Chapter 6

Electron Transfer in Fullerene

Dye-Sensitized Solar Cells
6.1 Extent of Charge Separation and Exciton Delocalization for Electronically Excited States in a Triphenylamine-C\textsubscript{60} Donor-Acceptor Conjugate: a Combined Molecular Dynamics and TD-DFT Study


*J.P.M. participated in the design of the project, performed all the calculations, analyzed the results, and co-wrote the manuscript.*
Extent of charge separation and exciton delocalization for electronically excited states in a triphenylamine-C$_{60}$ donor–acceptor conjugate: a combined molecular dynamics and TD-DFT study

Juan Pablo Martínez · Silvia Osuna · Miquel Solà · Alexander Voityuk

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Abstract Triphenylamine-pyrorolidine-C$_{60}$ is a potential material to construct high-efficient dye-sensitized solar cells. A combined molecular dynamics and time-dependent density functional theory study has been carried out to analyze charge separation and exciton delocalization in excited states of two constitutional isomers of this compound. Insight into the intrinsic structure of the excited states is provided. The presence of states with a hybrid excitonic and charge-transfer character is suggested to promote the direct charge separation process by excitation, which could have a significant impact on the efficiency of the light-harvesting species. A greater amount of such hybrid states is found at short distances between the triphenylamine fragment and the C$_{60}$ cage.

Keywords Fullerene dye-sensitized solar cells · Triphenylamine · Charge-transfer state · Molecular dynamics · TD-DFT

1 Introduction

Organic photovoltaic devices (OPVs) are particularly interesting due to their many applications in the field of molecular electronics. These materials can be used to manufacture light-harvesting ensembles [1], molecular transistors able to store excess of energy [2], and long π-conjugated molecules with better charge transport properties [3, 4]. Moreover, OPVs also represent a cheap and clean source of energy, which is increasingly more efficient [5, 6].

A dynamic area of research in OPVs is focused on dyesensitized solar cells (DSSCs) wherein two main concepts have been introduced: bulk heterojunctions (BHJs) [7] and molecular heterojunctions (mHJs) [8]. In the design of DSSCs constructed under the mHJ approach, there are several examples, in which fullerene C$_{60}$ is covalently linked to an electron donating group; as a matter of fact, unlike the polymeric approach, it has been pointed out that the use of relatively small molecular moieties as electron donors allows a better structural control and charge mobility tuning, which are remarkable advantages when investigating charge separation processes [8]. Among covalently connected dyes, triphenylamine (TPA) and its derivatives appear in interesting studies related to mHJs [9–11] (it is noteworthy to mention that these species have been used by the industry field as photoactive molecules during several decades [12], and also their applicability in the construction of DSSCs is of technological interest [13]). TPA is able to confine cationic charge and hamper aggregation between molecules, which induce self-quenching and reduce the
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2 Computational details

All calculations were completed with the program Gaussian 09 [27]. Ten structures for isomer a and other ten for isomer b (a and b being two TPA-C60 isomers with the TPA linked to the N-position and the two-position, respectively, of the pyrroldine ring as shown in Fig. 1) were taken from 100 ps MD trajectories (i.e., one snapshot every 10 ps was taken for further analysis). We consider that the analysis of ten snapshots in a 100 ps trajectory is enough to provide a semiquantitative description of the nature of excited states. MD simulations were performed in explicit solvent with the AMBER12 program [28] (see supporting information for full details on the MD simulations). Vertical electronic excitations were calculated using TD-B3LYP [29, 30] and its long-range corrected version, TD-CAM-B3LYP method [31]. Overall, the last version provides a more reliable description of CTS; that is, excitation energies for Rydberg and intermolecular charge-transfer transitions can be estimated within an error of 0.5 eV by a long-corrected approach, as well as reasonable oscillator strength (OS) values [32, 33]. The standard 6-31G* basis set was employed. Recently, Thiel et al. [34] assessed the performance of several TD-DFT schemes using for comparison the “best theoretical estimates” based on the coupled cluster and MS-CASPT2 data [34, 35]. TD-B3LYP/TZVP and TD-CAM-B3LYP/TZVP performed well in calculating excitation energies; the mean absolute deviations are found to be 0.27 and 0.30 eV, respectively. On the other hand, some studies involving CTS in fullerene-based dyes showed that the TD-B3LYP/6-31G* method is able to reproduce experimental trends related to emission energies for a set of oligomer fullerene dyes [36] and calculate, with a reasonable degree of accuracy, the different energetic parameters affecting charge-transfer reactions [37]. The study of the excited states with the TD-DFT method was carried out in gas phase. Based on a preliminary study, in which excited states are determined in the presence of a polarizable medium (see Figs. S1 and S2 in the SI), we consider that our calculations are still valid for a semiquantitative description of the nature of electronically excited states despite the omission of the solvent.

