Electronic Supplementary Information

Irreversible Tautomerization as a Powerful Tool to Access Unprecedented Porous Organic Polymers with Tris(β-Keto-Hydrazo)-cyclohexane Subunit

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1. Experimental details

1.1 Materials

Reagents and solvents were purchased from commercial sources and used without further purification. Phloroglucinol, sodium carbonate anhydrous, aniline were purchased from Tianjin Guanfu Fine Chemical Research Institute. 4,4'-Oxydianiline was purchased from Sinopharm Chemical Reagent Co., Ltd. 4,4'-Diphenylmethanediamine was obtained from Shanhai Titanchem Co., Ltd. Benzidine was purchased from WHAWN[®]. Tetrafluoroboric acid was obtained from Aladin[®]. Sodium nitrite was purchased from Beijing Tong Guang Fine Chemicals Company.

1.2 Instrumentation

¹H-NMR (400 MHz), ¹³C-NMR (101 MHz), ¹⁹F-NMR (370.5 MHz) and ¹⁵N-NMR (40.5 MHz) spectra and nuclear overhauser effect spectroscopy (NOESY) NMR were determined on an Oxford AS-400 magnetic resonance spectrometer (Varian, USA). Solid-state ¹³C crosspolarization magic angle spinning (CP-MAS) NMR spectra of solid samples were obtained using a Bruker Avance III 600 MHz Wide Bore spectrometer (14.2 T). A 3.2 mm MAS probe and ZrO_2 motor were used, and spin rates at 12 kHz. Chemical shifts (δ) are reported in ppm. Fourier Transform Infrared (FT-IR) spectra were recorded on a PerkinElmer Spectrum Two Fourier transform spectrometer from 500-4000 cm⁻¹. High-resolution ESI mass spectra (HR-ESI-MS) were recorded on a GCT CA127 Micronass UK mass spectrometer. Elemental analysis was measured by Vario EL elemental analyzer (Elementar Analysensysteme GmbH, Germany). Thermogravimetric analysis (TGA) was carried out on a Q600 SDT (TA, USA) thermogravimetric analyzer, heated from 25 °C to 800 °C at a rate of 20 °C/min under N₂ atmosphere. Nitrogen adsorption/desorption isotherms at 77 K were obtained using a BELSORP Max II (MicrotracBEL Corp.) static volumetric analyzer. Prior to adsorption measurements, the samples were degassed for 12 h at 120 °C to remove residual moisture and other trapped gases. The Brunauer-Emmett-Teller (BET) surface area was calculated within the relative pressure (P/P_0) range 0.05 to 0.35. The total pore volume was calculated at P/P_0 of about 0.995. The non-local density functional theory (NLDFT) methods was used to establish the pore size distribution and pore diameter (DP). Volatile organic compounds (VOCs) adsorption isotherms of the TKH-POPs after degassing for 12 h at 120 °C were investigated on a vapor sorption system (Belsorp MaxII). The saturated vapor pressures of VOCs were

calculated by the Antoine equation.¹ Scanning electron microscopy (SEM) images were taken by a Hitachi S4800 scanning electron microscope. Transmission electron microscopy (TEM) was performed using a FEI Tecnai G2 F30 high resolution transmission electron microscope operating at 300 kV. Powder X-ray diffraction (PXRD) patterns were recorded by a X-Pert3 Powder (PANalytical, Netherlands) diffractometer.

1.3 The synthesis of model compound

1.3.1 The synthesis of model compound 1

Benzenediazonium tetrafluoroborate ($C_6H_5N_2^+BF_4^-$): A pre-cooling sodium nitrite (1.4 g, 20 mmol, 1 eq.) in water (5 mL) was added into a mixture solution of HBF₄(50 wt% in water, 6 mL) and aniline (1.8 mL, 20 mmol, 1 eq.) in water (6 mL) in an ice-water bath. After 10 min of vigorous stirring, the precipitate was collected by filtration followed by washing with little ice-cold water, and the white crystalline was obtained by re-dissolved in acetone and then precipitated with the addition of diethyl ether, then drying to give benzenediazonium tetrafluoroborate ($C_6H_5N_2^+BF_4^-$) (3.3 g, 87% yield).

