

Synthesis of high-performance polycrystalline metal-organic framework membranes at room temperature in a few minutes

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Preparation of Precursor Solutions:

Metal and ligand solutions for ZIFs synthesis were prepared by separately dissolving 2.75 g zinc nitrate hexahydrate ($\geq 99.0\%$, Sigma-Aldrich), 2.69 g cobalt nitrate hexahydrate (98%, Sigma-Aldrich) and 56.75 g HmIm (99%, Acros) in 500 ml deionized (DI) water. For ZIF-90 synthesis, 0.74 g zinc nitrate hexahydrate and 2.40 g Hlca (97%, abcr GmbH) in 500 ml DI water respectively.

Characterization:

SEM images were collected on the FEI Teneo scanning electron microscope at an electron beam voltage of 1 kV to observe the surface and the cross-section of ZIF membranes. Dynamic light scattering (DLS, Malvern Nano ZS) was used to characterize the particle size of the ZIF-8 precursor solution at different dwell times. For the DLS experiments, the ZIF-8 precursor solution was prepared under the same condition as that for the ZIF-8 film. For measurements, 1 ml of the precursor solution at a certain dwell time was transferred into a 20 ml glass bottle containing 9 ml of deionized water at 0 °C to quench the reaction. After shaking the glass bottle for a few seconds, 2 ml of the diluted precursor solution was added into the sample cell to quickly start the measurement. Each sample was measured for a duration of 2 min for 3 times. Precursor solutions without dilution were also measured. The concentration of the HmIm in the ZIF-8 precursor solution was determined by a UV-Vis spectrophotometer (PerkinElmer LAMBDA 365). First, a series of HmIm solutions with known concentrations ranging from 2×10^{-6} to 2×10^{-4} mol L⁻¹ was measured using UV absorbance (205 nm) to prepare a calibration dataset. Then, similar to DLS experiments, the ZIF-8 precursor solution was diluted in deionized water at 0 °C by 10000 times and quickly collected for the measurement. The measurements were conducted at least twice. Fourier transform infrared spectra (FTIR, PerkinElmer Spectrum two™) were collected by 32 scans with a resolution of 2 cm⁻¹ in the range of 4000 – 400 cm⁻¹. The crystal structure of the films was analyzed by X-ray diffraction (XRD, Bruker D8 discover diffractometer) between 5 and 30° 2 θ at a rate of 1.5 s/step and a step size of 0.02°.

Gas Permeation Measurements:

The gas permeation measurements were carried out on a homemade Wicke-Kallenbach type permeation cell (Figure S12). All gases were delivered into the membrane cell by pre-calibrated mass flow controllers (MKS Instruments). The pressure of the feed and the permeate side was maintained at 1 bar. High purity Ar (99.999 %) was used as the sweep gas. The permeate compositions were analyzed using a calibrated mass spectrometer (Hiden Analytical, HPR-20). The as-synthesized membranes were sealed by epoxy on a stainless-steel disk with a hole of 5 mm diameter in the center. ZIFs/AAO membranes were heated inside an oven at 130 °C under the H₂/Ar atmosphere to remove the absorbed gases and moisture. All the measurements were recorded after reaching a steady state.

