Supporting Information

Mobility and separation of linear and branched C_5 alkanes in UiO-66 (Zr) probed by ^2H NMR and MD simulations

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Material synthesis and characterization

A typical synthetic procedure involved mixing under Argon atmosphere of 0.965 g of $ZrCl_4$ with 1.37 g of Terephthalic Acid in 24 mL of dimethylformamide (DMF) solvent with 0.64 mL of aqueous solution of HCl acid (37%) within a Teflon-lined steel Parr-autoclave. After mixing for 1 hour and sealing, the reactor was heated at 220 ^oC for 16 hours with 1 hour to heat up. After opening the reaction, the white power was collected by filtration. The product was rinsed 3 times with DMF. The resulting powder was washed in DMF (125 ml) at 80 ^oC for 9 hours and then filtered via hot filtration. The procedure was repeated twice with a fresh solvent. Then the DMF was exchange with MeOH by washing in MeOH (100 mL) for 12 hours at normal conditions. After filtration the resulting UiO-66 powder was dried in an oven at 100 ^oC. To obtain dehydroxylated form the material was activated at 250 ^oC.

The resulting material was studied by powder SEM, XRD and nitrogen porosimetry:

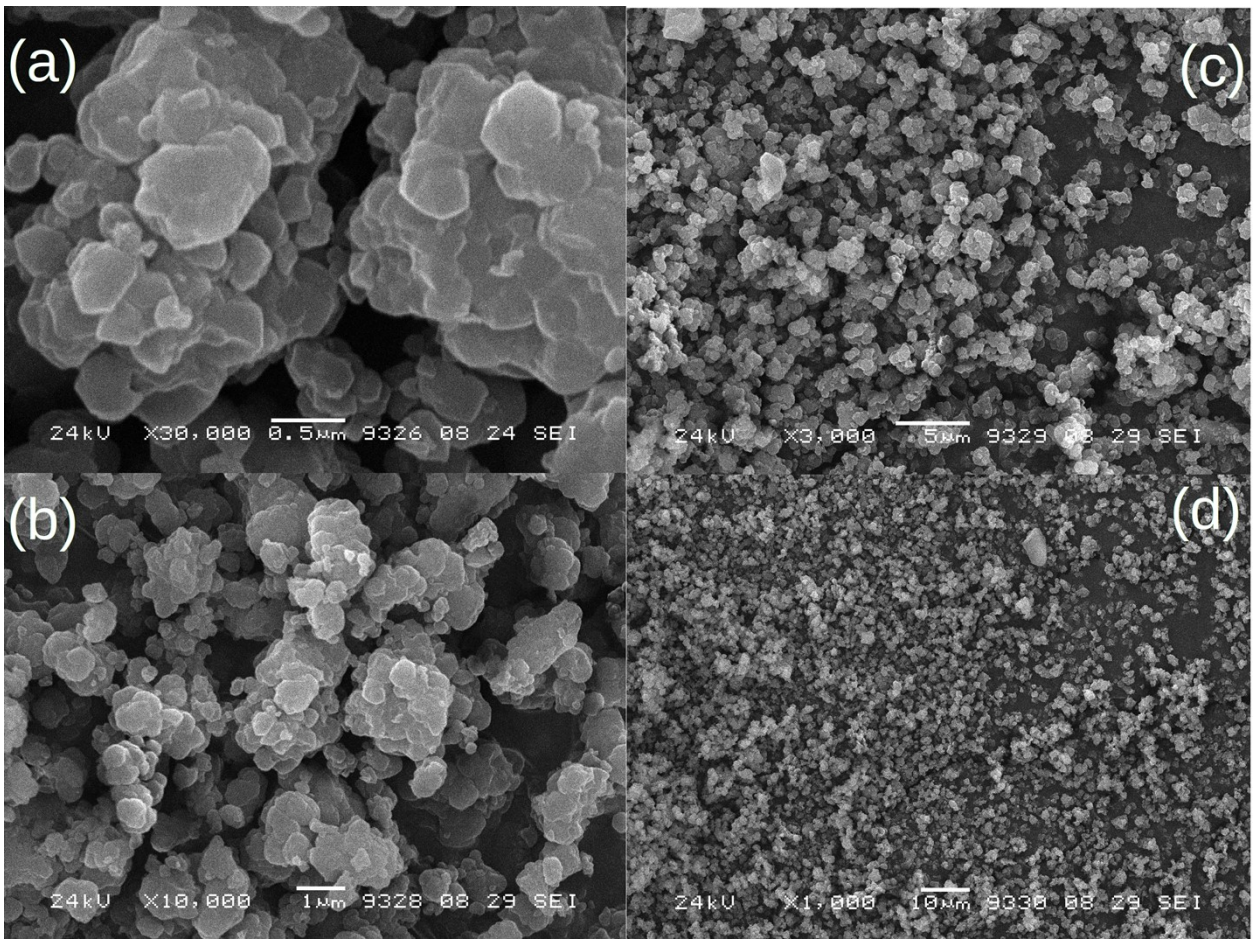

Figure S1. (a-d) SEM images of the synthesized and dried UiO-66 compound.

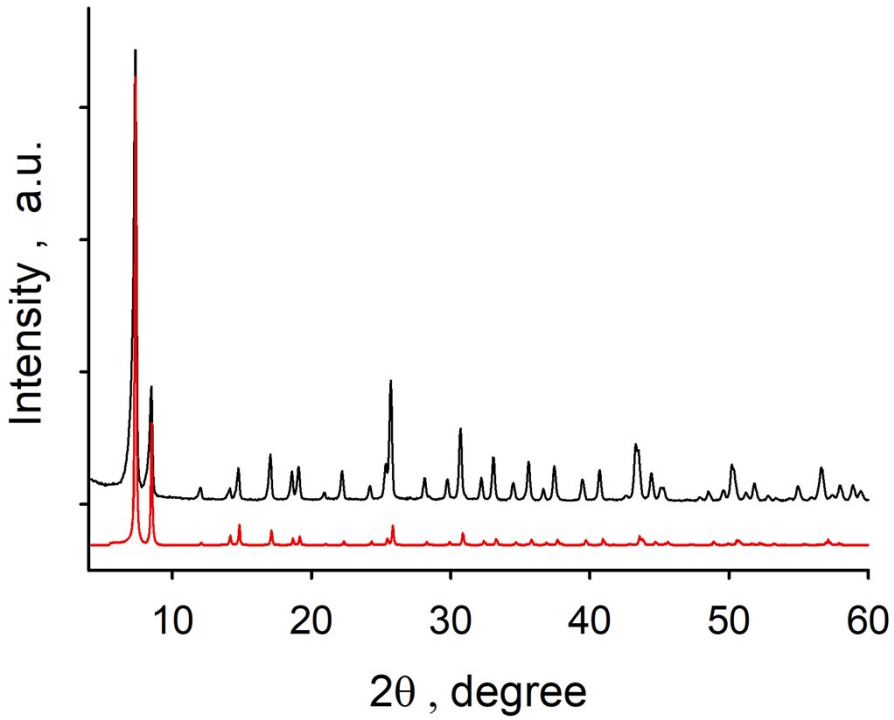

Figure S2. Experimental (black) and simulated (red) XRD patterns of the synthesized and dried UiO-66 compound.

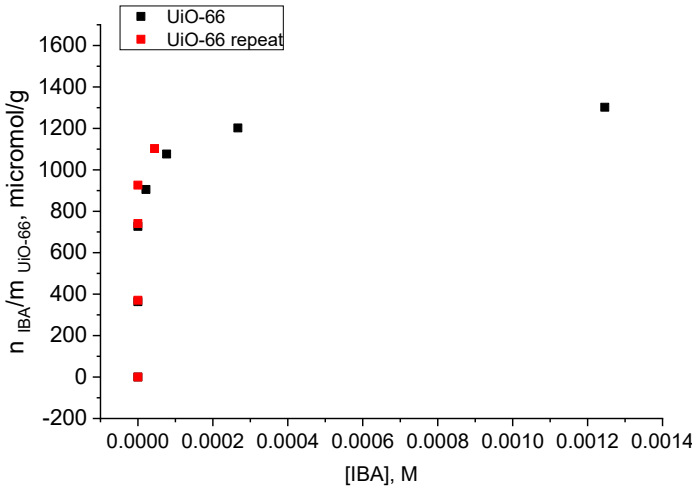

Figure S3. Nitrogen adsorption isotherms and textural characteristics for for UiO-66 (Zr) activated at 250 °C. S_{BET} = 1145 m^2/g, S_{ext} = 33 m^2/g, V_{total} = 0.46 cm^3/g, V_{micro} = 0.42 cm^3/g.

