Can MP(P)$_4$ Compounds Form Complexes with C$_{60}$?

Aleksey E. Kuznetsov*

Instituto de Química, Universidade de São Paulo - SP, Brasil

Abstract: Numerous complexes between versatile derivatives of metalloporphyrins MP (with M being Mn, Co, Ni, Cu, Zn and Fe) and C_{60} have been synthesized and characterized recently. Favorable van der Waals attractions between the curved π-surface of the fullerene and the planar π-surface of MP assist in the supramolecular recognition, overcoming the necessity of matching a concave-shaped host with a convex-shaped guest structure. Recently, we reported the computational studies of the structures and electronic properties of the series of metalloporphyrins where all the four pyrrole nitrogen atoms are replaced with P-atoms, MP(P)$_4$, M = Sc-Zn. Motivated by the numerous examples of the complex formation between regular planar or quasi-planar MP and C_{60}, we computationally investigated possibility of the complex formation between two MP(P)$_4$ species, ZnP(P)$_4$ and NiP(P)$_4$, and C_{60} without any linkers, using the CAM-B3LYP/6-31G* approach, both in the gas phase and with implicit effects from C_6H_6. We found that the binding energies in the MP(P)$_4$-C_{60} complexes for these two MP(P)$_4$ compounds are relatively low, ca. 1-1.6 kcal/mol and ca. 5 kcal/mol for M = Zn and Ni, respectively. The ZnP(P)$_4$ species was found to be noticeably distorted in the ZnP(P)$_4$-C_{60} complex whereas NiP(P)$_4$ inside the NiP(P)$_4$-C_{60} complex essentially retained its bowl-like shape. Thus, we showed the possibility of the formation of complexes between MP(P)$_4$ species and C_{60} without any linkers and showed dependence of the complex stability on the transition metal M. Further investigations are in progress.

Keywords: Porphyrin-fullerene complexes, tetraphosphorus-metalloporphyrins, DFT, binding energies, NBO charges.

INTRODUCTION

Porphyrins are among the most studied macrocyclic systems because of their prominent characteristics including photochemical and photophysical properties [1]. The porphyrin molecule has an 18π-electrons conjugated system within a square-planar or quasi planar framework giving rise to the aromatic character responsible for the porphyrin species stabilization [1]. Also, porphyrins are important chromophores that absorb visible light and are good candidates for photoelectronic materials which are used, for instance, in photosensitized solar cells [2, 3]. The rich and extensive absorptions (i.e., π–π* transitions) of porphyrins hold particular promise for an efficient use of the solar spectrum. During recent years porphyrins have attracted significant attention as light-harvesting building blocks for the construction of molecular architectures [1].

Fullerene C_{60}, on the other hand, is an excellent novel three-dimensional multielectron acceptor with a favorable reduction potential (−0.169 V). It has played an important role in the development of molecular building blocks for photovoltaic applications [4, 5]. High electron affinity combined with low reorganization energy in charge-transfer processes make the fullerenes ideal electron acceptors [6]. The delocalization of charges within the spherical carbon framework (diameter > 7.5 Å) together with the rigid, confined structure of the aromatic π-sphere offers unique opportunities for stabilizing charged entities.

A variety of supramolecular assemblies with porphyrin moieties was proposed as functional models for light-harvesting and photoinduced electron transfer systems [7-9]. Porphyrins and fullerenes are *complementary* compounds due to their strongly aromatic large structures, and thus they can form molecular architectures with strong π−π interactions [10, 11]. Also, formation of such supramolecular assemblies has been shown to occur due to metal−ligand bonds [12, 13], hydrogen bonds [14-16], electrostatic interactions [17], mechanical bonds [18, 19], or a combination of several of these interactions [20-22]. The assemblies of porphyrins and fullerenes are considered as one of the most extensively organic donor−acceptor pairs studied [23-34]. So far, numerous complexes between versatile derivatives of metalloporphyrins MP (with M = Mn, Co, Ni, Cu, Zn, and Fe) or a free porphyrin and C_{60} have been synthesized and characterized [10-35]. Virtually any functional group can be covalently linked to the highly reactive C_{60} carbon framework. As mentioned above, the formation of MP-C_{60} complexes involves the utilization of strong π–π interactions between metalloporphyrins and fullerenes. Favorable van der Waals attractions between the curved π-surface of the fullerene and the planar π-surface of MP assist in the supramolecular recognition, overcoming the necessity of matching a concave-shaped host with a convex-shaped guest structure. This leads to complexes with

---

*Correspondence Address to this author at the Av. Prof. Lineu Prestes, 748 – Butantã, CEP: 05508-000, São Paulo - SP, Brasil; Tel: +551633518062; E-mail: aleksey73kuznets@gmail.com

E-ISSN: 1929-5030/17

unusually short contacts (2.7–3.0 Å), shorter than ordinary van der Waals contacts (3.0–3.5 Å), and a variety of crystal structures [see, for instance, Ref. 10].

