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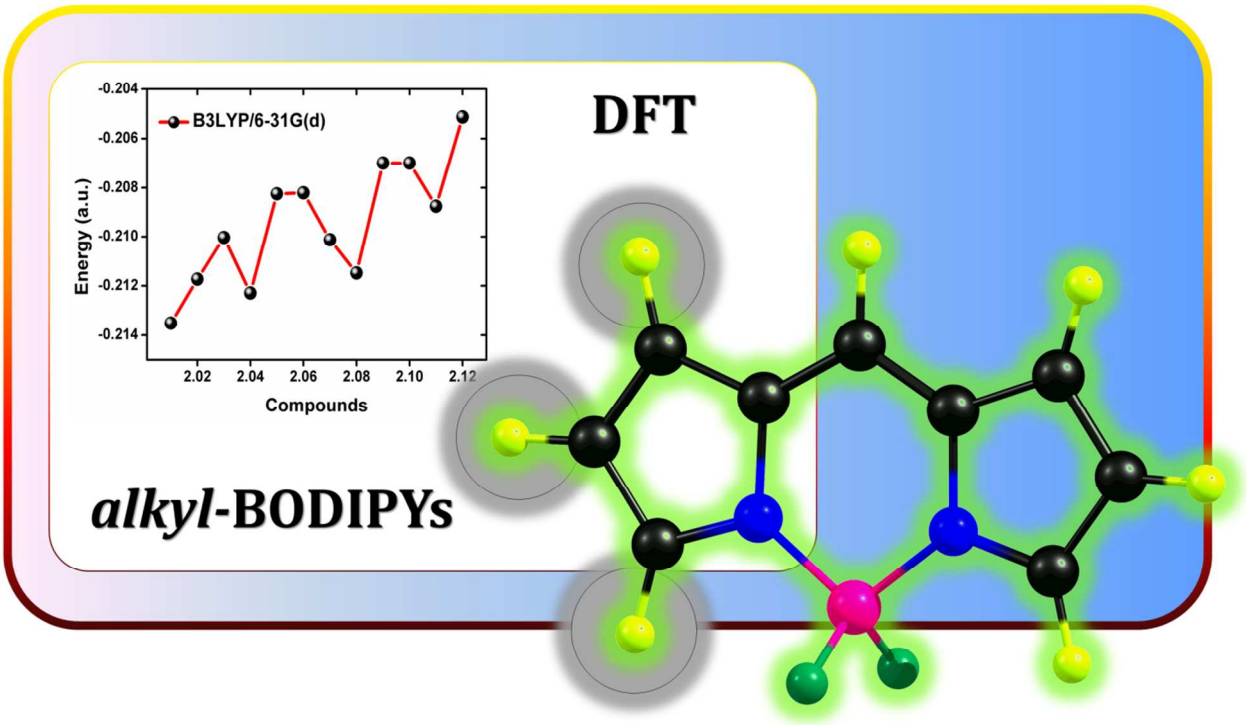
Graphical Abstract



A detailed computational investigation encompassing the effects of alkyl groups in the structural and electronic properties of BODIPY dyes is presented.

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Abstract:

Random changes in the alkyl substitution patterns in fluorescent dyes e.g. BODIPYs often accompany with significant changes in their photophysical properties. To understand such alteration of properties in closely related molecular systems, a comparative DFT (density functional theory) computational investigation was performed in order to comprehend the effects of alkyl substitutions in controlling the structural and electronic nature of BODIPY dyes. In this context, a systematic strategy was utilized considering all possible outcomes of constitutionally-isomeric molecules to understand the alkyl groups' effects on the BODIPY molecules. The usage of four different computational methods {i.e. B3LYP/6-31G(d); B3LYP/6-311++G(d, p); wb97xd/6-311++G(d, p) and mpw1pw91/6-311++G(d, p)} was employed to rationalized the unanimity of the trends associated with the molecular properties. In line with experimental observations, it was found that alkyl substituents in BODIPY dyes situated at 3/5-positions effectively participate in stabilization as well as planarization of such molecules. Screening of all the possible isomeric molecular systems was used to understand the individual properties and overall effects of the typical alkyl substituents in controlling several basic properties of such BODIPY molecules.

Introduction:

The recent progress of luminescent materials would remain largely incomplete if one does not take the accounts of BODIPYs (boron-dipyrromethenes).[1] BODIPYs are a considerably large class of tetracoordinate boron containing dyes where the dipyrrin type ligands act as the chelating group towards boron atom. With its sharp and tunable absorption and emission profiles coupled with their photo-stability and frequently observed high quantum yields, BODIPYs have found paths in almost all directions of modern applications. BODIPYs find applications in biological live-cell imaging, [2]

fluorescent recognition, [3] light-harvesting systems, [4] photo-catalysis [5] etc. Although the progress of applications of the BODIPY based compounds have been remarkable, the understanding of the origins of their excellent properties are yet not well-understood.

