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Molecular dynamics studies on the aggregation of Y-shaped fluoroalkanes

Abstract Molecular dynamics (MD) calculations have been performed on the aggregation of clusters with up to 128 Y-shaped perfluoroalkylated molecules of the type $C_{10}F_{20}[C_7H_{15}]_2$ (Y-A/128) and $C_{10}H_{20}[C_7F_{15}]_2$ (Y-B/128) as well as mixed clusters (Y-A/64+Y-B/64) using the AMBER 5 program. The effect of the segregation tendency of the chemically different parts and the influence of the steric repulsion due to the wedge shape of the molecules on the structure formation have been studied. The results have been analyzed by snapshots, radial atom pair distribution functions, orientational correlation functions as well as diffusion coefficients and are compared with the corresponding findings on clusters of alkanes and perfluoroalkanes. Electronic supplementary material to this paper can be obtained by using the Springer LINK server located at http://dx.doi.org/10.1007/s00894-002-0092y.

Keywords AMBER 5 · Fluorine effect · Distribution functions · Diffusion coefficients

Introduction

The covalent linking of chemically incompatible moieties is a successful concept to vary or create new liquid crystalline structures. The insertion of fluorinated segments into molecules causes remarkable changes in their mesomorphic behavior. [1, 2, 3, 4, 5] In a recent paper, we used MD simulations on clusters of alkanes and per-

fluoroalkanes [6] to show that perfluorinated alkyl chains have a significantly different flexibility and aggregation tendency in comparison to the alkane analogues.

Moreover, the molecular shape has a strong influence on structure formation by steric repulsion. Polyphilic compounds with partially fluorinated alkyl chains are of interest as non-chiral potentially ferroelectric crystals. [7, 8, 9] The Y-shaped molecules Y-A ($C_{10}F_{20}[C_7H_{15}]_2$) and the inverse form Y-B ($C_{10}H_{20}[C_7F_{15}]_2$) are suitable model compounds for studying the influence of the combined effect of phase separation and steric repulsion on the aggregation with respect to the length and position of the perfluorinated parts. Therefore, we have performed molecular dynamics (MD) calculations on the clusters Y-A/128 and Y-B/128 as well as the mixed clusters (Y-A/64+Y-B/64) using the full resolution force field of the AMBER 5 program [10]. Up to now, other MD simulations on the fluorine effect were mostly based on a united atom model that treats the CF_x and CH_x (x=2, 3) groups as pseudo-atoms. [11, 12, 13, 14] The results of the MD calculations have been analyzed by snap shots, radial atom pair distribution functions $g(r)$ and orientational correlation functions $g(o)$ with respect to the corresponding basic atoms and vectors as well as by diffusion coefficients.

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Details of computation

The MD simulations have been carried out with a version of AMBER 5 [10] implemented for the parallel computer HP SPP 2000 of the computational center of the university of Halle. For the fluorine atom, standard parameters of the AMBER 5 Program, verified on small molecules, were used. PM3, ab initio HF-SCF/6-31G and AMBER results of perfluoroeicosane (PFES) show that the force field reproduces the structural features indicating a helical torsionality of the chain of PFES monomer in contrast to the all-*trans* form of eicosane. [6] Atomic net charges for the molecules were adapted

from the fit to reproduce the electrostatic potential within the PM3 method. This procedure is frequently used to evaluate atomic charges in force field methods and is consistent with the defined atomic charges for amino acid fragments in the AMBER program. Moreover, ab initio and PM3 net charges both from Mulliken population analysis and from the fit of the electrostatic potential were checked. The used PM3 net charges reproduce the structural features of small fluorinated molecules in a suitable way. Classical MD studies within the (n, p, T) ensemble [6] have been performed at a temperature of 300 K and with simulation times of 400 ps. For the pressure the default value (1 bar) of the AMBER program was used. During the MD run a decrease of the box size was observed.

