Synergistic Adsorption of Polyaromatic Compounds on Silica Surfaces Studied by Molecular Dynamics Simulation

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ABSTRACT

The adsorption on silica surface of polyaromatic compounds: N-(1-hexylhepyl)-N'-(5-carboxylicpentyl)-perylene-3,4,9,10-tetracarboxylic bisimide (C5Pe), N-(1-undecyldodecyl)-N'-(5-carboxylicpentyl)-perylene-3,4,9,10-tetracarboxylic bisimide (C5PeC11) individually and their binary mixture in heptol (mixture of heptane and toluene) solutions was studied by molecular dynamics (MD) simulation, Quartz Crystal Microbalance with Dissipation (QCM-D) and Atomic Force Microscopy (AFM). The MD simulation results showed that C5Pe molecules tend to aggregate and form a large cluster rapidly in the oil phase, reducing the energy of the system. In contrast, C5PeC11 molecules with high solubility tend to disperse in the system. As a result, more C5PeC11 molecules exhibited a stronger adsorption than C5Pe molecules on silica surfaces. In the binary mixture system, the overall solubility is only slightly lower than that in the C5PeC11 system due to the association of C5Pe with C5PeC11 molecules through π-π stacking and T-stacking interactions, leading to more polyaromatic compounds available for adsorption onto silica surfaces. The enhanced adsorption of both polyaromatic compounds on silica surfaces clearly illustrates the synergy of adsorption in the mixed systems of C5Pe and C5PeC11 than the systems of their individual species. The adsorption characteristics revealed in MD simulations were confirmed by QCM-D measurement and AFM imaging. The observed synergy of adsorption provides insights into the molecular assembly at silica-oil interfaces for the fabrication of devices or sheds lights on petroleum processing.

■ INTRODUCTION

Polyaromatic compounds such as perylene bisimide (PBI) derivatives, possess large π-conjugated rings, which makes these molecules owning favorable physical and chemical properties as well as special functions. It has been widely researched in the fields of material science, supramolecular assembly, biology, photochemistry, analytical chemistry and so on. The self-assembly of π-conjugated organic molecules has always been an active research topic, due to the high thermal stability and photostablity at ambient conditions, which make it feasible for the application in optoelectronic devices. The property of easy chemical modification by various functional groups promotes the formation of well-defined nanostructures fabricated by PBIs, and inspires the research on self-assembly of n-type organic semiconductor molecules.[1-2] As a result, more and more efforts have been dedicated to expanding the possible applications of PBIs.[3-4]

Asphaltenes are the most aromatic of the largest, densest and heaviest components with remarkable surface-active properties in crude oil. They are defined as a solubility class, not by their structure, i.e., insoluble in alkanes such as pentane or heptane, but soluble in aromatic solvents such as toluene or xylene.[5-7] Such practical definition of asphaltenes means that the exact molecular structures of asphaltenes are still unknown. Asphaltenes are not a homogeneous fraction, but a mixture of molecules of fused polyaromatic rings with polar groups, branches and tails of variable lengths. The complexity and unknown molecular structure of asphaltenes make the understanding of their properties difficult. Archipelago model

and island model have been the recognized structure models of asphaltene molecules till now.[8-10] Therefore, developing and studying the model compounds with well-defined structure and properties similar to crude oil asphaltenes appear to be an excellent strategy for researchers.[11] Sjöblom's group designed and synthesized a series of model compounds of asphaltenes. These model compounds are derivatives of perylene imide molecules with branched alkyl chains and polar groups attached to the polyaromatic core.[12-15] Great efforts have been made to understand interfacial behaviors of these model compounds.[16-19]

As well documented, asphaltene adsorption at solid-oil interfaces is an ubiquitous phenomenon, which results in altering the wettability of solid surfaces, thus causing lots of problems in industry, such as production, transportation, petroleum refining and environmental treatment.[9] The adsorption of asphaltenes at liquid-solid interfaces has been studied in a wide range of systems, in order to develop the removal strategies of asphaltenes.[20-22] Adams reviewed the different adsorption systems. Asphaltene adsorption was determined to be a multifaceted process and sensitive to many system variables such as source and concentration of asphaltenes, physical aspects of sorbents, type of solvents, properties of rock surfaces, etc.[7] The adsorption of polyaromatic asphaltenes onto solid surface has been studied extensively by experimental methods, such as depletion method, quartz crystal microbalance, photothermal surface deformation spectroscopy, and contact angle measurements.[11] These experiments provided a great deal of valuable information on asphaltene adsorption. However, the critical information on molecular adsorption process, orientation of molecules, binding sites on solid surfaces, interaction type of asphaltenes, the state of molecular aggregates, etc., remain unavailable.

Molecular dynamics (MD) simulation has been extensively used to investigate the molecular aggregation of polyaromatic compounds systems.[23-25] The adsorption of model compounds with charged and uncharged terminal groups were studied and the stacked polyaromatic rings were identified to be orthogonally oriented to the oil-water interface. The results are in agreement with the experiments of the perylene-based type model compounds. Lots of evidences from experiments and simulations of adsorption process showed that the perylene-based type model compounds can be successfully used to mimic asphaltenes in crude oil. Recently, the mixture of different polyaromatic compounds published by Liu in a given solvent was found to significantly reduce the apparent average nanoaggregation number, indicating the influence of interactions between polyaromatic compounds on system properties.[26]

Other model compounds have also been investigated with MD simulation methods. Greenfiled reviewed the averaged-structure of asphaltene model compounds and the MD simulation studies.[27] These early studies and results provide an improved tool for relating asphalt chemical compositions to their interfacial behavior. Goual et al., for example, simulated the removal of asphaltenes from calcite mineral surfaces with surfactants and microemulsions. The results revealed that microemulsions were more effective than surfactants by swelling the oil phase.[28] Boek's group utilized the constraint force method to calculate the potential mean force (PMF) of asphaltene and calcite surface in vacuum, subsequently obtained the reasonable value of adsorption free energy.[29] Murgich et al. calculated the interaction energy of model asphaltenes and resins on neutral kaolinite surface. The results showed that van der Waals forces are the major driving force for the observed adsorption.[30] Increasingly, more MD simulation studies on aggregation and adsorption of polyaromatic compounds at oil-water or oil-solid interfaces

have been published recently.[24, 31-32] In summary, Boek et al. reviewed the insights and limitations of molecular dynamics simulation methods on studying asphaltene aggregation.[33] These authors provided a critical view on MD simulations as applied to asphaltene molecules from a number of aspects, including asphaltene structures, simulation systems and modeling, simulation details and analysis methods, etc.