The prediction of electronic properties of the BODIPY compounds using available computational tools and theoretical models mostly deviate largely from the actual experimentally observed properties. [6] Despite of the limitations, the usage of computational methods as DFT etc. have found important role in understanding the chemistry of boron based dyes. [7] The comparative nature of closely related molecules is better understood from regular computational results rather than the exact natures of individual compounds. In recent times, a number of computational efforts have been implemented to gain a comparative insight into the photophysics of BODIPY dye analogues. [6, 8] However, prior to this report, there has been no substantial work on the effect of alkyl substituents in controlling the nature of these dyes. It is notable that due to the synthetic convenience and to control physical properties e.g. solubility, often alkyl substituents are preferred as a part of the pyrollic moieties in BODIPYs. However, it has been observed that in many cases, such alkyl groups significantly alter the photophysical properties of BODIPYs. [9, 10] In this work, a closer theoretical perspective of such observations is explored. A comparative understanding on the effect of alkyl groups in control over the total energy, ring-planarity and FMO energies of BODIPY dyes are discussed.

The molecular structure of BODIPY core closely resemble to the geometry of indacenes. As shown in Figure 1, a close look at the {B3LYP/6-31G(d) optimized} molecular structure (see the Supporting Information) would suggest that the substituents at *meso*-position would experience comparatively less steric interactions of neighboring groups whereas the same is expected to be comparatively greater for 1, 2, 6 and 7-positioned substituents. Due to the presence of a borate moiety, the substituents at 3 and 5 positioned alkyl moieties are expected to experience the highest extents of steric interactions with the neighboring environment. If the interactions of such substituents are solely governed by steric interactions, 3/5-alkyl substituted BODIPYs can be expected to be energetically relatively less stable or puckered compared to its constitutional isomers. However, the experimental

observations found in previous reports as well as computational results found in this work provide completely opposing results.

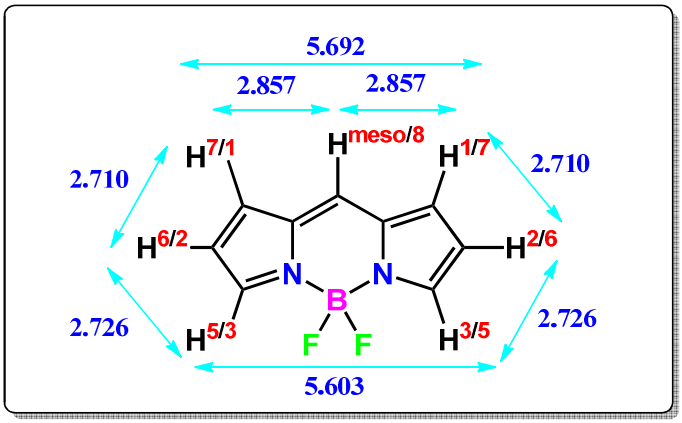

Figure 1: Molecular structure of BODIPY core showing atom numbering scheme and distances between neighboring H atoms in angstroms (B3LYP/6-31G(d) optimized structure)

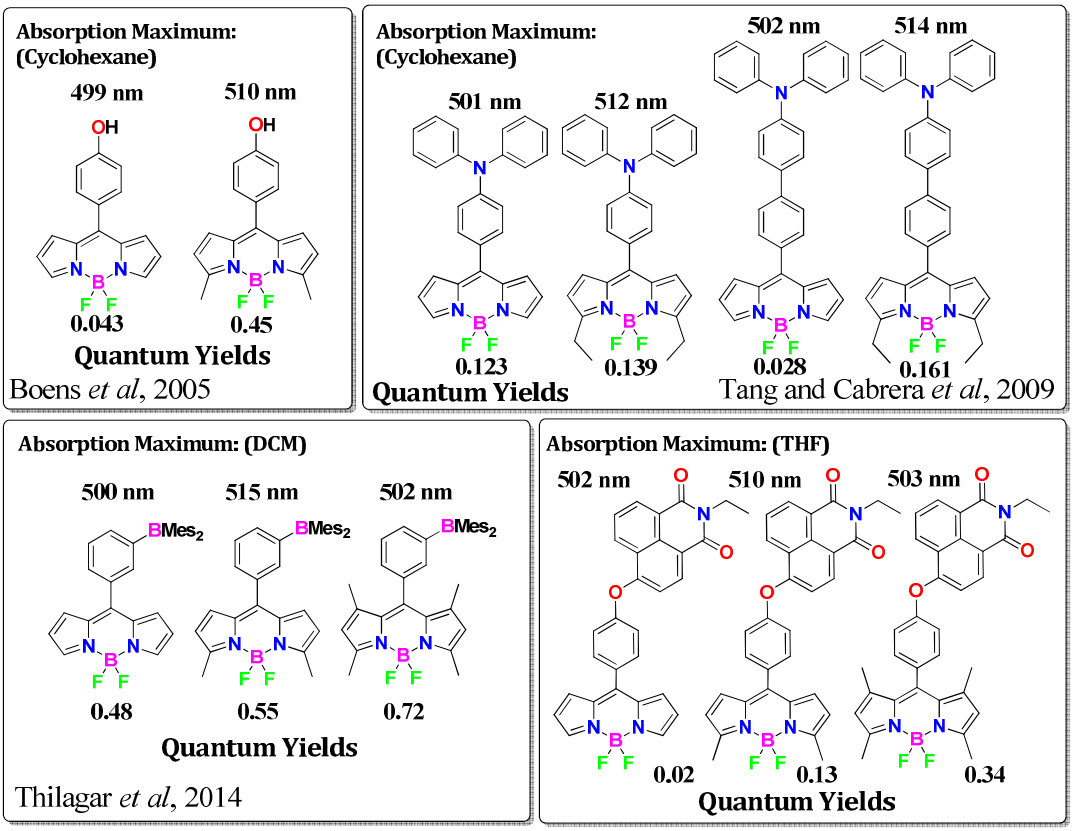

Figure 2: Comparison of optical properties of series' of structurally close BODIPY compounds differing only in alkyl substitution on the BODIPY unit. (Reference 9 and 10)

