Photo-excitation of a light-harvesting supra-molecular triad: a Time-Dependent DFT study

N. Spallanzani,1,2 C. A. Rozzi,2 D. Varsano,2,3 T. Baruah,4 M. R. Pederson,5 F. Manghi,1,2 and A. Rubio6,3

1Department of Physics, University of Modena e Reggio Emilia, via Campi 213a, 41100 Modena, Italy
2INFN-CNR National Research Center "SS", Modena, Italy
3European Theoretical Spectroscopy Facility (ETSF)
4Department of Physics, University of Texas at El Paso, El Paso, Texas 79968
5Center for Computational Materials Science, Code 6390, Naval Research Laboratory, Washington, DC 20375-5345
6Nano Bio Spectroscopy group, Dpto. de Física de Materiales, Universidad del País Vasco and Centro Mixto CSIC-UPV/EHU and DIPC, Av. Tolosa 72, E-20018 San Sebastián, Spain

We present the first time-dependent density-functional theory (TDDFT) calculation on a light harvesting triad carotenoid-diaryl-porphyrin-C60. Besides the numerical challenge that the ab initio study of the electronic structure of such a large system presents, we show that TDDFT is able to provide an accurate description of the excited state properties of the system. In particular we calculate the photo-absorption spectrum of the supra-molecular assembly, and we provide an interpretation of the photo-excitation mechanism in terms of the properties of the component moieties. The spectrum is in good agreement with experimental data, and provides useful insight on the photo-induced charge transfer mechanism which characterizes the system.

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I. INTRODUCTION

The quest for efficient ways to exploit renewable energy sources has become one of the key problems of our times. The idea of a solid-state device capable of transforming solar light energy into electric potential energy is quite old, and enormous progress has been made in optimizing traditional junction-based devices with respect to their thermodynamical efficiency and production cost. Recently entirely new classes of materials have been proposed as building blocks for next-generation solar cells. Among these nanostructured semiconductors, organic-inorganic hybrid and supra-molecular assemblies appear to be the most promising.

In the class of supra-molecular assemblies the donor-acceptor dyads and triads are objects of careful experimental study. They are in fact considered an ideal mimic for the primary photo-synthetic process, which basically consists of a photo-excitation followed by a charge-transfer between the component units. The same process on the other hand can be exploited in photo-conversion units like dye-sensitized (or Grätzel) solar cells. The research for ideal components of light-harvesting dyads has led to porphyrin-C60 assemblies.

Porphyrin molecules show extensive absorption of visible light, and an optical gap of approximately 2 eV and are therefore ideal photo-reaction centers and electron donors. C60, on its side, is the ideal electron acceptor. It has a particularly deep triply degenerate LUMO at approximately -4.3 eV vs vacuum, capable of accommodating six electrons from neighboring molecules. Moreover the highly conjugated nature of its bonds, together with a cage radius of 3.45 Å, stabilizes the extra charges in a very efficient way, so that little repulsive forces are felt by the excess electrons. A further step toward solar cells based on these components consisted in transforming the donor-acceptor unit into a donor-bridge-acceptor unit. This change has the main purpose of obtaining a better charge separation and a longer life time of the final (excited) state.

While many experimental properties of porphyrin-C60 based dyads and triads are known, less is known from an ab-initio theoretical point of view. The main reason is that the large size of the systems yields traditional accurate quantum-chemistry methods such CI impractical or infeasible. Less accurate but computationally efficient methods such as DFT have successfully been employed to describe the ground state of such compounds, but unfortunately, the prediction of excited state properties, like the optical absorption spectrum, from the ground state Kohn-Sham orbitals and eigenvalues usually leads to results that are in discord with the observed spectra. In particular the role of the interfaces between different parts of the triad and between the molecule and the solvent are not understood in spite of the fact that they are of paramount relevance to the problem of improving the energy conversion efficiency of next generation solar cells.

TDDFT is a rigorous and in principle exact method that allows for the calculation of excited-states through an extension of DFT to the domain of time-dependent external potentials. In this letter we report the first TDDFT calculation of the electronic structure and absorption spectrum of Carotenoid-diaryl-Porphyrin-C60 triad (abbreviated hereafter as triad or C-P-C60).

II. RESULTS AND DISCUSSION

The C-P-C60 system is composed by 207 atoms with 632 valence electrons. Its structure corresponds to the
formula C_{132}H_{46}N_{6}O. For all our calculations we used an optimized geometry obtained by Baruah et al. using the LBFGS scheme. The earlier calculation by Baruah and Pederson was carried out at the all-electron generalized gradient level using the NRLMOL code. This code uses a large gaussian basis set within the LCAO formulation. In this structure the molecule can be entirely embedded in a box approximately 55 × 16 × 20 Å wide, the longest side being along the x axis. As it is also clear following a steric argument, the porphyrin ring is perpendicular to the aryl rings, which, in turn, are coplanar with the carotenoid. The optimized geometry shows a slight bend in the carotenoid chain (see 1).

