

Supporting information for:

A Flexible, porous, cluster-based Zn-pyrazolate-dicarboxylate framework showing selective adsorption properties

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Liquid-phase adsorption and separation experiments.

Single-component adsorption experiment.

The desolvated sample of 1 (50 mg) was immersed in 2 mL of one of three C₉H₁₂ alkylbenzene isomers in a 5 mL vial at room temperature for 2 days. The sample were dried in air and stayed in the N₂ flow with 40 ml/min at 30 °C for 20 mins. The uptakes were calculated by the weight loss of TG curves with a heating rate of 5 °C/min.

Binary and ternary separation experiments.

The desolvated sample of 1 (50 mg) was immersed in a 1:1 binary mixture or a 1:1:1 ternary mixture of C₉H₁₂ alkylbenzene isomers at room temperature for 2 hours. The sample were dried in air and stayed in the N₂ flow with 40 ml/min at 30 °C for 20 mins. After that, the sample was extracted by MeOH (5 mL × 3) for 24 hours at 80 °C, which was adopted to ensure the thorough extraction. The molar ratio of the isomers in the extracted MeOH was determined by the Gas Chromatograph-Mass Spectrometry (GC-MS).

Gas Chromatograph-Mass Spectrometry Analysis.

All GC-MS measurements were performed by an Agilent 7890A-5975C apparatus with a HP-5MS capillary column (30 m × 0.25 mm × 0.25 μm). In each case, the analyte of 1 μl was injected to determine the molar ratio of the isomers. The condition of temperature settings: column temperature 80 °C (hold for 1min) and then increases to 120 °C at 10 °C/min, and cooled to 80 °C; front injection temperature 250 °C. The He flow was 1.2 mL/min, and the split mode was 10:1 for the measured samples.

Molecular dynamics simulations.

Grand canonical Monte Carlo (GCMC) simulations were performed to investigate the lowest energy sites for the C₉H₁₂ alkylbenzene isomers by using the loading task in the Sorption module of MS modeling 5.0 package. The simulation box consisted of 8 (2 × 2 × 2) unit cells and the Metropolis method based on the universal forcefield (UFF) was used. The model of both framework and the C₉H₁₂ alkylbenzene isomers were regarded as rigid and the QEq partial charges were employed to the atoms of the framework while that of the guests were adopted the ESP charges. The cutoff radius was chosen as 18.5 Å for the LJ potential. The loading steps and the equilibration steps were both 2 × 10⁶ and then followed 1 × 10⁷ production steps. Molecular dynamics (MD) simulation were carried out to study the mobility behaviors of the three isomers in the frameworks. The starting state of the MD simulations were produced from the GCMC loading results with global geometry optimizations by molecular mechanics with the same partials charges as mentioned above. All the MD processes were performed in the canonical (NVT) ensemble with constant volume and temperature using Nose thermostat and random initial velocities. In order to shorten the equilibration time of the simulation, the dynamic temperature was chosen as 1500 K. The timestep was 1 fs and the relaxation time was 1 ps. This was then followed by a 1000 ps total simulation time. The electrostatic interactions and the van der Waals interactions were evaluated by the Ewald summation method, while all the Buffer widths were set as 0.5 Å.

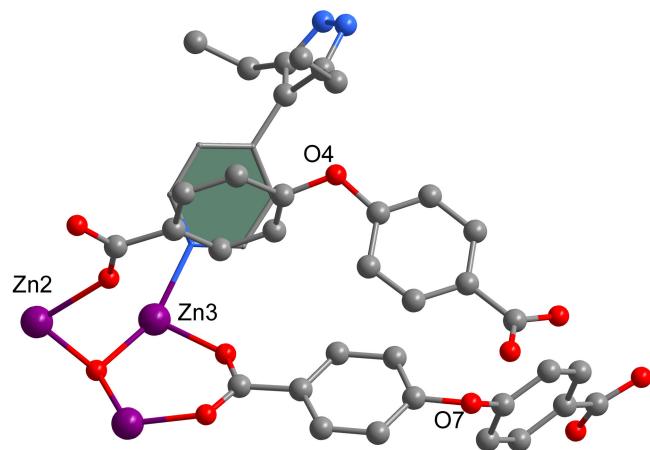


Figure S1. The coordination environment of **1-HT** (H atoms were omitted, and one set of disordered phenyl rings and ethyl groups was shown for clarity; green plane represents the mirror plane).