The effect of solvent properties on adsorption of polyaromatic compounds on silica was studied in heptane and toluene.[34] In this work, the adsorption process and interactions of different polyaromatic compounds from organic solutions on a silica surface were investigated by molecular dynamics (MD) simulation method. The adsorption kinetics and capacities were determined by quartz crystal microbalance with dissipation (QCM-D), with molecular orientation on silica surfaces in different solvents being characterized by atomic force microscopy (AFM) imaging.

■ SIMULATION MODELS AND METHODOLOGY

In this study, N-(1-hexylhepyl)-N'-(5-carboxylicpentyl)-perylene-3,4,9,10-tetracarboxylic bisimide (C5Pe) and N-(1-undecyldodecyl)-N'-(5-carboxylicpentyl)-perylene-3,4,9,10-tetracarboxylic bisimide (C5PeC11) (shown in Figure 1) were used as the polyaromatic compounds. The molecules both consisted of a polar terminate (carboxylic acid: -COOH) group and fused polyaromatic rings with two aliphatic chains on the other end. The difference between these two polyaromatic compounds is that C5PeC11 molecules have longer aliphatic chains than C5Pe molecules, which leads to a higher solubility in toluene. All the MD simulations were carried out using the GROMACS 5.1.4 software package with GROMOS96-53a6 united atom force field. [35] The details on silica slab structure and force field parameter settings are all the same as used in our previous paper. [34] Moreover, the optimized geometry and topology files of C5Pe and C5PeC11 were generated by Automated Topology Builder (ATB) of Repository Version 2.2. [36]

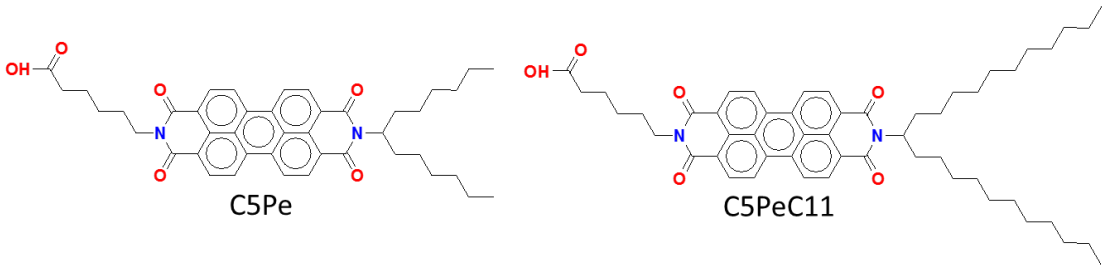


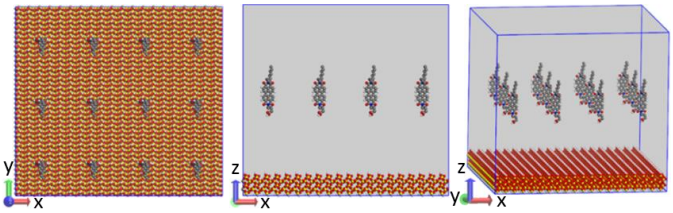
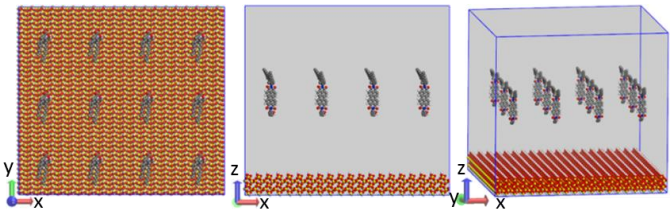
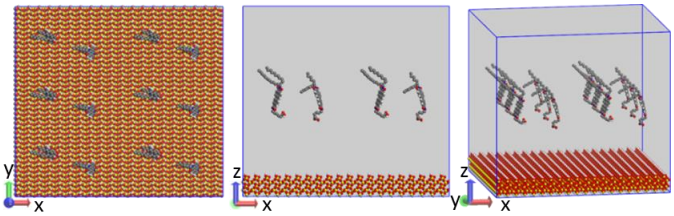
Figure 1. Structure of C5Pe and C5PeC11 polyaromatic compounds.

1. Configuration and Simulation Details

In order to investigate the adsorption of different polyaromatic compounds, it is critical to make sure that all the molecules run from the same distance to the silica surface. In this study, a box of 10.8 × 9.8 × 10 nm with a silica slab was created first. The polyaromatic compounds were arranged orderly over the surface with the distance of the closest atoms of the polyaromatic molecules being set at 3 nm away from the surface of the silica slab (shown in the inserted picture

in Table 1 and in the Supporting Information Figure S1). The box was then filled with heptol (a binary mixture of equal volume of heptane and toluene). The details on the number of molecules in box are given in Table 1.

Table 1. Number of molecules and molecular arrangement of initial simulation box

Molecules	Toluene	Heptane	View [a]
12 C5Pe	2484	1699	
12 C5PeC11	2478	1693	
6 C5Pe 6 C5PeC11	2478	1689	

[a] Colors for atoms are dark grey = C, white = H, blue = N, yellow = Si, and red = O. Heptane and toluene solvents are not shown for clarity.

In the entire MD simulation, the periodic boundary conditions were used in x-y directions, which made it possible for the adsorption study on only one silica-oil interface and simplified the subsequent analysis. Other simulation processes were almost the same as used in our previous paper.[34] Briefly, energy minimization was performed by the steepest descent method and followed by the conjugate gradient method for further eliminating the steric clashes and inappropriate geometry. The MD simulations were then performed in canonical (NVT) ensembles at 300 K using V-rescale thermostat coupling algorithm, and continued in isothermal−isobaric (NPT) ensembles at 300 K and 1 bar pressure using V-rescale thermostat and Berendsen pressure coupling algorithm in the Z direction, each for 500 ps to relax the system within the position constrain of polyaromatic compounds. The MD simulations were continued for 100 ns in NVT ensemble with the same parameter settings used in the above NVT simulation, but without the position constrain. During both the equilibration and production MD simulations, leapfrog Verlet algorithm with a time step of 2 fs was used for integration of the trajectories. The LINCS algorithm was used for all bonds, and the cutoff distance of the neighbor list was set at 1.2 nm. The cutoff distance of 1.4 nm was adopted to calculate the L-J potential and electrostatic interactions using particle mesh Ewald (PME) summation method.