Experimental observations often encounter the uncorrelated behaviors of several 3/5-substituted BODIPYs. Previous reports from Boens *et al*, Cabrera and Tang *et al* [9] followed by our recent investigations [10] have demonstrated that the alkyl substituents on BODIPY dyes can significantly alter their photophysical properties. As shown in Figure 2, in the series of BODIPYs depicted in the schemes, the 3,5-dimethyl substituted compounds show significantly red-shifted absorption (~10-15 nm) profiles compared to the BODIPYs with no substituents at all or 1,3,5,7-tetramethyl substituted compounds. As the first and third members of the last two series show same absorption pattern based on the BODIPY core, the sudden alteration of the band gap of the 3,5-dimethyl substituted BODIPYs cannot be accounted considering only π-π conjugation throughout the molecular backbone. Also, the 3,5-dimethyl substituted BODIPYs show higher quantum efficiencies compared to the BODIPYs with no methyl substituents. As observed, the 3,5-dimethyl substitutions participate actively in somehow rigidifying the BODIPY system and also effectively diminishing the effective band-gap. Such small changes in electronic and structural properties render considerably great effects on the photophysical properties of BODIPYs and other multichromophoric molecular conjugates. [11] In order to understand the effect of alkyl substituents in controlling the properties of BODIPYs, a comparative computational study was performed considering all possibilities of such substation patterns.

Methodology:

All the density functional theoretical (DFT) calculations were performed using standard computational methods and basis sets as incorporated in the *Gaussian 09* software package. [12] The most commonly used B3LYP functional with 6-31G(d) basis sets for all the atoms was taken into consideration in this regard (Table S1-1, ESI). [13] Frequency tests of the optimized structures were performed to ascertain stationary points. Additionally, the calculations were also performed using B3LYP/6-311++G(d, p); wb97xd/6-311++G(d, p) [14] and mpw1pw91/6-311++G(d, p) [15] methods to ascertain that the results obtained in the previous method are not dependent on the choices of either functional or basis-sets (see the Supporting Information). TD-DFT 1st excited state geometry optimizations were performed using only the B3LYP/6-31G(d) methodology.

In order to obtain a complete understanding of the effect of small alkyl groups on the nature of BODIPY dyes, systematic alteration of substituents were taken into considerations. For this purpose, five hypothetical series of compounds were taken in account for the computational studies. For instance, series **1** consists of all possible structures possible on single methyl substitution around the BODIPY core. As only four possibilities arise, models **1.01** to **1.04** are the constituents of this series. Similarly, series **3** considers single ethyl substitution whereas series **5** refers to single tert-butyl substitution, which was taken into considerations for understanding the steric effects of the alkyl groups. On the other hand, series **2** consists of possibilities where two simultaneous methyl substitutions are performed around the BODIPY dyes. In such a case, twelve different possibilities arise which can provide a relatively large series for comparative understanding of the constitutional isomers. Similarly, series **4** consists of models comprised of two simultaneous ethyl substitutions. In a complete picture, total **37** model systems were taken into account.

