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Molecular Dynamics of a Dendrimer−Dye Guest−Host System

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Abstract: We use molecular dynamics to investigate the instantaneous structure of a fourth generation (dansyl terminated) dendrimer of propylene amine dissolved in CH_2Cl_2, and of the same system upon the subsequent encapsulation of several eosin Y dyes. Calculations, in a cubic box with up to ∼3500 solvent molecules and a maximum of 12 eosins, show that one of the effects of the presence of the guest molecules is to "close" the structure of the box where they are contained. Multiple entrances-exits of the guest molecules in the dendrimer are observed in less than a nanosecond, until the excess eosins are irreversibly expelled and their number is finally brought down to the experimental limit of 6. The guest molecules are distributed at two main distances from the center of the dendrimer and their surroundings are far from static. Eosins move inside the hyperbranched molecule in a way similar to what the solvent molecules do and sometimes aggregate.

I. Introduction

Dendrimers are a class of macromolecules named after the ancient Greek words δϵνδρον and μϵροσ, which mean tree and part, respectively. Given a structural motif, dendrimers radiate from a central core branches-upon-branches to form well-defined macromolecules.[1] Repetitive synthetic steps form successive shells that yields generations of perfectly monodispersed hyper-branched polymers.[2] High control is now achieved over size, shape, and terminal functionalization of the branches (i.e., surface chemistry).[1,2] The three main synthetic approaches of Tomalia (namely, the Starburst divergent strategy),[1,2] Fréchet (i.e., the convergent strategy)[3] and Zimmerman (viz., the self-assembly strategy)[4] have generated dendrimers with a variety of properties and applications, which range from the preparation of new drug delivery systems to inks.[5] An important potential application of dendrimers is the encapsulation of molecules, that is the formation of guest−host systems.[6]

The present work was prompted by that of Balzani et al.[7] who showed that a 4-th generation poly(propylene amine) dendrimer, in short POPAM-4D, functionalized in the periphery with dansyl units, accepts a varying number of guests. Their experiment is a classical example of simplicity in chemistry: Two solutions, one aqueous with dissolved eosin Y and one organic with dissolved POPAM are brought in contact. This dye is water-soluble and is not soluble in CH_2Cl_2. It is, however, transferred to the organic phase through the interaction with the macromolecule, which hosts up to six molecules and modifies their photophysical properties.[7]

To understand the details of the interactions in the guest−host system (see Scheme 1), we decided to perform molecular dynamics, MD, calculations of the dendrimer in CH_2Cl_2 solution and then repeat the calculations with an excess number of eosins with the intent of obtaining instantaneous structural information.

The phenomenon we investigate is quite general. The same macromolecule can, in fact, accept even more molecules of Rose Bengal.[7] Other dendrimers accept varying numbers of guests. For instance, hyperbranched polyglycerols take in Congo Red,[8] and polyphenylene dendrimers host Pinacyanol.[9] Importantly, the dis-homogeneity of the latter system has recently been

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Scheme 1
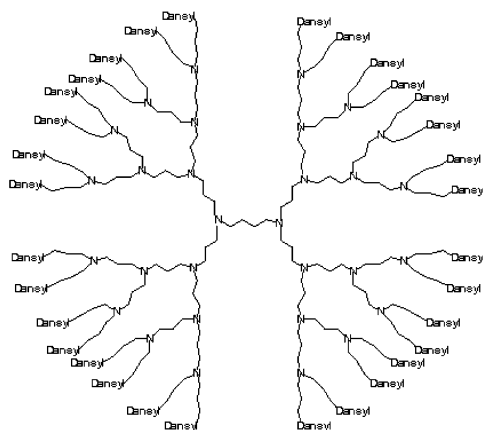
POPAM-4D
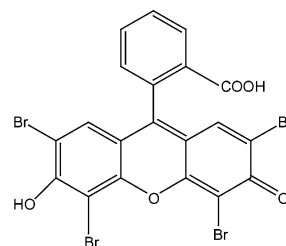
Eosin Y

investigated by single-molecule spectroscopy experiments in the solid,[9] which proved, among the rest, that the guests experience a variety of environments.

