## Supplementary information

# Diquaternary ammonium surfactant-directed synthesis of single-

## unit-cell nanowires of ZSM-5 zeolite

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### **Experimental section**

#### Materials

Tetraethyl orthosilicate (TEOS, 99%), sodium hydroxide (NaOH, 99%), tripropyl amine (99%), sodium metaaluminate (NaAlO<sub>2</sub>, 99%), N,N-dimethyldodecylamine (98%), N,N-didodecylmethylamine (85%), 1,6-dibromohexane (99%), methanol (99%), ethanol (99%), toluene (99%), acetonitrile (99%), iron chloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O, 99%), phenol (99%), catechol (CAT, 99%), hydroquinone (HQ, 99%), benzoquinone (BQ, 99%), ethylbenzene (EB, 99%), H<sub>2</sub>O<sub>2</sub> (30 wt%) were purchased from Aladdin Co.,Ltd. and used without any further purification. Prior to use, the concentration of H<sub>2</sub>O<sub>2</sub> was tested by direct iodine titration method.

### Preparation of bifunctional templates with different hydrophobic group

The intermediate  $Br-C_6H_{12}-N^+(C_3H_7)_3(Br^-)$  was synthesized as described in the Ref. 1. Typically, a mixture of 10 mL tripropyl amine (0.05 mol) and 10 mL toluene was slowly added to a mixture of 16 mL 1,6-dibromohexane (0.1 mol) and 16 mL acetonitrile at 60 °C stirring for 24 hours. After the solvent was removed via rotary evaporation, the intermediate was extracted through a diethyl ether/water system that separated residual 1,6-dibromohexane from the mixture.

The bifunctional soft template  $C_{12}H_{25}-N^+(CH_3)_2-C_6H_{12}-N^+(C_3H_7)_3(Br)_2$  was synthesized as follows: a mixture of 19.35 g Br-C<sub>6</sub>H<sub>12</sub>-N<sup>+</sup>(C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>(Br) and 30 mL acetonitrile was slowly added into a mixture of 10.88 g N,N-dimethyldodecylamine and 30 mL toluene at 75 °C stirring for 72 h. After the solvent was removed via rotary evaporation,  $C_{12}H_{25}-N^+(CH_3)_2-C_6H_{12}-N^+(C_3H_7)_3(Br)_2$  was extracted through a diethyl ether/water system that separated residual 1,6-dibromohexane from the mixture.

The bifunctional soft template  $(C_{12}H_{25})_2$ -N<sup>+</sup>(CH<sub>3</sub>)-C<sub>6</sub>H<sub>12</sub>-N<sup>+</sup>(C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>(Br<sup>-</sup>)<sub>2</sub> was synthesized as follows: a mixture of 19.35 g Br-C<sub>6</sub>H<sub>12</sub>-N<sup>+</sup>(C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>(Br<sup>-</sup>) and 30 mL acetonitrile was slowly added into a mixture of 20.42 g N,N-didodecylmethylamine and 30 mL toluene at 80 °C stirring for 72 h. After the solvent was removed via rotary evaporation,  $(C_{12}H_{25})_2$ -N<sup>+</sup>(CH<sub>3</sub>)-C<sub>6</sub>H<sub>12</sub>-N<sup>+</sup>(C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>(Br<sup>-</sup>)<sub>2</sub> was extracted through a diethyl ether/water system that separated residual 1,6-dibromohexane from the mixture.



Fig. S1 The chemical structures and <sup>1</sup>H NMR spetra of the prepared bifunctional soft templates

## Preparation of NS-ZSM-5 Zeolite

In a typical procedure, 0.067 g NaAlO<sub>2</sub> and 0.41 g NaOH were first dissolved in 62 g H<sub>2</sub>O. Then, 4.20 g TEOS were slowly adding into the solution at 25 °C. After stirring for 2 h, a mixture of 3.15 g  $C_{12}H_{25}$ -N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>12</sub>-N<sup>+</sup>(C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>(Br)<sub>2</sub> and 3 g H<sub>2</sub>O was added into the mixture under vigorous stirring (500 rpm). The final mixture was further stirred for 2 hours. The mother liquid was then moved into a teflon-coated stainless-steel autoclave and kept at 150 °C for 7 days (molar ratios: 1 Al<sub>2</sub>O<sub>3</sub>:14 TPAOH:6.6 C<sub>12-6</sub>:14 Na<sub>2</sub>O:8800 H<sub>2</sub>O:49 SiO<sub>2</sub>). The obtained material was separated by centrifuge, washed with ethanol for three times, dried at 80 °C overnight and calcined in air at 550 °C for 6 hours.

