Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Reverse Shape Selectivity of Hexane Isomer in Ligand Inserted MOF-74

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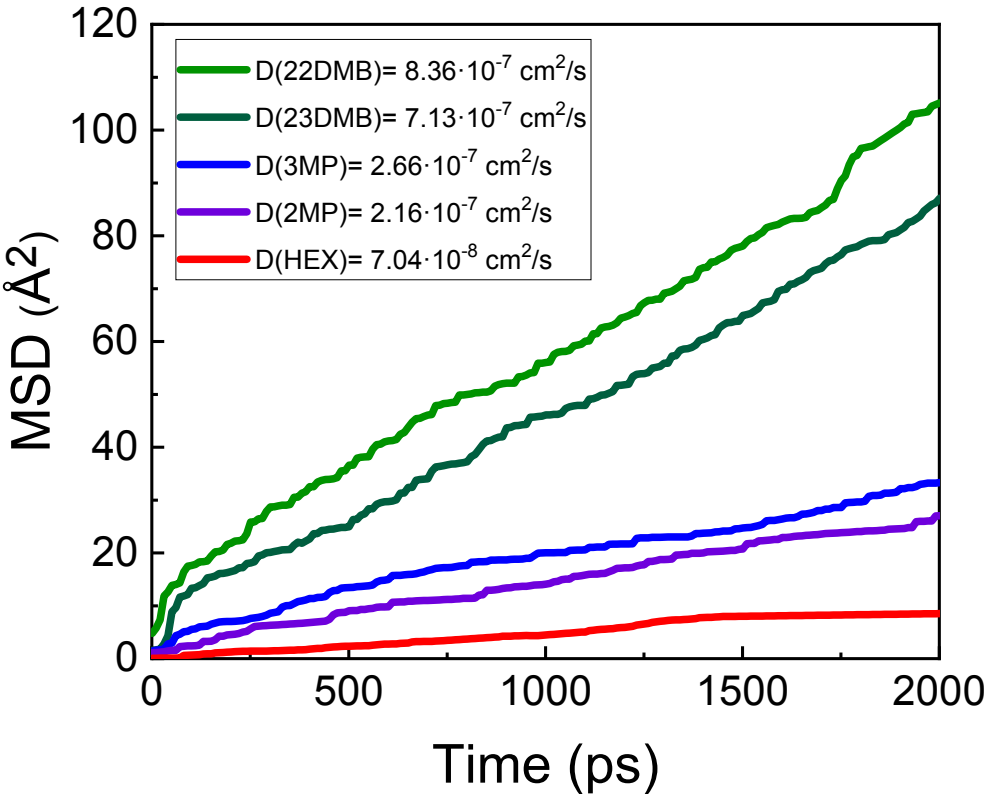

Figure S1. Mean-squared displacement (MSD) of hexane isomer at 433 K for 2 ns. Linear hexane (HEX, red), 2-methylpentane (2MP, purple), 3-methylpentane (3MP, blue), 2,3-dimethylpentane (23DMB, dark green), and 2,2-dimethylpentane (22DMB, green) are shown respectively.

