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Theoretical Study of Bis-porphyrin-Fullerene Supramolecular Complex Designed for Photovoltaic Devices

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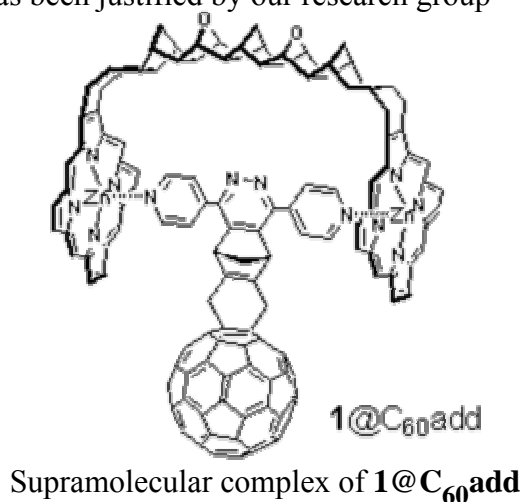
Abstract. A computational study of a bis-porphyrin-fullerene supramolecular complex designed for photovoltaic devices using semiempirical AM1 method is presented. The study of the frontier molecular orbitals in the ground state has revealed that porphyrin part is an electron donor moiety, while fullerene guest is an electron acceptor. The electronic properties of the excited singlet states of **1@C$_{60}$add** complex indicate electron transfer from porphyrin to fullerene moiety.

Introduction. Porphyrin-fullerene supramolecular systems and dyads have been extensively studied in order to examine donor-acceptor interactions. These systems are highly interesting in view of the possible supramolecular modulation of electronic properties of fullerenes.[1] Donor-acceptor interactions within fullerene-porphyrin architectures are important for multi-component model systems designed for transmission and process of solar energy. [2] Various fullerene-porphyrin donor-acceptor dyads were reported [3],[4],[5] and photovoltaic cells based on a fullerene-porphyrin dyads exhibited good quantum efficiency.[6],[7] Most of these supramolecular photocurrent-generating devices are based on covalently linked components using fullerenes and porphyrins. There are also literature examples of self-assembled supramolecular donor-acceptor (D-A) model systems employing metal complexation, such as zinc-porphyrin (ZnP), ZnP-C$_{60}$ systems and DABCO[8],[9] and bisZnP (D)-pyridine (A) systems.[10],[11] It was found that dipyridine-linked acceptors can be assembled with two coordination bonds to bisZnP donors.[12] Time-resolved fluorescence studies showed that the coordination bonds between the donor and acceptor do not make significant influence on the electron transfer (ET).[4] Therefore, supramolecular ET systems

with coordination bonds can be treated in a similar manner as covalently linked D-A systems.

The aim of this computational study is to investigate self-assembled bis-porphyrin-fullerene supramolecular complex **1@C$_{60}$add** designed for photovoltaic devices. It is assembled from the recently synthetized bis-porphyrin **1**[13],[14] possessing a semi-flexible polycyclic spacer and fullerene Diels-Alder adduct (**C$_{60}$add**) (Shown below). This design was based on previously synthetized supramolecular systems possessing various linkers between two porphyrin rings which were employed in host-guest studies.[15],[16] In order to understand the charge-separated behavior of the **1@C$_{60}$add** complex, we modeled ground state structure of the complex and investigated the spatial distribution of the frontier orbitals in ground and excited states.

Literature gives some examples of high level theoretical studies of electron-donor-fullerene complexes such as phthalocyanine-fullerene and chlorin-fullerene supramolecular complexes designed for a high efficiency photovoltaic devices using HF/3-21G calculations obtained by Mizuseki.[17],[18] However, in this study, due to the size of molecular system studied, we used semiempirical AM1 method, which was proven to accurately model ZnPy complexes[19] and related rigidly, space separated bis-porphyrin supramolecular systems.[10,11] The use of AM1 method to model large polycyclic systems has been justified by our research group[20] and other authors. [21]

