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SUPPORTING INFORMATION for

A systematic examination of the impacts of MOF flexibility on intracrystalline molecular diffusivities

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Tables S1-S9

Cell and pore parameters of the experimentally reported, DFT optimized, FF energy minimized and NPT relaxed structures of 17 MOFs; self-diffusion coefficients of the adsorbates in flexible and rigid frameworks; average window diameter of the flexible empty and loaded windows; standard deviation of the flexible empty and loaded window size distribution; comparison of Self-diffusion coefficients of the alkanes in flexible and rigid MOF-5; fitted adsorbate equivalent diameter and uncertainty; fitted slopes k and R-squared values in Figure 11.

Figures S1-S8

Illustration of MAPCIP; comparison of unit cell volume, LCD and PLD between energy minimized and NPT relaxed structures using UFF4MOF; comparison of LCD and (b) PLD between FF optimized and DFT optimized structures; comparison of LCD and PLD between experimental structures and DFT optimized, FF energy minimized and NPT relaxed structures; an example MSD profile of discrete hops in rigid frameworks; differences between the rigid and average flexible window diameters plotted as a function of average empty window size for 17 MOFs; ratio of self-diffusivities in flexible frameworks to diffusivities in rigid frameworks plotted as a function of corrected window size; comparison of self-diffusivities between simulations with rigid and flexible small pore MOFs.

Inputs examples of each type of simulation (ZIP)

0	README.txt
1	Example input files for DFT optimization
2	Example input files for force field optimization
3	Example input files for conventional MD simulation
4	Example input files for dcTST simulation
5	LAMMPS data files of the 17 MOFs and MOF-5

Table S1. Lattice parameters of the experimentally-reported, DFT optimized, FF energy minimized and NPT relaxed structures of 17 MOFs, with all distances in Å.

	Experimental				DFT			
	a Å	b Å	c Å	Volume Å^3	a/a_{exp}	b/b_{exp}	c/c_{exp}	V/V_{exp}
LOGBAK	18.740	18.740	9.439	3314.860	1.002	1.002	1.006	1.010
EZOFOP	26.816	26.816	26.816	19283.330	1.005	1.005	1.005	1.015
HIFVUO01	14.576	14.576	14.576	2383.700	1.001	1.001	1.001	1.004
HOLQIK	25.384	25.384	25.384	16356.120	1.011	1.011	1.011	1.034
KUCDIW	26.815	26.815	26.815	19281.600	0.996	0.996	0.996	0.988
MAPCIP	15.261	15.261	28.898	6730.290	0.976	0.976	0.975	0.929
BUKRUW01	20.162	20.162	20.162	8195.860	1.006	1.006	1.006	1.018
ABAYIO	26.771	26.771	26.771	19186.410	0.990	0.990	0.990	0.970
LUXFOA	26.291	26.291	26.291	18172.780	0.992	0.992	0.992	0.975
HUJGEA	17.926	17.926	28.063	9017.410	1.003	1.003	1.013	1.019
VIXPUP01	18.663	27.916	32.364	15560.450	1.000	1.019	0.999	1.023
GEGDED	12.247	25.914	25.914	8224.530	1.012	1.010	1.012	1.035
WULJUJ	26.326	26.326	26.326	18244.620	1.007	1.007	1.007	1.022
LAQNID	18.692	18.692	35.920	12550.520	1.008	1.008	1.004	1.021
KOZQEX	27.860	27.860	27.860	21624.370	1.006	1.006	1.006	1.017
XICZAM	27.584	27.584	27.584	14841.100	0.998	0.998	0.998	0.995
IYOWID	27.736	27.736	27.736	21337.830	1.005	1.005	1.004	1.014

	Supercell*	FF Energy Minimized				FF NPT			
		a/a_{exp}	b/b_{exp}	c/c_{exp}	V/V_{exp}	a/a_{exp}	b/b_{exp}	c/c_{exp}	V/V_{exp}
LOGBAK	2×2×3	1.001	1.001	0.993	0.994	0.995	0.991	0.987	0.973
EZOFOP	2×1×1	0.997	0.997	0.997	0.992	0.959	0.995	0.958	0.914
HIFVUO01	3×3×3	0.980	0.964	0.977	0.927	0.979	0.971	0.978	0.926
HOLQIK	2×1×1	0.994	0.994	0.994	0.981	0.990	0.992	0.987	0.970
KUCDIW	2×1×1	0.972	0.972	0.972	0.918	0.973	0.972	0.967	0.914
MAPCIP	2×2×1	0.970	0.970	1.128	1.061	0.972	0.972	1.125	1.063
BUKRUW01	2×2×2	0.990	0.990	0.990	0.969	0.998	0.994	0.995	0.987
ABAYIO	2×1×1	1.024	1.024	1.024	1.072	1.024	1.020	1.024	1.069
LUXFOA	2×1×1	0.978	0.982	0.980	0.941	1.020	1.015	1.018	1.054
HUJGEA	2×2×1	1.025	1.025	1.007	1.057	1.026	1.027	0.997	1.051
VIXPUP01	2×1×1	1.029	1.017	1.027	1.064	1.030	1.005	1.028	1.056
GEGDED	3×1×1	1.007	1.044	1.043	1.096	0.978	1.032	1.036	1.046
WULJUJ	2×1×1	1.028	1.028	1.028	1.085	1.028	1.028	1.021	1.079
LAQNID	2×2×1	1.027	1.027	1.008	1.064	1.025	1.022	1.006	1.054
KOZQEX	1×1×1	1.007	1.010	1.014	1.032	1.018	1.005	1.003	1.026
XICZAM	1×1×2	0.988	0.988	0.988	0.965	0.990	0.989	0.862	0.974
IYOWID	1×1×1	0.978	0.973	0.974	0.927	0.972	0.967	0.966	0.908