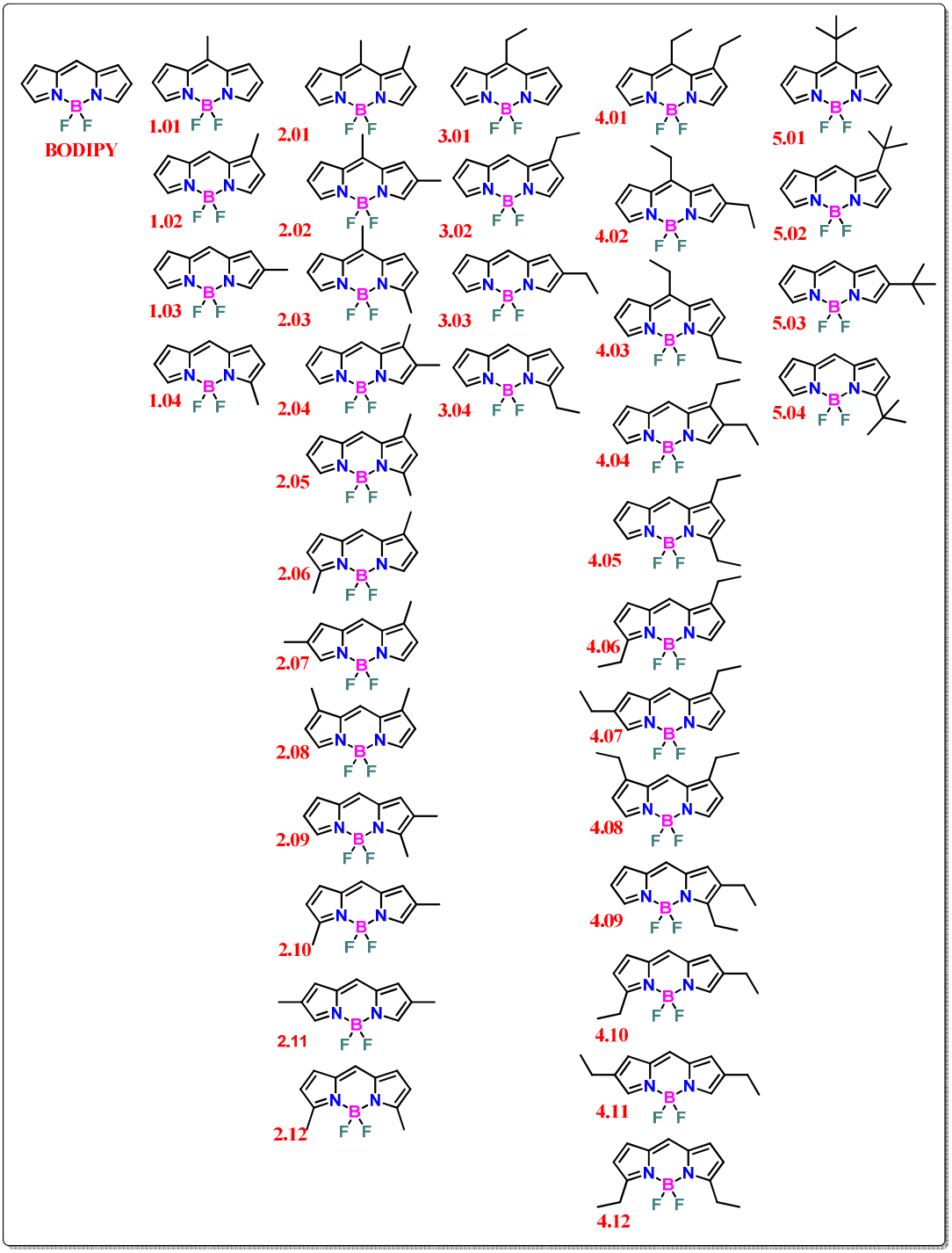

Figure 3: Structural formulae of the BODIPY compounds taken into considerations for the current study.

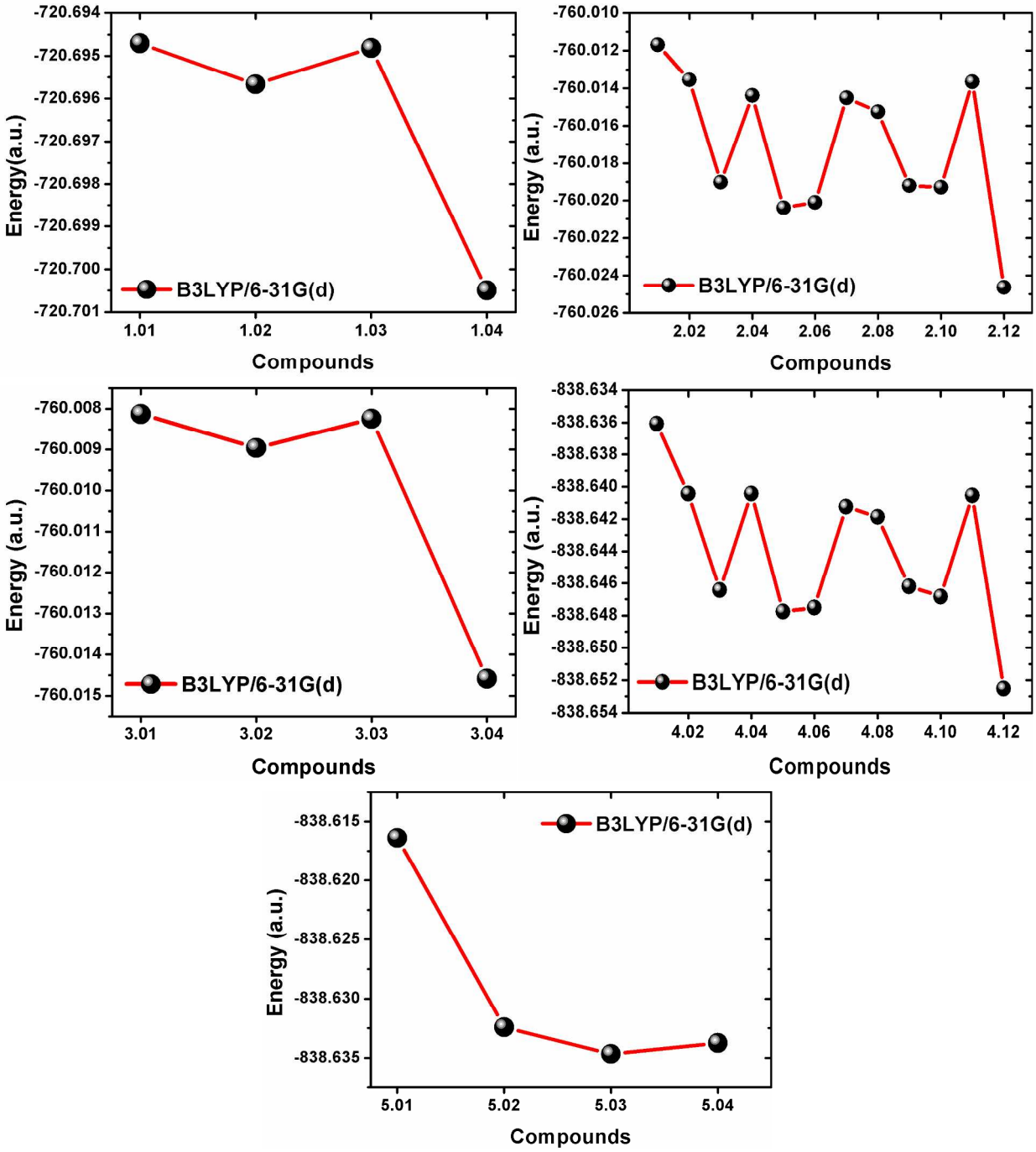

Figure 4: Comparison of the relative total energies of the BODIPY isomers represented in each series (Series **1-4**) as obtained from DFT B3LYP/6-31G(d) optimizations.

