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

Supplementary Information

An integrated computational tool to model the broadening of absorption bands of flexible dyes in solution: cationic chromophores as test cases

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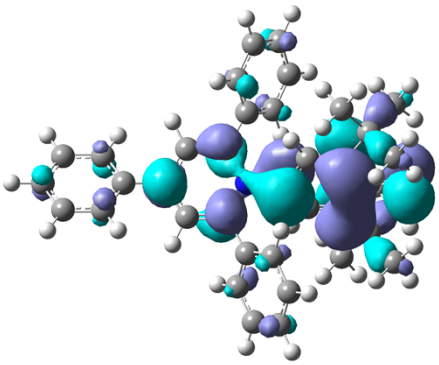
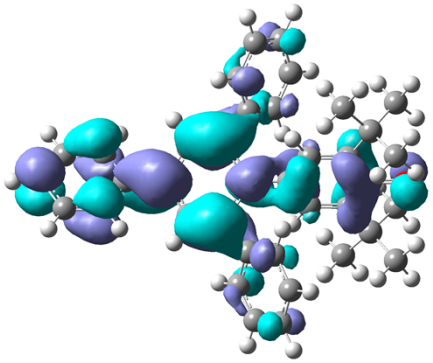


HOMO

(−4.6730 eV)



LUMO

(−3.182 eV)

Figure SI.1. Plot of the frontier molecular orbitals of the betaine dye **B**. Level of theory: DFT PBE0/SNSD/IEF−PCM (solvent = 1,4−dioxane).

Table SI.1. Sum of partial atomic Mulliken charges (Q) of the atoms forming the methyl−pyridinium or methyl−quinolinium ring (moiety A) and of the rest of the system (moiety B), and electric dipole moment *moduli* ($\boldsymbol{\mu}$), when S_0 or the adiabatic S_1 are populated. $\theta(\boldsymbol{\mu_0},\boldsymbol{\mu_1})$ is the angle defined by the two vectors $\boldsymbol{\mu_0}$ and $\boldsymbol{\mu_1}$. Level of theory: DFT CAM−B3LYP/6−31+G*/IEF−PCM (solvent = DCM).

	S_0			S_1			
	Q_0(A) / $\|e\|$	Q_0(B) / $\|e\|$	μ_0 / D	Q_1(A) / $\|e\|$	Q_1(B) / $\|e\|$	μ_1 / D	$\theta(\boldsymbol{\mu_0},\boldsymbol{\mu_1})$ / degs
1	0.488	0.512	7.1	0.206	0.794	3.1	116
2	0.230	0.385	0.9	−0.074	0.537	4.2	6
3	1.409	−0.409	9.9	0.567	0.433	2.6	92
4	2.155	−1.155	1.6	0.174	0.826	9.4	112
5	1.041	−0.041	2.9	0.631	0.369	8.5	137
6	0.943	0.057	17.7	0.640	0.360	6.0	14
7	1.291	−0.291	17.9	1.016	−0.016	5.0	13

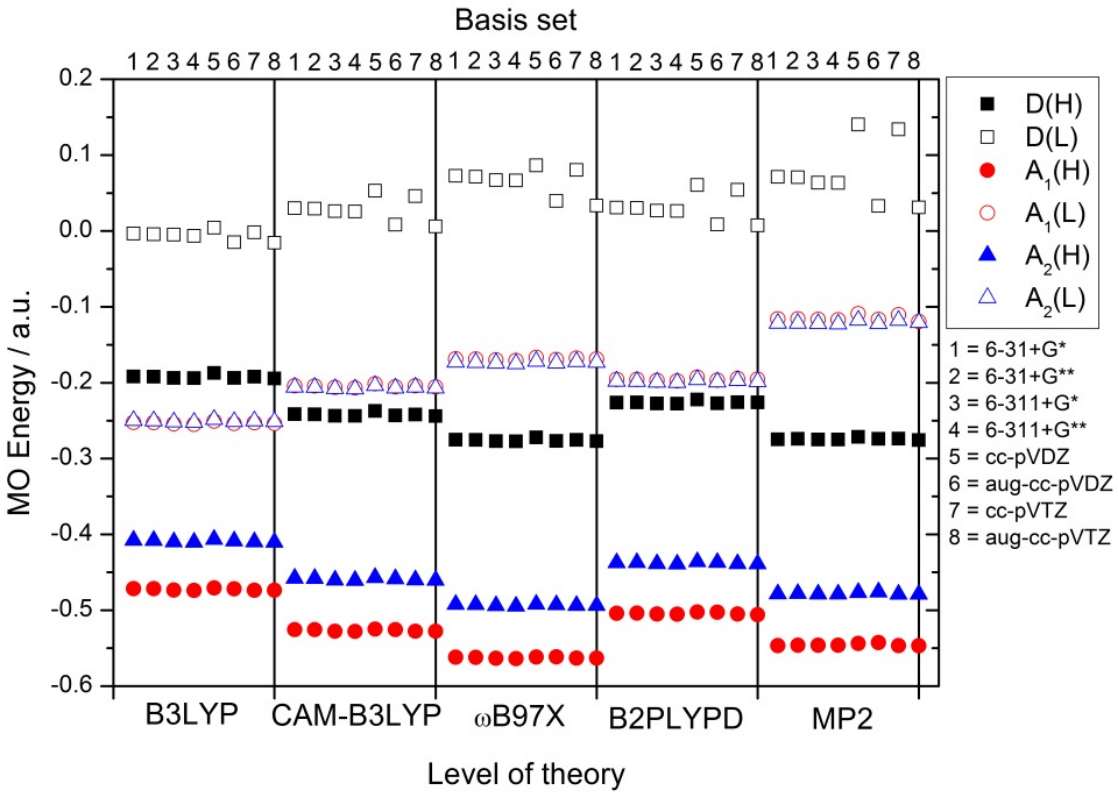


Figure SI.2. Evaluation of the frontier MOs of dimethylamino−benzene (D), methyl−pyridinium (A_1) and methyl−quinolinium (A_2), at different levels of theory.