

# A Molecular Dynamics Simulation of a Homogeneous Organic-Inorganic Hybrid Silica Membrane

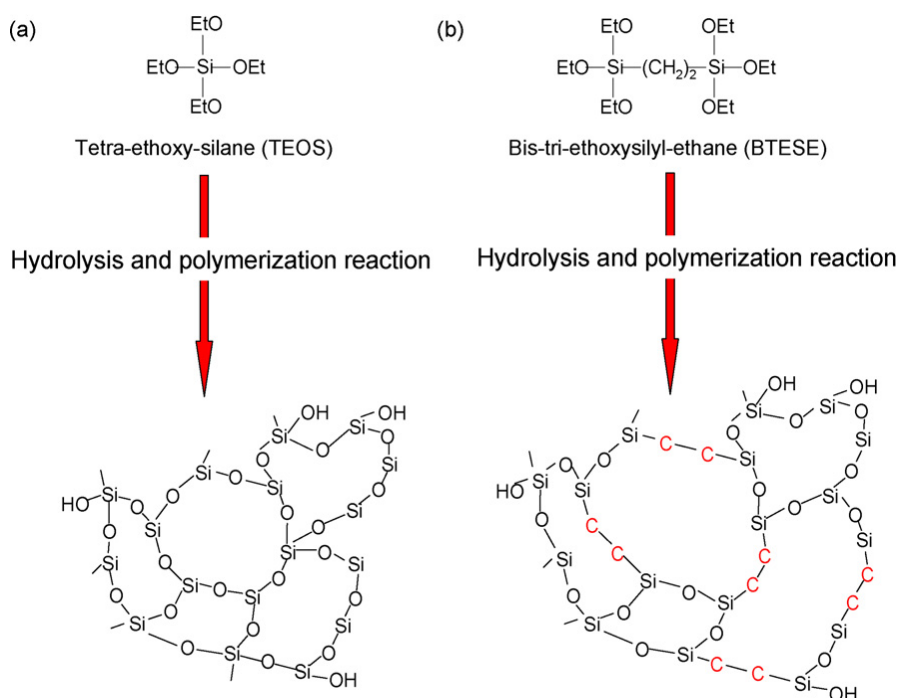
## Supplementary Information: Simulation Procedure and Physical Property Analysis

### Simulation Procedure

The molecular models in this work were built using the Materials Studio package from Accelrys. Details of the model construction and physical property estimation are described below.

#### Membrane Model Construction

The pure silica membrane model was first constructed using a cristobalite crystalline structure consisting of 512 silicon and 1024 oxygen atoms. The initial silica model was melted at 8500 K during the first 250 ps and then cooled to 300 K in 150 ps to form the amorphous silica structure. The amorphous silica structure built in this work was validated by comparing the radial distribution functions of the atom pairs to those in previous simulation reports.<sup>1,2</sup> Subsequently, the Si-O-Si segments in the silica network were randomly replaced by Si-C-C-Si segments to form the hybrid bis(triethoxysilyl)ethane (BTESE) structure. In the hybrid BTESE silica model, the number of carbon and silicon atoms were set to be equal, which corresponds to the properties of the actual material produced from the ideal hydrolysis and polymerisation reaction, as shown in **Figure S1**. The hybrid silica model processed the geometrical optimisation by energy minimisation over 3,000 iterations to obtain a stable molecular structure. To simulate how the Si-C-C-Si segments affected the hybrid silica network, the MD calculations were performed for 500 ps at 300 K under an NPT ensemble (with fixed atom numbers, cell volume, and system pressure).



**Figure S1** Schematic images of amorphous silica networks derived by (a) TEOS and (b) BTESE.<sup>3</sup>

### **Potential Function**

To couple the silica network and organic groups of the hybrid system into the simulation work, an accurate and reasonable potential function is necessary. All the current available potential functions could not be directly applied to reasonably construct organic-inorganic hybrid matrix. We proposed a new molecular dynamics simulation method by modifying the polymer consistent force-field (*pcff*) computational model. The parameters of bond stretching terms and bond angle terms with were estimated using Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies (COMPASS) force-field computational model. The newly proposed hybrid-*pcff* (*h-pcff*) computational model can be applied to accurately construct the homogeneous organic-inorganic hybrid BTESE silica membrane. Why we proposed the *h-pcff* model and how does it work are explained in the followings.

