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# The Nature of Absorption Electronic Spectrums of Porphyrin–Fullerene Dyads with a Different Type of Bonding

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**Abstract**

Donor–acceptor porphyrin–fullerene dyads are promising materials for the creation of artificial photosensitive systems. The general requirements for these compounds are light absorption at the visible field of the spectrum, long excited state lifetimes and the possibility of forming a system with separated charges. The DFT quantum–chemical calculations of geometry and the ground and excited electronic states of such structures with two kinds of bonds (covalently and non–covalently bound porphyrin and fullerene) are presented in this work. The formation of a system with separated charges is more probable in the case of covalent bonding than in the case of non–covalent bonding, but the lifetimes of excited states in the first case are sufficiently lower than in the second case.

**Keywords.** Systems with separated charges; photoinduced electron transfer; quantum–chemical simulation; photovoltaic elements; porphyrin–fullerene dyad.

**Abbreviations and notations**

| | |
|---|---|
| B, benzene | P, porphyrin |
| F, fullerene | P–2B–F, porphyrin–fullerene dyad linked by two benzene rings |
| HOMO, the highest occupied molecular orbital | P–B–F, porphyrin–fullerene dyad linked by benzene ring |
| MO, molecular orbital | P–F, porphyrin–fullerene dyad linked covalently |
| LUMO, the lowest unoccupied molecular orbital | P···F, porphyrin–fullerene dyad linked non–covalently |

## 1 INTRODUCTION

Photovoltaic elements are devices for converting light energy (including sun light) to electric energy. Investigations are currently aimed to obtain materials with 30–60% of power conversion efficiency [1]. Photovoltaic elements are also being used to create polymer films from organic substances. They become excited under light with a next electron transfer [2–10] to an electrode. Their use over inorganic materials is advantageous because of the relative low cost of obtaining a plastic structure for covering surfaces curved for architecture compatibility [2].

Organic semiconductor films can be used with good chromophores to produce optoelectronic

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devices [9]. The variability of their band gap by chemical modifications and their high–charge carrier mobility make these substances competitive for amorphous silicon.

Experimental application of organic polymer films began more than 20 years ago [3]; these films are usually placed between two electrodes on a glass surface. However, they are not used often in practice because of their low power conversion efficiency (6%) [4] due to the small spectral overlap of organic substances with sun light absorption [5]. The low intensity of red light absorption is especially problematic [6]. Therefore, the creation of new substances with satisfactory spectral characteristics is needed, and several of these substances are known at the present time [5–10].

Organic photovoltaic elements consist of two parts – an electron donor and acceptor. For the donor, groups of small heterocyclic molecules (pyrrole or pyridine) are used as heterocyclic macrocycles (porphyrins and phthalocyanines) that absorb light within the visible spectrum and are included in photosensitive compounds, such as chlorophyll. Fullerenes serve as electrons acceptors because of their unique ability to accumulate electrons [11] with the formation of multi–anions. Different substances, which are potential photovoltaic elements with fullerenes and porphyrins, have been examined by experimental [12–15] and theoretical [16–20] methods, and can be combined into dyads and triads depending on the quantity of the component parts.

In such types of substances, a photoinduced electron crosses from porphyrin (P) to $C_{60}$ fullerene (F). These molecules can be covalently linked [16–18] or non–linked [19]. Complex compound formation with atoms of transition metals binding a fullerene molecule in the center of porphyrin has been studied [20]. Electron transfers from the occupied molecular orbitals localized on porphyrin on the unoccupied molecular orbitals localized on fullerene are especially interesting. Many works have addressed the geometrical, energetic, electron and spectral characteristics of dyads [12–20].

Photoinduced electron transfer leads to the formation of a system with separated charges. The lifetime should be large enough for the effective conversion of excitation energy into electric energy with electron transfer from fullerene on an electrode without dispersion, such as by heat. The formation of electron states with long lifetimes increases the efficiency of power conservation.

Further understanding of photochemical processes involving photoinduced electron transfer in dyads is important for the synthesis of artificial photosystems used for creation of molecular electronic devices. Our work and investigations by other groups have aimed to study the electron structure features of donor–acceptor dyads and their changes due to light.