The elucidation of the structural and dynamical properties of dendrimers and their guest–host systems is one of the crucial steps toward their practical exploitation. The ability to modify the properties of guest molecules can have practical consequences, for instance, in the field of chemical sensors. However, the flexible branches, which characterize the majority of dendrimers, can rearrange to form a myriad of conformations. Their interconversion is rapid in the liquid and this exchange can be partly transmitted to the solid, making the structural characterization very difficult, (see, however, ref 9). It is believed that molecular modeling can assist the process of developing a quantitative understanding of the geometrical and dynamical properties of dendrimers.[1,10] Section II summarizes the theoretical methods, section III applies them to the host and the guest–host system and illustrates the results also in view of the experiments.

II. Computational Background

The calculation were performed with the MM3 force field that has been found to be accurate for organic systems[11] and was parametrized explicitly to describe the π–π stacking interactions that govern a sizable part of the interactions in this system. The S–C and S–N torsional potential energy curves of the sulfonamide of the dansyl units were not properly parametrized. The rigid torsions about the two types of bonds were calculated using B3LYP/6-31G* level of theory taking, as a model system, *N*-ethyl-phenylsulfonamide. The quantum chemical data were fitted to the standard MM3 torsional potential that reads

$$V_{\text{tors}} = \left(\frac{V_1}{2}\right)(1 + \cos\omega) + \left(\frac{V_2}{2}\right)(1 - \cos2\omega) + \left(\frac{V_3}{2}\right)(1 + \cos3\omega)$$

(1)

see Table 1 for the parameters.

Table 1. V_n, n = 1,2,3, kcal mol^{-1}, of the Potential Energy Curve of the S–C and S–N Torsions

torsion	V_1	V_2	V_3
NSCC	−9.06	4.64	5.33
OSCC	−2.18	3.72	−1.66
$C_{sp}2SNC_{sp}3$	3.08	−0.83	1.34
OSN $C_{sp}3$	−4.90	3.69	0.73
$C_{sp}2SNH$	−1.40	−0.91	−0.12
OSNH	−2.59	3.62	−0.98

Comparison between the points calculated for the torsional energy potentials is shown in Figure 1a for S–C and Figure 1b for S–N. The largest deviation is a few percent.

The molecular dynamics (MD) calculations were run at constant volume and at a temperature equal to 300 K, using periodic boundary conditions (PBC),with the Tinker 3.8 program.[12] The approach of Berendsen et al.[13] was used along with a cubic box with a maximum linear dimension of 75.84 Å. The approach based on MM3 implemented in the Tinker program has been rather successful in a variety of applications carried out in our laboratory.[14]

Solvent molecules of CH_2Cl_2 were treated explicitly. To reduce the total number of atoms in the calculations, CH_2Cl_2 was parametrized in the form of a dipole of 1.6 D, described by two pseudo-atoms separated by 2.22 Å and interacting with a force constant of 4.0 mdyn Å^{-1}. The smaller positive center has a van der Waals radius of 1.88 Å and a well depth of 0.19 kcal mol^{-1}; the larger negative center has a van der Waals radius of 2.38 Å and a well depth of 0.71 kcal mol^{-1}. Table 2 compares the performance of the present CH_2Cl_2 parametrization with previous work and with experimental data.[15] The agreement is quite satisfactory.

The fourth generation POPAM dendrimer was built in successive steps by an in-house written computer program and the geometry was initially optimized in the vacuum. Eosin Y was also optimized in the vacuum and then inserted in the dendrimer in regions that are