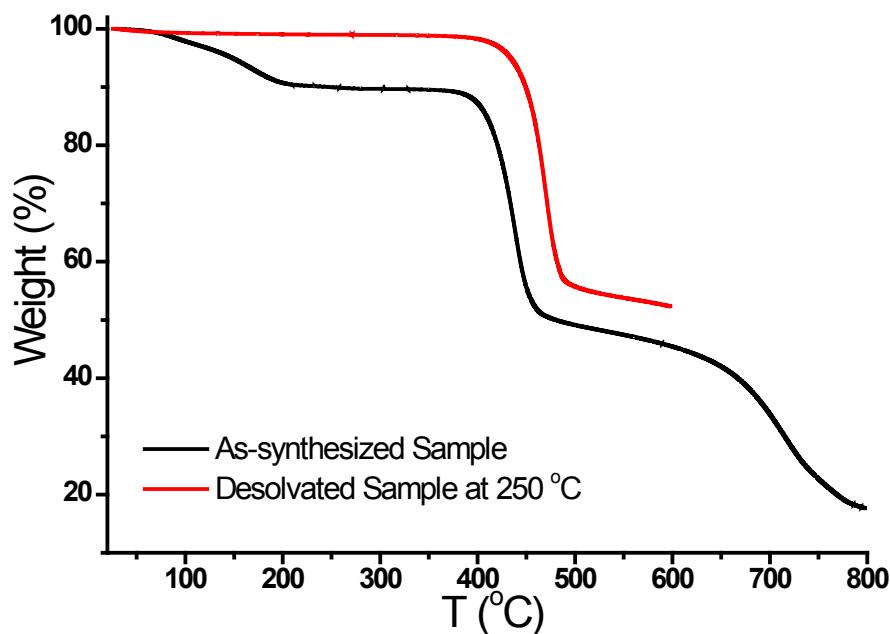


Figure S2. TG curves of the as-synthesized and desolvated samples.

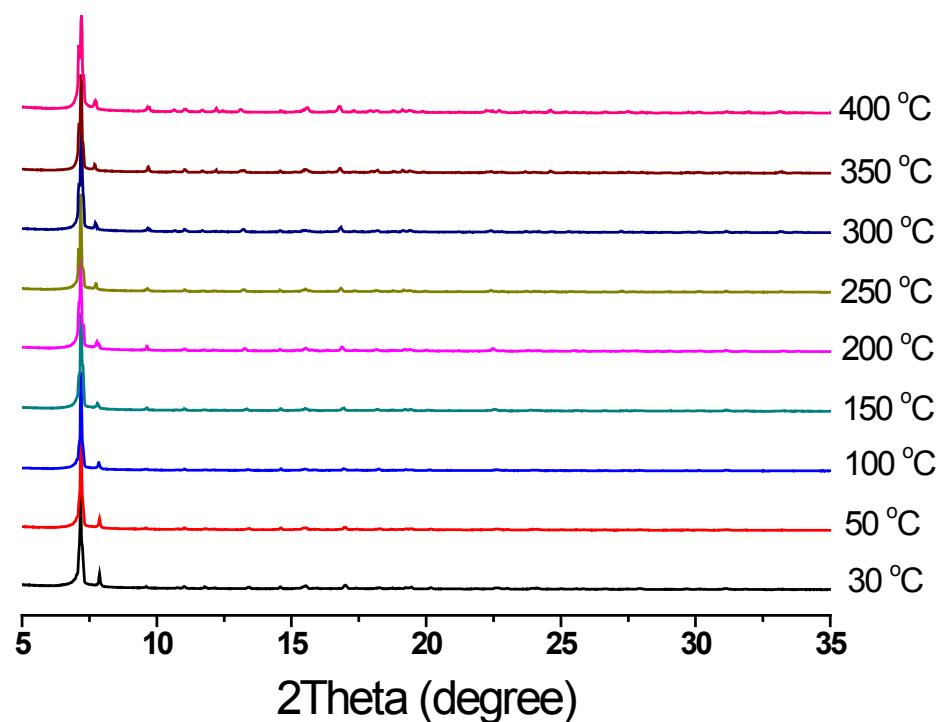


Figure S3. Variable temperature powder X-ray diffraction (PXRD) measurements of 1.

