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STUDY OF PHOTOINDUCED PROCESSES OF A DYAD BDP-C_{60} UNDER EXCITED BOTH ITS DONOR AND ACCEPTOR MOIETIES

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ABSTRACT

In this paper, A BODIPY-C_{60} Dyad system composed of a BDP donor and a Fullerene acceptor has been studied photoinduced processes using ultrafast transient absorption spectroscopies. Under excitation at 380 nm, both donor (BDP) and acceptor (C_{60}) were excited. The existence of three conformers of BDP-C_{60} structures was indicated as a result of different photoinduced processes under excitation wavelength at 380 nm, including both electron transfer and energy transfer. The ultrafast - Femtosecond transient absorption spectra deciphered the charge transfer and energy transfer between two parts of the dyad systems. The shortest donor-acceptor distance conformer (8.8 Å), which is noted as conformer 1, was designated as the cause of two fast and ultrafast electron transfers from the Frank-Condon region and singlet excited state of BDP to C_{60}. The rates of two-electron transfer processes were estimated at about 2.5×10^{12} and 1.7×10^{11} s^{-1}. Likewise, the longer donor-acceptor distance conformers (17.5 and 20.5 Å) were responsible for two energy transfer processes in the BDP-C_{60} dyad system.

NGHIÊN CỨU CÁC QUÁ TRÌNH TƯƠNG TÁC VỚI ÁNH SÁNG CỦA HỆ PHÂN TỬ DYAD BDP-C_{60} KHI KÍCH THÍCH CẢ HAI THÀNH PHẦN DONOR VÀ ACCEPTOR

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TỪ KHÓA

BODIPY
Fullerene
Hấp thụ phân giải thời gian
Trao đổi điện tử
Trao đổi năng lượng

TÓM TẮT

Trong bài báo này, hệ phân tử dyad được tạo thành từ hai thành phần donor – BDP và acceptor – Fullerene đã được nghiên cứu các quá trình xảy ra khi tương tác với năng lượng photon sử dụng hệ đo hấp thụ phân giải thời gian cực nhanh Femto giây. Dưới bước sóng kích thích 380 nm, cả hai thành phần donor (BDP) và acceptor (C_{60}) đều được kích thích. Các quá trình xảy ra khi tương tác với ánh sáng đã được chỉ ra là do sự tồn tại của ba đồng phân của phân tử dyad BDP-C_{60}. Phổ hấp thụ phân giải thời gian Femto giây đã chỉ rõ các quá trình xảy ra khi phân tử dyad BDP-C_{60} tương tác với ánh sáng ở bước sóng 380 nm bao gồm cả quá trình trao đổi năng lượng và điện tử. Đồng phân có khoảng cách donor-acceptor ngắn nhất (8.8 Å) (đồng phân 1) gây ra 02 quá trình trao đổi điện tử từ trạng thái Frank-condon và trạng thái kích thích singlet của BDP sang thành phần C_{60}. Hai hằng số của quá trình truyền điện tử được đánh giá tương ứng là 2.5×10^{12} và 1.7×10^{11} s^{-1}. Trong khi đó, hai đồng phân có khoảng cách donor-acceptor dài hơn (17.5 và 20.5 Å) gây ra các quá trình trao đổi năng lượng giữa hai thành phần BDP và C_{60}.

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1. Introduction

Global energy consumption is constantly rising. Solar power is one of the finest renewable energy sources for meeting this requirement, and it has received a lot of attention for replacing depleted fossil fuels. A well-studied strategy is to develop photoelectrochemical devices and cells that convert solar energy into electrical energy. Organic solar cells have several advantages over other choices, including being low-cost, lightweight, and adaptable [1], [2]. As a result, a wide range of donor-acceptor dyad systems has been designed to construct organic solar cells [3] - [5]. Strong light absorption, effective charge separation, and slow charge recombination should be required for a Dyad system in organic solar cells. Boron-dipyrromethene (referred to henceforth as BDP) donors and Fullerene acceptors stand out among a large variety of donor-acceptor candidates. BDP and its derivatives serve a dual function: they act as efficient light-harvesting antennae and as electron donors during photoexcitation [6], [7]. They also have a reasonably broad spectral range in both absorption and emission, as well as a high molar extinction coefficient in the visible area [6]. The system also requires an acceptor candidate, and Fullerene (C_{60}) has lately emerged as one of the most promising electron acceptors thanks to its low reorganization energies and a high degree of charge delocalization [8] - [10]. Donor-acceptor Dyad systems have been immobilized on a wide range of surfaces in order to build photoelectrochemical devices [11], [12]. Taking advantages of all these features, a BDP-C_{60} dyad system was constructed by a clickable fullerene, and BDP-thiol derivative (denoted as BDP-C_{60} dyad) was synthesized [13] and, then it will be immobilized on a gold surface through association with a helical peptide.