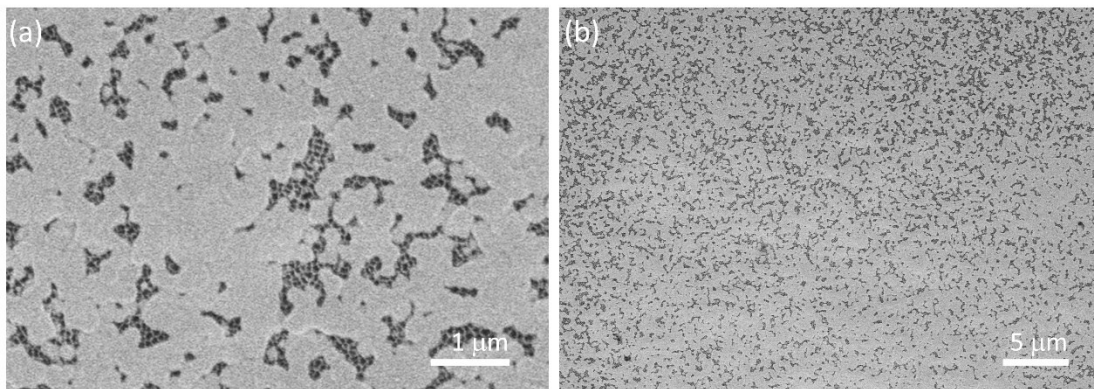


Figure S1. ZIF-8 nuclei film deposited on an AAO substrate with 100 nm pores under different magnifications.

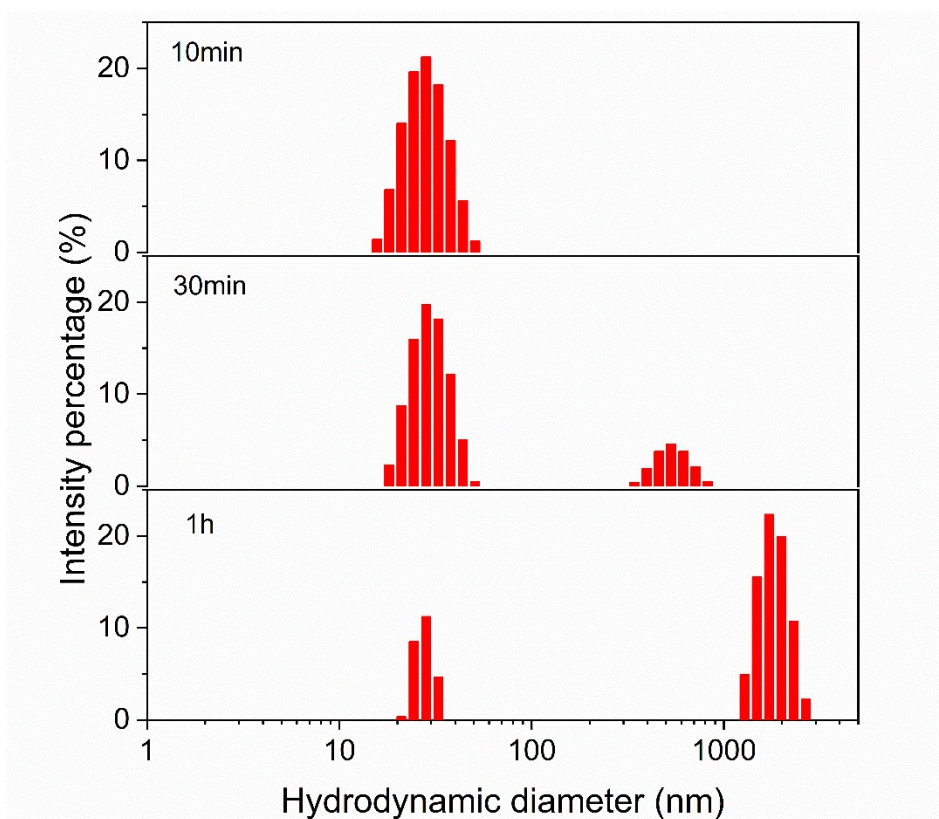


Figure S2. The hydrodynamic diameter of ZIF-8 particles in the precursor solution at different growth time.