In this work, we present the results of our quantum–chemical calculations of the molecular and electronic structures of several compounds containing porphine (the simplest porphyrin) bound covalently (P–F) or non–covalently (P···F) (by intermolecular forces only) to fullerene $C_{60}$. The electronic Absorption spectra and lifetimes of the excited states were calculated. We show that the spectral properties, such as wavelengths and oscillator strengths, and excited state lifetimes depend on the geometrical structures of the compounds and especially on the distance between the mass centers of P and F.

## 2 COMPUTATIONAL DETAILS

Density functional theory (DFT) with B3LYP [21] exchange–correlation potential and the 6–31G(p,d) atomic basis set was used for the calculations. The geometry of each structure was initially optimized, and then their excited states were calculated by the Time–Dependent DFT (TDDFT) [22–24]. It is well known that singlet–triplet and triplet–singlet electronic excitations have low intensities due to restrictions of such kinds of electron transfers. Therefore singlet–singlet excitations only were in the focus of this work, and restricted type of wave function was used. All calculations were done using the NWChem 5.1 software package [25,26].

The lifetimes of the excited states were estimated from the wavelengths ($\lambda$) and oscillator strengths ($f$) by

$$\tau = \frac{g_i}{g_j}\frac{C\lambda^2}{f}, \tag{1}$$

where $C$=1.49919·10$^{-14}$ nm$^{-2}$·s is a constant, $g_i$ and $g_j$ are the numbers of degenerate states on energy levels $i$ and $j$, respectively, between which a transition occurs [27].

## 3 RESULTS AND DISCUSSION

*Dyads linked covalently*. The P–F dyad structures for two examples of covalently bound P and F molecules were modeled and studied. In the first example (compound 1), the P molecule was linked between two six–membered rings of F (Figure 1, left). In compound 2, the P molecule was bound between the six– and five–membered rings of F (Figure 1, right). The similar structure was experimentally observed and described in the work [28].

Binding occurred by means of two methyl groups: one bound to a carbon atom of F and one to a carbon atom of the P pyrrole group.

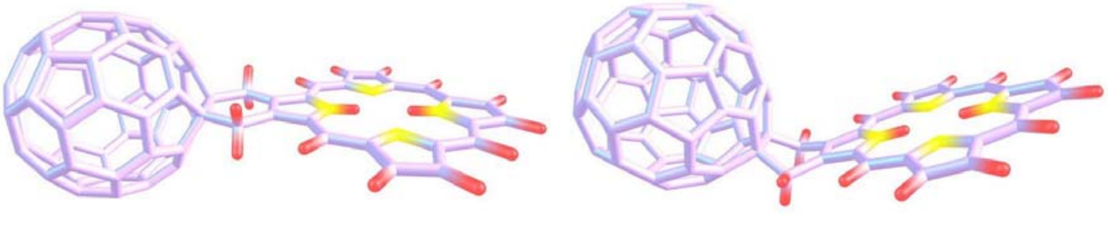

**Figure 1.** Models of compounds 1 (left) and 2 (right) optimized with $C_s$ symmetry restriction.

Geometry optimization of both structures was performed with symmetry restrictions: $C_s$ for compounds 1 and 2 and $C_{2v}$ for compound 1. Molecules were considered to have two spin states with multiplicities of 1 and 3. The calculated values of the total energies are presented in Table 1.

The structures were modeled so that the carbon atoms of the methyl groups and P were in one plane before the optimization procedure. There were no distortions of compound 1 after optimization. By contrast, compound 2 experienced sufficient distortion and the carbon atoms of the methyl groups and P are in different planes (Figure 1, right).

Based on the results presented in Table 1, the structure with P connected along the bond between the six–membered rings of F with a spin multiplicity of 1 and $C_{2v}$ symmetry is preferable because the total energy of the structure was minimized. Notably, the energy difference of compounds is small (0.019 a.u. or 0.52 eV). Therefore, the next calculations of covalently linked dyads were done for compound 1 and its derivatives with the same type of binding. In all cases, including P···F, $C_{2v}$ symmetry restriction and a spin multiplicity of 1 were applied.

**Table 1.** Total energies of covalently linked dyads

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

In the next step, the P–B–F and P–2B–F structures of dyads bound covalently, where an increasing distance between P and F was executed by adding two consecutive benzene (B) rings and the resulting compound was studied (Figure 2). There were no distortions of the compounds' geometries after optimization. Benzene rings were chosen as possible linkers from an idea that it should help to electron motion from porphyrin to fullerene through benzenes' $\pi$–conjugated systems, which are well movable.

