Supplementary Information (SI) for Journal of Materials Chemistry A.

Supporting Information for

High Toluene Uptake at the Trace Concentration in a Novel Gallium-Based Metal−Organic Framework

Thach N. Tu,[a] Hyuk Taek Kwon,[b] Manfred Scheer*[c] and Jinsoo Kim*[a]

[a] Department of Chemical Engineering (Integrated Engineering), Kyung Hee University, 1732 Deogyeong-daero, Giheung-gu, Yongin-si, Gyeonggi-do 17104, Republic of Korea.

[b] Department of Chemical Engineering, Pukyong National University, 45 Yongso-ro, Nam-gu, Busan 48513, Republic of Korea.

[c] Institute of Inorganic Chemistry, University of Regensburg, 93040 Regensburg, Germany.

Email: jkim21@khu.ac.kr; Manfred.Scheer@chemie.uni-regensburg.de

Section S1: Materials, Analytical Techniques and Experimental Methods

Materials

Biphenyl-3,4′,5-tricarboxylic acid (H_3BPT, 98% purity) were purchased from TCI Co. Ga(III) iodide anhydrous (GaI_3, 99.99% purity), benzoic acid (ben, 99%), ethanol (MeOH, 99%) and were obtained from Sigma Aldrich. Anhydrous cyclohexane (99% extra dry grade) and *N*,*N*-dimethylformamide (DMF, 99% extra dry grade) were obtained from Daejung Chemical Company.

Analytical Techniques

A single crystal of Ga-BPT$_{sc}$ was mounted on a cryoloop and cooled down to 100 K by a nitrogen flow. A XtaLAB Synergy using Cu K_α radiation source (λ = 1.54178 Å) was used for structure determination. The diffraction data was collected by HyPix-Arc 150. The unit cell and data reduction were determined using CrysAlisPro software. The data set was reduced, and data correction was carried out by a multi-scan spherical absorption method. The structure was solved by direct methods and further refinement was carried out using the full-matrix least-squares method in the SHELX-2013 program package. After locating the framework backbone and the adsorptive guest, the Solvent Mask routine was optionally used to remove residual electron density from solvent molecules. Powder X-ray diffraction (PXRD) patterns of grounded Ga-BPT were collected by a RIGAKU MiniFlex600 diffractometer. The N_2 adsorption isotherms were measured at 77 K using BELSORP-max. The surface area of the samples was calculated from the N_2 isotherms using the Brunauer–Emmett–Teller (BET) method. The benzene, toluene and xylenes isotherms was collected automatically at room temperature using the BELSORP-max II adsorption analyzer. The balance time was set at 1000 s / 0.1%. Toluene and xylenes isotherms were measured on one sample, which were reactivated overnight at 150 °C before each measurement. Thermal gravimetric analysis (TGA) was performed under a gas

mixture of O_2 (20%) and N_2 (80%) with temperature ramp of 5 °C min^{-1}. Fourier transform infrared (FT-IR) spectra were measured on a PerkinElmer FT-IR spectrometer (Frontier model) using the ATR protocol.

GCMC simulation of toluene adsorption in Ga-BPT$_P$ was performed using the adsorption tool of the Material Studio software. Before calculation, the atom charges of the toluene molecules were adjusted based on literature data: H (CH): 0.11; H (CH3): 0.06; C (CH): −0.11; C (CH3): −0.06 e−.[1] The Universal forcefield was employed to simulate the interaction between toluene and the Ga-BPT$_P$ framework. The Ewald & Group was used as electrostatic model. GCMC simulation (configurational bias method) was performed at 298 K and at a loading of 11 toluene molecules per unit cell.

1. F. D. Lahoz-Martín, A. Martín-Calvo and S. Calero, *J. Phys. Chem. C*, 2014, 118, 13126.

Section S2: Material Characterizations for Ga-BPT$_{sc}$

Table S1. Crystal data and structure refinement for Ga-BPT$_{sc}$

Empirical formula	$C_{37}H_{19}O_{16}Ga_3$
Formula weight	928.68
Temperature (K)	123
Wavelength (Å)	1.54178
Crystal system	*orthorhombic*
Space group	*Pmn2$_1$*
Unit cell dimensions (Å)	*a* = 22.997(3)
	b = 9.7823(5)
	c = 15.749(2)
Volume (Å^3)	3542.9(7)
Z	2
Density (g cm^{-1})	0.871
Absorption coefficient (mm^{-1})	1.681
F(000)	924
Crystal size (mm)	0.082 × 0.052 × 0.037
θ range (°)	3.401 to 67.684.
Index ranges	-27 ≤ *h* ≤ 28, -11 ≤ *k* ≤ 6, -19 ≤ *l* ≤ 19
Reflections collected	38244
Independent reflections	7060 [R_{int}= 0.1769]
Completeness to *θ* = 67.684°	0.995
Data / restraints / parameters	7060 / 99 / 263
S (GOF)	0.953
R_1, wR_2 [$I > 2\sigma(I)$]	0.1108, 0.2792
R_1, wR_2 (all data)	0.1669, 0.3242
Largest diff. peak and hole (e·Å^{-3})	0.886 and –0.834

CCDC number	2386132

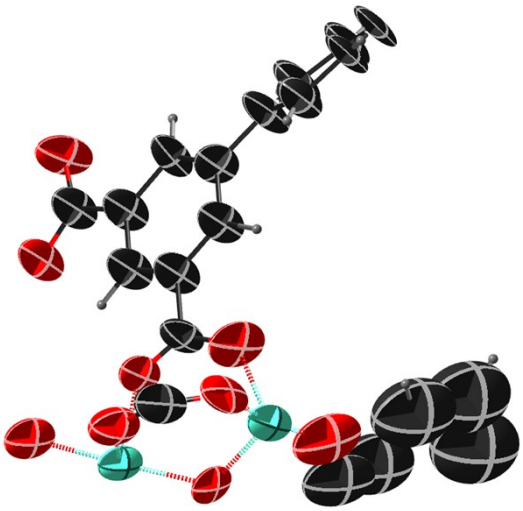


Figure S1. Thermal ellipsoid plot at 50% probability of the asymmetric unit Ga-BPT$_{sc}$.

