Supporting Information for

Heterogeneous Single-Molecule Diffusion in One- Two- and Three-Dimensional Microporous Coordination Polymers: Directional, Trapped and Immobile Guests

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Supplementary movies

Segments of raw data. Frame rate: 35 ms/frame. Contrast is adjusted for better visualization:

- Movie_1.avi – Isolated single Nile red molecules in UMCM-1 (frames 1-300). 7.1 × 9.4 μm^2.
- Movie_2.avi – Isolated single Nile red molecules in UMCM-2 (frames 1-150). 12.5 × 12.7 μm^2.
- Movie_3.avi – Isolated single Nile red molecules in UMCM-4 (frames 1-75). 22.7 × 20.4 μm^2.

Color tracks corresponding to trajectories in Figure 2 of the main text superimposed on raw data. Frame rate: 35 ms/frame. Contrast is adjusted for better visualization:

- Movie_4.avi - Quasi 1D track in MCM-1 corresponding to Figure 2b. 1.7 × 3.0 μm^2.
- Movie_5.avi - Confined motion in UMCM-1corresponding to Figure 2c. 1.0 × 1.1 μm^2.
- Movie_6.avi - Heterogeneous motion in UMCM-1 corresponding to Figure 2d. 1.2 × 2.2 μm^2.
- Movie_7.avi - Confined track in UMCM-2 corresponding to Figure 2f. 1.0 × 1.0 μm^2.
- Movie_8.avi - Free diffusion in UMCM-2 corresponding to Figure 2g. 1.8 × 2.4 μm^2.
- Movie_9.avi - 2D diffusion in UMCM-4 corresponding to Figure 2i. 2.6 × 2.9 μm^2.
- Movie_10.avi - Confined motion in UMCM-4 corresponding to Figure 2j. 1.1 × 1.1 μm^2.

Experimental Details:

Sample Preparation

Crystals of UMCM-1, UMCM-2, and UMCM-4 were prepared as previously described and their structures were confirmed by powder X-ray diffraction analysis.[1-3] A solution of 5 pM Nile red in 1-butanol was added to UMCM crystals (with 10% mineral oil for the UMCM-1 experiments) and the mixture was mounted between two cover slips immediately before imaging.

Single-Molecule Imaging

Widefield single-molecule epifluorescence microscopy was performed as previously reported.[4] Briefly, samples were imaged with a 1.40 NA oil-immersion objective in an Olympus IX71 inverted microscope and detected on a 512x512 pixel Photometrics Evolve EMCCD at a rate of 35 ms/frame. Samples were initially photobleached under 488-nm illumination (Coherent Sapphire 488-50), and then imaged 2 – 5 min later with 561-nm excitation (Coherent Sapphire 561-50). Appropriate filters (Semrock Di01-R561 and Semrock BLP01-561R) were chosen to maximize signal and minimize scattered laser light.

Angle Distribution of an Immobile Molecule in the Presence of Gaussian Fitting Noise

Due to the limited localization accuracy and the associated Gaussian fitting noise, an immobile molecule will appear as moving within a small region centered on its true position, which gives rise to an artificial trajectory. The angles between consecutive displacement vectors for such trajectory follow a U-shaped distribution with maxima at ±180^{o}. The mathematical justification can be found elsewhere,[5] and below we show the angle distribution from a simulated trajectory constructed from 10,000 data points centered about (0,0) with added Gaussian fitting noise. The resulting distribution of angles indeed follows a U-shaped pattern and resembles the one obtained for molecules in UMCM-2 crystals.

