Supporting Information

Interaction of fullerene chains and a lipid membrane via computer simulations

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Model

Force Field: The MARTINI coarse-grained (CG) force field (version of 2.1) developed by Marrink et al. [1] was employed to model all components under investigation. The MARTINI model maps about 3 or 4 heavy atoms into one effective particle in general. Each of these particles is assigned a diameter, 0.47 nm. van der Waals interactions are modeled using the Lennard-Jones (LJ) potential. Covalent bonds between CG particles are described by harmonic spring potentials. Angular potentials are modeled with a harmonic cosine potential. In the framework of MARTINI force field, the interaction matrix for LJ potential was given in Table S1. [2]

Lipid and Membrane: The mapping of the dipamitoyl phosphatidylcholine (DPPC) lipid into the coarse-grained beads is shown in Figure.S1 (a). The CG force field of these lipids and their topologies were downloaded from http://md.chem.rug.nl/cgmartini/. We construct a symmetrical bilayers with charge-neutral lipids of DPPC. The simple model of lipid bilayers do not include cholesterol, sphingolipid, and proteins, which indeed exist in the natural cell membrane. [3] The lipid bilayer consists of 512 lipid molecules, surrounded by more than 15000 CG water particles (corresponding to 60000 water molecules). Construction of the lipid bilayer consists of the following steps: a preassembled DPPC lipid bilayer configuration with 128 lipids, equilibrated for 1 μs, then it is replicated across the X and Y directions. Each system is then equilibrated for 500 ns in NPT ensemble to prepare further simulations.

Fullerenes: The mapping of the C_{60} fullerene into the coarse-grained bead of CNP type, is given in Figure.S1 (b). The C60 is mapped into 16 CNP beads by Monticelli et al[4,5]. The CG force field and its topologies were downloaded from http://md.chem.rug.nl/cgmartini/images/applications/fullerene/. For modelling the functionalizated fullerene, the CNP bead type was replaced with P4 type with hydrophilicity. This kind of bead can model the suface-modified C_{60} by, such as –(OH), -(NH_2), which can make C60 hydrophilic. We just pay attential to the general hydrophilic-hydrophobic effect, so we do not concente on what is the exact representation by P4. A simple main-chain fullerene polymer was constructed through the covalent connection modeled by the harmonic potential of fullerene beads.

Table S1 [a] :The interaction matrix of LJ interaction [1,2,5]

	Q0	Qa	Na	C1	CNP	P4
Q0	IV					
Qa	II	I				
Na	III	III	III			
C1	VI	IX	VI	IV		
CNP	T2	T2	T3	T4	T1	
P4	O	O	III	VIII	T2	I

a. The leves of LJ interaction is given below. For level O, ε =5.6 KJ/mol, σ =0.47nm ; for level I, ε =5.0 KJ/mol, σ =0.47 nm; for level II , ε =4.5 KJ/mol, σ =0.47 nm ; for level III , ε =4.0 KJ/mol, σ =0.47 nm; for level IV, ε =3.5 KJ/mol, σ =0.47 nm; for level VI, ε =2.7 KJ/mol, σ =0.47 nm ; for level VIII, ε =2.0 KJ/mol, σ =0.47 nm; for level IX , ε =2.0 KJ/mol, σ =0.62 nm; for level T1, ε =3.6 KJ/mol, σ =0.43 nm; for level T2, ε =2.7 KJ/mol, σ =0.43 nm; for level T3, ε =3.25 KJ/mol, σ =0.43 nm; for level T4, ε =3.15 KJ/mol, σ =0.43 nm.

