

**Supporting information's:**

**Germanosilicate zeolite ITQ-44 with extra-large 18-rings synthesized by using commercial quaternary ammonium as structure-directing agent**

Kun Qian,<sup>\*ab</sup> Yilin Wang,<sup>b</sup> Zhiqiang Liang,<sup>b</sup> Jiyang Li<sup>\*b</sup>

<sup>a</sup> Liaoning Medical University, Jinzhou 121001, P. R. China.

<sup>b</sup> State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, P. R. China.

**Table S1** The products obtained in the reaction gel with molar composition of  $m\text{SiO}_2$ :  $n\text{GeO}_2$ :  $0.25\text{SSDAOH}$ :  $y\text{NH}_4\text{F}$ :  $(0.25-y)\text{NH}_4\text{Cl}$ :  $x\text{H}_2\text{O}$  ( $x = 1-3$ ;  $y = 0-0.25$ ;  $m+n=1$  and  $n/m=0.5-1.0$ ) at 170 °C for 1 day.

F/T	Ge/Si=0.5		Ge/Si=1.0	
	H <sub>2</sub> O/T=1	H <sub>2</sub> O/T=2	H <sub>2</sub> O/T=1	H <sub>2</sub> O/T=2
0.25	ITQ-44	ITQ-44	ITQ-44	ITQ-44
0.20	ITQ-44	ITQ-44	ITQ-44	ITQ-44
0.10	ITQ-44	ITQ-44	ITQ-44	ITQ-44
0.05	ITQ-44	ITQ-44	ITQ-44	ITQ-44
0	ITQ-	ITQ-	ITQ-	ITQ-
	44+GeO <sub>2</sub>	44+GeO <sub>2</sub>	44+GeO <sub>2</sub>	44+GeO <sub>2</sub>

**Table S2** Products obtained in the reaction gel with molar composition of  $m\text{SiO}_2$ :  $n\text{GeO}_2$ :  $0.25\text{SDAOH}$ :  $0.25\text{NH}_4\text{F}$ :  $x\text{H}_2\text{O}$  ( $x=1-2$ ;  $m+n=1$ ,  $n/m=0.1-1.0$ ) at  $170^\circ\text{C}$  for 1-10 day.

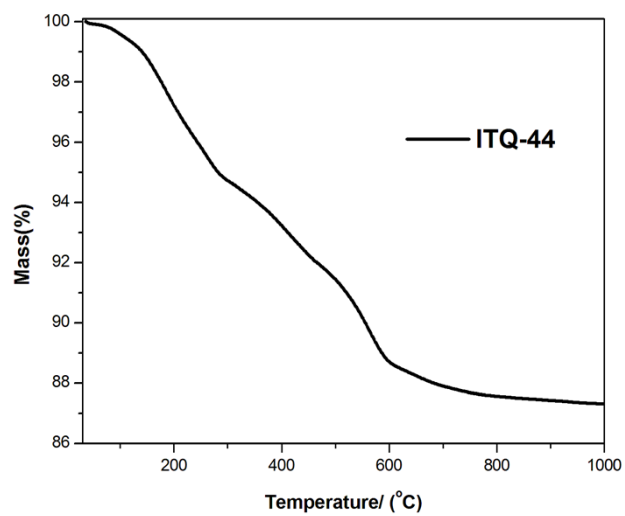
Ge/Si	Time (days)			
	1	5	7	10
0.1	Amorphous	Amorphous	Amorphous	Amorphous
0.5	ITQ-44	ITQ-44	ITQ-44	ITQ-44
1.0	ITQ-44	ITQ-44	ITQ-44+ITQ- 17	ITQ-44+ITQ- 17

**Table S3** Products obtained in the reaction gel with molar composition of  $m\text{SiO}_2$ :  $n\text{GeO}_2$ :  $0.25\text{SDAOH}$ :  $0.25\text{NH}_4\text{F}$ :  $x\text{H}_2\text{O}$  ( $x=1-2$ ;  $m+n=1$ ,  $n/m=0.1-1.0$ ) at 140-200 °C for 1 day.

