Supporting Information

Preparation and characterization of cationic water-soluble pillar[5]arene-modified zeolite for adsorption of methyl orange

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1. Materials and methods

All reagents were commercially available and used as supplied without further purification. WPA5 was synthesized as described previously. ^{1}H and 13C NMR spectra were recorded on a Bruker Avance 400 nuclear magnetic resonance spectrometer using tetramethylsilane (TMS) as the internal standard. SSNMR data were recorded on JNM-ECZ600R. The absorbance was measured using an Agilent 8453 UV-Vis spectrometer. The fluorescence data were recorded on a Cary Eclipse fluorescence spectrophotometer. FTIR spectra were measured with a Thermo Nicolet Avatar 360 spectrometer using the KBr pellet. XRD patterns of powder samples were recorded using a D/Max-3B diffractometer with Cu Kα radiation (λ = 0.15406 nm, 100 mA, 40 kV). The scan rate was 5°/min and the range of 2θ = 0.02° varied between 3° and 80°. The sample microstructure was analyzed using a FEL QUANTA 200 scanning electron microscope. Optical microscopy was performed using SOPTOP CX40. TG measurements were conducted with a NETZSCH STA 449F3 by increasing the temperature to 900 °C at a heating rate of 10°C/min in a dynamic nitrogen atmosphere.

2. Synthesis of **WPA5**

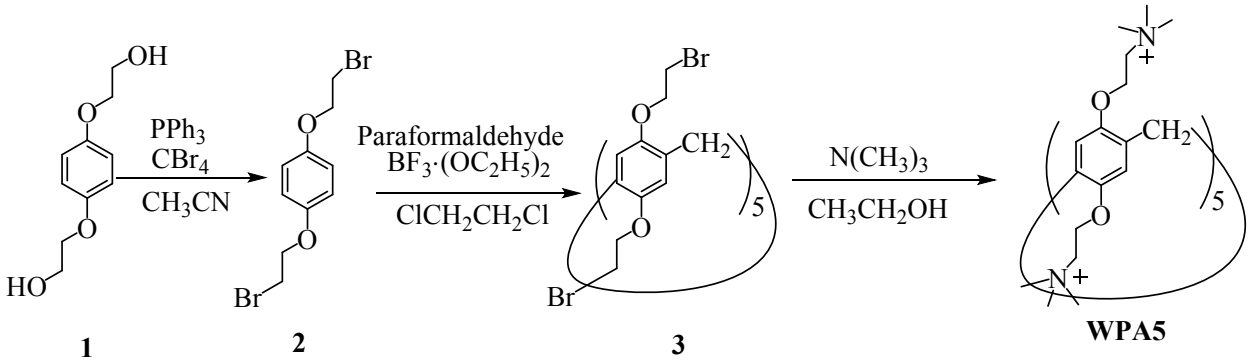

Figure S1. Synthetic route of WPA5

Synthesis of compound **2**:

After dissolving CBr_4 (33.46 g, 100.90 mmol) in acetonitrile solution, it was added dropwise to the acetonitrile solution of hydroquinone bis(2-hydroxyethyl)ether (10.0 g, 50.45 mmol) and PPh_3 (36.46 g, 100.90 mmol) under the protection of nitrogen, and reacted at room temperature for 4 h. Then, 150 mL of cold water was added to the reaction mixture to give a white precipitate. The white solid was filtrated and thoroughly washed with methanol and petroleum ether to give compound **2** (Yield:85%). The ^{1}H NMR spectrum of compound **2** was shown in Figure S2. ^{1}H NMR (400 MHz, chloroform-*d*) δ (ppm): 6.86 (s, 4H), 4.24 (t, J = 6.3

Hz, 4H), 3.61 (t, J = 6.3 Hz, 4H). The ^{13}C NMR spectrum of compound **2** was shown in Figure S3. ^{13}C NMR (100 MHz, Chloroform-*d*) δ (ppm): 151.83, 115.09, 67.72, 28.22, 28.20.

