Supporting Information

for

Lattice-Gas Modeling of Adsorbate Diffusion in Mixed-Linker Zeolitic Imidazolate Frameworks: Effect of Local Imidazolate Ordering

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KMC Implementation Validation and Percolating Cluster Determination

Figure S1 shows a representative MSD plot of an adsorbate in a parent material. The analytical self-diffusivity and the KMC self-diffusivity have a percent difference of ~5%.

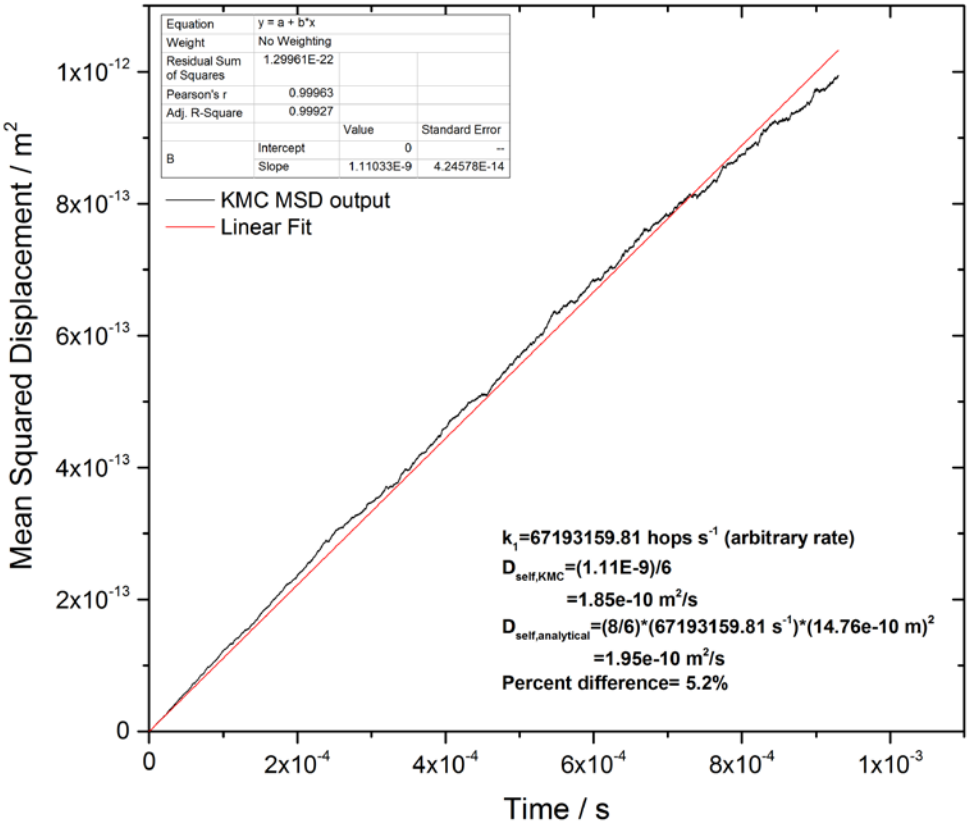

Figure S1. Example MSD of a lattice-gas in the parent material with a linear fit.

Figure S2 shows representative MSD plots of an adsorbate in a percolating (black) and non-percolating (blue) cluster. Adsorbates with final MSD values not larger than the longest distance on the 10x10x10 lattice were not included in the averaged diffusivity calculation.