¹H NMR (400 MHz, DMSO-d₆) δ (ppm): 8.59 (d, J = 8.0 Hz, 2H), 8.31 (t, J = 8.0 Hz, 1H), 7.98 (t, J = 8.0 Hz, 2H).

¹³C NMR (101 MHz, DMSO-d₆) δ (ppm): 140.88, 132.72, 131.29, 116.14.

¹⁹F NMR (370.5 MHz, DMSO-d₆) δ (ppm): -148.12, -148.17.

FT-IR (ATR, cm⁻¹): 3108 (w), 2295 (m), 1570 (m), 1462 (w), 1312 (w), 1290 (w), 1023 (s), 990 (s), 944 (m), 756 (s), 665 (m), 530 (m).



The above prepared diazonium salt (1.28 g, 6.7 mmol) solved in methanol (5 mL) was added into a solution of phloroglucinol (162 mg, 1 mmol) and sodium hydroxide (NaOH, 120 mg, 3 mmol) in methanol (10 mL). The reaction mixture was stirred for $1\sim$ 2 h. The resulting precipitate was filtered, washed by methanol and dried to afford model compound **1** (345 mg, 79% yield).

¹H NMR (400 MHz, CDCl₃) δ (ppm): 16.33 (s, 3H), 7.66 (d, J = 8.0 Hz, 6H), 7.47 (t, J = 8.0 Hz, 6H), 7.31 (t, J = 8.0 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 178.81, 141.37, 129.98, 128.94, 127.72, 117.77.

FT-IR (ATR, cm⁻¹): 3063 (w), 3014 (w), 1603 (m), 1583 (m), 1475 (s), 1450 (s), 1403 (s), 1308 (m), 1219 (s), 1186 (s), 1157 (s), 1099 (w), 1077 (m), 1046 (s), 996 (m), 903 (w), 838 (m), 790 (m), 750 (s), 683 (s), 645 (m), 506 (m), 496 (m), 466 (m).

MS (ESI): m/z 439.15052 (M+H⁺, required 439.15131).

Anal. Calculated (%) for C₂₄H₁₈N₆O₃ (438.14): C, 65.75; H, 4.14; N, 19.17; O, 10.95. Found: C, 65.76; H, 4.10; N, 18.72; O, 11.42.

1.3.2 The synthesis of ¹⁵N-labled model compound 1

Benzenediazonium tetrafluoroborate ($C_6H_5N_2^+BF_4^-$ **):** A pre-cooling ¹⁵N-labled sodium nitrite (0.7 g, 10 mmol, 1 eq.) in water (3 mL) was added into a mixture solution of HBF₄ (50 wt% in water, 3 mL) and aniline (0.9 mL, 10 mmol, 1 eq.) in water (3 mL) in an ice-water bath. After 10 min of vigorous stirring, the precipitate was collected by filtration followed by washing with little ice-cold water, and the white crystalline was obtained by re-dissolved in acetone and then precipitated with the addition of diethyl ether, then drying to give ¹⁵N-labled benzenediazonium tetrafluoroborate ($C_6H_5N_2^+BF_4^-$) (1.2 g, 61% yield).



The above prepared ¹⁵N-labled diazonium salt (1.2 g, 6 mmol) solved in methanol (5 mL) was added into a solution of phloroglucinol (162 mg, 1 mmol) and sodium hydroxide (NaOH, 120 mg, 3 mmol) in methanol (10 mL). The reaction mixture was stirred for 1~2 h. The resulting precipitate was filtered, washed by methanol and dried to afford ¹⁵N-labled model compound **1** (311 mg, 71% yield).

