Supporting Information

Assembly and spontaneous resolution of the chiral inorganic

polyoxometalates-based frameworks via helical chains association

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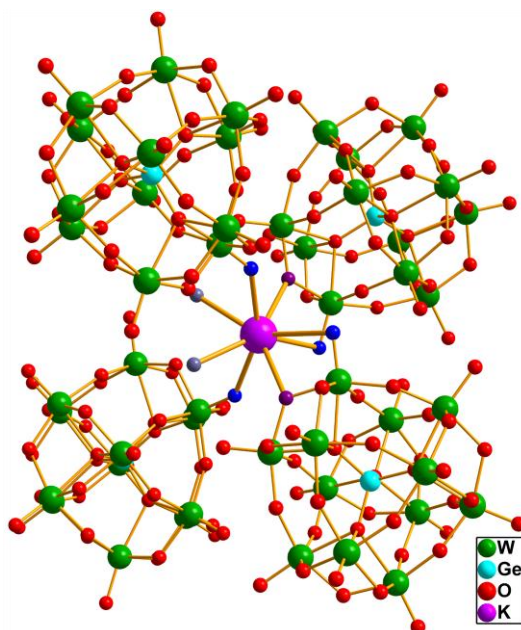*E-mail: liusx@nenu.edu.cn*

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Fig. S1 The K^+ cation eightfold coordinates to four terminal oxygen atoms (blue) of four $[GeW_{12}O_{40}]^{4-}$ polyoxoanions, two μ_2-bridging oxygens (violet) of two $[GeW_{12}O_{40}]^{4-}$ polyoxoanions, and two water molecules (blue gray).
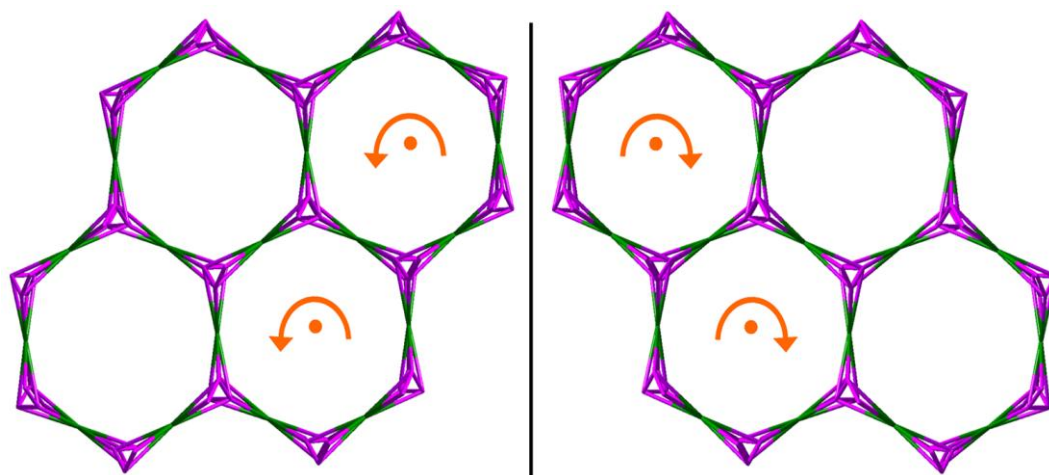