* The supercells listed were used for force field energy minimization and relaxation to ensure the simulation box sides are larger than doubled LJ potential cutoff (12.5 Å). A single unit cell was used to compare the lattice parameters between different methods.

Table S2. Pore parameters of the experimentally-reported, DFT optimized, FF energy minimized and NPT relaxed structures, with all distances in Å.

	Original		**DFT**		**FF Energy Minimized**		**FF NPT**	
	LCD Å	PLD Å	LCD Å	PLD Å	LCD Å	PLD Å	LCD Å	PLD Å
LOGBAK	8.339	3.643	8.481	3.702	7.126	2.975	7.150	3.076
EZOFOP	16.097	3.034	16.121	3.183	14.687	3.590	14.007	2.938
HIFVUO01	11.713	3.299	11.708	3.172	11.399	3.175	11.237	3.198
HOLQIK	12.108	3.446	12.109	3.389	10.191	3.280	11.109	3.247
KUCDIW	15.330	4.287	14.834	4.165	14.418	3.867	14.231	3.813
MAPCIP	9.537	5.448	9.251	5.103	8.542	4.615	8.660	4.501
BUKRUW01	10.640	5.176	10.951	4.993	9.821	4.951	9.649	5.018
ABAYIO	11.408	4.323	11.266	4.324	11.068	4.699	11.300	5.006
LUXFOA	13.739	4.318	13.878	4.227	11.808	4.310	13.752	5.045
HUJGEA	12.539	4.791	12.468	4.623	13.258	4.915	13.332	5.143
VIXPUP01	10.939	6.908	11.376	6.556	11.918	6.604	11.918	6.604
GEGDED	10.731	6.574	10.877	6.625	11.837	6.435	11.842	6.402
WULJUJ	13.252	6.696	13.500	6.761	13.875	6.870	13.895	6.833
LAQNID	13.514	6.533	13.468	6.609	13.803	6.878	13.723	6.808
KOZQEX	22.424	6.861	22.744	6.738	21.868	6.736	22.298	6.905
XICZAM	19.521	6.646	19.224	6.852	19.510	7.649	19.709	7.563
IYOWID	20.517	7.748	20.207	7.949	15.332	7.752	15.040	7.725

Table S3 Self-diffusion coefficients [cm^2/s] of the adsorbates in flexible frameworks.

	He	CH_4	SF_6	CCl_4	O_2	N_2	CO_2	C_6H_6	H_2O	n-C_4	i-C_4	n-C_6
LOGBAK	1.04E-04	1.76E-06	1.32E-32	1.26E-85	1.00E-06	3.53E-07	7.42E-07	*	7.48E-08	1.00E-37	*	1.00E-25
EZOFOP	2.09E-04	1.27E-06	8.72E-16	4.59E-25	2.84E-05	1.04E-05	1.08E-05	2.50E-08	1.93E-05	9.16E-07	1.64E-10	1.06E-09
HIFVUO	9.74E-05	6.10E-07	8.88E-17	1.77E-32	5.46E-05	2.96E-05	4.41E-06	7.73E-07	9.94E-06	1.11E-08	5.15E-13	1.51E-08
HOLQIK	9.38E-05	3.17E-06	3.15E-10	1.31E-11	6.36E-05	1.53E-05	4.52E-05	5.60E-07	2.35E-06	2.33E-07	1.62E-07	1.69E-07
KUCDIW	3.70E-04	2.02E-05	1.93E-11	3.15E-29	1.08E-04	7.42E-05	1.14E-05	5.12E-05	1.32E-06	2.50E-07	6.30E-31	2.84E-07
MAPCIP	7.32E-04	1.43E-04	1.18E-05	1.40E-07	2.97E-04	2.92E-04	1.26E-04	9.82E-06	3.27E-06	4.33E-05	2.50E-05	1.36E-05
BUKRUW01	8.07E-04	1.83E-04	3.42E-06	1.66E-08	2.62E-04	2.76E-04	1.29E-04	1.59E-05	8.63E-06	3.38E-05	7.40E-06	2.15E-05
ABAYIO	5.72E-04	6.46E-06	1.64E-08	1.66E-13	2.77E-05	2.14E-05	1.30E-05	2.50E-08	9.90E-06	9.16E-07	1.26E-08	6.53E-08
LUXFOA	6.56E-04	1.20E-04	8.67E-07	1.11E-08	1.10E-04	1.22E-04	7.30E-05	5.75E-07	3.50E-06	6.92E-06	2.26E-06	7.86E-06
HUJGEA	8.15E-04	1.14E-04	1.16E-06	1.38E-07	1.37E-04	1.42E-04	4.22E-05	1.42E-07	4.48E-07	4.88E-07	1.35E-06	4.95E-07
VIXPUP01	1.21E-03	2.10E-04	1.16E-05	1.10E-05	2.98E-04	3.27E-04	4.48E-05	2.49E-07	3.12E-06	8.53E-06	3.33E-06	5.43E-06
GEGDED	1.13E-03	7.95E-05	3.21E-05	1.46E-05	2.18E-04	2.30E-04	2.01E-05	7.28E-05	4.31E-06	5.56E-06	4.54E-05	5.66E-06
WULJUJ	9.13E-04	4.88E-05	7.96E-06	1.38E-06	1.70E-04	2.50E-04	5.22E-05	5.15E-05	7.98E-06	4.72E-06	1.15E-05	5.68E-07
LAQNID	1.58E-03	1.33E-04	9.51E-06	1.42E-06	2.31E-04	3.03E-04	5.95E-05	2.57E-05	5.03E-06	3.04E-07	2.28E-06	3.54E-07
KOZQEX	2.13E-03	4.31E-04	2.11E-05	1.12E-06	2.95E-03	2.29E-03	6.09E-04	1.76E-06	5.95E-06	1.49E-05	1.59E-05	3.67E-06
XICZAM	1.32E-03	1.80E-04	8.94E-06	1.78E-06	1.10E-04	1.22E-04	7.30E-05	5.75E-07	3.50E-06	6.92E-06	2.26E-06	7.86E-06
IYOWID	1.05E-03	1.42E-04	7.59E-06	1.92E-06	8.56E-05	3.06E-05	2.09E-05	6.66E-06	4.07E-06	7.85E-06	1.02E-05	3.32E-06