For the analysis of excited states, we utilized the methodology described recently [38, 39]. The extent of excitation localization in the excited state \( \psi_i \) can be measured as:

\[
X_{\text{d}(F)} = \frac{1}{2} \sum_{\alpha,\beta \in F} \left[ (S^{\text{ph}})_{\alpha\beta} \left( P^{\text{ph}} S \right)_{\alpha\beta} \right],
\]

where \( S \) is the atomic orbital overlap matrix and \( P^{\text{ph}} \) the symmetrized one-electron transition density matrix between the ground state \( \psi_0 \) and the excited state \( \psi_i \).
overall charge-transfer $\Delta q$ between fragments $F_1$ and $F_2$ is estimated as:

$$
\Delta q = \sum_{\alpha \in F_1} \sum_{\beta \in F_2} \left[ \left( SP^{0}\right)_{\alpha \beta} \left( P^{0}\right)_{\alpha \beta} + \left( SP^{0}\right)_{\beta \alpha} \left( P^{0}\right)_{\beta \alpha} \right],
$$

(2)

These quantities $X_{\chi}(F)$ (being $F$ either C$_{60}$ or TPA moieties) and $\Delta q$ are obtained for the 30 lowest excited states calculated for every structure of $a$ and $b$. Errors due to the functional and basis set are expected; however, we think that the selected methodology is consistent enough to provide a semiquantitative picture of the nature of the electronic excited states.

Finally, it is worth mentioning that real-time electron dynamics of photoexcited states can be very important for these systems. In fact, CTS and hybrid states (HS) can be generated because of the excited-state couplings after photoexcitation [40–42]. Despite its importance, the study of the dynamics of photoexcited states is out of the scope of the present work.

3 Results and discussion

The parameters $X_{\chi}(F)$ and $\Delta q$ are useful descriptors of the intrinsic structure of electronic transitions from which, depending on their value, we distinguish three different excitations that can give rise to a local excitation (LE), CTS, or HS. In the TPA-C$_{60}$ system, the nature of a particular excited state $\psi_i$ depends upon the contributions of the states $(F_{C_{60}})^{\pm}(F_{TPA})^{\pm}$ and $(F_{C_{60}})^{\pm}(F_{TPA})^{\pm}$, in which the two former terms, respectively, stand for excitations localized at the C$_{60}$ or TPA fragments, and the two latter ones represent excited states with strong charge-transfer character. Figure 2 shows the distribution of $X_{\chi}(F)$ and $\Delta q$ as a function of the excitation energy, and the discussion is reserved for the subsequent subsections.