Supramolecular complex of **1@C$_{60}$add**

Geometry. Full geometry optimization of **1@C$_{60}$add** complex at semiempirical AM1 level yielded structure shown in Figure 1. We have also computationally explored rotation of fullerene guest around Zn-N$_{py}$ axis. Several stable rotational isomers were located (Figure 2), and it was found that their energies lie within 1.6 kcalmol^{-1} indicating very low rotational barrier.
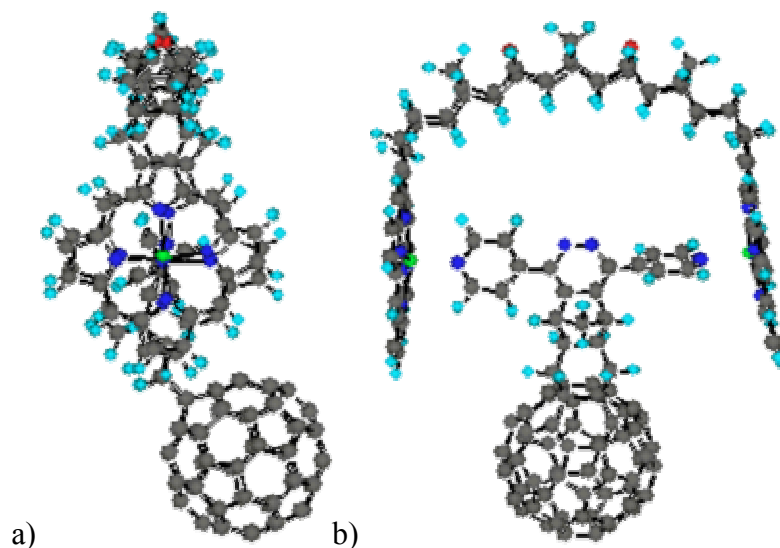
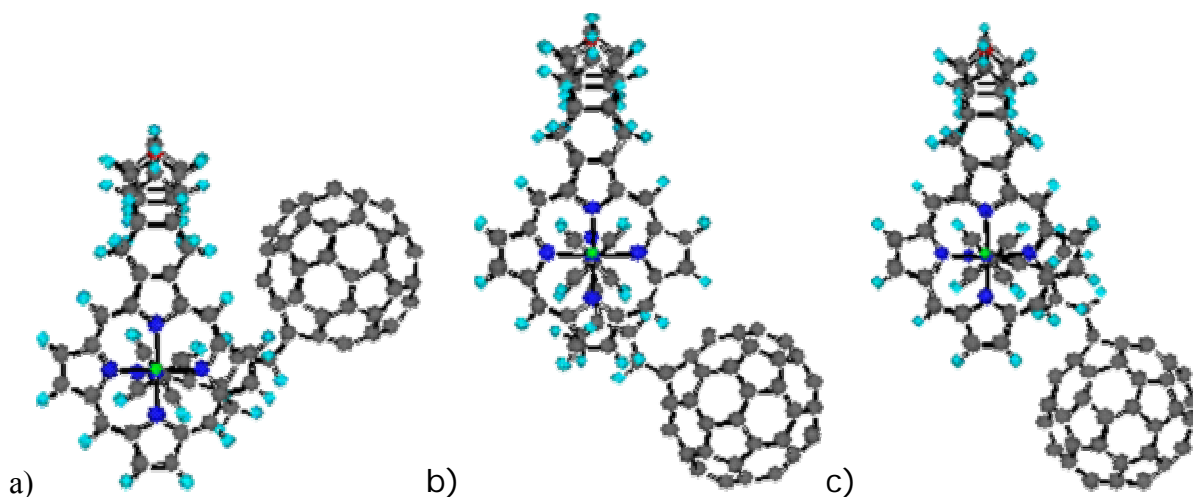Figure 1. AM1 optimized structure of **1@C$_{60}$add** complex a) front, b) side-view

Figure 2. AM1 calculated rotational isomers of **1@C$_{60}$add** complex

Furthermore, conformations of C$_{60}$adduct were computed and shown in Figure 3. This adduct is able to adopt two nondegenerate boat conformations, namely, an extended conformer and folded conformer. We found that extended(linear) conformer is more stable by only 0.43 kcalmol^{-1}. Transition state for interconversion from linear to bent conformer was also located, possessing a single imaginary frequency of vibration ($v^{\neq}$=-12 cm^{-1}). Activation energy for this process (E$_{act}$) was estimated to be 4.48 kcalmol^{-1}, indicating very low interconversion barrier. These AM1 results are in good accordance with reported value for flipping of structurally related C$_{60}$ ball-and-chain adducts around cyclohexene ring that connects the polycyclic bridge to the fullerene cage. It was found that in solid state (X-ray) these adducts adopt the extended conformation. In solution both isomers are present and one isomer is by 0.65 kcalmol^{-1} higher in energy than the other.[22] Literature AM1 calculations has shown that the conformational energy difference between extended and folded conformations is small, with a slight preference for folded conformation (0.02-1.02 kcalmol^{-1}). Conformational activation barriers are in the range 2.65-17.61 kcalmol^{-1},[23] which is close to experimental value (14.6 kcalmol^{-1}).[24]
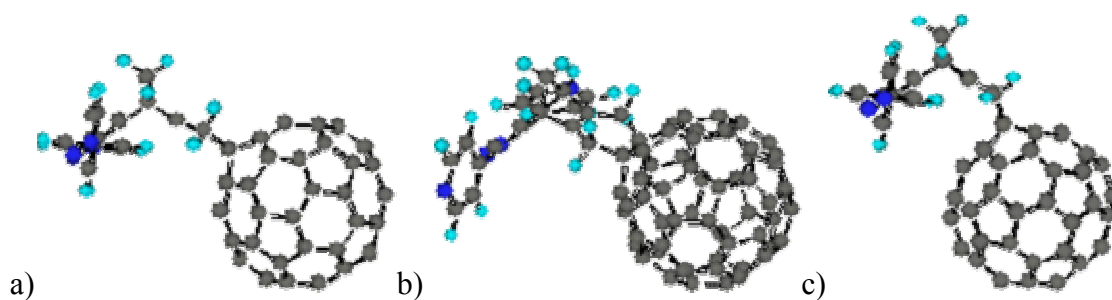
Figure 3. AM1 conformers of C_{60}adduct a) TS; b) linear; c) bent

Frontier molecular orbitals[25]

Molecular orbital analysis has been performed using AM1 semi-empirical method in order to gain insights into the intramolecular interactions and the electronic structure of **1@C$_{60}$add** complex, and results are combined in Table 1.