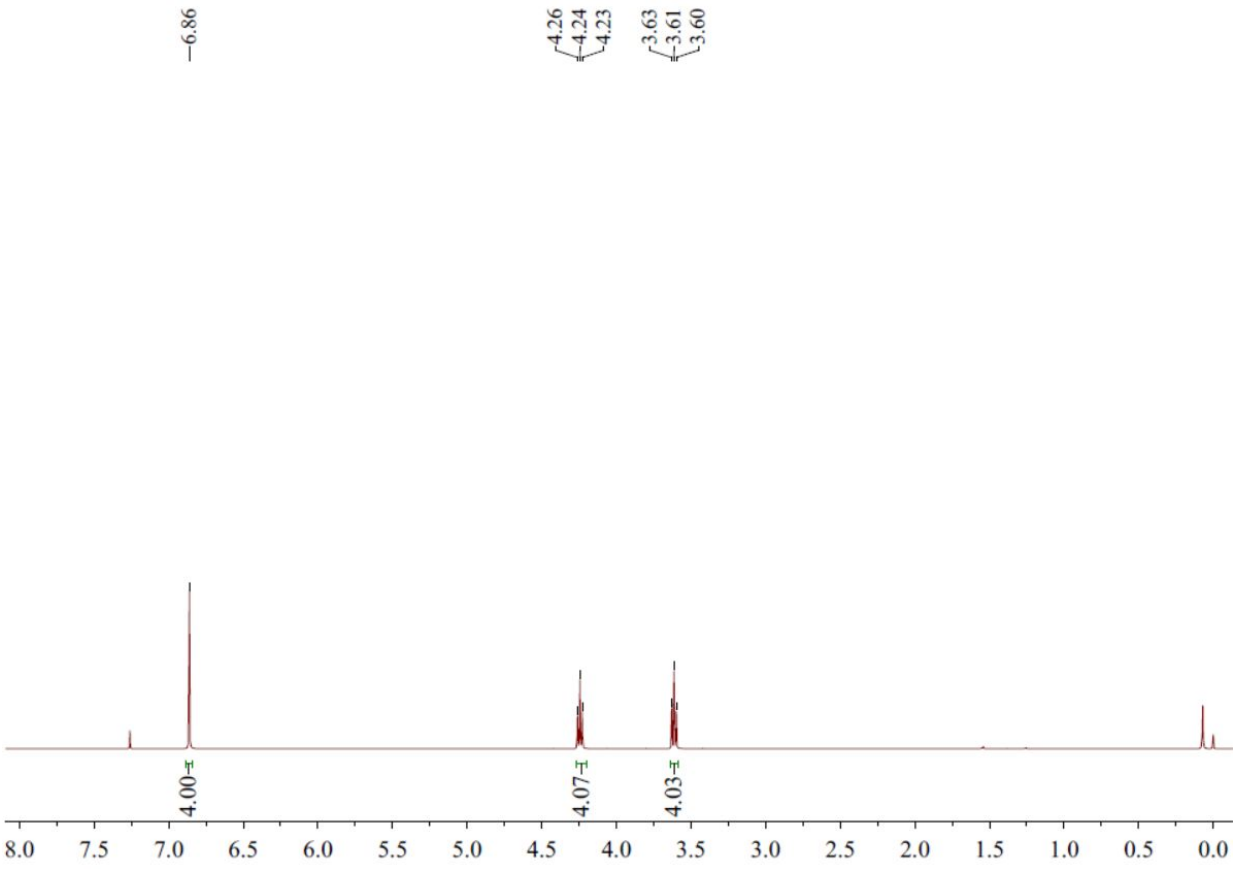

Figure S2. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 293 K) of compound **2**.