Recently, we reported the computational studies of the structures and electronic properties of the series of metalloporphyrins where all the four pyrrole nitrogens are replaced with P-atoms, $MP(P)_4$, M = Sc-Zn [36-38]. We showed that the prominent structural feature of all the $MP(P)_4$ compounds is the significant bowl-like distortion from planarity. Furthermore, motivated by the phenomenon of stack formation by regular metalloporphyrins, we performed the computational check of the stack formation between the $MP(P)_4$ species without any linkers or substituents, choosing the $ZnP(P)_4$ species as the simplest $MP(P)_4$ compound [39]. For the current research, we were motivated by the numerous examples of the complex formation between regular planar or quasi-planar MP and C_{60}, along with the recent report by Anand and co-workers about the complex formation between the dimer of *antiaromatic tetraoxaisophlorin* and C_{60} [40]. Thus, we decided to computationally investigate possibility of the complex formation between $MP(P)_4$ species, taking as examples $ZnP(P)_4$ and $NiP(P)_4$ compounds, and C_{60} *without any linkers or substituents.*

The paper is organized as follows. The next section describes computational details of the study. Then, we consider the results obtained and make discussion. Finally, conclusions and perspectives are provided.

COMPUTATIONAL DETAILS

The study described here was performed using the Gaussian 09 package [41]. The $MP(P)_4$ (M = Zn, Ni), C_{60}, and $MP(P)_4$-C_{60} species were optimized without any symmetry constraints, and the resulting structures were assessed using vibrational frequency analysis to probe whether they represent true minimum-energy geometries. We performed the geometry optimizations and frequencies calculations using the Handy and coworkers' long range corrected version of B3LYP, CAM-B3LYP [42] with the split-valence 6-31G* basis set [43, 44], further referred to as CAM-B3LYP/6-31G*. So far, different theoretical approaches have been used to study the complexes between porphyrins and their derivatives and fullerenes, for example: pure generalized gradient approximation (GGA) functional PBE, global hybrid meta-GGA functional M06, hybrid functional B3LYP, and wB97XD hybrid density functional including empirical atomic-pairwise dispersion corrections following the Grimme's D2 dispersion scheme (D) by Baruah and co-workers in the studies of systems based on fullerene/graphene oxide and porphyrin/smaragdyrin [33]; hybrid functional B3LYP in the recent study of noncovalent interactions between C_{60}-dipyridyl and zinc porphyrin dimer by Stangel *et al*. [45]; B97-D3 functional including dispersion corrections in the study of supramolecular ensembles of conjugated porphyrin dimers with C_{60} by Moreira *et al*. [32]; PBE with included semi-empirical 'DFT+D3' term in the studies of fullerene-porphyrin supramolecular nanocables by Buldum and Reneker [31]; CAM-B3LYP along with wB97XD, TPSSh, M06, and M06L functionals in the studies of Rhoda *et al*. on noncovalent complexes of subphthalocyanine derivatives with C_{60} and C_{70} fullerenes [46]. We decided to choose the CAM-B3LYP approach because of its superiority over the standard "pure" and "hybrid" exchange-correlation functionals in treating noncovalent weak long-distance interactions which should take place in the studied complexes.

Computational studies were performed using the CAM-B3LYP/6-31G* approach, both in the gas phase and with implicit effects from C_6H_6 (dielectric constant 2.2706). With implicit solvent effects the geometries and vibrational frequencies were calculated using the self-consistent reaction field IEF-PCM method [47] (the UFF default model used in the Gaussian 09 package, with the electrostatic scaling factor α set to 1.0).

The binding energies (E_{bind}) of the complexes studied were computed using the following formula:

$$E_{bind} = E(complex) - E(C_{60}) - E(MP(P)_4),$$

where E(complex) is the energy of the $MP(P)_4$-C_{60} species and $E(C_{60})$ and $E(MP(P)_4)$ are the energy of C_{60} and $MP(P)_4$, respectively. Below we consider the gas phase and implicit solvent results without the zero-point correction ZPE (ΔE_0). The charge analysis was performed using the Natural Bond Orbital (NBO) scheme with the 'pop=nbo' command as implemented in the Gaussian 09 package [48]. Molecular structures were visualized using OpenGL version of Molden 5.0 visualization software [49]. The work was partially done using the Extreme Science and Engineering Discovery Environment (XSEDE) [50].

