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Short communication

A dimension map for molecular aggregates

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ABSTRACT

A pair of gyradius ratios, defined from the principal radii of gyration, are used to generate a dimension map that describes the geometry of molecular aggregates in water and in organic solvents. Molecular dynamics simulations were performed on the aggregation of representative biomolecules and polyaromatic compounds to demonstrate application of the dimension map. It was shown that molecular aggregate data on the dimension map were bounded by two boundary curves, and that the map could be separated into three regions representing three groups of structures: one-dimensional rod-like structures; two-dimensional planar structures or short-cylinder-like structures; and three-dimensional sphere-like structures. Examining the location of the aggregates on the dimension map and how the location changes with solvent type and solute material parameter provides a simple yet effective way to infer the aggregation manner and to study solubility and mechanism of aggregation.

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Aggregation of molecules is a universal phenomenon which occurs in many processes. For instance, proteins or peptides are associated together to form fibrils in a number of human diseases; phospholipid molecules in water can spontaneously aggregate into bilayer membranes; organic molecules possessing polyaromatic (PA) cores, such as perylene tetracarboxylic diimide, can assemble into semiconductors of nanobelt structures in solutions; heavy aromatics in crude oil known as asphaltenes aggregate during petroleum processing [1–5]. Depending on the aggregation mechanisms, various shapes can be formed, examples including spherical micelles or rod-like micelles [6–8]. These structures have been revealed by imaging techniques such as scanning electron microscopy, atomic force microscopy, transmission electron microscopy, circular dichroism, nuclear magnetic resonance, small-angle neutron scattering, as well as molecular dynamics (MD) simulations [4,6–11]. Many parameters have been used to define the shapes of various aggregates, such as radii of curvature employed in the work of Israelachvili et al. [12]. However, most of them are difficult to obtain numerically and/or experimentally, and hence, are not widely used. On the other hand, a consistent and generalized method quantifying dimension characteristics will facilitate direct comparison among different observations, which helps not only to track the morphology variations of molecular aggregates but also gain insight into the aggregation manner and driving forces. In this communication, we introduce a dimension map based on a pair of unitless quantities, defined from the ratios between the principal radii of gyration of the aggregated structures, as a simple way to quantify their dimension characteristics. Applications of the dimension map are demonstrated using aggregates formed by biomolecules as well as PA compounds in water and organic solvents, obtained from MD simulations. Its potential use in experimental studies, such as microscopic analysis of molecular aggregates, is discussed.

Seven different compounds selected from the categories of peptides, lipids and PA compounds were simulated using MD. Their chemical structures are shown in Fig. 1. Tetra-peptide (TYR-TYR-TYR-TYR, TYR-4; Fig. 1a) was selected as a representative for peptide. Dodecylphosphocholine (DPC; Fig. 1b) and dipalmitoylphosphatidylcholine (DPPC; Fig. 1c) were chosen as representatives for single- and double-chained lipids, respectively. Peptides and lipids are known to aggregate in aqueous environment [1,2]; hence they were simulated in water. PA compounds are often used as surrogates in petroleum engineering for probing the aggregation behaviors of asphaltenes [13], which are defined as toluene soluble but *n*-heptane insoluble heavy aromatic compounds [14–17]. Four PA models, developed from Viloanthrone-78 [18,19], were employed in the MD simulations. These four models have the same PA core but differ by the length of their aliphatic side chains. Based on the number of interconnected aliphatic hydrocarbons on each chain, the four models are respectively referred to as VO-4C (Fig. 1d), VO-8C (Fig. 1e), VO-12C (Fig. 1f) and VO-16C (Fig. 1g). Three solvents (water, toluene and *n*-heptane) were

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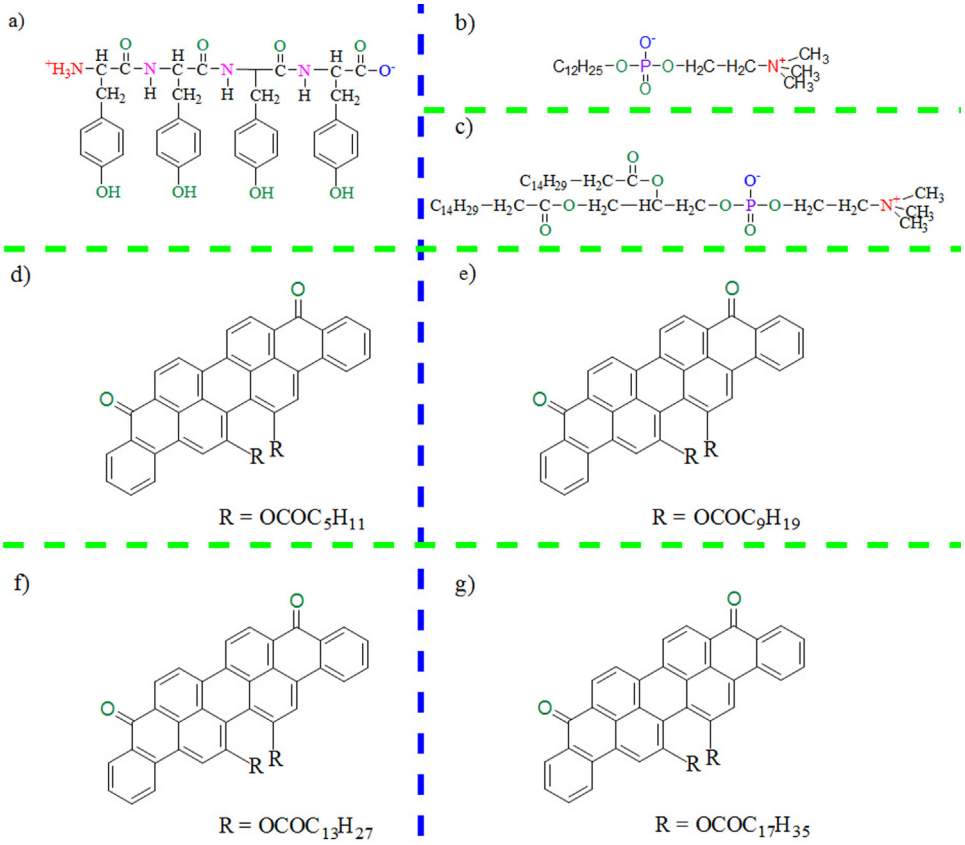

