

## Coupling between Plasmonic and Molecular Excitations: TDDFT Investigation of an Ag-Nanorod/BODIPY–Dye Interaction

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**ABSTRACT:** A time-dependent density functional theory (TDDFT) computational approach is employed to study the optical coupling between a plasmonic system (a  $Ag_{50}$  nanorod) and a fluorescent dye (BODIPY). It is found that the BODIPY dye can interact with a plasmonic system in a rather different and selective way according to the mutual orientation of the fragments. Indeed, (i) the plasmon excitation turns out to be sensitive to the presence of the BODIPY transition and (ii) this can lead to amplify or suppress the resonance accordingly to the relative orientation of the coupling mechanism, we analyze the shape of the induced density in real space and the Individual Component Map of the Oscillator Strength (ICM-OS) plots and achieve a simple rationalization and insight on



the origin and features of the coupling. The resulting possibility of understanding plasmon/fluorophore interactions by simple qualitative arguments opens the way to a rational design of hybrid (plasmon + dye) systems with the desired optical behavior.

#### 1. INTRODUCTION

Fluorescence of molecular dyes<sup>1</sup> is a phenomenon that has a wide range of applications in several diverse fields, ranging from biology and medicine (sensing, imaging)<sup>2,3</sup> to food <sup>-7</sup> etc. Among analysis,<sup>4</sup> as well as in optoelectronic devices,<sup>5–</sup> the class of fluorescent dyes, 4,4-difluoro-4-bora-3a,4a-diaza-sindacene, commercially known as BODIPY, is one of the most robust and versatile compound, giving rise to a large and extensively employed family of derivative species.<sup>8-10</sup> Of great current interest in this field are the effects arising from the interaction between fluorescent molecules with semiconductor or metal nanoparticles.<sup>11-14</sup> The coupling of extended and sometimes collective resonant excitations in the nanostructures with the localized excited states of the fluorescent molecule can give rise to varied and subtle phenomena, such as energy transfer processes, that can, e.g., enhance or, in general, finely tune (also anisotropically) the absorption cross-section of the system<sup>15-18</sup> or quench the fluorescence signal by surface energy transfer with the metal nanostructure,<sup>19</sup> thus greatly extending the scope of potential applications. Although the basic concepts and theoretical framework of these phenomena have been established,<sup>20-22</sup> the number of possible combinations of different systems and the need to understand the details of the nanostructure/fluorophore interaction to be able to properly control the final response together with new effects arising, e.g., in the strong coupling regime, etc.<sup>23,24</sup> make investigations in this field represent an active topic of current

research.<sup>2</sup> An ideal tool to provide a rigorous ground to such investigations is via predictive simulations,<sup>25,26</sup> whose controlled accuracy can simultaneously cross-validate experimental results in complex systems thus helping their interpretation,<sup>27</sup> as well as suggest configurations and combinations<sup>28</sup> which would otherwise be difficult to single out even from highthroughput techniques,<sup>29</sup> or explore exotic confinement effects on the interaction between electromagnetic cavity fields and quantum emitters.<sup>30</sup> To this purpose, among the possible theoretical approaches time-dependent density functional theory  $(\text{TDDFT})^{31-33}$  currently represents the most convenient and effective compromise between accuracy and computational effort.<sup>34</sup> Although the exact prediction of the excitation spectrum of some fluorescent dyes, including BODIPY, presents accuracy issues at the TDDFT level and alternative post-Hartree-Fock methods have been proposed to overcome these issues,<sup>35</sup> in addition to including possible effects such as solvent,<sup>36</sup> the possibility of treating systems of realistic dimensions<sup>37</sup> that is offered by recent software and

TDDFT algorithmic advances<sup>38–40</sup> makes TDDFT the method of choice for shedding theoretical light on the coupling of plasmonic-nanostructure/fluorophore optical excitations. When the plasmonic system size is larger than the mean free electron path (typically several nanometers) the classical electrodynamics method can be employed to describe the plasmon, although recent analysis has shown that classical methods can be usefully applied even when quantum confinement effects are present.<sup>41</sup>