The initial atomic velocities of the system were generated by Maxwell−Boltzmann distribution at the specified temperature of 300 K.

2. Experiments of QCM-D and AFM

The synthesis and the structural characterization of C5Pe and C5PeC11 molecules were performed in Sjöblom's group. Toluene and heptane were all of HPLC grade (Aladdin, China, >99.9%). Ethanol (Aladdin, China, 99%) and sodium dodecyl sulfate (SDS) salt (Aladdin, China, ≥99%) were used to clean the QCM crystals. All chemicals were used as received. The polyaromatic compound solutions were prepared by dissolving 0.02 g C5Pe, 0.02 g C5PeC11 or the mixture of 0.01 g C5Pe and 0.01 g C5PeC11 in 20 mL of toluene under sonication for 10 min. Additional 20 mL heptane was injected into each of the three polyaromatic compounds-in-toluene solutions under sonication for 10 min before being used for the QCM-D experiments.

A detailed description of the QCM-D experimental protocols is available elsewhere. [37] Quartz Crystal Microbalance with Dissipation (QCM-D) (Q-Sense E4, Biolin Scientific, Sweden) was used in this study. The silica-coated crystals were cleaned before their use by immersing them in ethanol for 30 min, and then washed with Milli-Q water. Next, the crystals were immersed in a solution of 2% sodium dodecyl sulfate in water for 30 min, followed by washing with Milli-Q water again. For further silica hydroxylation, the above cleaned crystals were immersed in NaOH solution (about pH = 11) for 30 min followed by washing with Milli-Q water several times. [34] Finally, the crystals were blown dried with N_2.

QCM-D adsorption experiments were performed with the following procedure: The machine was placed upside down in order to remove the possible effect of gravity. Heptol (equal volume of heptane and toluene) solution is initially passed through the chamber containing the crystal at 25 °C to obtain a baseline. The baseline was considered to be stable if the frequency change was less than ±1 Hz for 5 min. Three solutions of polyaromatic compounds in heptol were then injected into three separate chambers using a pump (flow rate = 500 μL/min).

The silica-coated crystals with polyaromatic compounds adsorbed as such were unloaded from Q-Sense E4 and blow-dried with pure nitrogen gas. Atomic force microscopy (AFM, Dimension Icon, Bruker) was used to image the morphology of the sensor surfaces in air at room temperature. Images of 10×10 μm were obtained using SCANASYST-AIR probe purchased from Bruker and Peak Force Tapping mode scan operated by ScanAsyst software. The experimental processes of QCM-D and AFM are shown in Figure 2.

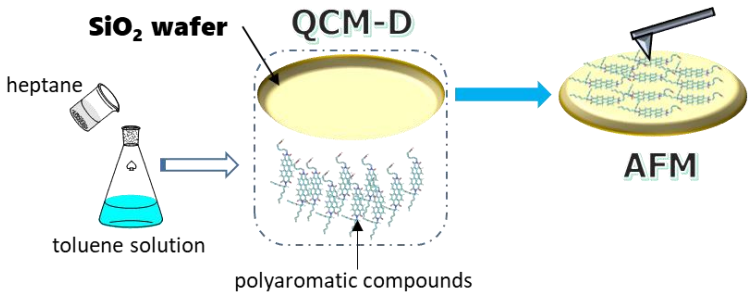


Figure 2. Schematic process of QCM-D and AFM experiments

■ RESULTS AND DISCUSSION

1. Molecular Dynamics Simulation on Adsorption Process

The number density of polyaromatic compounds and mass density profile of solvent (heptane and toluene) molecules in the systems of C5Pe, C5PeC11 or their binary mixture in heptol were analyzed along the Z-axis by taking the time average over the last 10 ns of 100 ns simulation time. For polyaromatic compounds, the distance in Figure 3 refers to the distance of COM normal to silica surfaces. The results are shown in Figure 3. Also shown in Figure 3 were snapshots of the molecular configuration on silica surfaces at 100 ns.

The results in Figure 3a-c showed a solvent layer of toluene adsorbed on silica surfaces with a density profile peaked at 1.8 nm, in contrast to a weak peak of heptane. Ledyastuti reported similar solvent density profiles and discussed the toluene adsorption on oil-silica interfaces in great detail. [38] In our study, the toluene solvent layers formed rapidly at the beginning of the simulations and were similar in all three systems, as shown in the Supporting Information Figure S2. The density profiles of toluene in Figure S2 were obtained as a time average over the first 1 ns of simulation time. The results show that the toluene adsorption layer formed long before the adsorption of polyaromatic compounds, which is shown in Figure 10 and will be discussed later.

Figure 3a shows a weak and broad number distribution peaks of C5Pe at z = 1.8 nm and a much stronger and broader peak at z = 4.5 nm. The first weak broad peak could indicate the adsorption of C5Pe as clusters as shown in the snapshot (Figure 3d). The second stronger and broader peak indicates the formation of C5Pe aggregates in bulk as also illustrated in the snapshot.

Compared with the C5Pe, the adsorption of C5PC11 molecules on silica in heptol is much stronger. Two distinct but overlapping peaks of C5PeC11 at z = 1.8 nm and 3.1 nm were observed. The first and relatively weak peak is attributed to C5PeC11 molecules directly bonded to silica surface through interactions between polar terminate (carboxylic acid: -COOH) group of C5PeC11 and geminal silanol groups (-Si-$(OH)_2$) on silica (shown in the Supporting Information Figure S3). The second and stronger peak located at 3.1 nm is attributed to C5PeC11 molecules associated in the form of nanoaggregates with the first layer of C5PeC11 molecules firmly attached to silica surface as illustrated in the snapshot of Figure 3e. The results in Figure 3 (b and e) also show a fraction of C5PeC11 remained in the bulk solution as indicated by broad and weak distinguishable peaks at and beyond z = 6 nm, mostly in the form of individual molecules or much smaller molecular aggregates.