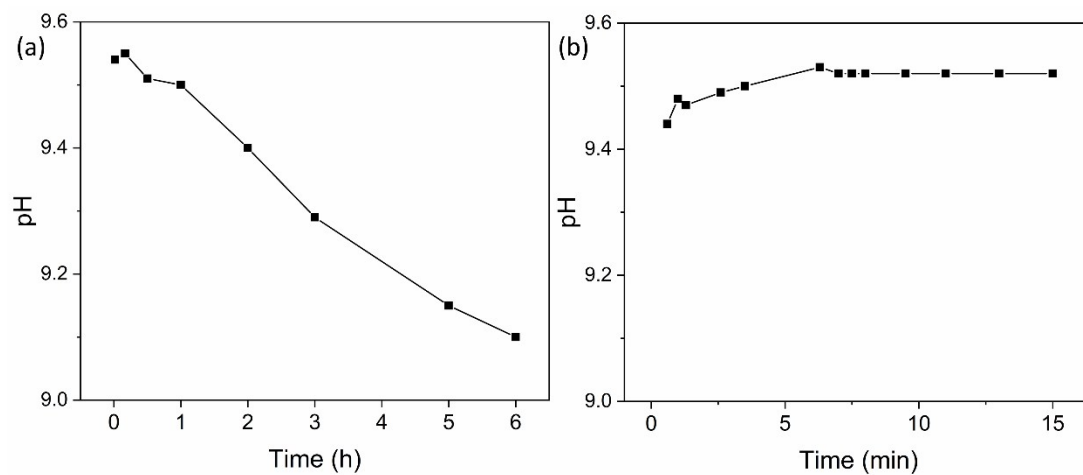


Figure S3. The change of pH value in ZIF-8 precursor solutions at different growth time by a) the ENACT and b) the CUSP approach.

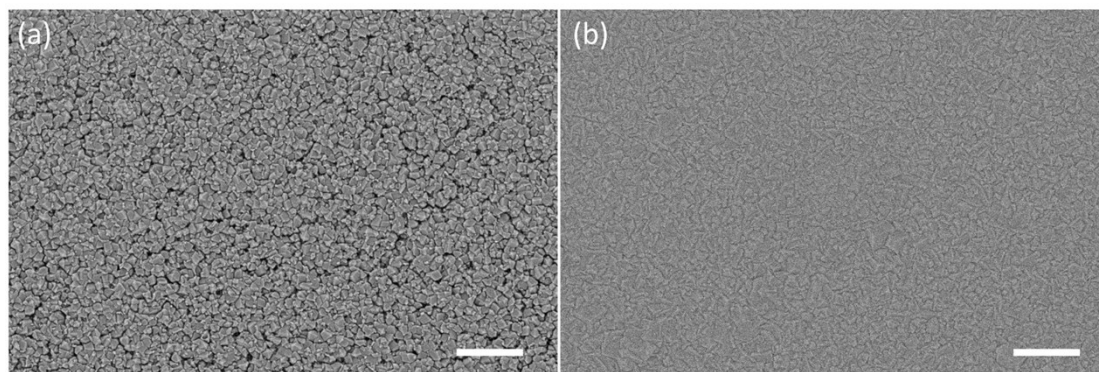


Figure S4. SEM images of ZIF-8 membrane synthesized with a dwell time of 3 min under a) 10 and b) 15 min of growth. Scale bars: 2 μm.

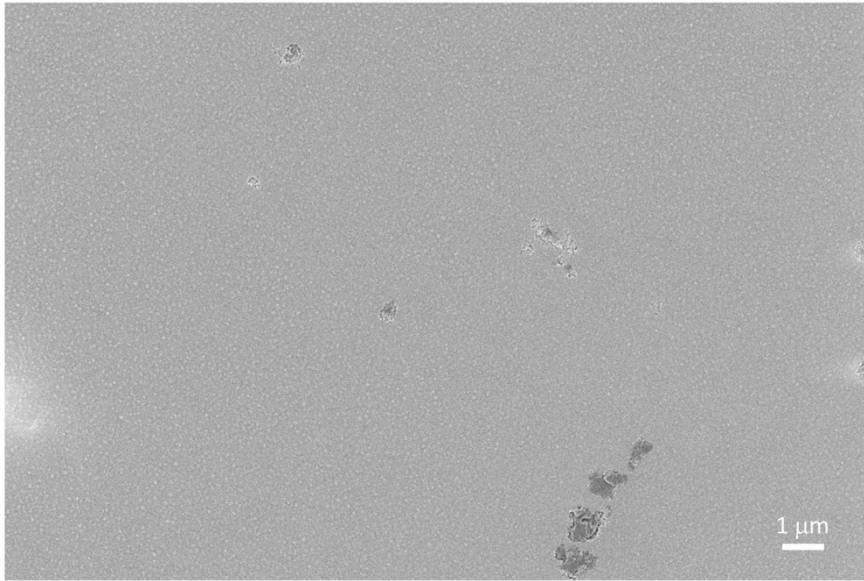


Figure S5. ZIF-8 nuclei film on AAO substrate holding 20 nm pores.