Effect of relative stability:

Although the individual members of a particular series are related to one another as constitutional isomers, their total energy i.e. stability differ in great manner (see the

Supporting Information). As shown in Figure 1, steric interactions between neighboring C1 and C8 substituents are expected to be less prominent compared to the C3/C5 and BF2 centers. However, the computational results differed vastly from our general expectations. As shown in Figure 4, in all the series **1-4**, the most stable isomers are those with isomers situated at the 3 and (or) 5 positions of the BODIPY moiety. The only exception is found in series **5** where the most stable isomer is **5.03**. It is also noteworthy that in all series **1-5**, the highest energy isomers are those particularly decorated with C8-substituents. The trends found in this regard are independent of the choice of functional or usage of either 6-31G(d) or 6-31++G(d, p) basis sets. As evident from the B3LYP/6-31G(d) obtained results, model system **1.04** is a ~15.2 KJ/mol more stable isomer compared to **1.01**. This is also followed in series **3** where **3.04** experiences ~17.0 KJ/mol stability compared to **3.01**. The minute differences in these relative stabilization energies of the 3-substituted isomers (i.e. **1.04** and **2.04**) compared to the *meso*-substituted isomers (i.e. **1.01** and **3.01**) indicates that these effects are mostly not due to steric interactions (see the Supporting Information).

The trends observed in series **2** and series **4** further supports that the lower ends of the energy profiles in the series of constitutional isomers are mostly hold by the 3-substituted members (i.e. **2.03**, **2.05**, **2.06**, **2.09**, **2.10** and **2.12** for series **2** and similarly for series **4**) whereas the 3,5-disubsituted members (i.e. **2.12** and **4.12**) are the most stable isomers with stabilization energies (compared to **2.01** and **4.01** respectively) ~34.0 KJ/mol for series **2** and ~43.2 KJ/mol for series **4** respectively. The trends in these two groups suggest that steric interactions between neighboring groups are most prominent for the *meso*-substituted compounds whereas the effects are least prominent for the 3 (and/or 5) substituted isomers. Compounds **2.09** and **4.09** are relatively stable isomers compared to **2.11** and **4.11** which is an apparent anomaly if one considers only steric interactions playing role in such energy differences. For instance, **4.09** contain two neighboring bulky ethyl units where in **4.11**; no such steric interactions are present except ethyl-hydrogen steric interactions. This statement is also evident from the observed trends in series **5** where **5.03** constitute the most stable isomer among **5.01**-**5.04**. The steric demand for 2,6-subsituted BODIPYs (e.g. **4.09**) should have been less than that for 2,3-substituted BODIPYs

(e.g. **4.11**). The explanations based on steric factors cannot completely justify the observations and the overall results indicate towards the active participation of the alkyl substituents' in governing the overall features of the BODIPY systems.

Effect on FMOs:

Further justifications of our interpretations are also followed from the tendencies observed in the FMO energies of the model BODIPY systems (see the Supporting Information). As shown in Figure 5, in either series **1**, **3** or **5**; the relative energies of the HOMO orbitals increase gradually in an almost linear fashion on going from the *meso*-substituted (**1.01** or **3.01**) to the 3-subsituted isomers (**1.04** or **3.04** respectively). The overall increment observed in these cases are rather considerable (~0.13 eV for series **1** and ~0.23 eV for series **3**), in complex molecular systems, such changes induced by the mare alkyl substituents might render great effects in their photophysical properties such as energy or electron transfer processes. Observations of the trends in the HOMO energies of series **2** and **4** make it evident that the trend is quite opposite to the trends observed in the total energy of the molecules. In these cases, the peaks of the energy profiles are hold by the **3** (and/or **5**) substituted isomers whereas the summits are constituted of the 1-substituted isomers. As shown in Figure 6, the interactions of C-H bonding interactions with the BODIPY based orbitals invest effectively in obtaining these trends. The *meso*-methyl substitution in compound **2.01** contributes rather low to the formation of the HOMO (compared to others in the same series). It is also qualitatively evident that the involvements of C-H δ-Bonds in the HOMO increase gradually on going from **2.02** to **2.04**. In the all the cases, it is found that the C-H δ-bonding orbitals are in destructive interference with the BOIPY centered orbitals and thus can only increase the HOMO energy. Consideration of only this idea can clearly describe the complete trends as observed in series **1-4**. For instance, in series **2**, model **2.01** has the lowest HOMO energy. A linear increase is followed up to **2.03** where the 3-subsitution results in a comparatively higher HOMO energy. In similar argument, model **2.12** has the highest HOMO energy resulting from the participation of C-H δ-bonds of the 3 and 5 substituents.