Table 1. Frontier molecular orbitals of **1@C$_{60}$add**

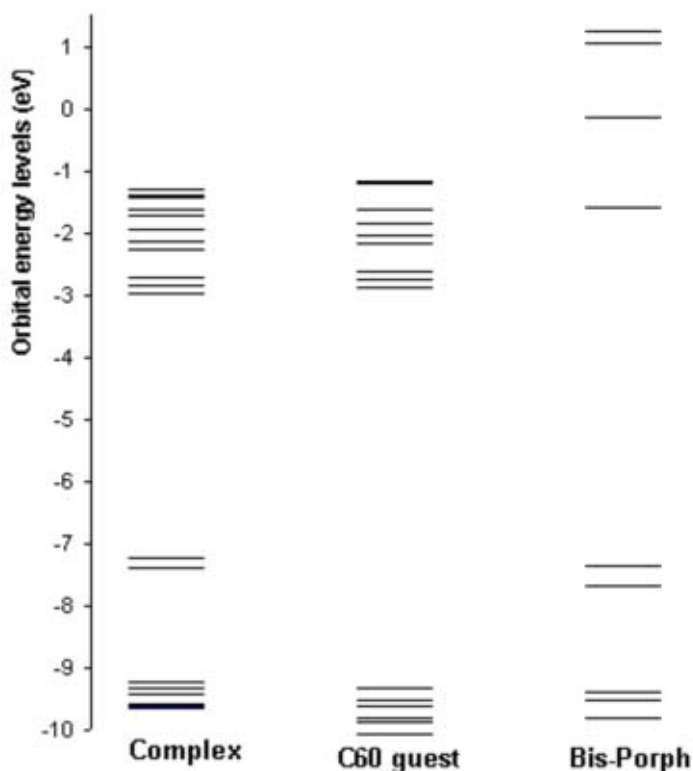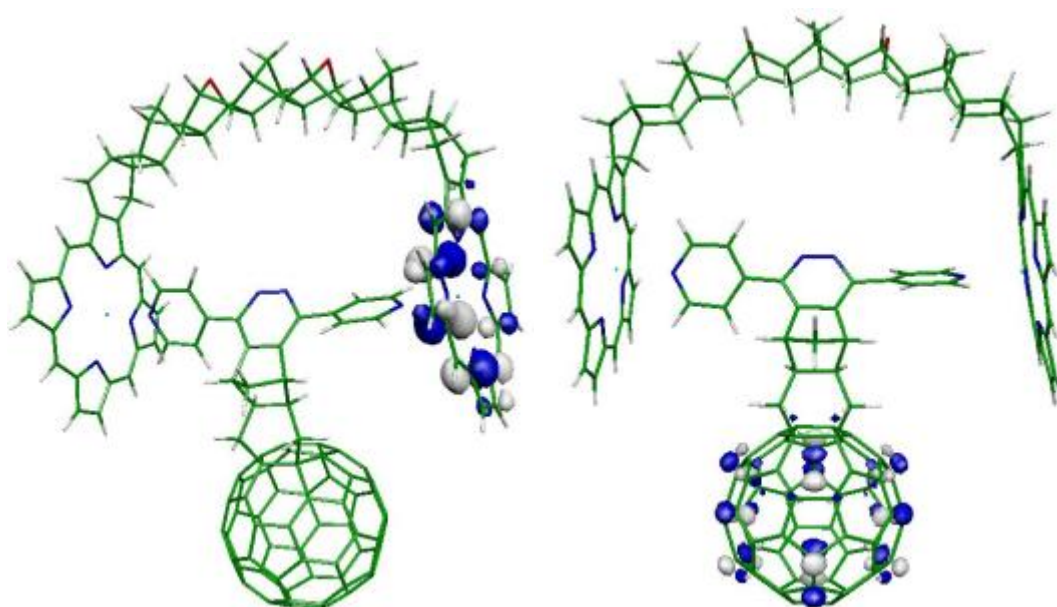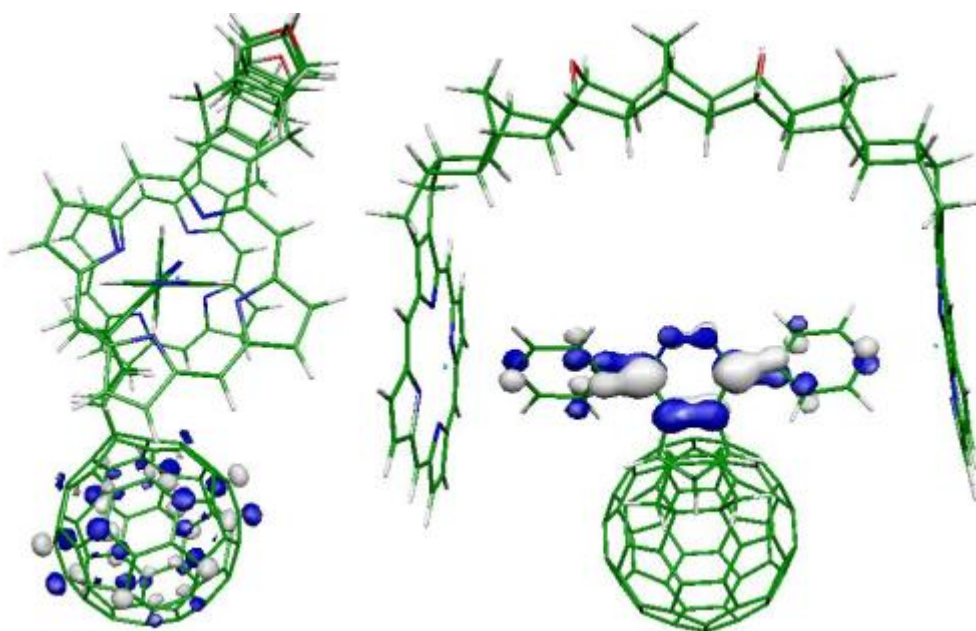| Orbital	FMO	energy	character	Orbital	FMO	energy	character
398	LUMO+12	-1.192	C_{60}	385	HOMO	-7.23	$Porph_1$
397	LUMO+11	-1.359	$Porph_1$	384	HOMO-1	-7.24	$Porph_2$
396	LUMO+10	-1.374	$Porph_2$	383	HOMO-2	-7.39	$Porph_2$
395	LUMO+9	-1.411		382	HOMO-3	-7.40	
394	LUMO+8	-1.414	$Porph_2$	381	HOMO-4	-9.18	$Porph_1$
393	LUMO+7	-1.613	$Porph_1$	380	HOMO-5	-9.22	$Porph_1+\sigma$
392	LUMO+6	-1.731	Pyr	379	HOMO-6	-9.29	$Porph_2$
391	LUMO+5	-1.938	C_{60}	378	HOMO-7	-9.34	
390	LUMO+4	-2.134	C_{60}	377	HOMO-8	-9.42	$Porph_1$
389	LUMO+3	-2.266	C_{60}	376	HOMO-9	-9.59	$Porph_2+\sigma$
388	LUMO+2	-2.715	C_{60}	375	HOMO-10	-9.60	C_{60}
387	LUMO+1	-2.855	C_{60}	374	HOMO-11	-9.62	C_{60}
386	LUMO	-2.972	C_{60}	373	HOMO-12	-9.66	C_{60}
			C_{60}				C_{60}
			C_{60}				$Porph_2$
			C_{60}				C_{60}

