

This is the pre-peer reviewed version of the following article: *Helv. Chim. Acta* 2017, 100, e1700093, which has been published in final form at <https://onlinelibrary.wiley.com/doi/full/10.1002/hlca.201700093>. This article may be used for non-commercial purposes in accordance with Wiley-VCH Terms and Conditions for Self-Archiving.

# Fluorescence Quenching in BODIPY Dyes: The Role of Intramolecular Interactions and Charge Transfer

Antonio Prlj,<sup>a</sup> Laurent Vannay,<sup>a</sup> and Clemence Corminboeuf<sup>\*,a</sup>

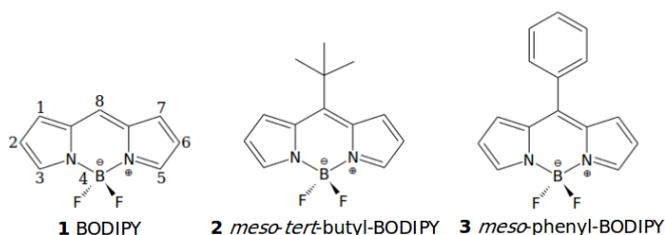
<sup>a</sup> Institut des Sciences et Ingénierie Chimiques, École polytechnique fédérale de Lausanne, CH-1015 Lausanne, Switzerland. E-mail: [clemence.corminboeuf@epfl.ch](mailto:clemence.corminboeuf@epfl.ch)

The fluorescence properties of the BODIPY dye and its two *meso*-substituted derivatives, *tert*-butyl- and phenyl-BODIPY, are rationalized. The non-emissive behavior of the latter two are attributed to the energetically accessible low-lying conical intersection between the ground state and the lowest excited singlet state. Both intramolecular non-covalent interactions and excited state charge transfer character are identified as being crucial for “stabilizing” the intersection and prompting the nonradiative decay. Similar crossing was located in the bare BODIPY dye, however, being energetically less accessible, which correlates well with the high fluorescence quantum yields of the parent dye.

**Keywords:** BODIPY • fluorescence quenching • conical intersection • minimum energy crossing point • ADC(2)

## Introduction

BODIPY derivatives have recently emerged as one of the most prominent classes of organic dyes, with wide applications in fields such as fluorescent imaging and sensing,<sup>[1][2]</sup> dye-sensitized solar cells,<sup>[3][4]</sup> lasing,<sup>[5]</sup> non-linear optics,<sup>[6]</sup> photocatalysis,<sup>[7][8]</sup> singlet oxygen generation and photodynamic therapy<sup>[9]</sup> etc. These *cis*-constrained cyanines<sup>[10]</sup> were first synthesized in 1968<sup>[11]</sup> (although the parent dye, **1** in Scheme 1, was only reported in 2009<sup>[12]</sup>), followed by an extensive synthetic efforts to functionalize the dye core and tune the chemical and photophysical properties.<sup>[13-15]</sup> Alternatively, the success of BODIPY derivatives inspired the design of various similar compounds such as aza-BODIPY,<sup>[13]</sup> PODIPY,<sup>[16]</sup> BODIHY,<sup>[17]</sup> BOPHY,<sup>[18]</sup> BOIMPY<sup>[19]</sup> and others.<sup>[20-22]</sup>



**Scheme 1.** Studied compounds.

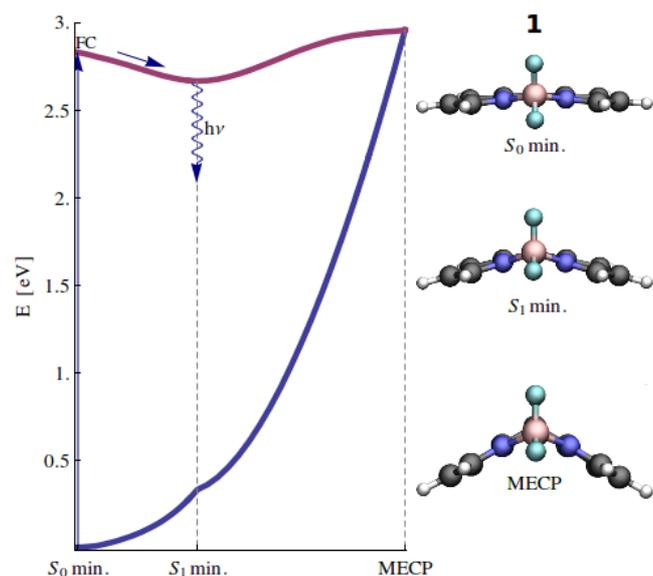
Of all possible positions, substitution at the *meso*-site (C8 atom in Scheme 1) is the most relevant, at least in terms of the fluorescence properties.<sup>[23-28]</sup> As summarized in the reference 27, alkyl-, alkenyl- and halo-substituted BODIPYs exhibit high fluorescence quantum yields ( $\Phi_f$ ), whereas for alkenyl- or aryl- substituents, the  $\Phi_f$  values are small, often close to zero. The BODIPY dye itself has a relatively high  $\Phi_f$  value (0.93 in ethanol, 0.77 in THF),<sup>[12]</sup> and the intense fluorescence, which is the basis for vast applications, persists in most of its derivatives. In our earlier work,<sup>[28]</sup> we addressed the contrast between fluorescence quenching in

*meso*-alkenyl-BODIPYs, versus the highly fluorescent *meso*-alkyl-BODIPYs. The divergent emissive properties can be well understood by the accessibility of the conical intersection upon excited state relaxation. Conical intersections,<sup>[29][30]</sup> *i.e.*, the crossings between the electronic states of the same multiplicity are of key importance to rationalize the fluorescence properties of many organic molecules (see for instance recent applications in ref 31-35). In the illustrative vinyl-BODIPY compound, the crossing between the lowest excited singlet state ( $S_1$ ) and the ground state ( $S_0$ ) lies energetically below the initial vertical excitation, the so-called Franck-Condon (FC) point, thus explaining the high nonradiative rates. In sharp contrast, the kinetic barrier in ethyl-BODIPY makes the crossing less accessible, promoting the radiative decay instead of the internal conversion. Nevertheless, one might still wonder if the basic principles demonstrated for these systems (*i.e.*, the existence of the low energy conical intersection and its accessibility) are broadly applicable to the photochemistry (fluorescence quenching in particular) of the other BODIPY compounds. The goal of the present work is to identify general underlying concepts based on three prototypical molecules depicted in Scheme 1: parent BODIPY (**1**), *meso*-substituted *tert*-butyl-BODIPY (**2**) which, in contrast to other *meso*-alkyl-BODIPYs, is very weakly fluorescent, as well as the ubiquitous *meso*-phenyl-BODIPY (**3**). We employ state-of-the-art quantum chemical computations to differentiate the excited state deactivation pathways and rationalize the fluorescence properties of these compounds.