RESULTS AND DISCUSSION

Figure **1** shows the calculated structures of the complexes $ZnP(P)_4$-C_{60} and $NiP(P)_4$-C_{60} and Table **1** provides selected computed data for these complexes along with $MP(P)_4$ and C_{60}. Interestingly, in the $NiP(P)_4$-

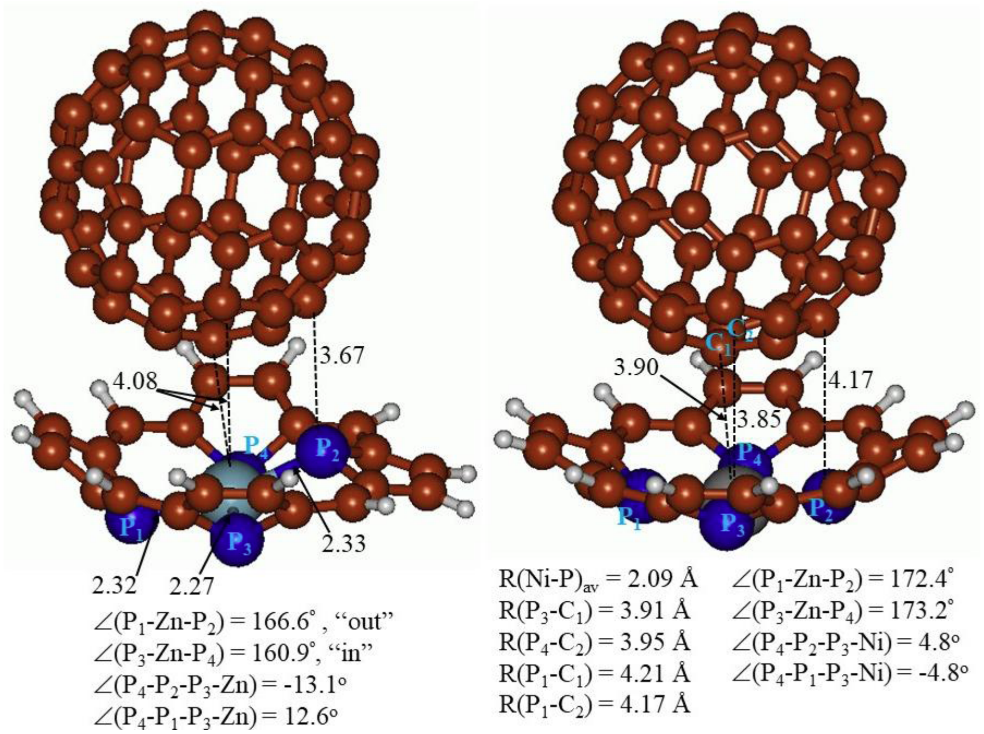

Figure 1: Structures of the complexes ZnP(P)$_4$-C$_{60}$ (left) and NiP(P)$_4$-C$_{60}$ (right) calculated using the CAM-B3LYP/6-31G* approach with implicit effects from C$_6$H$_6$ included. The color coding is as follows: dark brown for C, light grey for H, dark blue for P, light blue for Zn, and dark grey for Ni. Bond distances are given in Å, bond angles and dihedral angles are given in degrees.

C$_{60}$ species the bowl-like shape of NiP(P)$_4$ is generally preserved ("an apple at a saucer" structure) whereas in the ZnP(P)$_4$-C$_{60}$ complex the ZnP(P)$_4$ molecule is quite noticeably distorted ("an apple on a crumpled paper plate" structure). It should be noticed that for the ZnP(P)$_4$-C$_{60}$ complex similar distortions were observed when we did test calculations at the lower levels of theory, too (B3LYP/3-21G* and B3LYP/6-31G*). A closer look at the two complexes and comparison with the bare MP(P)$_4$ species shows the following. (i) In ZnP(P)$_4$-C$_{60}$, the two Zn-P bond distances, Zn-P$_{3,4}$ (Figure **1**), shorten by 0.09 Å compared to the Zn-P bond distances in the free ZnP(P)$_4$ species (cf. Table **S1** in Supporting Information), and the two other Zn-P bond distances, Zn-P$_1$ and Zn-P$_2$, are shortened by 0.04 and 0.03 Å, respectively. The phosphole unit containing P$_2$ becomes tilted oppositely relative to the other three phospholes in the porphyrin ring, and the C$_{60}$-P$_2$ distance, 3.67 Å, is the shortest distance between ZnP(P)$_4$ and fullerene in this complex (compare with 4.08 Å between Zn and C$_{60}$, see Figure **1**). The P-Zn-P bond angles in the complex are smaller by ca. 14 and 9^o compared to free ZnP(P)$_4$ (Table **S1**), and dihedral angles (P-P-P-Zn) increase by ca. 10^o. While in the free ZnP(P)$_4$ Zn-center is slightly "in" the plane formed by the four P-atoms, in the complex it is located essentially inside this plane. (ii) In NiP(P)$_4$-C$_{60}$, all the Zn-P bond distances have the same length as in the free NiP(P)$_4$ species (Table **S1**). The P-Ni-P bond angles in the complex are essentially the same as in free NiP(P)$_4$ (Table **S1**), and dihedral angles (P-P-P-Ni) are just diminished by merely 0.7^o (see Table **S1**). Both in the free NiP(P)$_4$ and in the complex Ni retains slightly "out" of the plane formed by the four P-atoms. The P-C$_{60}$ distances in this complex vary from 3.91 to 4.21 Å (Figure **1**), being longer than the Ni-C$_{1,2}$ distances, 3.85 and 3.90 Å, respectively (Figure **1**). (iii) Comparison of the two complexes shows that ZnP(P)$_4$-C$_{60}$ should be considered as essentially having C$_s$ symmetry, and NiP(P)$_4$-C$_{60}$ as having C$_{2v}$ symmetry. We agree that the calculated M-C$_{60}$ distances in our complexes, 3.85–4.08 Å, and the P-C$_{60}$ distances, 3.67–4.21 Å, should be considered as relatively long, compared to the previously reported values for other complexes, for instance, experimentally determined distances of 2.7–3.0 Å [10], or computed distances of 2.88–3.14 Å (metal•••C$_{60}$ distances) [32], or experimentally determined very close contacts (2.58 and 2.61 Å) between the isophlorin π-surface and the curved surface of C$_{60}$ [40]. However, the differences in considered complexes and in the computational approaches employed should be taken into account here.