Regarding amorphous silica modelling, the modified Born–Mayer–Huggins (BMH) pair potential and the Stillinger–Weber (SW) potential are widely considered to be the potential functions of choice for amorphous silica simulations.<sup>1, 2, 4, 5</sup> However, the

BMH pair potential and the SW potential do not provide information on organic groups or silica-organic group interactions. Therefore, a universal potential function was necessary in this study to couple the silica network and organics for the simulation of organic-inorganic hybrid silica structures. Here, we adopted the well-known *pcff* force field<sup>6</sup> as the basis of our potential function in this work. The *pcff* force-field is one member of the *ab initio* consistent force-field family (composed of CFF91, CFF, *pcff*, and COMPASS force-field) with the same functional form. The functional form can be illustrated as follows:

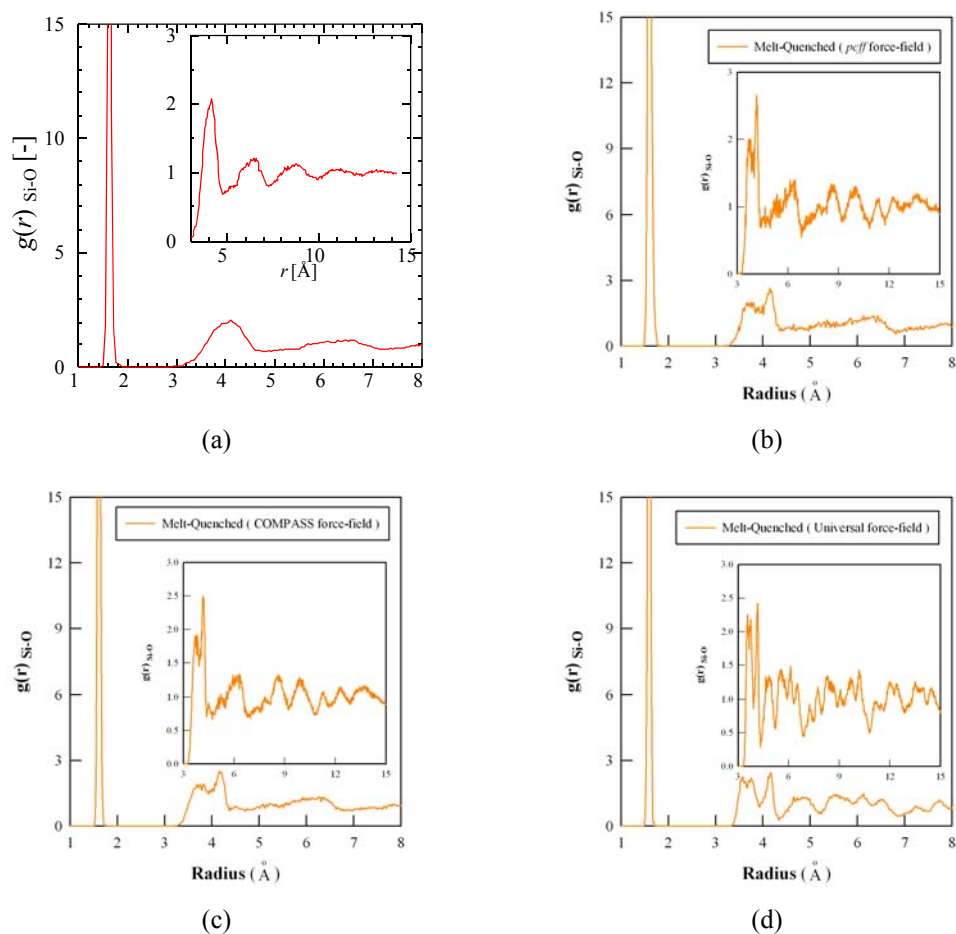
$$\begin{aligned}
 E = & \sum_b \left[ K_2 (b - b_0)^2 + K_3 (b - b_0)^3 + K_4 (b - b_0)^4 \right] & \text{(a)} \\
 & + \sum_\theta \left[ H_2 (\theta - \theta_0)^2 + H_3 (\theta - \theta_0)^3 + H_4 (\theta - \theta_0)^4 \right] & \text{(b)} \\
 & + \sum_\phi \left\{ V_1 [1 - \cos(\phi - \phi_0^1)] + V_2 [1 - \cos(2\phi - \phi_0^2)] + V_3 [1 - \cos(3\phi - \phi_0^3)] \right\} & \text{(c)} \\
 & + \sum_x K_x x^2 + \sum_b \sum_{b'} F_{bb'} (b - b_0)(b' - b'_0) + \sum_\theta \sum_{\theta'} F_{\theta\theta'} (\theta - \theta_0)(\theta' - \theta'_0) & \text{(d)} \quad \text{(e)} \quad \text{(f)} \\
 & + \sum_b \sum_\theta F_{b\theta} (b - b_0)(\theta - \theta_0) + \sum_b \sum_\phi (b - b_0) [V_1 \cos \phi + V_2 \cos 2\phi + V_3 \cos 3\phi] & \text{(g)} \quad \text{(h)} \\
 & + \sum_{b'} \sum_\phi (b' - b'_0) [V_1 \cos \phi + V_2 \cos 2\phi + V_3 \cos 3\phi] & \text{(i)} \\
 & + \sum_\phi \sum_\theta \sum_{\theta'} K_{\phi\theta\theta'} \cos \phi (\theta - \theta_0)(\theta' - \theta'_0) + \sum_{i>j} \frac{q_i q_j}{\epsilon r_{ij}} + \sum_{i>j} \left[ \left( \frac{A_{ij}}{r_{ij}^9} \right) - \left( \frac{B_{ij}}{r_{ij}^6} \right) \right] & \text{(j)} \quad \text{(k)} \quad \text{(l)}
 \end{aligned} \tag{1}$$