Atom colours: Ga, blue balls; C, black; O, red.

Section S3: Structural Solution of Ga-BPT$_P$

Structural Modeling of Ga-BPT$_P$. The modeled structure of Ga-BPT$_P$ was constructed based on the structure of Ga-BPT$_{SC}$ with a change of unit cell parameters. The full profile pattern fitting (Rietveld method) of Ga-BPT$_P$ was performed against the powder diffraction pattern using the *Materials Studio* software. This gave the satisfactory result with the fitting that converged at reasonable residual values (R_{wp} = 4.51%, R_p = 2.39%) and the final unit cell parameters (*(a* = 22.042; *b* = 9.896; *c* = 17.960 Å). The fractional atomic coordinates, refined cell parameters and crystal structure information of Ga-BPT$_P$ after the Rietveld fitting is shown in Table S2.

Table S2. Atomic coordinates and refined unit cell parameters of Ga-BPT$_P$.

Name		Ga-BPT$_P$		
Space group		*Pmn2$_1$*		
a (Å)		22.042		
b (Å)		9.896		
c (Å)		17.960		
Unit Cell Volume (Å^3)		3918		
Rp		2.39%		
Rwp		4.51%		
Atom Name	*x*	*y*	*z*	Site Occupancy
O1	0.61334	0.40019	0.52974	1
C1	0.5969	0.52093	0.54734	1
Ga1	0.57144	0.22864	0.5538	1
O2	0.62582	0.23769	0.64178	1
C2	0.62508	0.63503	0.51509	1
C3	0.60415	0.76142	0.53331	1
H1	0.56619	0.76995	0.57617	1
O3	0.63017	1.11661	0.50011	1
C4	0.628	0.87696	0.501	1
O4	0.56881	0.36503	0.7157	1
C5	0.67358	0.86255	0.44885	1
H2	0.69411	0.95568	0.42127	1
C6	0.74195	0.72669	0.37285	1
C7	0.79033	0.63299	0.37841	1
H3	0.79249	0.56014	0.42751	1
O5	0.55325	0.54098	0.59322	1
C8	0.83692	0.6268	0.32399	1
H4	0.87569	0.55149	0.33052	1
O6	0.56091	1.03422	0.56168	1
C9	0.83662	0.71253	0.26107	1
C10	0.61729	0.29625	0.70423	1
C11	0.55514	0.32245	0.30779	1
H5	0.60013	0.31018	0.33836	1
C12	0.55498	0.3533	0.23198	1
H6	0.59971	0.36599	0.20088	1
O7	0.55061	0.2625	0.46037	1
C13	0.69587	0.73688	0.42824	1
C14	0.6714	0.62399	0.46237	1
H7	0.68987	0.52028	0.4466	1
C15	0.78789	0.80493	0.25512	1
H8	0.78497	0.87581	0.20521	1
C16	0.60627	1.00796	0.5211	1
C17	0.7419	0.81247	0.30993	1
H9	0.70419	0.89011	0.30241	1

H10	0.53739	0.58963	0.7447	1
C18	0.5	0.30647	0.34658	0.5
Ga2	0.5	0.41792	0.64914	0.5
O8	0.5	0.53934	0.72276	0.5
C19	0.5	0.36867	0.19411	0.5
H11	0.5	0.39259	0.13543	0.5
O9	0.5	0.27937	0.58977	0.5
C20	0.5	0.27484	0.42698	0.5

Section 4: Characterization of Ga-BPT$_P$

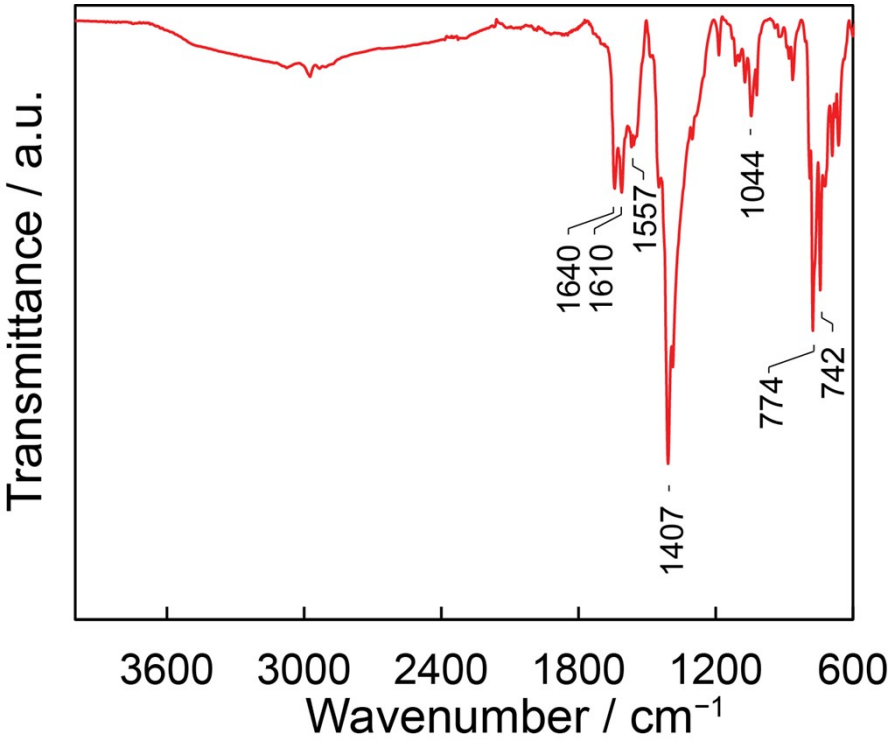


Figure S2. FT-IR of Ga-BPT$_P$.