#### **Preparation of NW-ZSM-5 Zeolite**

In a typical procedure, 0.067 g NaAlO<sub>2</sub> and 0.41 g NaOH were first dissolved in 62 g H<sub>2</sub>O. Then, 4.20 g TEOS were slowly adding into the solution at 25 °C. After stirring for 2 h, a mixture of 4.1 g  $C_{12}H_{25}$ -N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>12</sub>-N<sup>+</sup>(C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>(Br)<sub>2</sub> and 3 g H<sub>2</sub>O was added into the mixture under vigorous stirring (500 rpm). The final mixture was further stirred for 2 hours. The mother liquid was then moved into a teflon-coated stainless-steel autoclave and kept at 150 °C for 7 days (molar ratios: 1 Al<sub>2</sub>O<sub>3</sub>:14 TPAOH:6.6 C<sub>2-12-6</sub>:14 Na<sub>2</sub>O:8800 H<sub>2</sub>O:49 SiO<sub>2</sub>). The obtained material was separated by centrifuge, washed with ethanol for three times, dried at 80 °C overnight and calcined in air at 550 °C for 6 hours.

#### Preparation of Fe-NS-ZSM-5 and Fe-NW-ZSM-5 Zeolites

The preparation steps of Fe-NS-ZSM-5 and Fe-NW-ZSM-5 Zeolites are similar with NS-ZSM-5 and NW-ZSM-5 zeolites. The only difference is the addition of iron chloride hexahydrate after the addition of the prepared bifunctional soft templates.

#### Characterizations

X-ray diffraction (XRD) were performed on a Bruker D8 ADVANCEX instrument with Ni-filtered Cu K $\alpha$  radiation ( $\lambda = 0.1541$  nm) with a scanning pace of 5°/min in the range of 2 $\theta = 5$ ~50°. The morphologies of the prepared samples were observed on a Hitachi S-4800 scanning electron microscopy instrument (SEM). Before measurement, a thin platinum film was sprayed on the samples by using an ion sputtering apparatus. The pore structures of the prepared samples were recorded on a JEM-2100F transmission electron microscopy instrument (TEM). Before texts, each sample was first dispersed in ethanol using an ultrasonic instrument for 45 min and then dropped on an ultrathin carbon supported film. Nitrogen adsorption-desorption isotherms of the prepared samples were measured on a BUIDER SSA-7000 instrument. Before measurements, all samples to be tested were degassed at 250 °C for 6 hours. The specific surface areas (S<sub>BET</sub>) were calculated according to the

Brunauer-Emmett-Teller (BET) method. The pore size distributions were calculated by the Horvath-Kawazoe (HK) or Barrett-Joyner-Halenda (BJH) models (adsorption branch). Fourier transforming infrared spectra (FT-IR) were collected in the range of 400~4000 cm<sup>-1</sup> on a Thermo Nicolet instrument through the KBr pellet technique. The prepared soft templates were characterized by Bruker Ascend 400 MHz liquid nuclear magnetic resonance apparatus. The UV-vis spectra in the range of 200-800 nm were recorded on a PE Lambda 750 spectrophotometer. The Si/Fe molar ratios in the prepared samples were measured on a PerkinElmer Optima 8300 inductively coupled plasma-optical emission spectrometry instrument (ICP-OES).

