Supporting Information for

Cooperativity between coordinative unsaturated Fe(III) and aryl-π electrons in MIL-100(Fe) for adsorption of small molecules

Yuiko Tasaki-Handa, Kazuki Shibuya, and Shingo Saito

Graduate School of Science and Engineering, Saitama University, Japan.

Email: handa-ytasaki@apc.saitama-u.ac.jp; Tel: +81-70-8819-4717

1. Characterization of the as-synthesized MIL-100(Fe) and the packed column

Fig. S1 shows the XPS high resolution Fe 2p spectrum with fitted curve. Fe^{3+} shows two distinguishing peaks at 712.5 and 725.7 eV attributed to Fe 2p3/2 and Fe 2p1/2, with corresponding satellites at 716.4 and 730.0 eV.
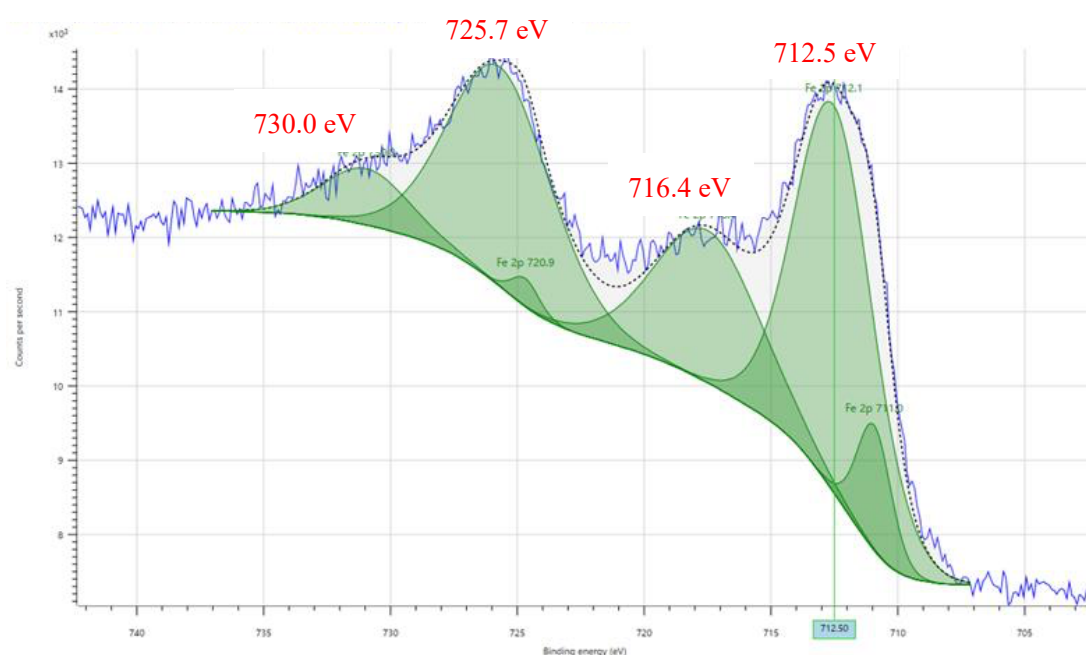

Figure S1. XPS high resolution Fe 2p spectrum of the as-synthesized MIL-100(Fe).

Figure S2 compares chromatograms before and after the flow of 1.0 L mobile phase.
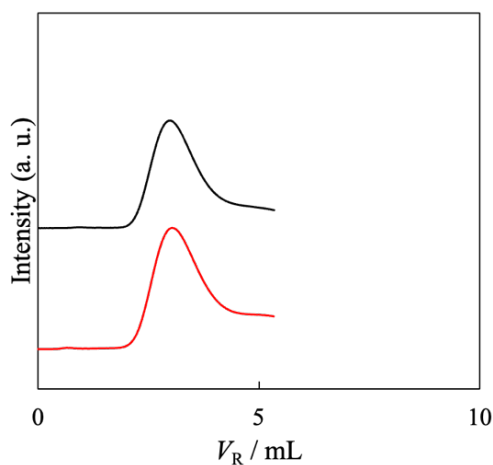

Figure S2　Chromatograms of 1-phenylethanol just after column packing (red) and after 1.0 L of mobile phase flow (black).