## Results and Discussion

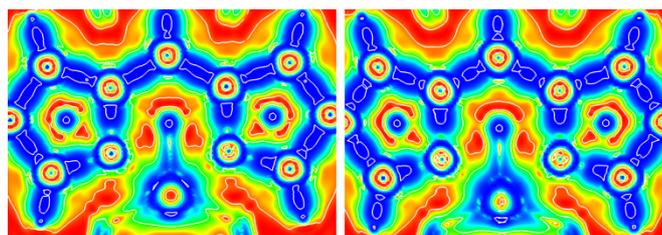
The emissive properties of the BODIPY dyes are intimately related to the topology of the  $S_1$  potential energy surface. Rare examples violating Kasha's rule exist (for instance certain BODIHY compounds).<sup>[36]</sup> The triplet state population *via* intersystem crossing is typically negligible, except for the heavy atom substituted BODIPYs<sup>[37][38]</sup> and the specific fused<sup>[39][40]</sup> and

oligomeric compounds.<sup>[41]</sup> For this reason, our attention is placed on the two lowest singlet electronic states, the ground and first excited state.



**Figure 1.** Energy profile (in eV) of compound **1**. The MP2/ADC(2) level and the def2-SVP basis set were used.

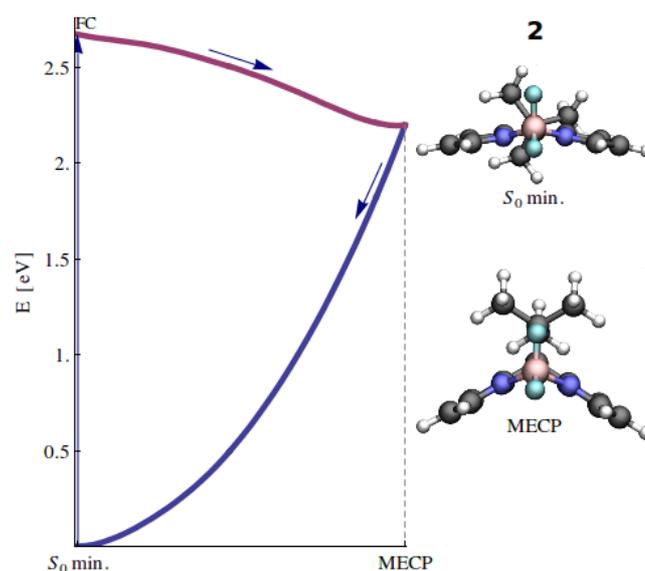
The electronic profiles of  $S_0$  and  $S_1$  of **1** along the interpolated reaction coordinate (see Computational Section) are shown in Figure 1. For both states, the energy minima were optimized (detailed photophysical data are given in the SI). Unlike the nearly planar ground state geometry, BODIPY in its first excited state is symmetrically bent over the *meso*C-boron line. Our Density overlap region indicator (*DORI*)<sup>[42][43]</sup> analysis of the bonding pattern in the  $S_0$  and  $S_1$  (Figure 2) reveals that the reduction of the CC bond order (most evident for the bonds involving *meso*C atom) is the main driving force for the bending.



**Figure 2.** 2D *DORI* map of **1** in  $S_0$  (left) and  $S_1$  (right) geometry. White contours represent the bonding pattern; a quasi-aromatic behavior characterizes the ground state, while the bond order is reduced in the excited state. Structures are oriented as in Scheme 1. See the Computational Section for details. The MP2/ADC(2) level and the def2-SVP basis set were used.

In addition to the minimum energy stationary points, the minimum energy crossing point (MECP in Figure 1) between the two states was also optimized. The geometry is in fact very similar to the ones of the *meso*-substituted BODIPYs computed in our earlier work,<sup>[28]</sup> with the characteristic excessive bending of the fused core, and the out-of-plane distortion of the *meso*-bonded substituent (H atom in case of bare dye). This similarity implies that the puckered conical intersection is a signature

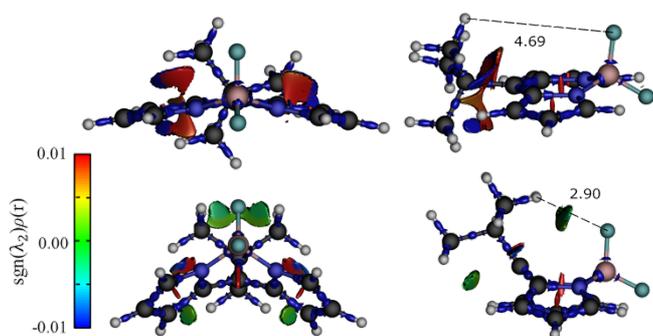
of all BODIPY dyes, while its energetic position critically depends on the substituents. If we turn our attention back to the Figure 1, we notice that upon photoexcitation the system can relax into the excited state minimum with a small excess energy ( $\sim 0.1$  eV). Although relatively close, the barrier to the conical intersection is roughly twice the reorganization energy. Therefore, the nonradiative decay is not expected to play a major role. Dede *et al.*<sup>[44]</sup> reported another  $S_1/S_0$  conical intersection, associated with the BN bond breaking in the nearly planar geometry (located at the MCSCF level). Similarity to the conical intersection of the dipyrin molecule was invoked. However, this crossing is almost 3 eV above the FC region, which makes it irrelevant for the photophysics of BODIPY, unless it is excited to very high energies.



**Figure 3.** Energy profile (in eV) of compound **2**. The ADC(2)/MP2 level and the def2-SVP basis set were used.

While most *meso*-alkyl BODIPYs are qualitatively similar to the parent dye, exhibiting intense fluorescence, compound **2** is an exception from the rule. It bears very low  $\Phi_f$  values (0.04 in methanol, 0.045 in THF) with large Stokes shifts and a broad fluorescence peak (as opposed to the rather typical small Stokes shifts and a sharp fluorescence).<sup>[27]</sup> The unusual properties were explained by Jiao *et al.*<sup>[27]</sup> who located the conical intersection at the CASSCF level. The structure identified in our computations (MECP in Figure 3) resembles closely that of Jiao *et al.* confirming our hypothesis on common conical intersection. However, no shallow minimum close to the conical intersection was located at the present theoretical level. Nevertheless, the qualitative picture is clear: upon photoexcitation the system readily relaxes towards the conical intersection, with the subsequent transition to the ground electronic state. The remaining question is why does the crossing appear at such low energy? The *DORI* analysis of the ground state minimum, and of the structure in vicinity of the crossing (Figure 4) help gaining further understanding. At the  $S_0$  geometry, there is a steric clash between the BODIPY ring and the bulky *tert*-butyl group (red color; blue islands correspond to attractive interactions). The ground state and the excited