Fig. S2 Schematic representations of mirror images of 3D chiral inorganic frameworks in compounds **1a** and **2a** (left), and **1b** and **2b** (right). (The handedness of some helices is illustrated as arrows). The K^+ cation as a four-connected node, and each $[GeW_{12}O_{40}]^{4-}$ or $[SiW_{12}O_{40}]^{4-}$ as an eight-connected node.
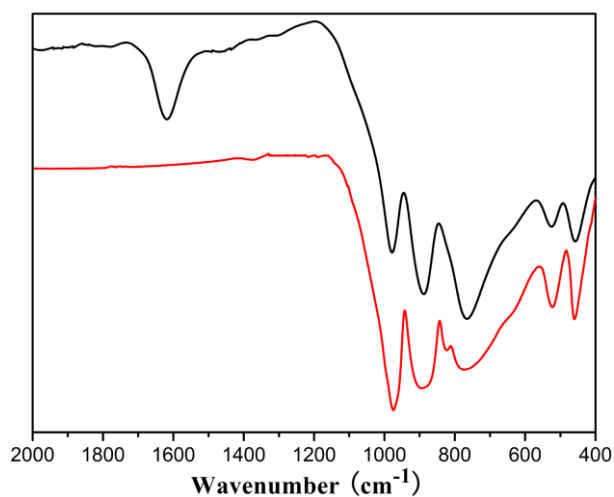
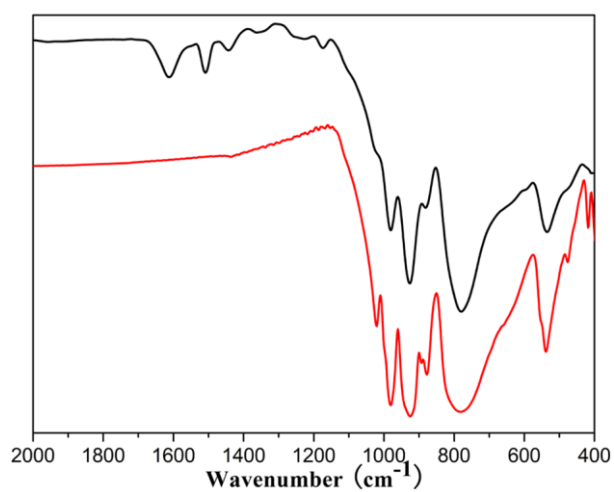**Fig. S3** The IR spectra of the compound **1** (black) and the thermally activated form of **1** (red).

Fig. S4 The IR spectra of the compound **2** (black) and the thermally activated form of **2** (red).
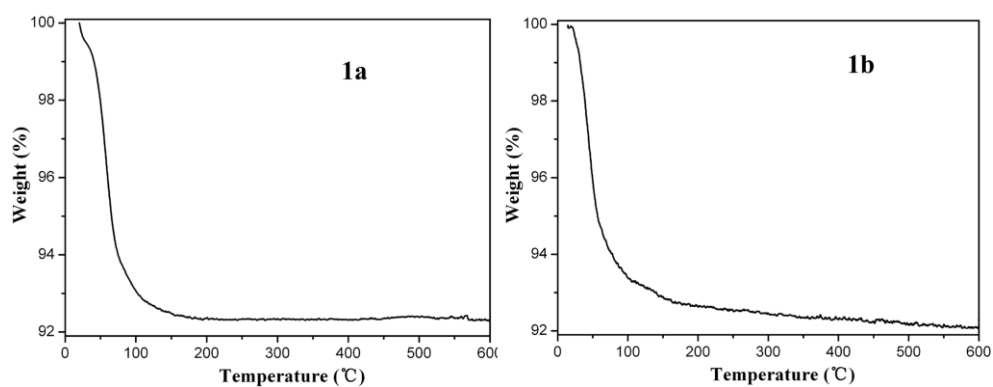