For the binary mixture system, the adsorption was obviously enhanced for both C5Pe and C5PeC11 molecules as compared with the systems of individual molecule type. As shown in Figure 3 (c and f), all the molecules accumulated on silica surface with a sharp and strong peak at z = 1.8 nm and a strong but board peak at z = 2.2 nm, illustrating more direct binding of molecules with the silica surface in the C5Pe and C5PeC11 binary mixture system. These results indicate a strong synergy between C5Pe and C5PeC11 on promoting the adsorption of polyaromatic compounds.

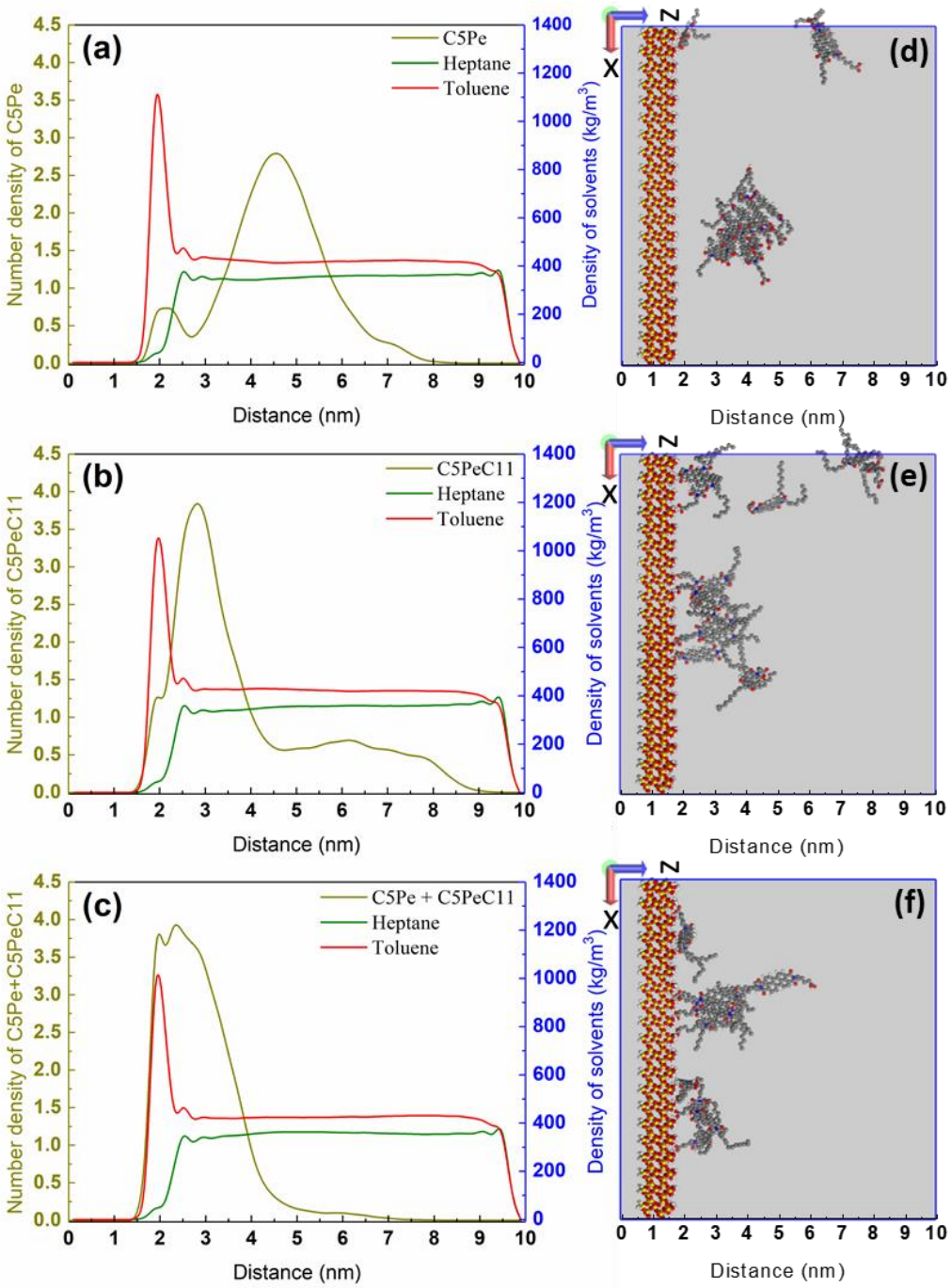


Figure 3. Number density of polyaromatic compounds (thick brown line) and mass density of heptane and toluene solvents (green and red line) along the Z-axis over the last 10 ns of simulation time: (a) 12 C5Pe system, (b) 12 C5PeC11 system, and (c) 6 C5Pe and 6 C5PeC11 binary mixture system. The right side is the snapshot of final adsorption configuration at 100 ns: (d) 12 C5Pe system, (e) 12 C5PeC11 system, and (f) 6 C5Pe and 6 C5PeC11 binary mixture system. The heptane and toluene are not shown in the snapshots for clarity. Colors for atoms are: dark grey-C, white-H, blue-N, yellow-Si and red-O.

To gain the insights on adsorption of different polyaromatic compounds, it is more valuable to analyze the time-dependent properties, not just the final configuration. Therefore, the trajectories of molecules were tracked by averaging the COM (center of mass) distance of

molecules on the silica surface. Since the COM of C5Pe and C5PeC11 is not the same due to the difference in the length of aliphatic chains, we considered the polyaromatic core of polyaromatic compound without aliphatic chains to assign the COM (shown in the Supporting Information Figure S4). The average distance between COM of polyaromatic compounds and silica surface of three systems in heptol were shown in Figure 4. The initial distance of COM to silica surface is about 4 nm. The polyaromatic molecules are clearly seen to move close to silica surface gradually in all systems. The final COM distance in C5Pe system fluctuated at about 2.6 nm away from the surface. While in the C5PeC11 system, the final COM distance is about 2.0 nm with less fluctuations, indicating a stronger binding of C5PeC11 than C5Pe on the silica surface. The trajectories in the binary mixture system provided more important information on the synergy effect of polyaromatic compound adsorption. The final average COM distance of all polyaromatic compounds is at about 1.1 nm with much smaller fluctuations (shown in Figure 4c black line), indicating a much stronger adsorption of C5Pe and C5PeC11 in the binary mixture system than that in the individual molecular species systems. More importantly, the average COM distance of C5Pe or C5PeC11 in binary mixture system is smaller than the average COM distance of corresponding single compound systems, shown by red and blue profiles, respectively.

