

Photoexcitation of a Light-Harvesting Supramolecular Triad: A Time-Dependent DFT Study

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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 photoabsorption spectrum of the supramolecular assembly, and we provide an interpretation of the photoexcitation 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 photoinduced charge-transfer mechanism which characterizes the system.

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.¹ 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 supramolecular assemblies appear to be the most promising.²

In the class of supramolecular 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 photoexcitation followed by a charge transfer between the component units.³ The same process on the other hand can be exploited in photoconversion units like dye-sensitized (or Grätzel) solar cells.^{4,5} The research for ideal components of light-harvesting dyads has led to porphyrin–C₆₀ assemblies.⁶

Porphyrin molecules show extensive absorption of visible light, and an optical gap of approximately 2 eV, and are therefore ideal photoreaction centers and electron donors. C₆₀, on its side, is the ideal electron acceptor. It has a particularly deep triply degenerate lowest unoccupied molecular orbital (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 of 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 lifetime 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 as Configuration Interaction impractical or infeasible. Less accurate but computationally efficient methods such as density functional theory (DFT) have successfully been employed to describe the ground state of such compounds,⁷ 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

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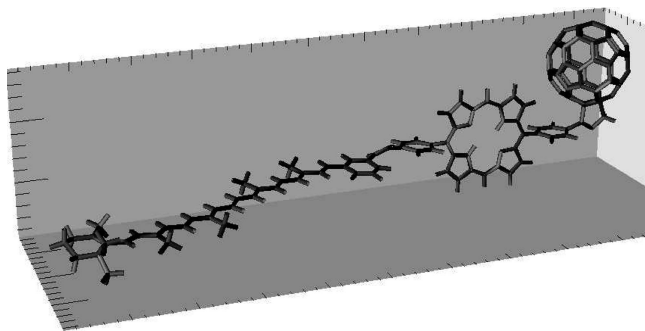


Figure 1. Optimized geometry of C–P–C₆₀ as in ref 7. Minor ticks are 1 Å wide apart.

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.⁸ In this Letter, we report the first TDDFT calculation of the electronic structure and absorption spectrum of the carotenoid–diaryl-porphyrin–C₆₀ triad (abbreviated hereafter as *triad* or C–P–C₆₀).

Results and Discussion

The C–P–C₆₀ system is composed of 207 atoms with 632 valence electrons. Its structure corresponds to the formula C₁₃₂H₆₈N₆O. For all of our calculations, we used an optimized geometry obtained by Baruah et al. using the LBFGS scheme.⁷ 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 Å × 16 Å × 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 Figure 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 functional.⁹ The core electrons were represented via Troullier–Martins¹⁰ pseudopotentials (for all of the components, the cutoff radii of the pseudopotentials are 1.25 au for hydrogen atoms, 1.47 au for carbon atoms, and 1.39 au for nitrogen and oxygen atoms), and the interpolating scaling functions method¹¹ was used to efficiently solve the Poisson equation in the calculation of the Hartree potential. All of the simulations in the present work, apart from the geometry optimization, were performed by discretizing all of 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 system.¹²

In Table 1, we report the Kohn–Sham energies of the highest occupied molecular orbital (HOMO) and LUMO for the isolated