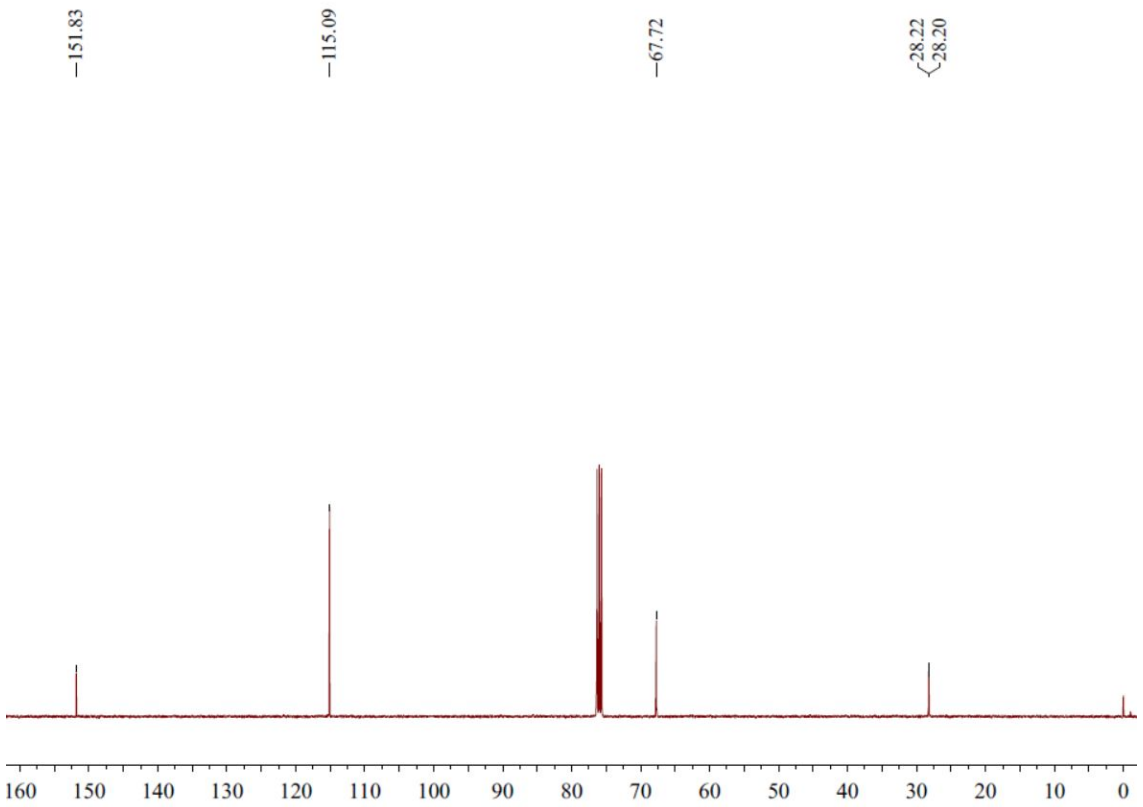

Figure S3. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 293 K) of compound **2**.

Synthesis of compound **3**:

To a solution of compound **2** (3.24 g, 10.00 mmol) in 1,2-dichloroethane (100 mL), paraformaldehyde (0.90 g, 30 mmol) was added under nitrogen atmosphere. Then $BF_3 \cdot OEt_2$ (1.39 mL, 10 mmol) was added to the solution and the mixture was stirred at room temperature for 6 h. A green solution was got. After the solvent was removed, the obtained solid was purified

by column chromatography on silica gel with petroleum ether/dichloromethane (1:1 v/v) as the eluent to get white powder compound **3** (Yield:85%). The ^{1}H NMR spectrum of compound **3** is shown in Figure S4. ^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm): 6.93 (s, 10H), 4.24 (t, J = 5.2 Hz, 20H), 3.85 (s, 10H), 3.69-3.61 (m, 20H). The^{13}C NMR spectrum of compound **3** was shown in Figure S5. ^{13}C NMR (100 MHz, Chloroform-*d*) δ (ppm): 148.61, 128.00, 115.04, 67.92, 29.72, 29.70, 28.36.