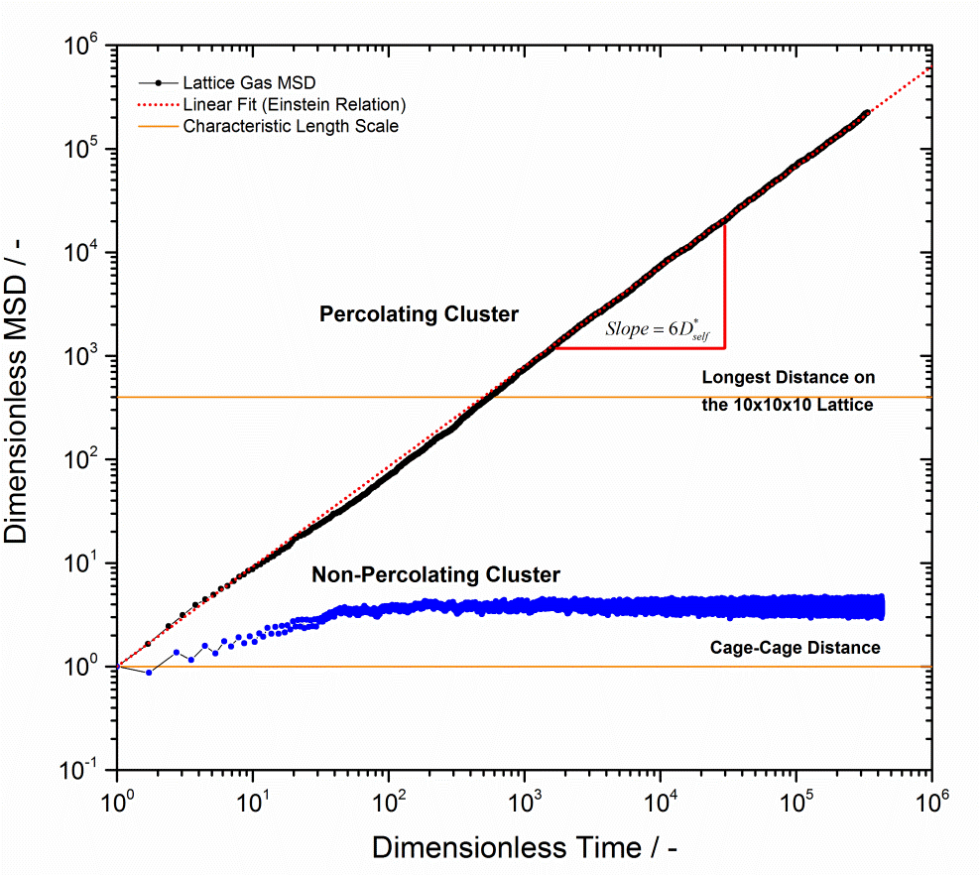

Figure S2. Example MSDs of a lattice-gas in both percolating and non-percolating clusters with characteristic length scales represented by gold lines.

Alternative Window Blocking Scenarios

A logical extension of the single blocking case would be to consider the scenario when more than one bulky imidazolate linker is needed for window blocking (e.g. a benzimidazolate linker in ZIF-7_x-8_{100-x} as shown in Figure S3a). We report in Figures S3b, S3c, and S3d normalized diffusivities as a function of the bulky imidazolate mole fraction for lattices with constant SRO. Figure S3b demonstrates the influence of SRO when 3 bulky imidazolate linkers are required for window blocking (k_4=0), and Figure S3c demonstrates the influence when 2 or 3 bulky imidazolate linkers are required for window blocking (k_3,k_4=0). Figure S3d contains the same information as Figure 4a of the main manuscript, but is duplicated for direct comparison. Window blocking with only k_4=0 shows that clustered linkers result in a faster decrease of the diffusivity as opposed to randomly placed or alternating linkers. Clustered linkers create lattices with a large population of blocked type 4 windows, hence lengthening diffusion pathways. Interestingly, the composition thresholds are the same for the three lattices. Window blocking with k_3,k_4=0 demonstrates that SRO has a negligible influence on the simulated diffusivities; interestingly, the composition threshold for lattices with clustered linkers is shifted to a larger mole fraction than the lattices with alternating or random SRO. These results suggest that window blocking requiring only one bulky imidazolate linker has the most promise for tuning adsorbate diffusion with SRO control.