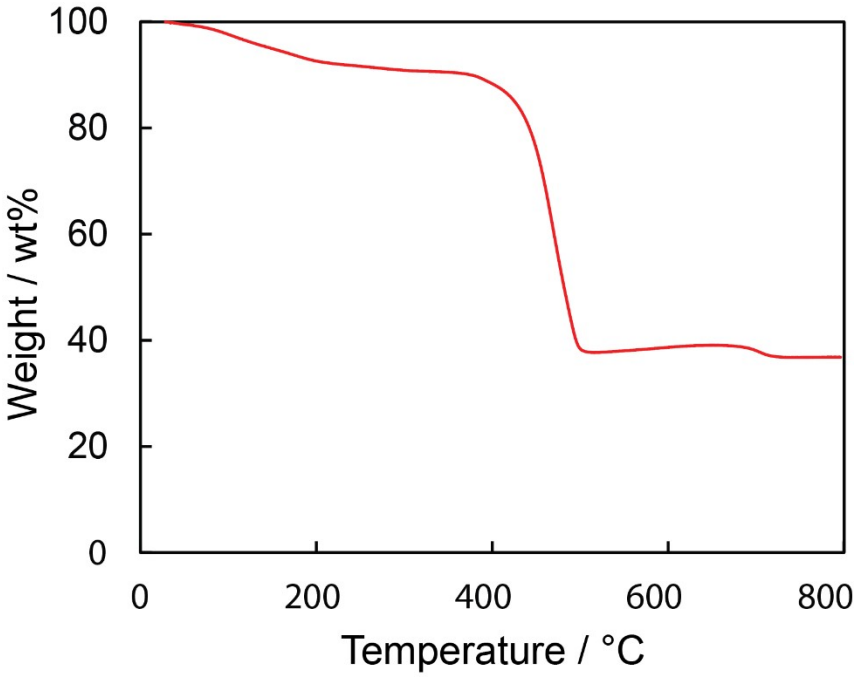


Figure S3. TGA of Ga-BPT$_{P}$.

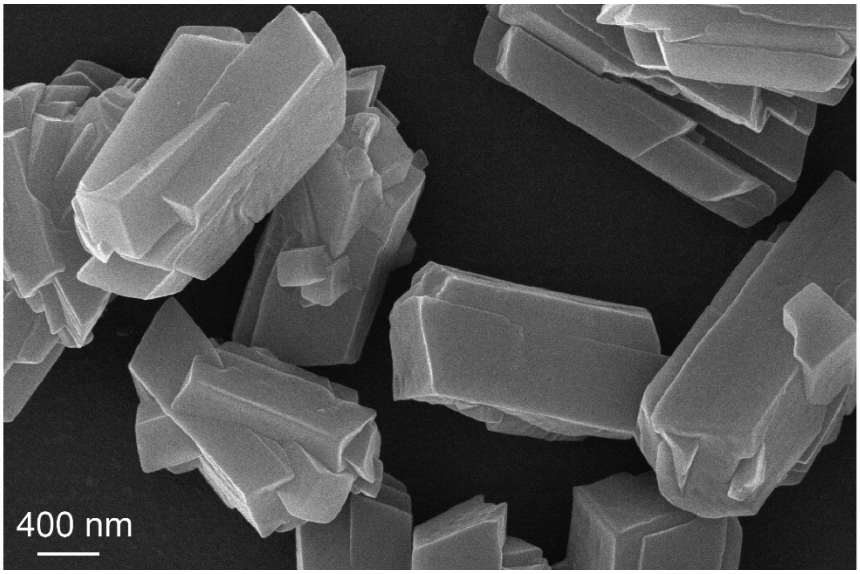


Figure S4. SEM images of Ga-BPT$_{\mathbf{P}}$.

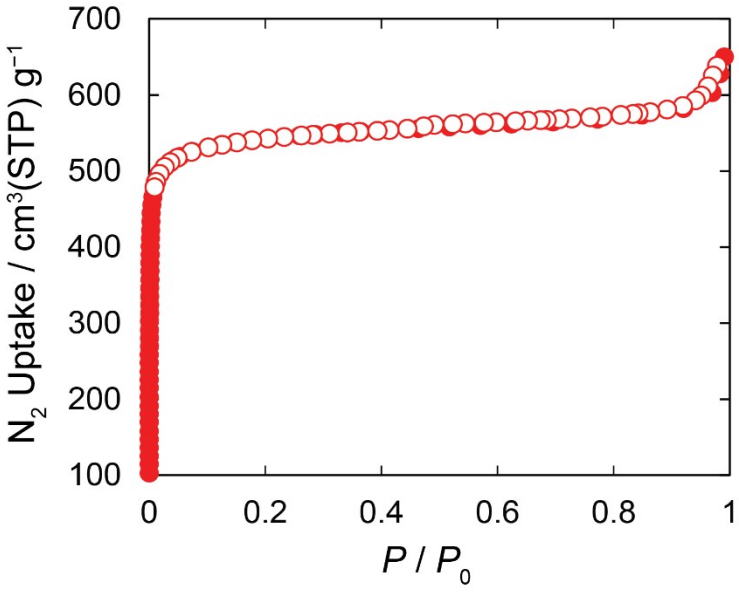


Figure S5. N_2 adsorption-desorption isotherm of Ga-BPT_p at 77 K.