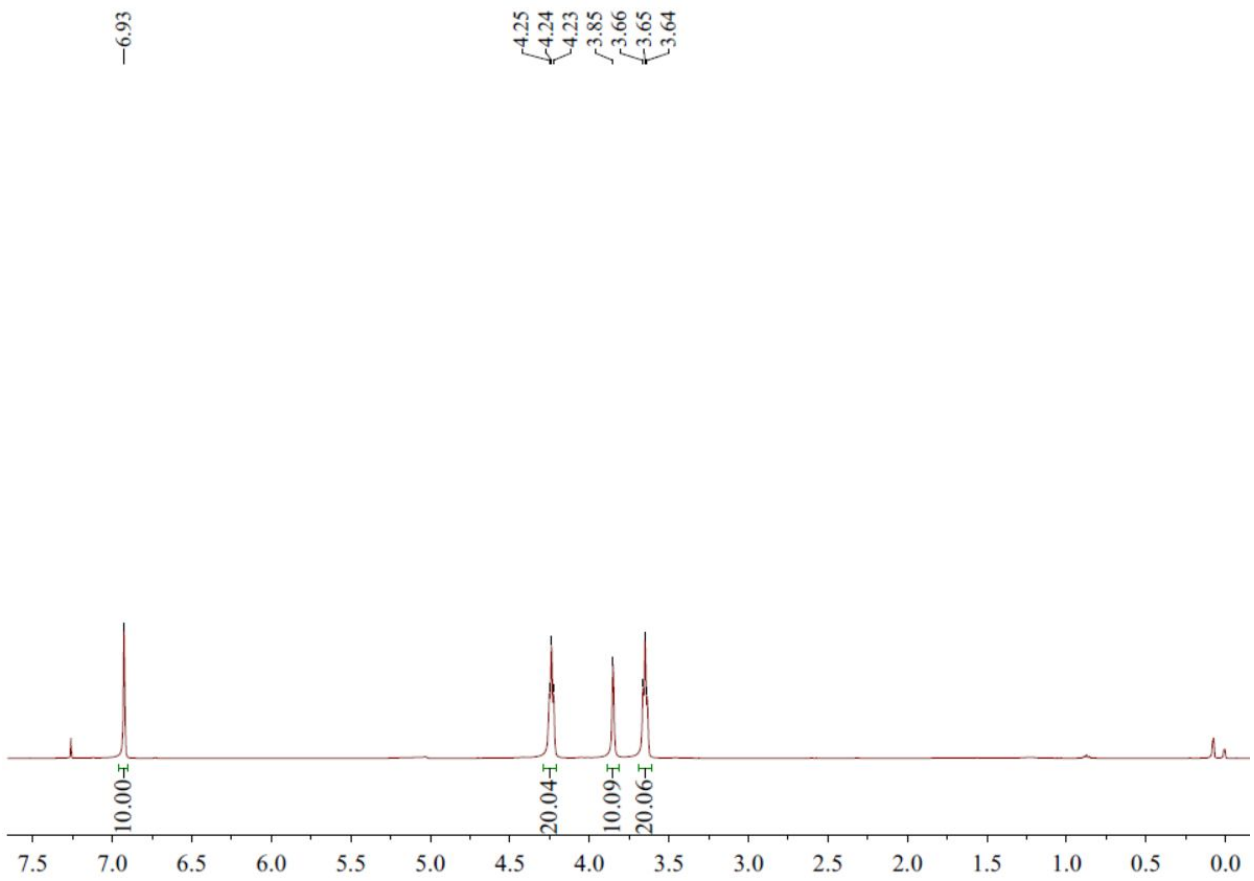

Figure S4. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 293 K) of compound **3**.