Considerations of the C$_6$H$_6$ calculated energies of the HOMO/LUMO and HOMO-LUMO gaps for the

Table 1: Studied Compounds Calculated Employing the CAM-B3LYP/6-31G* Approach with Implicit Effects from C_6H_6 Included

Property	C_{60}	$MP(P)_4$ (M = Zn//Ni)	$MP(P)_4$-C_{60} (M = Zn//Ni)
E_{bind} (kcal/mol)	-	-	1.1//4.7
E(HOMO), A.U.	-0.26199	-0.22519//-0.24462	-0.21833//-0.24530
E(LUMO), A.U.	-0.07997	-0.07887//-0.07005	-0.08150//-0.07893
Gap, eV	4.95	3.98//4.75	3.72//4.53
NBO charge (M), e	-	0.66//-0.27	0.59//-0.23
NBO charge (P), e	-	0.45//0.72	0.61(P_2),0.49($P_{3,4}$),0.41(P_1)^a// 0.72

[a] For P-center numbers, see Figure **1**.

$MP(P)_4$-C_{60} complexes and free C_{60} and $MP(P)_4$ show the following upon the complex formation: (i) the HOMO-LUMO gaps become noticeably smaller, decreasing by 1.23(Zn)/0.42(Ni) eV when compared to free C_{60} and by 0.26(Zn)/0.22(Ni) eV when compared to free $MP(P)_4$ (we understand that calculating the HOMO-LUMO gaps as energy differences of HOMO and LUMO should be taken with caution, but our task here is to show general trends in change of the compounds properties); (ii) the $MP(P)_4$-C_{60} HOMO is somewhat *destabilized* for M = Zn and slightly *stabilized* for M = Ni compared to free $MP(P)_4$; (iii) the $MP(P)_4$-C_{60} LUMO is *stabilized* for both M compared to free $MP(P)_4$; (iv) the $MP(P)_4$-C_{60} HOMO is noticeably *destabilized* for both M compared to free C_{60}; (v) the $MP(P)_4$-C_{60} LUMO is noticeably *stabilized* for M = Zn and slightly *destabilized* for M = Ni compared to free C_{60}. So, the LUMO energies of the two complexes are quite close to the LUMO energy of C_{60}, whereas the HOMO energies of the two complexes are quite close to the HOMO energies of the $MP(P)_4$ (see Table **1** and Table **S1**). Thus, the HOMO of the $MP(P)_4$-C_{60} complexes would have dominating contributions from the $MP(P)_4$ moieties, and the LUMO of the $MP(P)_4$-C_{60} complexes would have dominating contributions from the fullerene part. Therefore, charge-transfer interactions within such complexes could have non-zero possibility, which, in turn, might result in appearing the charge-transfer absorption band in the spectra of these complexes. To further analyze the possibilities for the charge transfer within the complexes, we performed the analysis of the NBO charges of the $MP(P)_4$-C_{60} complexes and free $MP(P)_4$. This analysis shows the following: (i) in $ZnP(P)_4$-C_{60}, the charge on the Zn-center becomes slightly smaller, by 0.07 e, whereas the charge on the P_2-center, the closest one to the C_{60}, increases noticeably, by 0.16 e, the charges on the $P_{3,4}$-centers increase by 0.04 e, and the charge on the P_1-center decreases by 0.04 e. Thus, there apparently exists certain charge transfer between the Zn-center and C_{60}, between the P_2-center and C_{60}, and between the total P4-unit and the rest of the porphyrin moiety. The NBO calculations show some small charges appearing on the C_{60} atoms in the $ZnP(P)_4$-C_{60} complex but they are generally in the order of 0.001 e. (ii) In $NiP(P)_4$-C_{60}, the charge on the Ni-center becomes slightly smaller, by 0.04 e, whereas the charges on the P-centers retain the same as in the free $NiP(P)_4$. Thus, the NBO analysis did not give the conclusive response to the question about the charge-transfer interactions within the complexes studied. Further, more profound, investigation will be necessary to clarify this issue.