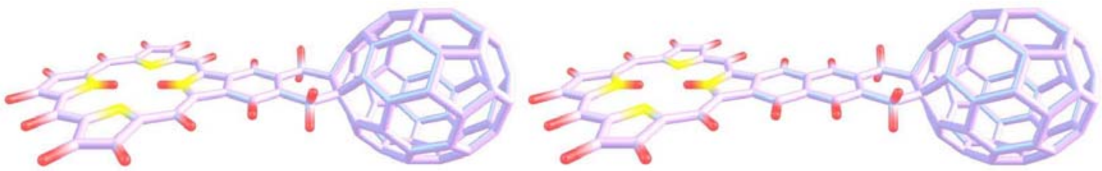

**Figure 2.** Models of P–B–F (left) and P–2B–F (right) structures optimized with $C_{2v}$ symmetry restriction

The distances between the mass centers of P and F in P–F, P–B–F and P–2B–F are 6.89, 9.38 and 11.84 Å, respectively, and their dipole moments are 2.79, 2.11 and 1.64 D.

The molecular orbitals (MOs) of the valence field are represented by the $\pi$–orbitals of P and F (at least the five highest occupied and five lowest unoccupied MOs) (Figure 3).

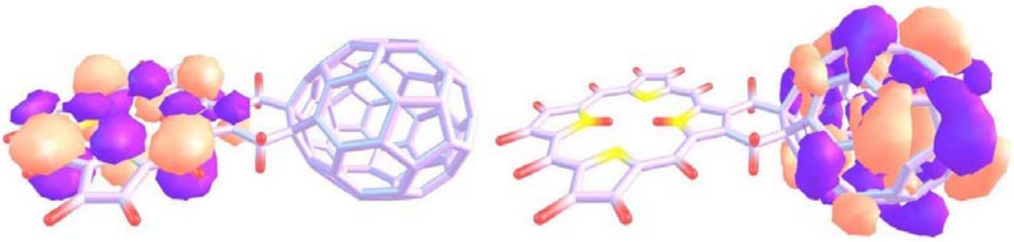

**Figure 3.** Highest occupied (left) and lowest unoccupied (right) MO of P–F

The energies and general localizations of these orbitals are presented in Table 2. The HOMO is the highest occupied MO, HOMO–1 is second highest MO, etc.; the LUMO is the lowest unoccupied MO, LUMO+1 is second lowest MO and so on.

**Table 2.** Energies and general localizations of the valence field MO of P–F

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

The introduction of benzene rings in P–F to form P–B–F and P–2B–F significantly changed the nature of the valence field MO of P–F. The overlapping of the conjugated electronic $\pi$–systems of B and P led to decreased MO localization (Figure 4), and the order of the MO changed due to their different energies (Table 3).

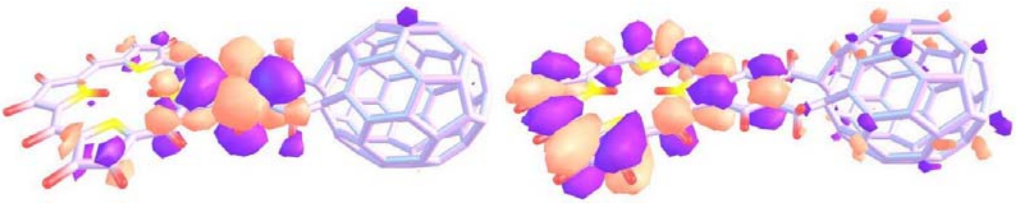

**Figure 4.** HOMO–3 (left) and LUMO+2 (right) of P–B–F.

The electronic structures of P–B–F and P–2B–F did not allow for us to consider these compounds as potential photovoltaic elements. Their valence fields were generally presented by the orbitals localized on the fullerene or belonging to different parts of the dyad at one time. Therefore, it was impossible to get clear transfers of electrons from porphyrin to fullerene. Moreover, HOMO localization on the electron donor (porphine) and LUMO localization on the electron acceptor (fullerene) are desirable, as observed for P–F but not for these two compounds.