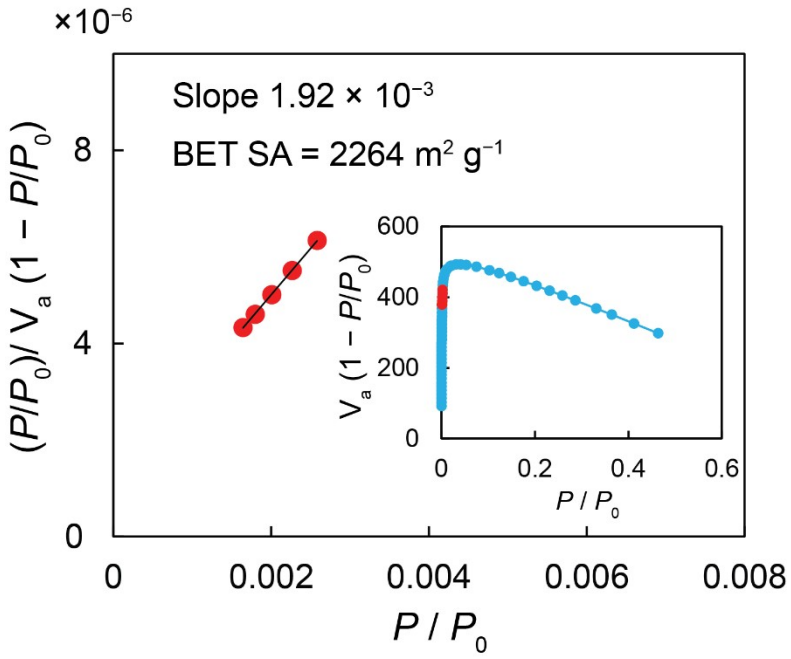


Figure S6. BET Surface area plot of Ga-BPT$_P$ and the supporting Rouquerol plot (inset).

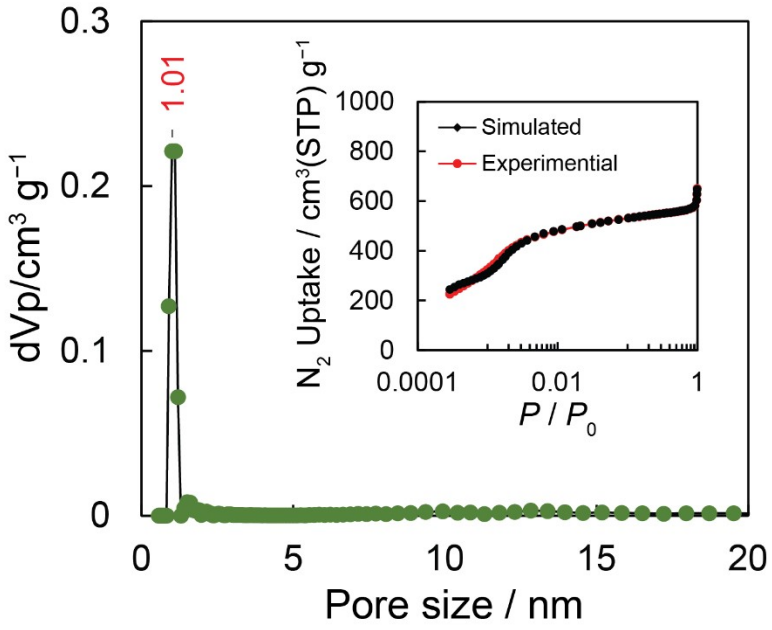


Figure S7. The pore size distribution of Ga-BPT$_P$ analyzed by the DFT method.

