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Computational analysis of the conformations of a doubly linked porphyrin–fullerene dyad

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Abstract

A doubly linked porphyrin–fullerene dyad is studied by molecular dynamics (MD) simulations in polar and non-polar solvent, as well as in vacuum. Two conformations representing the most probable vacuum structures are optimised with semi-empirical and density functional methods (DFT) and the structural differences are assessed. The distances between the centres of the porphyrin and fullerene appear very similar in MD simulations regardless of the environment. Optimization with DFT calculations produces centre-to-centre distances that are within 0.07–5% of the corresponding MD values of realistic environments. The results validate the electronic structure calculations relevant to describing photoinduced electron-transfer and related properties in the dyad.

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1. Introduction

In recent years, the issue of designing novel supramolecular donor–acceptor (D–A) complexes that may lead to efficient conversion of solar energy has attracted special attention. In this context, covalently linked porphyrin–fullerene dyads having porphyrin acting as electron donor and fullerene as electron acceptor have proved to be very promising candidates [1–4]. The spatial arrangement of D–A molecules is a subject of primary interest, as the rate of electron transfer (ET) depends considerably on the intermolecular distance and relative orientation of these molecules.

In a previous study [5] we have investigated the possible conformations of a porphyrin–fullerene dyad in which the D–A molecules were connected by a single relatively flexi-

ble linker – molecular chain – that allowed a substantial degree of conformational flexibility in the molecular topology. In the present study, we address the same issues for the case of a porphyrin–fullerene dyad (*DHD6ee*) in which the geometrical freedom of the D–A moieties appears to be strongly restricted by two interconnecting chains (see Fig. 1) [6,7]. In order to study the conformational behavior of *DHD6ee* in different environments, molecular dynamics (MD) simulations are performed both in non-polar (C_6H_6 , benzene, dielectric constant, $\epsilon_r = 2.28$) and polar solvents (C_2H_6SO , dimethyl sulfoxide, DMSO, $\epsilon_r = 47.2$). In addition, MD simulations are performed in vacuum with the purpose of assessing the differences between solvent and vacuum structures, and therefore, the usability of the vacuum structure for the more detailed electronic structure calculations relevant to the photoinduced ET. The most probable conformations obtained from the vacuum MD simulations are optimized with semi-empirical (SE) and density functional theory (DFT) methods and the extent of the structural changes is assessed.

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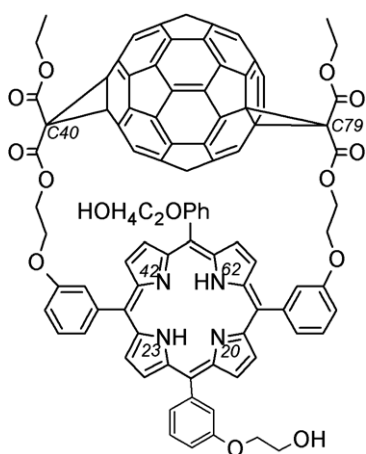


Fig. 1. A 2-dimensional view of the *DHD6ee* dyad.

2. Computational methods

2.1. Molecular dynamic simulations

Molecular dynamics simulations are performed with the GROMACS MD simulation package (versions 3.1.4 and 3.2.1) applying the GROMACS force field (based on the GROMOS-87 force field parameters [8,9] with some modifications [10,11]). Hydrogen atoms bound to the carbon atoms of the porphyrin–fullerene dyad are treated as united atoms. Otherwise atomic detail is used. Periodic boundary conditions are applied to the simulation box (size of 54–73 nm³) to minimize the artificial boundary effects. The simulations are performed with a time step of 0.5 fs. The solvents are included explicitly in the calculations to make the environment as realistic as possible for the molecule of interest. In addition to the 144 atoms of the dyad, there are 371–608 solvent molecules in the simulation box resulting in the total of 2720 atoms with DMSO and 4740 with benzene. To avoid the artifacts created when cutting off the long range electrostatic interactions the Particle-Mesh Ewald [12,13] method is applied to the electrostatic interactions. The charge group-based pairlist is updated every 10 steps. The temperature is controlled using weak coupling to a heat bath of 300 K with a time constant of 0.1 ps [14]. The pressure is kept at 1 bar with a similar procedure using a time constant of 1.0 ps. Initial velocities of the atoms are randomly generated from the Maxwell distribution at 300 K.

The system is first energy-minimized (EM) with the steepest descent method until the maximum of the force gradient components is smaller than 100 kJ/mol/nm or the maximum of 1000 steps is reached. The solvent is then equilibrated at least for 10 ps to remove solvent based bad contacts, while the dyad is restrained applying harmonic potentials with the force constant of 1000 kJ/mol/nm². After the equilibration, the production runs are performed for 50 ns. The results presented are the averages of two to three separate 50 ns runs started with different initial velocities.