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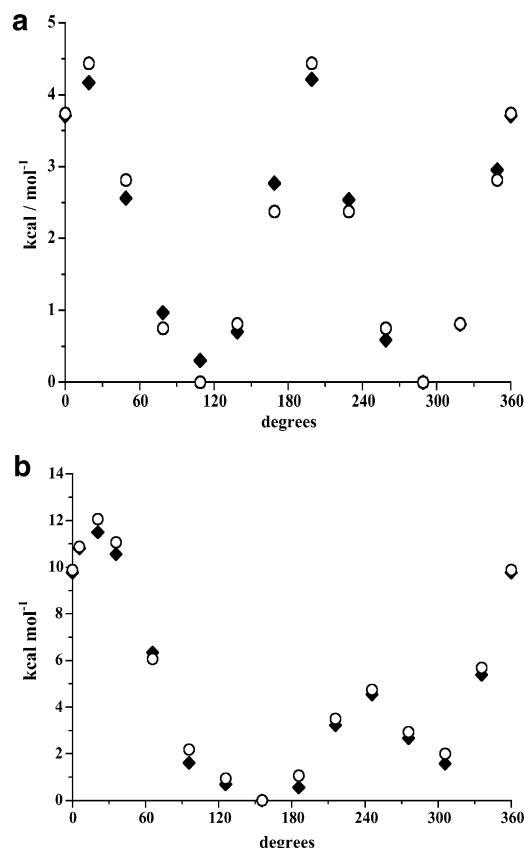
Figure 1. Comparison of the potential energies for the rigid torsion about the (a) S−C and (b) S−N bonds: solid circles B3LYP/6-31G*, diamonds present parametrization.

Figure 2. Instantaneous ratios of moments of inertia I_1/I_2 and I_1/I_3, with $I_1 > I_2 > I_3$ of POPAM-4D in CH_2Cl_2 solution. The "middle" curve is the gyration radius.

III. Results and Discussion

Before presenting the results of the simulations, it is worth summarizing the experiments. Eosin is water-soluble, where it forms a colored solution, and is not soluble in CH_2Cl_2. The dendrimer is soluble only in CH_2Cl_2. Shaking together two solutions, one made by water + eosin, the other made by CH_2Cl_2 + dendrimer, removes eosins from the aqueous phase, the color of water fades, whereas the CH_2Cl_2 solution becomes colored. Spectroscopic measurements, with varying volumes of the two solutions, indicate that each dendrimer molecule can interact with up to six eosins. The concentration of the dendrimer in CH_2Cl_2 is less that 10^{-5} M (2.7×10^{-6} M). The concentration of eosin in water is 10^{-5} M. Aggregation and dis-homogeneity in solution should therefore be unimportant on a long time scale, but may occur inside the macromolecule.

Flexibility of POPAM-4D. In solvents, dendrimers tend to have collapsed, compact conformations.[16] Internal mobility is, however, high because of the low activation barrier of the torsional degrees of freedom and to the high flexibility of the branches. Figure 2 displays, as a function of the simulation time, the instantaneous ratios of the largest moment of inertia divided by either one of the other two. A spherical static dendrimer would have both ratios constant and equal to one. On the contrary, the figure shows that during the dynamics I_1/I_2 ranges between 1 and 2, whereas I_1/I_3 ranges between 2 and 3 ($I_1 > I_2 > I_3$). A further index of the internal mobility of the dendrimer is the instantaneous gyration radius that changes by nearly 25% during the simulations and is also represented in Figure 2.

This variation is in good agreement with other MD simulations of dendrimers.[17] The nonsphericity of the macromolecule makes the use of r_{gyr} not entirely significant to investigate its properties. A sphere with this radius includes regions where only solvent molecules are present and, conversely, does not reach regions where there may be dendrimer atoms. In principle, however, r_{gyr} can still be useful to define roughly an inner part, or core, and an outer part, or surface/periphery, of the dendrimer.

Solvent Molecules Inside POPAM-4D. Figure 3 presents the evolution of the number of solvent molecules with either a

Table 2. Comparison of Calculated and Experimental Data for CH_2Cl_2

	ΔH_{vap} (kcal mol^{-1})	ρ (g cm^{-3})	D (10^{-5} cm^2 s^{-1})[a]
exp	6.89	1.317	3.3, 3.7, 3.8
ref 15 (flex. model)	6.57	1.284	2.6
ref 15 (rigid model)	6.09	1.251	2.5
present parametrization	6.95	1.332	3.5

[a] self-diffusion coefficient.

characterized by the largest cavities. The whole guest−host structure was then further optimized. The dendrimer, with up to 12 randomly placed eosins was then placed in the solvent box where the solvent had been previously equilibrated. All solvent molecules with center of mass less than 4.2 Å away from any atom of dendrimer were removed. The 4.2 Å value was determined by trial and error to replace an equal number of atoms. This leads to a system of 3526 CH_2Cl_2 molecules plus the guest−host system. Equilibration was performed in the NVT ensemble at 300 K until the potential energy converged.