#### **Catalytic activity**

Phenol hydroxylation over Fe-NS-ZSM-5 and Fe-NW-ZSM-5 catalysts were conducted in a three-necked flask (50 mL) with a constant temperature water bath mixer under vigorous stirring (600 rpm). In a typical procedure, 1 g phenol, 10 mL deionized water and 0.1 g catalyst were added into the three-necked flask at 25 °C. Then,  $H_2O_2$  was added into the flask to start the reaction. After reaction, catalysts were separated from reaction mixture by centrifugation. Gas chromatograph analyses were conducted by using a shimadzu GC-2010 plus instrument equipped with a SE-30 chromatographic capillary column ( $\emptyset$  0.25 mm × 0.25 µm × 30 m). Gas chromatography-Mass spectrometry analyses were performed on a Shimadzu QP2010 instrument. Ethyl benzene was used as the internal standard to calculate the mass of reactant and products. The conversion rate of phenol and the selectivity to dihydroxybenzenes (e.g. CAT, HQ) were defined as follows:

The conversion of phenol:  $X_{(P)} = 100 \times (C_{0, phenol} - C_{1, phenol}) / C_{0, phenol}$ The selectivity to CAT:  $S_{(CAT)} = 100 \times C_{1, CAT} / (C_{0, phenol} - C_{1, phenol})$ The selectivity to HQ:  $S_{(HQ)} = 100 \times C_{1, HQ} / (C_{0, phenol} - C_{1, phenol})$ The selectivity to dihydroxybenzenes:  $S_{(DHB)} = S_{(CAT)} + S_{(HQ)}$ 

Here,  $C_{0, phenol}$  and  $C_{1, phenol}$  are the molar concentration of phenol before reaction and after reaction, respectively,  $C_{1, CAT}$  and  $C_{1, HQ}$  are the molar concentrations of CAT and HQ after reaction, respectively.

# Supplementary figures and tables



Fig. S2 The FT-IR spectra of NS-ZSM-5 and NW-ZSM-5 samples.



Fig. S3 The XRD patterns and FT-IR spectra of Fe-NS-ZSM-5 and Fe-NW-ZSM-5 samples.



Fig. S4 The  $N_2$  adsorption-desorption isotherms and pore size distributions of Fe-NS-ZSM-5 and Fe-NW-ZSM-5 samples.

Samples	Si/Al <sup>a</sup>	$\mathbf{S}_{\text{BET}}^{\mathbf{b}}$	S <sub>micro</sub>	$V_{micro}{}^{c}$	$V_{\text{meso}}{}^{d}$
		$[m^2/g]$	[m <sup>2</sup> /g]	[cm <sup>3</sup> /g]	[cm <sup>3</sup> /g]
Fe-NS-ZSM-5	26	518	152	0.11	0.52
Fe-NW-ZSM-5	24	622	206	0.13	0.85

Table S1 Textural properties of Fe-NS-ZSM-5 and Fe-NW-ZSM-5 samples

<sup>a</sup> Measured by ICP-OES. <sup>b</sup> Brunner-Emmet-Teller (BET) Surface Area. <sup>c</sup> Determined by t-plot method. <sup>d</sup> Pore volume in the range of 2-50 nm.



Fig. S5 SEM images of (c1, c2, c3) Fe-NS-ZSM-5 and (d1, d2, d3) Fe-NW-ZSM-5 samples.



Fig. S6 TEM images of (C1, C2, C3) Fe-NS-ZSM-5 and (D1, D2, D3) Fe-NW-ZSM-5 samples.



Fig. S7 UV-vis spectra of Fe-NS-ZSM-5 and Fe-NW-ZSM-5 samples.



Fig. S8 Reaction pathway for the hydroxylation of phenol



Fig. S9 Catalytic stability of the Fe-NW-ZSM-5 sample in phenol hydroxylation.



Fig. S10 (A) XRD pattern and (B) UV-vis spectrum of R-Fe-NW-ZSM-5. Where R-Fe-TH-ZSM-5(4.2) is the sample collected after the reaction ran five cycles.



Fig. S11 (A) SEM and (B1, B2) TEM images of R-Fe-NW-ZSM-5 sample.

## References

1 Q. W. Tian, Z. H. Liu, Y. H. Zhu, X. L. Dong, Y. Saih, J.-M. Basset, M. Sun, W. Xu, L. K. Zhu, D. L. Zhang, J. F. Huang, X. J. Meng, F. S. Xiao and Y Han, *Adv. Funct. Mater.*, 2016, **26**, 1881-1891.