¹⁵N NMR (40.5 MHz, CDCl₃) δ (ppm): 7.73. (CH₃NO₂: 0 ppm)

1.3.3 The synthesis of model compound 2

4-Methylbenzenediazonium Tetrafluoroborate (p-CH₃C₆H₄N₂+BF₄-): A pre-cooling sodium nitrite (1.4 g, 20 mmol, 1 eq.) in water (5 mL) was added into a mixture solution of HBF₄ (50wt% in water, 6 mL) and p-toluidine (2.15 g, 20 mmol, 1 eq.) in water (6 mL) in an ice-water bath. After 10 min of vigorous stirring, the precipitate was collected by filtration followed by washing with little ice-cold water, and the white crystalline was obtained by redissolved in acetone and then precipitated with the addition of diethyl ether, then drying to give 4-Methylbenzenediazonium Tetrafluoroborate (p-CH₃C₆H₄N₂+BF₄-) (3.74 g, 91% yield). ¹H-NMR (400 MHz, DMSO-d₆) δ (ppm): 8.53 (d, *J*=8.8 Hz, 2H), 7.78 (d, *J*=8.8 Hz, 2H), 2.57 (s, 3H).

¹³C-NMR (100 MHz, DMSO-d₆) δ (ppm): 153.94, 132.65, 131.75, 111.93, 23.27.



The above prepared diazonium salt (1.38 g, 6.7 mmol) solved in methanol (5 mL) was added into a solution of phloroglucinol (162 mg, 1 mmol) and sodium

hydroxide (NaOH, 120 mg, 3 mmol) in methanol (10 mL). The reaction mixture was stirred for $1\sim2$ h. The resulting precipitate was filtered, washed by methanol and dried to afford model compound **2** (378 mg, 79 % yield).

¹H NMR (400 MHz, CDCl₃) δ (ppm): 16.41 (s, 3H), 7.54 (d, *J* = 8.0 Hz, 6H), 7.26 (d, *J* = 7.6 Hz, 6H), 2.39 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 178.75, 139.23, 137.95, 130.55, 128.67, 117.71, 21.37. FT-IR (ATR, cm⁻¹): 3029 (w), 3007 (w), 2916 (w), 2858 (w), 1601 (m), 1579 (m), 1466 (s), 1401 (s), 1315 (s), 1228 (s), 1189 (s), 1163 (s), 1086 (m), 1072 (m), 1049 (s), 806 (s), 754 (m), 638 (w), 508 (m), 462 (w).

MS (ESI): m/z: 481.19922 (M+H+, required 481.19827).

1.3.4 The synthesis of model compound 3

4-Methoxybenzenediazonium Tetrafluoroborate (p-CH₃OC₆H₄N₂⁺BF₄⁻): A pre-cooling sodium nitrite (1.4 g, 20 mmol, 1 eq.) in water (5 mL) was added into a mixture solution of HBF₄ (50wt% in water, 6 mL) and p-anisidine (2.46 g, 20 mmol, 1 eq.) in water (6 mL) in an ice-water bath. After 10 min of vigorous stirring, the precipitate was collected by filtration followed by washing with little ice-cold water, and the white crystalline was obtained by redissolved in acetone and then precipitated with the addition of diethyl ether, then drying to give 4-Methoxybenzenediazonium Tetrafluoroborate (p-CH₃OC₆H₄N₂⁺BF₄⁻) (4.28 g, yield 96%).

¹H-NMR (400 MHz, DMSO-d₆) δ (ppm): 8.62 (d, *J*=8.8 Hz, 2H), 7.50 (d, *J*=9.6 Hz, 2H), 4.04 (s, 3H).

¹³C-NMR (100 MHz, DMSO-d₆) δ (ppm): 168.81, 136.15, 117.30, 103.36, 57.49.



The above prepared diazonium salt (1.38 g, 6.7 mmol) solved in methanol (5 mL) was added into a solution of phloroglucinol (162 mg, 1 mmol) and sodium hydroxide (NaOH, 120 mg, 3 mmol) in methanol (10 ml). The reaction mixture was stirred for 1~2 h. The resulting precipitate was filtered, washed by methanol and dried to afford model compound **3** (459 mg, 87 % yield).

