Electronic Supplementary Information for

Excess adsorption of acetonitrile and water on MIL-100(Fe) and its potential application in mixed-mode chromatography

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1 Partial molar volume of water and ACN in water/ACN binary solution

The partial molar volumes of acetonitrile (ACN) and water, $\overline{V_A}$ and $\overline{V_W}$, respectively, in ACN/water binary solution are given as

$$\overline{V_A} = \frac{M_A}{\rho(c_A)} \cdot \left\{ 1 + \frac{c_A - 100}{\rho(c_A)} \cdot \frac{d\rho(c_A)}{dc_A} \right\} \tag{S-1}$$

$$\overline{V_W} = \frac{M_W}{\rho(c_A)} \cdot \left\{ 1 + \frac{c_A}{\rho(c_A)} \cdot \frac{d\rho(c_A)}{dc_A} \right\} \tag{S-2}$$

where M_A and M_W represent the molecular weights of ACN and water, respectively, c_A is weight concentration of ACN, and $\rho(c_A)$ is density of ACN/water binary mixture as a function of c_A.
Relation between $\rho(c_A)$ and c_A is shown in Fig. S2, where the solid curve was obtained by curve fitting and is given by

$$\rho(c_A) = -0.0468 \cdot \exp\left(\frac{c_A}{57.9}\right) + 1.05 \tag{S-3}$$

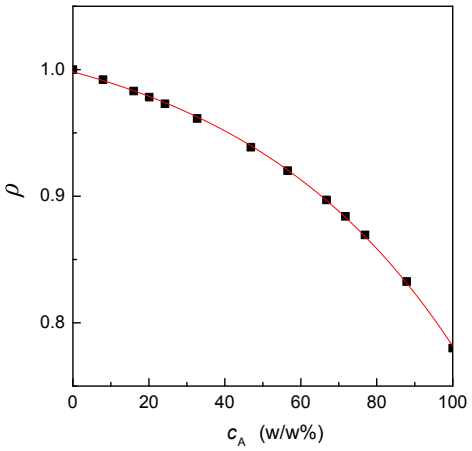

Fig. S 1: Relation between $\rho(c_A)$ and c_A.

The values of x_A was calculated by using the relation between $\overline{V_A}$ and x_A described as Eq. (4).

$$n_A \cdot \overline{V_A} = x_A \tag{S-4}$$

$$n_A = \frac{10 c_A \rho}{M_A} \tag{S-5}$$

2 X-ray photoelectron spectroscopy (XPS) analysis

Fig. S2 shows XPS Fe(2p) spectrum obtained from as-synthesized MIL-100(Fe). There are no spectra assigned to Fe(II), indicating that Fe(II) was oxidized to Fe(III) via hydrothermal reaction.

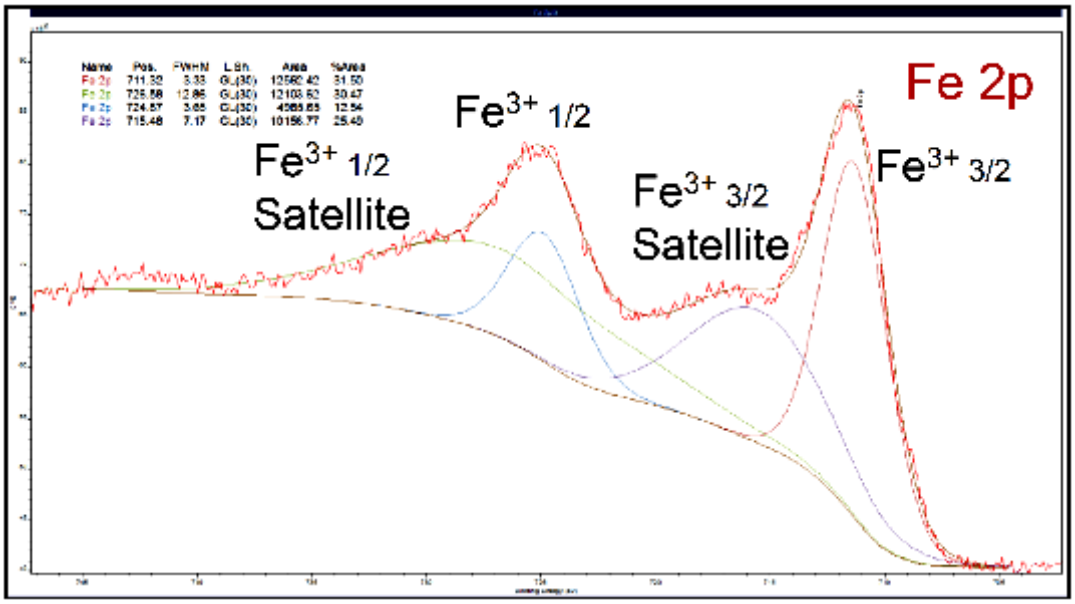

Fig. S 2: XPS spectra of the as-synthesized MIL-100(Fe).

3 FT-IR spectra

Fig. S3 shows FT-IR spectra of BTC and the as-synthesized substance. The spectra are completely different, indicating that the synthesized product does not contain BTC.