Figure S3 shows the excess adsorption isotherm for the MIL-100(Fe) packed column. The excess adsorption of ACN can be calculated as:

$$y_{ACN} - x_{ACN} = \frac{V_{ACN} - V_0}{V_0} x_{ACN}$$

where y_{ACN} and x_{ACN} are the volume fractions of ACN in the column and the mobile phase, respectively.[1] The experimental details are shown in the previous paper.[2] When x=0.3 (i.e., 30:70 vol% ACN-water), the excess adsorption ratio is approximately 0.75, indicating the presence of an excess ACN adsorption layer on the MIL-100(Fe). This is consistent with the results of the previous study.[2] Figure S3 compares chromatograms before and after the flow of 1.0 L mobile phase. There is no significant change in the elution time, indicating that the column can be used repeatedly.
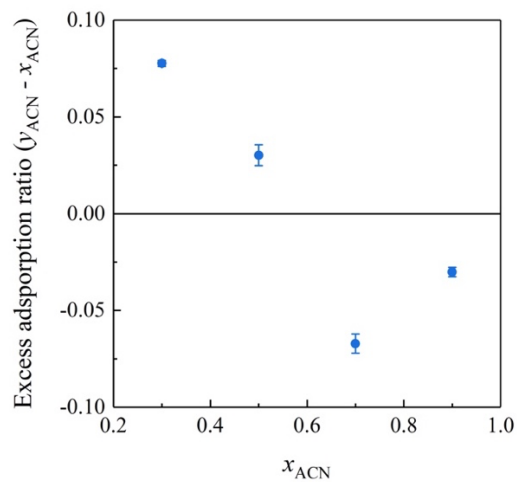
Figure S3 Excess adsorption isotherm of ACN on the as-synthesized MIL-100(Fe).

2. Prediction of retention volumes

Retention volumes of benzene, toluene, naphthalene, o-xylene, ethylbenzene, and m-xylene on C18 and Phe stationary phases were too strong under 30:70 vol% ACN-water mobile phase. Their retention volumes under 30:70 vol% ACN-water were determined by prediction of the linear relationship between log k and ACN concentration in the range from 45 to 70 vol% (Fig. S4).
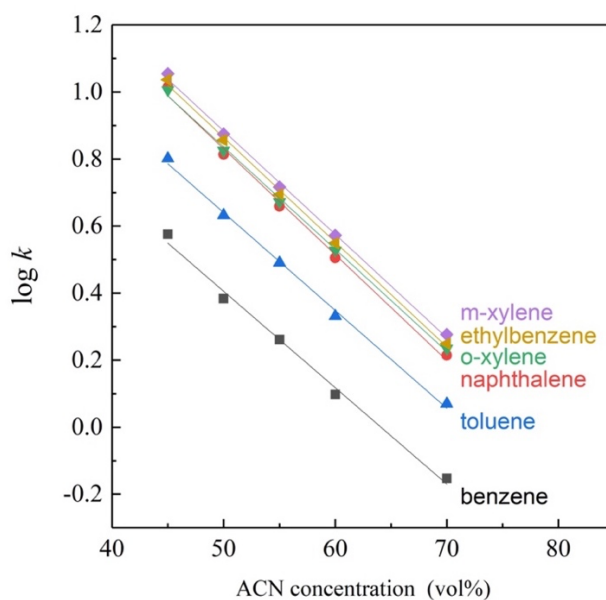

Figure S4   Change in log k with ACN concentration in the mobile phase for six aromatic hydrocarbons.

References

1   J. H. Knox and R. Kaliszan, *J. Chromatogr. A*, 1985, **349**, 211–234.

2   Y. Tasaki-Handa, M. Yoshikawa, S. Saito and M. Shibukawa, *New J. Chem.*, 2019, **43**, 16566−16571.