**Table 3.** Energies and general localizations of valence field MO of P–B–F and P–2B–F

| MO | P–B–F | | P–2B–F | |
|---|---|---|---|---|
| | Energy, eV | Localization | Energy, eV | Localization |
| LUMO+4 | –2.18 | F | –2.11 | P+B |
| LUMO+3 | –2.40 | F | –2.45 | P |
| LUMO+2 | –2.78 | P+B+F | –2.78 | B |
| LUMO+1 | –3.02 | F+P+B | –3.03 | F |
| LUMO | –3.15 | F | –3.15 | P |
| HOMO | –5.17 | F | –5.03 | F |
| HOMO–1 | –5.27 | F | –5.25 | F+B |
| HOMO–2 | –5.68 | F | –5.68 | P |
| HOMO–3 | –5.82 | B+P | –5.81 | F |
| HOMO–4 | –5.85 | F | –5.85 | F |

The results of ten electronic transfers in the P–F structure are presented in Table 4. Every electron transfer is a combination of a one–electron excitation from an occupied to unoccupied MO. Such excitations and the weight of their corresponding transfers are presented in Table 4.

**Table 4.** Electron transfers in P–F

| № | $\lambda$, nm | $f$, $\times 10^{-3}$ | One–electron excitations (weights)* |
|---|---|---|---|
| 1 | 664 | 0.02 | H→L (100 %) |
| 2 | 655 | 2.11 | H–3→L+1 (2 %), H–2→L (97 %) |
| 3 | 647 | ~0 | H–3→L (12 %), H–1→L (88 %) |
| 4 | 621 | 4.01 | H→L+1 (100 %) |
| 5 | 612 | ~0 | H–5→L (11 %), H–3→L (3 %), H–2→L+1 (85 %) |
| 6 | 611 | ~0 | H–3→L (82 %), H–2→L+1 (5 %), H–1→L (12 %) |
| 7 | 603 | 0.01 | H–1→L+1 (98 %) |
| 8 | 602 | 0.03 | H–4→L (98 %) |
| 9 | 562 | ~0 | H–5→L (82 %), H–4→L+2 (6 %), H–3→L (3 %), H–2→L+1 (8 %) |
| 10 | 561 | 0.05 | H–5→L+1 (84 %) |

*Values larger than 1%

These transfers occurred at wavelengths of 664 and 621 nm. They are in the orange and red diapasons of the electromagnetic irradiation spectrum, which is optimal for the use of photovoltaic elements in the conversion of solar to electric energy. The concerned transfers are formed due to one–electron excitations from HOMO to LUMO and LUMO+1. The energy of the heat oscillations can be estimated as $kT$, where $k$ and $T$ are the Boltzmann constant and temperature, respectively, and is 0.02 eV under standard conditions. Therefore, the HOMO, LUMO and LUMO+1 are not degenerate or pseudo–degenerate electron states because an energy difference from the neighboring MO is much larger than the energy of the heat oscillations (Table 2). Therefore, the coefficients $g_i$ and $g_j$ of the equation 1 are equal one. The lifetimes of the first and forth excited states can be estimated using this equation and are equal to 330 and 1 μs, respectively, that has a place in the interval of values experimentally observed early [29] for the similar kinds of objects. These values are sufficiently larger than the average lifetimes of the excited states of most atoms and molecules. The absence of MO degeneracy is supported by the slight distortion of the F structure due to the covalent interaction. Initially F had icosahedron ($I_h$) symmetry. Fullerene detached from the whole structure adopts $C_{2v}$ symmetry, which is the symmetry of the whole dyad. Molecules of such symmetry group do not have degeneracy of electron states, which occurs when the structure has at least one third–order rotation axis.

*Dyads linked non–covalently*. In accordance with another work [19] that modeled a C6C6/90° structure, the P and F of P···F were not linked covalently (Figure 5). There are several possible orientations of P and F relative to each to other there. The C6C6/90° was chosen because these geometrical characteristics from DFT calculations were much closer to the experimental values. The F molecule is oriented along the axis perpendicular to the porphyrin plane through its mass center; the centers of the two opposite edges are found on this axis. Every one of the noted edges has a place between the two six–membered rings. Pervious results from DFT methods [19] revealed that the distance from the porphyrin plane to the nearest carbon atom of F was equal to 3.1 Å or 3.5 Å when a PBE exchange–correlation potential with an SVP basis set or B3LYP exchange–correlation potential, respectively. X–ray diffraction experiments revealed distances of 2.7–3.0 Å [30], but they were obtained for individual porphyrin chain and fullerene structures. Therefore, these values should be less than that of the structure consisting of a single P and F moiety. Our calculations indicated a distance of 3.3 Å, which is acceptable because the difference from experimental data is negligible.