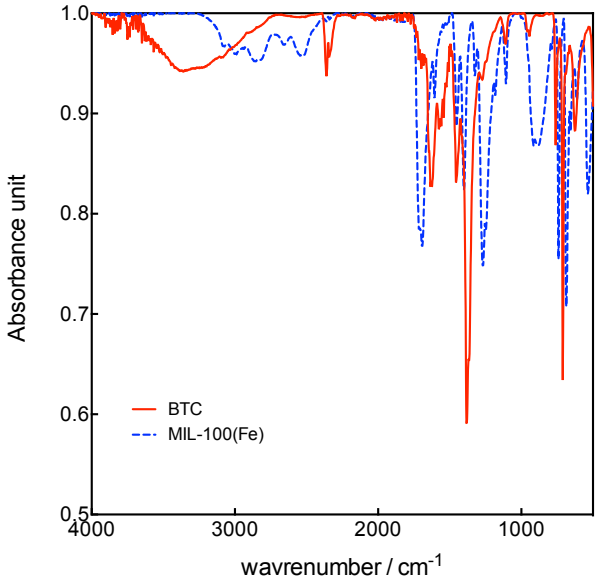

Fig. S 3: FT-IR spectra of BTC and the as-synthesized substance.

4 Repeatability of chromatographic measurements

Fig. S4 shows chromatograms when the same sample was repeatedly injected. The error was $< 0.1\%$.

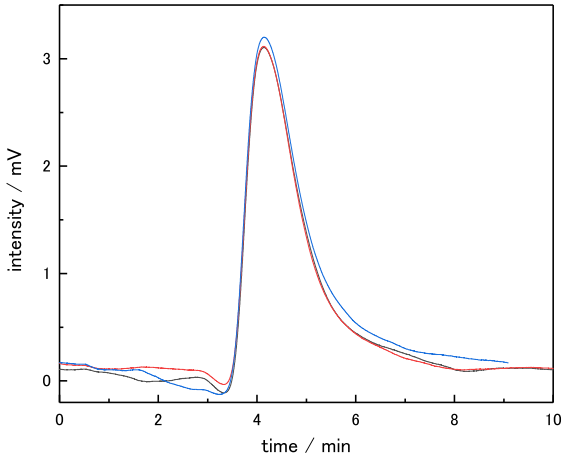

Fig. S 4: Chromatograms of solvent disturbance peak. Mobile phase: 90/10 vol% acetonitrile/water, sample: 100 μL water-added 90/10 vol% acetonitrile/water.