Fig. S5 The TG curves of **1a** and **1b** exhibit one weight loss stages in the temperature ranges 20–600 °C. Heating rate: 10 deg min^{-1}, N$_2$ atmosphere.
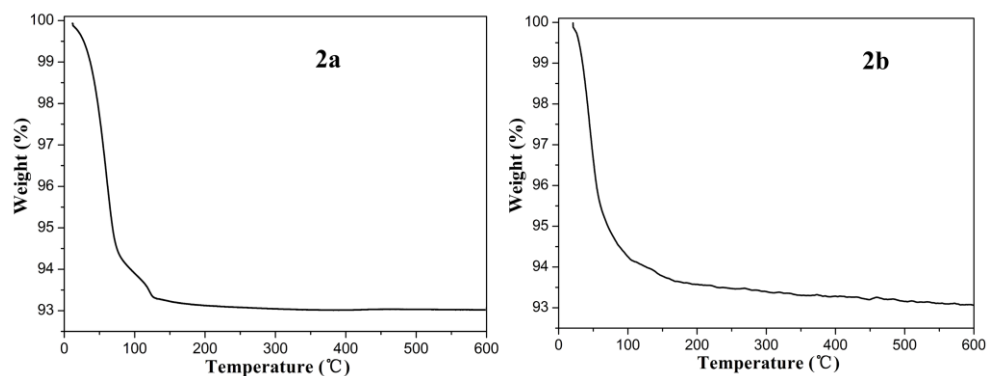
Fig. S6 The TG curves of **2a** and **2b** exhibit one weight loss stages in the temperature ranges 20–600 °C. The weight loss of 6.78% (calcd. 6.64%) for **2a** and 6.69% (calcd. 6.64%) for **2b** at 150 °C, which correspond to the loss of all the crystallization and coordination water molecules. Heating rate: 10 deg min^{-1}, N_2 atmosphere.
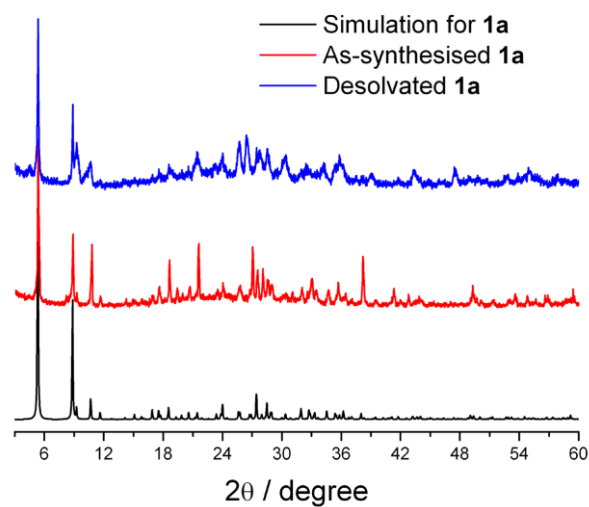

Fig. S7 The XRPD patterns for simulated, as-synthesised, and desolvated samples of **1a**.
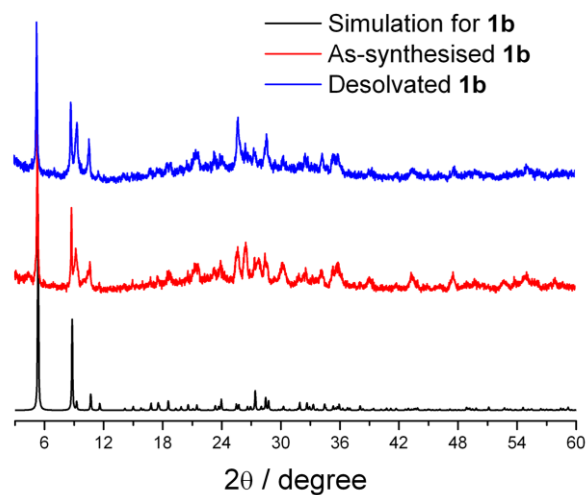
Fig. S8 The PXRD patterns for simulated, as-synthesised, and desolvated samples of **1b**.
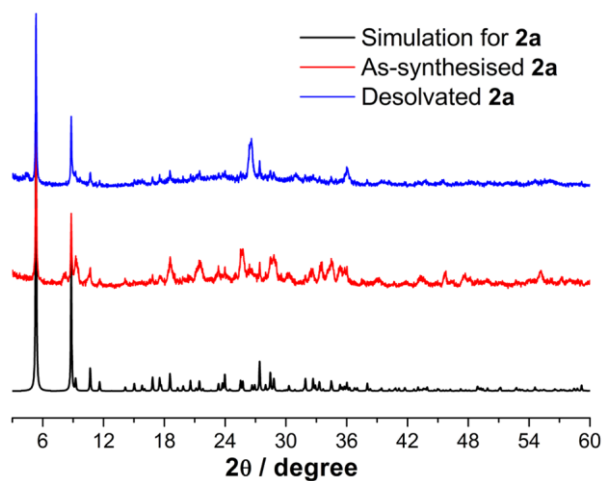