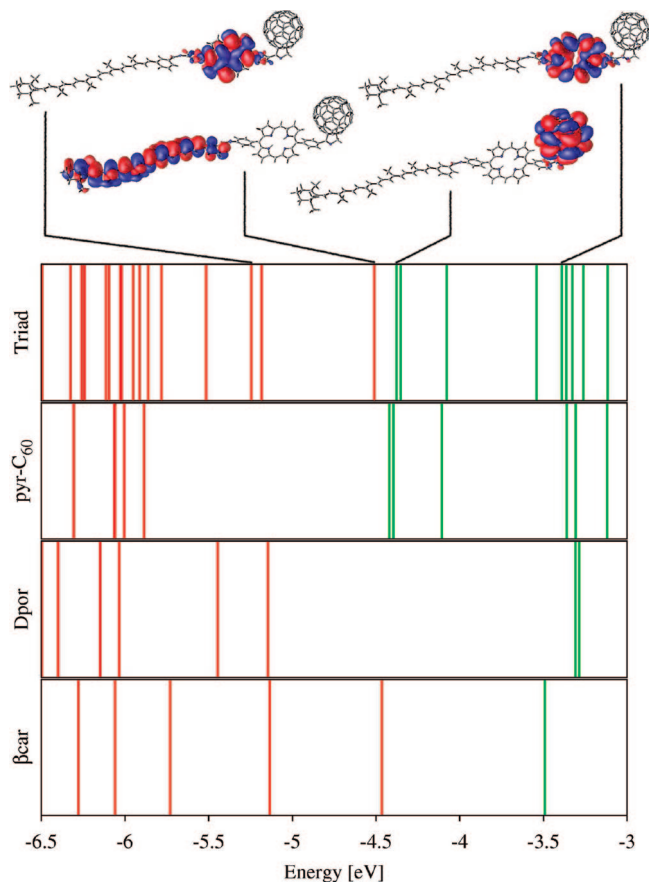


Figure 2. Ground-state energy levels of the triad. Red, occupied states; green, unoccupied states. The orbitals involved in the photoabsorption and charge-transfer processes are shown on top.

TABLE 1: Kohn–Sham Energy of HOMO and LUMO, Respectively, for β -Carotenoid, Diaryl-Porphyrin, Pyrrole-C₆₀, and the Whole Triad

molecule	ϵ_{HOMO} (eV)	ϵ_{LUMO} (eV)
β -carotenoid	−4.47	−3.49
diaryl-porphyrin	−5.15	−3.31
pyrrole-C ₆₀	−5.89	−4.42
triad	−4.51	−4.38

moieties and for the full triad. The detailed energy levels for other orbitals are depicted in Figure 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-C₆₀. 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 C₆₀ and it corresponds to the LUMO of the C₆₀ alone (see Figure 2). These features are in agreement with the earlier results obtained in ref 7 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 C₆₀ LUMO is split into three separate levels in the triad. Finally, some orbitals present a mixed character, such as LUMO+5, LUMO+6, and LUMO+7 with

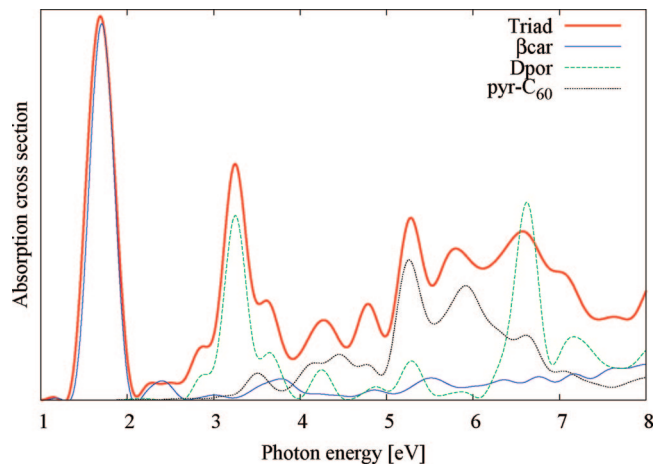


Figure 3. Calculated absorption spectrum of the triad, and the isolated pyrrole- C_{60} , diaryl-porphyrin, and β -carotenoid.

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 photoexcitation 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 preoptimized molecular components.

We have calculated the optical absorption spectra of the triad and its separated components using the time-dependent DFT, as described in ref 13. 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 $\delta v_{\text{ext}}(\mathbf{r}, t) = -\mathbf{k}_0 \cdot \mathbf{r} \delta(t)$). The magnitude of the perturbation is kept small in order to keep the dipolar response linear.¹² In this way, all of the frequencies of the system are excited with the same weight. The perturbed Kohn-Sham orbitals, $\phi_j(\mathbf{r}, t=0^+) = \exp(i\mathbf{k}_0 \cdot \mathbf{r})\phi_j(r)$, are then propagated on a real-time grid using the enforced time-reversal symmetry method.¹⁴

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 photoabsorption cross section, is obtained by averaging the polarizability over the three Cartesian directions. More detail on this procedure can be found in ref 12. 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 method.¹⁵ The orbitals were evolved, respectively, for a total of 15 fs, which corresponds to a spectral resolution of about 0.15 eV.

The TDDFT photoabsorption cross section of the triad and of the separated molecules is shown in Figure 3. 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

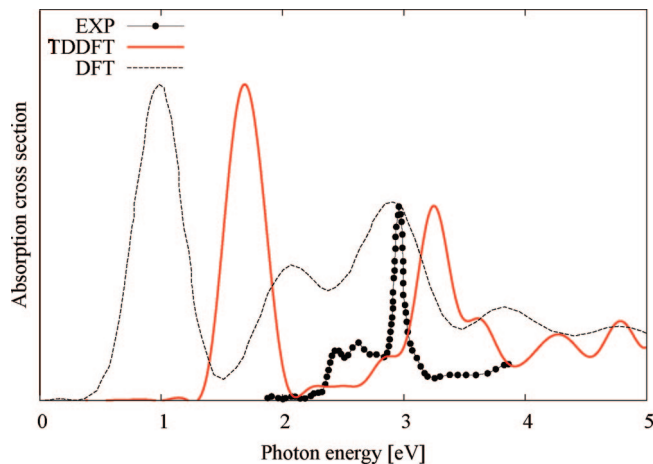


Figure 4. Comparison between theoretical and observed optical absorption for the full C-P- C_{60} . DFT is the calculated spectrum as in ref 7. TDDFT represents the present work. EXP depicts the observed spectrum as reported in ref 16.