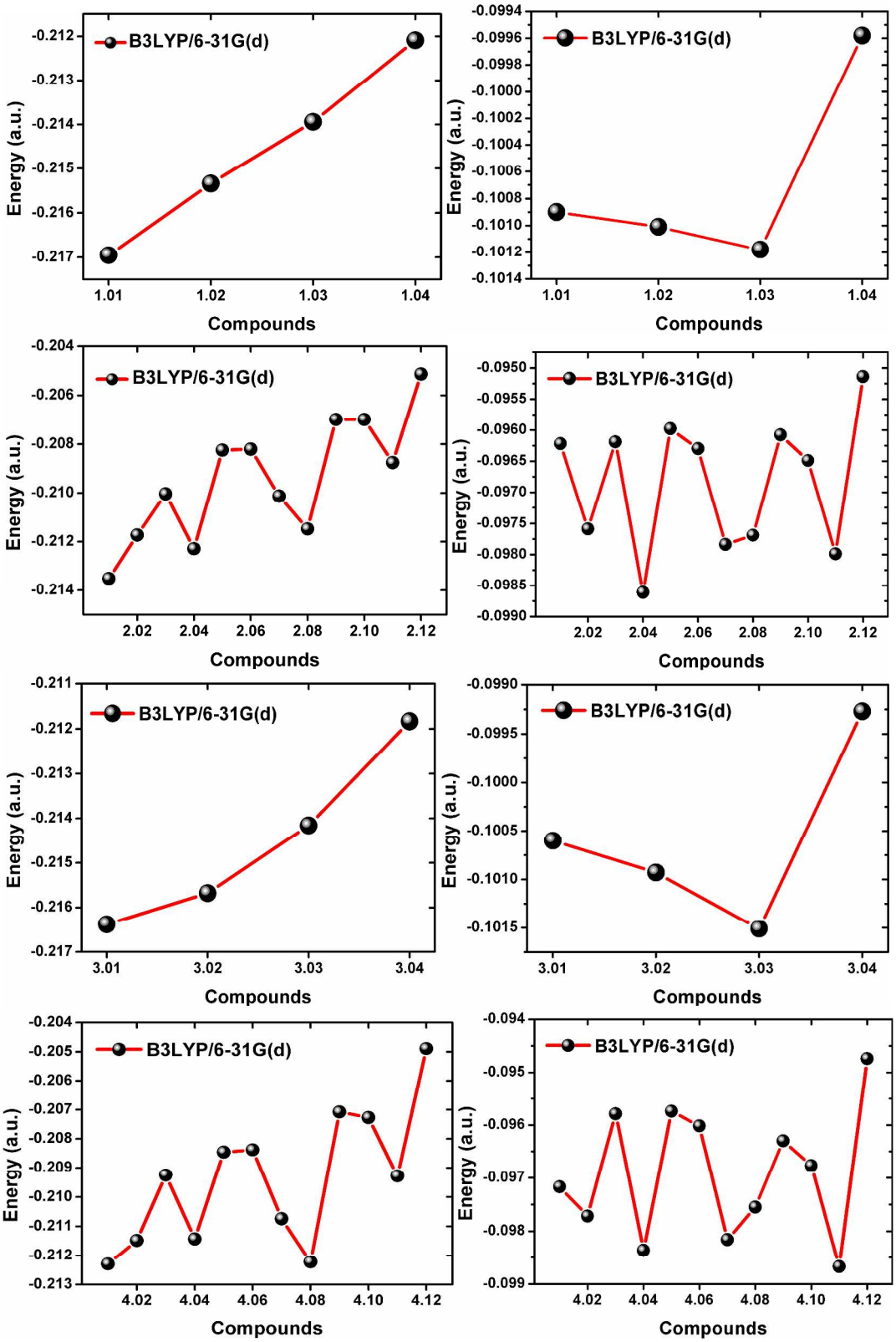

Figure 5: Comparison of the relative HOMO (left) and LUMO (right) energies of the BODIPY isomers represented in each series (Series **1-4**) as obtained from DFT B3LYP/6-31G(d) optimizations.

Similar observations are not followed in case for the LUMOs of the model BODIPY systems. In series **1**, the LUMOs energies decrease gradually on going from **1.01** to **1.03** whereas the LUMO energy of **1.04** is highest in the series **1**. Similar observations are followed in case of series **3** and series **5**. The observations can be well explained considering the interactions observed in these LUMO orbitals. As shown in Figure 7, from **1.01** to **1.03**, the effective involvement of C-H δ-orbitals in formation of the LUMOs gradually decrease whereas it regains its efficiency on going to **1.04**. It is also evident that the 2-subsituents almost not at all participate in formation of the LUMO orbitals and remain electronically inactive. So, the minimum of the LUMO energy profiles in series 2 and 4 consists of compounds with 2-substituted BODIPYs (i.e. **2.02**, **2.04**, **2.07** and **2.11**) without having any neighboring interactions.

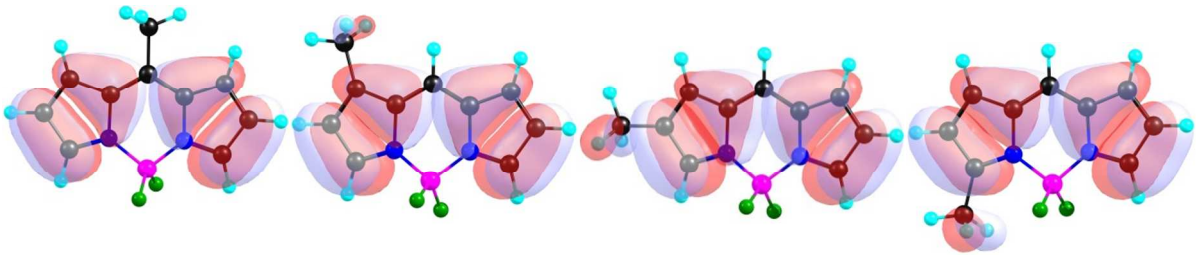

Figure 6: DFT B3LYP/6-31G(d) obtained HOMOs of **1.01** to **1.04** (from left to right respectively, isovalue = 0.02)