Figure 4. Schematic molecular orbital diagram of orbital levels for the **1@C$_{60}$add** complex, fullerene guest and bis-porphyrin molecular tweezers

Figure 4 depicts a schematic molecular orbital diagram and the comparison of the highest occupied and the lowest unoccupied orbital levels for the optimized structure of bis-porphyrin molecular tweezers, fullerene guest and **1@C$_{60}$add** supramolecular complex. It can be seen that LUMO energy levels of **1@C$_{60}$add** complex compare well with the fullerene guest (acceptor moiety)[6], while the HOMO energy levels of **1@C$_{60}$add** complex are close to that of the non-complexed bis-porphyrin molecular tweezers (donor moiety). Moreover, HOMO-LUMO energy gap in **1@C$_{60}$add** complex (4.26 eV) is smaller than those of non-complexed molecular tweezers and C$_{60}$adduct (5.75 and 6.44 eV, respectively), indicating electronic interactions between two moieties.

HOMO   LUMO
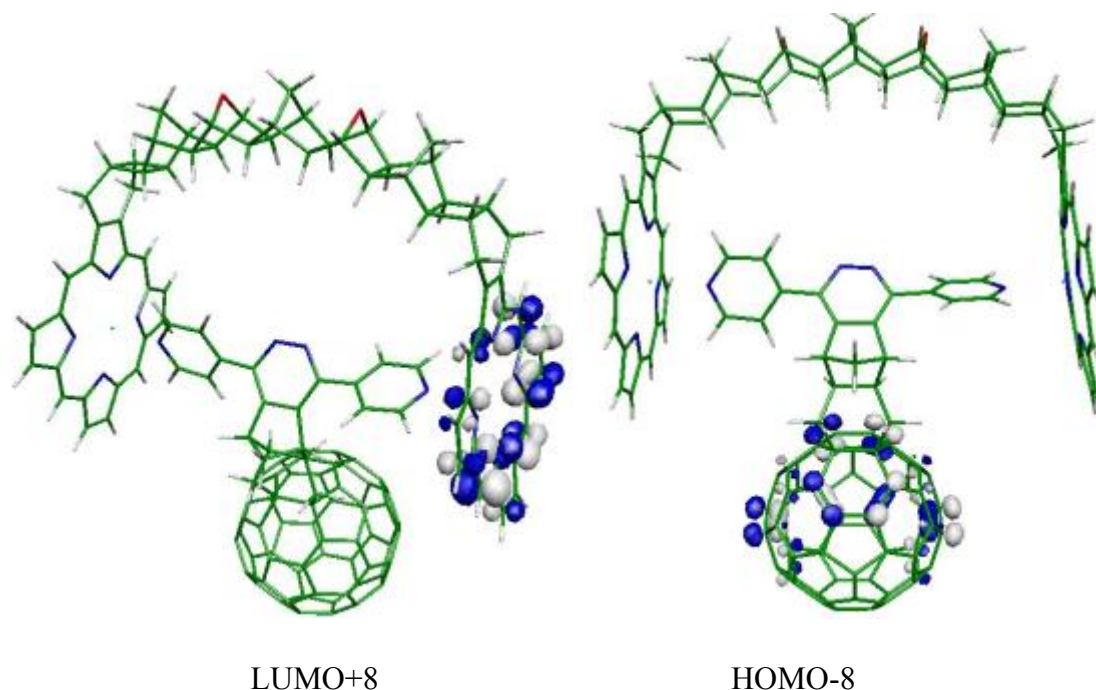
LUMO+1   LUMO+7

LUMO+8	HOMO-8

Figure 5. Visualization of the decisive occupied FMOs of the **1@C$_{60}$add** complex

Frontier molecular orbitals of the **1@C$_{60}$add** complex listed in Table 1 are illustrated in Figure 5. All decisive molecular orbitals of the complex are located on one of the components, *i.e.* either on the porphyrin or on the fullerene subunit. The two porphyrin, one pyridazine and three fullerene frontier orbitals are visualized in Figure 5. None of the investigated orbitals has a partial expansion of virtual orbital character into the fullerene subunit. The HOMO+6 and HOMO are of porphyrin character and correspond to the frontier orbitals according to the Gouterman four-orbital model for porphyrin.[26] The energy of porphyrin HOMO is significantly higher than the energy of the fullerene HOMO (HOMO-8), thus assigning the subunit as the electron donor of the complex. [27] Also the fullerene LUMO is lower in energy compared to the porphyrin LUMO (LUMO+8) by approximately 2.1 eV, assigning this unit as the electron acceptor. Therefore, charge-separate state of complex can be predicted to be **Porph$^{\cdot+}$@C$_{60}^{\cdot-}$**.[28] This result is in good agreement with experimental and computational results for other porphyrin-fullerene dyad systems.[29],[30]

Computational predictions of charge-separate state of complex were further corroborated by calculations of ZINDO/S//AM1 total spin density of **1@C$_{60}$add** radical anion. Results are depicted in Figure 6 revealing an electron transfer from porphyrin to fullerene moiety (*i.e.* **Porph$^{\cdot+}$@C$_{60}^{\cdot-}$**).
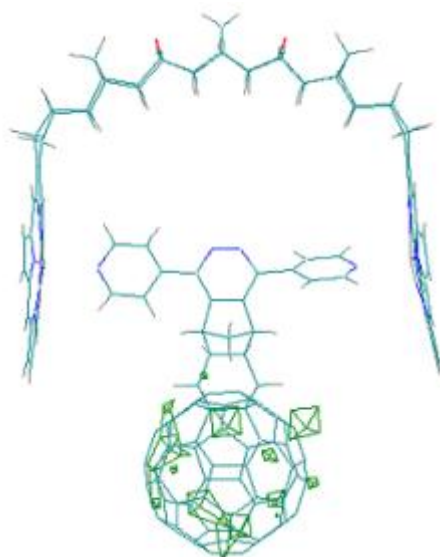
Figure 6. ZINDO/S//AM1 total spin density of **1@C$_{60}$add** radical anion (contour value= 0.001)

Electronic excitations

Electronic excitation of the ZnP portion of **1@C$_{60}$add** complex by visible light, leads predominantly to the population of its first singlet excited state, ^{1}*ZnP, which is followed by rapid intramolecular electron transfer (k$_{CS}$) to yield a long-lived charge-separated state (Equation 1).[31]

$$ZnP\text{-}C_{60}add \xrightarrow{\ h\nu\ } {}^{1*}ZnP\text{-}C_{60}add \xrightarrow{\ k_{CS}\ } ZnP^{\cdot+}\text{-}C_{60}add^{\cdot-} \quad (1)$$

