

Supporting Information

**Atomic/Molecular Layer Deposited Iron–Azobenzene Framework  
Thin Films for Stimuli-Induced Gas Molecule Capture/Release**

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## Characterization Techniques

The films thicknesses and densities were determined through X-ray reflectivity (XRR; X'Pert MPD PRO Alfa 1, PANalytical) measurements. The film thickness value was further divided by the number of deposition cycles to obtain the film growth rate, or the so-called growth-per-cycle (GPC) value. The density value was calculated from the XRR pattern based on the dependency of critical angle  $\theta_c$  on mean electron density  $\rho_e$  of the film material, namely,  $\rho_e = (\theta_c^2 \pi) / (\lambda^2 r_e)$ , where  $\lambda$  is the X-ray wavelength and  $r_e$  is the classical electron radius. The mass density was then calculated from  $\rho_m = (\rho_e A) / (N_A Z)$ , where  $A$  is the average molar mass,  $N_A$  is the Avogadro constant and  $Z$  is the average atomic number.

The degree of crystallinity of the films was investigated by grazing incidence X-ray diffraction (GIXRD; X'Pert MPD PRO Alfa 1, PANalytical; Cu K $\alpha$  radiation) with the incident angle ranging from 5° to 60°. Atomic force microscopy (Bruker dimension icon afm) images were taken in tapping mode to investigate the surface morphology of representative thin films. For each sample, scans of 5X5  $\mu\text{m}^2$  were mapped.

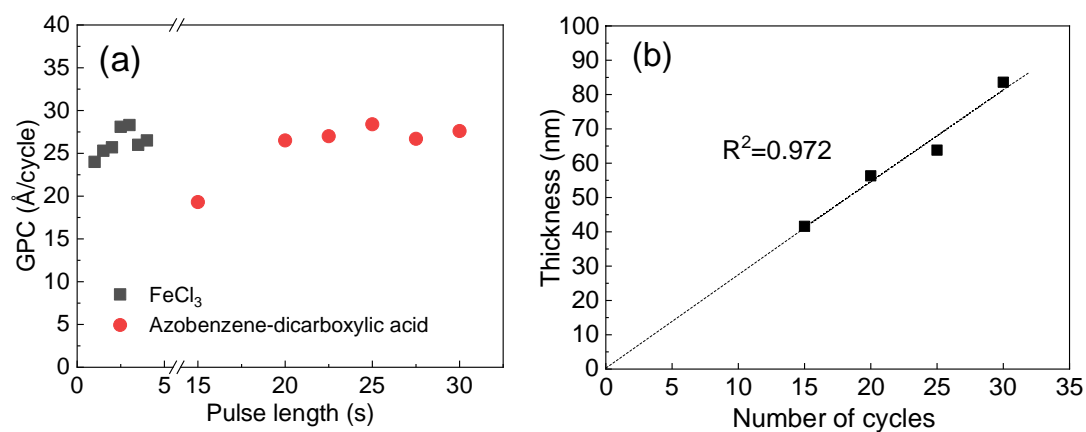
X-ray photoemission spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR) were used to analyze the chemical state of the samples deposited on Si. The FTIR measurements were carried out in transmission mode using a Bruker alpha II in the 4000-400  $\text{cm}^{-1}$  region at 2  $\text{cm}^{-1}$  resolution. A background spectrum was collected using an uncoated Si wafer and subtracted from the spectra measured for the samples. The XPS measurements were carried out using a Kratos Axis Ultra spectrometer with monochromatic Al K $\alpha$  radiation. For the spectra acquisition, a pass energy of 40 eV and an X-ray power of 100 W was used. The analysis area was roughly 700  $\mu\text{m}$  x 300  $\mu\text{m}$ . The FTIR measurements were carried out in transmission mode using a Bruker alpha II in the 4000-400  $\text{cm}^{-1}$  region at 2  $\text{cm}^{-1}$  resolution. A background spectrum was collected using an uncoated Si wafer and subtracted from the spectra measured for the samples.

The photoisomerization characteristics of our iron azobenzene thin films under irradiation by UV light (365 nm) using a 200 W xenon-doped mercury lamp (Hamamatsu Lightning cure LC8) equipped with a cut off filter ( $\lambda = 300\text{--}480$  nm). The photon flux was 3000  $\text{mW}/\text{cm}^2$  at the working distance of 10 mm. Furthermore, an optical fiber was employed to direct the irradiation beam to the sample holder, which considerably reduces the nominal power of the xenon-doped mercury lamp, leading to cold light. The UV-vis transmittance spectra (Shimadzu UV-2600 spectrometer) were recorded for samples in the wavelength range of 200–800 nm.