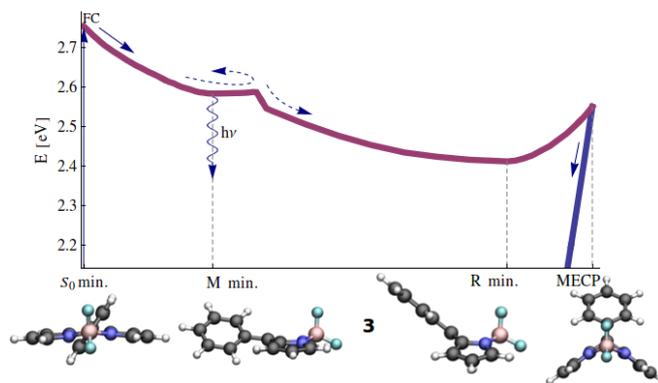
state potential energy surfaces (near the FC region) are expected to be destabilized. However, as the structure approaches the crossing geometry, the *tert*-butyl group is pushed away from the BODIPY core and the steric interactions are less significant. Therefore, the energy of the crossing is not lifted higher. In addition, a weakly attractive interaction appears between the *tert*-butyl group and the fluorine atom. This rather directional and fairly electrostatic interaction, further stabilizes the crossing relative to the FC region. Finally, our analysis of the density difference (between excited and the ground state; see SI) revealed a weak charge transfer from the pyrrole rings to the *meso*C atom and even to the substituent, which can also contribute to the stabilization of the excited state. This charge transfer appears surprising owing to the aliphatic nature of the *tert*-butyl group, but can possibly be explained by invoking hyperconjugation effects. Although charge transfer may weaken the aforementioned electrostatic interaction, both effects are expected to lower the energy of the excited state. In summary, the combination of intramolecular non-covalent interactions and charge transfer character can significantly modify the shape of the excited state potential energy surface, leading to the unexpected fluorescence quenching.



**Figure 4.** 3D *DORI* representation (isovalue=0.995) of compound **2** in the geometry of the ground state minimum (top) and near the conical intersection (bottom). *DORI* isosurfaces are color-coded ranging from blue (attractive) to red (repulsive interaction). For details on *DORI* see the Computational Section. The shortest hydrogen – fluorine distance [Å] is plotted in black dashed line. The MP2/ADC(2) level and the def2-SVP basis set were used.

Finally, we discuss *meso*-aryl-BODIPYs which are among the most popular BODIPY derivatives.<sup>[13-15][23][24][45-48]</sup> Illustrative compound **3** is very weakly fluorescent in various solvents ( $\Phi_f = 0.053$  in toluene,<sup>[23]</sup> 0.065 in THF<sup>[45]</sup>). However, if the methyl groups are attached to the BODIPY core (on atoms C1 and C7) or alternatively to the *ortho*-positions of the phenyl group, the  $\Phi_f$  values become rather high;  $\Phi_f = 0.65$  in the case of former (in methanol),<sup>[13]</sup>  $\Phi_f = 0.93$  in the case of latter (in toluene).<sup>[24]</sup> Fluorescence intensity also strongly depends on the viscosity of the solvent, *i.e.*, being larger in very viscous environments.<sup>[46]</sup> This implies that the torsions of the aryl group are crucial for the nonradiative decay. Time-resolved spectroscopy of Lindsey *et al.*<sup>[23]</sup> revealed a biphasic excited state decay (in toluene), with a major slow component of 440 ps, and a fast component of 17 ps. The complex excited state dynamics was explained based on semiempirical molecular orbital computations, which revealed the existence of two conformers in the  $S_1$  state, the higher energy metastable state (**M**) responsible for the slow component, and the lower

energy relaxed state (**R**) responsible for the fast component in decay. In a more recent study,<sup>[24]</sup> time constants of  $\sim 400$ , 10 and 1 ps were determined (in toluene). Accompanying computations (at the SAC-CI level), however, suggest that the “barrierless or nearly barrierless” relaxation to the **R** minimum takes place directly from the FC region. In both studies, a nonradiative relaxation was ascribed to the (more or less) favorable vibrational overlap factors with the ground state at the excited state minimum geometries. Here, we would like to reconcile the picture of the excited state decay of **3** with the concept of conical intersection accessibility, and provide a somewhat different explanation for its complex excited state behavior.

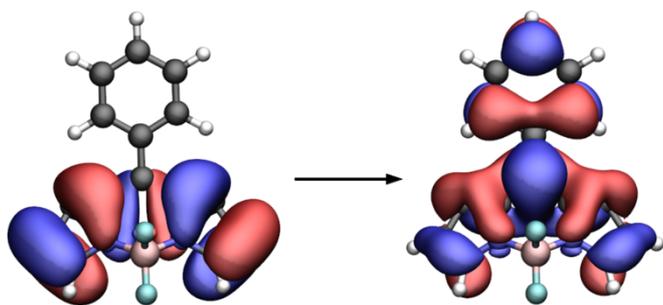


**Figure 5.** Energy profile (in eV) of compound **3**. The MP2/ADC(2) level and the def2-SVP basis set were used.

The energy profile of the  $S_1$  state between the  $S_0$  geometry and the located minimal energy crossing point is shown in Figure 5. The crossing structure certainly resembles those of **1** and **2** (Figures 1 and 3). Both the **M** and **R** minima were optimized, though the torsional barrier of the former appears almost non-existent ( $< 0.01$  eV). Since our standard procedure consisting in the interpolation of internal coordinates leads to unphysical barriers between the **M** and **R** conformers (due to the steric clashes in the intermediate geometries), we performed a constrained optimization, which presumably follows the reaction coordinate close to the minimal energy path. In the ground state, the phenyl ring is almost orthogonal to the BODIPY core (Figure 5). In the excited state, the relaxation proceeds through both the ring torsion and the core bending. The rotational axis of the phenyl moiety in **M** still lies approximately in the plane of the BODIPY ring. Pure rotation and excessive core bending are both strongly hindered by the steric interaction. However, the concerted motion (torsion plus bending) appears unhindered (as indicated by vanishingly small barrier). At the critical torsional angle (sharp feature in Figure 5), the phenyl ring is released from the structural constraints imposed by the H1 and H7 atoms and the large out-of-plane distortion, accompanied by a sudden drop in energy towards the **R** minimum, takes place. The excess in reorganization energy is certainly sufficient to reach the conical intersection (which is energetically below the **M** minimum). Lindsey *et al.* argue that upon photoexcitation both the **M** and **R** conformers are formed on the ultrafast time scale, with little interconversion between them. **M** decays via both the radiative and

