A study of the density functional methods on the photoabsorption of bodipy dyes

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Tunability of the photoabsorption and directional charge injection characteristics of Bodipy-based dye molecules with different carbonyl groups make them promising candidates for photovoltaic applications. In order to study the effect of screening in the Coulomb interaction on the electronic and optical properties of two Bodipy derivatives, we have used linear response time-dependent and exact exchange hybrid density functional approaches. The effect of linear and non-linear solvation models on the electrochemical properties of the dyes has also been discussed.

I. INTRODUCTION

The dye-sensitized solar cells (DSSC) form an important line of research as renewable energy sources. 1, 2 As being simple, economical and environmentally friendly, the DSSC attracts attention as a good alternative over expensive thin film solar cell technologies. The energy conversion efficiency-price ratio allows it to compete with the other energy generation technologies. The strong demand for a reasonable efficiency drives researchers to improve and find better sensitizers. Bodipy-based dyes are promising in light harvesting with their modifiable structures by adding different functional groups. 3, 4 The stability and efficiency of a cell mostly depend on the characteristics of the sensitizer. Light-harvesting electronic spectra, adsorption, charge injection efficiency and durability of the dye molecule during the cycles are important features for DSSC applications. In addition, their purification and cost should also be taken into consideration. For this reason, instead of metal-driven dye molecules 5, 6, organic sensitizers for DSSC applications have become the key issue of the many researchers.

Boron dipyrrins, which are widely known as Bodipy dyes, provide high incident photon current efficiency (IPCE) for DSSCs. The adjustable structures of Bodipy dyes allow them to absorb all frequencies within the visible range extending to near IR 3, 4, 7–9. The Bodipy molecules 5, 6, organic sensitizers for DSSC applications have become the key issue of the many researchers. Boron dipyrrins, which are widely known as Bodipy dyes, provide high incident photon current efficiency (IPCE) for DSSCs. The adjustable structures of Bodipy dyes allow them to absorb all frequencies within the visible range extending to near IR 3, 4, 7–9. The Bodipy compounds were reported as supporting the directional charge injection efficiency. In this manner we consider two derivatives referred as Bodipy 1 and Bodipy 2 (Fig. 1) which were synthesized by Erten-Ela et al. and Kolemen et al., respectively 3, 4. The parent Bodipy dye condensed through phenyl substituents as donor groups and cyanoacetic acid derived electron-withdrawing anchor groups 3, 4.

We have studied the absorbance of the two Bodipy-derived molecules using time-dependent density functional perturbation theory 10–14 as well as using the hybrid method fractionally incorporating the exact exchange interaction with and without its long-range part 15, 16. Our primary aim is to shed light on how these methods describe optical absorption spectra of such molecular structures with charge transfer (CT) excitations with an emphasis on the charge localization effects due to screening of the Coulomb interaction. In order to make a reasonable comparison with available experimental results, we repeated our calculations including a recent solvation model 17 that also elucidates the effect of chloroform solution in which the dye absorbs light.

II. COMPUTATIONAL DETAILS

We performed first-principles total-energy calculations using ultrasoft pseudopotentials (USPPs) 20 in plane wave based DFT. The exchange-correlation contributions have been treated using Perdew–Burke–Ernzerhof (PBE) 21 gradient corrected functional as implemented in the Quantum Espresso package 22, 24.

After having Kohn-Sham states and energies, optical properties were computed using turboTDDFT code 14, which is one of the modules of the Quantum Espresso code and implements the Liouville-Lanczos approach 25–28 to TDDFT 10, 12. The response of the molecular systems to an external field is measured by dynamic molecular polarizability,

$$\alpha_{ij}(\omega) = \text{Tr}(X_i \rho_j^r(\omega))$$

where $X_i$ is the $i$-th component of the position operator, $\rho_j^r(\omega)$ is the response density matrix of the system polarized along the $j$-th axis, oscillating at the frequency $\omega$. 14 The polarizability can be expressed as an off-diagonal matrix element of the resolvent of the Liouvillian superoperator and can be evaluated using the Lanczos algorithm, by means of the representation of density matrices transferred from time-independent density functional perturbation theory. 14, 25–28 The Liouville-Lanczos method implemented time-dependent density functional perturbation theory (TDDFPT) calculation provides spectroscopic features of molecular systems that is composed of hundreds of atoms. Since this approach does not require the calculation of the individual Liouvillian eigenvalues and allows to reach the full optical
spectrum directly, it needs a computational effort which is not so large than a standard DFT calculation.\[14\]

The next method that we used is the hybrid density functional approach which partially admixes exact Hartree-Fock (HF) and PBE exchange energies. One of the well known flavors is the PBE0 exchange-correlation (XC) functional defined as,

\[
E_{\text{PBE0}}^{\text{XC}} = \frac{1}{4} E_{\text{HF}}^{\text{X}} + \frac{3}{4} E_{\text{PBE}}^{\text{X}} + E_{\text{PBE}}^{\text{C}}.
\]