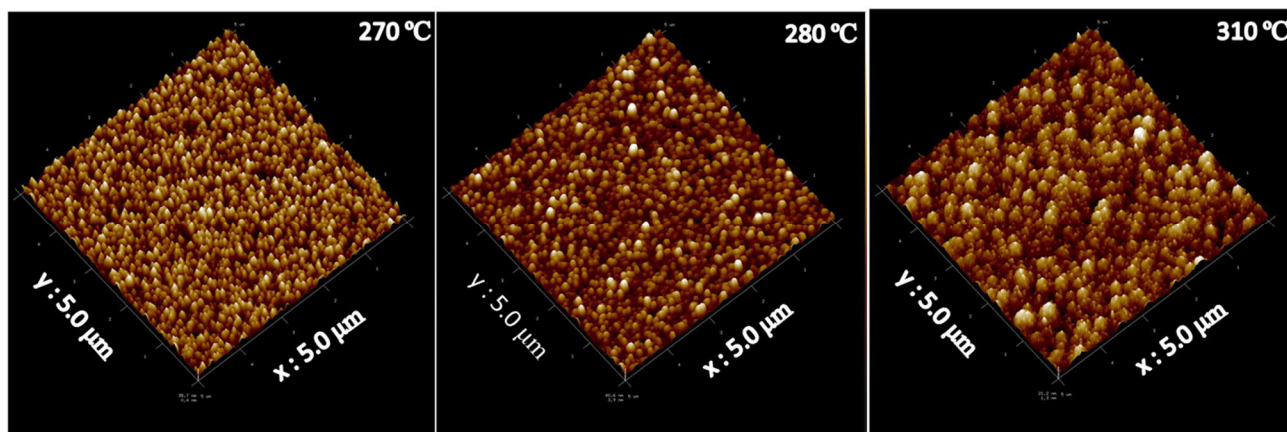
## Experimental Procedures

The crystalline iron-azobenzene-4,4'-dicarboxylate (Fe-azobenzene dicarboxylic acid) coordination network thin films were deposited in a commercial flow type hot-wall ALD reactor (F-120 by ASM Microchemistry Ltd.) using FeCl<sub>3</sub> (Merck, 95%) and azobenzene-4,4'-dicarboxylic acid (azobenzene dicarboxylic acid; TCI, 95%) as precursors. To reach the precursor vapor pressures required for the efficient transport of the precursor to the substrate, FeCl<sub>3</sub> and azobenzene dicarboxylic acid powders were placed in an open boat inside the reactor and heated, respectively, to 158 and 240 °C for sublimation. Nitrogen (>99.999%, Schmidlin UHPN 3000 N<sub>2</sub> generator) was used as a carrier and purging gas. The depositions were performed under a 3–4 mbar pressure onto Si (100) and quartz slide substrates; the latter substrates were used for the UV-vis transmittance spectroscopy measurements.

