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Excited Electronic States of Porphyrin-Fullerene Dyads with Different Type of Bonding

Pavel O. Krasnov*

Siberian State Technological University,
Mira 82, Krasnoyarsk, 660049,
Russia

Yuliya M. Milyutina

Siberian Federal University,
Svobodny 79, Krasnoyarsk, 660041,
Russia

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The general requirements to the artificial photosensitive systems are the light sorption at the visible field of spectrum, the long excitation states lifetime and the possibility to form system with separated charges. Donor-acceptor dyads porphyrin-fullerene are considered as promising materials possessed of noted features. The quantum-chemical calculations? results of geometry, general and excited electronic states of such structures with two kinds of bonds (porphyrin and fullerene are bonded covalently and non-covalently) are presented in this work. It has been shown that formation of system with separated charges in the first case happens more probably than in the second case, but the lifetimes of their excited states sufficiently lower.

Keywords: systems with separated charges, photoinduced electron transfer, quantum-chemical simulation, photovoltaic elements.

Introduction

Photovoltaic elements are devices for conversion of light energy (including sun light) to the electric energy. Their development and creation are very perspective directions of modern science and technique evolution. Investigations carried out at the present time are directed to obtaining of materials with 30-60% of power conversion efficiency [1]. It is not a single way in which investigations are performed. The second and a very interesting way for photovoltaic elements creation is the use of polymer films from organic substances being able to become excited under the action of light with a next electron transfer [2–10] to electrode. The advantages of their use over inorganic materials consist in a relative cheapness of obtaining and plastic structure allowed us to cover by them the surfaces curved for architecture compatibility of the last ones [2].

Moreover, organic semiconductor films can be used by way of good chromophores for creation of optoelectronic devices [9]. It is caused by two reasons: the easiness of variation of their band gap by the way of chemical modifications and a high charge carrier mobility, which makes these substances competitive for amorphous silicon.

Experimental application of organic polymer films has begun more then 20 years ago [3]. They are placed between two electrodes on a glass surface. The general problem of their practice

*kpo1980@gmail.com

use is a low power conversion efficiency amounting to 6% at presented time [4]. Such a low value is explained by the causes set, one of them is a small overlap of organic substances and sun light adsorption spectrums [5]. The low intensity of the red light adsorption is a key moment especially [6]. The solving of this problem is not only concerned with creation of new substances having satisfactory spectral characteristics, but combination of substances known at the present time [5–10].

Organic photovoltaic elements have to be consisted of two parts - electrons donor and acceptor. For the first one the groups of small heterocyclic molecules (pyrrole or pyridine type) are used as heterocyclic macrocycles (porphyrins and phthalocyanes). It is known that the last ones absorb the light of a visible spectrum range and are belonging to the photosensitive compounds, such as chlorophyll. Therefore their use is quite logical. Fullerenes are taken up as electrons acceptors due to their unique ability to accumulate electrons [11] with formation of multi-anions. Different substances, which are potential photovoltaic elements with fullerenes and porphyrins inside, have been already examined earlier by experimental [12–15] and theoretical [16–20] methods, and combine into dyads and triads, in general case, distinguished by a quantity of the component parts. It has been shown that in such types of substances the photoinduced electron crossing happens from porphyrin (P) on C_{60} fullerene (F). These molecules can be linked [16–18] or non-linked [19] covalently at that. The situation of complex compounds formation, where the atoms of transition metals binding fullerene molecule additionally as a ligand had a place in the center of porphyrins, has been studied either [20]. Electron transfers from the occupied molecular orbitals localized on porphyrin on the unoccupied molecular orbitals localized on fullerene are interesting in all cases. The presented works have been addressed to study of geometrical, energetic, electron and spectral characteristics of dyads.

Photoinduced electron transfer leads to formation of a system with separated charges. And the question about the lifetime of such system is fundamental here. It should be quite large for effective conversion of excitation energy into electric energy with electron transfer from fullerene on electrode without dispersion by way of heat, for example. Formation of long lifetime electron states increases power conversion efficiency exactly. Understanding of photochemical processes, which involves photoinduced electron transfer in the dyads, is an important moment for purposeful synthesis of artificial photosystems possessing the properties of natural objects and used for creation of molecular electronic devices. Our work and investigations mentioned above have been directed to studying of electron structure features of donor-acceptor dyads and features of its changing due to light effect in particular.