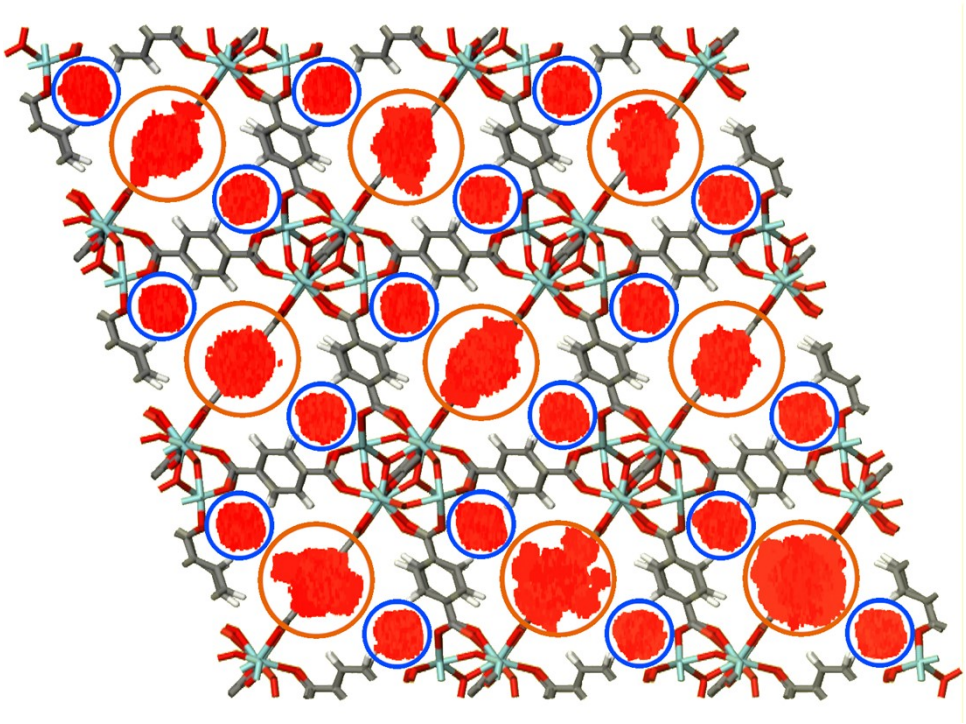

Figure S4. Localization of adsorbed pentane molecules in dehydroxylated UiO-66 at 100 kPa and 373 K. Orange circles depict position of octahedral cages, blue circles depict the position of tetrahedral cages.

NMR experiment

^{2}H NMR spectra were obtained by a Fourier transform of a quadrature-detected and phase-cycled quadrupole echo (quadecho) after two phase-alternating 90°-pulses in the pulse sequence ($90°_{\varphi1}$ – d6 – $90°_{\varphi2}$ – d7 – $acquisition_{\varphi3}$– t). Time delay between pulses d6=20 μs. Second time delay d7=18.5 μs was adjusted in order to start the acquisition of echo signal from the maximum. Inversion–recovery (IR) experiments for measurements of spin–lattice relaxation times (T_1) were carried out using the pulse sequence $180°_{\varphi0}$ – vd – $90°_{\varphi1}$ – d6 – $90°_{\varphi2}$ – d7 – $acquisition_{\varphi3}$ – t. The variable delay between 180° and the 90°-pulses was changed in 10 steps from 1 ms to approximately $5T_1$.

Spin-spin relaxation time (T_2) was measured by a Carr-Purcell-Meiboom-Gill pulse sequence: $90°_{\varphi1}$ – $(d20 - 180°_{\varphi2} – d20)_n$ − d20 − $180°_{\varphi2}$ – d21 − $acquisition_{\varphi3}$ – t. Time delay d20 = 200 μs was kept fixed for all temperatures. Time delay d21 was adjusted in order to start the acquisition of echo signal from the maximum. Phase cycles for all pulse sequences are shown in Table S1.

Table S1. Phase cycles used for NMR experiment.

	φ_0	φ_1	φ_2	φ_3
Quadecho	-	x -x -x x	y y -y -y	x -x -x x
IR	x -x -x x	x -x -x x	y y -y -y	x -x -x x
CPMG	-	x x -x -x y y -y -y	y -y y -y x -x x -x	x x -x -x y y -y -y

Table S2 Langmuir adsorption isotherm parameters of pentane isomers in UiO-66 at 373 K.

	Isopentane	*n*-Pentane
a_1	3.3	2.1
b_1, kPa^{-1}	2.4	0.15
a_2	9	11.2
b_2, kPa^{-1}	100	15.5