Theoretical investigation of effect of alkylation and bromination on spin-orbit couplings in BODIPY based photosensitizers

Mirza Wasif Baig,[a] Marek Pederzoli,[a] Mojmir Kyvala,[b] Lukasz Cwiklik[a,b] Jiri Pittner,[a]

[a]*J. Heyrovský Institute of Physical Chemistry of the Czech Academy of Sciences, Dolejškova 2155/3, 18223 Prague 8, Czech Republic*

[b]*Institute of Organic Chemistry and Biochemistry of the Czech Academy of Sciences, Flemingovo nám. 2, 16610 Prague 6, Czech Republic*

wasifbaig.mirza@jh-inst.cas.cz

Halogenated and alkylated BODIPY derivatives are emerging as important photosensitizers for their use in photodynamic therapy of cancer cells due to their high triplet quantum yield [1]. Spin-orbit couplings (SOCs) inducing intersystem crossing in these molecules is evaluated with an effective one-electron spin–orbit Hamiltonian. Matrix elements of an effective one-electron spin–orbit Hamiltonian between singlet and triplet configuration interaction singles (CIS) auxiliary wave functions are calculated using a new code capable of dealing with singlets and both restricted and unrestricted triplets built up from up to three different and independent sets of (singlet, alpha and beta) molecular orbitals [2].
BODIPY's with halogen atoms are found to have SOCs significantly greater than BODIPY's possessing just alkyl moieties. Excited state dynamics of brominated-BODIPY was further explored with TD-DFT surface hopping molecular dynamics on potential energy surfaces resulting from the eigenstates of the total electronic Hamiltonian including the spin-orbit (SO) coupling. For the surface hopping trajectories, an accelerated MD approach was used, in which the SO couplings are scaled up, to make the calculations computationally feasible and the life times are extrapolated back to unscaled SO couplings. The life time of the first excited singlet state estimated by semi-classical surface hopping simulations is 180±75 ps [3].

References

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