2.2. Semi-empirical

The semi-empirical Austin model (AM1)[15] and the parametric method number 3 (PM3) [16,17] are employed for geometry optimization. Both parameterizations are known to provide reliable ground-state geometries for porphyrins and porphyrin–fullerene dyads [18–21]. The calculations were carried out using the AMPAC software [22].

2.3. DFT

Both local-density and general-gradient approximations (LDA and GGA) to the exchange–correlation functional are employed for geometry optimization. In particular, the Slater–Vosko–Wilk–Nusair (SVWN) [23,24] and the Perdew–Burke–Ernzerhof (PBE) [25–28] functionals are used. The Karlsruhe split-valence basis set augmented with polarization functions (SVP) [29,30] is used. The SVP basis set consists of two basis functions for H (4s)/[2s], six basis functions for C (7s4p1d)/[3s2p1d], and six basis functions for N (7s4p1d)/[3s2p1d]. The terms in parentheses represent the numbers of primitive functions of each type and the terms in square brackets represent the numbers of contracted basis functions of each type. The resolution of identity approach (RI) is used to reduce the computational effort, and accordingly, the time needed for calculations [31]. All DFT calculations were performed with the TURBO-MOLE software package [32].

3. Results and discussions

3.1. Molecular Structures: MD studies

Fig. 2a,b show two structures as the representative conformations most frequently found during the vacuum MD simulations at 300 K. The distributions of different atom or atom group distances within the *DHD6ee* dyad obtained from the MD runs of 50 ns in vacuum at 300 K are depicted in Fig. 2c. The peak of the distribution exhibiting the distance between the centres of the porphyrin and fullerene is located at about 0.62 nm with the full width of half maximum (FWHM) of approximately 0.03 nm. The relatively narrow peak indicates that there is not much variation in the distance between the centres of the two moieties. This is an expected result due to the two interconnecting linker chains restricting the motional freedom of the dyad. However, the linkers show some flexibility by allowing the donor and acceptor parts to rotate with respect to each other, as can be observed from Figs. 2a,b, as well as from the atomic distances of Fig. 2c having multiple peaks and larger FWHM values (~0.06–0.09 nm). Fig. 2 also shows that the fullerene is not just rotating about the normal of the plane of the porphyrin ring, but it also has some freedom about the other rotational axes (see the attachment points of the linkers to the fullerene in the side views of Fig. 2a,b). However, the direction of the side chains of the linkers remain roughly the same