This time range has been proven to be sufficient in simulations on biochemical and mesogenic systems. [15, 16, 17] In an initial time period of about 60 ps the temperature was raised from 0 to 300 K. A time step of 0.5 fs and periodic boundary conditions were used in all simulations of the clusters. Non-bonded interactions were calculated with a cut-off radius of 4,000 pm. Bond lengths were constrained for all atoms using the SHAKE algorithm. The edge lengths of the box were generated by the program from the dimensions of the molecular clusters considered. Further information on the AMBER calculations (atom types, charges and related parameters) is given as supplementary material and is also available from. [6]

Results and discussion

The aggregation behavior of the wedge-shaped molecules with perfluorinated segments at different positions was investigated by comparing MD studies of the clusters Y-A/128 and Y-B/128 as well as mixed systems (Y-A/64+Y-B/64). The clusters were built up from smaller sub-units with extended chains to obtain suitable initial configurations. On the basis of such relatively high ordered configurations including different arrangements of the Y-shaped molecules the MD procedure was performed. Some of the starting structures of the clusters are schematically illustrated in Fig. 1.

Snapshots

First impressions of the aggregation process of the Y-shaped molecules in the clusters were obtained by looking at the snapshots during the MD run using graphics tools. The snapshots of the clusters after a simulation time of about 300 ps are shown in Fig. 2. The hydrogen and fluorine atoms are not drawn in the figures to give a clearer representation of the main features. The relatively ordered initial configurations break down after a simulation time of a few picoseconds. The fluorinated chains have a higher stiffness and show domains with layer-like structures. The covalently bound alkyl seg-
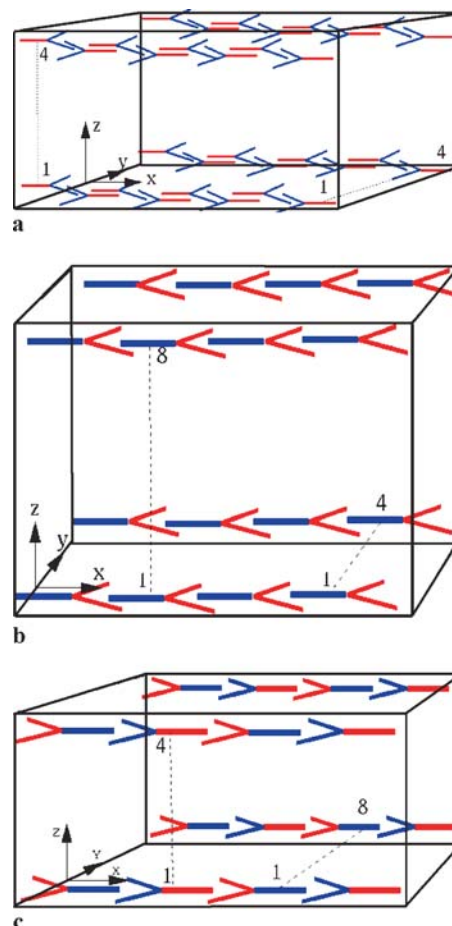

Fig. 1 Arrangements of the Y-shaped molecules in some of the considered initial configurations of the clusters. **a** Y-A/128. **b** Y-B/128. **c** Y-A/64+Y-B/64. (Perfluorinated chains *red*, alkyl chains *blue*)

ments indicate a higher flexibility and folded arrangements, which limit the structure formation of the perfluorinated chains. This effect is also illustrated in Fig. 2d, e by a comparison of the snapshots with those of the corresponding clusters of the non-branched alkane and perfluoroalkane systems eicosane (ES/128) and perfluoroeicosane (PFES/128).

Distribution functions $g(r)$

These features are supported by the calculation of the radial atom pair distribution function $g(r)$ related to suitable basic atoms. The $g(r)$ values for the Y-shaped molecules were related to the central C5 atoms of the individual non-branched perfluorodecane and decane segments of the clusters Y-A/128, Y-B/128 and (Y-A/64+Y-B/64), respectively.