The electronic properties of the excited singlet states of **1@C$_{60}$add** complex are summarized in Table 2 as obtained by ZINDO/S-CIS(6,6)//AM1 calculations of its UV spectrum[32]. The excited singlet states result from the combination of exciting one electron from one of the nearly degenerate orbitals HOMO, HOMO-1, HOMO-2 and HOMO-3 into LUMO+1, LUMO+3, LUMO+4 or LUMO+5. The S$_1$ and S$_2$ states have excitation energies of 4.53 and 4.54 eV, with corresponding oscillator strengths of 0.90 (1.00) and a dipole moments of 26.4 D and 4.4 D, respectively. This excitation can be assigned to the Q band of experimental absorption spectrum. The excitations energies of the next two states (S$_3$ and S$_4$) are calculated to lie between 5.29 and 5.27 eV, with small oscillator strength. Accordingly, these excitations can be assigned to the Q$_1$ and Q$_2$ bands of experimental absorption spectrum. A comparison with ZINDO/S-CIS//AM1 calculations of the excited singlet states of noncomplexed ZnP (Table 3) has revealed that this computational method correctly predicts the experimentally observed red-shift of porphyrin Soret and Q bands upon complexation.

Table 2. ZINDO/S-CIS//AM1 Excitation energies (*ΔE* in eV), dipole moments (μ in D), oscillator strengths (f), and characterization of the first excited states for the bis-porphyrin complex **1@C$_{60}$adduct**

		nm	ΔE	μ	f	Character[a]
S	P→C$_{60}$	337.75	5.11	6.15	2.990	HOMO-1→LUMO+4 HOMO-3→LUMO+5
S	P→C$_{60}$	341.60	4.54	26.43	0.901	HOMO-3→LUMO+1
S	P→C$_{60}$	396.24	4.53	4.43	1.028	HOMO-2→LUMO+3
S	P→C$_{60}$	472.90	4.96	10.84	1.190	HOMO→LUMO+3
S	P→C$_{60}$	559.62	5.29	10.26	0.138	HOMO-1→LUMO+4 HOMO-1→LUMO+5
S	P→C$_{60}$	601.50	5.27	8.75	0.100	HOMO-1→LUMO+5 HOMO-3→LUMO+4

[a]characters describe the main configuration of the excitations

Table 3. ZINDO/S-CIS//AM1 Excitation energies (ΔE in eV), dipole moments (μ in D), oscillator strengths (f) and characterization of the first excited states for **ZnP**

		nm	ΔE	μ	f	Character[a]
S	P→P	328.0	6.07	3.35	5.586	HOMO-3→LUMO+3
S	P→P	329.8	6.06	2.51	5.827	HOMO-2→LUMO+2 HOMO-3→LUMO
S	P→P	332.9	5.77	2.35	0.329	HOMO-1→LUMO+2 HOMO-2→LUMO+1
S	P→P	334.7	5.78	1.61	0.261	HOMO→LUMO+3 HOMO-2→LUMO+2 HOMO-3→LUMO
S	P→P	558.5	5.75	4.22	0.172	HOMO-1→LUMO+1 HOMO-2→LUMO+2
S	P→P	561.4	5.76	3.35	0.156	HOMO→LUMO HOMO-1→LUMO+3

[a]characters describe the main configuration of the excitations

Conclusion. Semiempirical AM1 method was used to model bis-porphyrin "molecular tweezers"-fullerene complex designed for photovoltaic cells. The study of the electronic structure of this complex in the ground state has revealed that porphyrin is an electron donor, while fullerene guest is an electron acceptor moiety. The electronic properties of the excited singlet states of complex indicate electron transfer from porphyrin to fullerene moiety.

Computational details. All geometry optimizations were carried out with semi-empirical calculations using the AM1 Hamiltonian[33], as implemented in the *Gaussian 03* suite of programs [34] on *Octane* Silicon Graphics workstations and Isabella computer cluster (24 dual processor HP ProLiant BLP20p nodes with Intel Xeon 2.8 GHz, 32 dual processor Dell 1850 1U nodes with Intel Xeon 3.4 GHz and 24 dual processor Pyramid GX28 nodes with AMD Opteron 248). ZINDO/S-CIS calculations[35] were performed on AM1 optimized geometries using *HyperChem* 7.01 Professional program.[36]

References.

[1]. Tashiro, K.; Aida, T.; Zheng, J.-Y.; Kinbara, K.; Saigo, K.; Sakamoto, S.; Yamaguchi, K. *J. Am. Chem. Soc.* **1999**, *121*, 9477.

[2]. Guldi, D. M. *Chem. Soc. Rev.* **2002**, *31*, 22.

[3]. Imahori, H.; Ozawa, S.; Ushida, K.; Takahashi, M.; Azuma, T.; Ajavakom, A.; Akiyama, T.; Hasegawa, M.; Taniguchi, S.; Okada, T.; Sakata, T. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 485.

[4]. Imahori, H.; Yamada, H.; Ozawa, S.; Ushida, K.; Sakata, Y. *Chem. Commun.* **1999**, 1165.