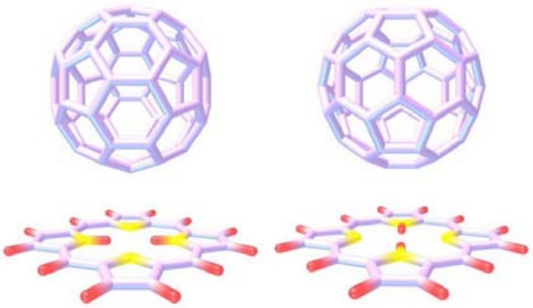

**Figure 5.** The P···F optimized structure with $C_{2v}$ symmetry (from two view points).

The energy values and localization of the valence field MO are presented in Table 5. The orbital energies differed slightly from those of the P–F structure and from previously reported values [19] (not more than 0.2 eV). The results from MO localization were also similar to those from the P–F compound and with previously presented work [19]. Therefore, we do not produce the MO schemes because they are identical to those published by Toivonen and co–authors. Some differences in energy can be explained due to the use of another basis set of atomic orbitals.

Following the criterion mentioned above for the assessment of the electron state degeneracy and because it is not possible for degeneracy due to the symmetry group, the HOMO–4, HOMO–3 and HOMO–2 are pseudo–degenerate. In addition, the LUMO, LUMO+1 and LUMO+2 are pseudo–degenerate and localize on fullerene. Low energy splitting in the first and second groups results from weak interactions of F and P, which do not lead to the essential distortion of the fullerene structure. Therefore, the structure maintains high symmetry of the tetrahedron (*T*) point group with degenerate electron states.

**Table 5.** Energies (energy relative to HOMO) and valence field MO localization of P···F

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

The nature of electron transfers (Table 6) allows for them to be separated into groups, according to the wavelengths and one–electron excitations. All of the ten transfers are carried out on the first three LUMO, such as in P–F. The first group consists of transfers from HOMO (1–3); the second group is from HOMO–1 (4–6); and the third group is from the much lower occupied MO. The transfers from the first and second groups are interesting because they lead to the formation of a system with separated charges due to electron crossing from P to F. Transfers 3 and 4 are more probable in these two groups because they have non–zero oscillator strengths, and their intensity in the spectrum should be more significant than that of the other lines.

**Table 6.** Electron transfers in P···F

| № | $\lambda$, nm | $f$, $\times 10^{-3}$ | One–electron excitations (weights)* |
|---|---|---|---|
| 1 | 694 | ~0 | H→L+1 (99%) |
| 2 | 693 | ~0 | H→L+2 (99%) |
| 3 | 689 | 0,34 | H→L (99%) |
| 4 | 637 | 0,04 | H–1→L+1 (99%) |
| 5 | 636 | ~0 | H–1→L+2 (99%) |
| 6 | 635 | ~0 | H–1→L (99%) |
| 7 | 595 | ~0 | H–5→L+1 (7%), H–4→L+2 (2%), H–3→L+1 (8%), H–2→L (83%) |
| 8 | 594 | ~0 | H–6→L+2 (12%), H–5→L (18%), H–3→L (63%), H–2→L+1 (5%) |
| 9 | 593 | 0,03 | H–6→L+1 (29%), H–4→L (37%), H–2→L+2 (33%) |
| 10 | 591 | ~0 | H–6→L+2 (3%), H–5→L (20%), H–2→L+1 (76%) |

*Values larger than 1%

The wavelengths of the two transfers are in the red field of the spectrum. The third transfer has the highest intensity, but is lower than in the P–F structure due to the absence of connecting elements between P and F within P···F than when only the porphyrin and fullerene $\pi$–orbitals overlap. As a result, the lower polarizability of the structure leads to a lower value of the dipole moment (1.49 D).

Because three LUMO are pseudo–degenerate, $g_i$=3 for both electron transfers. The HOMO and HOMO–1 are not degenerate, so $g_j$=1 for both transfers. Therefore, the lifetimes in the third and fourth excited states are 63 and 456 μs, which are slightly higher than in the excitation of the P–F structure.

