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Simulation of some dynamical aspects of the photophysics of dye molecules encapsulated in a dendrimer

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Abstract

We use a combination of molecular dynamics and quantum chemical calculations to investigate the photophysics of Eosin Y encapsulated in a fourth generation of poly-propylene amine dendrimer functionalized in the periphery with dansyl units. Once in contact with the macromolecule, the guests display a double exponential decay of the excited states that is reproduced by the present model.

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Keywords: Dendrimers; Guest–host systems; Molecular dynamics; Quantum chemistry; Kinetics

1. Introduction

The hyper-branched structure of dendrimers has often been advocated as an ideal cove for the encapsulation of molecules [1–6]. The macromolecule can then be used as a carrier to deliver the guest through hostile or aggressive environments. While one of the main practical purposes of the creation of these guest–host systems lies in the sheltering of the guest from the outside environment, the interactions with the dendrimer modify some of the electronic properties of the encapsulated molecule. Indeed, Balzani et al. [7] showed that poly(propylene amine), in short POPAM, dendrimers, functionalized in the periphery with dansyl units, accept a varying number of guests that undergo changes of their photophysical properties. The guest–host interactions modify the photophysical properties of Eosin and turn its mono-exponential decay—typical of the aqueous solution—into a bi-exponential one in CH_2Cl_2. The existence of two lifetimes may be taken as an indication that there are two types, or two families, of sites in the dendrimer, or, alternatively as a signal that there are two types of average interactions. The ability to tune and

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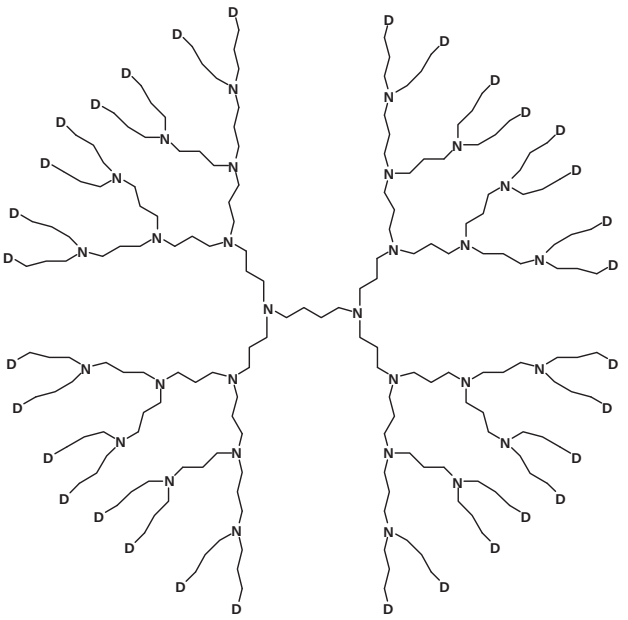
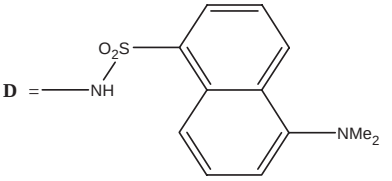
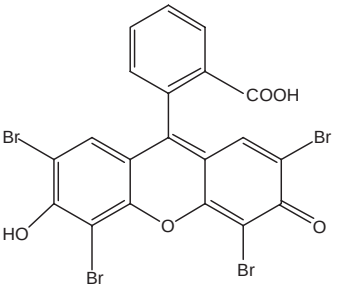


POPAM-4D



Dansyl



Eosin Y

Scheme 1.

modify the electronic properties of one, or more, guest molecules can have practical consequences and be exploited practically, for instance in the field of chemical sensors.

In the past, we presented molecular dynamics, MD, calculations of a guest–host system made by the fourth generation, 4D, dansyl functionalized POPAM dendrimer, with a varying number of Eosin Y, Scheme 1 [8]. The calculations successfully accounted for the ability of POPAM-4D to extract up to six molecules of Eosin Y from an aqueous solution to a CH_2Cl_2 solution that contained the macromolecule. However, they did not consider the variation of the excited state decay of the dye in the presence of the dendrimer. Here, we analyze the molecular dynamics runs performed previously and develop a simple model able to explain the photophysical properties of Eosin@POPAM-4D.

The work is presented as follows: Section 2 summarizes succinctly the theoretical methods, Section 3 applies them to the guest–host system and compares experiments to theory; Section 4 contains the conclusions.

2. Computational background

The molecular dynamics, MD, calculations were performed with the MM3 force field that has been found to be accurate for organic systems [9] and was parameterized explicitly to describe the $\pi-\pi$ stacking interactions that govern a sizeable part of the interactions in this system. Modifications of some of the torsional parameters were necessary and details have been published elsewhere [8].

MD calculations were run with the Tinker 3.8 program [10] using the approach of Berendsen et al. [11] with periodic boundary conditions (PBC), a cubic box with a linear dimension of 73 Å at constant volume and at a temperature equal to 300 K. The approach based on MM3 implemented