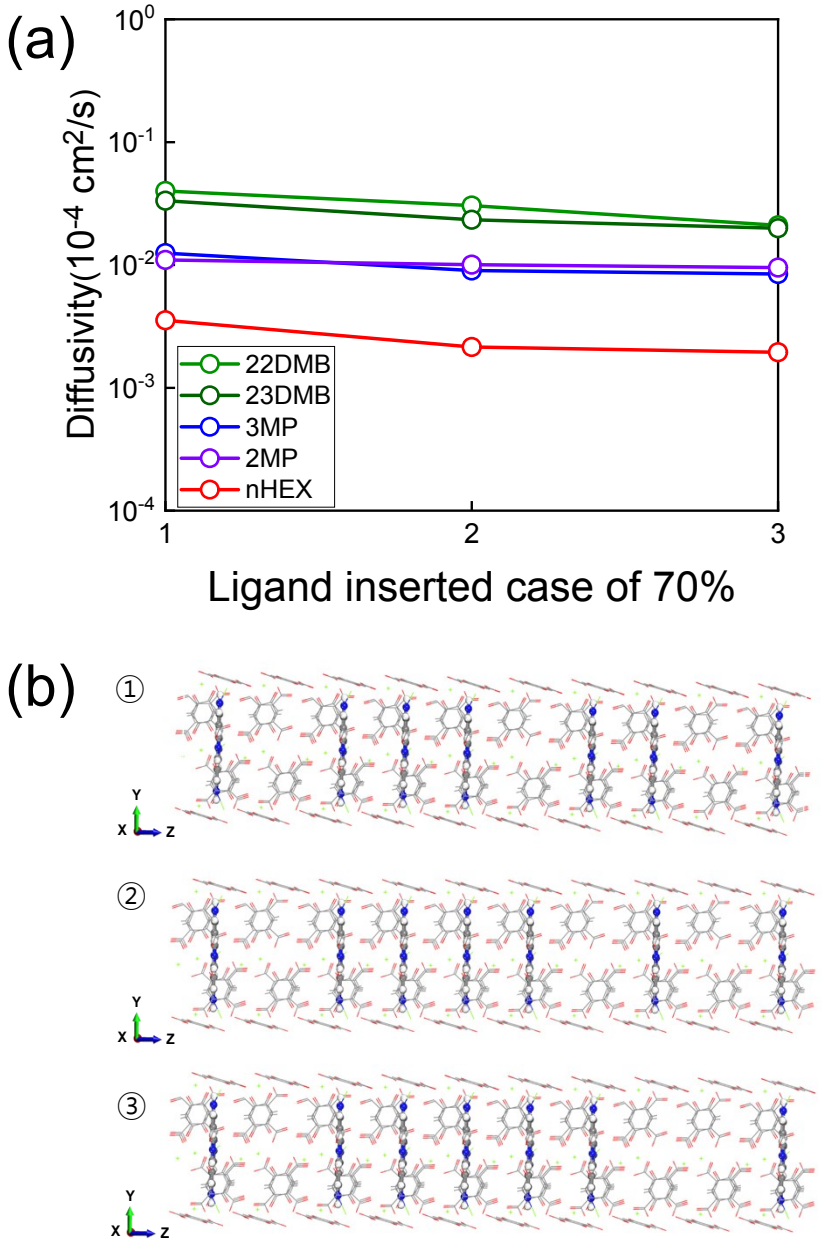

Figure S2. (a) Diffusivity versus inserted dpt ligand cases of 70% in Mg-MOF-74 at 300K for 2ns. The linear hexane (nHEX, red), 2-methylpentane (2MP, purple), 3-methylpentane (3MP, blue), 2,3-dimethylpentane (23DMB, dark green), and 2,2-dimethylpentane (22DMB, green), respectively. (b) Illustration of ligand inserted cases along the channels.