Here we follow such a line of research and investigate at the TDDFT level a system composed of BODIPY and a model of a plasmonic metal nanorod (Ag<sub>50</sub>). We have selected BODIPY as one of the most common fluorophores, and a silver nanostructure (in particular a Ag<sub>50</sub> nanorod) because silver nanostructures support plasmons already at small cluster size, typically already with few tens of atoms. We investigate different configurations of the two fragments and try to analyze/understand the interaction mechanisms between the plasmon and the dye excitations. We find that the interaction is significant only when the transition dipole of the dye excitation is parallel to the plasmonic one. The interaction can be constructive or destructive; i.e., it can increase or decrease the intensity of the plasmon resonance, and which of these two opposite effects is predominant can be discriminated and predicted by inspecting the induced density plots at the excitation energy, where a parallel or antiparallel interaction among the corresponding dipoles corresponds to an increase or a decrease, respectively, in the absorption intensity.

The article is structured as follows. In section 2 we describe briefly the theoretical methods employed in our calculations. In section 3, the results are presented and discussed, as grouped in three sections: free BODIPY, free plasmonic  $Ag_{50}$ , and the adduct BODIPY- $Ag_{50}$ . Finally, the conclusions are given.

# 2. THEORETICAL METHODS AND COMPUTATIONAL DETAILS

Initial atomistic configurations of the Ag<sub>50</sub> plasmonic cluster were taken from a previous work on Au nanowires,<sup>42</sup> simply by substituting the element Au with Ag in the Au<sub>50</sub> (110) nanowire. For BODIPY we employed the experimental geometry from ref 43. Note that we do not relax geometries because here we want to focus on optical interaction phenomena between plasmonic and finite systems in a "pure" form, separately from geometry effects.

Photoabsorption spectra were evaluated using the Casida formalism<sup>31</sup> as well as the complex polarizability algorithm,<sup>44</sup> both available in the ADF program.<sup>45</sup> In the complex polarizability algorithm, the absorption spectrum is extracted from the imaginary part of the complex dynamical polarizability, solving the TDDFT equations over the space of the density instead of the occupied-virtual pairs of the density matrix. The induced time-dependent density is represented by employing an auxiliary basis set of Slater type orbitals (STO).<sup>44,46</sup> Such a method (referred to as the complex polarizability TDDFT algorithm, or polTDDFT) has proven to be efficient in describing metal particles with many hundreds of atoms.<sup>47</sup>

It is worth noting that in the present work we consider two fragments at different distances, and this may represent a delicate issue in terms of accuracy due to the numerical integration employed in ADF. We carefully checked this point and found that the default integration scheme based on Becke Fuzzy Cells<sup>48</sup> is quite accurate and robust when the distance between the two fragments is varied. On the contrary, we noticed that the Voronoi grid<sup>49</sup> scheme is less robust, and the Voronoi integration technical parameters need a very careful fine-tuning in order to obtain accurate results. We thus employed the default Becke Fuzzy Cells as the numerical integration scheme. The numerical robustness of the simulation is further corroborated by the regular behavior of the transition intensity with distance; see the discussion below.

The BP86 exchange–correlation (xc) functional<sup>50,51</sup> is chosen to solve the KS equations while the Adiabatic Local Density Approximation<sup>52</sup> (ALDA) is used in the TDDFT part for the exchange–correlation kernel. The basis set employed is included in the ADF code and consists of Slater type orbitals (STO) of triple- $\zeta$  polarized (TZP) quality for the H atom and with frozen core (FC) of 1s shell for B, C, N, and F atoms, while for Ag a DZ basis with FC up to the 4p shell has been employed.

Although relativistic effects are rather weak for Ag, we have employed the zero-order regular approximation (ZORA) to include relativistic effects at the scalar level in the calculations.<sup>53</sup>

In terms of analysis tools, we have used two complementary ones.