To analyze quantitatively the results, one can use two distances. The first is the gyration radius, r_{gyr}

$$r_{gyr} = \left[\frac{\sum_i^{N_d} m_i(r_i - r_{CM,d})^2}{M_d} \right]^{1/2} \quad (2)$$

where m_i and r_i run over all the masses and the positions of the atoms of the dendrimer, $r_{CM,d}$ is the location of the center of mass of the dendrimer, and M_d is the dendrimer mass; the second and more relevant distance is the shortest distance between an eosin atom and a dendrimer atom.
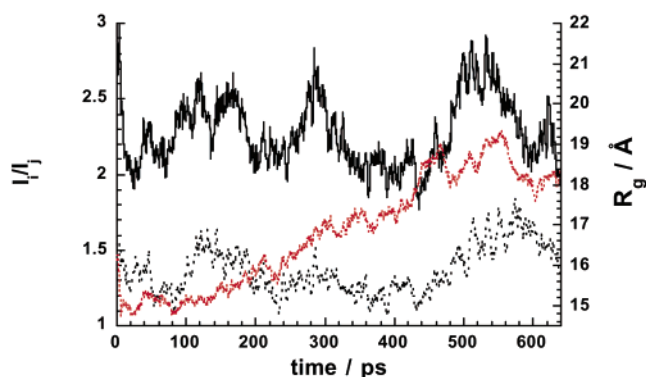
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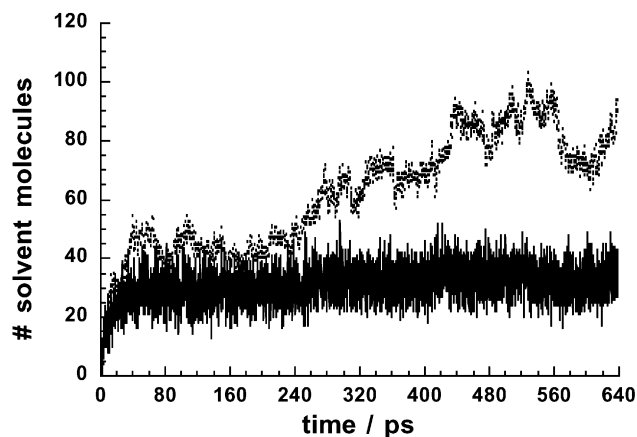(17) Karatasos, K.; Adolf, D. B.; Davis, G. R. *J. Chem. Phys.* **2001**, *115*, 5310−5318.

Figure 3. Instantaneous number of solvent molecules inside POPAM-4D in CH_2Cl_2 solution: the solid line is the number of solvent molecules with at least one atom less than 2.8 Å away from an atom of the dendrimer, the dotted line is the number of solvent molecules inside the dendrimer gyration radius.
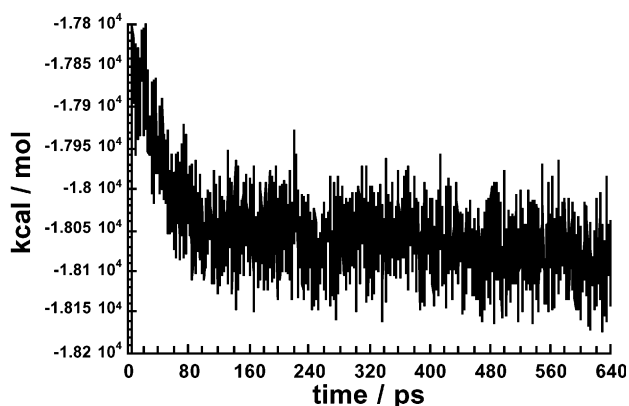

Figure 4. Instantaneous potential energy during the simulation of POPAM-4D inside the CH_2Cl_2 box.