Our first goal was to study the ground state properties of the molecule within the same methodology that we use for the time-dependent calculation of the excited states, and compare the electronic structure of the triad to the electronic structures of the separated components. For the calculations of the separated moieties the same geometries used in the triad have been utilized.

We have first performed a standard DFT calculation at the LDA level, using the Perdew-Zunger correlation functional11. The core electrons were represented via Troullier-Martins pseudo-potentials26, and the Interpolating Scaling Functions method27 was used to efficiently solve the Poisson’s equation in the calculation of the Hartree potential. All the simulations in the present work, apart from the geometry optimization, were performed discretizing all the quantities in real space over a uniform mesh made of overlapping spheres with a radius of 4.0 Å centered around each nucleus. The adopted grid spacing of 0.2 Å guarantees the convergence of the total energy of the system12.

In 7 we report the Kohn-Sham energies of HOMO and LUMO for the isolated moieties and for the full triad. The detailed energy levels for other orbitals are depicted in 2.

Comparing the values of the HOMO and LUMO energies of the triad with those of the isolated moieties we notice that the energy of the HOMO in the triad and in the isolated β-carotenoid differ by only 40 meV, as well as the energy of the LUMO in the triad and in the isolated pyrrole-C_{60}. It is also possible to find a close correspondence between many of the orbitals localized on each molecule, and orbitals of the full triad. In particular the HOMO wave-function of the triad is localized on the carotenoid, and it corresponds to the HOMO of the isolated β-carotenoid, while the LUMO of the triad is fully localized on the C_{60} and it corresponds to the LUMO of the C_{60} alone (see 2). These features are in agreement with the earlier results obtained in Ref2 using an all-electron GGA approach.

In some other cases the correspondence between the localization of orbitals remains, but some degeneracies are lifted, for example the triply degenerate C_{60} LUMO is split into three separate levels in the triad. Finally some orbitals present a mixed character, such as the LUMO+5, LUMO+6, LUMO+7 with mixed P-C_{60} character, or HOMO-6, with mixed C-P character. These orbitals however do not appear to have a major role in the photo-excitation process (see below).

From the above results we conclude that the electronic structure of the ground state of the triad is well approximated by the sum of the electronic structures of the isolated molecules. This conclusion implies that it is possible to design triad-based photoconversion devices adopting a divide et impera strategy, by covalently joining pre-optimized molecular components.

We have calculated the optical absorption spectra of the triad and its separated components using the time-dependent DFT as described in Ref28. Starting from the ground state Kohn-Sham orbitals φ_{j}, the system is instantaneously perturbed with a weak external electric potential of magnitude k_{0} along the principal cartesian direction (i.e. by applying the external potential δu_{ext}(r, t) = −k_{0} · r δ(t)). The magnitude of the perturbation is kept small in order to keep the dipolar response linear12. In this way all the frequencies of the system are excited with the same weight. The perturbed Kohn-Sham orbitals, φ_{j}(r, t = 0^{+}) = exp(δk_{0} · r)φ_{j}(r), are then propagated on a real-time grid using the enforced time-reversal symmetry method29.

From the Fourier transform of the real-time response to this perturbation the dynamical polarizability is obtained in the frequency range of interest, and finally the dipole strength function, which is proportional to the photo-absorption cross section, is obtained by averaging the polarizability over the three cartesian directions. More detail on this procedure can be found in Ref12. The time evolution of the Kohn Sham orbitals was calculated with a time step of 1.7 attoseconds (as) for the triad, where a fourth order Taylor expansion approximates the propagator. A time step of 7.9 as (resulting in a spectral range window for the dynamical polarizability of at least 8 eV) could be used on the isolated parts, where the propagator was approximated with the Lanczos method30. The orbitals were evolved respectively for a total of 15 fs, that corresponds to a spectral resolution of about 0.15 eV.

The TDDFT photo-absorption cross-section of the triad and of the separated molecules is shown in 8. We can easily distinguish one dominant peak at 1.7 eV, several small features between 2.0 and 3.0 eV, another peak at 3.3 with a shoulder at 3.6 eV, and a group of peaks between 4.0 and 8.0 eV.