* No data available. The adsorbate is too large to fit in the pore, so we could not get reliable quality of sampling in either regular MD or umbrella sampling simulation.

Self-diffusion coefficients highlighted grey were calculated with dcTST.

Table S4 Self-diffusion coefficients [cm^2/s] of the adsorbates in rigid framework.

	He	CH_4	SF_6	CCl_4	O_2	N_2	CO_2	C_6H_6	H_2O	n-C_4	i-C_4	n-C_6
LOGBAK	4.50E-04	8.00E-08	*	*	9.78E-07	2.25E-08	2.83E-07	*	5.50E-04	*	*	*
EZOFOP	1.17E-03	6.42E-05	*	*	7.32E-06	2.10E-06	3.39E-06	1.78E-08	5.62E-04	1.57E-04	1.64E-07	2.77E-05
HIFVUO	5.47E-04	1.73E-05	*	*	1.95E-06	4.81E-08	6.93E-09	2.00E-09	2.89E-05	6.00E-09	*	7.00E-09
HOLQIK	3.29E-04	1.48E-06	*	*	8.20E-07	6.07E-08	6.34E-07	3.00E-08	1.40E-04	3.84E-07	2.00E-08	2.00E-08
KUCDIW	2.55E-03	2.48E-04	*	*	4.21E-05	2.78E-05	6.14E-06	3.00E-08	1.00E-03	2.19E-04	*	3.04E-05
MAPCIP	4.36E-03	6.87E-04	1.04E-05	1.31E-06	3.20E-04	2.72E-04	1.40E-04	1.09E-05	1.37E-03	6.28E-04	5.13E-04	4.76E-04
BUKRUW01	1.76E-01	4.53E-02	3.42E-06	8.00E-11	1.94E-04	2.42E-04	9.13E-05	1.16E-05	3.88E-03	2.46E-03	6.74E-04	6.12E-04
ABAYIO	2.74E-03	2.96E-04	*	*	2.56E-05	2.72E-05	1.30E-05	4.49E-08	1.01E-03	4.85E-04	1.81E-04	5.73E-04
LUXFOA	9.43E-03	7.20E-04	1.55E-06	3.03E-07	1.76E-04	2.09E-04	7.14E-05	8.43E-07	8.21E-04	1.35E-03	4.18E-04	4.34E-03
HUJGEA	3.30E-03	7.74E-04	1.58E-07	2.00E-09	1.49E-04	1.69E-04	3.85E-05	1.31E-07	1.39E-03	2.66E-04	4.65E-05	1.18E-04
VIXPUP01	6.78E-03	1.33E-03	1.76E-05	3.77E-06	3.44E-04	2.68E-04	9.74E-05	1.92E-07	2.43E-03	7.53E-04	5.06E-04	7.09E-04
GEGDED	8.79E-03	1.55E-03	3.84E-06	1.53E-06	2.63E-04	2.34E-04	6.02E-05	2.49E-05	3.88E-03	9.62E-04	6.73E-04	3.64E-04
WULJUJ	6.69E-03	8.10E-04	1.97E-05	8.29E-06	1.85E-04	1.55E-04	4.03E-05	4.00E-11	1.73E-03	7.04E-04	3.60E-04	5.50E-04
LAQNID	6.62E-03	1.16E-03	2.15E-06	1.31E-06	2.39E-04	2.58E-04	6.05E-05	1.00E-08	1.96E-03	1.04E-03	7.74E-04	7.03E-04
KOZQEX	1.06E-02	3.01E-03	6.64E-05	7.44E-06	5.40E-04	6.10E-04	1.96E-04	1.79E-06	5.12E-03	1.27E-03	1.10E-03	1.13E-03
XICZAM	1.40E-02	1.83E-03	1.17E-05	2.77E-06	2.95E-04	4.07E-04	8.02E-05	4.30E-07	2.36E-03	2.78E-03	1.73E-03	1.21E-03
IYOWID	5.33E-03	9.37E-04	1.37E-05	7.30E-06	4.34E-04	3.01E-04	1.37E-04	7.07E-06	4.12E-03	7.90E-04	6.43E-04	1.49E-03

* No hops were observed on the MD time scale.