In this work we are presenting the quantum-chemical calculations results of adsorption spectrums character properties of porphyrin-fullerene dyads with two types of bonding: P and F are bonded covalently (P-F) in one case and bonded by the attracting intermolecular forces without covalent bonds formation ($P \cdots F$) in another case.

1. Computational Details

Density functional theory (DFT) method with B3LYP [21] exchange-correlation potential and 6-31G(p,d) atomic basis set was used for calculations. In the beginning the geometry optimization of each structure has been done, and further the excited states calculations of optimized molecules have been performed by the Time-Dependent DFT (TDDFT) [22–24] procedure. All calculations have been done in NWChem 5.1 software package [25,26]. Lifetime of excited states was estimated approximately from wavelengths (λ) and oscillator strengths (f) observed in the

results of calculations by equation

$$\tau = \frac{g_i}{g_j} \frac{C\lambda^2}{f} \quad (1)$$

where $C = 1.49919 \cdot 10^{-14} \text{ nm}^{-2} \cdot \text{s}$ is a constant, g_i и g_j are the numbers of states degenerated on i and j energetic levels, correspondingly, between which transition had a place [27].

2. Results and Discussion

Dyads linked covalently. P-F dyads structures for two cases of P and F covalent binding have been modeled and studied. In the first case P molecule has been linked along bond sited between six-fold rings of F — compound 1. In the second case P molecule has been linked along bond sited between six- and five-fold rings of F — compound 2 (1).

Binding took a place in both cases by means of two methyl groups; each of them was connected to respective carbon atom of F by one end and to respective carbon atom of P pyrrole group by another one. The geometry optimization of the both structures has been performed with

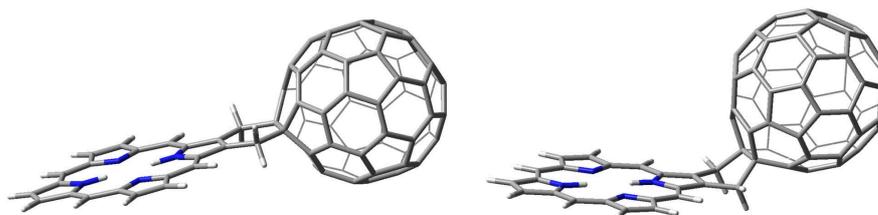


Fig. 1. Models of compounds 1 (left) and 2 (right) optimized with C_s symmetry restriction

symmetry restrictions: C_s for compounds 1 and 2, C_{2v} for compound 1. Molecules have been considered in two spin states with multiplicities 1 and 3. Calculated values of total energies are presented in Table 1.

Structures have been modeled in the way, when carbon atoms of methyl groups and P were in one plane, before optimization procedure of them. There were no any distortions of compound 1 after optimization. Whereas compound 2 has been exposed to sufficient distortion and as a result carbon atoms of methyl groups and P got places in the different planes (1).

Based on the results presented in the Table 1 it follows that structure with connection of P executed along bond between six-fold rings of F, with spin multiplicity equal to 1 and symmetry C_{2v} is more preferable, because the total energy of the structure in this case is minimal. It should be noted that the energy difference of compounds concerned is not very large and equals 0.019 a.u. (0.52 eV). So, the next calculations of covalently linked dyad have been done for compound 1 which is identified as P-F for comparing with covalently non-linked dyad $P \cdots F$. In both cases C_{2v} symmetry restriction and spin multiplicity equal 1 have been applied. Talking about electronic structure of P-F it should be noted that its molecular orbitals (MO) of valence field are presented by π -orbitals of P and F (five highest occupied and five lowest unoccupied at least) (2). Energies and general localizations of these orbitals are presented in the Table 2. Note that HOMO is highest occupied MO, HOMO-1 is previous for the last one MO and so on, and LUMO is lowest unoccupied MO, LUMO+1 is next after the last one MO and so on.