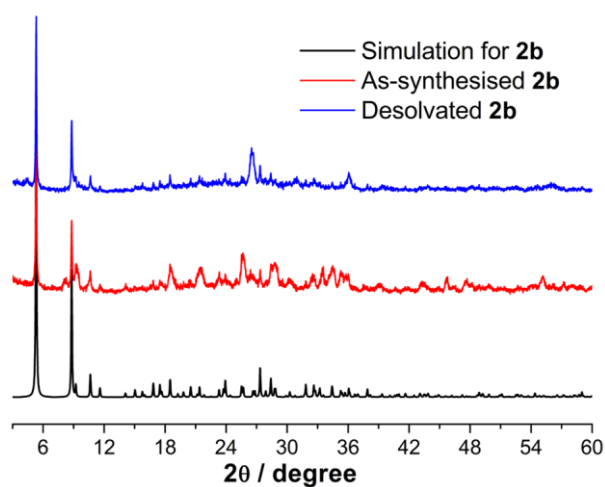**Fig. S9** The PXRD patterns for simulated, as-synthesised, and desolvated samples of **2a**.

Fig. S10 The PXRD patterns for simulated, as-synthesised, and desolvated samples of **2b**.
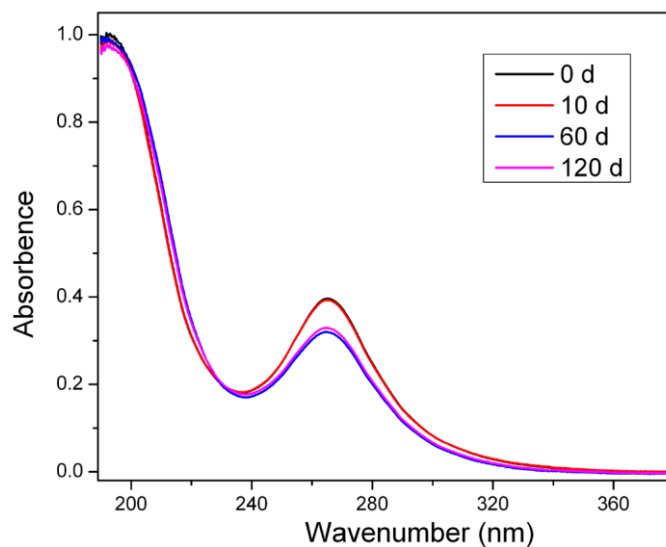
Fig. S11 The influence of time on the stability of compound **1** in the aqueous solution. Conditions: the pH value that **1** was dissolved in water (1×10^{-5} mol L^{-1}) is 6.0.
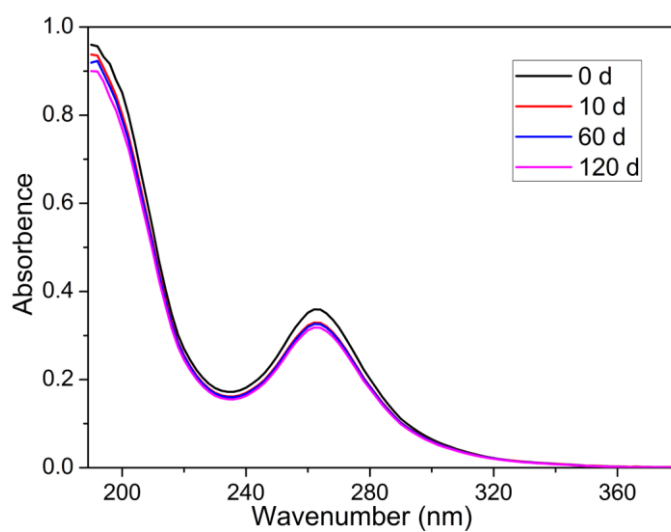

