Self-assembled micellar structures of Lipopeptides with variable number of attached lipid chains revealed by atomistic molecular dynamics simulations

Article

Supplemental Material

Supporting Information

Self-Assembled Micellar Structures of Lipopeptides with Variable Number of Attached Lipid Chains Revealed by Atomistic Molecular Dynamics Simulations

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PS1. Definitions of Moment of Inertia Tensor, Relative Anisotropy Shape and Body Reference Frame

The moment of inertia tensor of a self-assembled structure, consisting of n atoms with masses m_i, is defined by a matrix I

$$I = \sum_{i=1}^{n} \begin{bmatrix} m_i(y_i^2 + z_i^2) & -m_i x_i y_i & -m_i x_i z_i \\ -m_i x_i y_i & m_i(x_i^2 + z_i^2) & -m_i y_i z_i \\ -m_i x_i z_i & -m_i y_i z_i & m_i(x_i^2 + y_i^2) \end{bmatrix}, \quad (1)$$

where x_i, y_i and z_i are the atomic coordinates with respect to the center of mass (COM) of a self-assembled structure. The eigenvalues of I are denoted by I_{xx}, I_{yy} and I_{zz}.
The relative shape anisotropy K^2 is of the form

$$K^2 = \frac{3}{2}\frac{\lambda_1^2 + \lambda_2^2 + \lambda_3^2}{(\lambda_1 + \lambda_2 + \lambda_3)^2} - \frac{1}{2}, \quad (2)$$

where λ_1, λ_2 and λ_3 are the recombination of eigenvalues of I, given by the following formulae

$$\lambda_1 = \frac{1}{2}\left(I_{yy} + I_{zz} - I_{xx}\right)$$

$$\lambda_2 = \frac{1}{2}\left(I_{xx} + I_{zz} - I_{yy}\right)$$

$$\lambda_3 = \frac{1}{2}\left(I_{xx} + I_{yy} - I_{zz}\right).$$

The body reference frame is identified by the principal axes obtained by diagonalizing the moment of inertia tensor I.

PS2. Comparison of Atomic Density Functions of Different Lipid Chains in the Same Lipopeptide Molecule

To further compare the ADFs of different lipid chains in the same Pam_2CSK4 and Pam_3CSK4 molecules, we plot the ADFs of selected components of $Pam^{(1, 2)}$ for Pam_2CSK4 and $Pam^{(1\text{-}3)}$ for Pam_3CSK4 in Figure S1. Figure S1a shows that the ADFs of "CT", "CM" and "CH" in $Pam^{(1, 2)}$ of Pam_2CSK4 almost overlap with each other, an indication of statistical equivalency of the two lipid chains in the same molecule. Similar distributions of the three lipid chains $Pam^{(1\text{-}3)}$ in Pam_3CSK4 can also be seen in Figure S1b.