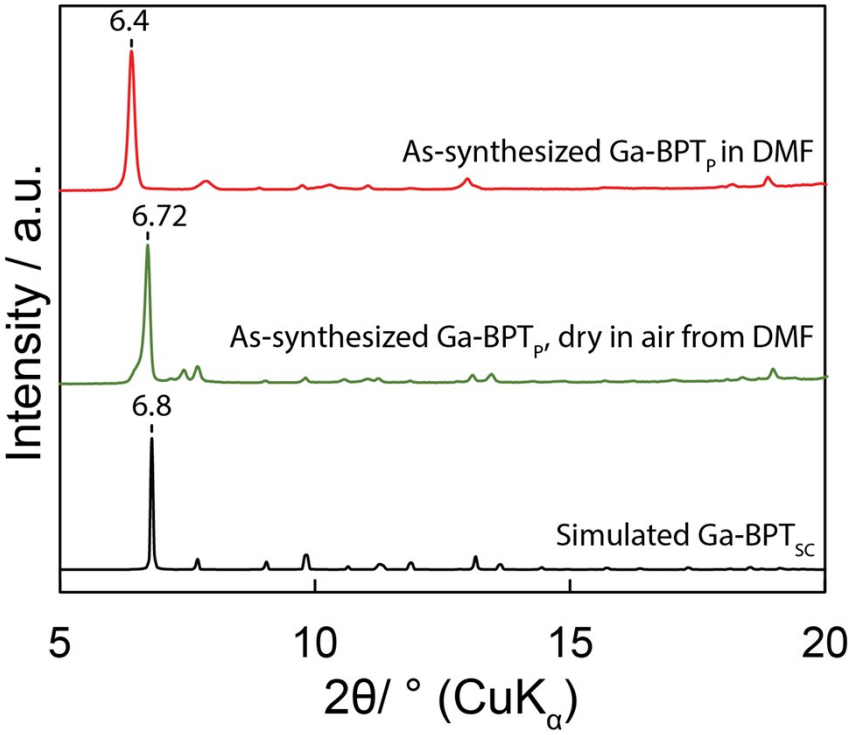


Figure S8. Monitoring PXRD patterns of Ga-BPTP upon slowly drying from DMF**.**

Section 5: Vapor adsorption isotherms of Ga-BPT$_P$

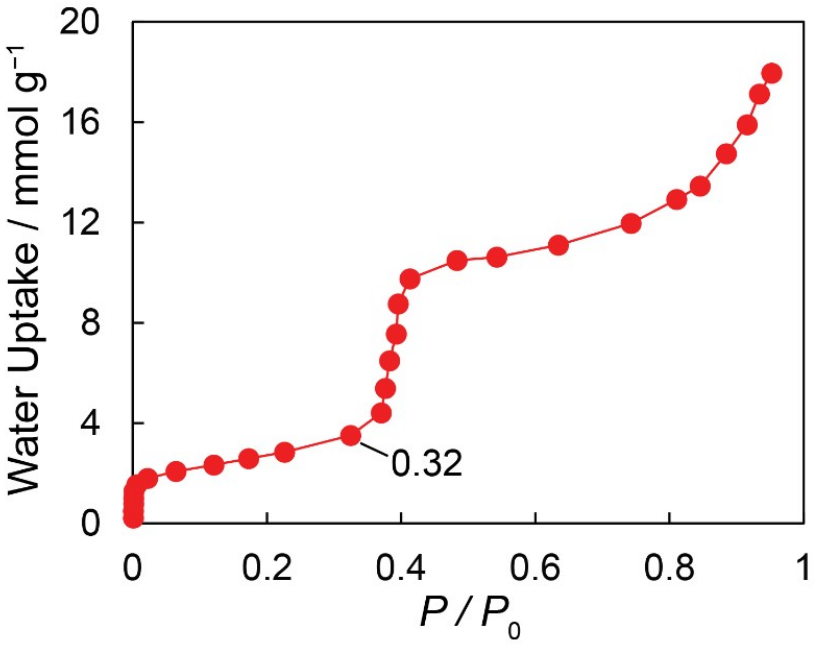


Figure S9. Water adsorption isotherm of Ga-BPT$_P$ at 298 K

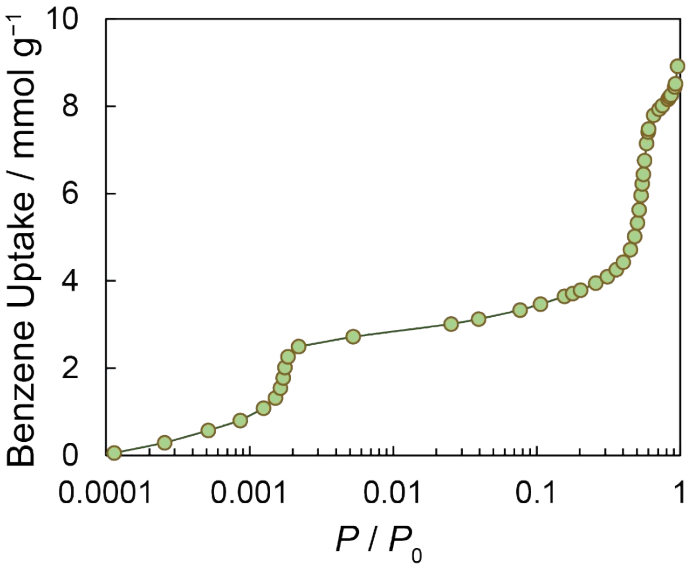
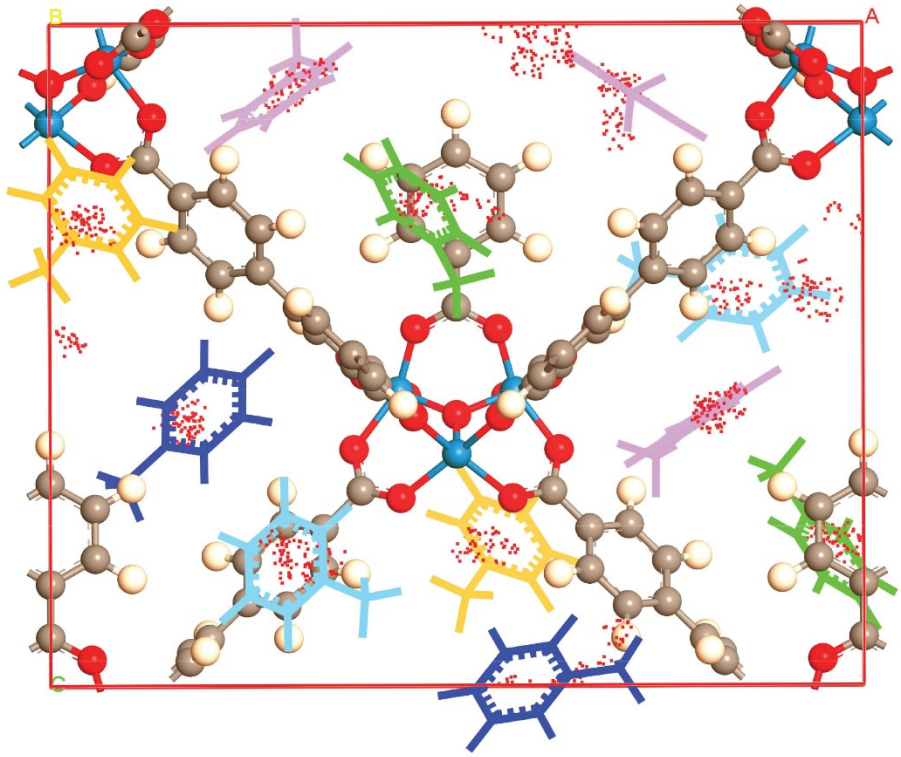


Figure S10. Benzene adsorption isotherm of Ga-BPT$_P$ at 298 K (P_0 = 12.778 kPa).

Section S6: Toluene adsorption sites in Ga-BPT$_P$



Red dots: Suggested toluene sites by GCMC

Green, yellow, light blue, purple molecules: Possible alignments of toluene in sites I, II, III, IV respectively

Figure S11. Toluene adsorption sites in Ga-BPT$_P$ by GCMC simulation.

