Substitution at BODIPY fragment effects on excited state potential energy surface

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4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) based dyes have extensive applications in optoelectronic and biosensing applications. Particular area of interest is application of BODIPY based dyes to viscosity sensing. Viscosity sensitivity of BODIPY dyes is related to structural changes in excited state, which involve rotation of group linked to 8 (*meso*) position of BODIPY fragment [1]. Upon excitation (I, Fig. 1) BODIPY molecule can relax radiatively (II, Fig. 1) or leave optically bright state by barrier-dependent rotation of *meso* group (III, Fig. 1). Calculated barrier heights can be correlated to experimentally determined viscosity sensitivity (x), which is a slope in Förster-Hoffmann equation:

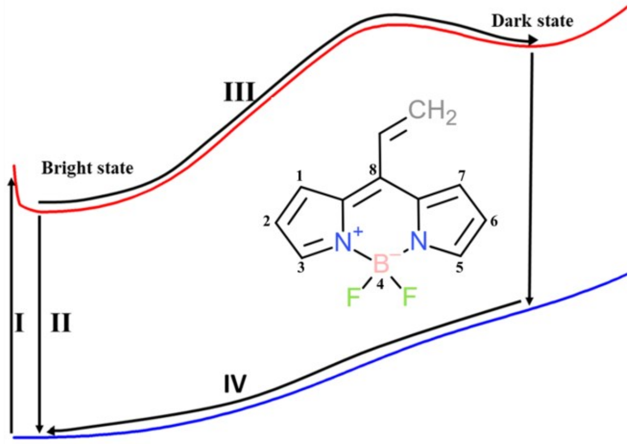

Fig. 1. Excitation and relaxation pathways of BODIPY based molecular rotors and molecular structure of 8VBDP rotor.

$$\log(\Phi) = C + x\log(\eta), \tag{1}$$

where Φ is quantum efficiency, η is bulk viscosity

It is empirically known that BODIPY dyes which are bound to sp^2 hybridized atom at *meso* position relax non-radiatively upon excitation unless bulky substituent groups, which hinder rotation of *meso* group, are introduced [2]. Bulky substituent groups induce energy barrier for rotation of *meso* group. Relaxation to optically dark state for 8-vinyl-DODIPY (8VBDP, Fig. 1) molecule is barrierless. The main objective of this study is to predict substituent effect on energy profile of 8VBDP molecule along dihedral angle between rotor and BODIPY fragment coordinate at TD-DFT/M06-2X level of theory. Energy profile scans along dihedral angle coordinate revealed that four additional methyl groups BODIPY fragment at 1, 3, 5, 7- BODIPY positions do not hinder rotation of *meso* group and, hence, do not induce energy barrier. Two additional phenyl groups at 2, 6- BODIPY positions change shape of potential energy curve, but they are not sufficient to prevent 8VBDP molecule's relaxation into optically dark state.

REFERENCES

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