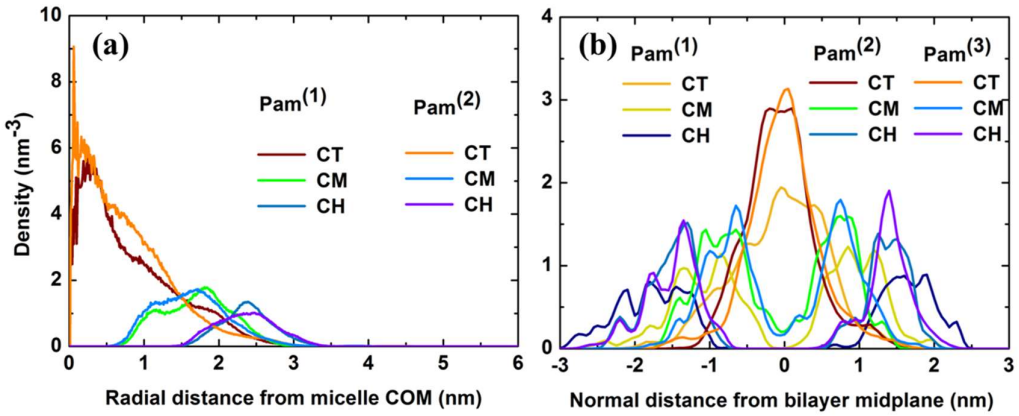

Figure S1. Atomic density functions (ADFs) of selected components of (a) the lipid chains $Pam^{(1, 2)}$ in Pam_2CSK4 and (b) $Pam^{(1\text{-}3)}$ in Pam_3CSK4. "CT", "CM" and "CH" denote the head and middle methylene groups and terminal methyl group on a lipid chain, respectively.

PS 3. Probability Distributions of the Length of Lipid Chains in Lipopeptide Molecules

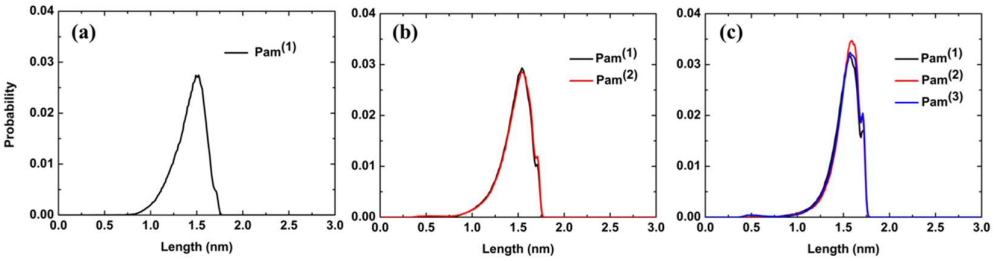

Figure S2. Probability distributions of the length of lipid chains of (a) PamCSK4, (b) Pam_2CSK4 and (c) Pam_3CSK4.

The narrow and sharp distributions of lipid chains on lipopeptides indicates that the lipid chains are straight and their lengths are of about 1.5 nm.

PS 4. Probability Distribution of Angles (Including Pam_3CSK4 Molecules at the Curved Side Edges of Flattened Wormlike Micelle)

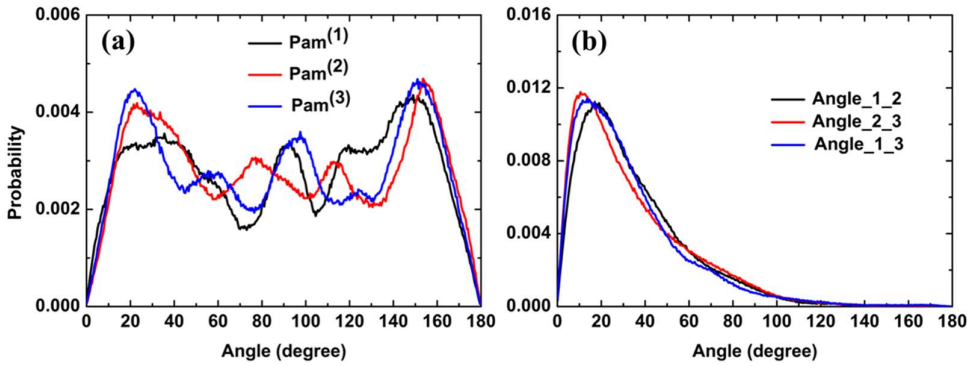

Figure S3. Probability distribution of the angle (a) between the vector of lipid chains and the normal of flattened wormlike micelle of Pam_3CSK4, and (b) between any two lipid chains on the same molecule.

When the Pam_3CSK4 molecules at the edge of the flattened wormlike micelle are considered, peaks around 90° appear in the Figure S3a and two peaks around 20° and 160° still exist. This indicates that molecules at the edge are almost distributed vertical to the normal of a flattened wormlike micelle, and the inclusion of these molecules has little impact on the recognition of bilayer stacking structures inner the flattened wormlike micelle.