The energy terms were divided into three categories: the bonded energy terms, the cross-terms, and the non-bonded energy terms. The bonded energy terms consisted of (a) the covalent bond stretching energy terms, (b) the bond angle bending energy terms, and (c) the torsion angle rotation energy terms of the polymer chain. The energy of the torsion angle was fit to a Fourier series function. The out-of-plane energy, or improper term (d), was described as a harmonic function. The terms for

cross interactions included the dynamic variations among the bond stretching, bending, and torsion angle rotation ( $e-j$ ). The last two terms, (k) and (l), represent the Coulombic electrostatic force and the van der Waals force, respectively, which are interactive forces between silica networks and small molecules.

The reasons we chose *pcff* as the basis of our potential function can be explained by the following:

- (1) *pcff* provided us the similar molecular structure of pure amorphous silica (checked by radial distribution function (RDF) of Si-O atom pair) in our simulation environment. We compared the results from several candidate force-fields with the data using the most convincing BMH and SW functions. **Figure S2** shows the RDF of Si-O atom pairs of SiO<sub>2</sub> structure from the three candidate potential functions and that from the BMH and SW functions.
- (2) The parameters of *pcff* are available to modify in our simulation software. In **Figure S2**, it was shown that *pcff* and COMPASS provided similar results with the data from BMH and SW potential. However, the parameters of COMPASS force-field are not available to modify in the software.
- (3) *pcff* has the same functional form with the COMPASS force-field. The COMPASS force-field is regarded as the first *ab initio* forcefield that enables accurate and simultaneous prediction of gas-phase properties (structural, conformational, vibrational, etc.) and condensed-phase properties (equation of



**Figure S2** RDF of Si-O atom pairs from (a) BMH and SW potential, (b) *pcff* force-field, (c) COMPASS force-field, and (d) Universal force-field.