Figure 5. Instantaneous ratios of moments of inertia I_1/I_2 and I_1/I_3, with $I_1 > I_2 > I_3$ of POPAM-4D in CH_2Cl_2 solution, 12 eosins are present in the simulations box. The curve that reaches the top on the right is the gyration radius.

Figure 6. Instantaneous shortest distance between an eosin atom and a dendrimer atom.

distance from any atom of the dendrimer shorter than 2.8 Å, or inside the gyration radius.

Because of the way the simulation is set up, CH_2Cl_2 molecules are not initially present inside POPAM-4D. The solvent molecules penetrate very rapidly inside the dendrimer and, in less than 60 ps, reach an average number that slightly exceeds 30. Figure 4 shows that, once the solvent has penetrated inside the macromolecule, the dynamics reaches equilibrium with a near constant value of the potential energy.

The present percolation process does not correspond to a real physical process. Its investigation is, however, useful to understand the rapidity of the solvent movements inside the dendrimer, which are, as expected, "virtually" unhindered. The number of CH_2Cl_2 molecules, inside the gyration radius, is larger than the number of molecules in contact with POPAM-4D (see the discussion in the previous subsection). Indeed, comparison of Figures 2 and 3 shows that when the radius is larger, more solvent molecules are inside it, although several of them belong to dendrimer-free regions. The overall conclusion of this subsection is that the solvent mobility inside the dendrimer is high.

POPAM-4D When the Guest Dyes are Present. Figure 5 shows the ratios of the largest moment of inertia divided either one of the others, together with the gyration radius in the presence of the eosins.
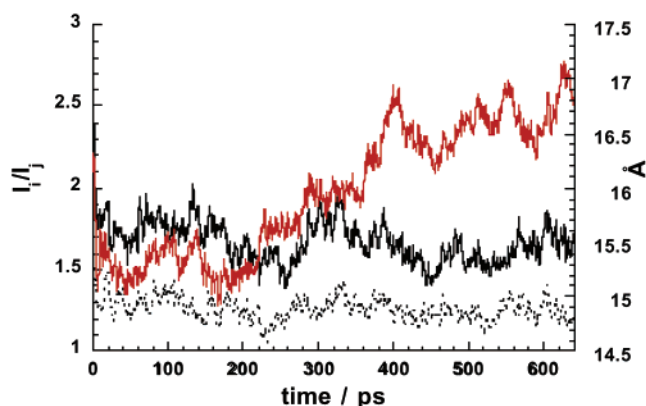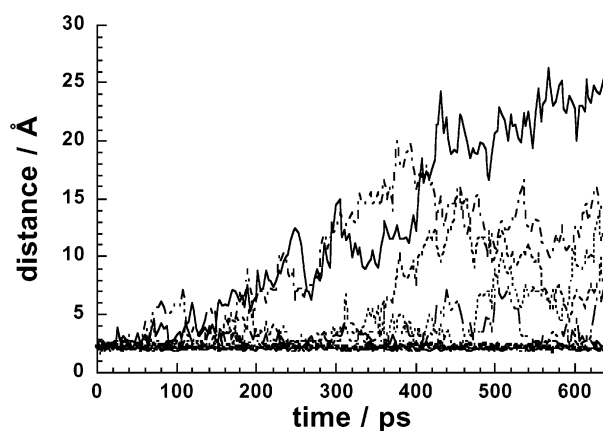
Comparison with Figure 2 shows that the guests compact further the dendrimer structure: the gyration radius is decreased by a few percent and the ratio between the largest and the smallest moment of inertia is diminished by ∼20%, so that the macromolecule is more spherical. Notice that in the equivalent of Figure 3 (not shown), the evolution of the number of solvent molecules in contact with the dendrimer shows that there is a 20% decrease in the number of solvent molecules inside POPAM-4D. Their total volume is smaller than that of the new guests.