Finally, consideration of the binding energies of the two complexes shows that they are indeed bound by the relatively weak van der Waals interactions: $ZnP(P)_4$-C_{60} has the binding energy calculated in implicit benzene mere 1.1 kcal/mol but a little higher E_{bind} in the gas phase, 1.6 kcal/mol (see Table **S1**) whereas $NiP(P)_4$-C_{60} is slightly stronger bound complex, with the E_{bind} 4.7 kcal/mol in the implicit C_6H_6 and 4.8 kcal/mol in the gas phase (Table **S1**). This could be explained by shorter distances between the Ni-center and C_{60} unit (see Figure **1**) compared to the $ZnP(P)_4$-C_{60} complex, apparently due to the smaller size of the Ni-center compared to Zn-center, and maybe also by negative charge on the Ni-center which might be – probably – donated to extended high-lying unoccupied orbitals of C_{60}. It would require further studies to figure out the exact picture of interactions between $MP(P)_4$ species and C_{60} leading to the formation of $ZnP(P)_4$-C_{60} and $NiP(P)_4$-C_{60}. Currently, we have demonstrated the *possibility* of the complex formation between the $MP(P)_4$ species and C_{60} leading to the formation of $MP(P)_4$-C_{60} complexes.

CONCLUSIONS AND PERSPECTIVES

Motivated by the numerous examples of the complex formation between regular planar or quasi-planar metalloporphyrins and their derivatives and C_{60}, along with the recent report by Anand and co-workers about the complex formation between the dimer of *antiaromatic tetraoxaisophlorin* and C_{60} [40], we decided to computationally investigate possibility of the complex formation between $MP(P)_4$ species, taking as examples $ZnP(P)_4$ and $NiP(P)_4$ compounds, and C_{60} *without any linkers or substituents.* We have demonstrated the *possibility* of the complex formation between the $MP(P)_4$ species and C_{60} leading to the formation of $MP(P)_4$-C_{60} complexes for M = Zn and Ni. In our computational studies, the CAM-B3LYP/6-31G* approach, both in the gas phase and with implicit effects from C_6H_6, was employed.

We found that the two $MP(P)_4$-C_{60} complexes for M = Zn, Ni, are indeed bound by the relatively weak van der Waals interactions: $ZnP(P)_4$-C_{60} has the binding energy calculated with implicit effects from C_6H_6 mere 1.1 kcal/mol (1.6 kcal/mol in the gas phase) whereas $NiP(P)_4$-C_{60} was calculated to be slightly stronger bound complex, with the E_{bind} 4.7 (4.8) kcal/mol. This could be explained by shorter distances between the Ni-center and C_{60} unit compared to the $ZnP(P)_4$-C_{60} complex, apparently due to the smaller size of the Ni-center vs. Zn-center, and maybe also by negative charge on the Ni-center which might be – probably – donated to extended high-lying unoccupied orbitals of C_{60}. The clarification of the picture of interactions between $MP(P)_4$ species and C_{60} requires further studies.

The $ZnP(P)_4$ unit was found to be noticeably distorted in the $ZnP(P)_4$-C_{60} complex giving rise to the "apple on the crumpled paper plate" structure whereas $NiP(P)_4$ inside the $NiP(P)_4$-C_{60} complex essentially retained its bowl-like shape giving rise to the "apple at the saucer" structure. Distances between M and C_{60} were computed to be 3.85-3.90 Å (for M = Ni) and 4.08 Å (for M = Zn). The shortest distances between $MP(P)_4$ and C_{60} were calculated to be ca. 3.67 (for M = Zn) and 3.91 (for M = Ni) Å. Upon the complex formation, the HOMO-LUMO gaps become noticeably smaller, decreasing by 1.23(Zn)/0.42(Ni) eV when compared to free C_{60} and by 0.26(Zn)/0.22(Ni) eV when compared to free $MP(P)_4$. In the $ZnP(P)_4$-C_{60} complex, there apparently exists certain charge transfer between the Zn-center and C_{60}, between the P_2-center and C_{60}, and between the total P4-unit and the rest of the porphyrin moiety. In $NiP(P)_4$-C_{60}, the charge on the Ni-center becomes slightly smaller than in the free $NiP(P)_4$ whereas the charges on the P-centers retain the same as in the free $NiP(P)_4$.

Based on the results obtained, the following questions to be answered can be formulated:

(i) How will the binding and structures in $MP(P)_4$-C_{60} complexes depend on the M nature (main group element or transition metal)? How will charge and size of M and number of unpaired d-electrons of M (spin state) affect the $MP(P)_4$-C_{60} complexes formation?

(ii) What is the exact nature of bonding between $MP(P)_4$ species and C_{60}?