For comparison, the findings of the clusters of decane (DC/184) and perfluorodecane (PFDC/184) were included. [6] The results are illustrated in Fig. 3. It is remarkable that the non-branched alkyl segments of the clusters
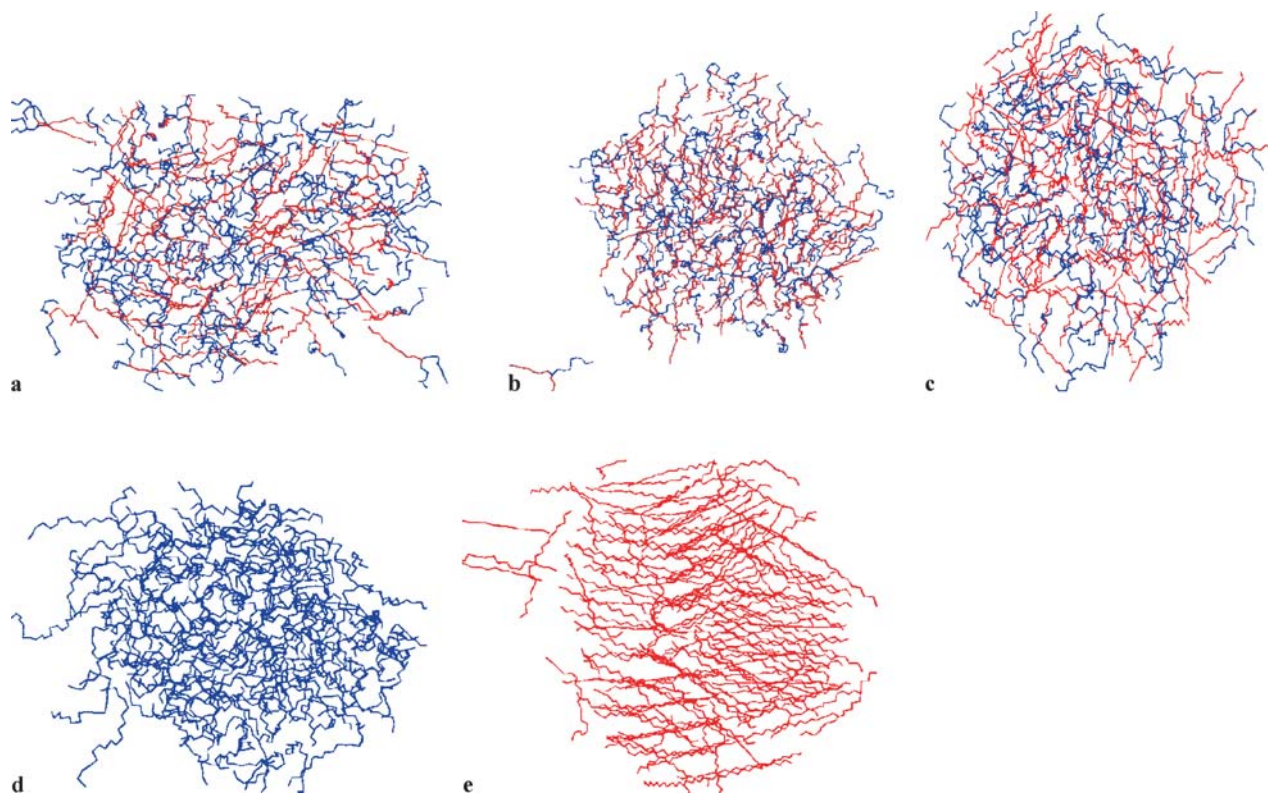
Fig. 2 Snapshots of the clusters. **a** Y-A/128. **b** Y-B/128. **c** Y-A/64+ Y-B/64. **d** ES/128. **e** PFES/128. (*T*=300 K, *t*=300 ps; perfluorinated chains *red*, alkyl chains *blue*)

Y-B/128 (Fig. 3b) and (Y-A/64+Y-B/64) (Fig. 3c) show a different aggregation behavior in comparison to the decane molecules in the cluster (DC/184). The non-branched decane segments of the Y-shaped systems indicate a certain long-range order comparable in some way with the findings for the perfluorinated chains. Especially, the mixed cluster (Y-A/64+Y-B/64) emphasizes this tendency (Fig. 3c). Obviously, the covalently bound perfluorinated segments and the wedge shape of the molecules cause the different aggregation behavior of the alkyl chains. The perfluorodecane segments of the clusters Y-A/128 and (Y-A/64+Y-B/64) show a similar tendency of the structure formation to the perfluorodecane chains of the system PFDC/184.

Orientational correlation function *g(o)*

The *g(o)* data are obtained by calculation of the radial dependency of the absolute values of the cosines between vectors related to defined initial and terminal atoms of the alkyl and perfluoroalkyl segments, respectively. The averaging procedure is carried out via the numbers of molecules and the time steps during the MD run. The orientational correlation functions *g(o)* of the clusters describing the mutual arrangement between the C1-C10 vectors of the non-branched chains support

the aggregation tendency of the Y-shaped molecules found from the *g(r)* functions (Fig. 4). The non branched segments have the tendency to organize themselves into layer-like structures. The effect is more distinct for the perfluorinated segments in comparison to the alkyl ones but is in both cases larger than for the perfluorodecane (PFDC/184) and decane (DC/184) clusters, respectively.