The decomposition of the spectrum into optical densities of the isolated moieties clearly shows again that the total spectrum is very well approximated by the sum of the spectra of the parts. In particular the main feature at 1.7 eV appears to be entirely originated by the β-carotenoid, which has a weak contribution on the rest of the spectral range, apart from a small feature at 2.3 eV that partially obscures the weak Soret Q-band of the diaryl-porphyrin. The B-band of the diaryl-porphyrin is the main contribution at 3.2 eV, and the diaryl-porphyrin has another prominent peak in the ultraviolet region at 6.6 eV. The contribution of pyrrole-C_{60} counts many...
peaks, notably two isolated at 5.3 and 5.9 eV, and several more from 4.0 to 5.0 eV.

The comparison of our calculations with the experimentally observed absorption in similar triads clearly shows that TDDFT improves on DFT in describing the main features of the spectra. In Refs. 16,17, that refers to a triad in 2-methyltetrahydrofuran solution. We observe a good one-to-one correspondence between the calculated and the observed peaks, whose positions appear overestimated in the calculation by an overall rigid shift of about 0.3 eV. We do not investigate here the possible role of the environment, that might well be responsible of the rigid shift, but is unlikely to qualitatively change the shape of the spectrum. In fact triads made of slightly different components, or immersed in different solvents, often have very similar spectra (see Ref.18). In particular the prominent porphyrin peak around 3 eV and the wide band between 2.0 and 3.0 eV seem to be common features in all the experimental data. Also notice that, despite the apparent superposition of the main experimental peak to a peak in the DFT calculation, the nature of the latter is predicted to be of C_{60} character, while the corresponding TDDFT feature at 3.5 correctly is attributed to the porphyrin. (see decomposition in [4]. The experimental data range in Refs.16,17 are limited above approximately 2.0 eV, but the β-carotenoid absorption does not appear to be relevant for the photo-conversion in the triad. On the other hand, Ref.18 report a peak for the isolated β-carotene at approximately 1.24 eV. A TDDFT calculation on the same system results again in a blue shift of about 0.4 eV. For an in depth discussion about the effect of exciton confinement in molecular chains see also Refs.19,20.

We have thus obtained the first ab initio optical absorption of the triad in agreement with the observed one. The comparison with a DFT spectrum, obtained by applying the Fermi golden rule to the Kohn-Sham levels confirms (see [4]) that TDDFT achieves a major improvement over DFT.

The analysis of the absorption of the diaryl-porphyrin alone allows us to clarify that, even if an intense peak appears in the UV region around 3.2 eV (see [5]), the actual very weak onset of absorption is in the orange-yellow visible region at approximately 2.0 eV. This transition corresponds to the calculated HOMO-LUMO in the diarylporphyrin alone, and it is also responsible for the optical excitation of the triad as a whole. This excitation was in fact obtained in laboratory condition with a laser at 590 nm.16.

In Refs.19,20 we have emphasized, among others, the two orbitals, localized on the porphyrin moiety, that are responsible for the optical excitation.

On the basis of structure, level, and orbital localization we are now able to achieve a theoretically motivated view of the photo-excitation process, and of the subsequent charge-transfer that can be summarized in the following chain of steps:

\[ \text{C-P-C}_{60} + h\nu \rightarrow \text{C-P}^+\cdot\text{C}_{60}^- \]
\[ \text{C-P}^+\cdot\text{C}_{60}^- \rightarrow \text{C-P}^+\cdot\text{C}_{60}^- \rightarrow \text{C}^+\cdot\text{P-C}_{60}^- \]

The first step corresponds to the optical transition from HOMO-2 to LUMO+4. A Casida analysis21 of this transition reveals that it is a pure transition, and the inspection of the involved orbitals clarifies that HOMO-2 are both mostly localized on the porphyrin. Let us call this excited state C-P^+\cdot C_{60}^-\text{C}. The electron in a previously unoccupied orbital on the porphyrin is now under the influence of the high affinity of the C_{60}, and it is easily accommodated on the almost-degenerate orbitals LUMO+1, LUMO+2 at 0.14 eV above LUMO localized on the C_{60}. In the assembled triad the three-fold degeneracy of the C_{60} T_{1u} LUMO is broken due to the presence of the Pyrrole and the LUMO of the triad is a singlet state. We have then reached a configuration C-P^+\cdot C_{60}^-\text{C}^\text{60}. The last step consists in a hole delocalization from the Porphyrin HOMO to the Carotenoid HOMO to give the final state C^+\cdot P-C_{60}^-\text{C}^\text{60}. Obviously only the study of the full dynamics of the whole process can support the latter two steps interpretation, which is inferred here on the basis of the analysis of the energy levels in [2] and on the electrochemical properties of the moieties. The analysis of the full dynamics is quite demanding, since the processes are estimated to occur on a time scale of tens of ns, and it is beyond the scope of the present work.