5 Chromatograms of alcohols and aromatics

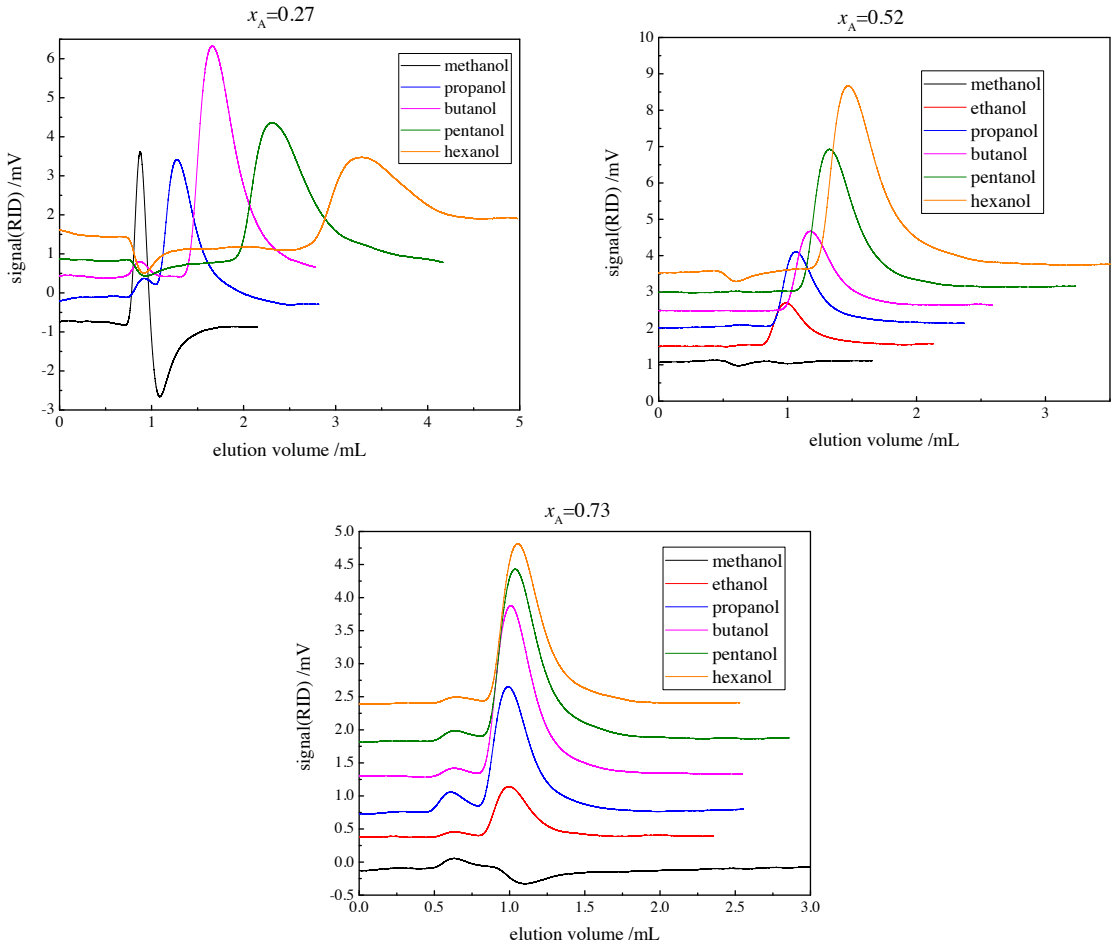

Fig. S 5: Chromatograms of alcohols at x_A=0.27, 0.52, and 0.73.

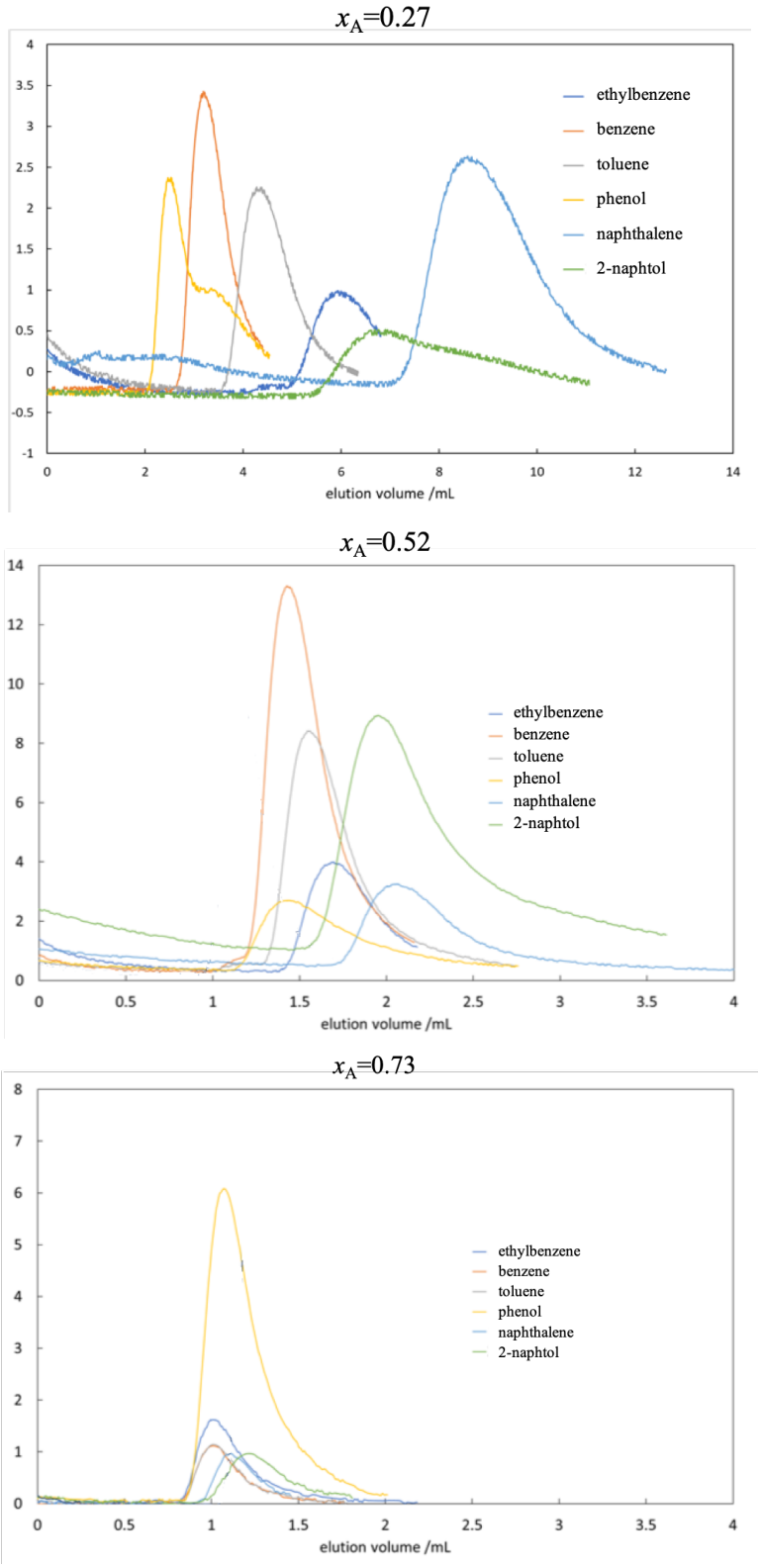

Fig. S 6: Chromatograms of aromatics at x_A=0.27, 0.52, and 0.73.