nonradiative pathways (long lifetime), while **R** decays mainly nonradiatively (short lifetime).<sup>[23]</sup> It is clear that the fast decay components correspond to the immediate relaxation to the **R** state and its subsequent internal conversion. However, due to the vanishing barrier associated with the **M** conformer, it is also likely that the excited state population initially trapped in **M** will slowly leak towards **R** and the nearby conical intersection. Accordingly, we propose the following scenario. Depending on the initially excited vibronic mode, part of the population will quickly relax to the **R** minimum and decay to the ground state *via* conical intersection. Larger part of the population will presumably be trapped in a metastable state **M**. The trapping is also consistent with the small Stokes shifts observed in experiments (*i.e.*, the emission from the **R** state would result with rather large Stokes shifts). Favorable pathway towards **R** is very narrow and implies the concerted ring torsion and the core bending motion. Therefore, slow relaxation to the conical intersection is expected to occur on a longer timescale. Hence, the energetically accessible conical intersection may play an essential role in the fluorescence quenching of the compound **3**, but the high-level wave packet simulations would be necessary to provide an unambiguous picture.

Why is the crossing stabilized relative to the FC region (when compared to the parent compound **1**) remains to be clarified? Although the intramolecular interactions (*i.e.*, steric clashes) play an important role in the dynamics, the primary reason is of electronic nature and can be rationalized by considering only the HOMO and LUMO. As noted earlier,<sup>[15][23][24]</sup> the HOMO has a node in the boron-*mesoC* vertical plane, and does not extend to the *meso*-group. On the other hand, the LUMO can delocalize on the *meso*-substituent, lowering its energy. Upon rotation of the phenyl ring, the  $S_1$  state of **3** will transfer charge through the delocalized LUMO (Figure 6).



**Figure 6.** Dominant natural transition orbitals (NTOs; coeff=0.99) of the  $S_1$  state of compound **3** in the minimum geometry of **R**. The ADC(2)/def2-SVP level was used; isovalue=0.02.

The portion of the potential energy surface with a charge transfer character is stabilized with respect to the FC region, and the conical intersection becomes energetically accessible. In our earlier work, we have found that the  $S_1$  state of non-emissive vinyl-BODIPY also achieves a partial charge transfer character upon torsion of the vinyl moiety. Therefore, the stabilization by charge transfer can be regarded as a general effect, which explains the weak fluorescence of the *meso*-BODIPY

dyes substituted with the conjugated  $sp^2$  moieties. Some caution should be taken for the large electron donating groups such as triphenylamine and pyrene.<sup>[47][48]</sup> Here an additional excited state appears in the low energy spectral region, exhibiting the charge transfer between the electron donating *meso*-substituent and the BODIPY acceptor (charge transfer has a direction opposite to that in **3**). In the polar environment, this state may be stabilized below the local BODIPY excitation, and the population transfer to the “dark” charge transfer state causes a loss of fluorescence.

## Conclusions

Fluorescence properties of BODIPY dyes were rationalized by exploring the topology of the lowest excited singlet state. The parent BODIPY exhibits a low lying conical intersection with the ground state, corresponding to the substantial bending of the molecular core over the boron-*mesoC* line. Since the conical intersection is located at an energy higher than the Franck-Condon point, nonradiative decay is not expected to be significant. However, different substituents, in particular those at the *meso* position, can “stabilize” the conical intersection, which prompts the internal conversion to the ground electronic state. We have identified two distinct situations, which lead to the relative lowering of the crossing energy and, as a consequence, to the quenching of fluorescence. In the case of *tert*-butyl-BODIPY, non-covalent interactions within the molecule play a key role, destabilizing the Franck-Condon region and stabilizing the crossing region. A partial charge transfer character was also detected. For phenyl-BODIPY, excited state achieves a significant charge transfer character upon torsion of the phenyl moiety, which lowers the energy of both the excited state global minimum and the nearby conical intersection. Since the intersection becomes energetically accessible, the excited state population is expected to decay to the ground state. The concept of the conical intersection accessibility was already successfully applied in our earlier study on *meso*-alkyl and *meso*-alkenyl compounds, explaining their distinct emissive properties observed in experiments.<sup>[28]</sup> Therefore the present methodology can be further generalized and used for the structure-property relationships and the rational design of the new BODIPY fluorophores.

## Computational Section

A variety of theoretical methods were previously employed to study excited states of BODIPY and its derivatives, including DFT based (TDDFT,<sup>[26][38][40][49-51]</sup>  $\Delta$ SCF,<sup>[45][52]</sup> ROKS,<sup>[53]</sup> DFT-MRC<sup>[54]</sup>), single reference wavefunction-based (ADC(2),<sup>[28][55]</sup> CC2,<sup>[56]</sup> SAC-CI<sup>[24]</sup>), mixed (SOS-CIS(D)/TDDFT<sup>[57]</sup>), multireference (CASCF,<sup>[27][41][44]</sup> CASPT2,<sup>[52]</sup> XMCQDPT2<sup>[58]</sup>), semiempirical<sup>[23]</sup> and machine learning<sup>[59]</sup> methods. The  $S_1$  state of various BODIPY compounds is well described by a single excitation from the highest occupied (HOMO) to the lowest unoccupied molecular orbital (LUMO), having a high oscillator strength which manifests in the intense and sharp absorption peaks.<sup>[10]</sup> However, BODIPYs are considered challenging due to the importance of dynamical