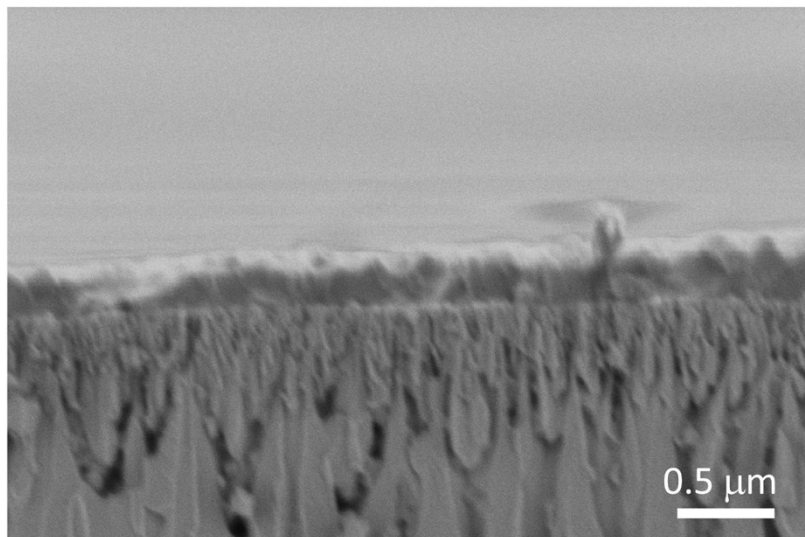


Figure S6. Cross-sectional view of ZIF-8 membrane prepared using 8 min of growth.

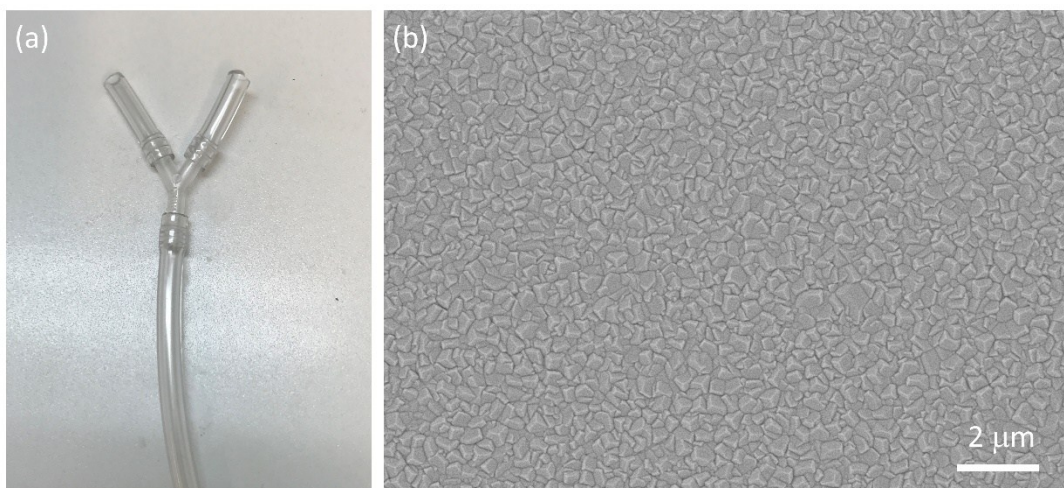


Figure S7. a) Photograph of Y-configuration mixing tube, and b) the top view of ZIF-8 membrane synthesized in 6 min by this approach.