Comparative analysis of data allows summarizing the effect of the presence of the dye molecules as a way to manipulate the structure of the dendrimer, which becomes more spherical and denser. Noteworthy is that, despite the smaller size and the increased compactness of the structure, the volume of the solvent molecules expelled by the eosins is smaller than that of the new guests. The partial conclusion of this subsection is that the presence of the dyes makes the macromolecule more box-like.

Eosins and POPAM-4D. The time evolution of the shortest interatomic distance of the eosin molecules from the dendrimer is shown in Figure 6.

Of the twelve guest molecules, at least six remain constantly in van der Waals contact with the host. The others six show multiple entrances-exits from the macromolecule van der Waals region with about half of them finally leaving permanently POPAM-4D. This trend emerges even more clearly from Figure
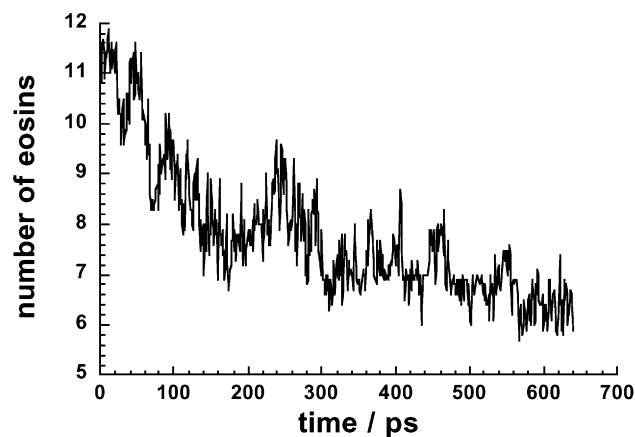
Figure 7. Instantaneous number of eosins with an atom less than 2.8 Å away from a dendrimer atom. The number of eosins is determined by averaging over every picosecond, the line that joins the points is intended only to assist the eye.

7, which presents the instantaneous number of eosins with an atom less than 2.8 Å away from a dendrimer atom: convergence toward the experimental number of six is observed. Notice that the number of eosins is determined by averaging over every picosecond, the line that joins the points is intended only to assist the eye.

An important issue to consider is the origin of the multiple entrances-exits observed in the short time frame of less than a nanosecond. Experiments and simulations concur that the hyperbranched molecule can accommodate only six eosins. Excess eosins therefore tend to leave the host and to find the "unfriendly" solvent environment, where they are not soluble. Low solubility implies, although not only, weak intermolecular interactions with the solvent. If, after departure from POPAM-4D, then the dye comes again in contact with the macromolecule, the favorable stabilizing interaction forces generated "suck" it in. In so doing, they may displace another guest molecule, or, alternatively, if the closest guest molecule is solidly embedded, then it may be difficult to displace and the eosin is expelled again. It is therefore expected that one would observe a large number of entrances/exits in the conditions of these simulations.

Notice that the periodic boundary conditions used here make some molecules first leave from a face of the simulation box, and then re-enter from the opposite one. Depending on the orientation of the dendrimer inside the box, and the region where a given eosin is located, both the path covered by the dye and the maximum distance between guest and host that can be reached may vary. When this technical event occurs, its equivalent, in a real solution, is the molecule moving toward another POPAM-4D.

Location of the Guest Molecules. Figure 8 shows the evolution of the distances between the centers of mass of the "permanent" guest eosins and that of the dendrimer. Although their location was randomly generated, they separate in two groups with three molecules residing in the core of the dendrimer and three in its periphery.