Table 1. Total energies of covalently linked dyads

Structure	Symmetry	Multiplicity	Energy (a.u.)
Compound 1	C_s	1	-3353.102
Compound 1	C_s	3	-3353.036
Compound 1	C_{2v}	1	-3353.102
Compound 1	C_{2v}	3	-3352.947
Compound 2	C_s	1	-3353.089
Compound 2	C_s	3	-3353.071

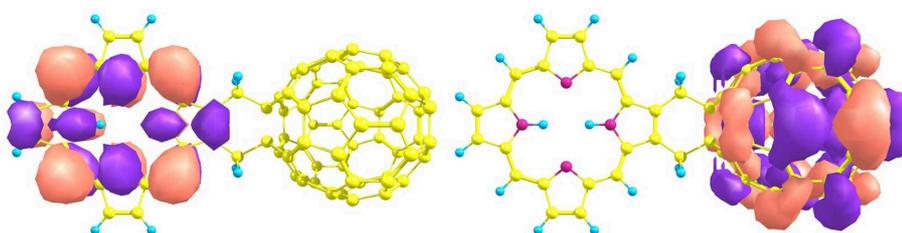


Fig. 2. Highest occupied (left) and lowest unoccupied (right) MO of P-F

The results of ten electronic transfers in P-F structure are presented in the Table 3. HOMO and LUMO symbols are changed by H and L, correspondingly, for short. Every electron transfer is combination of one-electron excitations from occupied on unoccupied MO. Such excitations with their weight in corresponding transfers are also presented in the Table 3 in percents. The

Table 2. Energies and general localizations of valence field MO of P-F

MO	Energy, eV	Localization
HOMO-4	-5.84	F
HOMO-3	-5.82	F
HOMO-2	-5.68	F
HOMO-1	-5.35	P
HOMO	-5.29	P
LUMO	-3.14	F
LUMO+1	-3.01	F
LUMO+2	-2.77	F
LUMO+3	-2.37	P
LUMO+4	-2.31	P

wavelengths of these transfers are equal 664 and 621 nm, correspondingly. So, they are in the orange and the red diapasons of electromagnetic irradiation spectra, which is optimal for potential photovoltaic elements in the purposes of their effective use for conversion of sun energy to electric. Concerned transfers are formed due to one-electron excitations from HOMO on LUMO and LUMO+1. Since the energy of heat oscillations can be estimated approximately as kT , where

k is Boltzman constant and T is temperature, so it is equal 0.02 eV at the usual conditions. It means that HOMO, LUMO and LUMO+1 separately are not degenerated or pseudo-degenerated electron states, because the difference of their energies from energies of neighboring MO is much larger than energy of heat oscillations (Table 2). Therefore the coefficients g_i and g_j of equation mentioned above are equal to one. In this case the lifetimes of the first and the forth excited states can be estimated using this equation and are equal 330 and 1 μ s, correspondingly. It is sufficiently larger than average lifetime of excited states most of atoms and molecules, therefore it can be concluded that these two excited states are long-living. The absence of MO degeneracy is confirmed by the fact that F structure distorts a little bit due to covalent interaction. Initially F has icosahedron (I_h) symmetry. It has been shown that the symmetry of fullerene detached from whole structure is C_{2v} that is a symmetry group of whole dyad. Molecules of such symmetry group do not have degeneracy of electron states, which has a place when structure has at least one rotation axis of the third order. *Dyads linked non-covalently*. By analogy with the work

Table 3. Electron transfers in P-F

N ^o	λ , nm	f , 10^{-3}	One-electron excitations (their weights)
1	664	0.02	H \rightarrow L (100%)*
2	655	2.11	H-3 \rightarrow L+1 (2%), H-2 \rightarrow L (97%)
3	647	~ 0	H-3 \rightarrow L (12%), H-1 \rightarrow L (88%)
4	621	4.01	H \rightarrow L+1 (100%)
5	612	~ 0	H-5 \rightarrow L (11%), H-3 \rightarrow L (3%), H-2 \rightarrow L+1 (85%)
6	611	~ 0	H-3 \rightarrow L (82%), H-2 \rightarrow L+1 (5%), H-1 \rightarrow L (12%)
7	603	0.01	H-1 \rightarrow L+1 (98%)
8	602	0.03	H-4 \rightarrow L (98%)
9	562	~ 0	H-5 \rightarrow L (82%), H-4 \rightarrow L+2 (6%), H-3 \rightarrow L (3%), H-2 \rightarrow L+1 (8%)
10	561	0.05	H-5 \rightarrow L+1 (84%)

*It was noted the values, which was larger than 1%.