Diffusion coefficients *D*

Diffusion coefficients were calculated using the Einstein model within the MD procedure [18, 19] in order to get some information about the mobility of the Y-shaped molecules. From the averaged mean-square displacement (MSD) of the center of mass $\langle \Delta r^2 \rangle = 6Dt$, valid at long simulation times, the diffusion coefficient *D* can be obtained. The scoring was carried out after an equilibrium time of 200 ps and during a further time period of 200 ps to avoid any influence of the starting structure on the results. The MSD values were collected at every 0.1 ps and plotted as a function of time. The diffusion coefficients can be calculated from a linear fit shown for the cluster Y-A/128 in Fig. 5. The linear fits obtained for the two components Y-A/64 and Y-B/64 of the mixed clusters are compared in Fig. 6a, b. The noise in the plot of the Y-A/128 system (Fig. 5) is much larger than that for the mixed clusters (Fig. 6a, b), where only half the number of molecules (64) are considered, respectively. A similar tendency was found in the non-branched systems [6]. The calculated diffusion coefficients for the Y-shaped
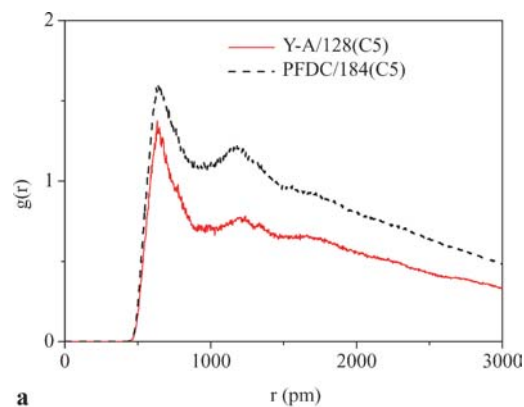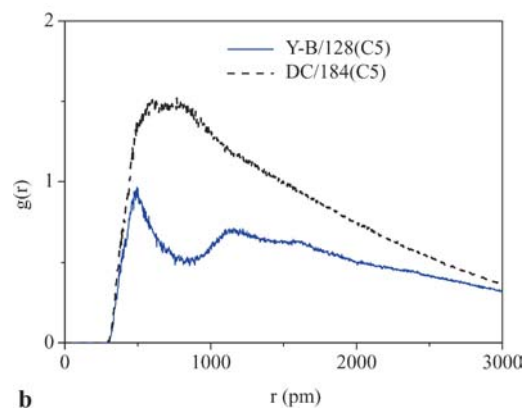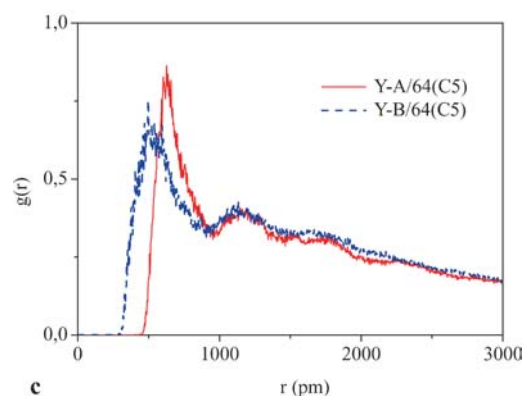
Fig. 3 Radial atom pair distribution functions $g(r)$ of the clusters (T=300 K, t=400 ps). **a** Y-A1/128. **b** Y-B1/128. **c** Y-A/64+Y-B/64 (mixed clusters). The C5 atoms of the non-branched chains are treated as basic atoms for the calculation of $g(r)$. For comparison the findings of the perfluordecane (PFDC/184) and decane (DC/184) clusters related to the same basic atoms are included [6]