[5]. Imahori, H.; Yamada, H.; Nishimura, Y.; Yamazaki, I.; Sakata, Y. *J. Phys. Chem. B* **2000**, 2099.

[6]. Imahori, H.; Sakata, Y. *Eur. J. Org. Chem.* **1999**, 2445.

[7]. Konishi, T.; Ikeda, A.; Shinkai, S. *Tetrahedron* **2005**, *61*, 4881.

[8]. Guldi, D. M.; Luo, C.; Swartz, A.; Scheloske M.; Hirsch, A. *Chem. Commun.* **2001**, 1066.

[9]. Cho, Y.-J.; Ahn, T. K.; Song, H.; Kim, K. S.; Lee, C. Y.; Seo, W. S.; Lee, K.; Kim, S. K.; Kim, D.; Park, J. T. *J. Am. Chem. Soc.* **2005**, *127*, 2380.

[10]. Flamigni, L.; Johnston, M. R. *New. J. Chem.* **2001**, *25*, 1368.

[11]. Flamigni, L.; Marconi, G.; Johnston, M. R. *Phys. Chem. Chem. Phys.* **2001**, *3*, 4488.

[12]. Sakata, Y.; Imahori, H.; Tsue, H.; Higashida, S.; Akiyama, T.; Yoshizawa, E.; Aoki, M.; Yamada, K.; Hagiwara, K.; Taniguchi, S.; Okada, S. *Pure Appl. Chem.* **1997**, *69*, 1951.

[13]. Gunter, M. J.; Tang, H.; Warrener, R. N. *Chem. Commun* **1999**, 803.

[14]. Gunter, M. J.; Tang, H.; Warrener, R. N. *J. Porph. Phthal.* **2002**, *6*, 673.

[15]. Yamada, K.; Imahori, K.; Yoshizawa, E.; Gosztola, D.; Wasielewski, M. R. Sakata Y. *Chem. Lett.* **1999**, 235; Haino, T.; Fujii, T.; Fukuzawa, Y. *Tetrahedron Lett.* **2005**, *46*, 257; Kubo, Y.; Sugasaki, A.; Ikeda, M.; Sugiyasu, K.; Sonoda, K.; Ikeda, A.; Takeuchi, M.; Shinkai, S. *Org. Lett.* **2002**, *4*, 925; Yamaguchi, T.; Ishii, N.; Tashiro, K.; Aida, T. *J. Am. Chem. Soc.* **2003**, *125*, 13934; Mizutani, T.; Wada, K.; Kitagawa, S. *J. Am. Chem. Soc.* **2001**, *123*, 6459; Sun, D.; Tham, F. S.; Reed, C. A.; Chaker. L.; Burgess, M.; Boyd, P. D. W. *J. Am. Chem. Soc.* **2000**, *122*, 10704; Anderson, S.; Anderson, H. L.; Bashall, A.; McPartlin, M.; Sanders. J. K. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1096; Dudić, M.; Lhoták, P.; Stibor, I.; Petříčková, H.; Lang, K. *New. J. Chem.* **2004**, *28*, 85; Drain, C. M.; Russell, K. C.; Lehn, J.-M. *Chem. Commun.* **1996**, 337; Sanders, J. K. M.; in Atwood, J. L.; Davies, J. E. D.; MacNicol, D. D.; Vögtle, F. Eds. Comprehensive Supramolecular Chemistry, Pergamon, Oxford, **1996**, vol 9, pp 131; Kieran, A. L.; Bond, A. D.; Belenguer, A. M.; Sanders, *J. K. M. Chem. Commun.* **2003**, 2674; Haycock, R. A.; Yartsev, A.; Michelsen, U.; Sundstrőm, V.; Hunter, C. A. *Angew. Chem. Int. Ed. Engl.* **2000**, *39*, 3616; Proni, G.; Pescitelli, G.; Huang, X.; Nakanishi, K.; Berova, N. *J. Am. Chem. Soc.* **2003**, *125*. 12914; Yagi, S.; Ezoe, M.; Yonekura, I.; Takagishi, T.; Nakazumi, H. *J. Am. Chem. Soc.* **2003**, *125*, 4068; Borovkov, V. V.; Lintuluoto, J. M.; Sugeta, H.; Fujiki, M.; Arakawa, R.; Inoue, Y. *J. Am. Chem. Soc.* **2002**, *124*, 2993; Kubo, Y.; Ohno, T.; Jamanaka, Y.; Tokita, S.; Iida, T.; Ishimaru, Y. *J. Am. Chem. Soc.* **2001**, *123*, 12700; Jokic, D.; Asfari, Z.; Weiss, J. *Org. Lett.* **2002**, *4*, 2129; Yagi, S.; Yonekura, I.; Awakura, M.; Ezoe, M.; Takagishi, T. *J. Chem. Soc., Chem. Commun.* **2001**, 557; Iwamoto, H.; Yamaguchi, M.; Hiura, S.; Fukazawa, Y. *Heterocycles* **2004**, *63*, 2005; Borowiec, J.; Trojnar, I.: Wolowiec, S. *Polyhedron* **2004**, *23*, 33.