electron correlation effects.<sup>[10][57][60]</sup> The same problem holds for linear cyanines as widely discussed in the literature.<sup>[61-65]</sup> The single excitation methods (such as TDDFT or CIS) as well as methods which lack dynamical correlation (CASSCF) are expected to have large errors.<sup>[60]</sup> In a benchmark study of Momeni and Brown,<sup>[60]</sup> the best performance was assigned to the CASPT2 and the local CC2 method. Here we use the ADC(2) method<sup>[66][67]</sup> which is closely related, and has a similar accuracy as CC2.<sup>[68]</sup> ADC(2) was recently applied to various organic molecules,<sup>[28][31][34][35][69-72]</sup> typically providing the results consistent with experiments. The method can also be used for optimizing conical intersections,<sup>[28][31][34][73-77]</sup> although it does not provide a correct dimensionality of the crossing seam (for  $S_1/S_0$  crossing).<sup>[78]</sup> The computations were performed with Turbomole 7.0.2 package<sup>[79]</sup> and the strict ADC(2) method implemented therein. Ground state computations were performed with MP2 method. The def2-SVP<sup>[80]</sup> basis set was systematically used; BODIPY compounds exhibit a relatively small basis set dependence, as shown in Table S2 in SI. The resolution of identity (along with the universal auxiliary basis set<sup>[81]</sup>) and the frozen core approximations were employed. Minimal energy crossing points were optimized with CIOpt code<sup>[82]</sup> coupled to Turbomole. For all optimized geometries, tight convergence criteria were chosen. While the interpolated energies are generally not representative of the minimum energy pathway in the excited state, the energetic positions of the optimized critical points provide a good description of the excited state dynamics. The coordinate interpolation serves essentially as a visual guideline. When this interpolation leads to an unnaturally high barrier, we employed a constrained optimization. For the segment between the **M** and **R** minima of compound **3**, the energies were computed by a constrained optimization in which the torsional angle  $\varphi$  (see SI for definition) was fixed and varied ranging from  $-49.2^\circ$  corresponding to the **M** structure and  $-4.3^\circ$  corresponding to the **R** structure. The relative distances between the points (*i.e.* minima and MECPs) on the reaction coordinate were scaled based on the root mean square deviation between the structures of the consecutive points. All the optimized structures (xyz) and the detailed photophysical data are given in the SI. Profiles in the Figures 1, 3 and 5 were computed in the vacuum, thus reflecting the intrinsic properties of the molecules. Continuum solvation models are challenging to apply in this case (equilibrium vs. nonequilibrium conditions<sup>[83]</sup> in the excited state). Nevertheless, earlier studies imply that the solvent effects are not very significant.<sup>[28][51]</sup> The state with the charge transfer character (as in molecule **3**) may be further stabilized in the polar environment but this is still fully compatible with the proposed interpretation of the excited state dynamics. The qualitative shape of  $S_1$  potential energy surface remains the same, even if there is an additional stabilization of the portion of potential energy surface with the charge transfer character.

Density overlap region indicator (*DORI*)<sup>[42][43]</sup> was used to describe bonding pattern and the intramolecular interactions. *DORI* detects regions where electron density stemming from different atoms overlap. However, while *DORI* provides the extent of the overlap, it is inapt at distinguishing whether the interaction is attractive or repulsive. This

information is retrieved using the second eigenvalue of the Laplacian of the electron density ( $\lambda_2$ ):  $\nabla^2\rho = \lambda_1 + \lambda_2 + \lambda_3$ , ( $\lambda_1 \leq \lambda_2 \leq \lambda_3$ ).  $\lambda_2$  is negative in bonding regions, and positive for repulsive interactions. The interaction strength is estimated using the value of the density itself:  $\text{sgn}(\lambda_2)\rho(r)$  (see ref. 42 and 84 for more details). For applications of *DORI* in excited states see ref. 43. Both *DORI* and  $\nabla^2\rho$  were computed numerically on optimized densities, with a precision of 10points/bohr on the grid mesh. *DORI* was obtained using a local script, whereas  $\nabla^2\rho$  was computed using the NCI-milano software.<sup>[85]</sup>

## Supplementary Material

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/MS-number>.

## Acknowledgements

We thank Dr Ewa Pastorzak for discussions. Fundings from the Swiss National Science Foundation (no. 156001) and the European Research Council (ERC Grant 306528, "COMPOREL") are acknowledged.

## Author Contribution Statement

A. P. computed excited state profiles, L. V. analyzed the densities, A. P., L. V. and C. C. prepared the manuscript.

## References

- [1] N. Boens, V. Leen, W. Dehaen, 'Fluorescent indicators based on BODIPY', *Chem. Soc. Rev.* **2012**, *41*, 1130-1172.
- [2] T. Kowada, H. Maeda, K. Kikuchi, 'BODIPY-based probes for the fluorescence imaging of biomolecules in living cells', *Chem. Soc. Rev.* **2015**, *44*, 4953-4972.
- [3] S. Erten-Ela, M. D. Yilmaz, B. Icli, Y. Dede, S. Icli, E. U. Akkaya, 'A Panchromatic Boradiazaindacene (BODIPY) Sensitizer for Dye-Sensitized Solar Cells', *Org. Lett.* **2008**, *10*, 3299-3302.
- [4] Z. Lu, M. Liang, P. Dai, K. Miao, C. Zhang, Z. Sun, S. Xue, 'A Strategy for Enhancing the Performance of Borondipyrromethene Dye-Sensitized Solar Cells', *J. Phys. Chem C* **2016**, *120*, 25657-25667.
- [5] F. López Arbeloa, J. Bañuelos, V. Martínez, T. Arbeloa, I. López Arbeloa, 'Structural, photophysical and lasing properties of pyrromethene dyes', *Int. Rev. Phys. Chem.* **2005**, *24*, 339-374.
- [6] G. Ulrich, A. Barsella, A. Boeglin, S. Niu, R. Ziessel, 'BODIPY-Bridged Push-Pull Chromophores for Nonlinear Optical Applications', *ChemPhysChem* **2014**, *15*, 2693-2700.
- [7] W. Li, L. Li, H. Xiao, R. Qi, Y. Huang, Z. Xie, X. Jing, H. Zhang, 'Iodo-BODIPY: a visible-light-driven, highly efficient and photostable metal-free organic photocatalyst', *RSC Adv.* **2013**, *3*, 13417-13421.
- [8] G. Magagnano, A. Gualandi, M. Marchini, L. Mengozzi, P. Ceroni, P. G. Cozzi, 'Photocatalytic ATRA reaction promoted by iodo-Bodipy and sodium ascorbate', *Chem. Commun.* **2017**, *53*, 1591-1594.
- [9] S. G. Awuah, Y. You, 'Boron dipyrromethene (BODIPY)-based photosensitizers for photodynamic therapy', *RSC Adv.* **2012**, *2*, 11169-11183.
- [10] B. Le Guennic, D. Jacquemin, 'Taking Up the Cyanine Challenge with Quantum Tools', *Acc. Chem. Res.* **2015**, *48*, 530-537.
- [11] A. Treibs, F.-H. Kreuzer, 'Difluorboryl-Komplexe von Di- und Tripyrlylmethenen', *Liebigs Ann. Chem.* **1968**, *718*, 208-223.