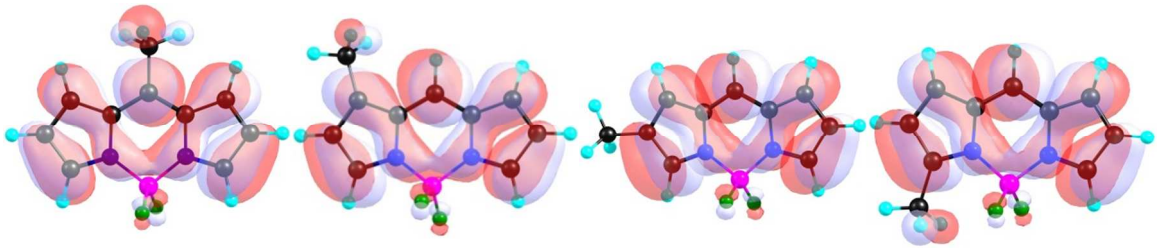

Figure 7: DFT B3LYP/6-31G(d) obtained LUMOs of **1.01** to **1.04** (from left to right respectively, isovalue = 0.02)

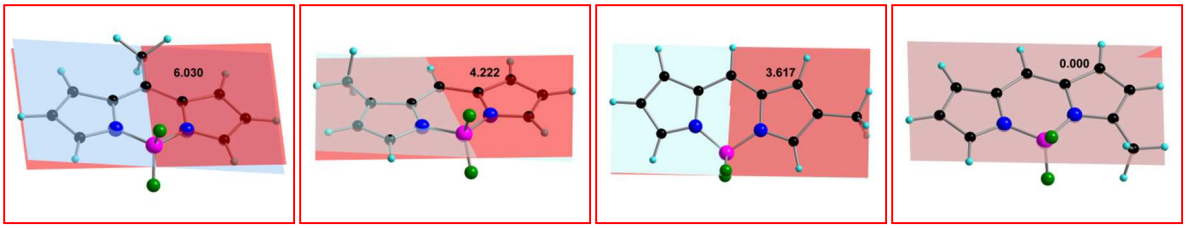

Figure 8: Dihedral arrangements of the two neighboring pyrrolic units in compounds **1.01** to **1.04** (from left to right respectively) as obtained from DFT B3LYP/6-31G(d) optimized ground-state structures.

