Conformational dynamics of $TPPS_4$ and theoretical simulation of $TPPS_4$ spectra

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Recently there has been growing interest in $TPPS_4$ for applications in photodynamic therapy.[1] The monomers of this porphyrin efficiently self-associate into H- and J-aggregates in aqueous media. It is not fully understood what kind of $TPPS_4$ configurations are building blocks of aggregates. For these reasons, the aim of this study is to determine tetramers and calculate their absorption spectra.

First of all, QM calculations was performed on geometry optimizations of the structures of $TPPS_4$ zwitterionic monomers. Two different types of the zwitterionic form of the $TPPS_4$ molecules were considered with respect to position of SO_3H protonized groups: either these groups are opposite (Z1 monomer) or adjacent (Z2 monomer). QM calculation were performed using the DFT B3LYP/6-311G(d,p) basis set and PCM methods. The Gaussian 16 program was used. The next step was to take parameters from the GAFF. It was also adjusted several parameters of monomers. MM geometry optimization was also performed. The second step was to construct Z1 and Z2 tetramers. The obtained tetramers were solvated with water boxes. Then MD simulation was performed with AMBER 22 program.

Theoretical calculations of the $TPPS_4$ tetramer's absorption spectra were performed for Z1 and Z2 tetramers. These calculations were performed by associating 4 optical transition dipole moment vectors μ_1, μ_2, μ_3 and μ_4 to each of the molecules constituting the tetramer, the first two vectors corresponding to the Q band and vectors three and four to the B band. Each vector's coordinates were associated with the coordinates of each molecules central nitrogen atoms and then normalised to 11.6 D for μ_1 and μ_2, as well as 3.9 D for μ_3 and μ_4 for all frames obtained from the MD simulation of the aggregate. The tetramer's spectral density was calculated and then averaged for all 5000 frames of the simulation and normalised to a maximum of 1.

It was determined two Z1 and Z2 linear (Figure 1 (a),(b)) tetramers. These tetramers have many different conformers which change during MD simulation. Conformers differing by protonized sulpho group positions: one/both/neither sulpho groups are interacting with porphyrin ring. Theoretically calculated absorption spectra (Figure 1 (c) and (d)) coincide with experimentally measured spectra.[2]

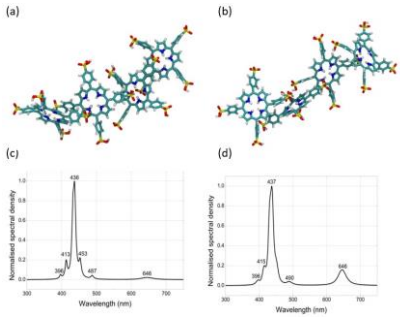

Fig. 1 $TPPS_4$ Z1 (a) and Z2 (b) linear tetramers, absorption spectra of $TPPS_4$ Z1 tetramer (c) and averaged $TPPS_4$ Z1 tetramer spectrum of 5000 frames (d).

References

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