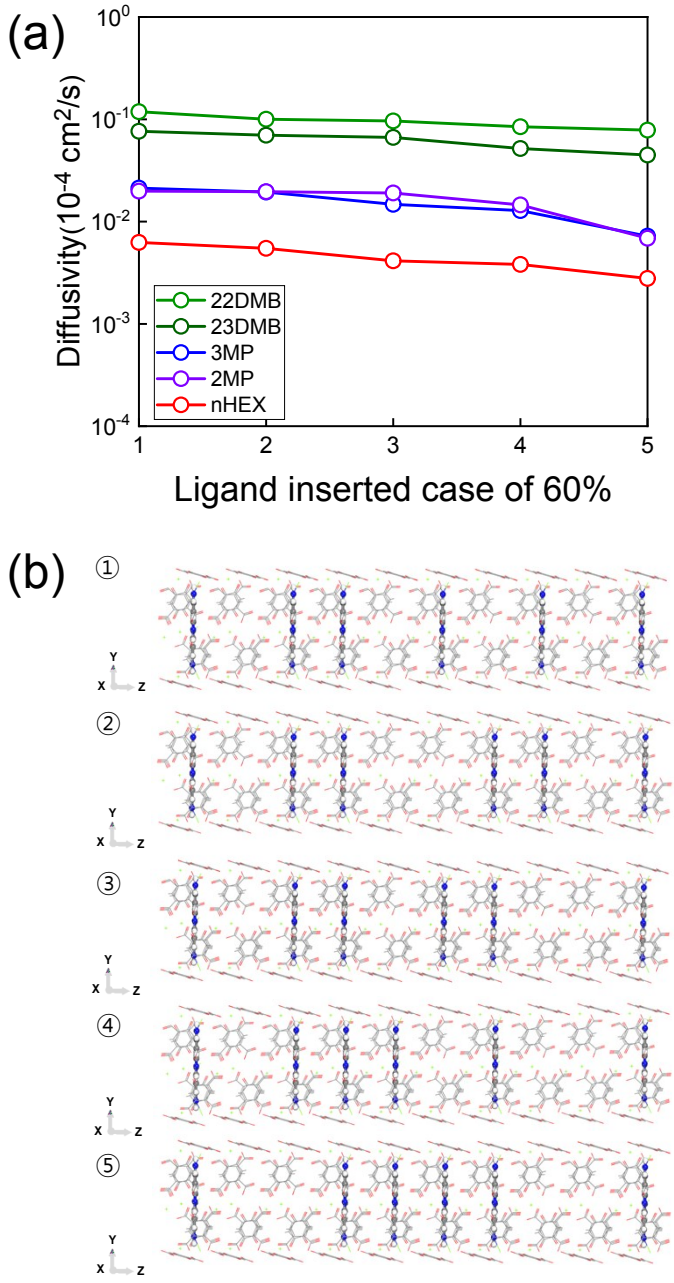

Figure S3. (a) Diffusivity versus inserted dpt ligand cases of 60% in Mg-MOF-74 at 300K for 2ns. The linear hexane (nHEX, red), 2-methylpentane (2MP, purple), 3-methylpentane (3MP, blue), 2,3-dimethylpentane (23DMB, dark green), and 2,2-dimethylpentane (22DMB, green), respectively. (b) Illustration of ligand inserted cases along the channels.