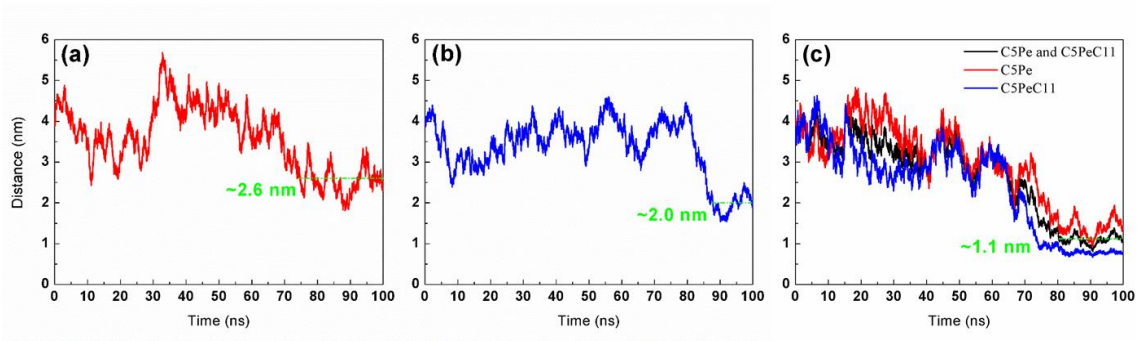


Figure 4. Average distance between COM (center of mass without aliphatic chains) of polyaromatic compounds and silica surface in heptol as a function of time: (a) 12 C5Pe system, (b) 12 C5PeC11 system, (c) 6 C5Pe and 6 C5PeC11 binary mixture system.

The number of molecules that adsorbed on the silica surface was analyzed at every 10 ns intervals and the results are shown in Figure 5. Here the number of polyaromatic molecules adsorbed on silica surfaces was calculated in two steps. First, we define the cluster (aggregation of polyaromatic compounds) using the same method published in our previous. [34] Briefly, the cluster was updated whenever a molecule moved into the cut off (0.55 nm) around a molecule in the cluster, including a single molecule as monomer. Next, we calculate the distance of the closest atom in a cluster to the silica surface. Once the distance is less than 0.5 nm, the cluster was regarded as being adsorbed. The number of cluster (including single molecules as adsorbed monomers) meeting this criterion was calculated as number of molecules adsorbed. C5Pe alone showed a negligible adsorption up to 80 ns, when only one out of 12 C5Pe molecules adsorbed. This result illustrates a weak adsorption of C5Pe alone on silica surfaces. For C5PeC11 alone, the adsorption of a single C5PeC11 was observed at 30 ns and increased gradually to 3 C5PeC11 molecules at 80 ns when a significant increase to 8 in the number of C5PeC11 molecules adsorbed was observed. In contrast, the adsorption of C5PeC11 and C5Pe was observed at as early as 10 ns, indicating

a strong synergy of C5Pe and C5PeC11 in promoting their adsorption on silica in heptol. The molecules adsorbed remained at 3 for an extended period with a step increase in the number of molecules adsorbed was observed at 90 ns simulation time. Although this step increase corresponded to the observed step increase in the C5PeC11 system, more C5Pe molecules were shown to be adsorbed. The results on the number of the adsorbed molecules and the average COM distance of polyaromatic molecules to silica surfaces clearly illustrate the synergy between C5PeC11 and C5Pe on their adsorption on silica in their binary mixture system.

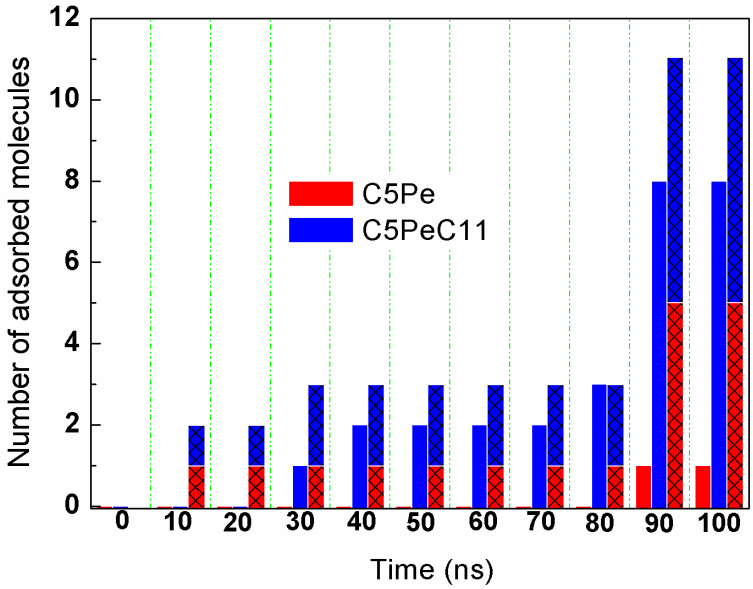


Figure 5. Number of molecules adsorbed on silica surfaces at different simulation time. (The stacked columns of shaded patterns represent the binary mixture system.)

To better understand the observed adsorption characteristics of polyaromatic molecules on silica surfaces in heptol, the number of hydrogen bonds between polyaromatic molecules and silica surface was determined as a function of simulation (adsorption) time, which allows us to elucidate when and how many molecules adsorbe on silica surface. It is not surprising to see the absence of hydrogen bonds until 84 ns for the C5Pe system (shown in Figure 6a) due to the absence of C5Pe adsorbed on the silica as shown in Figure 5. On the contrary, polyaromatic compounds gradually adsorbed on silica surfaces after 10 ns with increasingly more hydrogen bonds formed in the C5PeC11 system (shown in Figure 6b). In the binary mixture system, much more hydrogen bonds were calculated compared with the individual molecular species systems, as anticipated. In the binary system, the polyaromatic compounds adsorbed rapidly on the surface at the beginning of the simulation (shown in Figure 6c). More interestingly, the number of hydrogen bonds between polyaromatic molecules and silica surface contributed by 6 C5Pe or 6 C5PeC11 is also more than the corresponding individual molecular species systems of 12 molecules. The number of hydrogen bonds in Figure 6 clearly shows a strong and rapid adsorption of C5Pe and C5PeC11 in the binary mixture system, which proved the synergy in the adsorption of polyaromatic compounds.