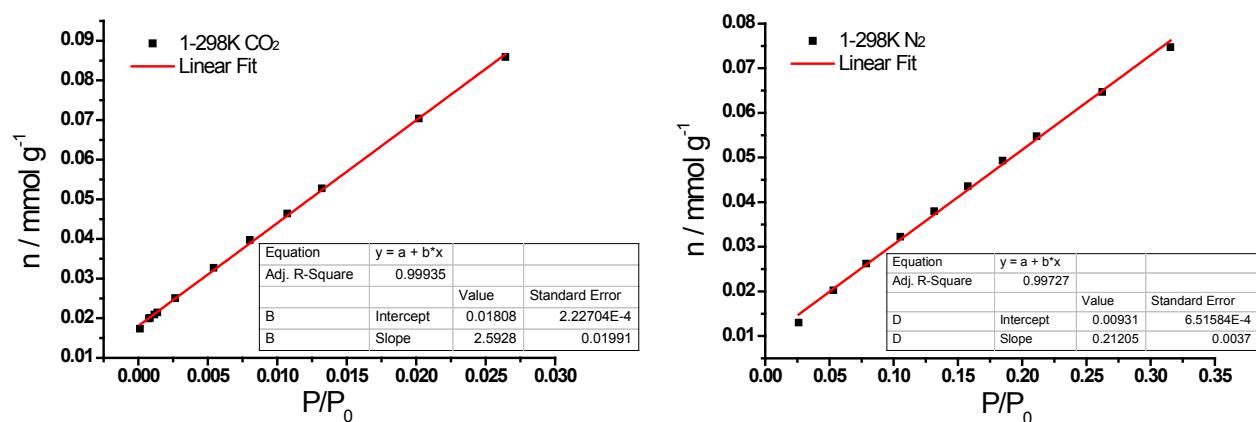


Figure S4. Henry's law CO₂/N₂ selectivity calculated by single-component isotherms.