Another one is based on a screened Coulomb potential for the exchange interaction.\[15–17\] Among all the other Coulomb terms of the Hamiltonian, only the exchange interaction uses a screened Coulomb potential. The exchange component of the XC energy is divided into two parts as long-range (LR) and short-range (SR) while the correlation component is represented by standard PBE \[21\] functional. In this hybrid approximation, which reduces the self-interaction (SI) error of the DFT, the exchange energy is given as,

\[
E_{\text{HSE}}^{\text{X}} = a E_{\text{HF,SR}}^{\text{X}}(\omega) + (1-a) E_{\text{PBE,SR}}^{\text{X}}(\omega) + E_{\text{PBE,LR}}^{\text{X}}(\omega)
\]

where \(a\) is the mixing coefficient that is determined by perturbation theory \[29\] and \(\omega\) is the range separation parameter controlling the extent of the SR interactions.\[15–17\] We performed Heyd-Scuseria-Ernzerhof hybrid functional (HSE06) \[15–17\] calculations with the Vienna Ab-initio Simulation Package (VASP) \[30\]. We used projector augmented waves (PAW) \[31, 32\] datasets and optimized atomic positions by minimizing the forces requiring a precision of 0.01 eV/A. For the computation of the absorption spectra, the transitions from occupied to unoccupied states are considered within the first Brillouin zone. The imaginary part of the dielectric function \(\varepsilon_2(\omega)\) can then be determined by the summation,

\[
\varepsilon_{\alpha\beta}^{(2)}(\omega) = \frac{4\pi^2e^2}{\Omega} \lim_{q\to0} \frac{1}{q^2} \sum_{c,v,k} 2w_k \delta(\epsilon_{c,k} - \epsilon_{v,k} - \omega) \times (\langle u_{c,k+e,q}|u_{c,k}\rangle\langle u_{v,k+e,q}|u_{v,k}\rangle)^*.
\]

In order to study the effect of the solvent environment (chloroform) on the electronic structure of the dye molecules, we performed calculations using the new non-linear polarizable continuum model (PCM) and its linear counterpart, both of which has been implemented in the open-source code JDFTx.\[19, 34\] These PCM approaches enable us to make better comparisons with experiment.

III. RESULTS & DISCUSSION

The placement of substituents that conjugated to the Bodipy core (Fig. 1) is very important for efficient charge injection. The absorption peaks of the compounds can be shifted to the lower energies, the intensity and broadening of those peaks rise depending on the increment of the added arms. We know that the parent Bodipy dye shows weak absorbance at only shorter wavelengths.\[9\] Addition of the styryl arms intensifies and shifts this major peak to the longer wavelengths while producing new weak absorbances at higher energies.\[3, 9\]

In our case there are four absorption peaks of each compound (Fig. 2). The Bodipy1 and Bodipy2 compounds absorb strongly at around 699 nm and 746 nm, respectively, in CHCl\(_3\).\[3, 4\] These lowest lying excitations involve \(S_0 \rightarrow S_1\) transitions which asymmetrically
increase the charge density on the meso-carbon and decrease it in the other parts. Such a directional charge redistribution is hoped to achieve better charge injection. TDDFPT predicts three distinct absorption peaks which are red-shifted similarly for both Bodipy1 and Bodipy2, while the width of their lowest lying excitations are well-described.

The HOMO-LUMO energy level characterization of the compounds had been made by cyclic voltammetry experiments. Standard DFT calculations underestimate the HOMO-LUMO gaps because of the SI error in the Coulomb term (Table I). Interestingly, the prediction of the gap with PBE for Bodipy1 of 0.60 eV is much worse than that of Bodipy2 being 0.90 eV. We also note that the correction to the energy gap by TDDFPT is much better for Bodipy1. Time dependent density functional perturbation approach shifts PBE-predicted absorption peaks toward longer wavelengths in the near IR region (Fig. 2). Although TDDFPT improves over the standard DFT gaps, there still remains a noticeable underestimation due to low-lying excitation energies associated with significant charge transfer (CT) errors. The extent of the error depends on the spatial separation of charge excitation from one carbonyl group to another. Other than the presence of CT states, the determination of optical spectrum of such a large molecular system over a broad frequency range is computationally expensive with linear response TDDFT. This has been made possible by TDDFPT with drastically less computational effort, but the main drawback that still exists is the localization of XC functionals, which yields the underestimation in orbital energy differences.