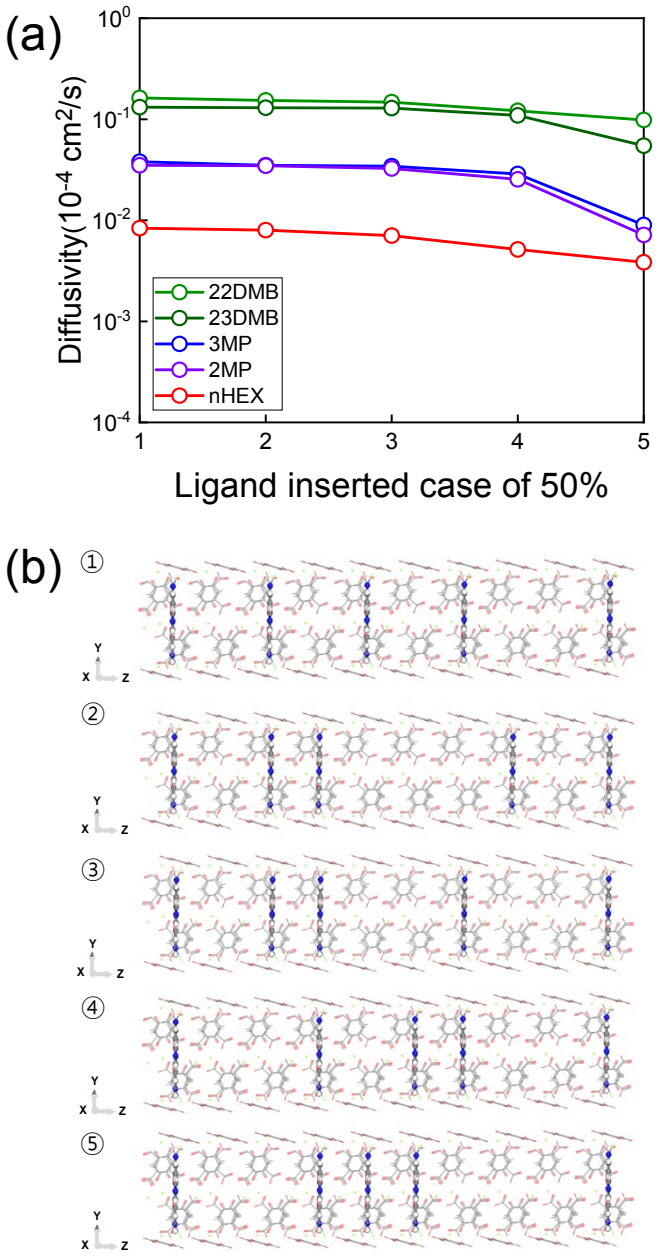

Figure S4. (a) Diffusivity versus inserted dpt ligand cases of 50% in Mg-MOF-74 at 300K for 2ns. The linear hexane (nHEX, red), 2-methylpentane (2MP, purple), 3-methylpentane (3MP, blue), 2,3-dimethylpentane (23DMB, dark green), and 2,2-dimethylpentane (22DMB, green), respectively. (b) Illustration of ligand inserted cases along the channels.

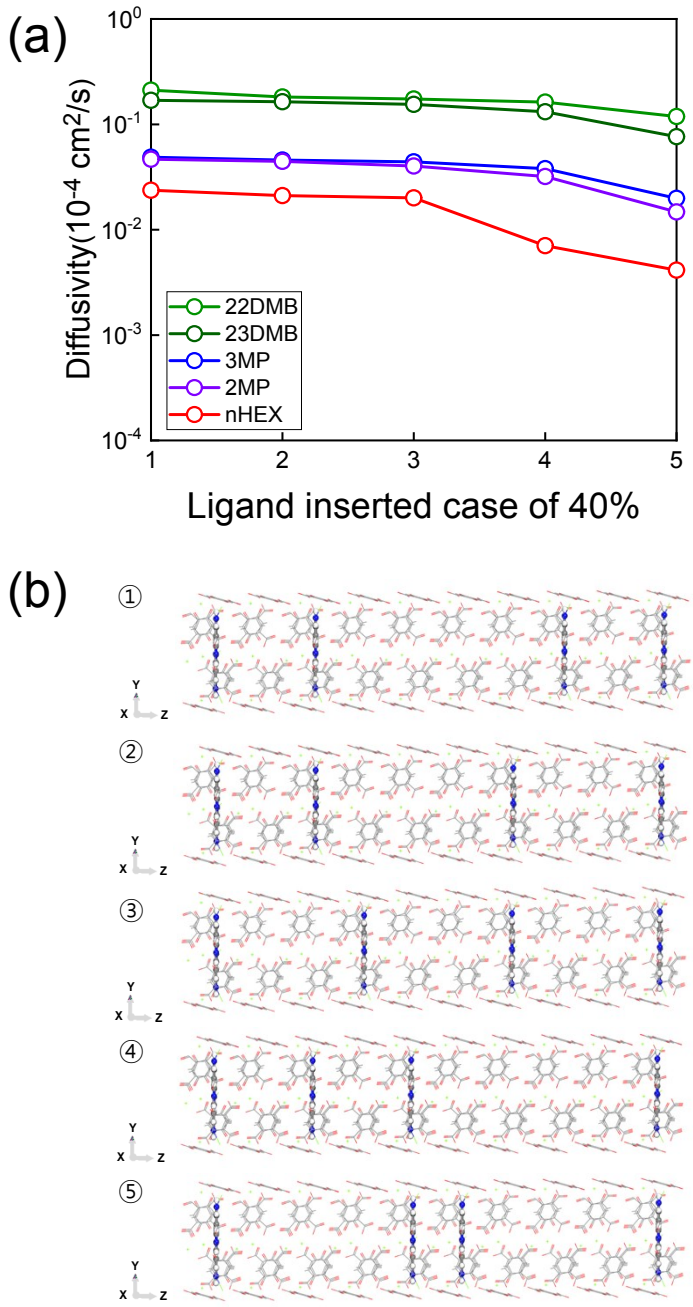

Figure S5. (a) Diffusivity versus inserted dpt ligand cases of 40% in Mg-MOF-74 at 300K for 2ns. The linear hexane (nHEX, red), 2-methylpentane (2MP, purple), 3-methylpentane (3MP, blue), 2,3-dimethylpentane (23DMB, dark green), and 2,2-dimethylpentane (22DMB, green), respectively. (b) Illustration of ligand inserted cases along the channels.