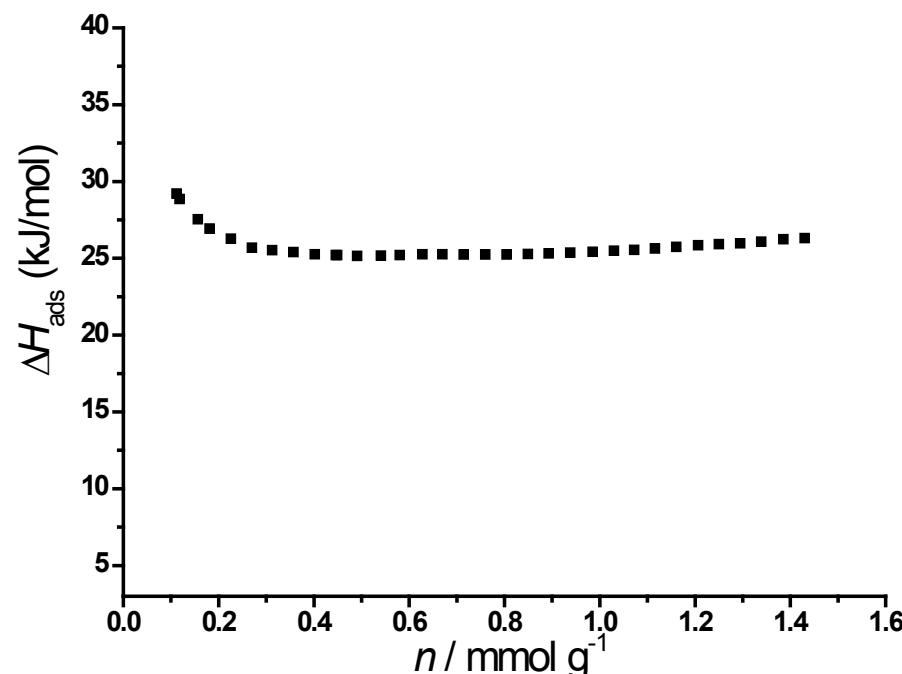


Figure S5. Isosteric heat of adsorption as a function of CO₂ uptake.

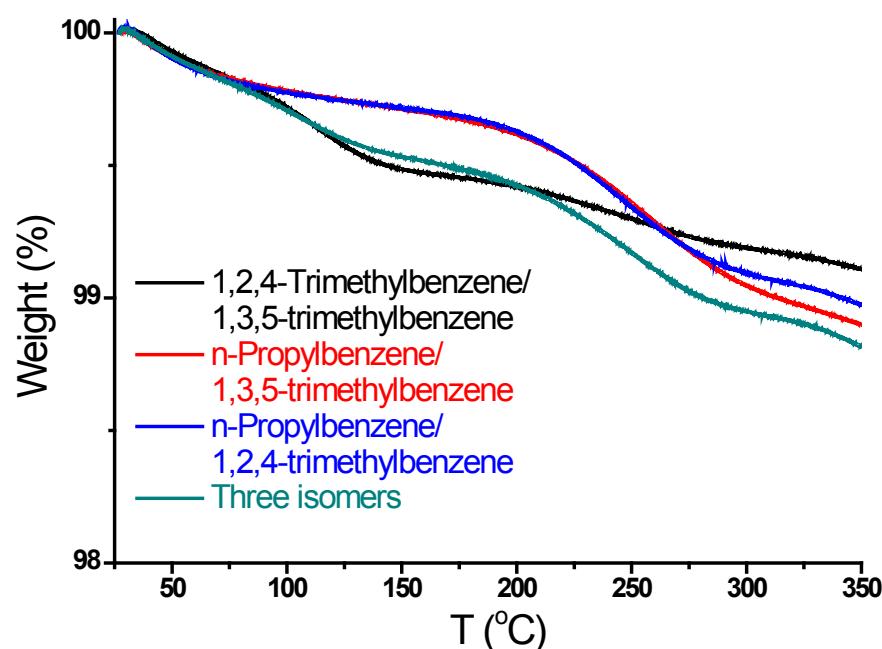


Figure S6. Thermogravimetry (TG) curves of desolvated **1** after adsorption of C₉H₁₂ alkylbenzene isomers in the binary and ternary mixtures.