Fig. 1. Molecular structures employed in this study: (a) TYR-4, (b) DPC, (c) DPPC, (d) VO-4C, (e) VO-8C, (f) VO-12C and (g) VO-16C.

used in their MD simulations. In total, 15 systems were studied, all of which were simulated using GROMACS 4.0.7 [20–23] based on the GROMOS96 force field parameter set 53A6 [24]. Each system was subjected to an NPT simulation of length varying from 30 to 180 ns. Details on the MD simulations are available in the Supporting Information, Section S1.

Fig. 2 shows snapshots of selected aggregated structures obtained at the equilibrium stage of the simulations. The achievement of dynamic equilibrium is demonstrated in the Supporting Information, Section S2. It can be clearly seen that these aggregates exhibit different geometries. For example, the stacked PA cores of VO-8C in *n*-heptane (Fig. 2f) form a nearly one-dimensional structure not observed in other subfigures. In order to quantitatively describe the dimension of each aggregate, we define a pair of unitless quantities called gyradius ratios, based on the principal radii of gyration (gyradii) [25,26]. Specifically, for an aggregate we denote the three principal axes that pass through its center of mass as x, y, z and the three principal mass moments of inertia as I_{xx}, I_{yy}, I_{zz}. The detailed procedure of determining the principal mass moments of inertia and principal axes are available in the Supporting Information, Section S3. The principal radii of gyration are defined by [27–29]:

$$R_x = \left(\frac{I_{xx}}{\sum_i m_i}\right)^{0.5} = \left(\frac{\sum_i m_i(y_i^2 + z_i^2)}{\sum_i m_i}\right)^{0.5} \quad (1)$$

$$R_y = \left(\frac{I_{yy}}{\sum_i m_i}\right)^{0.5} = \left(\frac{\sum_i m_i(x_i^2 + z_i^2)}{\sum_i m_i}\right)^{0.5} \quad (2)$$

$$R_z = \left(\frac{I_{zz}}{\sum_i m_i}\right)^{0.5} = \left(\frac{\sum_i m_i(x_i^2 + y_i^2)}{\sum_i m_i}\right)^{0.5} \quad (3)$$

where m_i and (x_i, y_i, z_i) are respectively the mass and coordinates for atom i and the summations are over all atoms in a given aggregate. One can always denote R_0 as the minimum of $\{R_x, R_y, R_z\}$, R_2 as the maximum of $\{R_x, R_y, R_z\}$, and R_1 as the intermediate value among $\{R_x, R_y, R_z\}$. The gyradius ratios r_1 and r_2 are then defined as:

$$r_1 = \frac{R_1}{R_0}, \quad r_2 = \frac{R_2}{R_0} \quad (4)$$

Clearly $r_1 \le r_2$. Furthermore, it can be shown that for any structure, $1 \le r_1 \le r_2 \le \sqrt{1 + r_1^2}$ (see Supporting Information, Section S4). Therefore, if we generate a dimension map with r_1 and r_2 being the horizontal and vertical axes respectively (Fig. 3), any one aggregate will correspond to a point on this map, and all the points will be bounded by two curves of $r_2 = r_1$ and $r_2 = \sqrt{1 + r_1^2}$. These two curves are plotted as black dashed lines in Fig. 3. As r_1 increases, the two curves will approach each other, and eventually become indistinguishable when $r_1 \gg 1$. We now examine the gyradius ratios of the aggregates formed in our MD simulations and their locations on this dimension map.

Examples of final aggregated structures formed by TYR-4 and DPC are shown in Fig. 2a and b, respectively. In each system, the molecules formed 2 aggregates (one shown in Fig. 2) and each aggregate is more or less isotropic, with approximately equal dimensions in all directions. The gyradius ratios (r_1, r_2) for these aggregates are depicted in Fig. 3 as purple diamonds and purple plus signs, respectively for TYR-4 and DPC. All data points are located in the lower left region of the dimension map and near the boundary line of $r_2 = r_1$. This corresponds to a geometry which has approximately equal principal axes and resembles a three-dimensional sphere-like structure. In the system of DPPC, on the other hand, a single bilayer structure was formed (Fig. 2c) where the tail groups (colored cyan) are sandwiched between the head groups (colored

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