[19] the structure called C6C6/90 $^\circ$ there and P \cdots F here has been modeled, where P and F were not linked covalently (3). There were some possible orientations of P and F relative to each to other there. The choice of C6C6/90 $^\circ$ was resulting from the fact that its geometrical characteristics obtained from DFT calculations were much closer to experimental values. The structure of this compound can be presented by the next way. F molecule is oriented along the axis coming perpendicular to porphyrin plane through its mass center in the way when centers of two opposite edges are cited on this axis. Every one of noted edges has a place between two six-fold rings at that. It has been shown [19] by DFT methods that distance from porphyrin plane to nearest carbon atoms of F is equal 3.1 \AA in the case when PBE exchange-correlation potential was used with SVP basis set and equal 3.5 \AA in the case of B3LYP exchange-correlation potential. X-ray diffraction results show the values in the interval of 2.7–3.0 \AA [28], but they were obtained for a chain of porphyrin and fullerene structures taking place there one by one. Therefore these values should be less than in the case of structure consisting of singles P and F. Our calculations have indicated that presented distance is equal 3.3 \AA that is allowable value, because the difference with experimental data is negligible. Energy values and localization of valence field MO are presented in Table 4. It is obvious that orbitals energies are differed slightly

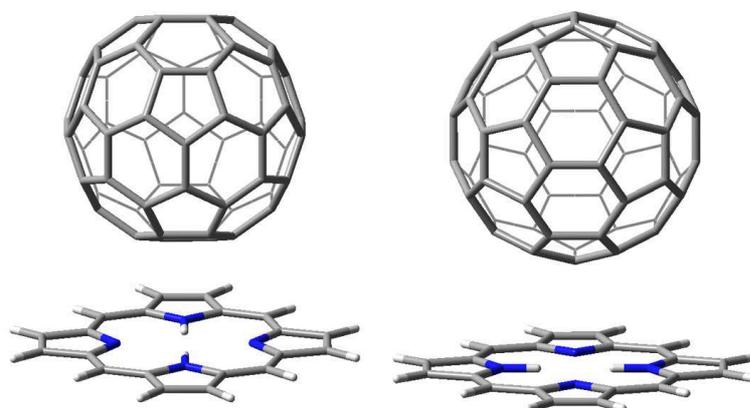


Fig. 3. The P···F optimized structure with symmetry C_{2v} (from two sides of view)

from mentioned above for P-F structure and mentioned in the work [19] (not more than 0.2 eV). It is the same situation for MO localization, because this one is similar to P-F compound and the same with presented early [19]. Therefore we do not produce the Mo schemes here, because they are fully agree with published by Toivonen and co-authors. The same differences of energies can be explained by the fact that another basis set of atomic orbitals has been used in the mentioned work. Following the criterion mentioned above for assessment of electron states degeneracy it

Table 4. Energies (energy relative to HOMO) and localization of valence field MO of P···F

MO	Energy,eV	Localization
HOMO-4	-5.80 (-0.57)	F
HOMO-3	-5.80 (-0.57)	F
HOMO-2	-5.80 (-0.56)	F
HOMO-1	-5.38 (-0.15)	P
HOMO	-5.23 (0.00)	P
LUMO	-3.05 (2.18)	F
LUMO+1	-3.04 (2.19)	F
LUMO+2	-3.04 (2.20)	F
LUMO+3	-2.33 (2.90)	P
LUMO+4	-2.31 (2.92)	P

should be noted that HOMO-4, HOMO-3 and HOMO-2 are pseudo-degenerated, taking into account the fact that it is not possible to call them as degenerated due to the symmetry group used. LUMO, LUMO+1 and LUMO+2 are also pseudo-degenerated and localized on fullerene. The low energy splitting in the first and the second groups is resulting from weak interaction of F and P, which does not follow the essential distortion of the fullerene structure. Therefore it keeps high symmetry that has been shown by analyzing of fullerene separately. Its symmetry agrees with tetrahedron (T) point group symmetry, and electron states of such type of symmetry molecules can be degenerated.