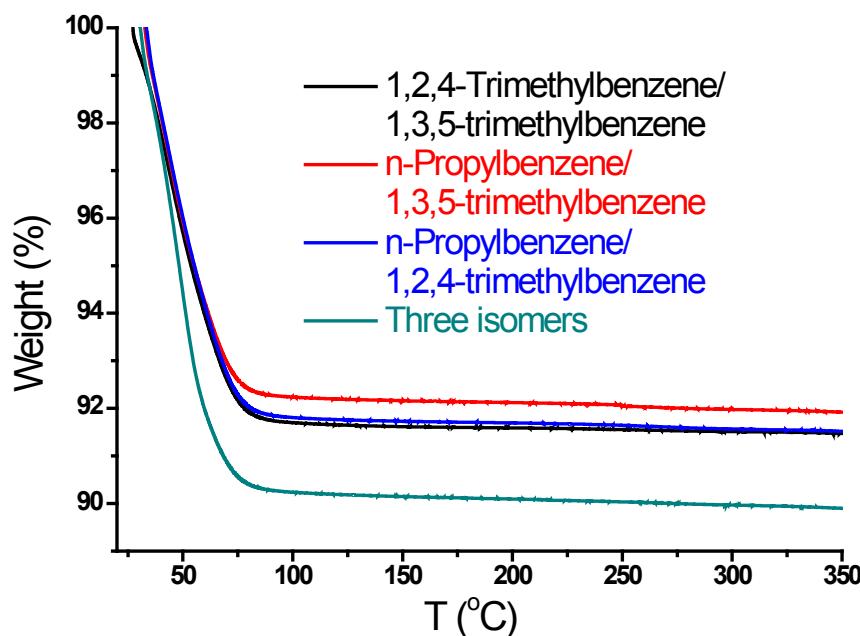


Figure S7. Thermogravimetry (TG) curves of C_9H_{12} alkylbenzene isomers adsorbed **1** after the exchange of MeOH.

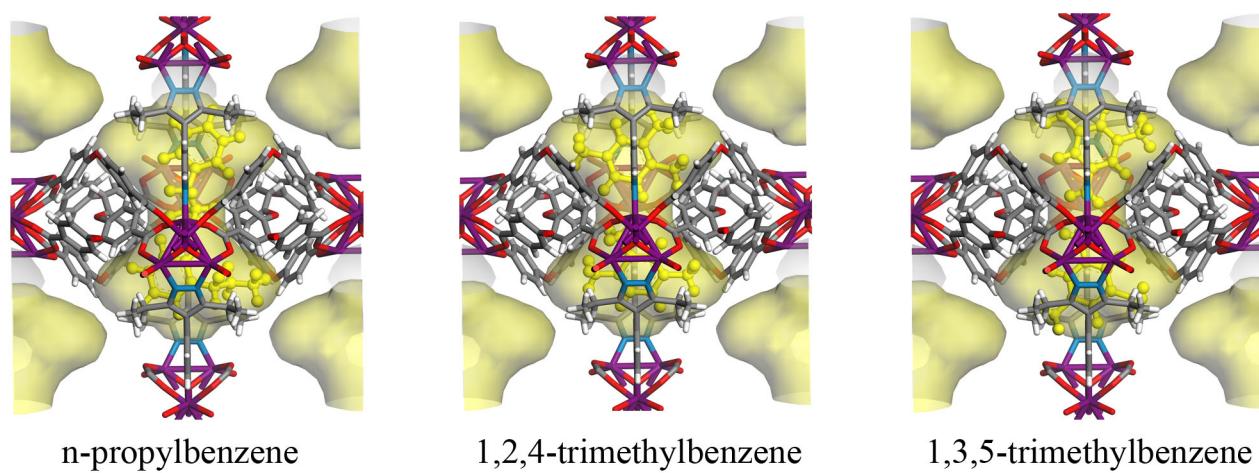


Figure S8. Configurational bias grand canonical ensemble Monte Carlo simulation of **1-HT** for the maximum filling of three C_9H_{12} alkylbenzene isomers highlighted with yellow spheres and sticks.