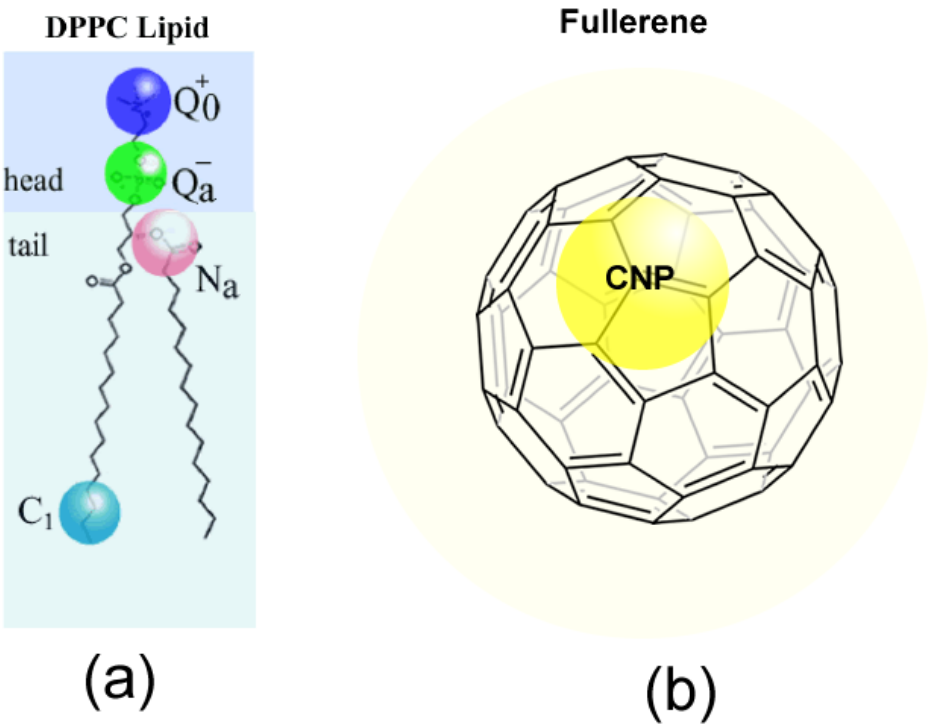

Figure S1. (((a) Mapping of the dipamitoylphosphatidylcholine (DPPC) lipid into the coarse grained beads within the MARTINI force field, which are mainly four types of interaction sites: polar (P), nonpolar (N), apolar (C), and charged (Q). Each type has a number of subtypes distinguished by a letter denoting the hydrogen-bonding capabilities (d= donor, a = acceptor, da = both, 0 = none), or by a number indicating the degree of polarity (from 1, low polarity, to 5, high polarity). (b) Mapping of the C_{60} fullerene into the coarse-grained bead, CNP, which was developed by Monticelli et al.. [3,4]

Analytical Methods

Radius of Gyration Rg is calculated by the equation $Rg = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(\vec{r}_i - \vec{r}_{cm})^2}$ where N is the number of beads on the chain. $\vec{r}_i$ is the position vector of the ith bead and $\vec{r}_{cm}$ is the center of mass of the chain

End-to-end Distance The end-to-end distance is the norm of the end-to-end vector defined by a vector from the center of mass of C60 at one end of the chain to the center of mass of C60 at the other end of the chain.

Shape Anisotropy The instantaneous shape of polymers can be analyzed quantitatively by means of the radius of gyration tensor $R_{\alpha\beta} = \frac{1}{N}\left[\sum_{i=1}^{N}(r_{i,\alpha} - r_{cm,\alpha})(r_{i,\beta} - r_{cm,\beta})\right]$, where α and β (= x, y, or z) are the three Cartesian components and $r_{i,\alpha}$, $r_{cm,\alpha}$ as well as $r_{i,\beta}$, $r_{cm,\beta}$ are the coordinates of the ith bead and of the center of mass of the chain, respectively. The two invariants, $I_1 = I_x + I_y + I_z$, $I_2 = I_x I_y + I_y I_z + I_z I_x$, are used to define the asphericity, $a = 1 - 3\langle I_2/I_1^2\rangle$, where Ix, Iy, Iz are the three eigenvalues, corresponding to the three semiaxes of equivalent ellipsoid of the $R_{\alpha\beta}$. The value of a is between 0 and 1. Specifically, a = 0, 1/4, and 1 represent spherical, oblate, and extremely elongated ellipsoids, respectively.

Order parameter The order parameter of lipid tail was define by, $S = 0.5\langle 3\cos^2\theta - 1\rangle$, where θ is the angle between the C1A-C4A bond vector of acl chain and the bilayer normal., and the angular brackets indicate averaging over time and lipid molecules.