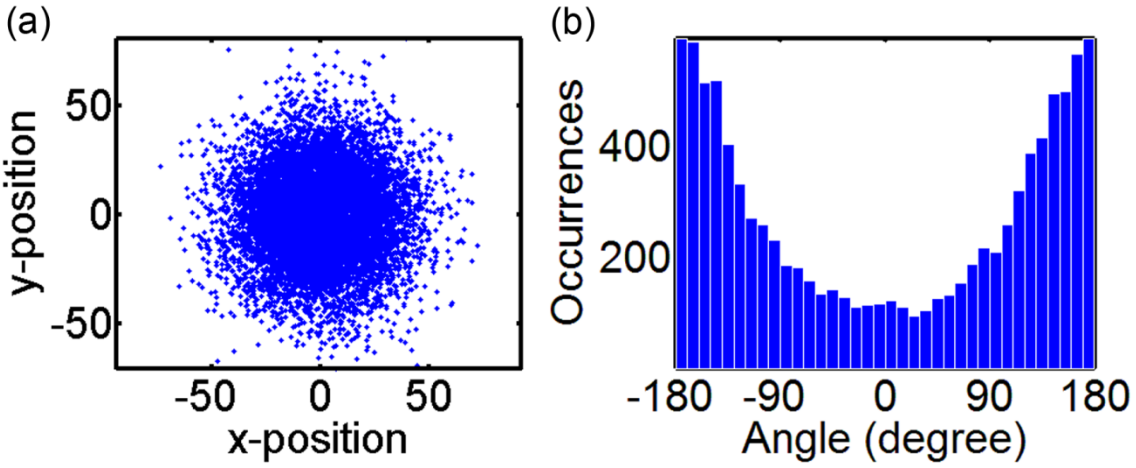

Figure S1. (a) 10,000 simulated data points are distributed around the origin in a Gaussian pattern and are connected sequentially to generate a trajectory similar to that obtained from tracking an immobile molecule in the presence of Gaussian fitting noise. For clarity, the connections between data points are not shown. (b) Angle distribution of the simulated trajectory.

Trajectory Backbones in UMCM-1:

To reduce the quasi-1D motion observed in UMCM-1 to ideal 1D motion for subsequent 1D cumulative probability distribution (CPD) analysis, all displacements in UMCM-1 are projected onto the track backbone prior to fitting the data to a one-dimensional diffusion model. The backbone for each trajectory is obtained from a least-square linear regression over all track positions. Even for those tracks that are qualitatively 1D along the crystal axis, any motion in the perpendicular direction will cause the backbone to tilt with respect to the crystal axis, therefore the projected displacements include contributions from motion in both the parallel and the perpendicular direction. This projection represents the overall shape of each trajectory, and one can see a large distribution of long-axis angles in Figure S2.

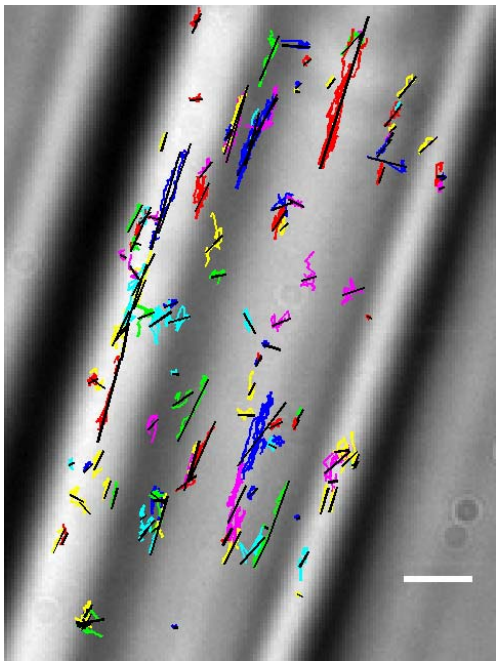

Figure S2. The backbone (solid black line) for each trajectory (colored line) is obtained from a least-square linear regression over all positions along the track. Scale bar: 1 μm.

Comparison of Two-Term and Three-Term Cumulative Probability Distribution Fitting Results

Cumulative probability distribution (CPD) functions with only two terms are not sufficient to describe the distribution of squared step sizes of molecules in either UMCM-1 or UMCM-4. As shown in Figure S3 (a and b), the residuals from two-term CPD fitting results are not only large in magnitude, but also show a pronounced oscillatory behavior, which is indicative of a systematic fitting function error. These issues are significantly remedied in both cases by fitting the squared step sizes to three-term CPD functions (Figure S3, c and d).