In this section, the synergy effect of C5Pe and C5PeC11 is further discussed. Although the polyaromatic compounds distribution was discussed in Figure 3, the results were not sufficient to explain the interactions between C5Pe and C5PeC11 molecules. The top views of the final configuration at 100 ns in the three systems are shown in Figure 7, which illustrate the strong aggregation of C5Pe, followed by C5PeC11 and then C5Pe and C5PeC11 in the mixture, as anticipated.

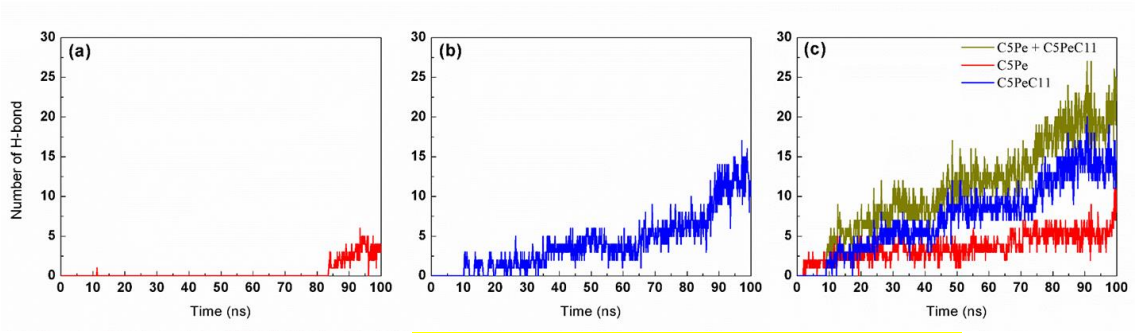


Figure 6. Number of hydrogen bonds between polyaromatic molecules and silica surface as a function of simulation time in (a) 12 C5Pe system, (b) 12 C5PeC11 system, (c) 6 C5Pe and 6 C5PeC11 binary mixture system.

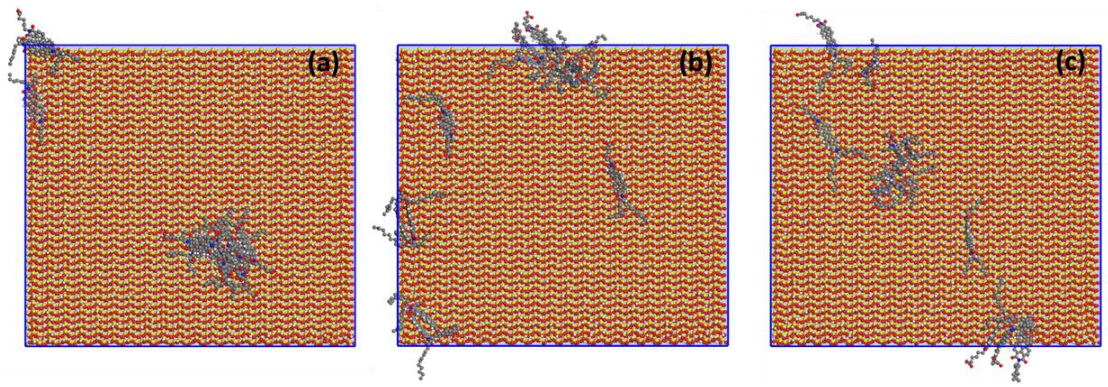


Figure 7. Top views of the final configuration at 100 ns: (a) 12 C5Pe system, (b) 12 C5PeC11 system, (c) 6 C5Pe and 6 C5PeC11 binary mixture system.

In order to explain the observed trend in molecular aggregation as a function of simulation time, the solvent accessible surface area (SASA) of polyaromatic compounds is calculated for the three systems and the results are shown in Figure 8. The SASA data is a measure on the interactions of polyaromatic compounds with solvents and hence among themselves in corresponding solvents. It is clear to see a rapid reduction in the SASA of C5Pe, with the value of SASA levelled off after 25 ns and with low fluctuations. The result indicates the formation of the aggregate within 25 ns in the system (shown in the Supporting Information Figure S5). The observed low fluctuations illustrate a strong aggregation of C5Pe molecules with each other in the solvent. The free energy of the system was reduced by the aggregation of molecules, resulting in a weak adsorption of polyaromatic compounds on silica surface. In contrast, the SASA reduced slowly with high fluctuations in the C5PeC11 system, most likely due to the high solubility of C5PeC11 in heptol solvents. The solubilization of C5PeC11 increases the

chance for polyaromatic compounds to adsorb on silica surface. For the binary mixture system, the SASA decreased slowly as in C5PeC11 system with the curve of SASA falling slightly below the curve for the C5PeC11 individual component system. It appears that the presence of C5PeC11 enhances the access of C5Pe by solvent molecules due to the association between C5Pe and C5PeC11. Such increase in SASA of C5Pe by C5PeC11 led to an increased adsorption of C5Pe and C5PeC11 on silica.

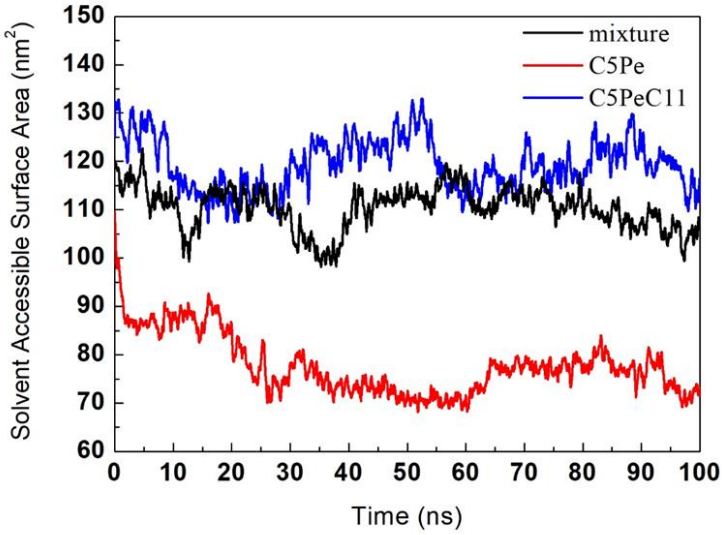


Figure 8. Solvent accessible surface area of the C5Pe, C5PeC11 and their binary mixture system as a function of simulation time.