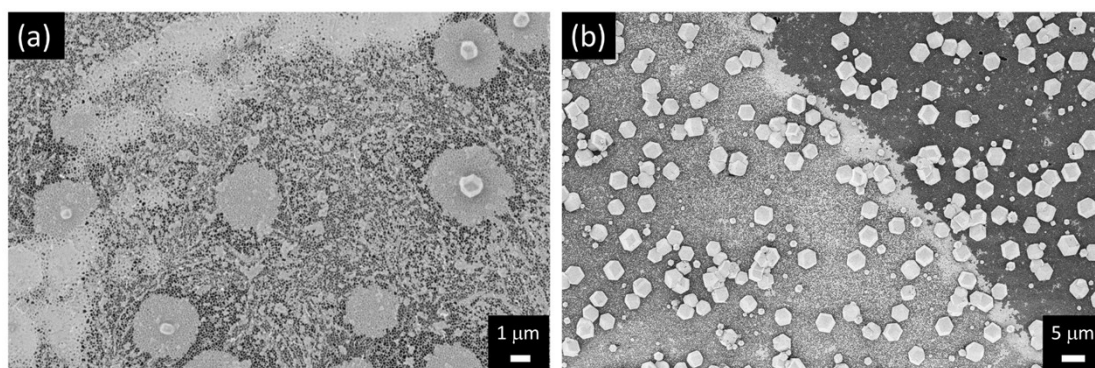


Figure S8. SEM images revealing a) poor heterogeneous nucleation of ZIF-90 on the porous support, and b) poor intergrowth of film in (a).

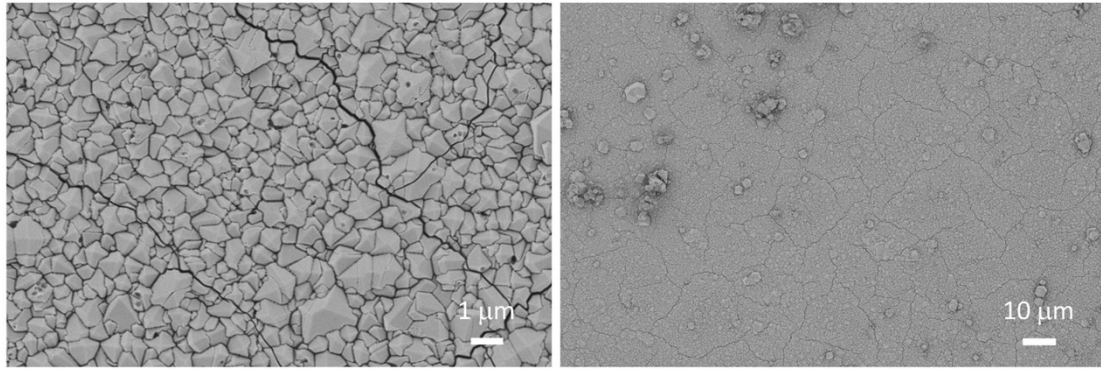


Figure S9. SEM images of ZIF-90 film synthesized in methanol showing cracks formed during activation.

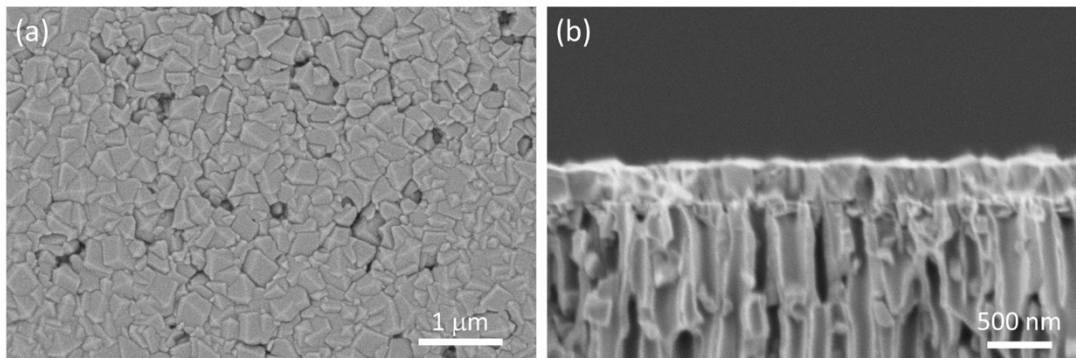


Figure S10. a) Top view and b) cross-sectional view of a defective ZIF-8 film as a substrate for ZIF-90 growth.