Fig. 4 Orientational correlation functions $g(o)$ of the clusters (T=300 K, t=400 ps). **a** Y-A/128. **b** Y-B/128. **c** Y-A/64+Y-B/64 (mixed clusters). The mutual orientation between the C1-C10 vectors of the non-branched chains are considered for the calculation of $g(o)$. For comparison the findings of the perfluordecane (PFDC/184) and decane (DC/184) clusters related to the same vectors are included [6]

systems are summarized in Table 1 together with the corresponding values of the clusters of the non-branched alkane and perfluoroalkane systems with different chain length for comparison. The diffusion coefficients of the Y-shaped systems are smaller than those of the linear molecules with different chain length. Obviously, the Y-shape of the molecules and the covalent binding of chemical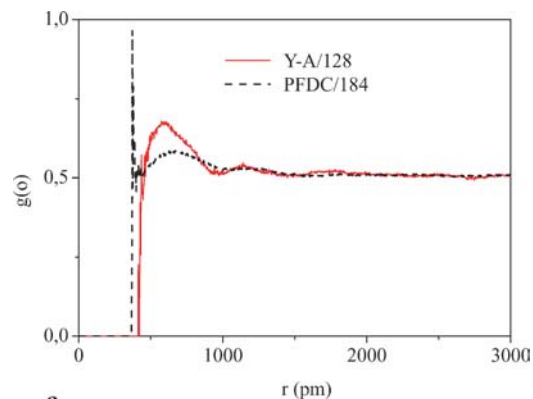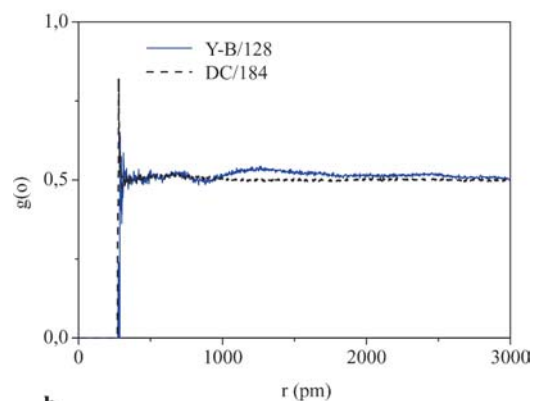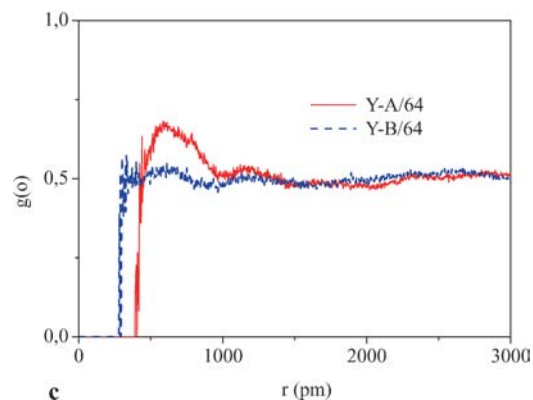ly incompatible segments decrease the mobility of the species. Moreover, the Y-shaped molecules with perfluorinated and non-fluorinated decane segments, respectively, show an opposite trend of the D values compared with their linear analogues PFDC/184 and DC/184. Similar findings were obtained for the diffusion coefficients of the different molecules of the mixed clusters. It is remarkable that the diffusion coefficients of the Y-shaped molecules of type Y-A and Y-B as well as of
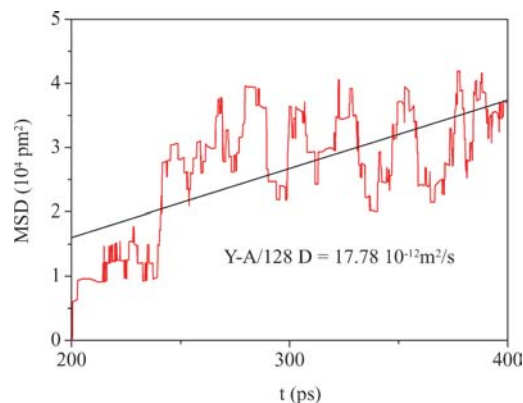
Fig. 5 Plot of the mean-square displacements (MSD) as a function of the time for the cluster Y-A/128 (T=300 K, t=400 ps)
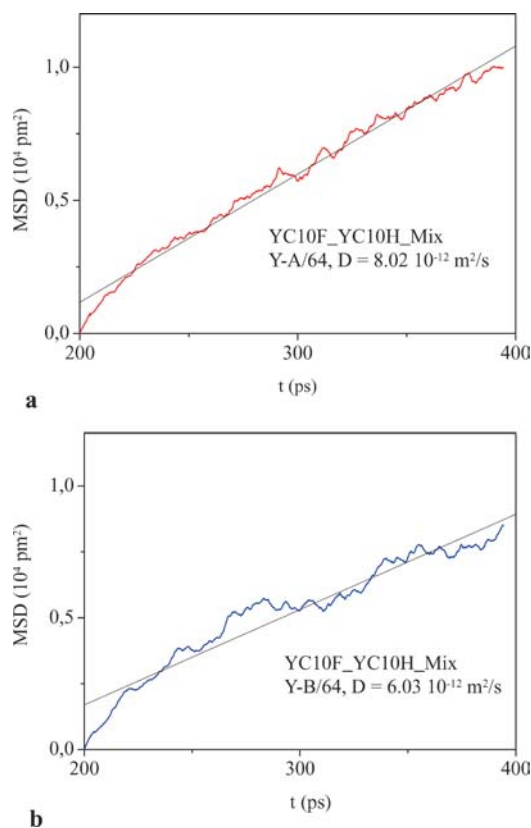