The aggregation between C5Pe and C5PeC11 in the binary mixture system was investigated. It is interesting to find two kinds of interaction configurations on the surface: (a) π-π stacking, and (b) T-stacking (shown in Figure 9). These two types of stacking between polyaromatic compounds have been reported in a number of studies.[23, 39]

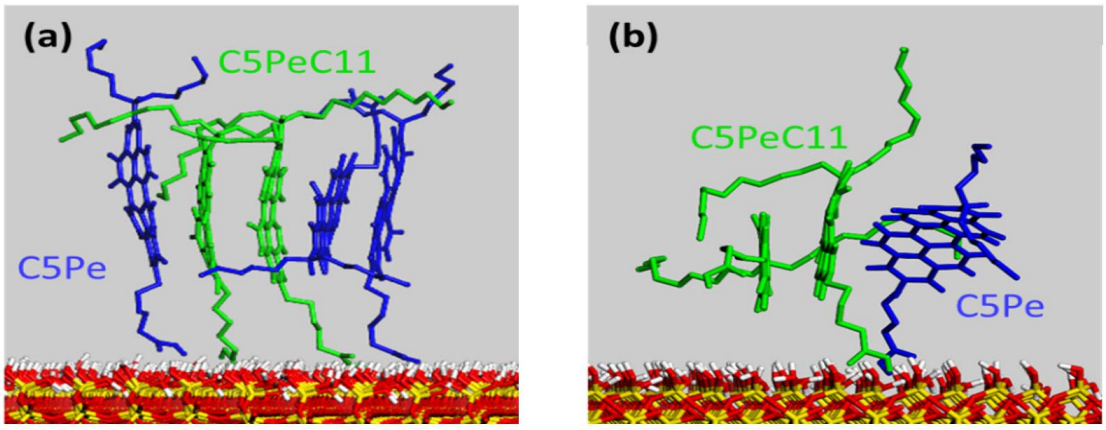


Figure 9. Configuration of C5Pe and C5PeC11 adsorption on silica surface in a binary mixture system. (a) π-π stacking, (b) T-stacking

The π-π stacking or T-stacking interaction between C5Pe and C5PeC11 in the bulk led to formation of small C5Pe-C5PeC11 clusters in the bulk. The small clusters of high diffusivity and large number binding sites exhibit more effective adsorption on silica surface than larger clusters of C5Pe (shown in the videos of Supporting Information SI-trimer and SI-pentamer). From the video, it is clear to see the trimer formed at 30 ns in bulk solvents and then adsorbed on silica surface. As for the pentamer, the situation is more complex. First, the dimer and trimer formed, respectively, in the bulk. The dimer then adsorbed after an extended simulation time. Next the interaction of the trimer from bulk solution with the dimer adsorbed led to the formation of pentamer on the silica surface and rearrangement on silica surface to the final state of adsorbed cluster (pentamer) configuration. From the final configuration at 100 ns of C5PeC11 system, the largest aggregate is dimer, while there are pentamer and trimer in the C5Pe-C5PeC11 mixture system. The steric hindrance of longer aliphatic chains impeded the aggregation of C5PeC11. The addition of C5Pe with shorter aliphatic chains provided a compromise to reduce the steric hindrance of C5PeC11 by its aggregation with C5PeC11, allowing more active polar terminals exposed for adsorption. This is the mechanism of the enhanced C5Pe adsorption in the mixed molecular system by its association with C5PeC11 molecules.

2. Experiments of QCM-D

To confirm the significant findings by MD simulations, the adsorption of polyaromatic compounds either individually or in the binary mixture was studied using QCM-D method. In each experiment, heptol was injected first into the QCM-D system to establish the baseline, followed by the flow of corresponding polyaromatic compound solutions to determine the adsorption process by recording the change in the resonance frequency (Δf) and dissipation (ΔD) of QCM-D silica sensors. Figure 10 shows a rapid but small decrease (15 Hz) in the resonance frequency accompanied by a small increase in dissipation of 8×10^{-6} when C5Pe in heptol solution was allowed to contact with the silica sensor surfaces, indicating a limited adsorption of C5Pe molecules from its heptol solutions. A much significant decrease by 80 Hz in the resonance frequency with a significant increase in ΔD by 43×10^{-6} was observed for the C5PeC11 system, indicating a much stronger adsorption of C5PeC11 than that of C5Pe on silica surfaces. It is however surprising to see an even larger decrease in the resonance frequency by 140 Hz, but with a much less increase in ΔD by 28×10^{-6} in the binary mixture system as compared with the case for C5PeC11 alone. At the same total polyaromatic compounds concentration (0.5g/L) for each system, the larger decrease in the resonance frequency indicates more molecules adsorbed on the silica sensor surfaces, which agrees with the MD simulation results in Figure 3, where two strong overlapping peaks were observed in the mixed system than that in the individual component systems. More importantly, the close distances of the two peaks to the silica surface would indicate a more compact configuration of the adsorbed polyaromatic molecules, which would correspond to a smaller ΔD increase as experimentally observed when compared with the case of C5PeC11 alone in heptol. Qualitatively, the observed decreases of Δf, which are in the order of C5Pe+C5PeC11 mixture > C5PeC11 > C5Pe, agreed well with the decreasing peak intensity of adsorbed polyaromatic molecules observed in MD simulations shown in Figure 3. Such agreement confirms not only the synergy effect of C5Pe and C5PeC11 adsorption, but also the accuracy and the value of MD simulations. In the current systems, the minimal dissipation change for C5Pe is linked with negligible adsorption of C5Pe

on silica surfaces due to its low solubility in heptol, which forces molecules to form compact aggregates in the bulk and hence the loss of their ability to bind with silica surfaces. For C5PeC11 of high solubility in the heptol and steric hindrance from its aliphatic chains, the aggregation of C5PeC11 in heptol is limited as such that there remain sufficient active sites from C5PeC11 to bind with silica surfaces in floppy configurations. In the case of C5Pe and C5PeC11 mixtures, the molecular aggregation between C5Pe and C5PeC11 is stronger than that among C5PeC11 molecules but much weaker than that among C5Pe molecules, as shown in our previous study with ESI-MS (Electrospray Ionization Mass Spectrometry).[26] Such interactions between C5Pe and C5PeC11 accounts for the observed significant increase in SASA of C5Pe systems that is close to the SASA value for C5PeC11 system as shown in Figure 8. Therefore, it is not surprising to see less dissipation change despite a larger change in Δf in the mixed systems than that in C5PeC11 alone system.