The transfer wavelengths, their conversion to energy units, the order of transfers and one–electron excitation included in these transfers are different from previously obtained results [19]. These differences are due to the use of different atomic orbital basis sets in the calculations; the TDDFT method is the most sensible choice as the basis set [31].

The distance between the P plane and its nearest F carbon atom in experimentally observed structure is less than in the calculated P···F structure herein. Additional calculations were performed to determine the influence of this distance on the compound electronic structure and Absorption spectrum. When the distance was changed by 0.5 Å in the both directions and became 2.8 and 3.8 Å, respectively. Geometry optimization was not performed. The change in distance was realized by P atom displacement on the noted value along the second–order rotation axis.

A slight change (Table 7, Figure 6) was observed in the MO localization with decreasing distance. As a result, it becomes difficult to separate the MOs of P or F because they become localized on both parts of the structure at one time. Therefore, there was a higher disappearance of electronic state degeneration, but they can still be assumed to be pseudo–degenerate if accounting for energy differences between them.

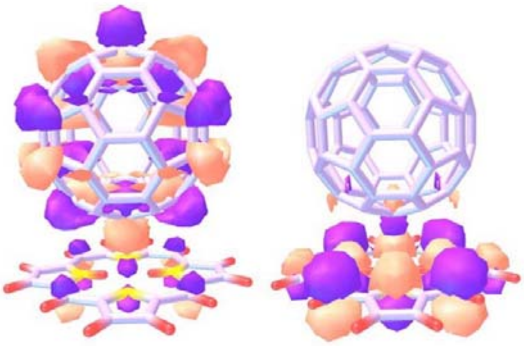

**Figure 6**. HOMO–4 (left) and HOMO (right) of P···F (2.8 Å)

**Table 7**. Energies and general localizations of valence field MO of P···F at different distances between porphyrin and its nearest fullerene carbon atom

| MO | P···F (2.8 Å) | | P···F (3.8 Å) | |
|---|---|---|---|---|
| | Energy, eV | Localization | Energy, eV | Localization |
| LUMO+4 | –2.37 | P | –2.28 | P |
| LUMO+3 | –2.39 | P | –2.30 | P |
| LUMO+2 | –2.97 | F | –3.07 | F |
| LUMO+1 | –2.98 | F | –3.07 | F |
| LUMO | –3.00 | F | –3.08 | F |
| HOMO | –5.25 | P+F | –5.21 | P |
| HOMO–1 | –5.43 | P | –5.35 | P |
| HOMO–2 | –5.72 | F | –5.83 | F |
| HOMO–3 | –5.73 | F | –5.83 | F |
| HOMO–4 | –5.75 | F+P | –5.83 | F |

The different electronic structures led to changes in the nature and energy of the electronic transfers (Table 8). The wavelengths of the first and second groups decreased by an average of 15 nm and 22 nm, respectively, whereas the wavelengths of the third group basically did not change. The number of one–electron excitations in every transfer and intensities (oscillation strengths) of the last transfers increased.

**Table 8.** Electron transfers in P···F (2.8 Å)

| № | $\lambda$, nm | $f$, $\times 10^{-3}$ | One–electron excitations (weights)* |
|---|---|---|---|
| 1 | 681 | 0.02 | H–4→L+1 (3%), H→L+1 (96%) |
| 2 | 676 | ~0 | H–4→L+2 (3%), H→L+2 (96%) |
| 3 | 675 | 0.45 | H→L (98%) |
| 4 | 616 | ~0 | H–6→L (11%), H–3→L (6%), H–1→L (82%) |
| 5 | 616 | 0.20 | H–6→L+1 (7%), H–2→L (3%), H–1→L+1 (90%) |
| 6 | 609 | 0.01 | H–6→L+2 (2%), H–5→L (2%), H–3→L+2 (2%), H–1→L+2 (92%) |
| 7 | 598 | 0.05 | H–3→L+1 (12%), H–2→L (83%), H–1→L+1 (3%) |
| 8 | 594 | ~0 | H–5→L+2 (2%), H–3→L (33%), H–2→L+1 (62%), H–1→L (2%) |
| 9 | 589 | ~0 | H–6→L+2 (4%), H–4→L+1 (2%), H–3→L+2 (92%) |
| 10 | 589 | ~0 | H–6→L (9%), H–5→L+2 (39%), H–3→L (22%), H–2→L+1 (22%), H–1→L (7%) |