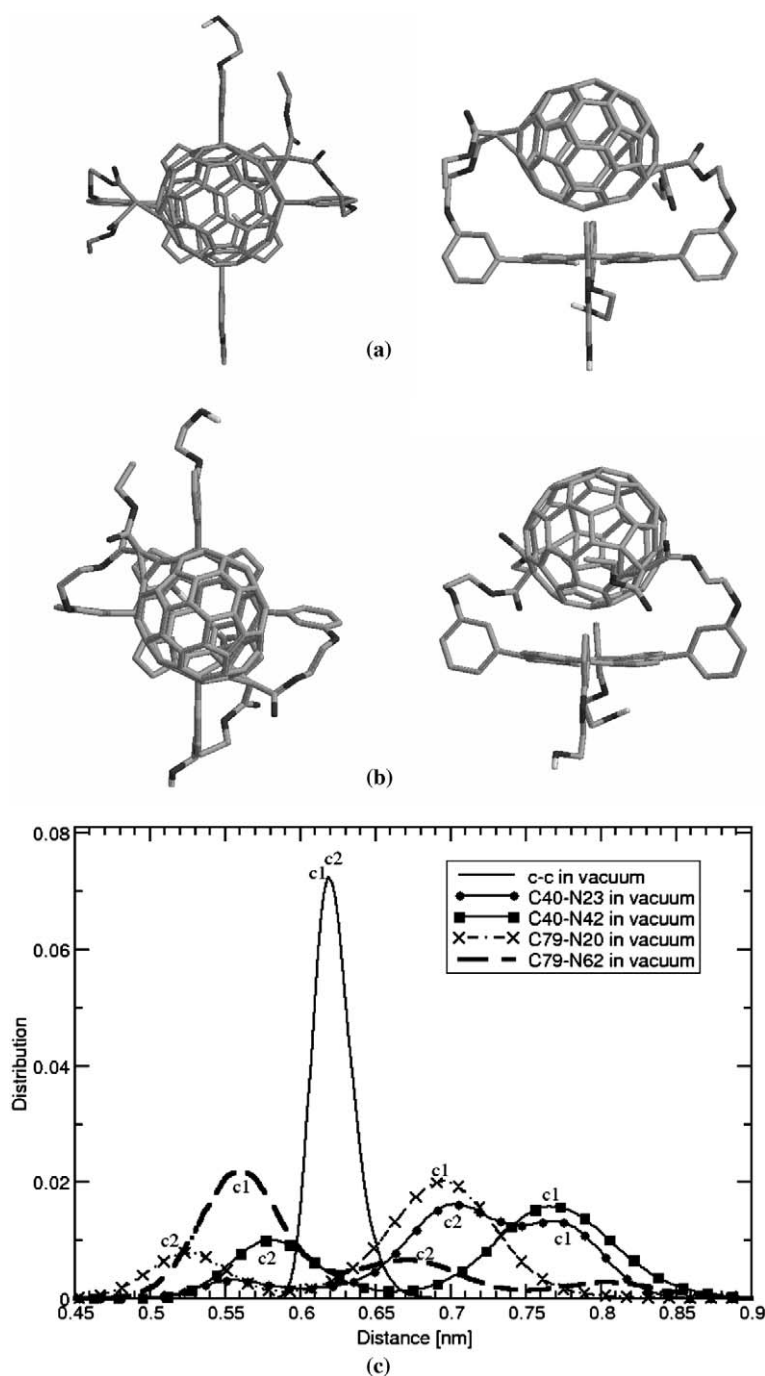


Fig. 2. Two conformations representing the cases most often found during the vacuum MD simulations at 300 K: (a) conformation 1 and (b) conformation 2 (the top views on the left and the side views on the right). (c) The distributions of different atom or atom group distances within the *DHD6ee* dyad obtained from three 50 ns MD runs in vacuum at 300 K: the distance between the centre of the fullerene and the centre of the four nitrogens of the porphyrin ring (c-c: solid line), the distance between atoms C40 and N23 (C40–N23), the distance between atoms C40 and N42 (C40–N42), the distance between atoms C79 and N20 (C79–N20) and the distance between atoms C79 and N62 (C79–N62). The codes c1 and c2 tell which of the peaks of the distributions correspond to the two conformations of (a) and (b), respectively.

meaning that the same half sphere of fullerene is always facing the porphyrin.

In addition to the vacuum runs at 300 K, some of the 300 K structures were used as starting conformations for simulated annealing (SA) runs from 300 K to 0 K. Although the fullerene is not able to move very much over

the porphyrin at 300 K, the simulated annealing leads to somewhat different structures each time when SA is repeated starting from a different 300 K structure of the trajectory. This suggests that the potential energy landscape is relatively rough with several local minima at 0 K. The variation of the distance between the porphyrin and