In the previous work, BDP-C_{60}, the photophysical properties of BDP-C_{60} dyad system were implemented using fast and ultrafast transient absorption spectroscopy under excitation wavelength at 532 nm [13]. This study indicated that, under laser excitation 532 nm, mainly donor – BDP moiety was excited, and the photoinduced electron and energy transfer processes were verified. In this work, photoinduced processes on the BDP-C_{60} dyad system were investigated upon laser excitation at 380 nm to excite both donor – BDP and acceptor – C_{60} moieties, using ultrafast Femtosecond transient absorption spectroscopy.

2. Methods

The BDP-C_{60} dyad was synthesized and reported in the previous work [13]. Figure 1 presents the structures of the BDP-C_{60} dyad system and their donor – BDP and acceptor – C_{60} moieties.

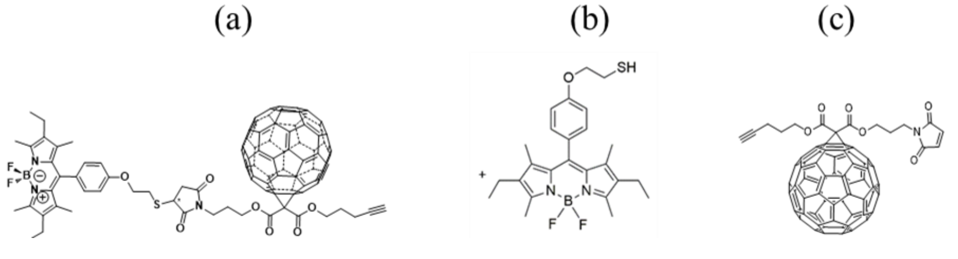

Figure 1. *The molecular structures of (a) BDP-C_{60} dyad; (b) donor – BDP; and (c) acceptor – C_{60}*

The primary method to study the photophysical properties of BDP-C_{60} dyad under the effect of light excitation was ultrafast – Femtosecond UV-vis-NIR transient absorption spectroscopy (Ultrafast systems, Helios model). The ultrafast laser system comprises a short-pulse titanium-sapphire oscillator followed by a high-energy titanium-sapphire regenerative amplifier. The pump pulse energy was 0.8 μJ. The absorbance was about 0.86 at the excitation wavelength. Before the experiment, the solution was saturated with argon.