¹H NMR (400 MHz, CDCl₃) δ(ppm): 16.59 (s, 3H), 7.58 (d, *J* = 8.4 Hz, 6H), 6.97 (d, *J* = 7.6 Hz, 6H), 3.85 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ(ppm): 178.52, 159.35, 135.04, 128.28, 119.17, 115.21, 55.78.

FT-IR (ATR, cm⁻¹): 3005 (w), 2956 (w), 2925 (w), 2837 (w), 1606 (m), 1510 (m), 1476 (s), 1430 (m), 1405 (s), 1319 (m), 1300 (m), 1233 (s), 1180 (m), 1031 (m), 1001 (w), 827 (w), 520 (w).

MS (ESI): m/z: 529.18304 (M+H+, required 529.18301).

1.4 The synthesis of TKH-POPs

Taking the preparation of TKH-POP-1 as an example, the diazo-coupling reaction was carried as follows. 100 mL of 4,4'-diaminobiphenyl (276 mg, 1.5 mmol) aqueous was mixed with 2.3 mL of HBF₄ (50 wt% solution in water) at 0 °C. After stirring for 15 min, 30 mL of sodium nitrite (3.1 mmol) aqueous was added and stirred for 25 min to get the bis(diazonium) salt. Subsequently, the mixture was neutralized to pH 7.0 with a diluted Na₂CO₃ solution, and then mixed with 30mL of aqueous solution of phloroglucinol (126 mg, 1 mmol) and Na₂CO₃ (3 mmol) at 0 °C. After stirring for 12 h, the solid sample was filtered, washed successively with water, methanol, DMF, methanol, and water, and then lyophilized to obtain the porous polymer (426 mg, 98% yield). Similarly, TKH-POP-2, TKH-POP-3 and TKH-POP-4 were prepared using the corresponding monomers in yields of 90%, 91% and 95%, respectively.

TKH-POP-1:

FT-IR (cm⁻¹): 3033 (w), 1599 (m), 1472 (s), 1432 (m), 1400 (s), 1317 (m), 1220 (s), 1167 (s), 1090 (m), 1051 (s), 1032 (m), 1002 (m), 820 (s), 764 (w), 732 (w), 630 (w), 552 (w), 517 (w). ¹³C CP/MS NMR, δ (ppm): 177.71, 140.93, 127.89, 117.62.

TKH-POP-2:

FT-IR (cm⁻¹): 2923 (w), 1603 (m), 1580 (m), 1475 (s), 1425 (s), 1404 (s), 1307 (m), 1222 (s), 1203 (s), 1168 (m), 1089 (m), 1050 (s), 1029 (m), 1000 (m), 916 (w), 822 (m), 773 (m), 707 (w), 638 (w), 623 (w), 515 (w).

¹³C CP/MS NMR, δ (ppm): 178.60, 140.09, 129.12, 118.04; 40.94.

TKH-POP-3:

FT-IR (cm⁻¹): 3061 (w), 1594 (m), 1477 (s), 1427 (m), 1402 (s), 1312 (m), 1220 (s), 1184 (s), 1106 (w), 1089 (m), 1051 (m), 1029 (m), 831 (m), 705 (w), 613 (w), 519 (w).

¹³C CP/MS NMR, δ (ppm): 177.90, 158.12, 137.77, 129.33; 119.09.

TKH-POP-4:

FT-IR (cm⁻¹): 3439 (w), 3060 (w), 1608 (m), 1475 (vs), 1448 (m), 1419 (vs), 1402 (vs), 1317 (s), 1220 (s), 1171 (s), 1115 (w), 1090 (m), 1050 (s), 1029 (s), 998(m), 914 (m), 823 (s), 747 (s), 732 (s), 629 (m).

¹³C CP/MS NMR, δ (ppm): 177.89, 149.60, 140.17, 127.48, 119.47, 64.95.

1.5 VOCs adsorption tested by weighing method

In the VOCs adsorption test by weighing method, a certain amount of porous polymer was weighed and loaded in a small beaker, which was then placed into a larger beaker with a small amount of ethanol. They were sealed by preservation film with some pinholes and placed in a fume hood to allow ethanol solvent to produce ethanol vapor around the porous polymers. After 12 h at the room temperature, the mass of the porous polymer was measured again. Adsorption capacity value was thus calculated. The other organic vapours adsorption experiments were done following the same procedure.