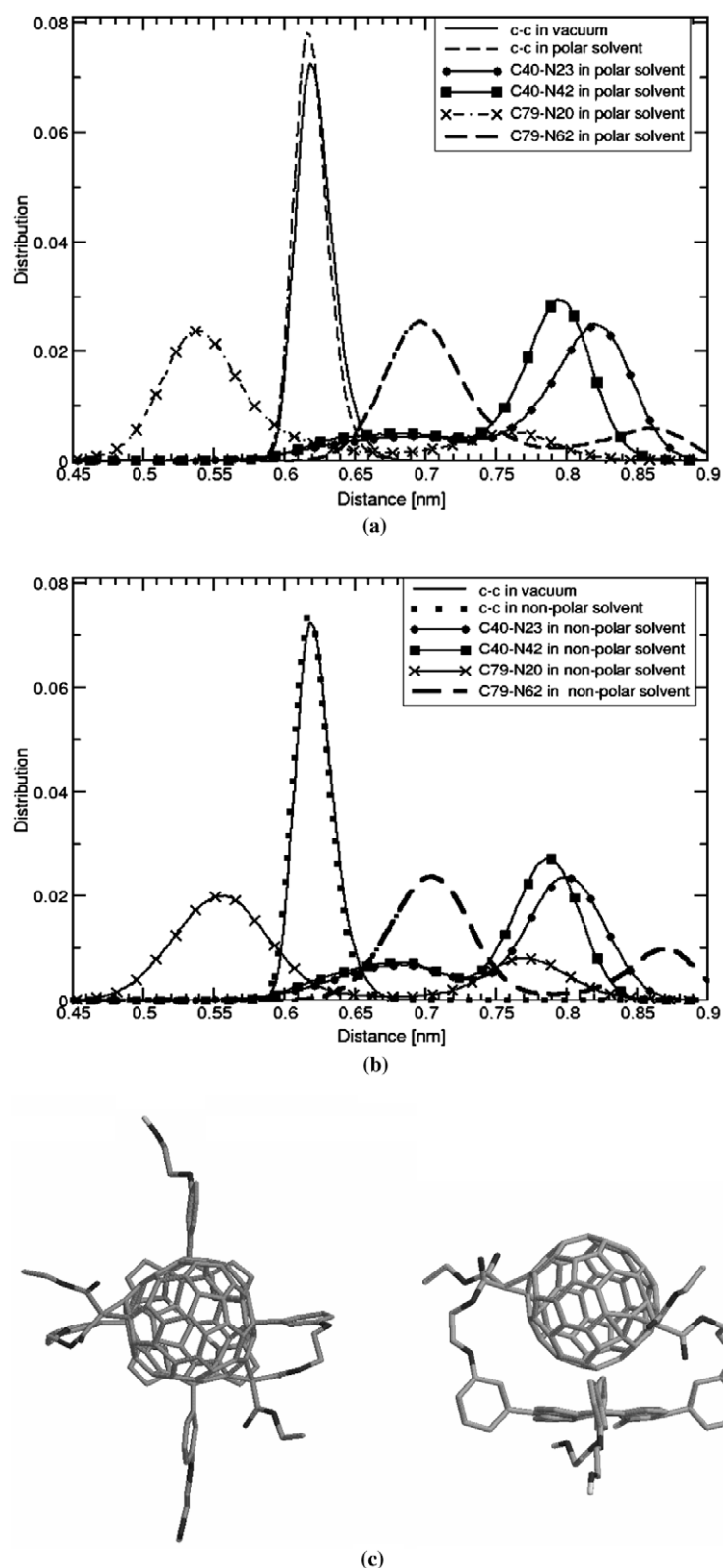


Fig. 3. The distribution of different atom or atom group distances within the *DHD6ee* dyad obtained from 50 ns MD runs in (a) polar and (b) non-polar solvent at 300 K (used similar naming to the one in Fig. 2). The distance between the centre of the fullerene and the centre of the four nitrogens of the porphyrin ring in vacuum (c-c in vacuum: solid line) is also shown as a reference. (c) The top and side views of the representative structure in solvent.

fullerene at 0 K is approximately 20% of the corresponding value measured at 300 K. In the 1-handed case [5], the ligand of the porphyrin never ended up exactly to the same

conformation after different SA runs. The case seems to be something similar here, but now it does not concern the ligand groups only.

The distributions of the different atom or atom group distances within the *DHD6ee* dyad in polar and non-polar solvent (Fig. 3) look very similar to each other. The peaks of the centre-to-centre distance between the porphyrin and fullerene are also very close to the one obtained in vacuum, but the atomic distances (C40–N23, C40–N42, C79–N20, C79–N62) are more confined in the solvents. Accordingly, the linkers seem to be more flexible, showing larger range of movements, in vacuum than in the solvents. The conformation most often found in the solvents (3c) looks similar to the vacuum conformation 1 (2a) with the exception that it is a kind of mirror image of the vacuum structure (see the top views).

3.2. Molecular structures from SE and DFT compared with the MD results

The two representative conformations (conf. 1 and conf. 2) selected from the vacuum MD simulations (see Figs. 2a, b) were optimized with both SE and DFT methods. The general characteristics of the two conformations, i.e. orientation of fullerene with respect to porphyrin (see Fig. 4) and the conformation of the two linkers, are retained also after optimization. Only the AM1 optimized structure of conf. 1 presents a different fullerene and porphyrin orientation. The two molecular units are shifted one with respect to the other, so that a line drawn through their centers of mass would be far from being perpendicular to the porphyrin plane, as it is the case of the other structures presented in Fig. 4. This can be seen from the ratios of the N23(N42)–C40 and N20(N62)–C79 distances, which are evidently larger than for the other conformers.

The porphyrin ring has independent of the calculation method a ruffled conformation, the degree of ruffling being least in the case of the structures optimized at SE level and highest for the representative MD structures. The degree of

ruffling of the porphyrin ring is evidently increasing when the porphyrin–fullerene center-to-center (c–c) distance is decreasing. Inspection of Fig. 4 reveals that the c–c distances for the several analyzed structures are decreasing in the following order $SE > GGA > MD_{vacuum} \geq LDA$. This is similar to the previous observations for a porphyrin–fullerene dyad with a single linker [5]. Additionally, it can be observed that the c–c distance is larger for conf. 2 than for conf. 1. The exception lies again with the AM1 optimized structures, in which the c–c distance of conf. 1 is increased due to the above mentioned shifting of fullerene with respect to porphyrin, thus being larger than in the case of conf. 2.