Self-diffusion coefficients highlighted grey were overestimated in the MSD method.

Table S5 Average window diameter of the flexible empty and loaded windows, with all distances in Å. The PLD refers to the result from the static FF-minimized MOF with no adsorbates.

MOF	PLD	Empty	He	CH_4	SF_6	CCl_4	O_2	N_2	CO_2	C_6H_6	H_2O	n-C_4	i-C_4	n-C_6	mean	std	max-min
LOGBAK	3.076	2.539	2.554	2.601	3.541	3.889	2.625	2.658	2.598	3.099	2.733	3.002	3.352	2.854	2.959	0.415	1.335
EZOFOP	2.938	2.660	2.771	2.974	3.831	4.462	2.812	2.972	2.871	3.251	2.924	3.252	3.633	3.394	3.262	0.483	1.691
HIFVUO01	3.198	2.923	3.084	3.840	4.862	5.065	3.485	3.664	3.378	4.137	4.287	3.909	4.633	3.912	4.021	0.579	1.980
HOLQIK	3.247	2.778	4.706	5.010	5.500	6.687	4.806	4.811	4.736	4.343	4.209	4.870	5.434	4.718	4.986	0.624	2.478
KUCDIW	3.813	3.678	3.683	3.935	4.606	5.047	3.813	3.839	3.757	4.122	3.803	3.916	4.380	3.922	4.069	0.392	1.364
MAPCIP	4.501	4.419	4.417	4.421	4.557	4.804	4.417	4.415	4.414	4.421	4.406	4.424	4.446	4.425	4.464	0.110	0.398
BUKRUW01	5.018	4.065	4.137	4.153	4.703	5.192	4.075	4.124	4.078	4.099	4.092	4.680	4.630	4.621	4.382	0.353	1.117
ABAYIO	5.006	4.435	4.462	4.446	4.879	5.319	4.461	4.500	4.462	4.667	4.466	4.562	4.845	4.542	4.634	0.252	0.873
LUXFOA	5.045	4.649	4.653	4.659	4.731	4.911	4.656	4.659	4.657	4.670	4.716	4.661	4.709	4.665	4.696	0.070	0.257
HUJGEA	5.143	4.649	4.772	4.719	4.802	5.390	4.724	4.749	4.623	4.767	4.705	4.784	5.053	4.890	4.832	0.197	0.767
VIXPUP01	6.604	6.375	6.356	6.380	6.392	6.515	6.362	6.373	6.357	6.342	6.004	6.320	6.738	6.620	6.397	0.171	0.735
GEGDED	6.402	5.673	5.701	5.703	5.832	5.932	5.858	5.692	5.717	5.730	5.673	5.684	5.870	5.694	5.757	0.086	0.259
WULJUJ	6.833	6.375	6.386	6.385	6.409	6.460	6.376	6.394	6.392	6.398	6.381	6.403	6.408	6.394	6.399	0.021	0.084
LAQNID	6.808	6.357	6.360	6.549	6.365	6.582	6.372	6.377	6.374	6.350	6.572	6.350	6.613	6.379	6.437	0.102	0.263
KOZQEX	6.905	6.243	6.280	6.294	6.302	6.395	6.271	6.279	6.275	6.250	6.277	6.279	6.293	6.290	6.290	0.034	0.145
XICZAM	7.563	6.712	6.645	6.708	6.863	6.926	6.699	6.719	6.769	6.793	6.791	6.737	6.781	6.704	6.761	0.074	0.281
IYOWID	7.725	7.175	7.230	7.041	7.179	7.358	7.111	7.135	7.228	7.138	7.060	7.127	7.260	7.167	7.169	0.085	0.318

Table S6 Standard deviation of the flexible empty and loaded window size distribution, with all distances in Å.