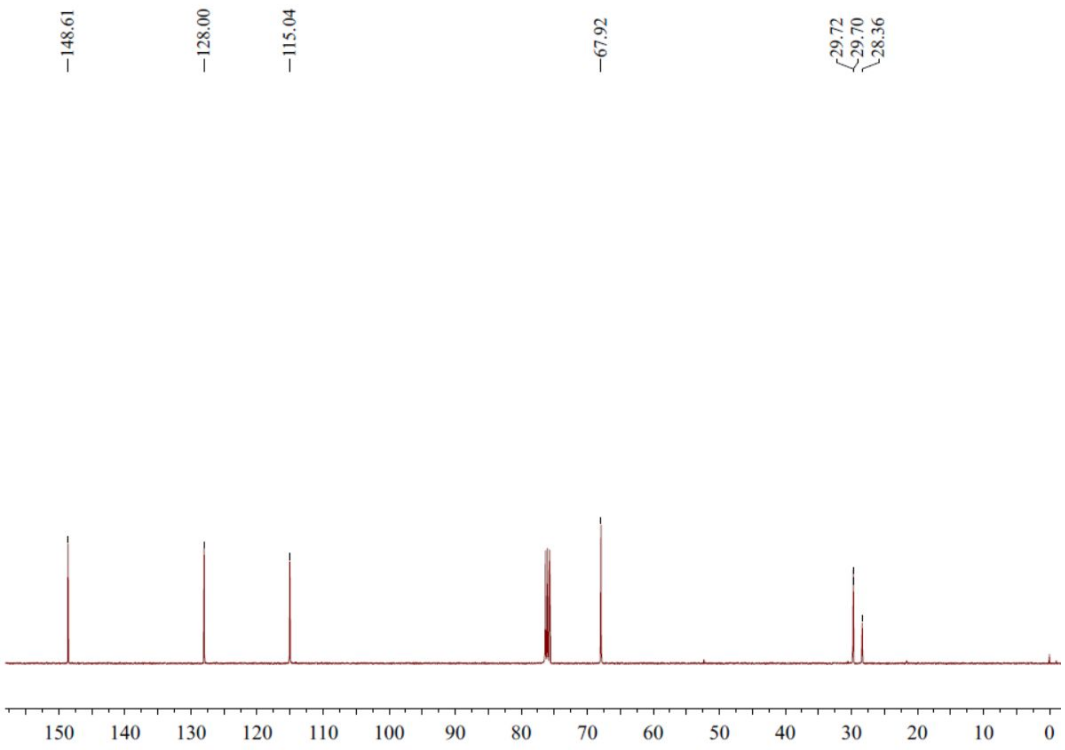

Figure S5. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 293 K) of compound **3**.

Synthesis of WPA5:

Compound **3** (0.4813 g, 0.2865 mmol) and excessive trimethylamine were added to ethanol (30 mL). The solution was refluxed 36 h. Then the solvent was removed by evaporation, deionized water 10 mL was added. After filtration, a clear solution was obtained. Then the water was removed by evaporation to obtain WPA5 as a colorless solid (Yield: 90%). The ^1H NMR spectrum of WPA5 was shown in Figure S6. ^1H NMR (400 MHz, D_2O) δ (ppm): 6.98 (s, 10H),

4.49 (s, 20H), 3.96 (s, 10H), 3.84 (s, 20H), 3.25 (s, 90H). The ^{13}C NMR spectrum of WPA5 was shown in Figure S7. ^{13}C NMR (100 MHz, D_2O) δ (ppm): 149.28, 129.85, 116.38, 64.81, 63.37, 53.96, 29.53.