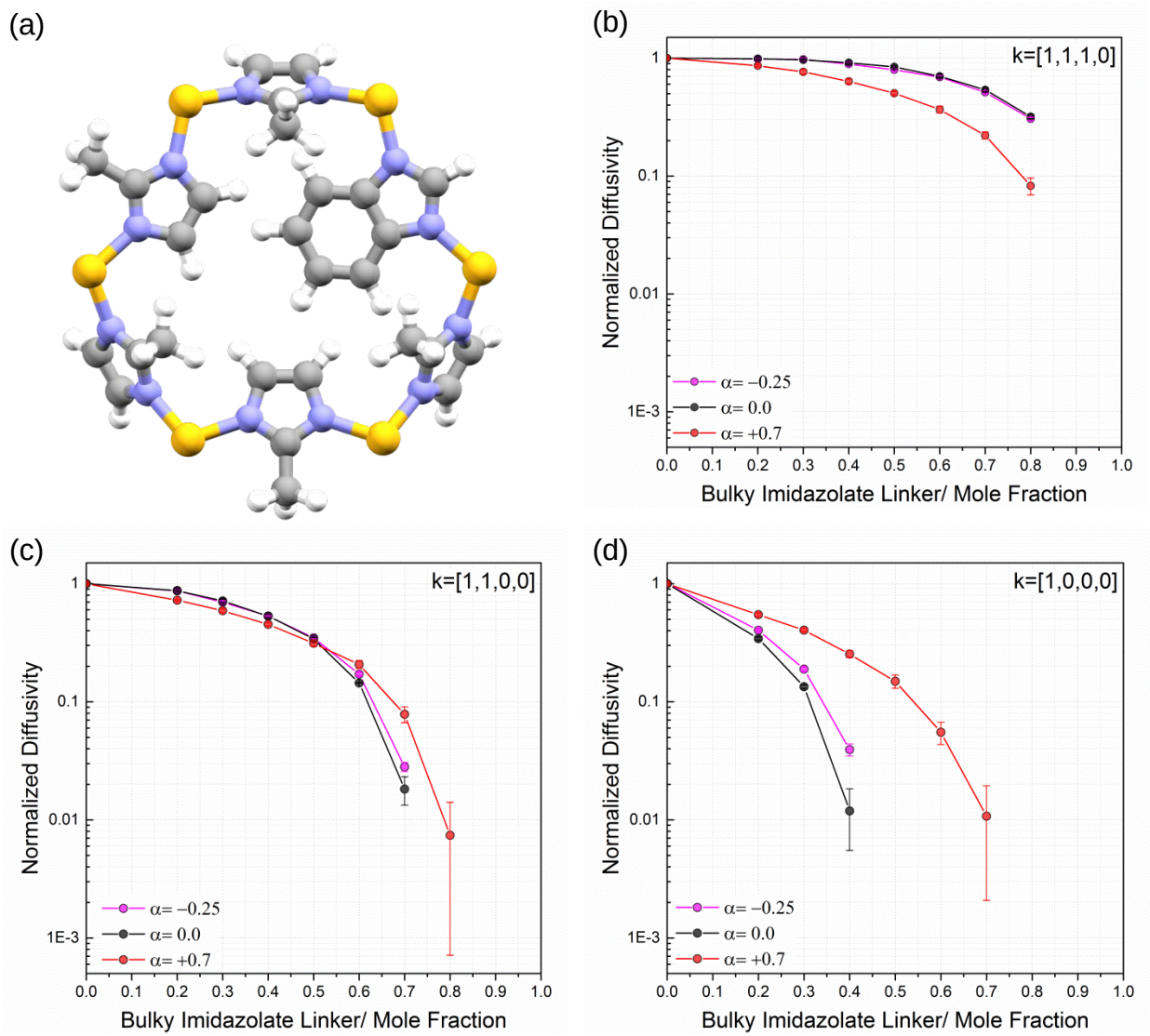

Figure S3. **(a)** Example of window blocking from a bulky imidazolate linker. Diffusivities as a function of composition at fixed SRO for **(b)** window blocking requiring three bulky linkers, **(c)** window blocking requiring two linkers, and **(d)** window blocking requiring only one bulky linker.

Divergent Hopping Rates through Hybrid and Parent Windows

To our knowledge, existing experimental data of adsorbate transport in binary mixed-linker ZIFs presents diffusion coefficients as monotonic functions of the organic linker composition. It is reasonable to consider that adsorbate diffusion may also be blocked (allowed) through either the hybrid or parent windows resulting in nonlinear diffusion behavior. This behavior is plausible when two distinct linkers surrounding a window interact in a cooperative manner. These interactions either impact linker flexibility (i.e. amplitude or frequency characteristics[1]) or (broaden) narrow the window aperture through attractive (repulsive) pair-wise interactions (e.g. van der Waals or electrostatics). Figures S4a and S4b demonstrate the impact of SRO when considering window blocking through the two hybrid windows and the two parent windows respectively. Figure S4a demonstrates that adsorbate diffusion is most reduced (by one order of magnitude) for SROs close to 0.0 (i.e. random local ordering). More striking is the observation that adsorbates can percolate through the structure over the entire range of compositions. This is a direct consequence of the window type probabilities as a function of composition[2]. Figure S4b demonstrates that structures with random local orderings enhance the diffusion properties over a composition range from 0.2-0.8 mole fractions. Percolation is only completely inhibited in the near parent ZIF lattices where the probability of observing a hybrid window of either type drops to near zero. Figures S4c and S4d demonstrate the impact of local ordering when adsorbate diffusion is depressed (accelerated) through the hybrid windows. Similar observations as those discussed for Figures S4a and S4b are made, with a difference that percolation in the parent materials in Figure S4d is not impeded completely, merely reduced according to the predetermined rates. Said another way, there are two percolation thresholds in Figure S4b and no percolation thresholds in Figure S4d. Ultimately, to predict this diffusion behavior, one needs the knowledge that the rates through the hybrid windows are faster (slower) than the rates in the parent materials; the magnitude of the hybrid window rates is not an important parameter.