1.6 Static adsorption measurements

The adsorption properties of H₂O, acetonitrile, benzene and ethanol on TKH-POPs and Azo-POP-4 were measured on a vapor sorption system (Belsorp MaxII). 298 K was selected as adsorption temperature for the VOCs adsorption, and 273 K was the extra selected temperature for the ethanol vapor adsorption to measure the isosteric heat of adsorption. The saturation vapor pressures of adsorbates were calculated by the Antoine equation.¹ The isosteric heat of adsorption, Q_{st} (sometimes it denoted as $-\Delta H$), is defined by the equation of the Clausius–Clapeyron type:^{2, 3}

$$\frac{Q_{st}}{RT^2} = \left[\frac{\partial(lnP)}{\partial(T)}\right]_N \tag{1}$$

where Q_{st} (kJ mol⁻¹) is the isosteric heat of adsorption, R (8.314 × 10⁻³ kJ mol⁻¹ K⁻¹) is the ideal gas constant, T (K) is the testing temperature, P (Pa) is the vapor feed pressure.

1.7 Computational methods

The unrestricted density functional theory (UDFT) with the hybrid functional B3LYP⁴⁻⁶ were used in all calculations, as implemented in the Jaguar 8.7 package (Jaguar, version 8.7, Schrodinger, Inc., New York, NY, 2015.). Geometry optimizations were carried out with the 6-31+G(d,p) basis set for all atoms. On the basis of the optimized geometries, more accurate energies were obtained by performing single-point calculations with a larger basis set cc-pVTZ(-f)+ for all elements. Using Gaussian 09 program package (Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford CT, 2013.), frequency calculations were performed at the same theory level as the optimizations to confirm the nature of the stationary points and to obtain zero-point energies (ZPE) and entropy effects. The solvation effects were estimated at the same theory level as the optimizations by performing single-point calculations on the optimized structures using the self-consistent reaction field (SCRF) method with a Poisson–

Boltzmann solver^{7, 8}, as implemented in Jaguar 8.7 (Jaguar, version 8.7, Schrodinger, Inc., New York, NY, 2015).

2. Tables

Entry	Purification of Diazonium Salt ^a	pН	Solvents	Isolated Yield (%)	BET Surface Area (m ² g ⁻¹)
1	Yes	2 ^b	H ₂ O	81	27
2	Yes	7	H_2O	52	114
3	Yes	7	EtOH ^c	46	12
4	No	7	H_2O	98	398

Table S1. Optimization of the preparation of TKH-POP-1.

All the experiments were carried out as following except other indication: The solubility of 1 mmol phlorogucinal in H₂O was achieved by mixing with 3 mmol Na₂CO₃, and the pH value of the reaction media was adjusted at 7 by dilute Na₂CO₃ solution. ^aThe diazonium salt was purified by filtration followed by washing with ice-cold water and lyophilized to powder. ^bThe pH value of the reaction media wasn't adjusted. ^cThe 1 mmol phlorogucinal was soluble in EtOH.

Samples ^[a]	N%	BET SA	Total Pore	Yield
	Content ^[a]	$(m^2 g^{-1})$	Volume	(%) ^[c]
			$(cm^3 g^{-1})^{[b]}$	(, 0)
TKH-POP-1	15.49	398	1.5	98
TKH-POP-2	15.36	437	1.4	90
TKH-POP-3	15.32	552	2.3	91
TKH-POP-4	11.79	639	2.2	95

Table S2 The physicochemical properties of the TKH-POPs

[a] Measured by Vario EL elemental analyzer. [b] Calculated from the N₂ adsorbted at $P/P_0 = 0.99$. [c] Isolated yield.

