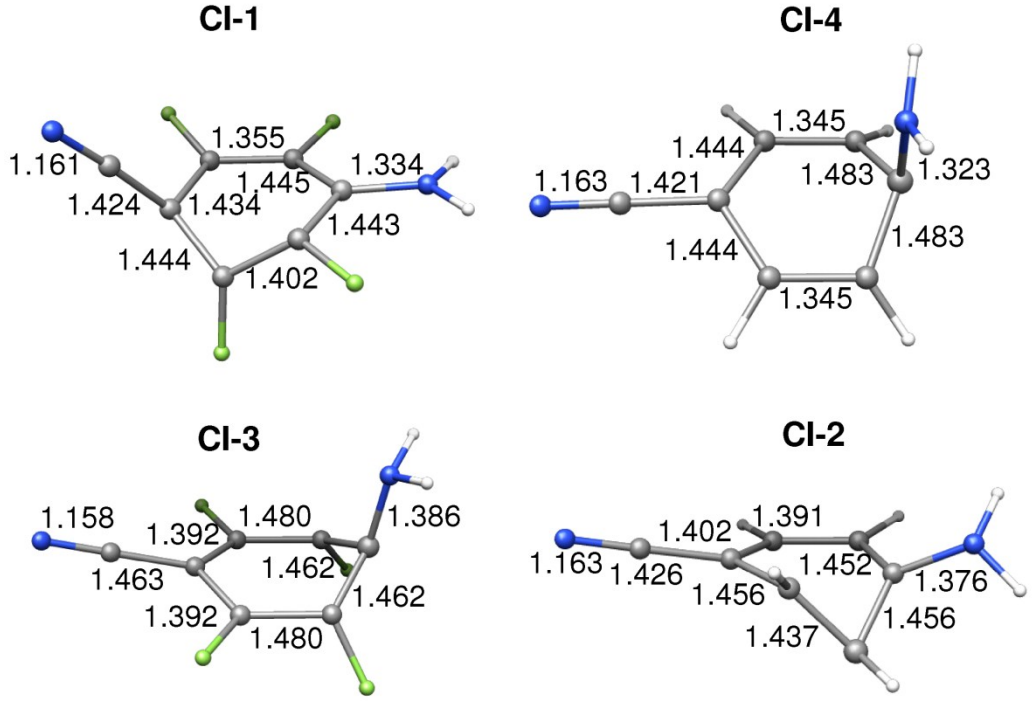


Figure S9.- MS-CASPT2 profiles of the LE and ground state potential energy surfaces of ABN-4F along LIIC path from the LE minima to different S_1/S_0 conical intersections: a) LE/GS CI-1; b) LE/GS CI-2; c) LE/GS CI-3.

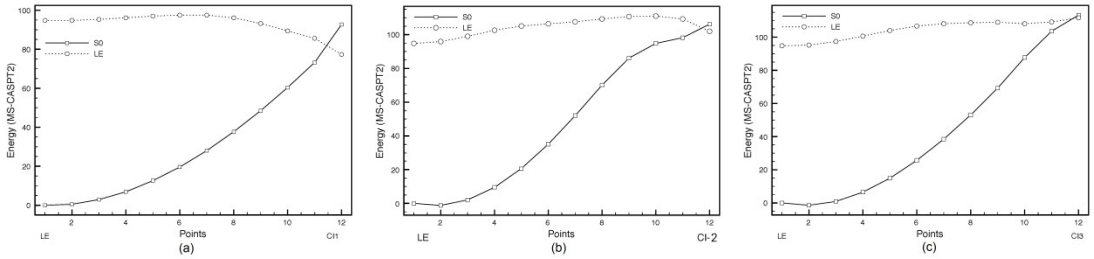


Figure S10.- Geometries of the S_1/S_0 conical intersections located for DMABN and DMABN-4F at CASSCF level: a) LE/GS CI in DMABN; b) LE/GS CI in DMABN-4F; c) CT/GS CI in DMABN; d) TS to CT/GS CI in DMABN.