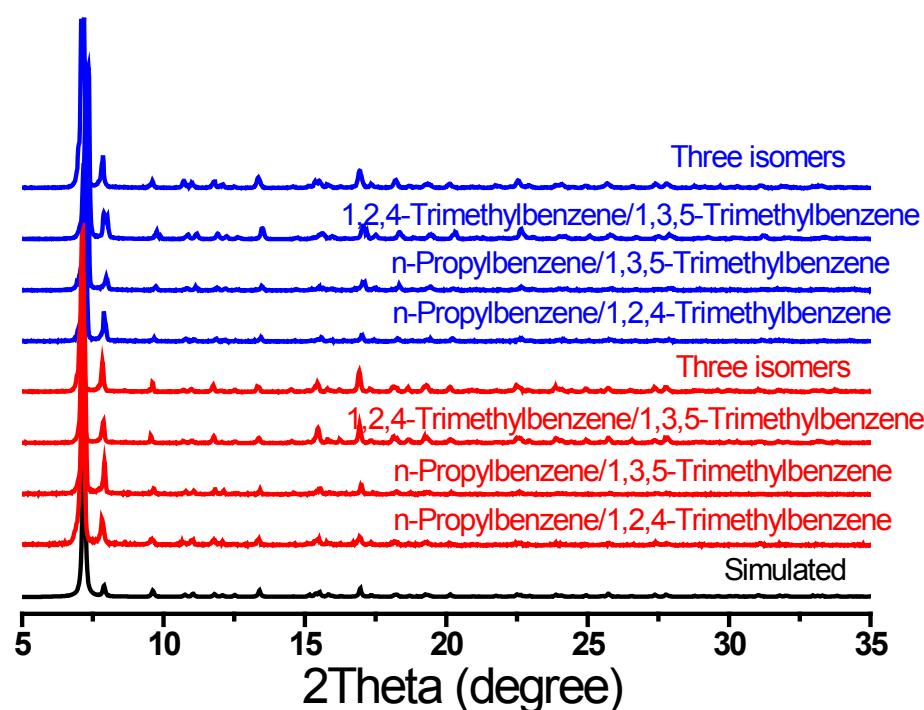
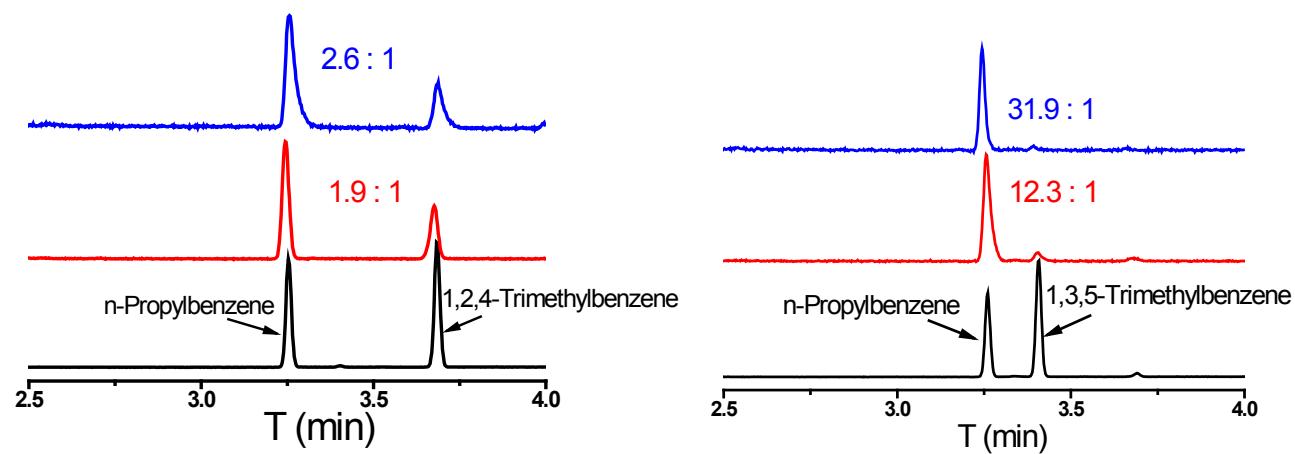


Figure S9. PXRD measurements of **1** immersed in different mixtures for 2 hours (red lines) and then exchanged by MeOH (blue lines).