3. Results and discussion

3.1. Absorption and fluorescence measurements

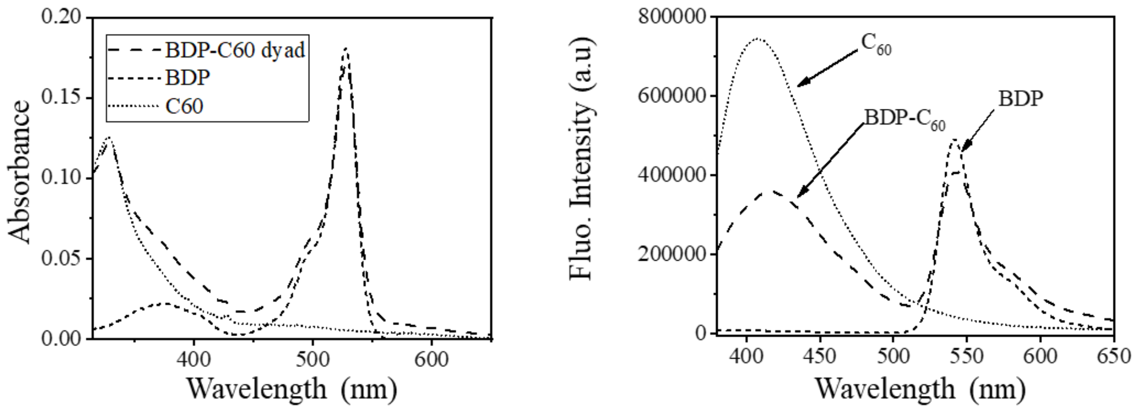

Figure 2. *(a) Absorption and (b) fluorescence spectra in benzonitrile of BDP-C_{60} dyad (dash lines), and their BDP (short dash lines) and C_{60} moieties (short dot lines); The wavelength excitation at 380 nm*

Figure 2 (a) shows the absorption spectra of BDP-C_{60} dyad, BDP, and C_{60} in benzonitrile (PhCN). It is clear that the absorption spectrum of BDP-C_{60} dyad is composed of two components: (i) a center band at 532 nm is attributed to the contribution of the BDP portion; (ii) a peak centered at 328 nm is ascribed to the C_{60} part [14]. The fluorescence spectra of these solutions were recorded under 380 nm wavelength excitation and displayed in figure 2 (b). Under using 380 nm wavelength, the purpose is that both donor-BDP and acceptor-C_{60} parts are excited. As expected, the characteristic of BDP-C_{60} dyad's fluorescence spectrum is contained two bands at 418 nm and 543 nm corresponding to the fluorescence of C_{60} and BDP moieties, respectively [13], [15]. Therefore, both BDP moiety and C_{60} portion were excited under excitation wavelength at 380 nm.

3.2. Femtosecond transient absorption measurement

Femtosecond transient absorption spectroscopy was implemented to elucidate the photoinduced processes occurring under 380 nm excitation. The femtosecond TA spectra of BDP-C_{60} dyad in argon-saturated PhCN at indicated delay times are shown in Figure 3. The femtosecond TA spectra range is from 330 nm to 1500 nm. To simplify, the TA spectra of the BDP-C_{60} dyad are separated into two temporal windows: UV-Vis [330 – 750 nm] and NIR-infared [600-1500 nm]. Parallel to that, the six basic kinetic traces that indicate particular characteristic states were selected and presented in Figure 4 and Table 1. The fitting time converged in five distinct times: (0.3-0.5) ps, (2-6) ps, (50-58) ps, (470-590) ps, and roughly 1300 ps. As indicated in the previous study [13], computational analyses have revealed the existence of at least three conformers with donor-acceptor distances of 8.8 Å (conformer 1), 17.5 Å (conformer 2), and 20.5 Å (conformer 3); thus, the times above must be attributed to the various conformers.

Under 380 nm excitation, the instantaneously generated $^1C_{60}^*$ with the broadband at 900 nm was detected concomitant with the creation of the singlet excited state of BDP ($^1BDP^*$) at 1278 nm (Figure 3a). Figure 3a also shows the rapid formation of the charge-separated state from the Frank-Condom (FC) region of BDP with the characteristic band at 1045 nm of the first reduced state of C_{60} ($C_{60}^{\bullet -}$) [13], [16]. This ultrafast process, with a formation time of roughly 0.3 ÷ 0.5 ps, is shown as the first stage, in which charge transfer must occur for conformer 1 with the shortest donor-acceptor distance (8.8 Å). The second temporal window [0.58-20 ps] (Figure 3 (b) and (c) reveals a concomitant drop of the ^{1}BDP* with an added rise of $C_{60}^{\bullet -}$ with a characteristic time of about 6 ps. This process is designated for a second charge transfer step from ^{1}BDP* to C_{60}. As a result, the two rates of two mechanism charge transfer caused conformer 1 are 2.5×10^{12} and 1.6×10^{11} s^{-1}, corresponding to two average times of 0.4 ps and 6 ps, respectively. It should be highlighted that these charge transfer rates are more efficient when compared to molecules of the same class [16], [17]. Moreover, the decay of the ^{1}BDP* occurs at the same time as the initial time constant of bleaching band recovery (Figure 3b). The second decay time of ^{1}BDP* is consistent with the energy transfer process from ^{1}BDP* to C_{60} that happened for conformer 2 (17.5 Å). The last decay time of ^{1}BDP* (~470 ps) might ascribe to the energy transfer to C_{60} corresponding to conformer 3 with the longest donor-acceptor distance of 20.5 Å.