(iii) Which approaches could be used to facilitate the complex formation between $MP(P)_4$ and C_{60}? Could further porphyrin core-modification (replacing P with other elements or using porphyrins with smaller number of core-modifying atoms) or adding various electron-donating/withdrawing substituents be helpful?

(iv) What are charge accumulation/charge transfer and photophysical properties of $MP(P)_4$-C_{60} complexes?

Some research projects aimed to answer these questions are ongoing currently.

ACKNOWLEDGEMENTS

This work was supported by the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) grant "Estudo Teórico Computacional de Sistemas Nanoestruturados com Potencial Aplicação Tecnológica", number 402313/2013-5, approved in the call N° 70/2013 Bolsa de Atração de Jovens Talentos - BJT - MEC/MCTI/CAPES/CNPq/FAPs / Linha 2 - Bolsa de Atração de Jovens Talentos – BJT. The computational resources of the centers Centro Nacional de Processamento de Alto Desempenho em São Paulo, Núcleo de Tecnologia da Informação, and Centro Nacional de Processamento de Alto Desempenho – UFC are highly apprecaited. This work also used the Extreme Science and Engineering Discovery Environment (XSEDE), which is supported by National Science Foundation grant number ACI-1053575.

SUPPORTING INFORMATION

The supporting information can be downloaded from the journal website along with the article.

REFERENCES

[1] Kadish KM, Smith KM, Guilard R, Eds. Handbook of porphyrin science with applications to chemistry, physics, materials science, engineering, biology and medicine. Singapore: World Scientific 2010.

[2] Urbani M, Grätzel M, Nazeeruddin MK, Torres T. Meso-substituted porphyrins for dye-sensitized solar cells. Chem Rev 2014; 114: 12330-96. https://doi.org/10.1021/cr5001964

[3] Cardenas-Jirón GI, Baruah T, Zope RR. Excited electronic states of porphyrin-based assemblies using density functional theory. In: Handbook of porphyrin science. River Edge, NJ: World Scientific Publishing Co. 2016; pp. 233-89. https://doi.org/10.1142/9789813149625_0004

[4] Guldi DM. Fullerenes: three-dimensional electron acceptor materials. Chem Commun 2000; 321-27. https://doi.org/10.1039/a907807j

[5] Dennler G, Scharber MC, Brabec CJ. Polymer-fullerene bulk-heterojunction solar cells. Adv Mater 2009; 21: 1323-38. https://doi.org/10.1002/adma.200801283

[6] Sariciftci NS, Smilowitz L, Heeger AJ, Wudl F. Photoinduced electron-transfer from a conducting polymer to buckminsterfullerene. Science 1992; 258: 1474-6. https://doi.org/10.1126/science.258.5087.1474

[7] Jung SH, Lee J-W, Kim H-J. Self-assembly of uncharged amphiphilic porphyrins and incorporation of C_{60} fullerenes in water. Supramol Chem 2016; 28: 634-9. https://doi.org/10.1080/10610278.2015.1092535

[8] Beletskaya I, Tyurin VS, Tsivadze AY, Guilard R, Stern C. Supramolecular chemistry of metalloporphyrins. Chem Rev 2009; 109: 1659-1713. https://doi.org/10.1021/cr800247a

[9] Drain CM, Varotto A, Radivojevic I. Self-organized porphyrinic materials. Chem Rev 2009; 109: 1630-58. https://doi.org/10.1021/cr8002483

[10] Guldi DM. Fullerene-porphyrin architectures; photosynthetic antenna and reaction center models. Chem Soc Rev 2002; 31: 22-36. https://doi.org/10.1039/b106962b

[11] Zope RR, Olguin M, Baruah T. Charge transfer excitations in cofacial fullerene-porphyrin complexes. J Chem Phys 2012; 137: 084317. https://doi.org/10.1063/1.4739272

[12] Stangel C, Schubert C, Kuhri S, *et al.* Tuning the reorganization energy of electron transfer in supramolecular ensembles--metalloporphyrin, oligophenylenevinylenes, and fullerene--and the impact on electron transfer kinetics. Nanoscale 2015; 7: 2597-608. https://doi.org/10.1039/C4NR05165C

[13] Garg V, Kodis G, Liddell PA, *et al.* Artificial photosynthetic reaction center with a coumarin-based antenna system. J Phys Chem B 2013; 117: 11299-308. https://doi.org/10.1021/jp402265e

[14] Đorđević L, Marangoni T, De Leo F, *et al.* Fullerene–porphyrin [n]pseudorotaxanes: self-assembly, photophysics and third-order NLO response. Phys Chem Chem Phys 2016; 18: 11858-68. https://doi.org/10.1039/C5CP06055A

[15] Sánchez L, Sierra M, Martín N, *et al.* Exceptionally strong electronic communication through hydrogen bonds in porphyrin–C_{60} pairs. Angew Chem Int Ed 2006; 45: 4637-41. https://doi.org/10.1002/anie.200601264