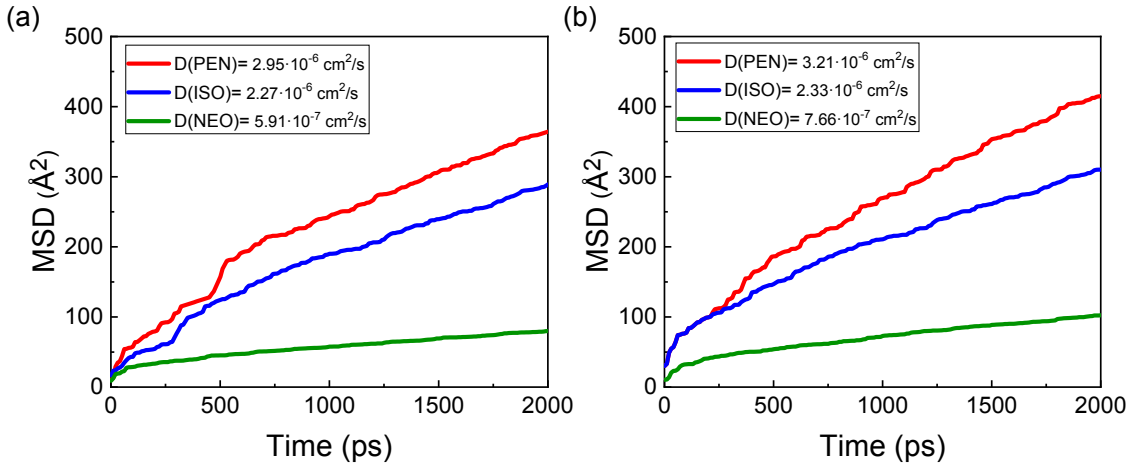

Figure S6. Mean-squared displacement (MSD) of pentane isomer at 300 K for 2 ns. Linear pentane (PEN, red), Isopentane (ISO, blue), and Neopentane (NEO, green) are shown respectively. (b) Same as (a) but at 433 K for 2 ns.