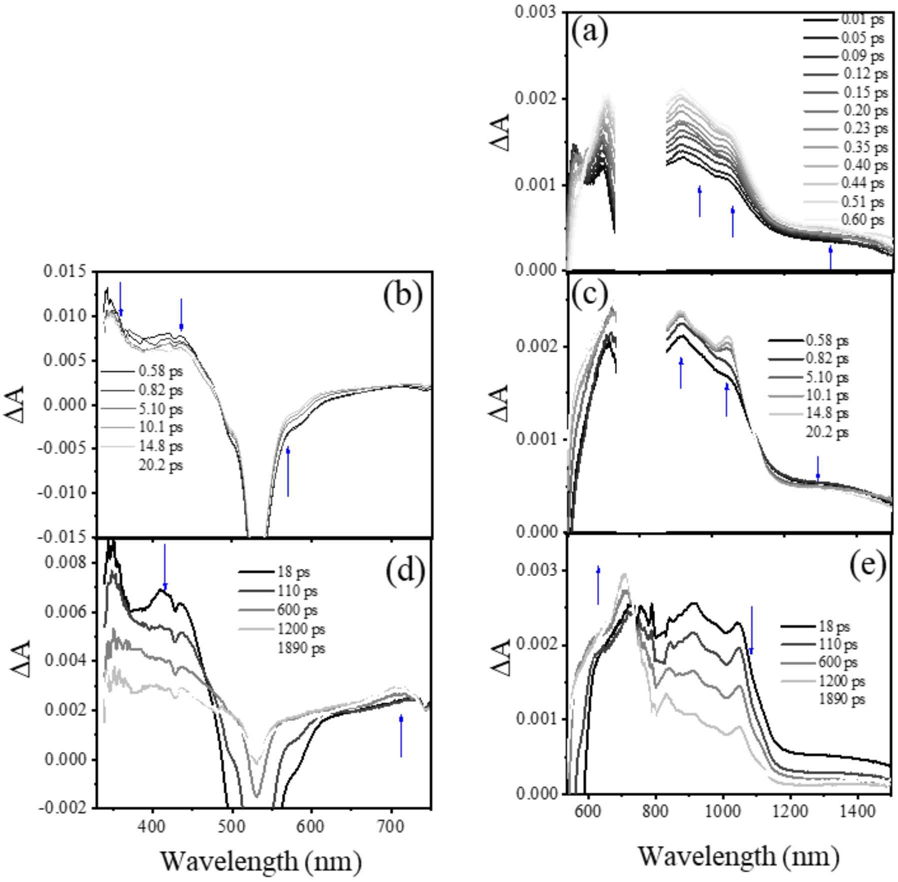

Figure 3. *Femtosecond transient absorption spectra at the indicated delay times of BDP-C_{60} dyad in argon saturated PhCN, λ_{exc} 380 nm; The range of the spectra is divided into two windows [350÷750] and [570÷14500]; The white blanks in figures (a and c) are due to laser excitation at short delay times*

In contrast to the case of using 527 nm excitation, the generation of $^1C_{60}^*$ under 380 nm excitation could not be recognized by monitoring the growth at 916 nm. It could be explained by a relatively low energy transfer from BDP in comparison to direct excitation BDP moiety, which limits the detection of $^1C_{60}^*$.

The kinetic traces of both $^1C_{60}^*$ and $C_{60}^{\bullet -}$ indicate the simultaneous appearance of a new band at 700 nm corresponding to the triplet excited state of C_{60} (noted as $^3C_{60}^*$) (Figure 3 (e)). The rate constants for charge recombination and intersystem crossing were both found to be 8.3×10^8 s^{-1}. This value is the same order of magnitude as the rise of the $^3C_{60}^*$. Consequently, these findings suggest that both $^1C_{60}^*$ and $C_{60}^{\bullet -}$ relax to the $^3C_{60}^*$ state before returning to the ground state.