Fig. S12 The influence of time on the stability of compound **2** in the aqueous solution. Conditions: the pH value that **2** was dissolved in water (1×10^{-5} mol L^{-1}) is 6.0.
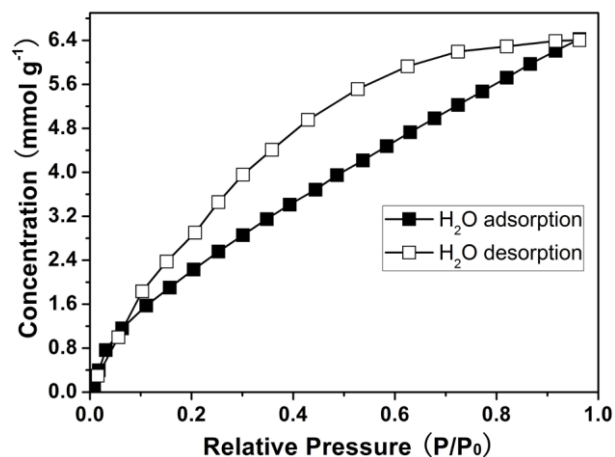
Fig. S13 The water adsorption and desorption curves of **1** at 298 K
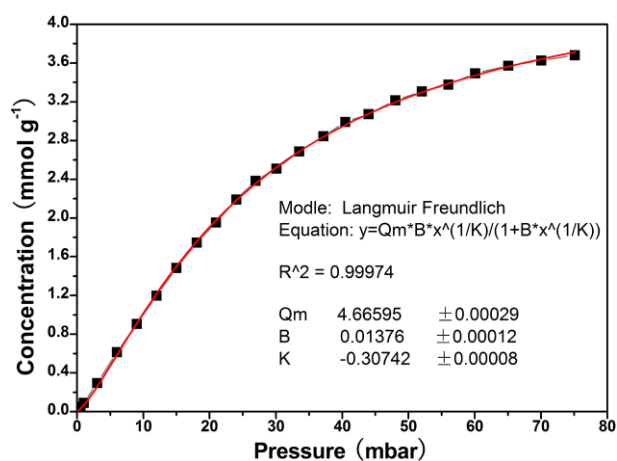

Fig. S14 Curve fitting of ethanol adsorption isotherm of **1** recorded at 298 K using Langmuir-Freundlich equation.
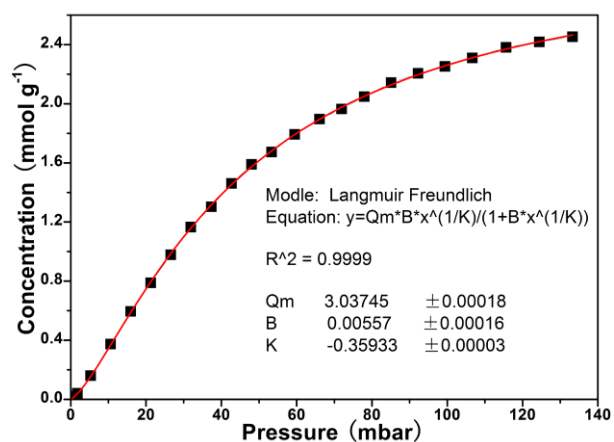

Fig. S15 Curve fitting of ethanol adsorption isotherm of **1** recorded at 308 K using Langmuir-Freundlich equation.

Fig. S16 Methanol and 1-propanol adsorption and desorption curves at 298 K for **1**.

Fig. S17 Cyclohexane, benzene, and toluene adsorption and desorption curves at 298 K for

1.