From the point of view of the c–c distance, the representative conformations of the MD runs are closest to the LDA results, see Fig. 4. In addition, the differences in the c–c distances between the MD and LDA results are smaller than the widths of the c–c distributions in Figs. 2 and 3 indicating that the distances may, in fact, be considered equal within the limits of thermal fluctuations, while the corresponding data of the other methods (GGA, AM1, PM3) show significantly larger deviation from the MD results. The atomic distances (C40–N23, C40–N42, C79–N20, C79–N62) exhibit in general larger variations than the c–c distance for both the LDA and GGA conformations as compared with the MD vacuum ones. However, as the relative orientation of porphyrin and fullerene is preserved after the DFT optimization one might consider the LDA conformation as a promising candidate for further electronic structure calculations and other properties and phenomena including the photoinduced ET in *DHD6ee*.

The conclusion is supported by the experimental results obtained for porphyrin–fullerene dyads having different lengths of the connecting linkers [6]. The results indicate that the main difference with respect to ET properties is related to the values of the electronic coupling between porphyrin and fullerene, while the other factors influencing the ET rates (reorganization energy, free energy change, etc.) vary only slightly with the length of the connecting linkers. For example, by comparing the dyads studied in Ref. [6], the nonradiative relaxation rate is expected to roughly double when the c–c distance increases ca 0.1 nm. However, when looking at the results presented in Fig. 4, we observe that the difference between the MD and LDA results is only a fraction ($\sim 1/5$) of the value of 0.1 nm. Thus, although the crystal structure of the dyad is not known, the experimental data discussed above supports the conclusion that the LDA conformation is a promising candidate for further electronic structure calculations. On the other hand, due to the very fact that the experimental crystal structure is not available, the MD data provided here can also be considered even more interesting.

4. Conclusions

The MD simulations of the doubly linked porphyrin–fullerene dyad in vacuum and in polar and non-polar solvent

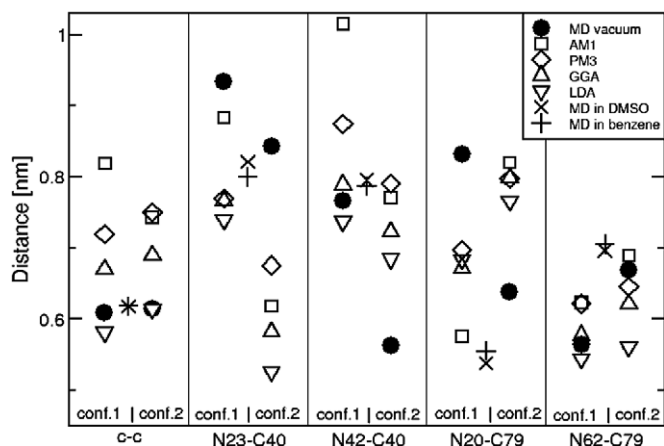


Fig. 4. Graphical summary of the SE, DFT and MD results for conformations 1 and 2 (conf. 1 and conf. 2) and for the solvent conformations: the center to center distance (c–c) between the fullerene and porphyrin, the distances between the atoms N23 and C40 (N23–C40), N42 and C40 (N42–C40), N20 and C79 (N20–C79) and N62 and C79 (N62–C79).

revealed that the distances between the centres of the porphyrin and fullerene are always very similar regardless of the environment. In spite of the relatively strongly restricted centre-to-centre distance, some rotational freedom is found in the relative orientations of the donor and acceptor parts, as well as conformational freedom in the linker conformations. In addition, the conformational freedom of the linker chains is higher in vacuum than in the solvents. The SE and DFT optimisations of two conformations representing the ones most often found in the MD vacuum simulations result in the following order of the centre-to-centre distances of the two moieties of the dyad: SE > GGA > MD_{vacuum} ≥ LDA. After optimization with LDA calculations the centre-to-centre distances are within 4.6% and 0.07% of the corresponding MD values for the two conformations.

Since the similar MD values are obtained also in the solvents, the results suggests that DFT based electronic structure calculations can be used with reasonable reliability to describe also other properties and phenomena including photoinduced electron-transfer in the doubly linked porphyrin–fullerene dyad.

Similar conclusions related to the reliability of the DFT based electronic structure calculations were previously drawn for a porphyrin–fullerene dyad with a single linker [5]. The order of the centre-to-centre distances with respect to the computational method also appeared similar for the two dyads. However, the higher flexibility of the singly linked dyad resulted in a more pronounced effect of solvents on the conformations of the dyad in the previous studies.

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