- [12] I. J. Arroyo, R. Hu, G. Merino, B. Z. Tang and E. Peña-Cabrera, 'The Smallest and One of the Brightest. Efficient Preparation and Optical Description of the Parent Borondipyromethene System', *J. Org. Chem.* **2009**, *74*, 5719-5722.
- [13] A. Loudet, K. Burgess, 'BODIPY Dyes and Their Derivatives: Synthesis and Spectroscopic Properties', *Chem. Rev.* **2007**, *107*, 4891-4932.
- [14] G. Ulrich, R. Ziessel, A. Harriman, 'The Chemistry of Fluorescent Bodipy Dyes: Versatility Unsurpassed', *Angew. Chem. Int. Ed.* **2008**, *47*, 1184-1201.
- [15] H. Lu, J. Mack, Y. Yang, Z. Shen, 'Structural modification strategies for the rational design of red/NIR region BODIPYs', *Chem. Soc. Rev.* **2014**, *43*, 4778-4823.
- [16] X. Jiang, J. Zhao, D. Xi, H. Yu, J. Guan, S. Li, C. Sun, L. Xiao, 'A New Water-Soluble Phosphorus-Dipyromethene and Phosphorus-Azadipyromethene Dye: PODIPY/aza-PODIPY', *Chem. Eur. J.* **2015**, *21*, 6079-6082.
- [17] Y. Yang, X. Su, C. N. Carroll, I. Aprahamian, 'Aggregation-induced emission in BF<sub>2</sub>-hydrazone (BODIHY) complexes', *Chem. Sci.* **2012**, *3*, 610-613.
- [18] I. Tamgho, A. Hasheminasab, J. T. Engle, V. N. Nemykin, C. J. Ziegler, 'A New Highly Fluorescent and Symmetric Pyrrole-BF<sub>2</sub> Chromophore: BOPHY', *J. Am. Chem. Soc.* **2014**, *136*, 5623-5626.
- [19] B. Lee, B. Gyu Park, W. Cho, H. Yong Lee, A. Olasz, C. Chen, S. Bum Park, D. Lee, 'BOIMPY: Fluorescent Boron Complexes with Tunable and Environment-Responsive Light-Emitting Properties', *Chem. Eur. J.* **2016**, *22*, 17321-17328.
- [20] Y. Yang, R. P. Hughes, I. Aprahamian, 'Visible Light Switching of a BF<sub>2</sub>-Coordinated Azo Compound', *J. Am. Chem. Soc.* **2012**, *134*, 15221-15224.
- [21] F. M. F. Santos, J. N. Rosa, N. R. Candeias, C. P. Carvalho, A. I. Matos, A. E. Ventura, H. F. Florindo, L. C. Silva, U. Pischel, P. M. P. Gois, 'A Three-Component Assemble Promoted by Boronic Acids Delivers a Modular Fluorophore Platform (BASHY Dyes)', *Chem. Eur. J.* **2016**, *22*, 1631-1637.
- [22] T. Mikysek, H. Kvapilová, H. Doušová, F. Josefík, P. Šimůnek, Z. Růžicková, J. Ludvík, 'Synthesis, electrochemical, structural and theoretical study of new derivatives of O-B-N and O-B-O heterocycles', *Inorg. Chim. Acta* **2017**, *455*, 465-472.
- [23] F. Li, S. Ik Yang, Y. Ciringh, J. Seth, C. H. Martin III, D. L. Singh, D. Kim, R. R. Birge, D. F. Bocian, D. Holten, J. S. Lindsey, 'Design, Synthesis, and Photodynamics of Light-Harvesting Arrays Comprised of a Porphyrin and One, Two, or Eight Boron-Dipyrrin Accessory Pigments', *J. Am. Chem. Soc.* **1998**, *120*, 10001-10017.
- [24] H. L. Kee, C. Kirmaier, L. Yu, P. Thamyongkit, W. J. Youngblood, M. E. Calder, L. Ramos, B. C. Noll, D. F. Bocian, W. R. Scheidt, R. R. Birge, J. S. Lindsey, D. Holten, 'Structural Control of the Photodynamics of Boron-Dipyrrin Complexes', *J. Phys. Chem. B* **2005**, *109*, 20433-20443.
- [25] I. J. Arroyo, R. Hu, B. Z. Tang, F. I. López, E. Peña-Cabrera, '8-Alkenylborondipyromethene dyes. General synthesis, optical properties, and preliminary study of their reactivity', *Tetrahedron* **2011**, *67*, 7244-7250.
- [26] R. Lincoln, L. E. Greene, C. Bain, J. O. Flores-Rizo, D. S. Bohle, G. Cosa, 'When Push Comes to Shove: Unravelling the Mechanism and Scope of Nonemissive *meso*-Unsaturated BODIPY Dyes', *J. Phys. Chem. B* **2015**, *119*, 4758-4765.
- [27] L. Jiao, C. Yu, J. Wang, E. A. Briggs, N. A. Besley, D. Robinson, M. J. Ruedas-Rama, A. Orte, L. Crovetto, E. M. Talavera, J. M. Alvarez-Pez, M. Van der Auweraer, N. Boens, 'Unusual spectroscopic and photophysical properties of *meso*-tert-butylBODIPY in comparison to related alkylated BODIPY dyes', *RSC Adv.* **2015**, *5*, 89375-89388.
- [28] A. Prlj, A. Fabrizio, C. Corminboeuf, 'Rationalizing fluorescence quenching in *meso*-BODIPY dyes', *Phys. Chem. Chem. Phys.* **2016**, *18*, 32668-32672.
- [29] J. Michl, V. Bonačić-Koutecký, 'Electronic Aspects of Organic Photochemistry', Wiley-Interscience, 1990.