Tuble 55. Elemental analysis of the TKTTTOTS.						
Polymer	Found			Calculated		
	N	С	Н	N	С	Н
TKH-POP-1	15.49	69.08	5.03	19.29	66.14	3.44
TKH-POP-2	15.36	65.02	4.32	18.40	63.09	3.29
TKH-POP-3	15.32	65.13	4.35	18.28	62.68	3.26

Table S3. Elemental analysis of the TKH-POPs.

Table S4. Comparison the adsorption capacity for H₂O of TKH-POP-1 at 298 K and relative pressure of 0.2 ($P/P_0=0.2$) with other functionalized porous materials.

Adsorbents	BET surface area (m ² g ⁻¹) ^a	Adsorption amount (mmol g ⁻¹)	Ref
NC100	1493	<1	9
Carbon nanotube	510 - 1650	< 0.02	10-12
Carbide-derived carbon	2479	0.02 - 0.04	13
 TKH-POP-1	398	2	This work

^aObtained from the N₂ isotherms at 77 K.

Table S5. Comparison the adsorption capacity for H_2O of TKH-POP-1 at 298 K and constant vapor pressure with other functionalized porous materials.

Adsorbents	BET surface area $(m^2 g^{-1})^a$	Adsorption capacity (mmol g ⁻¹)	Ref
NC100	1493	37.8	9
Activated carbon fiber cloth ACC-5092-25	1763	36.1	14
De-solvated $[ZnL(HCO_2)]_{\infty}$		27.4	15
1-Gly functionalized porous materials		12.8	16
Coordination polymer [Cu(4-pmntd) (opd)] _n		5.6	17
Cobalt(II) coordination polymer $\{[Co(3-pmpmd)_{1.5}(NO_3)_2] \cdot 0.8CH_3OH\}_n$		5.4	18
Hydrophilic covalent organic nanosheet TpASH		11.3	19
TKH-POP-1	398	39.6	This work

^aObtained from the N₂ isotherms at 77 K.

Adsorbents	BET surface area (m ² g ⁻¹) ^a	Adsorption capacity (mmol g ⁻¹)	Ref
NENU-28	470	4.78	20
NENU-29	466	4.25	20
NENU-3	405	3.97	20
$Cu_3(BTC)_2$	1507	3.54	20
Microorous MOF {[Dy(ox)(Bpybc)(H ₂ O)]·OH·13H ₂ O} _n		0.08	21
FJI-C1	1726	1.24	22
Cu-L3 MOF		2.5	23
Porous frameworks [CuCl(BCbpy)(Ser)] · 5 H ₂ O		3.91	16
Commercial Activated carbon	316	4.5	This work
TKH-POP-1	398	22.2	This work

Table S6. Comparison the adsorption capacity for ethanol of TKH-POP-1 at 298 K with other adsorbents.

^aObtained from the N_2 isotherms at 77 K.

Table S7.	Comparison	the adsorption	capacity for	acetonitrile	of TKH-PO	P-1 at 2	98
K with oth	her adsorbent	S.					

Adsorbents	BET surface area (m ² g ⁻¹) ^a	Adsorption capacity (mmol g ⁻¹)	Ref
Micrporous MOF {[Dy(ox)(Bpybc)(H ₂ O)]·OH·13H ₂ O} _n		2.2	21
Coordination network [Cu(4-pmntd) (opd)] _n		0.45	17
$MOF \ \{[Ni^{II}(dpzca)_2Ag](BF_4)(acetone)_{0.5}\}_{\infty}$	3.5 ^b	0.68	24
Unoxidized VPCs		<26.5°	25
Commercial activated carbon	316	17.0	This work
TKH-POP-1	398	35.8	This work

^aObtained from the N_2 isotherms at 77 K.

^bObtained from the Ar_2 isotherms at 77 K.

^cObtained from simulated CH₃CN adsorption isotherms by the hyper parallel tempering Monte Carlo (HPTMC) method.