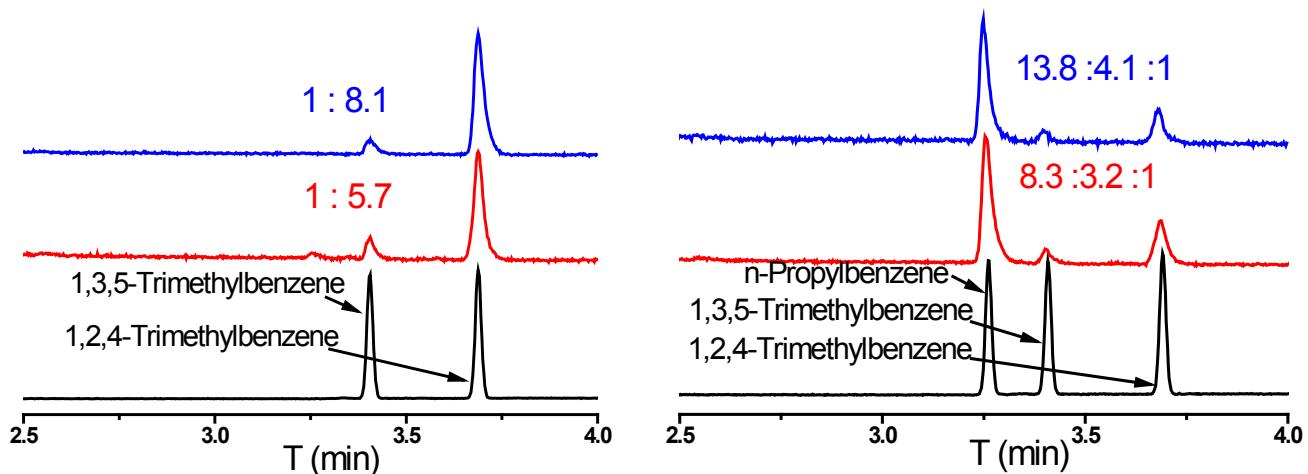


Figure S10. GC results of **1** for the liquid-phase separation experiments (red lines represent the samples dried in air, blue lines represent the samples dried at 150 °C and black lines represent the contrast samples).

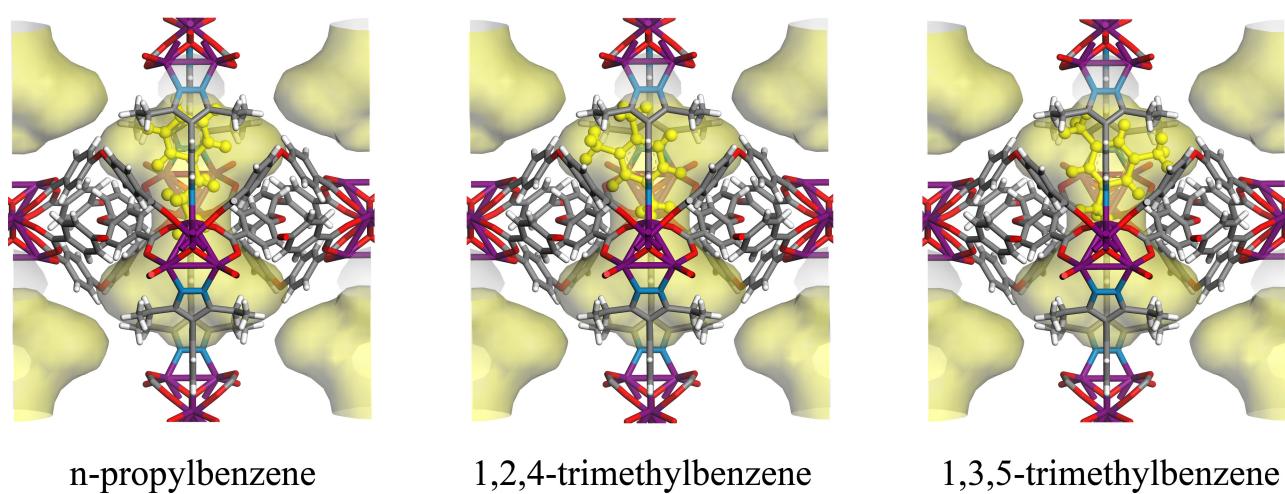


Figure S11. The calculation of preferred locations of three isomers (highlighted with yellow spheres and sticks) in **1-HT** as the starting state of molecular dynamics simulations.