- [30] W. Domcke, D. R. Yarkony, H. Köppel, 'Conical Intersections: Theory, Computation and Experiment', World Scientific, Singapore, 2011.
- [31] M. Barbatti, H. Lischka, 'Why water makes 2-aminopurine fluorescent?', *Phys. Chem. Chem. Phys.* **2015**, *17*, 15452-15459.
- [32] X. Peng, S. Ruiz-Barragan, Z. Li, Q. Li, L. Blancafort, 'Restricted access to a conical intersection to explain aggregation induced emission in dimethyl tetraphenylsilole', *J. Mater. Chem. C* **2016**, *4*, 2802-2810.
- [33] A. Prlj, N. Došlić, C. Corminboeuf, 'How does tetraphenylethylene relax from its excited states?', *Phys. Chem. Chem. Phys.* **2016**, *18*, 11606-11609.
- [34] M. Dommett, R. Crespo-Otero, 'Excited state proton transfer in 2'-hydroxychalcone derivatives', *Phys. Chem. Chem. Phys.* **2017**, *19*, 2409-2416.
- [35] Q. L. Nguyen, V. A. Spata, S. Matsika, 'Photophysical properties of pyrrolocytosine, a cytosine fluorescent base analogue', *Phys. Chem. Chem. Phys.* **2016**, *18*, 20189-20198.
- [36] H. Qian, M. E. Cousins, E. H. Horak, A. Wakefield, M. D. Liptak, I. Aprahamian, 'Suppression of Kasha's rule as a mechanism for fluorescent molecular rotors and aggregation-induced emission', *Nat. Chem.* **2017**, *9*, 83-87.
- [37] J. Zhao, K. Xu, W. Yang, Z. Wang, F. Zhong, 'The triplet excited state of Bodipy: formation, modulation and application', *Chem. Soc. Rev.* **2015**, *44*, 8904-8939.
- [38] B. C. De Simone, G. Mazzone, J. Pirillo, N. Russo, E. Sicilia, 'Halogen atom effect on the photophysical properties of substituted aza-BODIPY derivatives', *Phys. Chem. Chem. Phys.* **2017**, *19*, 2530-2536.
- [39] S. Ji, J. Ge, D. Escudero, Z. Wang, J. Zhao, D. Jacquemin, 'Molecular Structure-Intersystem Crossing Relationship of Heavy-Atom-Free BODIPY Triplet Photosensitizers', *J. Org. Chem.* **2015**, *80*, 5958-5963.
- [40] G. Mazzone, A. D. Quartarolo, N. Russo, 'PDT-correlated photophysical properties of thienopyrrole BODIPY derivatives. Theoretical insights', *Dyes Pigm.* **2016**, *130*, 9-15.
- [41] Y. Cakmak, S. Kolemen, S. Duman, Y. Dede, Y. Dolen, B. Kilic, Z. Kostereli, L. Tatar Yildirim, A. Lale Dogan, D. Guc, E. U. Akkaya, 'Designing Excited States: Theory-Guided Access to Efficient Photosensitizers for Photodynamic Action', *Angew. Chem. Int. Ed.* **2011**, *50*, 11937-11941.
- [42] P. de Silva, C. Corminboeuf, 'Simultaneous Visualization of Covalent and Noncovalent Interactions Using Regions of Density Overlap', *J. Chem. Theory Comput.* **2014**, *10*, 3745-3756.
- [43] L. Vannay, E. Brémond, P. de Silva, C. Corminboeuf, 'Visualizing and Quantifying Interactions in the Excited State', *Chem. Eur. J.* **2016**, *22*, 18442-18449.
- [44] M. Buyuktemiz, S. Duman, Y. Dede, 'Luminescence of BODIPY and Dipyrrin: An MCSCF Comparison of Excited States', *J. Phys. Chem. A* **2013**, *117*, 1665-1669.
- [45] A. Orte, E. Debroye, M. J. Ruedas-Rama, E. Garcia-Fernandez, D. Robinson, L. Crovetto, E. M. Talavera, J. M. Alvarez-Pez, V. Leen, B. Verbelen, L. Cunha Dias de Rezende, W. Dehaen, J. Hofkens, M. Van der Auweraer, N. Boens, 'Effect of the substitution position (2, 3 or 8) on the spectroscopic and photophysical properties of BODIPY dyes with phenyl, styryl or phenylethynyl group', *RSC Adv.* **2016**, *6*, 102899-102913.
- [46] M. K. Kuimova, G. Yahioglu, J. A. Levitt, K. Suhling, 'Molecular Rotor Measures Viscosity of Live Cells via Fluorescence Lifetime Imaging', *J. Am. Chem. Soc.* **2008**, *130*, 6672-6673.
- [47] R. Hu, E. Lager, A. Aguilar-Aguilar, J. Liu, J. W. Y. Lam, H. H. Y. Sung, I. D. Williams, Y. Zhong, K. S. Wong, E. Peña-Cabrera, B. Z. Tang, 'Twisted Intramolecular Charge Transfer and Aggregation-Induced Emission of BODIPY Derivatives', *J. Phys. Chem. C* **2009**, *113*, 15845-15853.
- [48] J. Bañuelos, I. J. Arroyo-Córdoba, I. Valois-Escamilla, A. Alvarez-Hernández, E. Peña-Cabrera, R. Hu, B. Z. Tang, I. Esnal, V. Martínez, I. López Arbeloa,