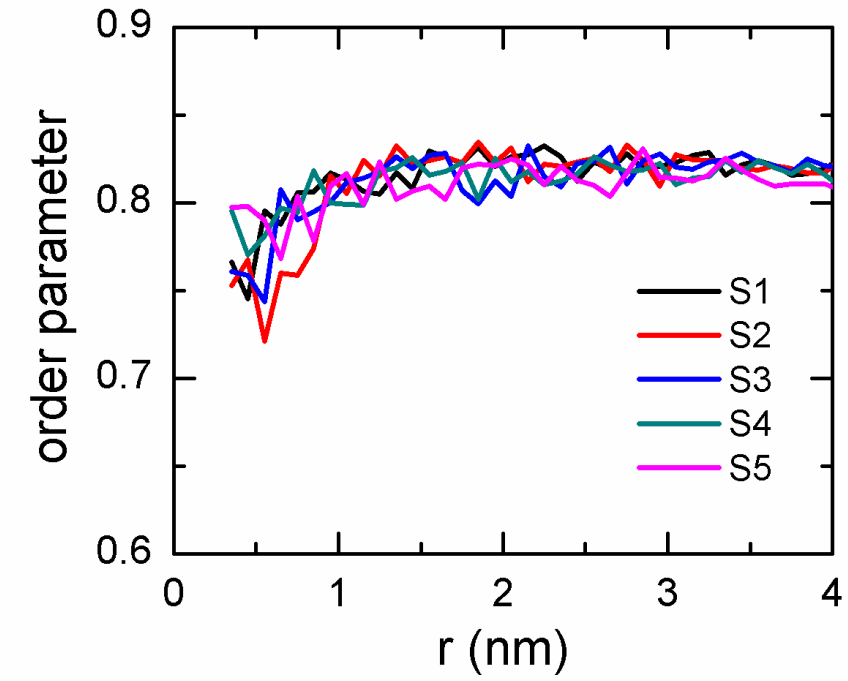

Fig.S2 Order parameter of the lipids as a function of distance from the center of mass the fullerene chain.

Table S2: Time for C_{60} molecules on the polymer penetrating into the membrane. The initial center-of-mass distance between the polymer and the membrane is 3.4 nm. Each system was simulated ten times and the effective time for each system is 1.4 μs.

System\Case	**C1/ns**	**C2/ns**	**C3/ns**	**C4/ns**	**C5/ns**	**C6/ns**	**C7/ns**	**C8/ns**	**C9/ns**	**C10/ns**	**Average/ns**
S1	214	39.5	43.5	19	369	Non-adsorption					137.0±151
S2	484	69	821	134	112.5	495.5	126.5	386.5	146	439	321.4±244
S3	140	380.5	1110	105.5	269.5	133.5	adsorption				322.0±361
S4	781.5	35.5	71.5	40	333	500	115	adsorption			268.0±285
S5	adsorption										--

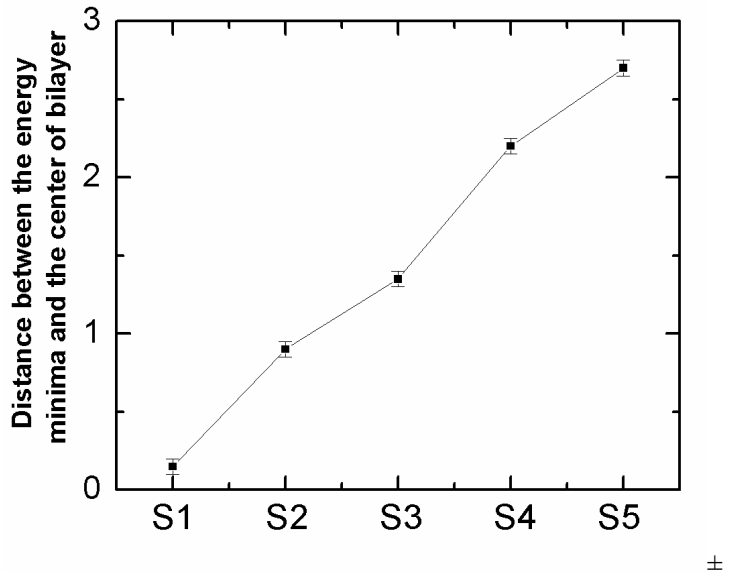

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Fig. S3: Distance between the energy minima (derived from the PMFs in figure 4(a) in the text) and the center of mass of the lipid membrane. Error bars are given.

Comparison with Qiao's work.[6]

Previous work by Qiao et al. also calculate the PMF of pristine C_{60} and $C_{60}(OH)_{20}$ interacting with membrane. They find the PMF minimum is located at Z ≈ 1.1 nm, not at zero. Our finding demonstrates that the PMF minimum of pristine C_{60} polymer (i.e. S1) is located at Z ≈ 0.21 nm, which is consistent with the Qiao' finding. The PMF by Qiao et al. suggested that a single $C_{60}(OH)_{20}$ prefers to adsorb onto the outer rim of the bilayer, which is also in agreement with our result of S5 system. Although we find the fullerene polymers can thin the membrane, we do not witness a micropore formation as suggest by Qiao et al.

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[2] Marrink SJ, Risselada HJ, Yefimov S, Tieleman DP, de Vries AH. J Phys Chem B. 2007 Jul 12;111(27):7812-24.

[3] R.H. Garrett, C. M. Grisham, *Biochemistry*, Tomson Brooks/Cole: Davis Drive, USA **2005**; pp:267.

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[5] L. Monticelli, *J. Chem. Theory Comput.,* **2012,** *8,* 1370-1378.

[6] R. Qiao, A. P. Roberts, A. S. Mount, S. J. Klaineand, P. Ke, Nano Lett., 2007, 7, 614.