Fig. S18 The water adsorption and desorption curves of **2** at 298 K
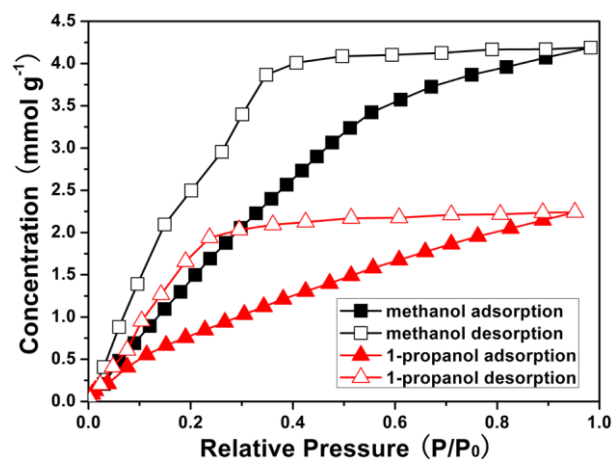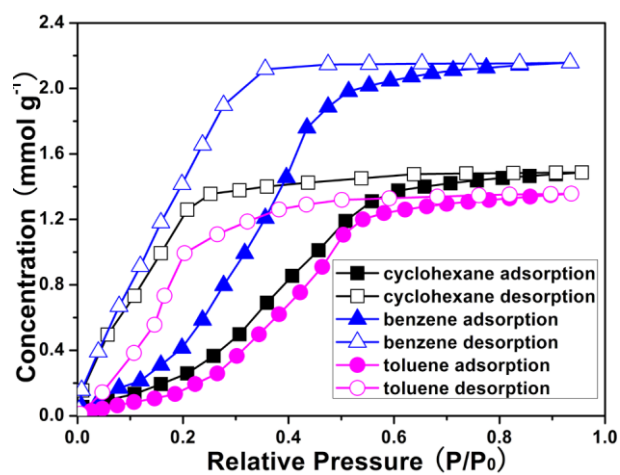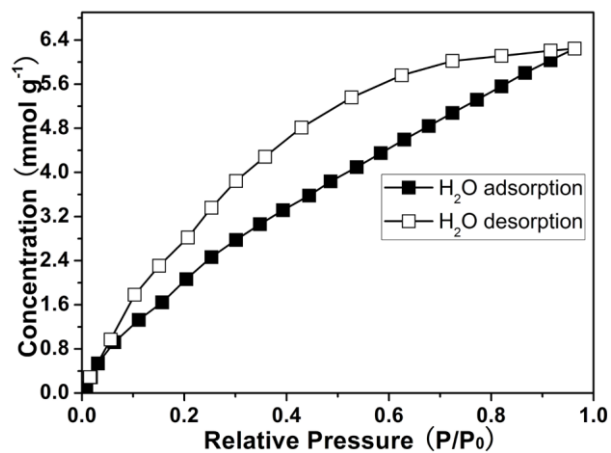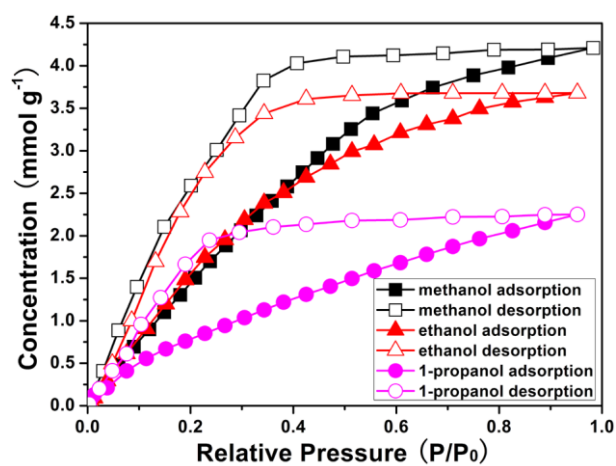

