**ABSTRACT**

The transport properties of oxygen in three amino-functionalized cubic polyhedral oligomeric silsesquioxanes (POSS) have been studied using classical molecular dynamics (MD) simulations over a timescale long enough to reach the Fickian regime for diffusion. An amount of O2 corresponding to an applied pressure of 3 bars was inserted into molecular models of hybrid organic/inorganic POSS with the chemical composition (RSiO3/2)8, which differed by the end-groups of their organic pendant chains, that is, R = −(CH2)3−NH−CO−X with X = −C6H4OH, −C6H5 or −C6H11. The oxygen … POSS energies were found to be small with respect to the POSS… POSS interactions. The O2 molecules permeate the organic phase and move through combinations of oscillations within available free volumes in the matrices and occasional jumping events. Gas mobility was more restricted in the system with the salicylic end-group and the largest hydrogen-bond network, whereas it was enhanced in the system with the cyclohexyl end-group. The most energetically-favorable sites for O2 insertion were either in the vicinity of the silica cages or close to the rings of the chain end-groups. On the other hand, the amide and hydroxyls groups engaging in H-bonds were less energetically favorable. This confirms that H-bonding networks are a hindrance for O2 transport in such systems.