- 'Modulation of the photophysical properties of BODIPY dyes by substitution at their *meso* position', *RSC Adv.* **2011**, *1*, 677-684.
- [49] C. Adamo, D. Jacquemin, 'The calculations of excited-state properties with Time-Dependent Density Functional Theory', *Chem. Soc. Rev.* **2013**, *42*, 845-856.
- [50] S. Chibani, B. Le Guennic, A. Charaf-Eddin, A. D. Laurent, D. Jacquemin, 'Revisiting the optical signatures of BODIPY with *ab initio* tools', *Chem. Sci.* **2013**, *4*, 1950-1963.
- [51] D. Jacquemin, S. Chibani, B. Le Guennic, B. Menucci, 'Solvent Effects on Cyanine Derivatives: A PCM Investigation', *J. Phys. Chem. A* **2014**, *118*, 5343-5348.
- [52] E. A. Briggs, N. A. Besley, D. Robinson, 'QM/MM Excited State Molecular Dynamics and Fluorescence Spectroscopy of BODIPY', *J. Phys. Chem. A* **2013**, *117*, 2644-2650.
- [53] K. T. Komoto, T. Kowalczyk, 'How Parallel Are Excited State Potential Energy Surfaces from Time-Independent and Time-Dependent DFT? A BODIPY Dye Case Study', *J. Phys. Chem. A* **2016**, *120*, 8160-8168.
- [54] J. D. Spiegel, M. Kleinschmidt, A. Larbig, J. Tatchen, C. M. Marian, 'Quantum-Chemical Studies on Excitation Energy Transfer Process in BODIPY-Based Donor-Acceptor Systems', *J. Chem. Theory Comput.* **2015**, *11*, 4316-4327.
- [55] S. Knippenberg, M. V. Bohnwagner, P. H. P. Harbach, A. Dreuw, 'Strong Electronic Coupling Dominates the Absorption and Fluorescence Spectra of Covalently Bound BisBODIPYs', *J. Phys. Chem. A* **2015**, *119*, 1323-1331.
- [56] M. R. Momeni, A. Brown, 'A Local CC2 and TDA-DFT Double Hybrid Study on BODIPY/aza-BODIPY Dimers as Heavy Atom Free Triplet Photosensitizers and Photodynamic Therapy Applications', *J. Phys. Chem. A* **2016**, *120*, 2550-2560.
- [57] A. Charaf-Eddin, B. Le Guennic, D. Jacquemin, 'Excited-states of BODIPY-cyanines: ultimate TD-DFT challenges?', *RSC Adv.* **2014**, *4*, 49449-49456.
- [58] R. R. Valiev, A. N. Sinelnikov, Y. V. Aksenova, R. T. Kuznetsova, M. B. Berezin, A. S. Semeikin, V. N. Cherepanov, 'The computational and experimental investigations of photophysical and spectroscopic properties of BF<sub>2</sub> dipyrromethene complexes', *Spectrochim. Acta Mol. Biomol. Spectrosc.* **2014**, *117*, 323-329.
- [59] J. Wang, J. Jin, Y. Geng, S. Sun, H. Xu, Y. Lu, Z. Su, 'An Accurate and Efficient Method to Predict the Electronic Excitation Energies of BODIPY Fluorescent Dyes', *J. Comput. Chem.* **2013**, *34*, 566-575.
- [60] M. R. Momeni, A. Brown, 'Why Do TD-DFT Excitation Energies of BODIPY/Aza-BODIPY Families Largely Deviate from Experiment? Answers from Electron Correlated and Multireference Methods', *J. Chem. Theory Comput.* **2015**, *11*, 2619-2632.
- [61] K. Schulten, U. Dinur, B. Honig, 'The spectra of carbonium ions, cyanine dyes, and protonated Schiff base polyenes', *J. Chem. Phys.* **1980**, *73*, 3927-3935.
- [62] S. Grimme, F. Neese, 'Double-hybrid density functional theory for excited electronic states of molecules', *J. Chem. Phys.* **2007**, *127*, 154116.
- [63] R. Send, O. Valsson, C. Filippi, 'Electronic Excitations of Simple Cyanine Dyes: Reconciling Density Functional and Wave Function Methods', *J. Chem. Theory Comput.* **2011**, *7*, 444-455.
- [64] B. Moore II, J. Autschbach, 'Longest-Wavelength Electronic Excitations of Linear Cyanines: The Role of Electron Delocalization and of Approximations in Time-Dependent Density Functional Theory', *J. Chem. Theory Comput.* **2013**, *9*, 4991-5003.
- [65] M. Filatov, M. Huix-Rotllant, 'Assessment of density functional theory based ΔSCF (self-consistent field) and linear response methods for longest wavelength excited states of extended π-conjugated molecular systems', *J. Chem. Phys.* **2014**, *141*, 024112.
- [66] J. Schirmer, 'Beyond the random-phase approximation: A new approximation scheme for the polarization propagator', *Phys. Rev. A* **1982**, *26*, 2395-2416.
- [67] A. B. Trofimov, J. Schirmer, 'An efficient polarization propagator approach to valence electron excitation spectra', *J. Phys. B: At. Mol. Opt. Phys.* **1995**, *28*, 2299-2324.
- [68] C. Hättig, 'Structure Optimizations for Excited States with Correlated Second-Order Methods: CC2 and ADC(2)', *Adv. Quant. Chem.* **2005**, *50*, 37-60.
- [69] M. Barbatti, 'Photorelaxation Induced by Water-Chromophore Electron Transfer', *J. Am. Chem. Soc.* **2014**, *136*, 10246-10249.
- [70] T. N. V. Karsili, D. Tuna, J. Ehrmaier, W. Domcke, 'Photoinduced water splitting via benzoquinone and semiquinone sensitisation', *Phys. Chem. Chem. Phys.* **2015**, *17*, 32183-32193.
- [71] A. Prlj, B. F. E. Curchod, C. Corminboeuf, 'Excited state dynamics of thiophene and bithiophene: new insights into theoretically challenging systems', *Phys. Chem. Chem. Phys.* **2015**, *17*, 14719-14730.
- [72] M. Sapunar, A. Ponzi, S. Chaiwongwattana, M. Mališ, A. Prlj, P. Decleva, N. Došlić, 'Timescales of N-H bond dissociation in pyrrole: a nonadiabatic dynamics study', *Phys. Chem. Chem. Phys.* **2015**, *17*, 19012-19020.
- [73] D. Tuna, A. L. Sobolewski, W. Domcke, 'Mechanisms of Ultrafast Excited-State Deactivation in Adenosine', *J. Phys. Chem. A* **2014**, *118*, 122-127.
- [74] X. Liu, T. N. V. Karsili, A. L. Sobolewski, W. Domcke, 'Photocatalytic Water Splitting with the Acridine Chromophore: A Computational Study', *J. Phys. Chem. B* **2015**, *119*, 10664-10672.
- [75] D. Tuna, W. Domcke, 'Excited-state deactivation in 8-oxo-deoxyguanosine: comparison between anionic and neutral forms', *Phys. Chem. Chem. Phys.* **2016**, *18*, 947-955.
- [76] R. Szabla, R. W. Góra, J. Šponer, 'Ultrafast excited-state dynamics of isocytosine', *Phys. Chem. Chem. Phys.* **2016**, *18*, 20208-20218.
- [77] J. Novak, A. Prlj, N. Basarić, C. Corminboeuf, N. Došlić, 'Photochemistry of 1- and 2-Naphthols and their Water Clusters: The Role of ππ\*(L<sub>a</sub>) Mediated Hydrogen Transfer to Carbon Atoms', *Eur. Chem. J.* **2017**, DOI: 10.1002/chem.201700691.
- [78] D. Tuna, D. Lefrançois, Ł. Wolański, S. Gozem, I. Schapiro, T. Andrúniów, A. Dreuw, M. Olivucci, 'Assessment of Approximate Coupled-Cluster and Algebraic-Diagrammatic-Construction Methods for Ground- and Excited-State Reaction Paths and the Conical-Intersection Seam of a Retinal-Chromophore Model', *J. Chem. Theory Comput.* **2015**, *11*, 5758-5781.
- [79] F. Furche, R. Ahlrichs, C. Hättig, W. Klopper, M. Sierka, F. Weigend, 'TurboMole', *WIREs Comput. Mol. Sci.* **2014**, *4*, 91-100.
- [80] F. Weigend, R. Ahlrichs, 'Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy', *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297-3305.
- [81] F. Weigend, 'Accurate Coulomb-fitting basis sets for H to Rn', *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057-1065.
- [82] B. G. Levine, J. D. Coe, T. J. Martínez, 'Optimizing Conical Intersections without Derivative Coupling Vectors: Application to Multistate Multireference Second-Order Perturbation Theory (MS-CASPT2)', *J. Phys. Chem. B* **2008**, *112*, 405-413.
- [83] B. Lunkenheimer, A. Köhn, 'Solvent Effects on Electronically Excited States Using the Conductor-Like Screening Model and the Second-Order Correlated Method ADC(2)', *J. Chem. Theory Comput.* **2013**, *9*, 977-994.
- [84] P. de Silva, J. Korchowicz, T. A. Wesolowski, 'Revealing the Bonding Pattern from the Molecular Electron Density Using Single Exponential Decay Detector: An Orbital-Free Alternative to the Electron Localization Function', *ChemPhysChem* **2012**, *13*, 3462-3465.

## Entry for the Table of Contents