MOF	Empty	He	CH_4	SF_6	CCl_4	O_2	N_2	CO_2	C_6H_6	H_2O	n-C_4	i-C_4	n-C_6	mean
LOGBAK	0.102	0.093	0.101	0.064	0.060	0.093	0.087	0.093	0.088	0.181	0.092	0.091	0.090	0.095
EZOFOP	0.200	0.203	0.161	0.145	0.151	0.178	0.188	0.158	0.158	0.200	0.151	0.166	0.183	0.172
HIFVUO01	0.260	0.311	0.269	0.187	0.129	0.326	0.301	0.327	0.254	0.302	0.266	0.229	0.276	0.264
HOLQIK	0.313	0.408	0.568	0.334	0.365	0.429	0.414	0.370	0.283	0.388	0.443	0.363	0.437	0.393
KUCDIW	0.277	0.265	0.214	0.153	0.114	0.240	0.233	0.257	0.237	0.254	0.231	0.213	0.223	0.224
MAPCIP	0.131	0.130	0.126	0.125	0.101	0.125	0.138	0.131	0.136	0.130	0.125	0.117	0.124	0.126
BUKRUW01	0.242	0.276	0.241	0.168	0.158	0.247	0.242	0.251	0.207	0.266	0.230	0.219	0.217	0.228
ABAYIO	0.226	0.224	0.222	0.181	0.164	0.232	0.222	0.227	0.214	0.224	0.217	0.230	0.217	0.215
LUXFOA	0.105	0.114	0.103	0.103	0.094	0.106	0.107	0.104	0.109	0.115	0.108	0.113	0.107	0.107
HUJGEA	0.315	0.314	0.295	0.233	0.164	0.362	0.302	0.376	0.287	0.319	0.294	0.254	0.278	0.292
VIXPUP01	0.341	0.354	0.337	0.336	0.296	0.336	0.320	0.331	0.321	0.344	0.440	0.340	0.348	0.342
GEGDED	0.194	0.216	0.204	0.227	0.213	0.259	0.206	0.211	0.214	0.206	0.192	0.208	0.205	0.212
WULJUJ	0.245	0.239	0.248	0.245	0.228	0.251	0.252	0.245	0.237	0.236	0.252	0.234	0.245	0.243
LAQNID	0.213	0.201	0.261	0.198	0.220	0.197	0.207	0.187	0.197	0.229	0.183	0.247	0.196	0.210
KOZQEX	0.238	0.250	0.239	0.237	0.225	0.249	0.247	0.254	0.254	0.234	0.238	0.243	0.248	0.243
XICZAM	0.356	0.452	0.429	0.362	0.347	0.321	0.362	0.381	0.414	0.393	0.440	0.415	0.439	0.393
IYOWID	0.338	0.375	0.329	0.330	0.377	0.313	0.332	0.375	0.324	0.346	0.325	0.364	0.290	0.340

Table S7 Comparison of Self-diffusion coefficients [cm^2/s] of the alkanes in rigid and flexible MOF-5 using UFF4MOF. Results shown as "Rigid adsorbate test" are for flexible adsorbates simulated without their internal degrees of freedom in a rigid framework.

	n-C_4	**n-C_6**	**i-C_4**
Flexible Framework	1.02E-04	4.03E-05	9.76E-05
Rigid Framework	1.33E-03	7.73E-04	1.09E-03
Rigid Adsorbate Test	1.19E-04	3.04E-05	8.38E-05

Table S8 Fitted adsorbate equivalent diameter and uncertainty.

Ads	**d_{eq} [Å]**	**ϵ [order of mag.]**
He	3.44	0.62
CH_4	3.80	1.47
SF_6	5.10	1.13
CCl_4	7.00	2.90
O_2	3.58	0.35
N_2	3.63	0.37
CO_2	3.72	0.51
C_6H_6	4.04	1.58
H_2O	3.84	1.44
n-C_4	4.09	1.15
i-C_4	5.21	5.18
n-C_6	4.24	1.19

* Uncertainty ϵ was calculated by:

$$\epsilon = \sqrt{\frac{\sum_i^N (logD_s^{sim} - logD_s^{pre})^2}{N}}$$

where N is the number of MOFs, D_s^{sim} is the simulated self-diffusion coefficient, D_s^{pre} is the predicted self-diffusion coefficient by assuming linear correlation between the self-diffusion

coefficient and adsorbate equivalent diameter. Benchmark points for the line locating are CH_4 and SF_6. The unit of ϵ is order of magnitude in diffusion coefficient.

Table S9 Fitted slopes, m, intercepts, b, and R-squared values in Figure 11.

MOF	m	b	R^2
LOGBAK	0.402	1.228	0.891
EZOFOP	0.483	1.183	0.950
HIFVUO01	0.511	1.820	0.741
HOLQIK	0.579	2.491	0.820
KUCDIW	0.388	2.397	0.932
MAPCIP	0.104	4.017	0.853
BUKRUW01	0.324	2.985	0.802
ABAYIO	0.253	3.544	0.962
LUXFOA	0.067	4.409	0.865
HUJGEA	0.187	4.027	0.855
VIXPUP01	0.082	6.045	0.218
GEGDED	0.068	5.466	0.590
WULJUJ	0.020	6.312	0.897
LAQNID	0.054	6.206	0.263
KOZQEX	0.031	6.157	0.783
XICZAM	0.064	6.487	0.704
IYOWID	0.062	6.900	0.510