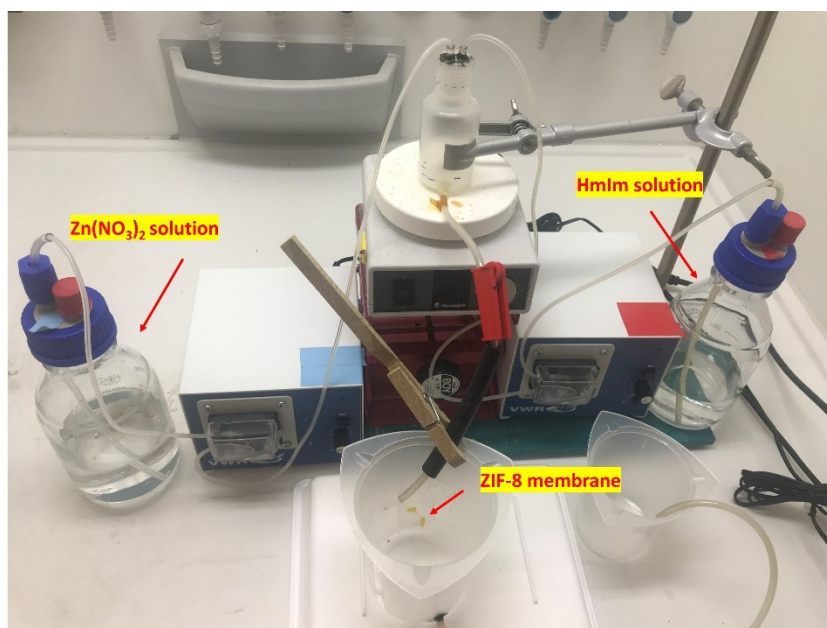


Figure S11. The CUSP setup.

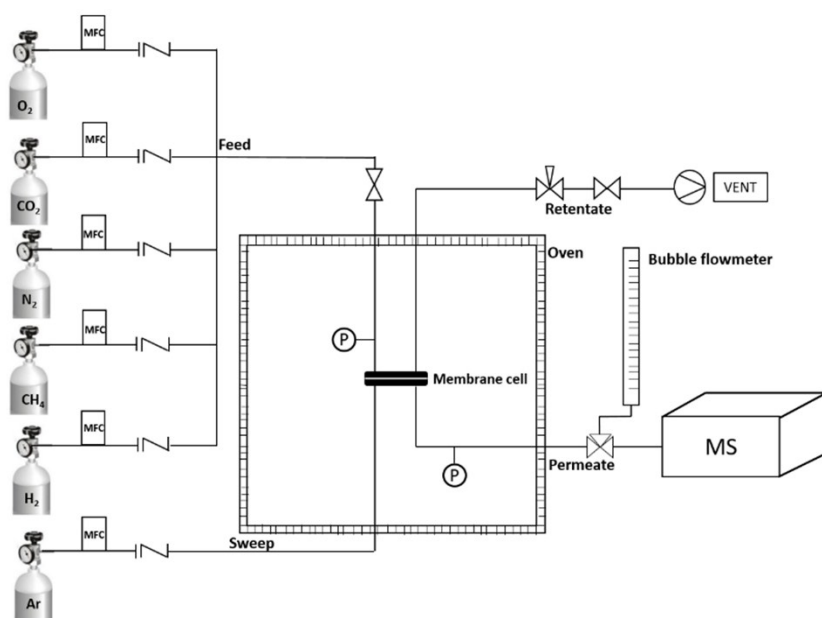


Figure S12. Schematic illustration of the gas permeance measurement setup.