The individual component map of the oscillator strength (ICM-OS)<sup>54</sup> tool has been employed to analyze and better understand the features of electronic transitions. This tool allows one to decompose a specific absorption peak in terms of electronic transitions labeled by the energy of the occupied (xaxis) and virtual (y-axis) orbitals involved. Briefly, the diagonal line formed by the most intense features in the ICM-OS plots corresponds to the energy of the exciting photon (indicated above each plot), which results from the energy difference between virtual and occupied molecular orbitals. Therefore, spots on the diagonal correspond to single-particle excitations, whereas the presence of off-diagonal features indicates a collective behavior typical of plasmons. These collective plasmonic features are characterized by occupied and virtual orbitals with smaller energy differences than the analyzed excitation energy, indicating that the excitation involves more than one single-particle excitation. Importantly, in addition to the weight of each pair of orbitals in the oscillator strength, ICM-OS also accounts for the signs of the associated dipole contributions, which may result in constructive or destructive interferences among excited configurations.

In this work we have also analyzed the induced density associated of selected excitations, which has proven to be very informative in order to discriminate between constructive and destructive interactions of the two interacting systems with a concomitant increase or decrease of the intensity, respectively. The induced density consists in the time-dependent first-order perturbation of the electron density as an effect of the external time-dependent electromagnetic field. This quantity is a fundamental ingredient of the complex polarizability algorithm and can be conveniently plotted for analysis as a 3D isosurface with a phase (positive and negative induced density means electron density accumulation or depletion respectively).

#### 3. RESULTS AND DISCUSSION

Our goal in the present study is assessing the mechanisms of interaction between a plasmon resonance and the molecular transitions of a fluorescent dye. For the dye, we have chosen BODIPY due to its major role in many photochemical processes.<sup>8,9</sup> As a model plasmonic system, we have chosen a silver nanorod (Ag<sub>50</sub>) because, as recalled in the Introduction, silver supports plasmonic excitations already in structures of small size, typically a few tens of atoms, at variance with gold which needs larger sizes.<sup>55</sup> As is well-known, this is due to the presence in gold of the quenching effect of the 5d band,<sup>56</sup> whereas in silver the 4d band is deeper and does not suppress the plasmon. The size and shape of Ag<sub>50</sub> has been chosen because for this nanocluster the plasmon resonance falls at the same energy as that of the lowest transition of the BODIPY, and this is expected to maximize their mutual interaction: we note, however, that, in general, it is easy to tune Ag nanorods to give the desired plasmon frequency to maximally interact with other transitions.<sup>57-59</sup> We start by briefly describing the excitation spectra of the isolated systems, then we couple them in a system which we shall designate as the adduct, and analyze and try to rationalize the changes occurred upon interaction. In the interaction system, the two fragments have been positioned in different mutual orientations, in order to have the dipole transition density of the BODIPY pointing toward or away from the nanorod, and at different distances.

**3.1. BODIPY Excitation Spectrum.** The three lowest TDDFT excitations of the BODIPY molecule calculated using the Casida approach<sup>31</sup> are reported in Table 1, while in Figure

Table 1. Three Lowest BODIPY Electronic Excitations Calculated at the TDDFT level with the BP86 XC Functional and TZP Basis Set

1B 2.00 0.121 55% $2_2 \rightarrow 7b \cdot 44\% 4_2$	
$1D_2$ $3.00$ $0.131$ $33\%$ $3a_2 \rightarrow 7D_1$ ; $44\%$ $4a_2 =$	→ 7b <sub>1</sub>
$1A_1$ 3.33 0.0182 97% $6b_1 \rightarrow 7b_1$	
$2B_2 \qquad \qquad 3.89 \qquad \qquad 0.404 \qquad 54\% \ 4a_2 \rightarrow 7b_1; \ 43\% \ 3a_2 -$	→ 7b <sub>1</sub>