*Values larger than 1%

When the distance between P and F increased, we observed the opposite response. First, MO energy splitting did not occur; however, there were some changes in their energies with decreasing distance. Second, the valence field MO localization was preserved and the orbitals can be presented schematically in the same way as for P···F without the distance changing. Third, the number of one–electron excitation in each transfer decreased (Table 9). The third transfer occurred due to electron excitation only from the HOMO to LUMO. In addition, the intensity (oscillator strength) of the transfers decreased. The wavelength of the transfers increased by 11 and 12 nm on average for the first and second group, respectively; by contrast, the wavelengths of the third group basically did not change.

**Table 9.** Electron transfers in P···F (3.8 Å)

| № | $\lambda$, nm | $f$, $\times 10^{-3}$ | One–electron excitations (weights)* |
|---|---|---|---|
| 1 | 705 | ~0 | H→L+2 (99%) |
| 2 | 705 | ~0 | H→L+1 (99%) |
| 3 | 700 | 0,10 | H→L (100%) |
| 4 | 649 | ~0 | H–1→L+1 (100%) |
| 5 | 649 | ~0 | H–1→L+2 (100%) |
| 6 | 647 | ~0 | H–1→L (100%) |
| 7 | 594 | ~0 | H–5→L+1 (13%), H–4→L (78%), H–3→L+1 (5%), H–2→L+2 (3%) |
| 8 | 594 | ~0 | H–6→L+2 (16%), H–5→L (21%), H–3→L (62%) |
| 9 | 593 | ~0 | H–6→L+1 (30%), H–4→L+2 (33%), H–2→L (37%) |
| 10 | 593 | ~0 | H–6→L (4%), H–5→L+2 (12%), H–3→L+2 (34%), H–2→L+1 (49%) |

*Values larger than 1%

Because the structure was not optimized, the fullerene geometry remained the same and its high symmetry was preserved. The MO energy changes were caused by the influence of the external electric field of the P charges polarizing the F molecule. With a smaller distance between P and F, the dipole moment of the whole structure increased by 0.77 D. With a greater distance, the dipole momentum decreased by 0.39 D. The non–linear dependence of the dipole moment on distance reveals the redistribution of the charge density at various distances. In particular, the MO energies, localizations (Table 7) and total effective charge of F change. The total effective charge is $19 \cdot 10^{-5}$ at the equilibrium state, $61 \cdot 10^{-5}$ at a shorter distance and $5 \cdot 10^{-5}$ at a longer distance. A decreased effective charge was previously observed with increasing distance between fullerene and porphyrin [32]. The charge values were much higher there than those presented here; both parts of the dyad were bonded covalently, but were oriented each to other in a similar way as in our study.

## 4 CONCLUSIONS

Through photoinduced excitation, the presented objects should form with separated charges due to electron transfer from porphyrin to fullerene, except for those having benzene rings. The lifetime of the excited states is large (microseconds), and the wavelengths of transfer induced irradiation are in the red range of the spectrum. The presented spectral features are satisfactory for the potential use of studied compounds as photovoltaic elements.

In the case of compounds with benzene rings, sufficient changes of the valence field electronic structures within the dyads were observed because of the benzene rings conjugated with the electronic $\pi$–systems of porphyrin and fullerene. It is difficult to produce a system with separated charges because the HOMOs, from which the electron transfer must occur, are localized on fullerene. In addition, the LUMOs do not belong to fullerene, but are of different parts of dyads. Therefore, we conclude that porphine and fullerene in the dyad with covalent binding should be linked by single bonds preventing of common electronic $\pi$–system formation.

Covalent binding of P with F slightly distorts the structure of F. Accordingly, the symmetry of F decreases, which is accompanied by the loss of the degeneracy of molecular orbitals localized on it. In addition, the excited state lifetime of the whole dyad decreases. Therefore, the non–covalently bound dyad chains are appropriate to use as the photovoltaic elements. The negative moment of P···F relatively to P–F is of sufficient low intensity for the electromagnetic radiation absorption of the wavelengths described above. The advantage of non–covalently bound dyads is the constant structure of their Absorption electronic spectra. Even if the last one depends on the distance between porphyrin and fullerene, the resulting changes are markedly smaller than when groups are covalently bound.

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