a

b

Fig. 6 Plots of the mean-square displacements (MSD) as a function of the time for the two components Y-A/64 and Y-B/64 of the mixed cluster (T=300 K, t=400 ps). **a** Y-A/64 in the mixture (Y-A/64+Y-B/64). **b** Y-B/64 in the mixture (Y-A/64+Y-B/64)

Table 1 Diffusion coefficients D (scoring period 200–400 ps) of the clusters calculated via the Einstein relation

System	D ($\times 10^{-12}$ m^2 s^{-1})
Y-A/128	17.8
Y-B/128	1.6
Y-A/64: (Y-A/64+Y-B/64)	8.0
Y-B/64: (Y-A/64+Y-B/64)	6.0
PFDC/184[a]	47.9
DC/184[a]	85.5
PFDC/92: (DC92+PFDC/92)[a]	34.4
DC/92: (DC/92+PFDC/92)[a]	115.6
PFES/128[a]	61.2
ES/128[a]	25.6

[a] From [6]

of the molecules significantly determine their aggregation behavior. Due to the limited total simulation time of 400 ps, the diffusion coefficients can only be used for a qualitative comparison. However, such a simulation time could be realized with maintainable computational effort for all systems considered in order to obtain comparable results.

Conclusions

MD simulations have been performed on clusters with Y-shaped perfluoroalkylated molecules as well as mixed clusters to study the combined effect of micro-phase separation and steric repulsion with respect to the length and position of the perfluorinated segments. The full atom resolution force field of the AMBER 5 program was used to investigate the fluorine effect on the aggregation behavior of the systems. From the analysis of snapshots, radial atom pair distribution functions $g(r)$ and orientational correlation functions $g(o)$ as well as diffusion coefficients D it can be concluded that both the amphiphilic character and the shape of the molecules significantly determine their structure formation. The covalent binding of chemically incompatible segments as in the case of the perfluoroalkylated Y-shaped molecules of type Y-A and Y-B causes remarkable differences of the aggregation behavior in comparison to the linear alkanes and perfluoroalkanes. Especially, the non-branched alkyl segments of the Y-B/128 and (Y-A/64+Y-B/64) clusters show an increased tendency to form layer-like domains which results from the $g(r)$ and $g(o)$ functions. Moreover, the Y-shaped molecules have smaller diffusion coefficients in comparison to the corresponding alkane and perfluoroalkane systems with different chain length. The same tendency was found for the D values of the molecules of the mixed clusters. Generally, the tendency of the D values of the Y-shaped molecules is more comparable with the longer than with the shorter alkanes and perfluoroalkanes. The MD simulations of the Y-shaped model systems support the experimentally found stabilization of smectic phases in perfluorinated swallow-tailed compounds compared to the non-fluorinated ones [9].

the eicosane and perfluoreicosane molecules show a similar tendency in the corresponding clusters (Table 1). Obviously, the limitations of the total simulation time (400 ps) and of the numbers of monomers in the clusters are reasons for the relatively small values of the diffusion coefficients obtained. The longer alkyl chains indicate a more distinct folding, which leads to a higher flexibility but a lower mobility of the molecules. These are further hints that the shape and the amphiphilic character

The simulations are first attempts to model the influence of chemical different segments and the steric repulsion of molecules on their aggregation behavior.

Supplementary material

The AMBER input files of the monomers are available as supplementary material.

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