1 we report the optical absorption spectrum calculated using two different methods: the Casida approach<sup>31</sup> and the polTDDFT method,<sup>44</sup> where the latter is an approximation of TDDFT that enables us to perform calculations on large systems such as those involving a nanorod. In Figure 1 we use the label of the  $C_{2\nu}$  point group symmetry to classify excitations and molecular orbitals, while the BODIPY structure is reported at the top of Figure 2, together with the main orbitals (the occupied  $3a_2$ ,  $4a_2$ , and  $6b_1$ , and the virtual  $7b_1$ ) involved in the low-energy excited states. Note that the  $C_2$  axis corresponds to the z direction, while the molecular plane lies in the yz plane (actually only the two F atoms do not belong to this plane). The lowest-energy  $1B_2$  transition corresponds to the y component of the electric dipole, and its assignment shows that it can be ascribed as a linear combination of two oneelectron excited configurations: 55%  $3a_2(HOMO-1) \rightarrow$  $7b_1(LUMO)$  and  $44\% 4a_2(HOMO) \rightarrow 7b_1(LUMO)$ . As apparent from Figure 2 where schematic depictions of these molecular orbitals are reported, they are all  $\pi$  orbitals, the molecular plane being nodal. The lowest-energy 1B<sub>2</sub> transition finds its counterpart in the third 2B<sub>2</sub> transition, that not only has the same symmetry but also has a similar percent composition in terms of the same two excited configurations. We can obtain a qualitative but very useful understanding of such configuration mixing by looking at the induced density plots reported at the bottom of Figure 1: while for the 2B<sub>2</sub> excitation a typical dipolar shape along the y direction is apparent, for the 1B1 it seems that two dipoles with opposite direction are interpenetrating each other. This finding has a



**Figure 1.** Discrete and smoothed (by Lorentzian function) Casida (black line) and polTDDFT (blue line) excitation spectrum of BODIPY up to 5 eV (upper panel). HWHM for Lorentzian broadening and imaginary photon energy both equal to 0.075 eV. Lower panel: induced density of the two most intense transitions (isolines  $0.03 \text{ e}^-/\text{bohr}^3$ ).

simple interpretation: when the dipoles have opposite direction, their energy is lower due to the stabilizing effect between charges of opposite sign, but concomitantly the oscillator strength is lower due to the destructive interference between the dipoles. This clearly rationalizes why the interpenetrating induced density corresponds to a lower excitation energy and a lower intensity in Figure 1. The second  $1A_1$  transition (see Table 1) corresponds to the z component of the electric dipole transition moment, it has an almost pure (97%)  $6b_1(HOMO-2) \rightarrow 7b_1(LUMO)$  nature but has a negligible intensity due to the reduced extension of the molecule along the z direction. We also note that the energy of the TDDFT-calculated lowest vertical excitation energy (3.00 eV) is overestimated with respect to the experimental value (2.46 eV).43 As recalled in the Introduction, such a discrepancy is well-known: previous ab initio studies on BODIPY and its derivatives<sup>60,61</sup> have shown that this shortcoming is not related to the choice of the exchangecorrelation functional within TDDFT, but rather is intrinsic to the TDDFT single-particle excitation formalism (only oneelectron excited configurations are used in the description of the excited state) and that two-electron excited configurations must be included in the calculation in order to obtain accurate excitation energies. We underline, however, that the goal of the present work is not an accurate description of an experiment, but rather a fundamental investigation of the nature of interaction between plasmonic and molecular excitations. To this end we must employ the same approach to describe the excited states of both the plasmonic system and the dye, and at the moment it is not computationally feasible to employ highly correlated post-Hartree-Fock ab initio methods to treat plasmonic systems, which typically consist of a metal



Figure 2. Molecular orbitals of BODIPY involved in the three lowest excitations. Isolines 0.03  $(e^{-})^{1/2}$  (bohr)<sup>-3/2</sup>.

nanostructure containing several tens of metal atoms. We expect that the neglect of two-electron excitations will deteriorate only the energy position of the transitions, but will not change the global description of the coupling mechanism between the plasmon and the dye.