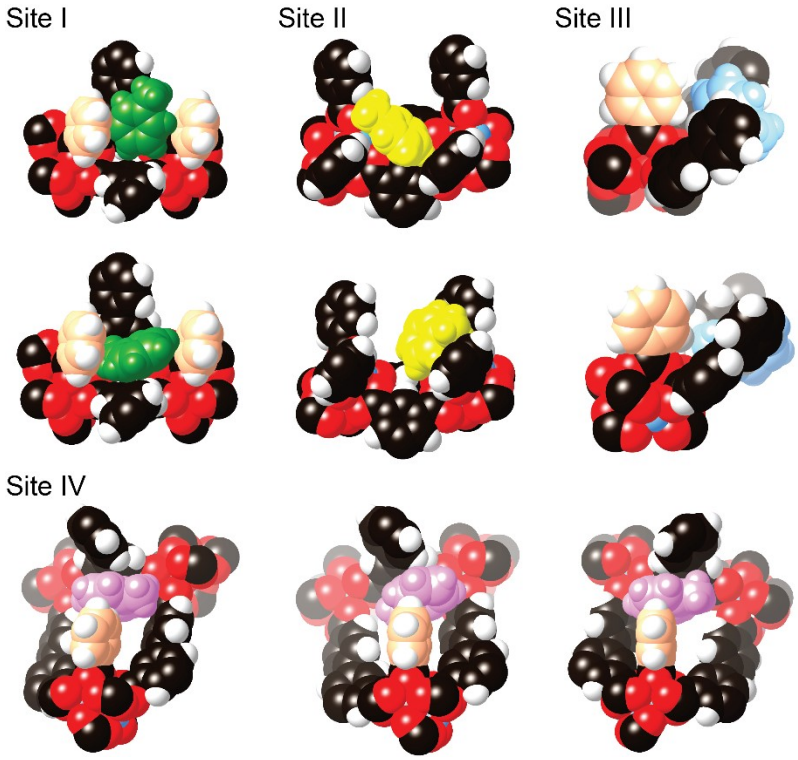


Figure S12. Possible interaction mechanism between toluene and Ga-BPT$_P$ suggested by GCMC simulation.

Section S7: Breakthrough Experiments

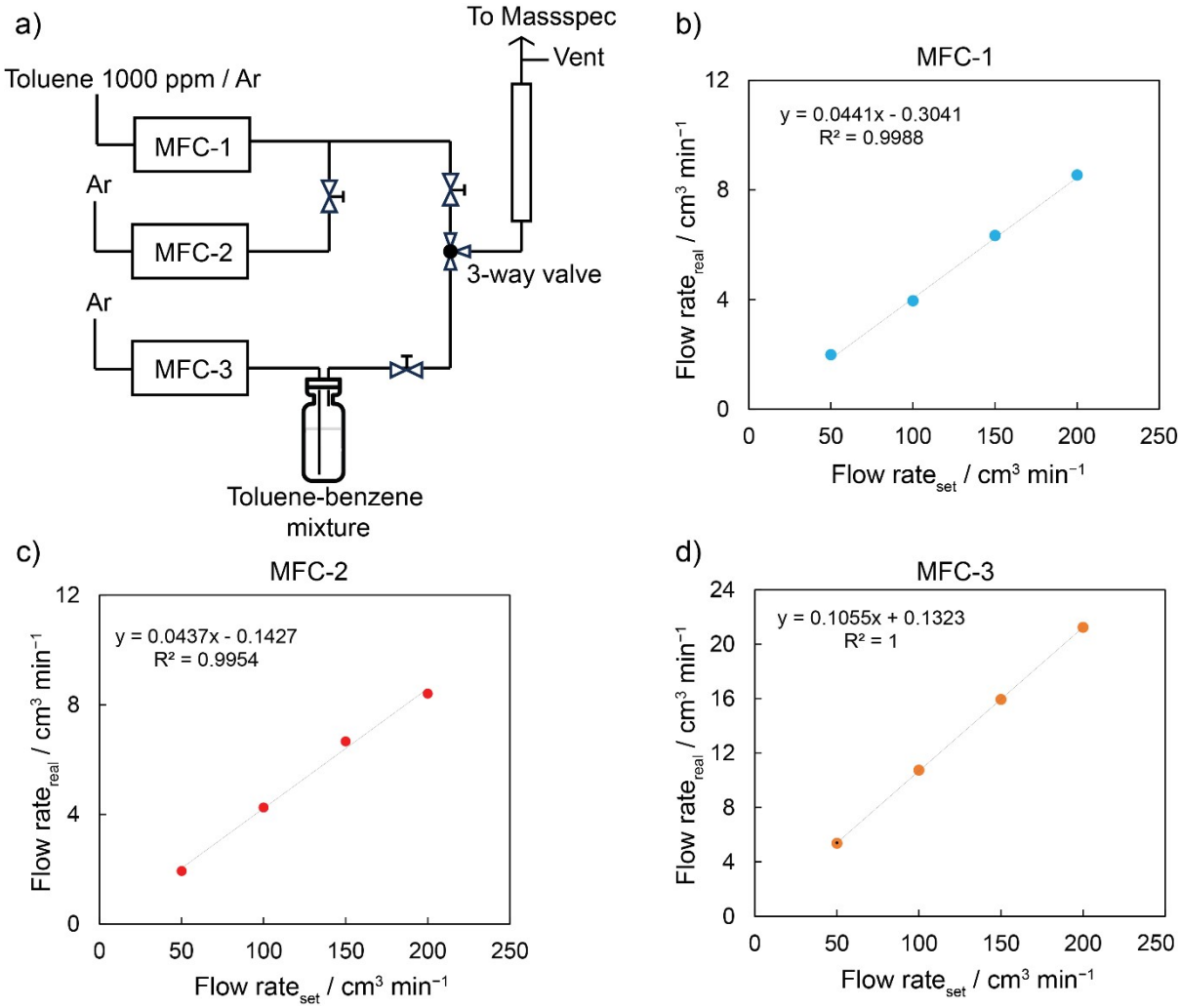


Figure S13. Customized system for analysis of the dynamic breakthrough adsorption: (a) the system diagram; and (b, c, d) the flow rate calibrations for MFC-1, 2 and 3.