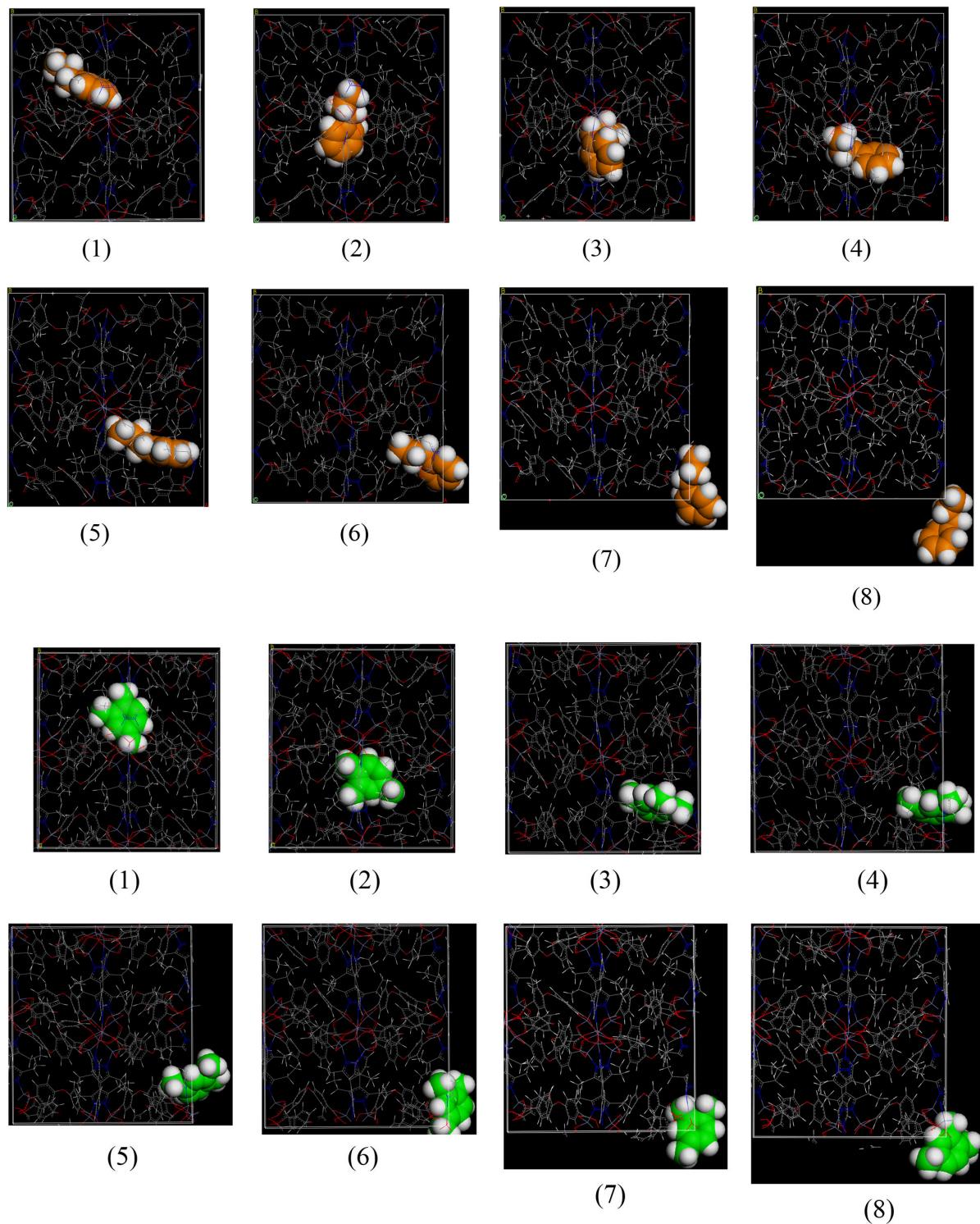


Figure S12. The schematic diagrams of the trajectories of n-propylbenzene (orange), 1,2,4-trimethylbenzene (green) in **1-HT**.

Table S1. The calculated selectivities of binary/ternary mixtures of C₉H₁₂ alkylbenzene isomers for **1** by the weight losses of TG curves.

Components of the mixtures	Selectivity ^a	
	r.t.–350 °C	150–350 °C
n-Propylbenzene/1,3,5-Trimethylbenzene	2.7	7.0
n-Propylbenzene/1,2,4-Trimethylbenzene	2.2	3.5
1,2,4-Trimethylbenzene/1,3,5-Trimethylbenzene	1.2	2.0
Three isomers	2.7:1.2:1	7.0:2.0:1