As we have already stressed, it is the almost non-interacting character of the moieties, demonstrated by the shape of the absorption spectrum, and the nature of the molecular orbitals, that makes it possible to describe this process in terms of orbitals localized on each component. In fact the charge-transfer states associated with this molecule are not dipole allowed transitions due to the fact that the hole on the (donor) carotene and the particle-state on the C_{60} (acceptor) molecule are essentially non overlapping. Additional work is required to fully understand the dynamics of the light-induced charge transfer process. As concluding remarks we must recall that the 15 fs time span of our simulation is unlikely to account for the complete charge transfer process, that occurs on a different time scale, but it is able to accurately describe the photo-excitation of the molecule. Nevertheless we have been able to get a valuable insight about the charge transfer from the careful examination of the energy levels and of the calculated absorption spectrum of the system. Finally many issues may be relevant for a full understanding of the mechanism we have devised in the steps indicated above, and many of them still are under investigation. Among them we stress the need of a full dynamical simulation of the molecule in an intense laser field, the study of the relaxation in the excited state, and the careful study of the predictive power of the different functionals in the correct description of the charge transfer. For more information about the latter point, and the
III. CONCLUSIONS

In summary, we have addressed the fundamental problem of describing the creation of electron-hole pairs and the efficient charge separation in a supramolecular assembly of interest for third generation solar devices. Since not all the effects leading to the final-state charge separation are fully known the accurate description of the excited states of such an object is a crucial step in order to understand the details of the photo-absorption and charge-transfer processes occurring in the system.

We have calculated for the first time the optical absorption cross section of such a large system using TDDFT as a rigorous ground for the excited states dynamics. In addition to the computational challenge, our calculations demonstrate that the simple ground-state DFT description of the system is not able to capture the correct shape of the photo-absorption spectrum. In contrast we have shown that the main features of the TDDFT spectrum are in good agreement with the experimental data, and the analysis of the total absorption in terms of the absorption of the isolated moieties indicates that even at the TDDFT level (at least in the weak field limit) the component molecules in the triad do not appear to strongly interact.

The system as a whole acts as the sum of its parts, each of which has a specific role in the photo-induced charge separation mechanism that makes this molecule a good candidate for third generation solar energy conversion devices. This fact has allowed us to sketch a diagram of all the states involved in the photo-absorption and charge transfer processes, and indicates that the design of solar devices based on similar assemblies can be performed by individually addressing the active components, and then chemically joining them into a unit capable of transforming the energy of an incoming photon into electric potential energy stored into a 50 A long dipole.

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* Electronic address: nicola.spallanzani@unimore.it

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26 For all the components the pseudo-potentials cutoff radii are 1.25 a.u. for hydrogen atoms, 1.47 a.u. for carbon atoms, and 1.39 a.u. for nitrogen and oxygen atoms.
Comparing HOMO and LUMO energies

\[
\begin{array}{lcc}
\text{molecules} & \epsilon_{HOMO} \text{ (eV)} & \epsilon_{LUMO} \text{ (eV)} \\
\hline
\beta\text{-carotenoid} & -4.47 & -3.49 \\
Diaryl-porphyrin & -5.15 & -3.31 \\
pyrrole-C_{60} & -5.89 & -4.42 \\
Triad & -4.51 & -4.38 \\
\hline
\end{array}
\]

Table I: Kohn-Sham energy of HOMO and LUMO respectively for $\beta$-carotenoid, Diaryl-porphyrin, pyrrole-C$_{60}$ and the whole triad.

Figure 1: Optimized geometry of C-P-C$_{60}$ as in Ref.\textsuperscript{7}. Minor tics are 1 Å wide apart.
Figure 2: Ground state energy levels of the triad. Red occupied, green unoccupied states. The orbitals involved in the photo-absorption and charge transfer processes are shown on top.
Figure 3: Calculated absorption spectrum of the triad, and the isolated pyrrole-C$_{60}$, Diaryl-porphyrin and $\beta$-carotenoid.
Figure 4: Comparison between theoretical and observed optical absorption for the full C-P-C$_{60}$. DFT is the calculated spectrum as in Ref. 7. TDDFT present work. EXP depicts the observed spectrum as reported in Ref. 16.
Figure 5: Comparison between theoretical TDDFT optical absorption in diaryl-porphyrin and observed free-base porphin absorption as in Ref. In the inset the region between 2 to 3 eV is magnified.