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 the main features of the spectra are better described within TDDFT than applying the Fermi golden rule to Kohn-Sham eigenvalues and eigenfunctions. In Figure 4, we compare our data to the absorption reported in ref 16, which refers to a triad in 2-methyltetrahydrofuran solution. We observe a good one-to-one correspondence between the calculated and 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, which might well be responsible for 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 17). 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 of 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 eV correctly is attributed to the porphyrin (see decomposition in Figure 3). The experimental data ranges in refs 16 and 17 are limited to above approximately 2.0 eV, but the β -carotenoid absorption does not appear to be relevant for the photoconversion in the triad. On the other hand, ref 18 reports a peak for β -carotene in dichloromethane solution 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 and 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

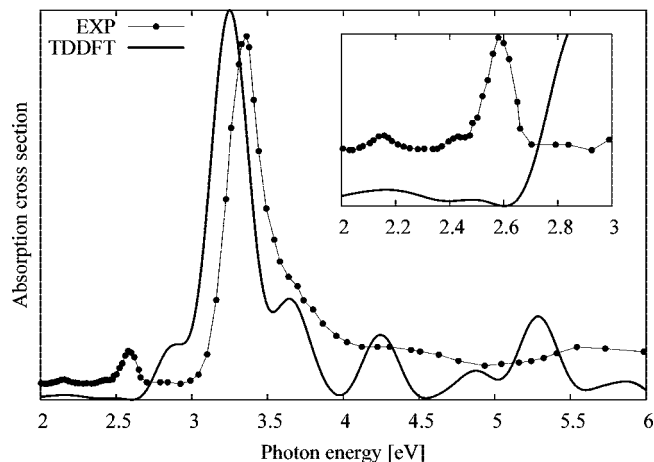


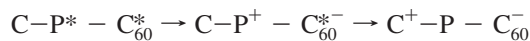
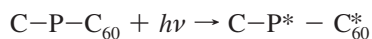
Figure 5. Comparison between theoretical TDDFT optical absorption in diaryl-porphyrin and observed free-base porphyrin absorption as in ref 25. In the inset, the region between 2 and 3 eV is magnified.

rule to the Kohn–Sham levels confirms (see Figure 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 Figure 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 diaryl-porphyrin alone, and it is also responsible for the optical excitation of the triad as a whole. This excitation was in fact obtained in laboratory conditions with a laser at 590 nm.¹⁶

In Figure 2, 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 photoexcitation process, and of the subsequent charge transfer that can be summarized in the following chain of steps:



The first step corresponds to the optical transition from HOMO-2 to LUMO+4. The decomposition of the corresponding TDDFT excitation into Kohn–Sham electron-hole pair excitations²¹ 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*–C₆₀^{*}. The electron in a previously unoccupied orbital on the porphyrin is now under the influence of the high affinity of the C₆₀, and it is easily accommodated on the almost-degenerate orbitals LUMO+1 and LUMO+2 at 0.14 eV above the LUMO localized on the C₆₀. In the assembled triad, the 3-fold degeneracy of the C₆₀ 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⁺–C₆₀^{–*}. The last step consists of a hole delocalization from the porphyrin HOMO to the carotenoid HOMO to give the final state C⁺–P–C₆₀[–]. Obviously, only the study of the full dynamics of the whole process can support the latter two steps of interpretation, which is inferred here on the basis of the analysis of the energy levels in Figure 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 nanoseconds, and it is beyond the scope of the present work.

As we have already stressed, it is the almost noninteracting 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 C₆₀ (acceptor) molecule are essentially nonoverlapping. Additional work is required to fully understand the dynamics of the light-induced charge-transfer process.²⁰ 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 photoexcitation of the molecule. Nevertheless, we have been able to get 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.²⁰ Among them, we stress the need for 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 role of the self-interaction problem, see also refs 19 and 22–24.

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 of 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 photoabsorption 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 photoabsorption 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 photoinduced 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 of the states involved in the photoabsorption 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 in a 50 Å long dipole.

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