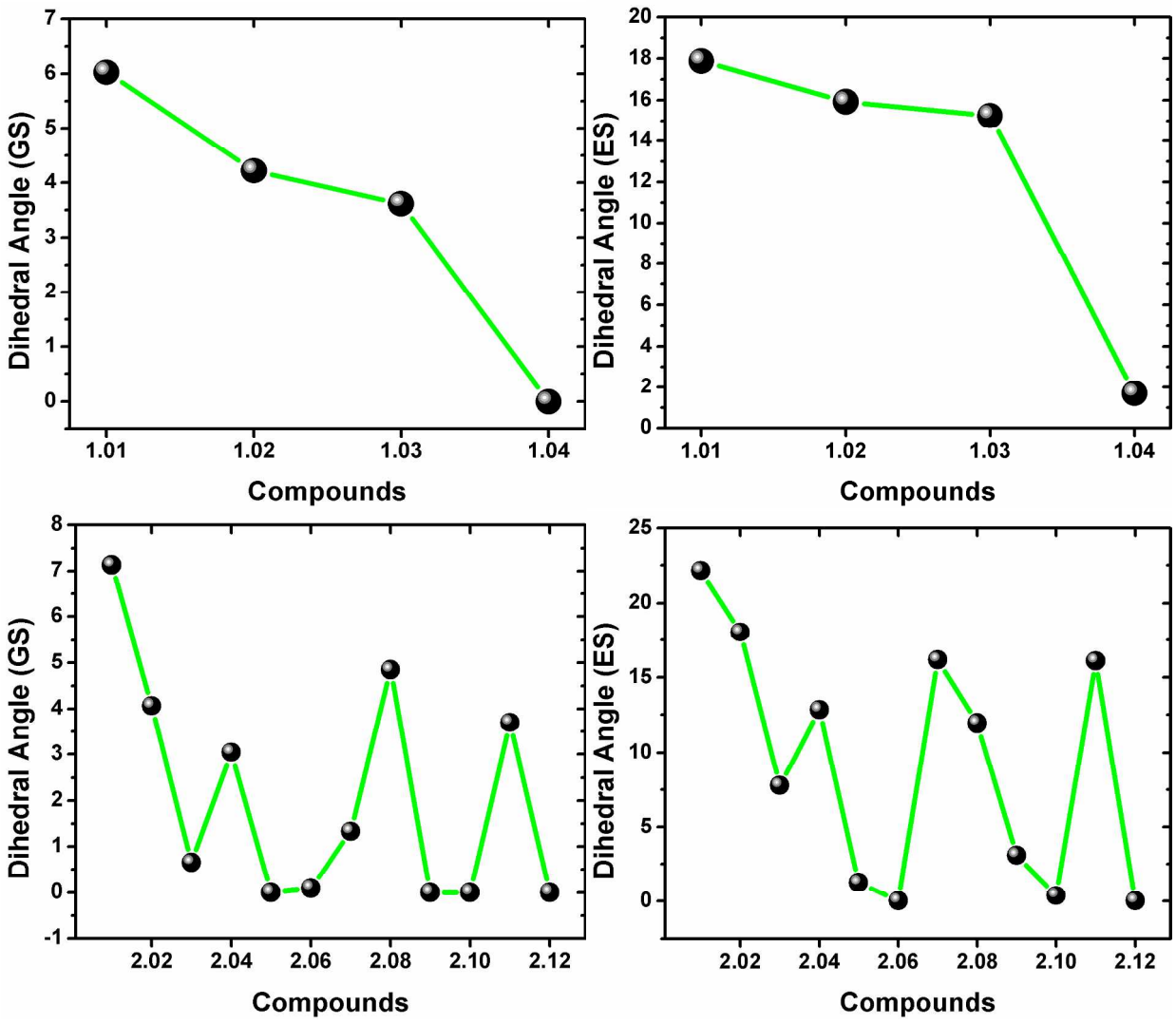

Figure 9: Comparison of the dihedral arrangements of the two neighboring pyrrolic units in compounds in series **1** (top) and **2** (bottom) in their ground states (left side pictures) and in their 1st excited states (right side pictures) as obtained from DFT B3LYP/6-31G(d) computations.

Effect on dihedral arrangement:

The alkyl substitution patterns around the BODIPY units also actively participate in controlling the overall planarity of the fluorescent chromophore (see the Supporting Information). In order to understand such effect, we considered measurement of the dihedral angle between the two pyrrolic units (defined as ∠Py-Py) which can be taken as a standard of quantifying the planarity of BODIPY. If the dihedral angle is 0.0°, the system can be considered as a planar system whereas larger values of this angle would indicate towards relatively more puckering of the BODIPY. As shown in Figure 8 and 9, the methyl/ethyl substituents participate actively in controlling the planarity of the BODIPY core.

In series **1**, on moving from **1.01** to **1.03**, the ∠Py-Py decrease gradually and takes a sudden drop on approaching **1.04**. In fact, the BODIPY ring takes on a complete planar geometry (∠Py-Py = 0.000°) in **1.04** which is unexpected considering the possible steric effects. However, similar observations are not followed for series **3** and series **5** where **3.02** and **5.03** (respectively) show minimum puckering of the molecules. The tendencies observed in the 1st excited state optimized geometries of the BODIPY systems are also in close similarities with the ground-state structures. As discussed, the 3 (and/or 5) alkyl substitutions in BODIPYs allow considerably minimal puckering of the ring structure in their ground states as well as upon electronic excitations. Such effects are intrinsically related to the total energy i.e. relative stabilities of the systems as well as contribute significantly in controlling conjugation through the molecular structures.

Collective comparison:

The results presented earlier open many explored avenues related to the chemistry of BODIPY dyes. It is evident that even a small change in the random arrangement of an alkyl substituent can render considerably large electronic and structural effects on the molecular systems. Although this study represents a qualitative outlook on the overall picture, it is evident that even such small changes cannot be put on randomly if the synthetic designs are really expected to be built from the scratch. If only alkyl substituents result in such a large diversity, other electronically active atoms (e.g. Br, I etc.) or functional entities would

result in furthermore larger effects at the molecular levels resulting in vastly different functionalities of closely related molecules.

As observed, the alkyl substitutions at the 3/5-positions of the BODIPY dyes participate in relative planarization of the molecular system increasing conjugation throughout which effectively results in its relatively higher stability compared to its other constitutional isomers. The results are unanimously supported from the observational consistencies of all four computational methods as used in this work {i.e. B3LYP/6-31G(d); B3LYP/6-311++G(d,p); wb97xd/6-311++G(d,p) and mpw1pw91/6-311++G(d,p) methods}. The 3/5-positioned substituents also result in higher HOMO energy but render less effective destabilization of the LUMO levels which result in an overall diminished band gap. These observations are line with the experimental observations as discussed *vide-supra*. The universality of the trends in isomeric molecules was tested using the four above mentioned computational methods (also see the Supporting Information) which unambiguously show the effect of alkyl groups in controlling the overall nature of BODIPYs.

Conclusions:

In summary, a systematic approach has been utilized in order to achieve a comparative and qualitative perspective of the BODIPYs with isomeric structures differing only in substituent positions. The universalities of the outcomes were also compared using different computational methods and the consistencies of any given trend were found to be unanimous in nature. The results found in this respect are potentially interesting and open new questions and prospects related to our available understanding of BODIPY based molecules. Even the alkyl moieties were found to be effective tools in altering the nature of BODIPY dyes and their intrinsic properties. It was found that the participation of such alkyl moieties in controlling the electronic signature of the BODIPYs (e.g. HOMO or LUMO energies) depend solely on the position of the substituent and almost irrespective of the nature of substituent (e.g. methyl or ethyl groups). It was also found that the planarization or the puckering of the BODIPY ring systems are also highly altered by the position of such alkyl substituents which can be of great effect in the cases of fluorescent chromophores. The results discussed in this work relate to the very basic and often puzzling experimental

observations and can be of potential interest to even finer-tuning of the photophysics of BODIPY dyes.

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