MOLECULAR DYNAMICS SIMULATIONS OF PORPHYRIN-DENDRIMER SYSTEMS: TOWARDS MODELLING ELECTRON-TRANSFER IN SOLUTION

Pedro M. R. Paulo, José N. C. Lopes and Sílvia M. B. Costa

Centro de Química Estrutural – Complexo I, Instituto Superior Técnico, Av. Rovisco Pais,
1049-001 Lisboa, Portugal

pedro.m.paulo@ist.utl.pt

Organic dendrimers are highly regular and branched polymers that assume a globular shape in solution with dimensions of some nanometers. Since its discovery more than two decades ago, dendrimers have become a very important building block in supramolecular chemistry and nanoscience. The set of potential applications for these molecules encompass a variety of areas, namely, biology (as mimetic systems of enzymes or redox proteins), medicine (in drug delivery, gene therapy and biochemical sensors) and optoelectronics (for transduction of signals or light-harvesting devices).

In previous studies we focused on the non-covalent interactions of a cationic porphyrin (TMPyP) with negatively charged poly(amido)amine dendrimers (PAMAM) in aqueous solution.[1] TMPyP experiences a strong fluorescence quenching effect upon association with PAMAM dendrimers. This effect was attributed to a photoinduced electron-transfer reaction from the tertiary amine groups of the dendrimer to the excited-state porphyrin. The fluorescence decays of the porphyrin-dendrimer ionic complex are multi-exponential and can be fitted with a dispersive kinetics model that considers a statistic distribution of quenching rates, $k^{i}_{\mathrm{ET}}(x)$. This distribution of rates was explained assuming a distribution of donor-acceptor distances that arise from the conformational flexibility of PAMAM dendrimers.[1]

In the present contribution we further explore this issue using Molecular Dynamics simulations. We employed a model based on OPLS/AMBER force field, which was developed for half-generation PAMAM dendrimers.[2] Initially we performed simulations without explicit solvent to achieve simulation times of about one nanosecond. From these trajectories, we could assess different geometries of the porphyrin-dendrimer complex (see figure 1) and retrieve distributions of donor-acceptor distances from the positions of the dendrimer tertiary amines relative to the porphyrin sitting on its *surface*. We have also performed simulations in the presence of explicit solvent (figure 2) and, using a procedure developed by Schulten and co-workers,[3] we were able to estimate the reorganization energy of the medium for different donor-acceptor pairs. The values obtained show a linear dependence with the inverse of the donor-acceptor distance, which is reminiscent of Marcus expression for two charged spheres in a dielectric continuum. Combining the results from the simulations with and without explicit solvent, we have calculated distributions of electron-transfer rates for two simulated configurations of the porphyrin-dendrimer pair using semi-classical Marcus theory of Electron-Transfer. The results obtained from the simulations will be discussed from a critical perspective and, whenever possible, compared to the experimental results.

References:

[1] P.M.R. Paulo, S.M.B. Costa, J. Phys. Chem. B, **109** (2005) 13928.

[2] P.M.R. Paulo, J.N. Canongia Lopes, S.M.B. Costa, J. Phys. Chem. B, **111** (2007) 10651.

[3] M. Nonella, K. Schulten, J. Phys. Chem., **95** (1991) 2059.

Figures:

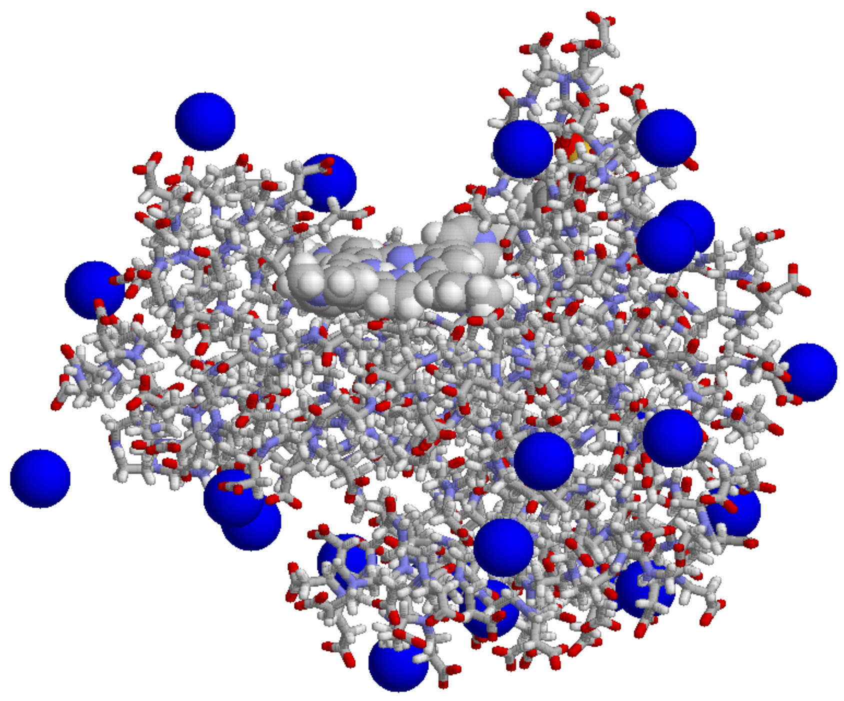

Figure 1 – Snapshot of simulated system without explicit solvent: porphyrin (spacefill) and PAMAM dendrimer (sticks) with sodium counterions (blue spheres).

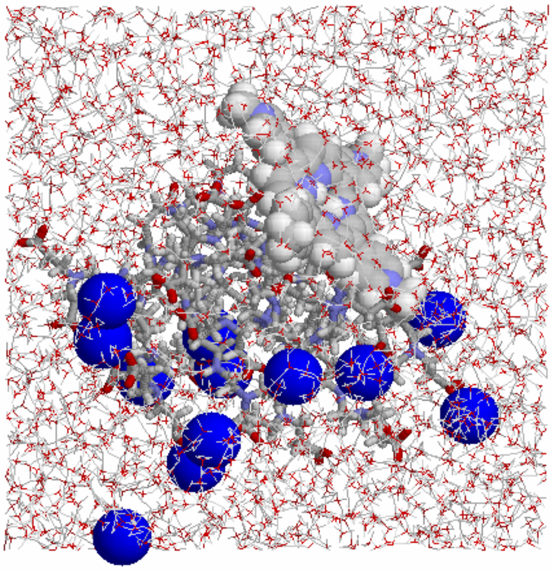

Figure 2 – Snapshot of simulated system with explicit solvent: same representation choice as in figure 1, but with water represented in wireframe.