3.1 Local excitations

A purely excitonic state has no contributions of CT states $(F_{C_{60}})^{\pm}(F_{TPA})^{\pm}$ and $(F_{C_{60}})^{\pm}(F_{TPA})^{\pm}$. Figure 2 shows that $X_{\chi}(F_{TPA})$ is zero, reflecting no contribution of TPA for all excited states calculated for both $a$ and $b$ isomers. Therefore, in our systems, states lacking charge separation are mainly characterized by single-molecule excitations (i.e., they correspond to local excitations, LE), for which $X_{\chi}(F_{C_{60}}) = 1$ and $\Delta q = 0$ given $\psi_i$ (let us define the ranges $X_{\chi}(F_{C_{60}}) = 0.9–1.0$ and $\Delta q = 0.0–0.1$ to identify a LE). Plots in Fig. 2 are conveniently sectioned to analyze the distribution of states through three different regions separated by vertical lines; horizontal lines indicate the previously defined range. On the whole, B3LYP results are different as compared to the CAM-B3LYP ones; however, a similar trend can be observed at the 2.0–3.0 eV range (see Figs. 2, 3). In the case of B3LYP, in a we calculate 86 excited states from which 65 are LE in the energy range equal to or $<2.0$ eV (i.e., 76% of the excitations lead to LE); on the other hand, 71% of the excitations in b correspond to LE in the same energy range considering 112 excited states. When changed to the 2.0–2.5 range, the relative population
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of LE increases to 86% in a and 97% in b; nonetheless, while excitations in a remain leading to LE with 83% in the 2.5–3.0 range, the number of LE in b decreases by a factor of 0.59 (from 97 to 57%) due to a considerable amount of excited states with mixed LE and charge-transfer character. It is illustrative to mention that Walton et al. [43] determined 26 bands in the absorption spectrum of pristine $C_{60}$ in the 1.8–3.2 range, where 14 bands were assigned to be in the 2.0–2.5 range, which is the region largely dominated by LE in a and b isomers. Now let us examine the CAM-B3LYP results at the 2.0–3.0 range. Plots c and d in Fig. 2 show that LE is only populated in the 2.0–2.5 range. Nevertheless, while 97% of the excitations in a remain LE in the 2.5–3.0 range, this population decreases by a factor of 0.74 in b, which resembles the tendency predicted by B3LYP. Higher-energy excitations (above 3.0 eV) give rise to mixed character states, and the amount of LE is diminished to 79 and 84% in a and b, respectively. Based on the B3LYP and CAM-B3LYP results, it is concluded that excitations in a are more likely to generate a LE, being $(F_{C_{60}})^*$ the main contribution to most of the calculated electronic transitions.

3.2 Charge-transfer states

The main contributions to form a CTS come from the states $(F_{C_{60}})^+(F_{TPP})^-$ and $(F_{C_{60}})^-(F_{TPP})^+$. In agreement with the preceding subsection, let us take the reference values $X_{a}(F_{TPP}) = 0.0$, $X_{b}(F_{C_{60}}) = 0.0–0.1$, and $\Delta x = 0.9–1.0$ to define a CTS given $\psi_{2}$, B3LYP results at 2.0 eV or less show that 20% of the excitations in a have strong charge-transfer character, and 19% in b. The 2.0–2.5 range is mainly dominated by LE; therefore, other CTS appear at higher-energy excitations. On this subject, Bakulin et al. [44] determined more electron and hole delocalization in higher-energy CTS, and their conclusions were based on charge distribution calculations via intermediate neglect of differential overlap/configuration interaction singles (INDO/CIS) for donor-acceptor organic semiconductors, including $C_{60}$ and derivatives. Moreover, in the BHJ approach where a conjugated polymer acts as the donor and a fullerene derivative as the acceptor, it has been demonstrated that the accessibility of high-energy excited CTS to the polymer exciton upon dissociation may facilitate charge separation [36].

It was proposed that charge separation is caused by a decreased coulombic barrier due to hole delocalization in higher electronically excited states with strong charge-transfer character at the donor–acceptor interface. In line with our results, 15% of the excitations lead to CTS in the 2.5–3.0 range in both a and b isomers as calculated with B3LYP (keeping in mind that there are more states with mixed character in b). On the other hand, only 3% of the excitations correspond to CTS in a as calculated by CAM-B3LYP at the same energy range, and 9% for b. Besides, above 3.0 eV there are almost three times more CTS (10%) as compared to the former energy range in a, although the amount of CTS in b is reduced to 6%. Accordingly, B3LYP does not only calculate high-energy CTS but also relatively low-energy CTS (below 2.0 eV); unlike CAM-B3LYP results, where CTS are only calculated above 2.5 eV. Nonetheless, low-lying CTS cannot be considered as physically reasonable.