Figure 5 summarizes the various photoinduced events of the BDP-C_{60} dyad in benzonitrile. The energy diagram depicts different photophysical processes of the BDP-C60 Dyad in benzonitrile that were constructed utilizing excited state energies of the donor and acceptor units as well as computed free energy data. Both the donor BDP and C60 moieties are activated in the diagram. The direct electronic excitation of the C_{60} moiety under 380 nm excitation can also produce some vibrational excitation [14], [18]. The energies of radical ion pairs and the singlet excited state of the C_{60} are greater than those of the $^3C_{60}^*$ state. Thus, it agrees with the results in femtosecond TA: both $C_{60}^{\bullet-}$ and $^1C_{60}^*$ occupy the $^3C_{60}^*$ state before returning to the ground state.

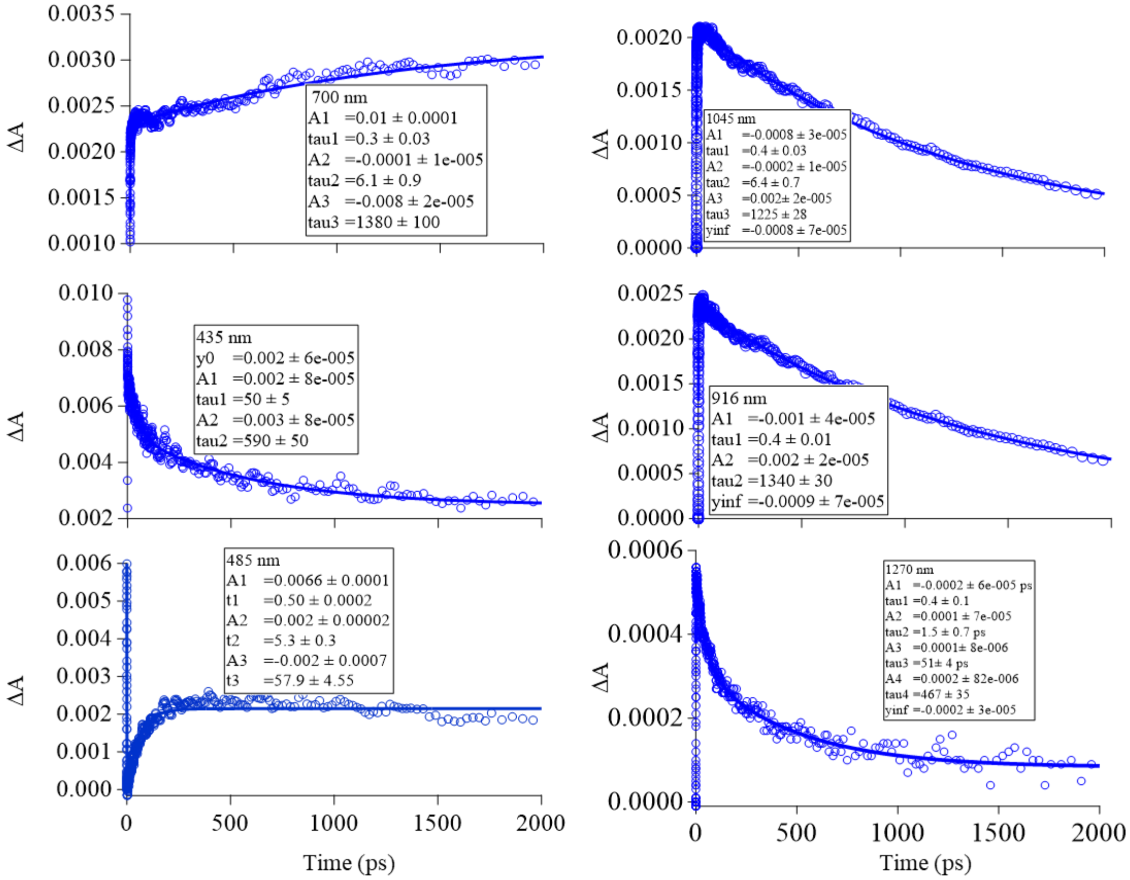

Figure 4. *Basic fits of some traces at specific characteristics bands of the BDP-C_{60} dyad in argon saturated benzonitrile, λ_{exc} 380 nm. 700 nm ($^3C_{60}^*$); 435 nm ($^1C_{60}^*$ + $^1BDP^*$); 485 nm (bleaching band of BDP); 1045 nm ($C_{60}^{\bullet-}$); 916 nm ($^1C_{60}^*$ + $C_{60}^{\bullet-}$); 1270 nm ($^1BDP^*$)*