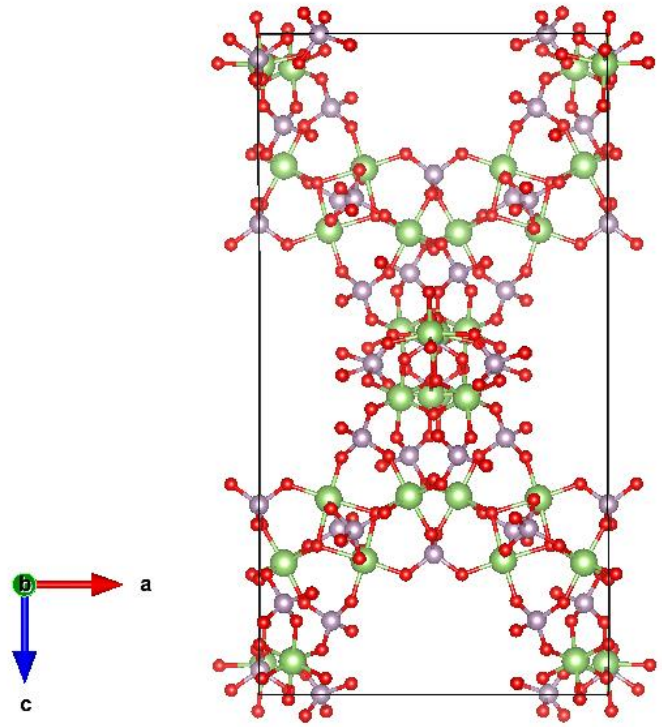

Figure S1. Illustration of MAPCIP.

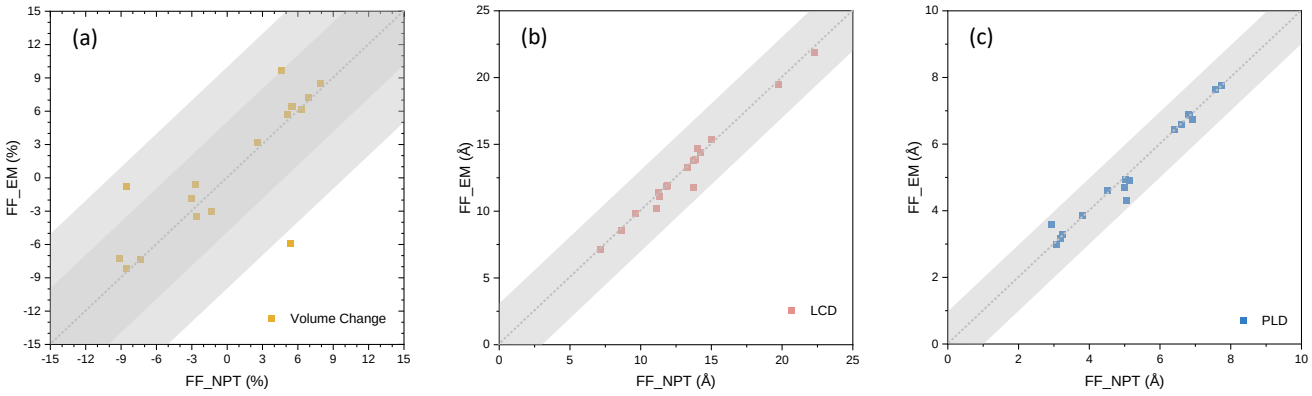

Figure S2. Comparison of (a) unit cell volume change compared to the experimental structures, (b) LCD and (c) PLD between energy minimized (EM) and NPT relaxed structures using UFF4MOF. The dark shading (light shading) in plot (a) indicates where the deviation between EM and NPT results are less than 5% (10%). The shading in (b) and (c) indicate where the deviation between EM and NPT results are less than 3 Å and 1 Å, respectively.

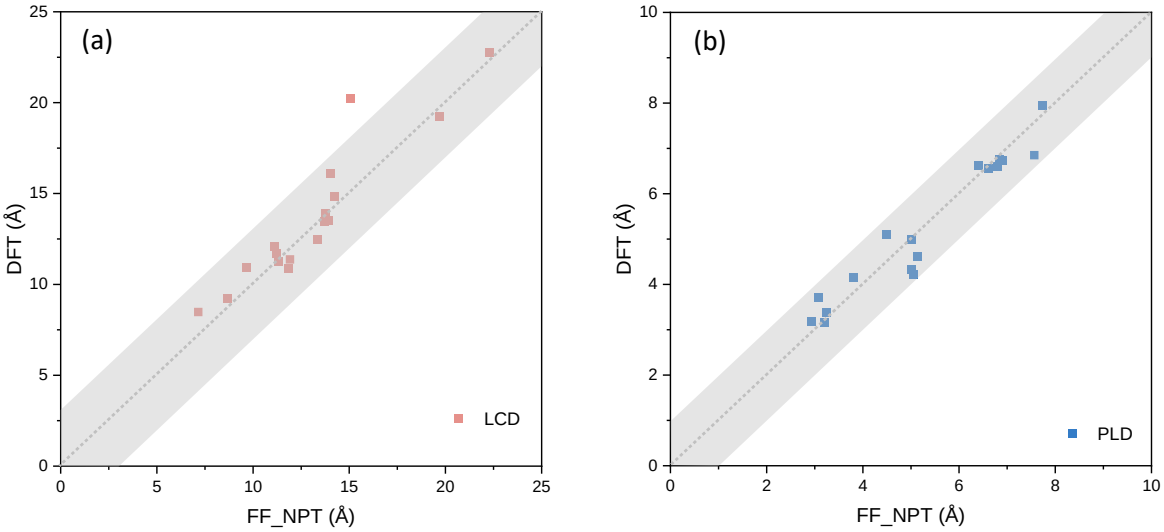

Figure S3. Comparison of (a) LCD and (b) PLD between FF optimized and DFT optimized structures. The shadings in plot (a) and plot (b) indicate where the deviation between FF and DFT results are less than 3 Å and 1 Å, respectively.