3.2. Ag<sub>50</sub> Excitation Spectrum. In Figure 3 we report the excitation spectrum of  $Ag_{50}$  calculated using the polTDDFT method, together with induced density plots of the two major excitations reported at the bottom of Figure 3. The shape and the structure of Ag<sub>50</sub> were constructed by following a suggestion taken from a previous work on gold nanowires:44 with respect to these previously derived nanorod atomistic arrangements, we simply tuned the length of the present Ag nanorod so that its plasmon falls at the same energy as the lowest-energy BODIPY absorption transition (differences in the excitation spectrum between the present results and those reported in refs 41 and 57 are due to differences in the geometry and in the exchange-correlation functionals employed in the DFT and TDDFT calculations). Indeed, as apparent from Figure 3, the first intense absorption peak of Ag<sub>50</sub> falls nearly at exactly at 3.00 eV. The plasmonic nature of this absorption peak is confirmed by the ICM-OS analysis, which is reported in Figure 4 for the z Cartesian component as 2D plot (upper panel) and 3D plot (lower panel). In fact, in the 2D plot we find two spots that are considerably far from the straight line connecting orbital energy differences equal to excitation energies, thus indicating strong coupling among different single-particle excitations, while the 3D plot shows in a clearer way the absolute scale of the ICM-OS components. Moreover, it can be observed that the shape of the induced density of the peak at 3 eV, reported in the bottom of Figure 3, displays a characteristic dipolar shape, typical of plasmons. The higher-energy peak at 3.76 eV exhibits about half the intensity of the main peak, and quite interestingly its induced density



Figure 3. PolTDDFT excitation spectrum of  $Ag_{50}$  up to 5 eV (upper panel). Lower panel: induced density of the two most intense transitions (isolines 0.10 and 0.03 e<sup>-</sup>/bohr<sup>3</sup> for the first and second peaks, respectively).



**Figure 4.** ICM-OS analysis of the first peak of  $Ag_{50}$  at 3.00 eV. Upper and lower panels report the 2D and 3D representations, respectively.

plot shows the interpenetration and thus the coupling of two parallel dipoles, located at different locations along the longitudinal cluster direction. We may describe this situation as a pair of plasmons, each one belonging to one-half of the cluster, coupled to give constructive interference (sum) of their dipoles. The shape of the induced density of the peak at 3.76 eV indicates that it corresponds to a longitudinal mode. We note in passing that we do not observe a transverse plasmon, since the present nanorod is too thin to support transverse plasmon.<sup>42,62</sup>

**3.3. BODIPY-Ag**<sub>50</sub> **Longitudinal and Lateral Adducts: Excitation Spectrum.** The interaction between the nanorod and the BODIPY will depend on their distance and the mutual orientation. To have a systematic picture, we have explored all the possible relative configurations, but here we will report

explicitly only those giving the most noticeable effects. In general, we noticed that the interaction effects are much larger when the BODIPY dipole component y of the most intense transitions (both with B<sub>2</sub> symmetry, see Figure 1) is parallel to the Ag<sub>50</sub> *longitudinal* direction, which is also the dipole orientation of the plasmon. This can be achieved in two different configurations: the longitudinal one (shown in the inset of Figure 5) and the lateral one (shown in the inset of Figure 7).

Starting with the longitudinal geometrical configuration, first, in Figure 5 we report two calculated absorption profiles: the absorption profile of the adduct system at a distance in which BODIPY is "touching" the cluster, with a Ag-H distance of 1.507 Å, and the absorption profile obtained by summing the spectra of the isolated Ag<sub>50</sub> + BODIPY fragments. This direct comparison allows us to appreciate even tiny effects on the optical features of the plasmon excitation following interaction with the BODIPY. From Figure 5 it is well apparent that both peaks at 3.00 and 3.75 eV gain intensity with respect to the sum of the isolated systems. Since the changes are of the order of 10-30% of the peak themselves, it is necessary to check that they are not due to numerical artifacts. Thus, in order to check the numerical stability of our approach, we have calculated the spectra at various BODIPY/nanorod distances, and we have integrated the oscillator strength as a function of this distance. The results of this exercise are reported in Figure S1 of the Supporting Information. As apparent from Figure S1, we obtain a smooth evolution of the spectrum, thus validating the numerical stability of our approach. Note in passing that in practice it is enough to increase the distance between the two fragments by 10 Å to recover a spectrum that is practically identical to that of the sum of the isolated species, pointing to a fast decrease of the coupling with interseparation distance.