[16] D'Souza F, Maligaspe E, Ohkubo K, Zandler ME, Subbaiyan NK, Fukuzumi S. Photosynthetic reaction center mimicry: low reorganization energy driven charge stabilization in self-assembled cofacial zinc phthalocyanine dimer-fullerene conjugate. J Am Chem Soc 2009; 131: 8787-97. https://doi.org/10.1021/ja903467w

[17] Grimm B, Karnas E, Brettreich M, Ohta K, Hirsch A, Guldi DM, Torres T, Sessler JL. Charge transfer in sapphyrin-fullerene hybrids employing dendritic ensembles. J Phys Chem B 2010; 114: 14134-9. https://doi.org/10.1021/jp906785f

[18] Megiatto JD, Schuster DI, de Miguel G, Wolfrum S, Guldi DM. Topological and conformational effects on electron transfer dynamics in porphyrin-[60]fullerene interlocked systems. Chem Mater 2012; 24: 2472-85. https://doi.org/10.1021/cm3004408

[19] Megiatto JD, Li K, Schuster DI, *et al.* Convergent synthesis and photoinduced processes in multi-chromophoric rotaxanes. J Phys Chem B 2010; 114: 14408-19. https://doi.org/10.1021/jp101154k

[20] Moreira L, Calbo J, Illescas BM, *et al.* Metal-atom impact on the self-assembly of cup-and-ball metalloporphyrin-fullerene conjugates. Angew Chem Int Ed 2015; 54: 1255-60. https://doi.org/10.1002/anie.201409487

[21] Calderon RMK, Valero J, Grimm B, de Mendoza J, Guldi DM. Enhancing molecular recognition in electron donor-acceptor hybrids via cooperativity. J Am Chem Soc 2014; 136: 11436-43. https://doi.org/10.1021/ja5052236

[22] Fang X, Zhu Y-Z, Zheng J-Y. Clawlike tripodal porphyrin trimer: ion-controlled on–off fullerene binding. J Org Chem 2014; 79: 1184-91. https://doi.org/10.1021/jo4026176

[23] Garg V, Kodis G, Chachisvilis M, *et al.* Conformationally constrained macrocyclic diporphyrin-fullerene artificial photosynthetic reaction center. J Am Chem Soc 2011; 133: 2944-54. https://doi.org/10.1021/ja1083078

[24] Al-Subi AH, Niemi M, Tkachenko NV, Lemmetyinen H. Effect of anion ligation on electron transfer of double-linked zinc porphyrin-fullerene dyad. J Phys Chem A 2011; 115: 3263-71. https://doi.org/10.1021/jp111234d

[25] Lemmetyinen H, Tkachenko NV, Efimov A, Niemi M. Transient states in photoinduced electron transfer reactions of porphyrin- and phthalocyanine-fullerene dyads. J Porphyrins Phthalocyanines 2009; 13: 1090-7. https://doi.org/10.1142/S108842460900139X

[26] D'Souza F, Chitta R, Gadde S, *et al.* Photosynthetic reaction center mimicry of a ″special pair″ dimer linked to electron acceptors by a supramolecular approach: self-assembled cofacial zinc porphyrin dimer complexed with fullerene[s]. Chem- Eur J 2007; 13: 916-22. https://doi.org/10.1002/chem.200600885

[27] D'Souza F, Maligaspe E, Karr PA, *et al.* Faceto-face Pacman-type porphyrin-fullerene dyads: design, synthesis, charge-transfer interactions, and photophysical studies. Chem-Eur J 2008; 14: 674-81. https://doi.org/10.1002/chem.200700936

[28] Fukuzumi S, Kashiwagi Y. Photoinduced electron transfer in a supramolecular triad system composed of ferrocene-zinc porphyrin-pyridylnaphthalenediimide. J Porphyrins Phthalocyanines 2007; 11: 368-74. https://doi.org/10.1142/S1088424607000412

[29] Sarova GH, Hartnagel U, Balbinot D, Sali S, Jux N, Hirsch A, Guldi DM. Testing electron transfer within molecular associates built around anionic C[60] and C[70] dendrofullerenes and a cationic zinc porphyrin. Chem-Eur J 2008; 14: 3137-45. https://doi.org/10.1002/chem.200701462

[30] Mironov AF. Synthesis, properties, and potential applications of porphyrin-fullerenes. Макрогетероциклы/ Macroheterocycles 2011; 4: 186-208. https://doi.org/10.6060/mhc2011.3.08

[31] Buldum A, Reneker DH. Fullerene-porphyrin supramolecular nanocables. Nanotechnology 2014; 25: 235201. https://doi.org/10.1088/0957-4484/25/23/235201

[32] Moreira L, Calbo J, Arago J, *et al.* Conjugated porphyrin dimers: cooperative effects and electronic communication in supramolecular ensembles with C$_{60}$. J Am Chem Soc 2016; 138: 15359-67. https://doi.org/10.1021/jacs.6b07250