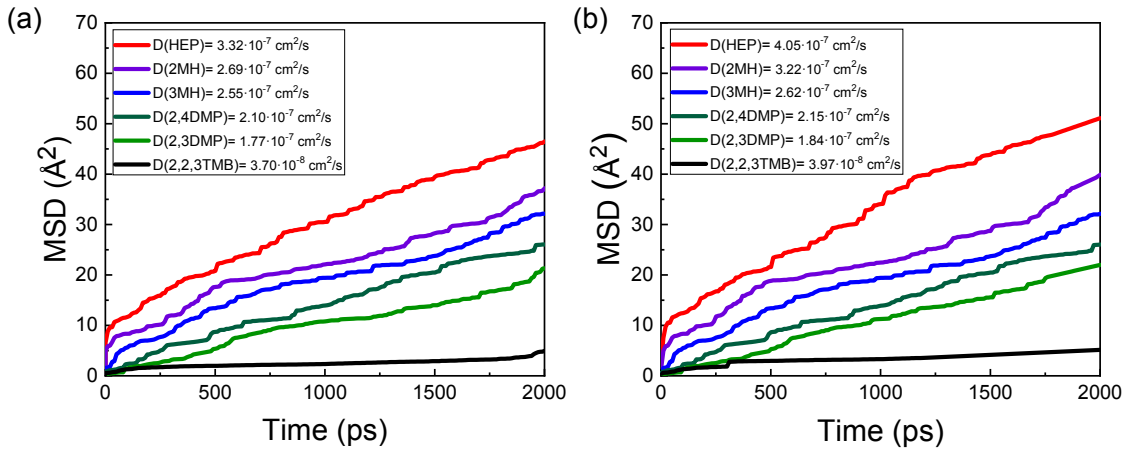

Figure S7. (a) Mean-squared displacement (MSD) of heptane isomer at 300 K for 2 ns. Linear heptane (HEP, red), 2-methylhexane (2MH, purple), 3-methylhexane (3MH, blue), 2,4-dimethylpentane (24DMP, dark green), 2,3-dimethylpentane (23DMP, green), and 2,2,3-trimethylbutane (2,2,3TMB, black) are shown respectively. (b) Same as (a) but at 433 K for 2 ns.

Table S1. Binding energies (in kJ/mol) for hexane isomers in MOFs

	Mg-MOF-74	dpt-Mg-MOF-74
HEX	- 46.28 kJ/mol	-51.04 kJ/mol
2-MP	-44.34 kJ/mol	-50.12 kJ/mol
3-MP	-43.10 kJ/mol	-49.57 kJ/mol
22-DMB	-42.85 kJ/mol	-48.62 kJ/mol
23-DMB	-42.45 kJ/mol	-47.93 kJ/mol

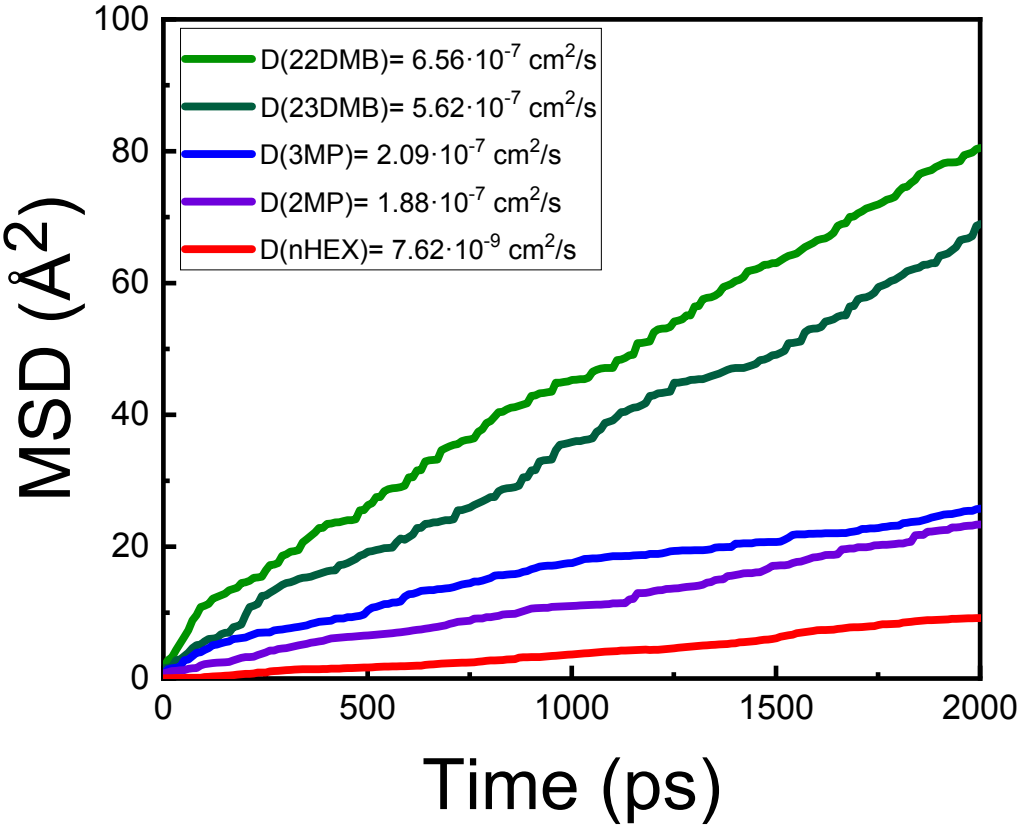

Figure S8. Mean-squared displacement (MSD) of mixed hexane isomer at 300 K for 2 ns. Linear hexane (HEX, red), 2-methylpentane (2MP, purple), 3-methylpentane (3MP, blue), 2,3-dimethylpentane (23DMB, dark green), and 2,2-dimethylpentane (22DMB, green) are shown respectively.