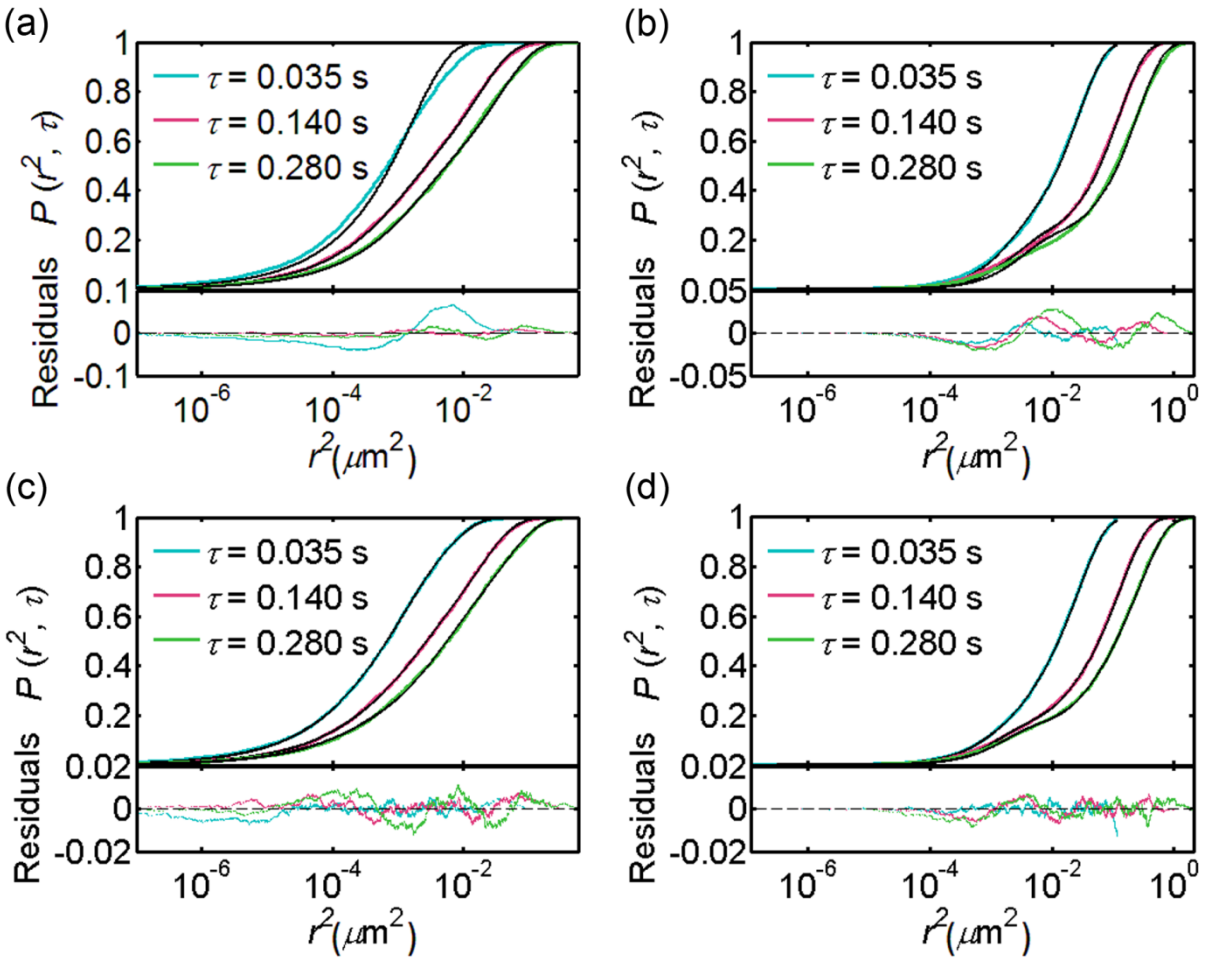

Figure S3. CPD fitting results of squared displacement distributions of Nile red molecules in (a) UMCM-1 with two mobile terms, (b) UMCM-4 with two mobile terms, (c) UMCM-1 with two mobile and one immobile terms, and (d) UMCM-4 with three mobile terms.

Supporting References

1. Koh, K.; Wong-Foy, A. G.; Matzger, A. J. *Angew. Chem.* **2008***, 47,* 677-680.

2. Koh, K.; Wong-Foy, A. G.; Matzger, A. J. *J. Am. Chem. Soc.* **2009***, 131,* 4184-4185.

3. Koh, K.; Wong-Foy, A. G.; Matzger, A. J. *J. Am. Chem. Soc.* **2010***, 132,* 15005-15010.

4. Biteen, J. S.; Goley, E. D.; Shapiro, L.; Moerner, W. E. *ChemPhysChem* **2012**, *13,* 1007-1012.

5. Kirstein, J. U. Diffusion of single molecules in nanoporous mesostructured materials, Ph.D. Dissertation, Ludwig Maximilian University of Munich, Munich, Germany, 2007.