To better analyze these findings, we have plotted the induced densities corresponding to the two main absorption peaks, also reported at the bottom of Figure 5. It is apparent from these plots that the dipolar-like main excitations of the silver cluster sum up constructively with the dipolar-like excitation of the BODIPY (note the opposite colors at the touching sides): this explains why we observe a gain in the absorption intensity for both bands. A similar conclusion can be drawn by inspecting the ICM-OS plot, reported in Figure 6 for the main, lowest-energy peak along the z Cartesian coordinate. From the 2D plot (upper panel in Figure 6), we find that the plasmonic peaks in the ICM-OS appear in the same region of the peaks observed in the previous Figure 4, but with a different intensity: in particular, the peaks associated with the virtual orbitals at higher energies acquire intensity with respect to the separated-fragment case, which is the main reason for the increase in total absorption strength. Additionally, the contribution of the interaction of the nanorod with BODIPY is also apparent in a small spot in the region of the BODIPY excitations, that we have highlighted with a white circle in Figure 6 (upper panel) to help the reader identify its position. The BODIPY contribution can be identified even more clearly in the ICM-OS 3D plot (lower panel of Figure 6); this time it is included in a yellow circle. It is noteworthy and quite interesting that the BODIPY spot is weak in terms of the ICM-OS contribution, so it cannot be considered as directly responsible for the increase in the intensity of the 3 eV band, but that the nanorod plasmonic spots are nevertheless amplified by the presence of the dye. We are led to conclude



**Figure 5.** PolTDDFT excitation spectrum of the longitudinal  $Ag_{50}$ -BODIPY adduct up to 5 eV (upper panel). Lower panel: induced density of the two most intense transitions (isolines 0.03 e<sup>-</sup>/bohr<sup>3</sup>).

that the intensity gain of the plasmonic peak is not due to the fact that the BODIPY absorption is summed with that of the silver cluster but rather that the presence of the fluorophore makes the silver plasmon more intense due to coupling matrix elements which increase the electric dipole transition moment. Finally, we checked if some charge transfer is present in the absorption spectrum for this systems. We have considered in Figure S2 of the Supporting Information an analysis of the oscillator strength projected onto fragment contributions, accordingly to the analysis method proposed in ref 63 for the absorption of the longitudinal Ag<sub>50</sub>-BODIPY adduct. We consider two cases: BODIPY at the distance of closest approach, corresponding to Figures 5 and 6 (upper panel of Figure S2) and BODIPY at a distance increased by 2 Å (lower panel of Figure S2). It is apparent from the fragment projection at the closest distance that some ligand to metal

(L-M) and metal to ligand (M-L) contributions do exist in the fragment analysis, proving that some charge transfer is present in this system. As a control system, it is reassuring to note that the mixed contributions (CT) to the plasmonic peak disappear when the Ag50–BODIPY is increased by 2 Å.

Second, we consider the lateral configuration and report the spectra of the adduct system in Figure 7: one at a distance in which BODIPY is almost "touching" the cluster before the formation of a chemical bond and one obtained by summing the spectra of the isolated  $Ag_{50}$  + BODIPY fragments. Interestingly, for this interaction configuration we find a behavior opposite to that observed for the longitudinal one: the first plasmonic peak is now strongly quenched, while the second peak is still slightly amplified by the fluorophore/ nanorod mutual interaction. Also in this case the induced densities reported at the bottom of Figure 7 help to explain





and fully rationalize the observed behavior. In the lowestenergy peak the excitation dipole of the BODIPY is antiparallel with respect to the plasmonic one, so that the intensity is finally reduced by about 35%. At variance, in the induced density plot corresponding to the second peak the excitation dipoles of the two fragments are parallel, so that the final intensity is slightly larger than that for the isolated systems. To further analyze and understand, the ICM-OS plot for the first peak of the lateral geometry is reported in Figure 8: the corresponding 2D plot in the upper panel shows that the BODIPY contribution is so weak that it cannot be identified. The 3D plot in the lower panel of Figure 8 allows us to identify a very weak negative BODIPY contribution, which has been included in a yellow circle for the sake of clarity, suggesting a suppressing effect (destructive interference). Also in this case



Figure 7. PolTDDFT excitation spectrum of the lateral  $Ag_{50}$ -BODIPY adduct up to 5 eV (upper panel). Lower panel: induced density of the two most intense transitions (isolines 0.03 e<sup>-</sup>/bohr<sup>3</sup>).

this tiny destructive effect cannot explain the significant amount of plasmon quenching: rather, this can be ascribed to the fact, apparent in Figures 6 and 8, that the plasmonic spots are less intense than in the longitudinal geometry.