Adsorbents	BET surface area $(m^2 g^{-1})^a$	Adsorption capacity (mmol g ⁻¹)	Ref
NENU-28	470	3.42	20
NENU-29	466	3.38	20
NENU-3	405	3.29	20
$Cu_3(BTC)_2$	1507	3.21	20
PAF-11	704	11.2	26
FJI-C1	1726	1.71	22
PCBs-3	1090	17.92	27
VACFs	1233	6.40	28
Commercial activated carbon	316	5.4	This work
TKH-POP-1	398	18.2	This work

Table S8. Comparison the adsorption capacity for benzene of TKH-POP-1 at 298 K with other adsorbents.

 $^{a}Obtained$ from the N_{2} isotherms at 77 K.

3. Figures



Figure S1. HR-ESI-MS spectrum of model compound 1.



Figure S2. HR-ESI-MS spectrum of model compound **2**.



Figure S3. HR-ESI-MS spectrum of model compound **3**.



Figure S4. Comparison of FT-IR between (a) TKH-POP-1 and model compound **1**, (b) TKH-POP-2 and model compound **2**, (c) TKH-POP-3 and model compound **3**.



Figure S5. ¹H-NMR spectrum of model compound **1** in CDCl₃.



Figure S6. ¹³C-NMR spectrum of model compound **1** in CDCl₃.



Figure S7. 15 N-NMR spectrum of model compound 1 in CDCl₃.



Figure S8. NOESY NMR spectrum of model compound 1 in CDCl₃.



Figure S9. C-H HSQC NMR spectrum of model compound 1 in CDCl₃.



Figure S10. C-H HMBC NMR spectrum of model compound 1 in CDCl₃.



Figure S11. N-H HSQC NMR spectrum of model compound 1 in CDCl₃.



Figure S12. ¹H-NMR spectrum of model compound **2** in CDCl₃.



Figure S13. ¹³C-NMR spectrum of model compound **2** in CDCl₃.



Figure S14. NOESY NMR spectrum of model compound 2 in CDCl₃.



Figure S15. C-H HSQC NMR spectrum of model compound **2** in CDCl₃.



Figure S16. C-H HMBC NMR spectrum of model compound **2** in CDCl₃.



Figure S17. ¹H-NMR spectrum of model compound **3** in CDCl₃.



Figure S18. 13 C-NMR spectrum of model compound **3** in CDCl₃.



Figure S19. NOESY NMR spectrum of model compound **3** in CDCl₃.



Figure S20. C-H HSQC NMR spectrum of model compound **3** in CDCl₃.



Figure S21. C-H HMBC NMR spectrum of model compound **3** in CDCl₃.



Figure S22. Adsorption (filled symbols) and desorption (empty symbols) isotherms of N₂ at 77 K for the TKH-POP-1 prepared by different ways shown in Table S1.



Figure S23. Micrographs for (a, b) TKH-POP-1, (c, d) TKH-POP-2, (e, f) TKH-POP-3 and (g, h) TKH-POP-4. (a, c, e, g) SEM images, scale bar: 100 nm. (b, d, f, h) TEM images, scale bar: 50 nm.



Figure S24. Powder X-Ray Diffraction analysis of TKH-POPs.



Figure S25. The TG Analysis of (a) TKH-POP-1, (b) TKH-POP-2, (c) TKH-POP-3 and (d) TKH-POP-4.



Figure S26. The adsorption rate of TKH-POP-1 towards organic vapours at 298 K.



Figure S27. Adsorption (filled symbols) and desorption (empty symbols) isotherms of N₂ at 77 K for the activated carbon, and the BET surface area was calculated from the N₂ adsorbted at $P/P_0 = 0.05 \sim 0.3$, the total pore volume was calculated from the N₂ adsorbted at $P/P_0 = 0.99$.



Figure S28. Adsorption isotherms of ethanol, acetonitrile and benzene on activated carbon at 298 K.



Figure S29. Adsorption isotherms of ethanol on TKH-POP-1 at 298 K.



Figure S30. Adsorption isotherms of ethanol on TKH-POP-1 at 273 K.



Figure S31. The isosteric heats of adsorption with ethanol adsorbed by TKH-POP-1.

4. Schemes



Scheme S1. The syntheses of model compound 1-3



Scheme S2. The syntheses of TKH-POP-1-4

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