Table S1. Gas separation data from membranes in this study at 25 °C.

Sample	H ₂ permeance (mol m ⁻² s ⁻¹ Pa ⁻¹)	Ideal selectivity			
		H ₂ /CH ₄	CO ₂ /CH ₄	H ₂ /C ₃ H ₆	C ₃ H ₆ /C ₃ H ₈
ZIF-8 on 20 nm AAO	1.6×10 ⁻⁶	8.8	3.6	78.7	30.9
ZIF-8 on 100 nm AAO	1.9×10 ⁻⁶	8.5	3.9	69.6	17.2
ZIF-8 on 100 nm AAO	2.1×10 ⁻⁶	13.9	3.8	122.5	13.7
ZIF-8 on 100 nm AAO	1.0×10 ⁻⁶	9.4	2.7	49.8	8.2
ZIF-67 on 100 nm AAO	1.9×10 ⁻⁶	9.1	4.0	98.4	11.3
ZIF-8-67/AAO hybrid membrane	2.3×10 ⁻⁶	9.3	1.5	59.3	6.1
ZIF-8-90/AAO hybrid membrane	6.3×10 ⁻⁷	19.2	7.9	79.1	C ₃ H ₈ below the detection limit.
ZIF-8-90/AAO hybrid membrane	4.8×10 ⁻⁷	16.3	7.5	107.1	10.7

Table S2. Gas permeance data of MOF membranes in literature at 25 °C. Permeance given in units of mol m² s⁻¹ Pa⁻¹.

MOF	H ₂	CO ₂	CH ₄	H ₂ /CH ₄	CO ₂ /CH ₄	Membrane thickness/μm	Synthesis period	Reference
ZIF-8	3.5×10 ⁻⁶	1.1×10 ⁻⁶	1.2×10 ⁻⁷	30.7	9.4	0.017	2 h	1
ZIF-7-8	3.0×10 ⁻⁷	6.0×10 ⁻⁸	1.4×10 ⁻⁸	21.4	4.3	1~2	24 h	2
ZIF-8	8.3×10 ⁻⁶	1.1×10 ⁻⁶	5.1×10 ⁻⁷	16.2	2.2	0.5	10 h	3
ZIF-8	2.0×10 ⁻⁶	4.6×10 ⁻⁷	1.4×10 ⁻⁷	14.3	3.3	15	40 h	4
ZIF-8	3.0×10 ⁻⁷	5.0×10 ⁻⁸	1.0×10 ⁻⁸	30.0	5.0	15	40 h	4
ZIF-8	2.7×10 ⁻⁷	1.6×10 ⁻⁸	6.4×10 ⁻⁹	41.9	2.4	20	48 h	5
ZIF-8	1.2×10 ⁻⁷	6.4×10 ⁻⁸	1.0×10 ⁻⁸	12.3	6.4	6.8	24 h	6
ZIF-67	2.8×10 ⁻⁷	3.1×10 ⁻⁸	5.8×10 ⁻⁹	48.2	5.4	3	48 h	7
ZIF-90	5.7×10 ⁻⁷	4.8×10 ⁻⁷	8.1×10 ⁻⁸	7.1	5.9	3.1	44 h	8
ZIF-90 (200 °C)	2.5×10 ⁻⁷	3.5×10 ⁻⁸	1.6×10 ⁻⁸	15.9	2.2	20	18 h	9
ZIF-90 (200 °C)	2.1×10 ⁻⁷	1.3×10 ⁻⁸	1.1×10 ⁻⁸	19.3	1.2	20	28 h	10
ZIF-8-90	6.3×10 ⁻⁷	2.6×10 ⁻⁷	3.3×10 ⁻⁸	19.2	7.9	0.9	20 min	This work
ZIF-8-90	3.4×10 ⁻⁷	1.6×10 ⁻⁷	2.1×10 ⁻⁸	16.3	7.5	0.9	20 min	This work

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