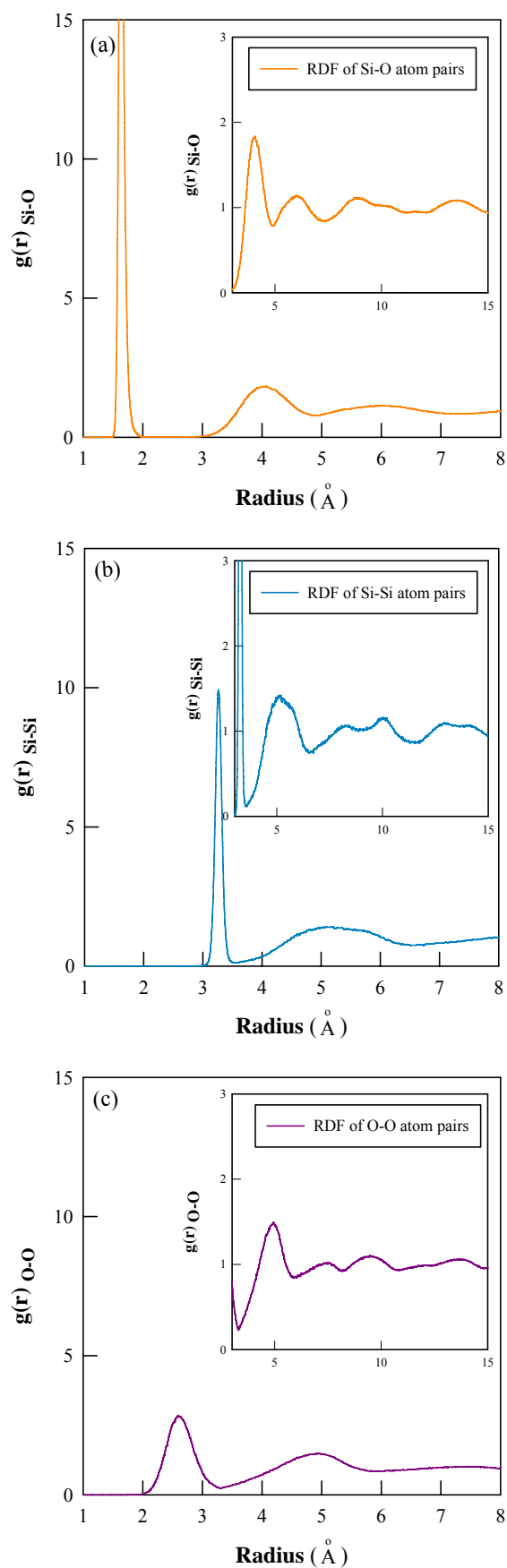
state, cohesive energies, etc.) for a broad range of molecules and polymers. It is also a high quality force-field to consolidate parameters of organic and inorganic materials<sup>7-9</sup>.

Thus, it might be possible to adopt some specific parameters from COMPASS into *pcff* for trying to obtain reasonable molecular structure since they are the consistent force-fields with the same functional form. Therefore, we adopted *pcff* as our initial potential function and modified its bonding terms and bond angle terms to achieve our pure amorphous silica model reasonably and stably.

The parameters of the Si-O bonding term and the O-Si-O bond angle term were modified to match the local regional structural modifications, while the parameters of Si-O, the Si-O cross term and the Si-O-Si bond angle term were modified to match the

longer range structural modifications. The radial distribution functions (RDF) of Si-O, Si-Si, and O-O atom pairs were analysed and then compared with those of past simulations to validate the feasibility and accuracy of the modified *pcff* force-field. **Figure S3** shows the RDF diagram obtained from the purple amorphous silica model at 300 K using the same modified *pcff* force-field used in this work.

Subsequently, we adopted the parameters of bond stretching terms (C-C, Si-C and C-H) and bond angle terms (Si-C-C, C-Si-C, C-Si-O, H-C-Si, H-C-H, and C-C-H) from the COMPASS force-field into the modified *pcff* force-field. The Si-C-C bond angle was also modified to address the expansion effect of Si-C-C-Si segment in the hybrid silica network. The potential energy and kinetic energy were at the same order of magnitude and rapidly archived equilibrium during the simulation process.