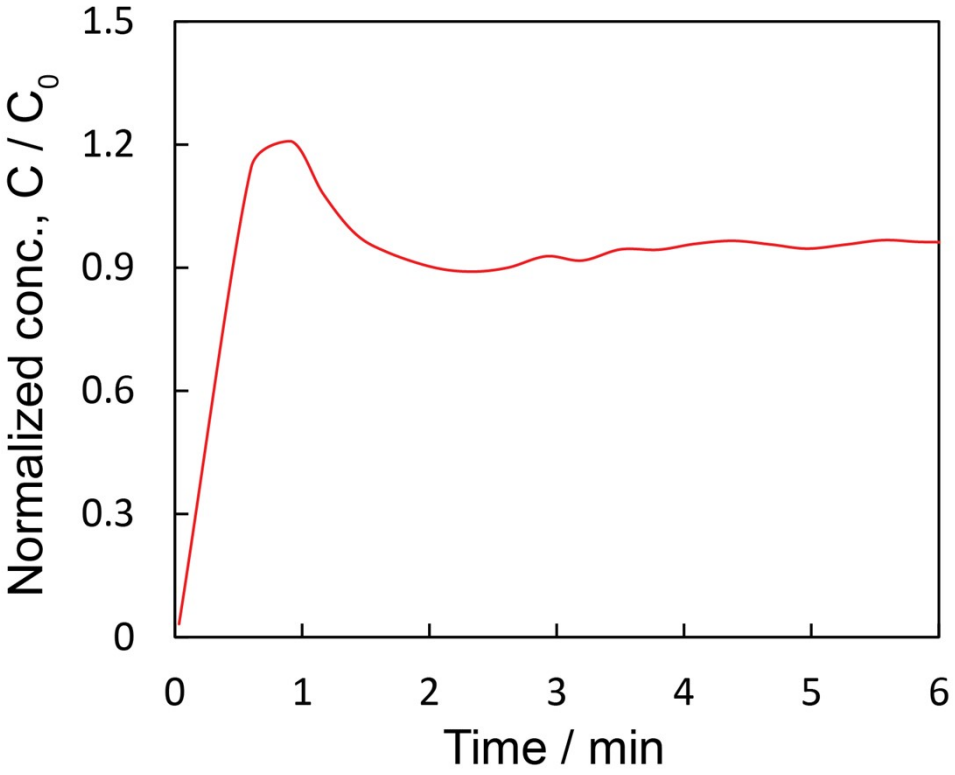


Figure S14. Toluene breakthrough profile of the dummy cell.

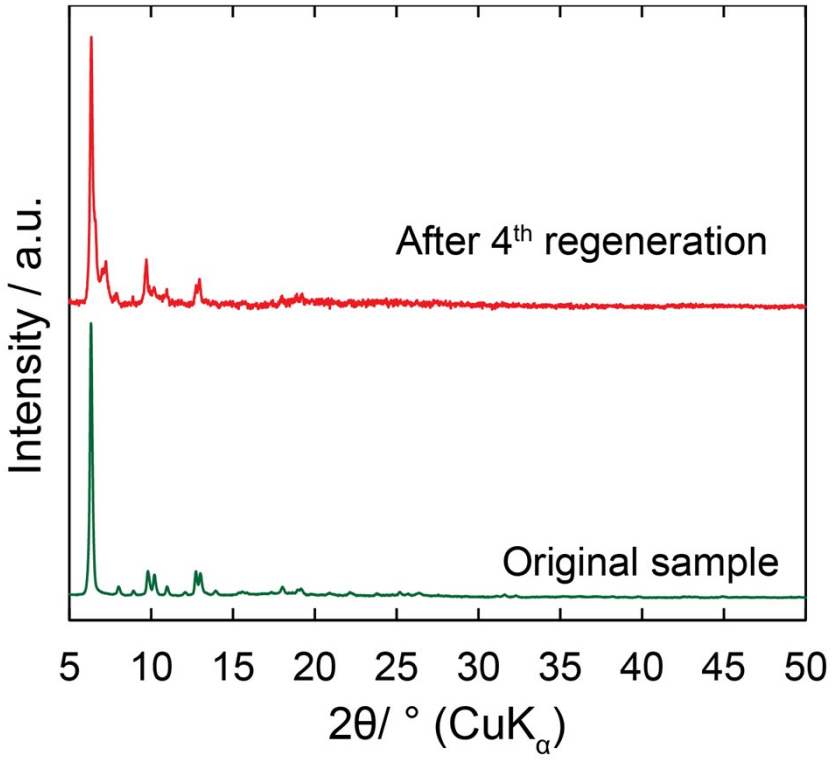


Figure S15. PXRD pattern of Ga-BPT$_{\mathbf{P}}$ after 4th-cycle breakthrough toluene capture and regeneration.