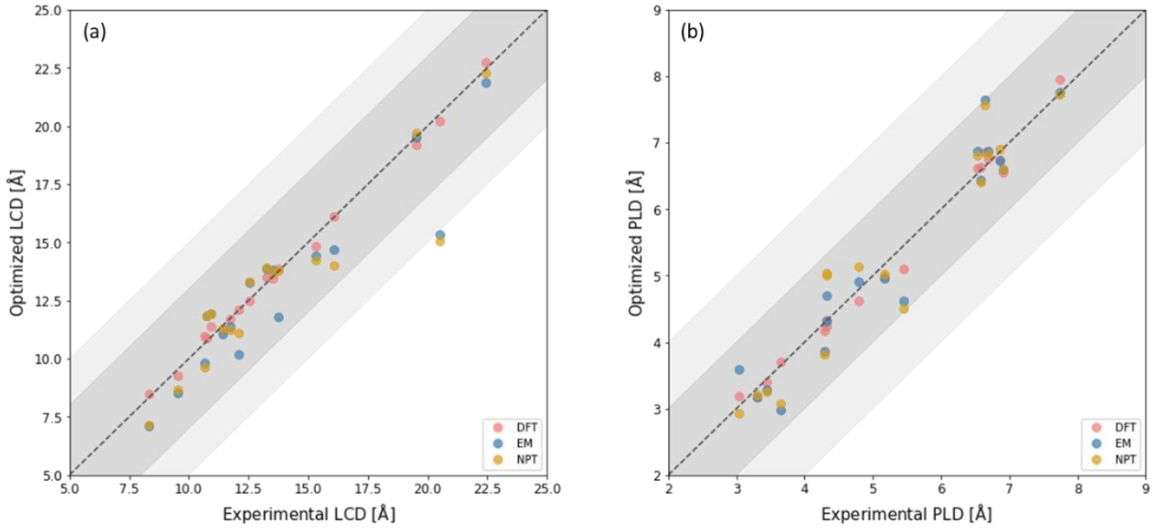

Figure S4. Comparison of (a) LCD and (b) PLD between experimental structures and DFT (red) optimized, FF energy minimized (blue) and NPT relaxed (yellow) structures. The dark shading (light shading) in (a) indicates where the deviation between optimized and experimental LCD are less than 3 Å (5 Å). The dark shading (light shading) in (b) indicates where the deviation between optimized and experimental PLD are less than 1 Å (2 Å).

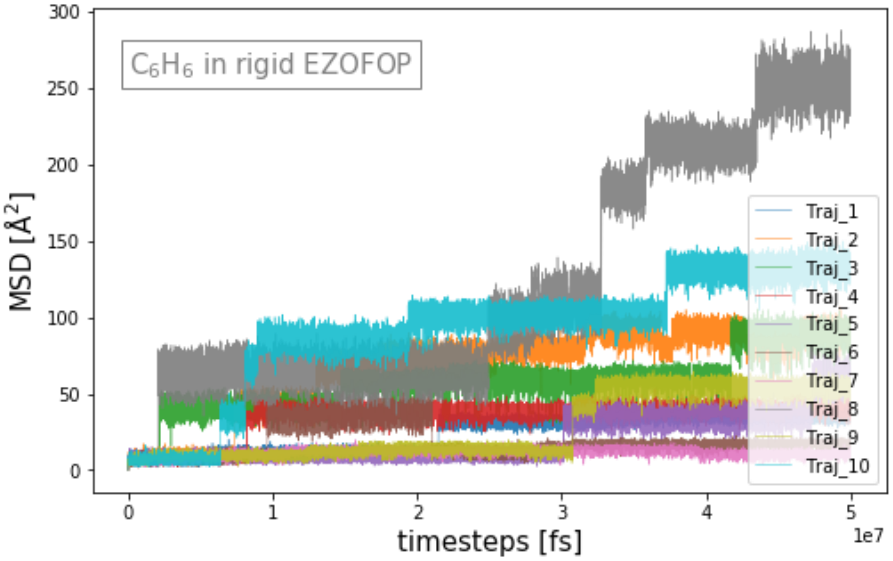

Figure S5. MSD profiles showing discrete hops of C_6H_6 in rigid EZOFOP at 308K.