Because of the necessity of non-local XC functionals to fix this problem, hybrid approaches with semi-local exchange terms have been used before. Although hybrid functionals do not include the excitation process, some CT states, depending on spatial orbital overlaps, can be generated with these functionals. In our case here, for Bodipy1 and Bodipy2 molecules, the occupied and virtual orbitals do not overlap. The CT excitation energies as mean orbital energy differences improve reasonably by using HSE06 hybrid XC functional which incorporates partial exact exchange energy through a screened Coulomb interaction. HSE06 method predicts HOMO-LUMO gaps as 1.58 eV and 1.39 eV for Bodipy1 and Bodipy2, respectively (Table I). These values show good agreement with the experimental counterparts, as also reflected in Fig. 2a and Fig. 2d, from the correspond-
TABLE I: Maximum optical absorption wavelengths, $\lambda_{\text{max}}$ (nm), and HOMO-LUMO energy gaps, $E_{\text{gap}}$ (eV), of compounds Bodipy1 and Bodipy2.

|           | Exp | PBE | TDDFPT | HSE | PBE0 | HSE+PCM$^a$ | PBE0+PCM$^a$ |
|-----------|-----|-----|--------|-----|------|-------------|--------------|
| Bodipy1   |     |     |        |     |      |             |              |
| $E_{\text{gap}}$ | 1.57 | 0.60 | 1.21   | 1.58 | 2.15 | 1.61        | 2.17         |
| $\lambda_{\text{max}}$ | 699$^b$ | 1542 | 867    | 695 | 450  | 684         | 522          |
| Bodipy2   |     |     |        |     |      |             |              |
| $E_{\text{gap}}$ | 1.43 | 0.90 | 0.96   | 1.39 | 1.95 | 1.41        | 1.97         |
| $\lambda_{\text{max}}$ | 746$^b$ | 1040 | 960    | 764 | 568  | 755         | 563          |

$^a$ Nonlinear PCM included for CHCl$_3$
$^b$ Absorption data collected in CHCl$_3$ solution, Ref. [4]

ing optical absorption thresholds involving excitations between the frontier molecular orbitals. For both of the dye molecules, HSE06 calculations also achieve a reasonable estimation the widths of those lowest lying peaks. Moreover, the positions of higher lying absorption peaks are properly described.

The PBE0 hybrid XC functional, on the other hand, significantly overestimates HOMO-LUMO gaps for both Bodipy1 and Bodipy2. Corresponding maximal absorption peak positions are shifted to shorter wavelengths in the visible region. The directional charge redistribution upon a light harvesting excitation on these dye molecules indicates the need for a proper description of the localization effects. In HSE06 functional, the mixing parameter and range of separation can be considered as an effective screening of the Coulomb interaction. In this way, a reasonable description of such localized states can practically be obtained. The main difference of HSE06 from PBE0 is the omission of long range part of nonlocal exact exchange and compensation of it with semilocal PBE exchange. For extended states and materials this may not cause much of a change in the calculated properties. Here, for Bodipy molecules the screened exact exchange kernel acts in favor of the HSE06 approach. PBE0 functional tend to substantially overestimate the gaps for Bodipy dyes due to relatively stronger charge localization as a result of the insufficient screening of the Coulomb interaction. Our PBE0 results are in agreement with previous theoretical studies such that the existence of the long-range HF exchange strongly enlarges the band gaps.

Our calculations revealed that Bodipy derivatives can be used as good sensitizers exhibiting strong absorption characteristics toward the longer wavelengths in the visible and near-IR region. We have performed calculations with TDDFPT as well as HSE06 and PBE0 hybrid functionals to determine electronic and optical properties of candidate dye molecules for DSSC applications. Lowest lying excitations in Bodipy-based sensitizers exhibit directional charge redistribution with no overlap between the occupied and virtual orbitals. When standard XC functionals are used TDDFPT calculations can not generate excitation energies of CT states accurately. PBE0 hybrid functional largely overestimates HOMO-LUMO gaps due to the presence of long-range exact exchange giving rise to strong localization effects. Screened Coulomb HSE06 functional reasonably describes the gaps and photo absorption characteristics indicating the effect of screening in the exchange term. We have shown that solvation models have a nonnegligible contribution in improving the band gaps of Bodipy dyes even in non polar solutions with low dielectric constants. Nonlinear PCM effects on the absorption characteristics of dye sensitizers might become more pronounced for polar electrolytes.

**IV. CONCLUSIONS**

Our calculations revealed that Bodipy derivatives can be used as good sensitizers exhibiting strong absorption characteristics toward the longer wavelengths in the visible and near-IR region. We have performed calculations with TDDFPT as well as HSE06 and PBE0 hybrid functionals to determine electronic and optical properties of candidate dye molecules for DSSC applications. Lowest lying excitations in Bodipy-based sensitizers exhibit directional charge redistribution with no overlap between the occupied and virtual orbitals. When standard XC functionals are used TDDFPT calculations can not generate excitation energies of CT states accurately. PBE0 hybrid functional largely overestimates HOMO-LUMO gaps due to the presence of long-range exact exchange giving rise to strong localization effects. Screened Coulomb HSE06 functional reasonably describes the gaps and photo absorption characteristics indicating the effect of screening in the exchange term. We have shown that solvation models have a nonnegligible contribution in improving the band gaps of Bodipy dyes even in non polar solutions with low dielectric constants. Nonlinear PCM effects on the absorption characteristics of dye sensitizers might become more pronounced for polar electrolytes.

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