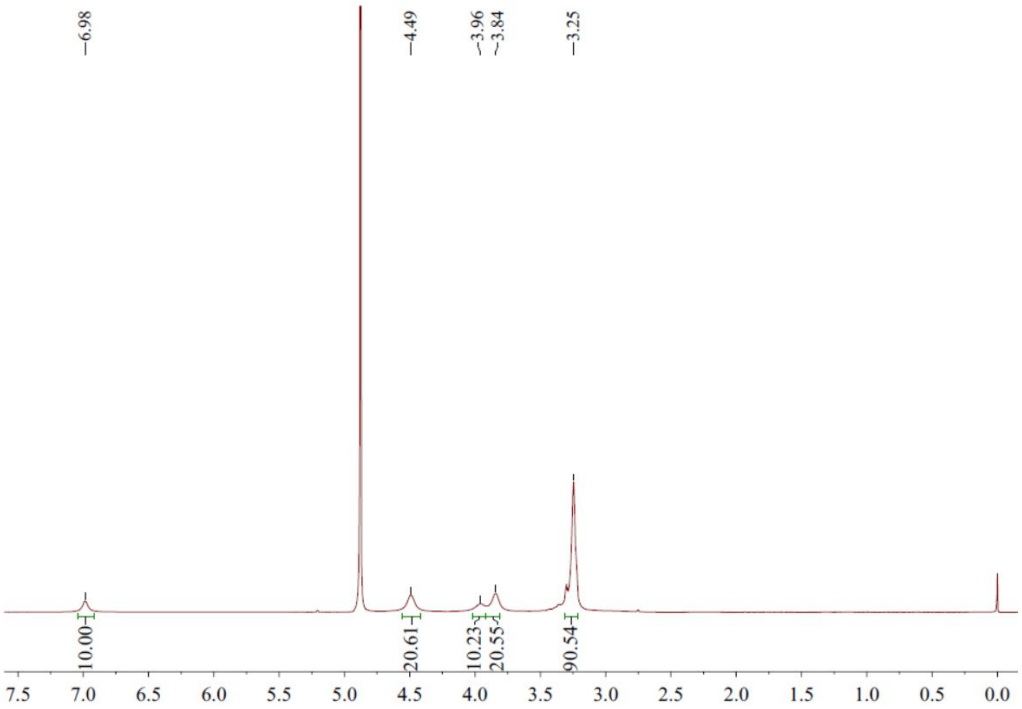

Figure S6. ^{1}H NMR spectrum (400 MHz, D_2O, 293 K) of WPA5.

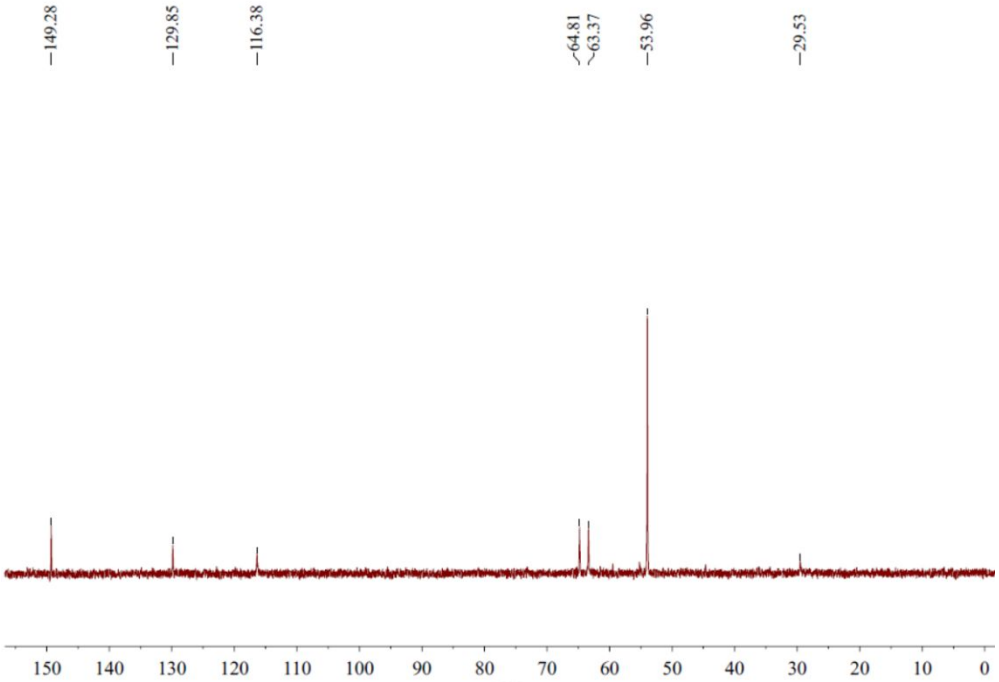

Figure S7. ^{13}C NMR spectrum (100 MHz, D_2O, 293 K) of WPA5.