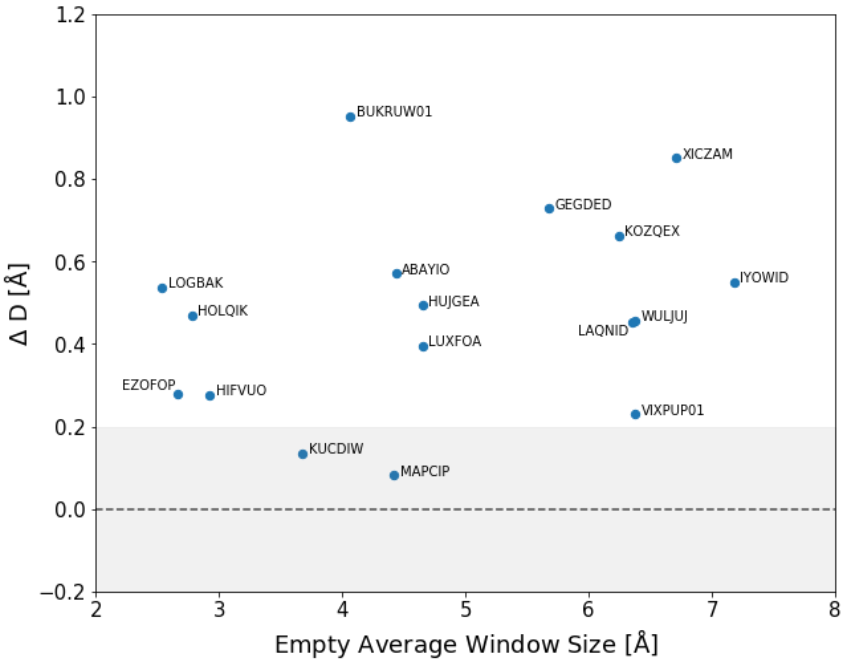

Figure S6. Differences between the rigid and average flexible window diameters plotted as a function of empty average window size for 17 MOFs. The shading indicates where the differences are within ±0.2Å.

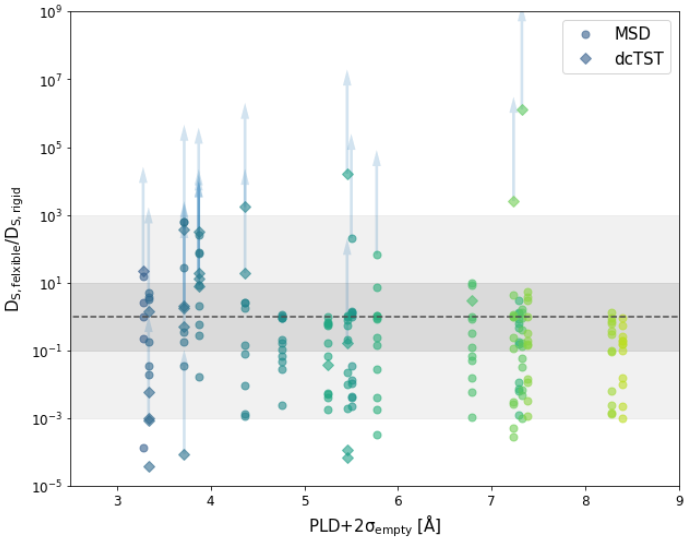

Figure S7. Ratio of self-diffusivities in flexible frameworks to diffusivities in rigid frameworks plotted as a function of corrected window size (PLD + 2σ of the empty window size distribution). In flexible frameworks, calculations performed with MD (dcTST) are denoted with circles (diamonds). . The dark shading (light shading) indicates where the deviation of the ratios are less than one order of magnitude (three orders of magnitude).

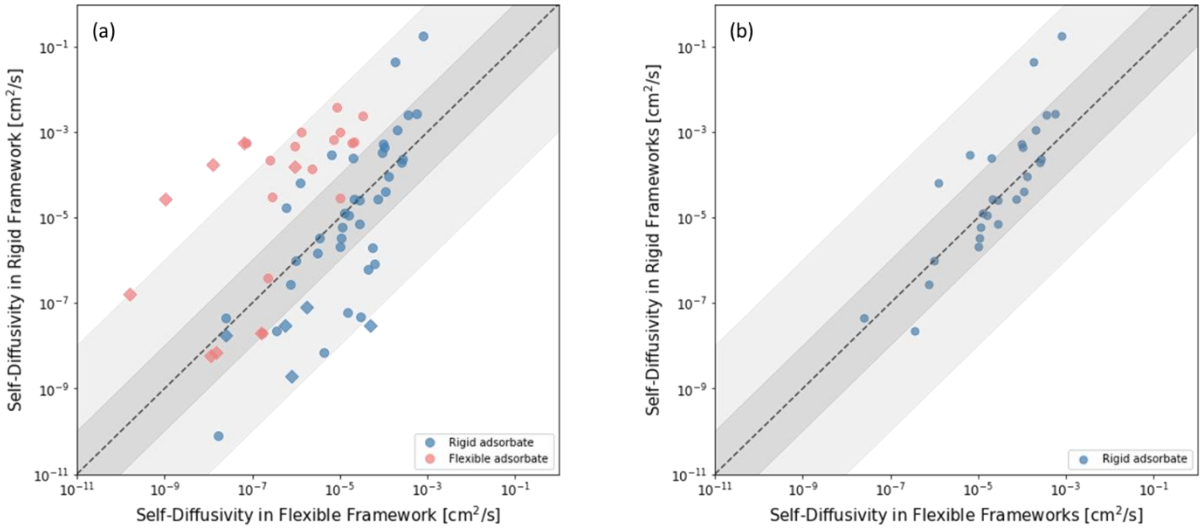

Figure S8. Comparison of self-diffusivities between simulations with rigid and flexible small pore MOFs. (a) all adsorbates; (b) rigid adsorbates who expand the corresponding window size smaller than 0.4 Å. In flexible frameworks, calculations performed with MD (dcTST) are denoted with circles (diamonds). . The dark shading (light shading) indicates where the

deviation between the rigid and flexible results are less than one order of magnitude (three orders of magnitude).