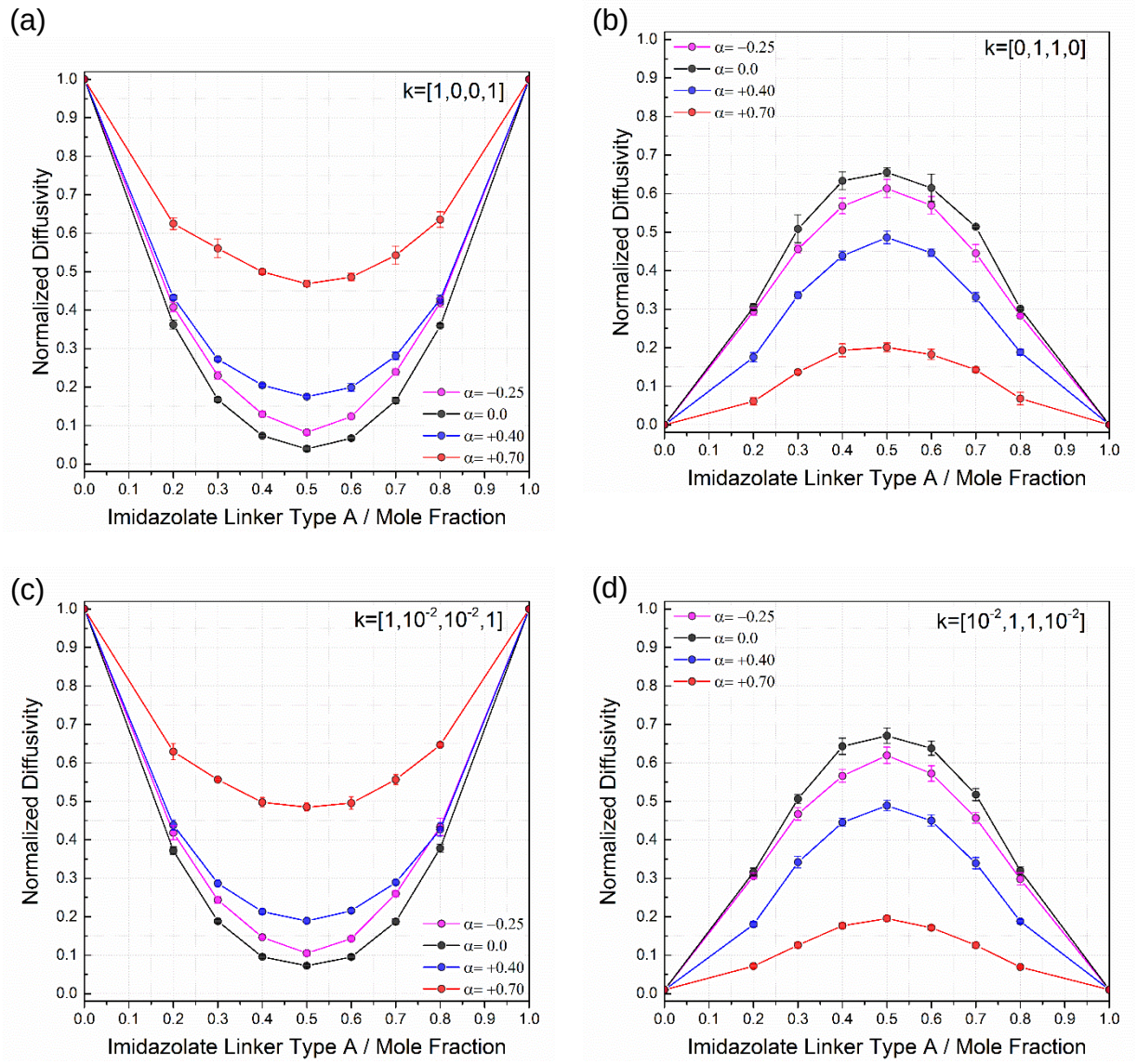

Figure S4. Normalized self-diffusivities as a function of SRO and the mole fraction of linker type A where **(a)** utilizes a rate convention of k=[1,0,0,1] to denote blocking of the hybrid windows, **(b)** utilizes a rate convention of k=[0,1,1,0] to denote blocking of the parent windows, **(c)** utilizes a rate convection of k=[1,10^{-2},10^{-2},1] to denote reduced diffusion through hybrid windows, and **(d)** utilizes a rate convection of k=[10^{-2},1,1,10^{-2}] to denote reduced diffusion through parent windows.

Supporting Information References

1. Kolokolov, D. I.; Stepanov, A. G.; Jobic, H., Mobility of the 2-Methylimidazolate Linkers in ZIF-8 Probed by 2H NMR: Saloon Doors for the Guests. *J. Phys. Chem. C* **2015**, *119*, 27512-27520.

2. Jayachandrababu, K. C.; Verploegh, R. J.; Leisen, J.; Nieuwendaal, R. C.; Sholl, D. S.; Nair, S., Structure Elucidation of Mixed-Linker Zeolitic Imidazolate Frameworks by Solid-State 1H Cramps NMR Spectroscopy and Computational Modeling. *J. Am. Chem. Soc.* **2016**, *138*, 7325-7336.