Similar results were obtained in other simulations that are not shown here. In practice, the eosins reside either in the inner core of the dendrimer or on its surface. In both case, they show a substantial mobility, which may even bring them in contact with each other.
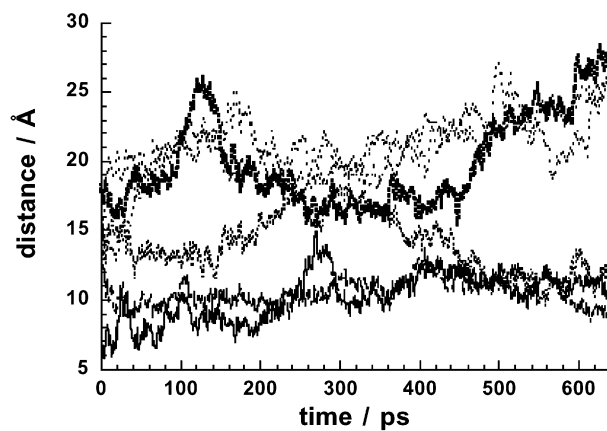

Figure 8. 6Eosin@POPAM-4D instantaneous distance between the centers of mass of the individual surviving eosins and the dendrimer's.
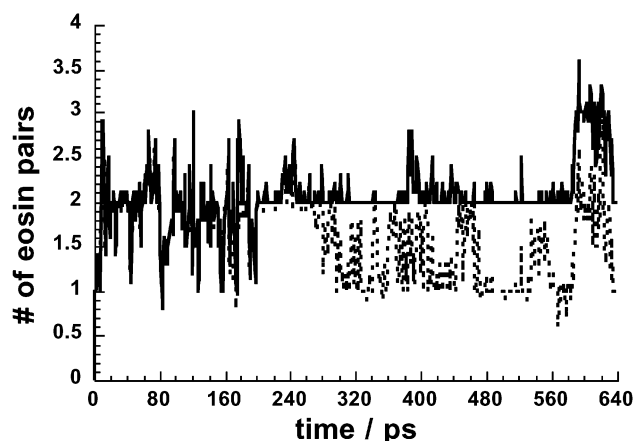

Figure 9. Number of eosin pairs with at least one atom−atom distance smaller than 2.8 Å. Solid line all eosins. Dotted line at least one atom of the pair is at a distance smaller than 2.8 Å from the dendrimer. The number of eosins pairs is determined every picosecond by averaging over the this time, the line that joins the points is intended only to assist the eye.

Figure 9 shows that a number of eosin pairs, with at least one atom−atom distance smaller than 2.8 Å, are instantaneously formed. Some of the pairs permanently leave the macromolecule. Because some contact-times are very rapid, it was thought that the best way to present the figure was to average, at each point in time, the number of pairs over 1 ps of simulation. In practice, there is always at least one eosin pair inside the dendrimer.

Comparison with Experiments. The original experiments on the eosins@POPAM-4D showed the presence of two lifetimes ($\tau_1 = 2.2$ ns, $\tau_2 = 0.6$ ns) for the dyes.[7] This is contrary to the single lifetime observed for eosin in water. It is tempting to ascribe these lifetimes to their distribution inside the dendrimer (Figure 8). One lifetime would be caused by the larger POPAM-4D-eosin interaction when they reside in the core, while the other by the eosins residing in the periphery. A second possible explanation of the two lifetimes is that one of them is caused by single eosins entrapped inside the macromolecule, whereas the other is due to pair, i.e., dimer, formation. It must be mentioned that the rapid movements of the eosins in the dendrimer make both these qualitative pictures not entirely satisfactory because of their static representation of highly dynamical processes. Importantly, however, differences in the environments of the eosins that may lead to the presence of

two lifetimes are well present here. The simulations are also in accord with the detailed microscopic picture obtained by single molecule spectroscopy investigation for another dendrimer−dye guest−host system, which show that the guests experience a wide variety of environments.[9]

IV. Conclusion

MD calculations find that POPAM-4D is a flexible system where a large number of solvent molecules move nearly freely. Introduction of 12 eosins in a thought-experiment shows that they tend to leave the macromolecule, first tentatively with several returns and then permanently until they reach the experimental limit of six. The presence of the guest molecules compacts and makes more spherical the dendrimer structure. Each of the guest molecules can still move inside the host substantially. The six dyes that remain in contact with POPAM-4D are found at two main distances from the center and are often in van der Waals contact with one another, forming at least one pair, at any given time. The simulations agree with recent spectroscopic findings on dendrimer-based guest−host systems and show that there are no static cavities in the dendrimer with eosins molecules inside.

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