3.3 Hybrid states

In the former two subsections, we mentioned that some excitations give rise to excited states with mixed LE and charge-transfer character. The nature of these states is rather complex, although some descriptions have been done in the literature. Let us consider again the BHJ scheme; in this framework, Kanai and Grossman [45] identified an electronic state extended across the oligomer–fullerene interface in the lowest excited state; that is to say, a hybridization between the lowest unoccupied molecular orbitals (LUMOs) of the oligomer–fullerene derivative with partial charge-transfer character. In the same system, a combined MD and unrestricted density functional theory (UDFT) calculations of the lowest triplet state study reveals that the structural variability of
the oligomer–fullerene interface gives rise to either a state with strong charge-transfer character or an extended state similar to the previously reported in Ref. [45]. The triplet state may be used to describe the equilibrium geometry and energy of an excited singlet state with strong charge-transfer character assuming negligible exchange interactions. Nevertheless, this assumption does not remain for states with partial charge-transfer character [46]. Additionally, the role of states with partial charge-transfer character in several oligomer–fullerene blends was also determined by Nelson et al. [36]. They argued that a hybridized lowest energy excited state is brought about by nearly degenerate LUMOs localized at the donor and acceptor as well, although this state strongly depends on the relative position of the oligomer–fullerene. The system under study in this contribution is not a blend of oligomer–fullerene, since the relatively small molecule TPA and C60 are covalently connected. However, we observe that some excitations have mixed character with partial contributions of $(F_{C60})^{-}(F_{TPA})^{+}$ and $(F_{C60})^{+}$; that is, $X_a(F_{TPA}) = 0.0$, $X_b(F_{C60}) = 0.1–0.9$, and $\Delta q = 0.1–0.9$. In the case of B3LYP, 5 and 10 % of the excitations below 2.0 eV give rise to HS in a and b, respectively. In the region mainly dominated by LE, there are more HS in a (8 %) than b (1 %); although a notable difference is observed at the 2.5–3.0 range, wherein 8 % and 28 % of the excitations correspond to HS in a and b, respectively. CAM-B3LYP does not calculate any HS in the 2.0–3.0 range for a; HS appear in b at the 2.5–3.0 range with 17 % of the excitations. For higher-energy states, a and b show the same population of HS, being 10 % for each one. Based on the relative population of HS across the whole energy range, we infer that adiabatic charge separation and charge recombination reactions are slower in a because it produces a fewer amount of excited states with mixed charge-transfer and LE characters, which are reported to promote charge separation at the donor–acceptor interface. This could have a direct impact in the design of high-efficient DSSCs as materials may be engineered such that their excitations lead to a small number of HS, thus avoiding a premature charge recombination. As a matter of fact, Scharf et al. [44] found that this generates longer-lived CTS as compared to b due to the longer distance between the TPA and C60 centers. They also reported rate constants to be slightly slower for charge-transfer reactions in a. In view of these findings, we are currently studying the main parameters that affect the reaction rates for charge-transfer reactions in TPA-C60.

### 3.4 Forbidden transitions

An electron may be migrated to a phase boundary through spatial translation of a Frenkel exciton. This coulomb-bound excited state enables the access to CTS after dissociation, since direct excitations to CTS are either completely forbidden or only weakly allowed according to the photoabsorption spectrum of C60. Indeed, in C60 nine bands from 3.0 to 6.4 eV are assigned to be allowed transitions ($1T_{1u} \rightarrow 1A_{2g}$) with OS ranging from 0.005 to 3.09, the latter at 5.78 eV, and 18 bands from 2.0 to 3.0 eV are assigned to be orbitally forbidden transitions [43]. The main contribution to the excited states calculated in TPA-C60 comes from $(F_{C60})^{+}$ as excitations are predominantly LE. In comparison with the forbidden bands in C60, it is observed a significant number of transitions with weak OS (less than $5 \times 10^{-3}$) as shown in Fig. 4. Among electronic transitions with a slightly stronger OS (above 0.02), B3LYP calculates two excitations for a and one for b, all of them in the 2.0–3.0 energy range. On the other hand, CAM-B3LYP calculates eight excitations for a (only LE) and seven for b (six LE and one HS), all of them above 2.8 eV. In some cases, the OS increases one order of magnitude in high-energy excitations as compared to weaker OS; this is the region where allowed bands of C60 are observed. In view of the nonvanishing values of the OS, electronic transitions in TPA-C60 may take place from the ground state by light absorption.
3.5 Structural analysis