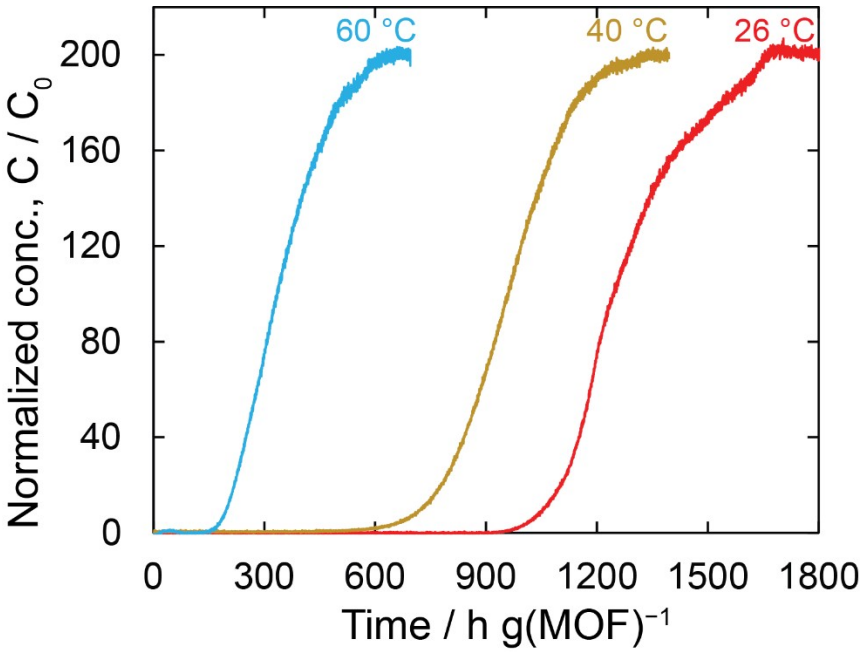


Figure S16. Toluene breakthrough profiles of Ga-BPT$_P$ at different temperature.

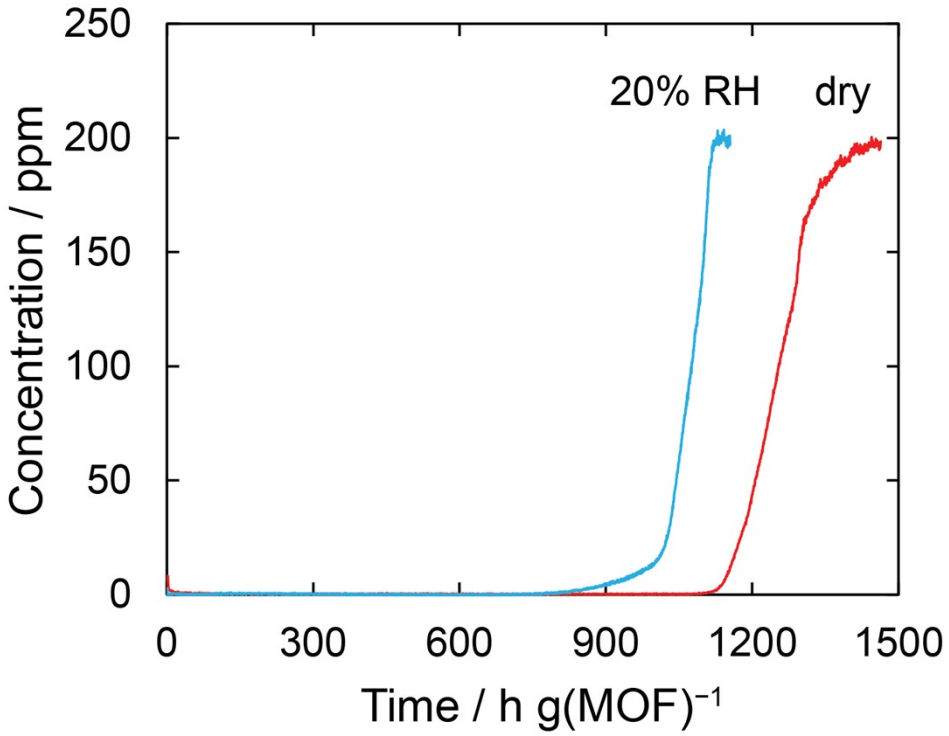


Figure S17. Toluene breakthrough profiles of Ga-BPT$_{\mathbf{P}}$ in presence of moisture.

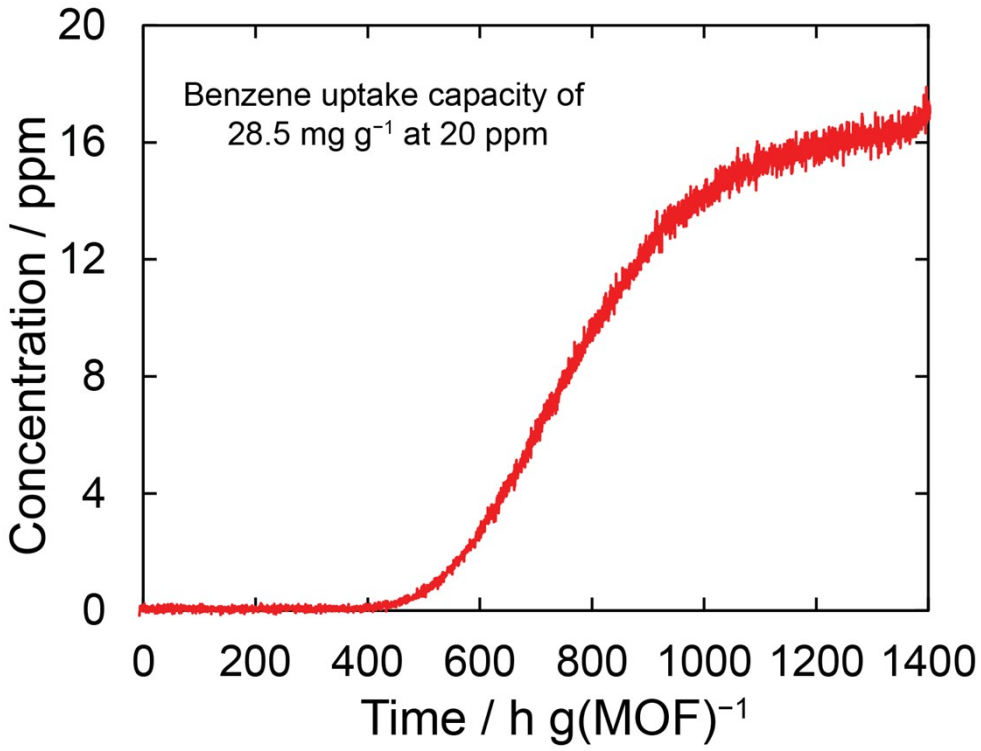


Figure S18. Benzene breakthrough profile of Ga-BPT$_{\mathbf{P}}$ at 25 °C.