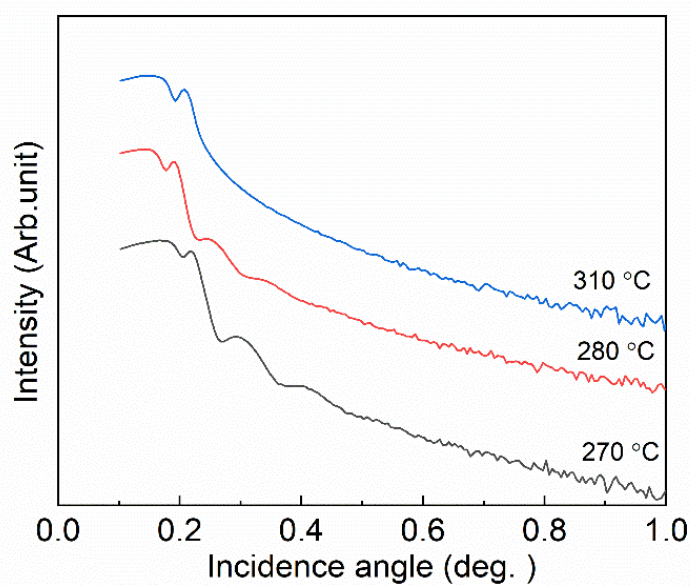
## Supporting Information Figures



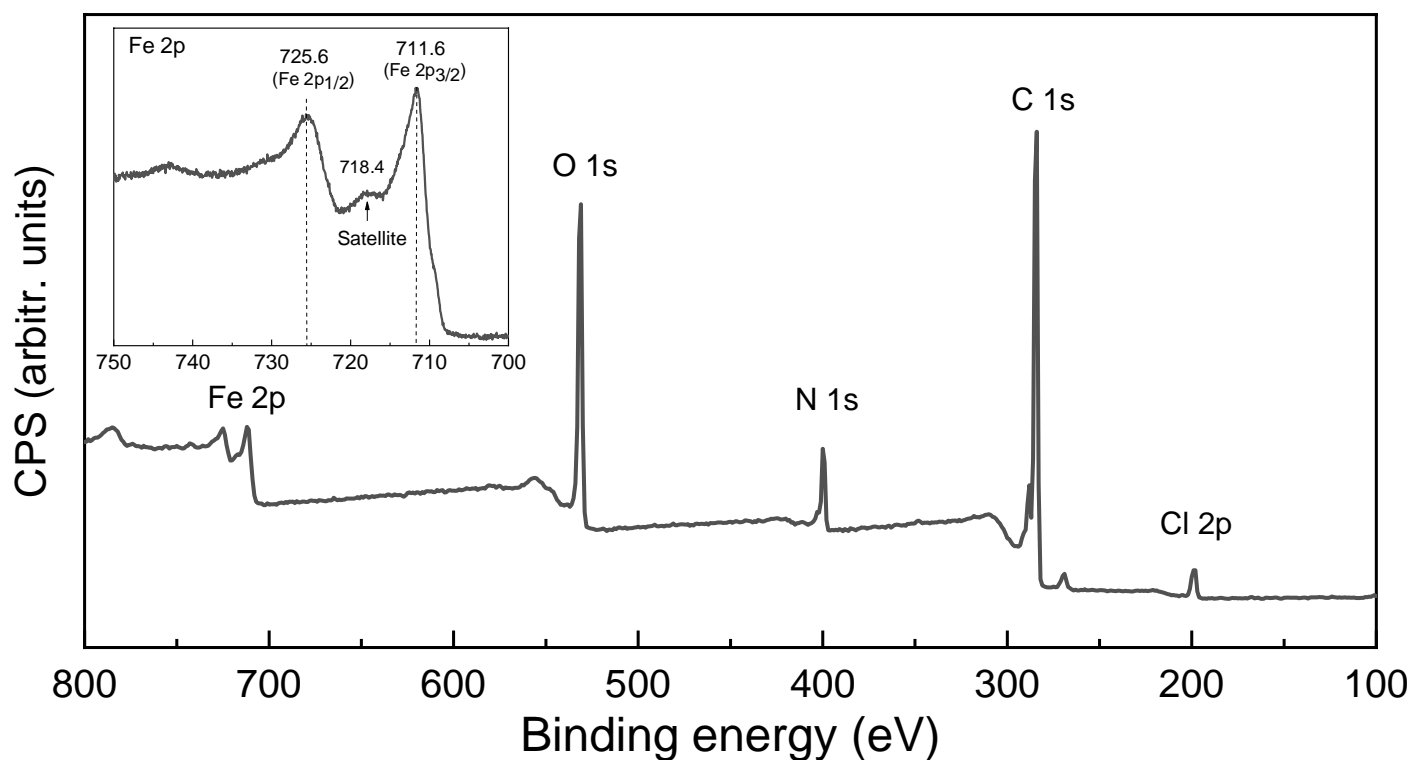
**SI Fig. 1.** Optimization of ALD/MLD parameters: (a) growth-per-cycle (GPC) at different pulse lengths of FeCl<sub>3</sub> (black squares; 20 s for azobenzene-dicarboxylic acid) and azobenzene-dicarboxylic acid (red balls; 4 s for FeCl<sub>3</sub>) at 280 °C, and (b) film thickness vs. the number of ALD/MLD cycles at 280 °C.



**SI Fig. 2.** AFM images of iron-azobenzene thin films deposited at different temperatures.



**SI Fig. 3.** XRR patterns of iron-azobenzene thin films deposited at different temperatures.



**SI Fig. 4.** High-resolution XPS spectra for a crystalline film deposited through the FeCl<sub>3</sub>+Azobenzene dicarboxylic acid process at 280 °C. Insert shows the Fe 2p XPS spectrum.

**Author Contributions**

Experimental work was carried jointly by A. K. and A. P. under the supervision of M. K. The manuscript was written with contributions from all the three authors.