**Figure S3** RDF diagram of (a) Si-O, (b) Si-Si, and (c) O-O atom pairs obtained using the modified *pcff* force-field.

## Physical Property Analysis

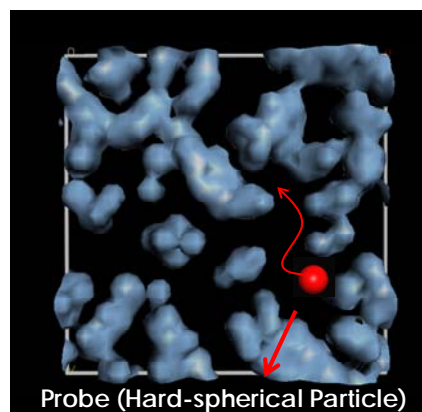
In our simulation, five independent molecular models were constructed for each membrane material to analyse their physical properties and obtain average calculated values. The reproducibility was also confirmed to validate that this was a reasonable simulation procedure.

### Fractional Free Space (FFS) and Fractional Accessible Volume (FAV)

The FFS of a membrane can be calculated using the following equation:

$$FFS = \frac{V_{\text{cell}} - V_{\text{vdw}}}{V_{\text{cell}}}, \quad (2)$$

where  $V_{\text{cell}}$  is the cell volume at  $T = 300$  K, and  $V_{\text{vdw}}$  is the van der Waals volume of the molecular model. For FAV analysis, the accessible volume was probed using a hard spherical particle with a specific radius, as shown in **Figure S3**. The FAV value can be estimated by dividing the accessible volume by the cell volume. In this study, different probe diameters were used to calculate the FAV values for equating to the gas permeance. The probe diameters were determined as the kinetic diameters of  $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ , and  $\text{SF}_6$ , which have kinetic diameters of 2.89 Å, 3.30 Å, 3.46 Å, 3.64 Å, 3.8 Å, 4 Å, 4.2 Å, and 5.5 Å, respectively.



**Figure S3** Schematic image of the accessible volume probed by a hard spherical particle.



## **Radial Distribution Function (RDF)**

In statistical mechanics, a radial distribution function (RDF) is adopted to analyse the micro-structure of the material. It describes how the specific atomic density varies as a function of the distance from one reference atom. In other words, the RDF counts the number of two-atom species with specific distances and is defined as:

$$g_{\alpha,\beta}(r) = \frac{V_0}{N_\beta} \frac{N_{\beta}(r)}{4\pi r^2 \Delta r}, \quad (3)$$

where  $V_0$  is the cell volume,  $N_\beta$  is the total number of  $\beta$  atoms, and  $N_{\beta}(r)$  is the number of  $\beta$  atoms found within a spherical shell with a radius of  $r$  to  $r+\Delta r$  corresponding to  $\alpha$  atoms. RDF is usually adopted to analyze the structure characteristic. Generally speaking, a higher intensity or sharper peak in the RDF pattern indicates a better ordering of atoms in the molecular model. In other words, the intensity of the peak in the RDF diagram is lowered or broadening as a result of higher molecular mobility or flexibility. The peak position of RDF diagram corresponding to x-axis indicates the distance between two specific atoms in the system, which can also be utilized to analyze the structure expansion or shrinkage.

## **References**

1. B. P. Feuston and S. H. Garofalini, *J. Chem. Phys.*, 1988, **89**, 5818.
2. T. Yoshioka, T. Tsuru and M. Asaeda, *Mol. Phys.*, 2004, **102**, 191.
3. M. Kanezashi, K. Yada, T. Yoshioka and T. Tsuru, *J. Membr. Sci.*, 2010, **348**, 310.
4. W. Chang and T. Y. Lee, *Comput. Chem. Eng.*, 2004, **29**, 209.
5. H. Takaba, E. Matsuda and S. I. Nakao, *J. Phys. Chem. B*, 2004, **108**, 14142.

6. J. R. Hill and J. Sauer, *J. Phys. Chem.*, 1995, **99**, 9536.
7. H. Sun, *Macromolecules*, 1995, **28**, 701-712.
8. H. Sun and D. Rigby, *Spectrochim. Acta, Part A*, 1997, **53**, 1301-1323.
9. H. Sun, *J. Phys. Chem. B*, 1998, **102**, 7338-7364.