We have analyzed some structural parameters of the geometries studied (see SI, Tables S1–S3). We first selected a set of length variables to account for the distance between the TPA center and the C60 surface (see Fig. S3). In isomer a, the absolute deviation of these length variables, in reference to an optimized geometry, range from 0.02 to 0.68 Å with an absolute arithmetic mean deviation of 0.12 Å (σ = 0.31 Å). The situation is very similar to isomer b, and the length variables deviate from 0.03 to 0.74 Å (absolute mean deviation 0.21 Å and σ = 0.28 Å). The distance between the TPA center and the C60 surface therefore remains, in comparison with an optimized geometry, almost unchanged through the ten different structures of each isomer. Our results show that the distance between the TPA center and C60 surface is closer in isomer b than in a. Consequently, the fact that isomer b tends to form more HS is attributed to the increased spatial orbital overlap resulting from the closer proximity between the donor and acceptor moieties. We looked into the planarity of TPA, by measuring a set of dihedral angles, so as to determine whether the structural conformation of TPA has some effect on the OS (see Fig. S4). We hypothesized that a more planar structure might favor an electronic transition by increasing spatial orbital overlap; however, TPA remains non-planar and has several orientations through the different examined structures; as a result, no correlation could be related to this structural parameter. Nonetheless, since the structures under study of each isomer are structurally similar to their respective optimized geometry, we infer that electronic transitions are mainly dominated by the inherent electronic structure of the isolated fragments TPA and C60; thus, the inclusion of more conformations to our analysis is considered superfluous as discussed below.

By taking the equilibrium geometry of the isolated fragments, we calculated a large gap (ca. 4.0 eV) between the highest occupied molecular orbital (HOMO) of TPA and LUMO of C60. This large HOMO–LUMO gap justifies the vanishing OS at a lower energy range calculated for all the geometries under study. A similar observation was done by Lin et al., who carried out DFT and Zerner’s INDO calculations in fluorene-thiophene/cyclopentadienylthiophene-based copolymers and observed that an increased HOMO–LUMO gap of the donor to the acceptor reduces the OS of transitions from the ground state to the first excited state [47]. Moreover, they concluded that electronic transitions from the ground state to higher electronically excited states may dominate the total transitions. Our CAM-B3LYP results obtained for every structure of both isomers also indicate that higher electronically excited states are more likely to occur as several transitions above 3.0 eV have nonvanishing OS for different structural conformations (see Fig. 4), which may be attributed to either an allowed transition localized at C60 or a smaller energy difference and better spatial orbital overlap between the involved molecular orbitals of TPA and C60. In fact, since we calculated one HS at 2.82 eV with an OS value of 0.029 in b, we conclude that an enhanced spatial orbital overlap can promote the formation of excited states with mixed character, thus increasing the probability to transport charge through those materials aimed at the construction of DSSCs.

4 Conclusions

Based on the analysis of intrinsic structure of excited states, the nature of electronic excitations in TPA-C60 has been studied in detail. The extent of charge separation and exciton delocalization has been determined for each of the 30 lowest excited states in TPA-C60. The effects of thermal fluctuations on the results have been considered. In a wide range of excitation energies, excited states are determined to be mainly localized at the C60 fragment. Some high-energy excited states are found to exhibit strong charge-transfer character, TPA-C60 (although unlike CAMB3LYP, B3LYP predicts also low-lying charge-transfer states, this result cannot be considered as physically reasonable). Isomer b, which has a closer distance between the TPA and C60 fragments, tends to form more states with mixed LE and charge-transfer character delocalized over the donor and acceptor sites; as a result, the formation of CTS is suggested to be more probable in isomer b. Finally, several hybrid excited states with nonvanishing OS have been identified, suggesting that light absorption may directly lead to charge separation in the TPA-C60 system.

5 Supporting information

Supporting information includes full details of the MD simulations, an estimation of solvent effects, and Cartesian coordinates of all considered structures.

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References

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