[16]. Satake, A.; Kobuke, Y. *Tetrahedron* **2004**, *61*, 13.

[17]. Mizuseki, H.; Igarashi, N.; Belosludov, R.; Farajian, A. A.; Kawazoe, Y. *Synth. Metals* **2003**, *138*, 281.

[18]. Mizuseki, H.; Igarashi, N.; Belosludov, R. V.; Farajian, A. A.; Kawazoe, Y. *Jpn. J. Appl. Phys.* **2003**, *42*, 2503.

[19]. Margetić, D.; Butler, D. N.; Warrener, R. N. *Theor. Chem. Acc.* submitted.

[20]. Warrener, R. N.; Butler, D. N.; Liu, L.; Margetić, D.; Russell, R. A. *Chem.-Eur. J.* **2001,** *7(15)*, 3406; Warrener, R. N.; Margetić, D.; Amarasekara, A. S.; Butler, D. N.; Mahadevan, I.; Russell, R. A. *Org. Lett.* **1999**, *1*, 199.

[21]. Lawson, J. M.; Oliver, A. M.; Rothenfluh, D. F.; An, Y.-Z.; Ellis, G. A.; Ranasinhe, M.; Khan, S. I.; Franz, A. G.; Ganapathi, P. S.; Shephard, M. J.; Paddon-Row, M. N.; Rubin. Y. *J. Org. Chem.* **1996**, *61*, 5032; Bell, T. D. M.; Jolliffe, K. A.; Ghiggino, K. P.; Oliver, A. M.; Shephard, M. J.; Langford, S. J.; Paddon-Row, M. N. *J. Am. Chem. Soc.* **2000**, *122*, 10661.

[22]. Khan, S. I.; Oliver, A. M.; Paddon-Row, M. N.; Rubin, Y. *J. Am. Chem. Soc.* **1993**, *115*, 4919.

[23]. Lawson, J. M.; Oliver, A. M.; Rothenfluh, D. F.; An, Y.-Z.; Ellis, G. A.; Ranasinghe, M. G.; Khan, S. I.; Franz, A. G.; Ganapathi, P. S.; Shephard, M. J.; Paddon-Row. M. N.; Rubin, Y. *J. Am. Chem. Soc.* **1996**, *61*, 5032.

[24]. Rubin, Y.; Khan, S. I.; Freedberg, D. I.; Yeretzian, C. *J. Am. Chem. Soc.* **1993**, *115*, 344.

[25]. Parusel, A. B. J. *J. Photochem. Photobiol. B* **2000**, *55*, 188.

[26]. Gouterman, M.; Wagniere, G. H.; Snyder, L. C. *J. Mol. Spectrosc.* **1963**, *11*, 108.

[27]. Kuciauskas, D.; Lin, S.; Seely, G. R.; Moore, A. L.; Moore, T. A.; Gust, D.; Drovetskaya, T.; Reed, C. A.; Boyd, P. D. W. *J. Phys. Chem.* **1996**, *100*, 15926.

[28]. Chen, Y.; El-Khouly, E. M.; Sasaki, M.; Araki, Y.; Ito, O. *Org. Lett.* **2005**, *7*, 1613.

[29]. Zandler, M. E.; Smith, P. M.; Fujitsuka, M.; Ito, O.; D'Souza, F. *J. Org. Chem.* **2002**, *67*, 9122.

[30]. D'Souza, F.; Gadde, S.; Zandler, M. E.; Arkady, K.; El-Khouly, M. E.; Fujitsuka, M.; Ito, O. *J. Phys. Chem. A* **2002**, *106*, 12393.

[31]. Liddell, P. A.; Sumida, J. P.; MacPerson, A. N.; Noss, L.; Seely, G. R.; Clark, K. N.; Moore, A. L.; Moore, T. A.; Gust, D. *Photochem. Photobiol*. **1994**, *60*, 537.

[32]. ZINDO/S CIS: Zerner, M. C.; Loew, G. H.; Kirchner, R. F.; Mueller-Westerhoff, U. T. *J . Am. Chem. Soc.* **1980**, *102*, 589; Ridley, J.; Zerner, M. C. *Theor. Chim Acta* **1973**, *32*, 111; Ridley, J. E.; Zerner, M. C. *Theor. Chim. Acta.* **1976**, *42*, 223; Karlsson, G.; Zerner, M. C. *Int. J. Quant. Chem.* **1973**, *7*, 35.

[33]. Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4499.

[34]. Gaussian 03, Revision B.03, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, A.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A.D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, A.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. I.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C., Pople, J. A. Gaussian, Inc., Pittsburgh PA, **2003**.

[35]. Ridley, J. E.; Zerner, M. C. *Theor. Chim. Acta* **1976**, *42*, 223.

[36]. Hypercube Inc*.,* Gainesville, USA, **2002**.