[33] Caŕdenas-Jiroń G, Borges-Martínez M, Sikorski E, Baruah T. Excited states of light-harvesting systems based on fullerene/graphene oxide and porphyrin/smaragdyrin. J Phys Chem C 2017; 121: 4859-72. https://doi.org/10.1021/acs.jpcc.6b12452

[34] Saegusa Y, Ishizuka T, Kojima T, Mori S, Kawano M, Kojima T. Supramolecular interaction of fullerenes with a curved π-surface of a monomeric quadruply ring-fused porphyrin. Chem Eur J 2015; 21: 5302-6. https://doi.org/10.1002/chem.201500389

[35] Imahori H, Fukuzumi S. Porphyrin- and fullerene-based photovoltaic devices. Adv Funct Mater 2004; 14: 525-36. https://doi.org/10.1002/adfm.200305172

[36] Barbee J, Kuznetsov AE. Revealing substituent effects on the electronic structure and planarity of Ni-porphyrins. Comp Theoret Chem 2012; 981: 73-85. https://doi.org/10.1016/j.comptc.2011.11.049

[37] Kuznetsov AE. Metalloporphyrins with all the pyrrole nitrogens replaced with phosphorus atoms, MP[P]$_4$ [M = Sc, Ti, Fe, Ni, Cu, Zn]. Chem Phys 2015; 447: 36-45. https://doi.org/10.1016/j.chemphys.2014.11.018

[38] Kuznetsov AE. How the change of the ligand from L = porphine, P^{2-}, to L = P$_4$-substituted porphine, P[P]$_4^{2-}$, affects the electronic properties and the M-L binding energies for the first-row transition metals M = Sc-Zn: comparative study. Chem Phys 2016; 469-470: 38-48. https://doi.org/10.1016/j.chemphys.2016.02.010

[39] Kuznetsov AE. Computational design of ZnP[P]$_4$ stacks: three modes of binding. J Theor Comp Chem 2016; 15: 1650043. https://doi.org/10.1142/S0219633616500437

[40] Reddy BK, Gadekar SC, Anand VG. The synthesis and characterization of the meso– meso linked antiaromatic tetraoxaisophlorin dimer. Chem Commun 2016; 52: 3007-9. https://doi.org/10.1039/C5CC10370C

[41] Frisch MJ, Trucks GW, Schlegel HB, *et al.* Gaussian 09: ES64L-G09RevD.01 24-Apr-2013, Gaussian, Inc., Wallingford CT. 2013.

[42] Yanai T, Tew D, Handy N. A new hybrid exchange-correlation functional using the Coulomb-attenuating method (CAM-B3LYP). Chem Phys Lett 2004; 393: 51-7. https://doi.org/10.1016/j.cplett.2004.06.011

[43] Hariharan PC, Pople JA. Accuracy of AH$_n$ equilibrium geometries by single determinant molecular orbital theory. Mol Phys 1974; 27: 209-14. https://doi.org/10.1080/00268977400100171

[44] Gordon MS. The isomers of silacyclopropane. Chem Phys Lett 1980; 76: 163-8. https://doi.org/10.1016/0009-2614(80)80628-2

[45] Stangel C, Charisiadis A, Zervaki GE, *et al.* Case study for artificial photosynthesis: noncovalent interactions between C$_{60}$-dipyridyl and zinc porphyrin dimer. J Phys Chem C 2017; 121: 4850-8. https://doi.org/10.1021/acs.jpcc.6b11863

[46] Rhoda HM, Kayser MP, Wang Y, *et al.* Tuning up an electronic structure of the subphthalocyanine derivatives toward electron-transfer process in noncovalent complexes with C$_{60}$ and C$_{70}$ fullerenes: experimental and theoretical studies. Inorg Chem 2016; 55: 9549-63. https://doi.org/10.1021/acs.inorgchem.6b00992

[47] Cancès E, Mennucci B, Tomasi J. A new integral equation formalism for the polarizable continuum model: Theoretical background and applications to isotropic and anistropic dielectrics. J Chem Phys 1997; 107: 3032-41. https://doi.org/10.1063/1.474659

[48] Reed AE, Curtiss LA, Weinhold F. Intermolecular interactions from a natural bond orbital, donor-acceptor viewpoint. Chem Rev 1988; 88: 899-926. https://doi.org/10.1021/cr00088a005

[49] Schaftenaar G, Noordik JH. Molden: a pre- and post-processing program for molecular and electronic structures. J Comput-Aided Mol Design 2000; 14: 123-34. https://doi.org/10.1023/A:1008193805436

[50] Towns J, Cockerill T, Dahan M, *et al.* XSEDE: accelerating scientific discovery. Comp Sci Eng 2014; 16: 62-74. https://doi.org/10.1109/MCSE.2014.80

Received on 13-06-2017 Accepted on 22-08-2017 Published on 31-10-2017

DOI: https://doi.org/10.6000/1929-5030.2017.06.03.1