This fact results from the nature of the electron transfers (Table 5). They can be separated

by the groups, following to wavelengths values and one-electron excitations nature. All of ten transfers are carried out on the first three LUMO as in the case of P-F. The transfers from HOMO (1–3) are the first group; from HOMO-1 (4–6) is the second group; from much lower lying occupied MO is the third group. It is obvious that the first and the second groups' transfers are much more interesting because they lead to formation of the system with separated charges taking a place due to electron crossing from P to F. The transfers number 3 and 4 should be noted in these two groups because they have non-zero oscillator strengths resulting to much high probability of them, and their intensity in the spectrum must be much significant than the one of other lines. The wavelengths of the two transfers noted are in the red field of spectrum. The third transfer

Table 5. Electron transfers in P···F

№	λ , nm	f , 10^{-3}	One-electron excitations (their weights)
1	694	~ 0	H \rightarrow L+1 (99%)*
2	693	~ 0	H \rightarrow L+2 (99%)
3	689	0.34	H \rightarrow L (99%)
4	637	0.04	H-1 \rightarrow L+1 (99%)
5	636	~ 0	H-1 \rightarrow L+2 (99%)
6	635	~ 0	H-1 \rightarrow L (99%)
7	595	~ 0	H-5 \rightarrow L+1 (7%), H-4 \rightarrow L+2 (2%), H-3 \rightarrow L+1 (8%), H-2 \rightarrow L (83%)
8	594	~ 0	H-6 \rightarrow L+2 (12%), H-5 \rightarrow L (18%), H-3 \rightarrow L (63%), H-2 \rightarrow L+1 (5%)
9	593	0.03	H-6 \rightarrow L+1 (29%), H-4 \rightarrow L (37%), H-2 \rightarrow L+2 (33%)
10	591	~ 0	H-6 \rightarrow L+2 (3%), H-5 \rightarrow L (20%), H-2 \rightarrow L+1 (76%)

*It was noted the values, which was larger than 1%.

has the maximal intensity, but it is lower that in the case of P-F structure. Apparently, it results from the absence of connecting elements between P and F of P···F along which the electron transfer must happen with much higher probability than in the case of porphyrin and fullerene π -orbitals overlap only. And, as a result, it is also can be explained by lower polarizability of the structure, that leads to lower value of dipole momentum which is equal 1.49 D.

Since three LUMO are pseudo-degenerated, it follows that $g_i=3$ for both electron transfers. HOMO and HOMO-1 do not have degeneracy therefore $g_j=1$ for both transfers. So, the lifetime in the third and the fourth excited states are equal, correspondingly, 63 and 456 μ s. It is a little higher than in the case of excitation of P-F structure.

The values of transfers wavelengths at the converting their to energy units, the order of transfers and one-electron excitation included in these transfers are different from those obtained earlier in [19]. It results from the use of different atomic orbitals basis set in the calculations, because it is known that TDDFT method is sensible to the basis set chose [29].

3. Conclusion

Through photoinduced excitation it should be observed the formation of presented objects with separated charges taking a place due to electron transfer from porphyrin to fullerene. The lifetime of excited states is quite large and equal to microseconds. The wavelengths of transfer

induced irradiation are in the red field of spectrum. The presented spectral features in general are satisfied for potential use of studied compounds in the way of photovoltaic elements.

It should be noted that covalent binding of P with F distorts a little the structure of the last one. It leads to the F symmetry decreasing, which is accompanied by the degeneracy losing of molecular orbitals localized on it. Excited state lifetime of the whole dyad decreases as a result. Therefore the dyad chains non-bonded covalently are appropriate to use as the photovoltaic elements. The negative moment of P···F relatively to P-F is sufficient low intensity of electromagnetic radiation sorption of the wavelengths mentioned above.

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Возбужденные электронные состояния диад порфирина-фуллера с различным типом связывания

Павел О. Краснов
Юлия М. Милютина

Основными требованиями к искусственным фоточувствительным системам являются поглощение света в видимой области спектра, возможность образовывать долгоживущие возбужденные электронные состояния и системы с разделенными зарядами. В качестве потенциальных материалов, обладающих указанными свойствами, рассматриваются донорно-акцепторные диады порфирина-фуллера. В работе представлены результаты квантово-химических расчетов методом теории функционала плотности геометрии, основных и возбужденных электронных состояний данных объектов с двумя типами связывания: порфирин и фуллерен связаны ковалентно и ковалентно не связаны, а взаимодействуют посредством межмолекулярных сил. Показано, что в первом случае образование систем с разделенными зарядами происходит более вероятно, чем во втором, но при этом время жизни возбужденных состояний значительно меньше.

Ключевые слова: порфирин-фуллерен, возбужденное состояние, донорно-акцепторная диада.