Fig. S19 Methanol, ethanol, and 1-propanol adsorption and desorption curves at 298 K for **2**.
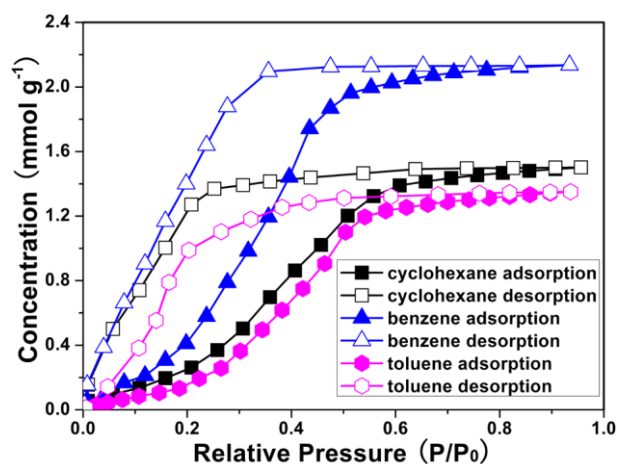
Fig. S20 Cyclohexane, benzene, and toluene adsorption and desorption curves at 298 K for **2**.

Table S1 The VOCs adsorption properties of **1** and **2** at 298 K.

Adsorption amount	**1** (mmol g^{-1})	**2** (mmol g^{-1})	**1** (molecules per formula unit)	**2** (molecules per formula unit)
water	6.42	6.24	57.75	56.19
methanol	4.19	4.21	37.69	37.89
ethanol	3.68	3.73	33.11	33.51
1-propanol	2.23	2.25	20.06	20.24
cyclohexane	1.49	1.50	13.45	13.50
benzene	2.16	2.13	19.47	19.21
toluene	1.36	1.33	12.25	11.98

Estimation of adsorption enthalpy

The adsorption isotherms were fitted using the Langmuir-Freundlich equation instead of the more commonly used Langmuir equation. The Langmuir-Freundlich model gives a better fit over the entire measured pressure range, resulting in a more accurate prediction of the adsorption capacity at saturation. The calculation of the enthalpy of VOCs adsorption using

Clausius-Clapeyron equation:

$$\ln\left(\frac{P_1}{P_2}\right) = \Delta H_{ads} \times \frac{T_2 - T_1}{RT_1 T_2} \tag{1}$$

P = pressure for isotherm

T = temperature for isotherm

R = 8.315 J K^{-1} mol^{-1}

Equation **(1)** can be used as a function of the quantity of adsorbed to calculate the adsorption enthalpy. The pressure as a function of the amount of adsorbed was determined by using Langmuir-Freundlich fit for the adsorption isotherms.

$$\frac{Q}{Q_m} = \frac{BP^{(1/t)}}{1 + BP^{(1/t)}} \tag{2}$$

Q = moles adsorbed

Q_m = moles adsorbed at saturation

P = pressure

B and t = constants.

Rearranging **(2)** to obtained:

$$P = \left(\frac{Q/Q_m}{B - BQ/Q_m}\right)^t \tag{3}$$

Replacing P in equation **(1)**, the $\triangle H_{ads}$ can be calculated from the following formula:

$$\Delta H_{ads} = \frac{RT_1T_2}{T_2-T_1} \times \ln \frac{\left(\dfrac{Q/Q_{m1}}{B_1 - B_1 Q/Q_{m1}}\right)^t}{\left(\dfrac{Q/Q_{m2}}{B_2 - B_2 Q/Q_{m2}}\right)^t} \qquad (4)$$

References

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2. S.Q. Ma, H.C. Zhou, J. Am. Chem. Soc. 128 (2006) 11734–11735.

3. B. Chen, X. Zhao, A. Putkham, K. Hong, E.B. Lobkovsky, E.J. Hurtado, A.J. Fletcher, K.M. Thomas, J. Am. Chem. Soc. 130 (2008), 6411–6423.