Computational method

The grand canonical MC (GCMC) simulations were employed to obtain the adsorption isotherms of the hexane isomers in the MOFs using RASPA program[1]. Each cycle of the GCMC simulations consisted of various moves of the molecules such as random translation, random rotation, reinsertion, swapping, and identity change for mixtures. Reinsertion movement is implemented with configurational biased MC (CBMC), where a chainlike molecule is developed part-by-part by selecting the first site randomly in an energetically favored location. To enable the description of the dpt ligand, UFF parameters were used, and the partial point charges obtained from the DFT calculations. Density functional theory (DFT) calculations were performed using a hybrid generalized gradient approximation with the B3LYP functional[2], implemented in GAUSSIAN 09 program(G09)[3] as the B3LYP has demonstrated to show accurate geometry optimization results[4]. The 6-31G(d) basis-set is used to describe all of the electrons in the system.

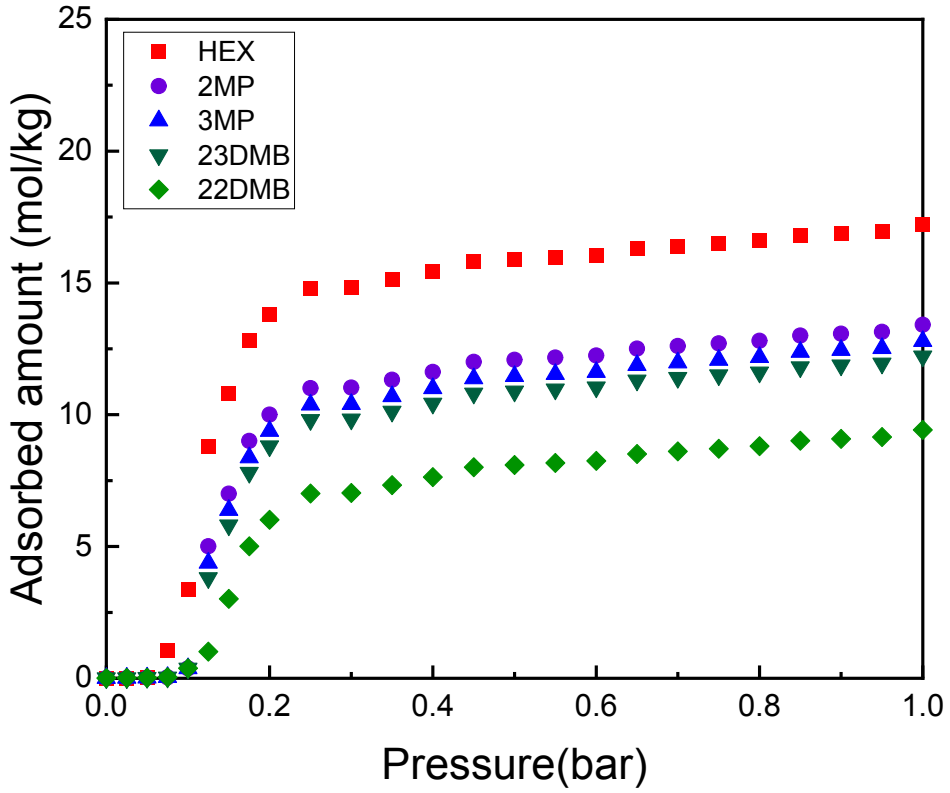

Figure S9. Hexane isomers adsorption isotherms of dpt-Mg-MOF-74 at 300K. Linear hexane (HEX, red square), 2-methylpentane (2MP, purple circle), 3-methylpentane (3MP, blue triangle), 2,3-dimethylpentane (23DMB, dark green triangle), and 2,2-dimethylpentane (22DMB, green diamond) are shown respectively.

References

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2. A. Becke, *J. Chem. Phys.,* 1993, **98**, 5648.
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