Table 1. *Specific times of certain states obtaining from basic kinetic fitting $^1C_{60}^*$*

	t_1 (ps)	t_2 (ps)	t_3 (ps)	t_4 (ps)
435 nm $^1C_{60}^*$ + $^1BDP^*$	-	(d) 50 ± 5	(d) 590 ± 50	-
485 nm Bleaching band BDP	(d) 0.5 ± 0.0002	(r) 5.3 ± 0.3	(r) 57.9 ± 4.55	-
700 nm $^3C_{60}^*$	(r) 0.30 ± 0.02	(r) 6.1 ± 0.9	(d) 1380 ±100	-
916 nm $^1C_{60}^*$ + $C_{60}^{\bullet-}$	(r) 0.4 ± 0.01	(d) 1340 ± 30	-	-
1045 nm $C_{60}^{\bullet-}$	(r) 0.4 ± 0.03	(r) 6.4 ± 0.7	(d) 1225 ±28	-
1270 nm $^1BDP^*$	(r) 0.4 ± 0.1	(d) 1.5 ± 0.7	(d) 51 ±4	(d) 467 ± 35

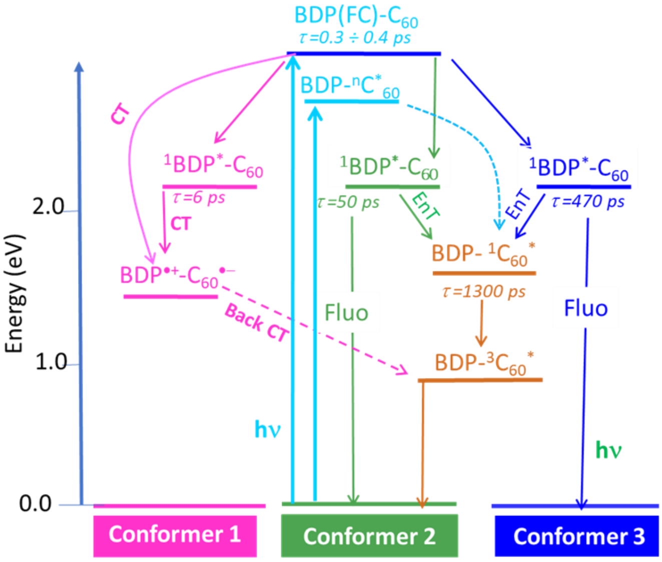

Figure 5. *The energy level diagram depicts the photoinduced processes observed in the three conformers of the BDP-*C_{60} *dyad in benzonitrile after laser excitation at 380 nm. Abbreviations: EnT= Energy transfer, CT = charge transfer, Back CT = back charge transfer, ISC = intersystem crossing, energies:* $^{1}\mathbf{BDP}^{*}$ *=2.33eV,* $^{1}\mathbf{C}_{60}^{*}$ *= 1.75eV ,* $^{3}\mathbf{C}_{60}^{*}$ *= 1.55eV [19], [20]*

4. Conclusion

In conclusion, both BDP and C_{60} portions in the BDP-C_{60} dyad were stimulated at 380 nm. However, the excited state of C_{60} appears to demonstrate no charge transfer to the BDP moiety. In contrast, conformer 1, which has the lowest donor-acceptor distance, demonstrated rapid charge transfer between the FC and $^{1}BDP^{*}$ states of the BDP to the C_{60}. It should be noted that our findings show a high efficiency of charge transfer, with rate constants of 2.5×10^{12} and 1.7×10^{11} s^{-1}. Finally, the excited state and the charge-separated state of C_{60} populated the triplet excited state of C_{60}.

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