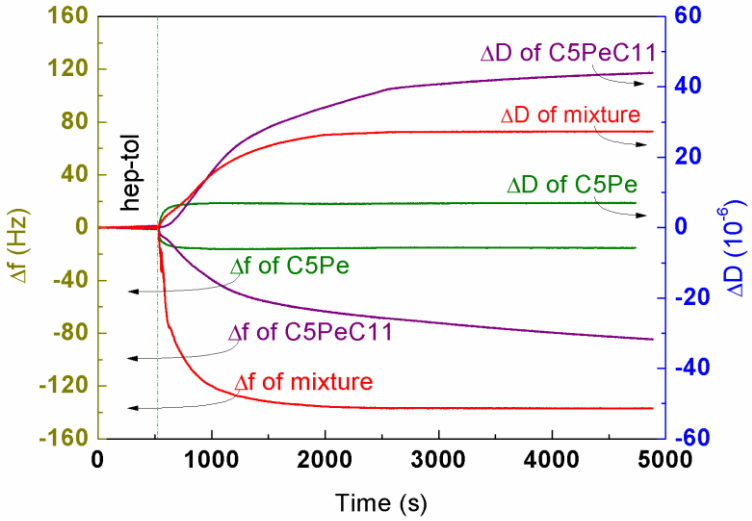


Figure 10. Frequency and dissipation shift as a function of the adsorption time in QCM-D experiments.

3. AFM Imaging of Adsorbed Layers

The silica wafers after adsorption were imaged by AFM to shed lights on the extent and the structure of adsorbed molecules. As anticipated, the results in Figure 11a showed a clear adsorption of C5Pe on silica in the form of aggregates with variable sizes and long strip shapes, which were also shown in our previous work.[34] In the C5PeC11 system as shown in Figure 11b, the aggregates were more compact and interconnected, in a long string of instant noodle shape. It is the crosslinking of polyaromatic compounds that enhanced the adsorption of C5PeC11 as compared with that of C5Pe alone. The image in Figure 11c for C5Pe and C5PeC11 binary mixture showed a more closely packed spongy layer of polyaromatic molecules covering the entire silica surface. This morphology of C5Pe and C5PeC11 adsorption from their binary mixture indicated a higher adsorption capacity as observed in QCM-D measurement and MD simulations. The results from AFM imaging confirmed the synergy adsorption of C5Pe and C5PeC11 mixture.

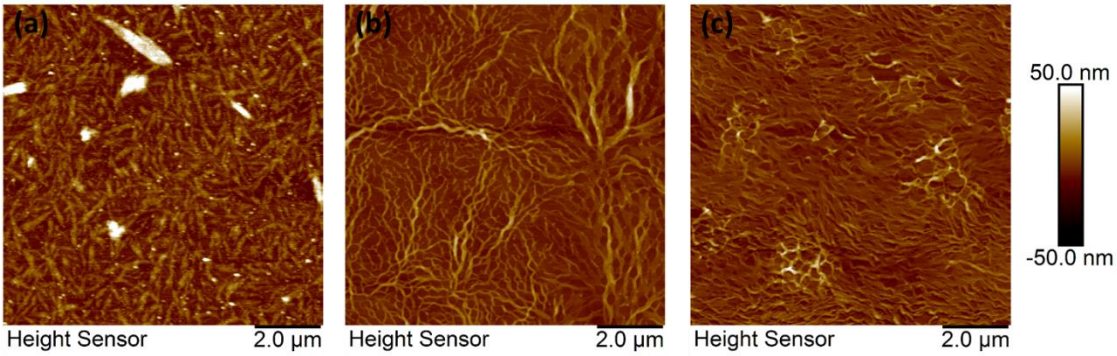


Figure 11. AFM images of (a) C5Pe, (b) C5PeC11 and (c) their binary mixture adsorbed on QCM-D silica wafer.

■ CONCLUSION

The adsorption of individual C5Pe or C5PeC11 and their binary mixture on silica surface in heptol solvents was investigated by molecular dynamics (MD) simulation, and further studied by QCM-D experiments and AFM imaging. MD simulation showed a lower solubility and stronger aggregation of short aliphatic chain C5Pe in its heptol solution as compared with the longer aliphatic chain C5PeC11. It is therefore not surprising to see a larger aggregation in heptol and fewer adsorptions on silica surfaces of C5Pe than C5PeC11 from corresponding heptol solutions. It is interesting to see a clear synergy between C5Pe and C5PeC11 to enhance their adsorption from their binary mixture system. The analysis on the trajectories of molecules and number of hydrogen bonds revealed that the interactions of π-π stacking and T-stacking between C5Pe and C5PeC11 molecules are advantageous for not only reducing the disparity, but also preventing rapid aggregation of polyaromatic compounds in the binary mixture system. As a result, more C5Pe and C5PeC11 molecules adsorbed on silica surface for reducing the system free energy. The QCM-D experiments and AFM imaging revealed a strong adsorption and a spongy morphology of adsorbed layers on silica surface from C5Pe and C5PeC11 mixture as compared with the cases of individual component systems, and the results were confirmed by MD simulations. The synergetic adsorption of polyaromatic compounds revealed and discussed in this work provides insights into the molecular assembly at silica-oil interfaces for the fabrication of smart devices and for resolving challenges in petroleum production.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available and free of charge on the ACS Publications website at DOI:

The detail of polyaromatic compounds arrangement in simulation box, the density distribution of toluene in the first 1 ns along Z direction in systems, the H-bonding interaction between polar terminate (carboxylic acid: -COOH) group and geminal silanol groups (-Si-$(OH)_2$), the detail of COM assigns in molecules and the snapshot of C5Pe in system at 25 ns.

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Notes
The authors declare no competing financial interest.

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