Finally, one can note that the main plasmonic peak of  $Ag_{50}$  actually exhibits an internal structure and is split into two subpeaks at 2.98 and  $\approx$ 3.2 eV. This is not a numerical artifact of our simulations. In fact, despite the fact that  $Ag_{50}$  is a plasmonic system, it still keeps molecular features due to its limited size, and the splitting in the adduct spectrum at  $\sim$ 3 eV is a consequence of these features. To demonstrate this interesting point, in Figure S3 of the Supporting Information we show that the ICM-OS and the induced density corresponding to the second subpeak of the main plasmonic peak of  $Ag_{50}$  differ from the analogous quantities of the first subpeak reported in Figures 7 and 8, indicating that the two subpeaks correspond to physically slightly different excitations.

#### 4. CONCLUSIONS

The goal of the present work is to investigate via TDDFT simulations the optical coupling between a plasmonic system (a  $Ag_{50}$  nanorod) and a fluorescent dye (BODIPY), a topic with several perspective applications<sup>2–7</sup> and on which rigorous information is strongly needed. As a major outcome of this study, we have found that the BODIPY dye can interact with plasmonic systems in a very different and selective way according to the mutual orientation of the fragments.



**Figure 8.** ICM-OS analysis of the first peak of the lateral  $Ag_{50}$ -BODIPY adduct at 2.98 eV. Upper and lower panels report the 2D and 3D representations, respectively.

The plasmon excitations of  $Ag_{50}$  (two major plasmonic peaks are found in the optical spectra of this nanorod) turned out to be sensitive to the presence of the BODIPY transition and can be amplified or suppressed accordingly to the relative orientation of the corresponding transition dipoles. We found that the alignment of the transition dipoles in the longitudinal configuration gives rise to a constructive interference and therefore to an enhancement of absorption intensity for both major plasmonic peaks of the nanorod, whereas in the case of the lateral arrangement the lowest-energy peak is quenched by an unfavorable interaction with the BODIPY excitations (destructive interference).

We have then shown that the coupling mechanism responsible for these effects can be clearly and easily singled out and understood via two analysis tools: (i) by inspecting the shape of the induced density in real space and (ii) by analyzing the ICM-OS plots in the space of one-electron excited configurations. The possibility of understanding plasmon/ fluorophore interactions by simple arguments and physical observables which can be easily represented in real space, such as the induced density plots, or in momentum space, such as the ICM-OS plots, opens the way to a rational design of hybrid (plasmon + dye) systems with a desired optical behavior. Moreover, the fact that it is possible to rationalize qualitatively the changes in absorption intensity in terms of simple interactions between dipoles, suggests that simplified models, for example based on exciton models, can be effective and efficient for predicting and for such a rational design activity, a fact that is especially convenient for studying large and complex systems. In perspective, the present simulations provide thus the basis for a multiscale modeling of complex materials composed of several plasmonic and BODIPY units simultaneously interacting, i.e., of a TDDFT-informed excitonic models describing the response of these systems.<sup>27,64,65</sup>

Finally, a further promising perspective of the present line of research is to combine BODIPY compounds<sup>66</sup> (possibly functionalized so as to be chiral) with chiral nanowires,<sup>67–69</sup> thus achieving circularly polarized luminescence.<sup>70–72</sup>

#### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpca.2c04168.

Integral of oscillator strength as a function of fragments distance, analysis of the oscillator strength, ICM-OS analysis, and Cartesian coordinates of the longitudinal and lateral adducts at minimum distance (PDF)

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#### Notes

The authors declare no competing financial interest.

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