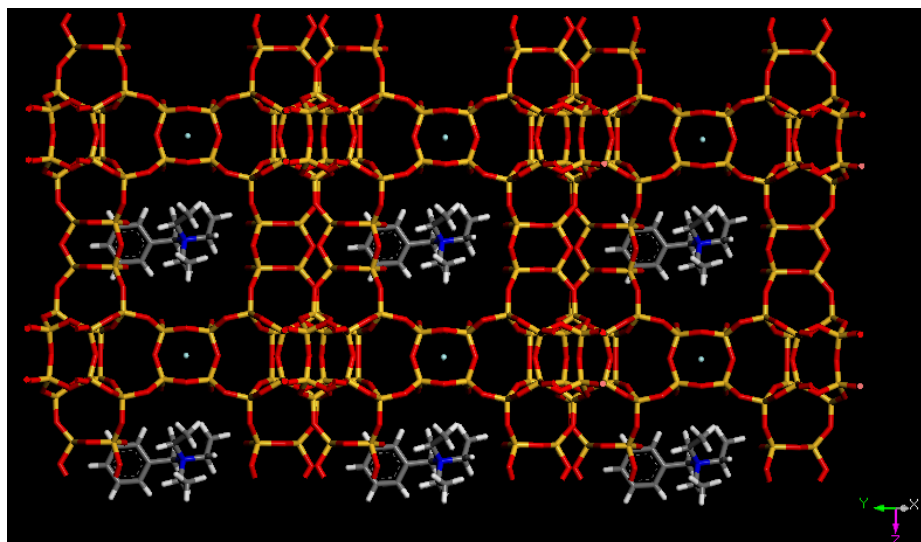
Ge/Si	Temperature (°C)				
	140	150	160	170	200
0.1	Amorphous	Amorphous	Amorphous	Amorphous	Amorphous
0.5	Amorphous	ITQ-44	ITQ-44	ITQ-44	ITQ-44
1.0	Amorphous	ITQ-44	ITQ-44	ITQ-44	ITQ-44

**Table S4** ICP analysis of the M-ITQ-37 obtained from the reaction system of 0.5SiO<sub>2</sub>: 0.5GeO<sub>2</sub>: zM<sub>2</sub>O<sub>3</sub>: 0.25OSDAOH: 0.20NH<sub>4</sub>F: 0.05NH<sub>4</sub>Cl: 5H<sub>2</sub>O at 170 °C for 24 hours.

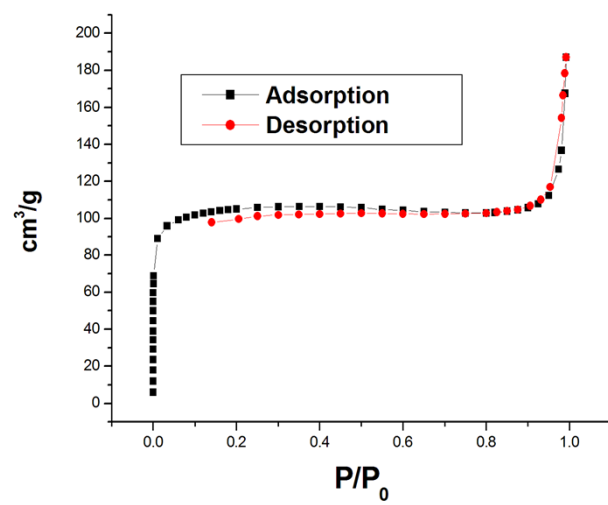
M source	M/ (Si+Ge)		
	0.01	0.05	0.10
Al(OH) <sub>3</sub>	0.01	0.04	0.07
Fresh Al(OH) <sub>3</sub>	0.01	0.04	0.09
B <sub>2</sub> O <sub>3</sub>	0.01	—	—
Ga <sub>2</sub> O <sub>3</sub>	0.01	—	—



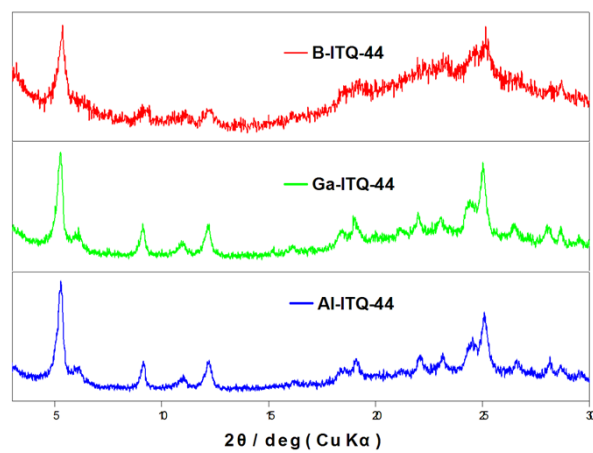
**Fig. S1** The TG curve of as-synthesized ITQ-44.



**Fig. S2** The positions of SDA-1 cations in ITQ-44.



**Fig. S3** The N<sub>2</sub> adsorption and desorption isotherms of calcined ITQ-44.



**Fig. S4** The XRD patterns of as-synthesized M-ITQ-44.