Supporting information for

Fe^{2+}-based layered porous coordination polymers and soft encapsulation of guest via redox activity

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Materials and general methods

All chemicals and solvents used in the syntheses were of reagent grade and used without further purification. Thermogravimetry analysis (TGA) were measured using a Rigaku TG8120 under flowing nitrogen with 10 K min^{-1} ramp rate. X-ray powder diffraction (XRPD) data were collected on a Rigaku RINT 2200 Ultima diffractometer with CuKα anode. Single crystal X-ray diffraction measurement were performed at 223 K with a Rigaku AFC10 diffractometer with Rigaku Saturn Kappa CCD system equipped with a MicroMax-007 HF/VariMax rotating-anode X-ray generator with confocal monochromated MoKα radiation. Data were processed by a direct method (SIR97) and refined by full-matrix least-squares refinement using the SHELXL-97 computer program. The hydrogen atoms were positioned geometry and refined using a riding model. The deposited numbers of Cambridge Crystallographic Data Centre (CCDC) are 901080 (FeCID-1), 901081 (FeCID-1⊃DMF), 901082 (FeCID-1⊃I), 901083 (FeCID-2⊃DMF), 901084 (FeCID-5⊃DMF), 901085 (FeCID-6⊃DMF), respectively. CO_2 gas adsorption isotherms were measured by BELSORP-mini with dryice/methanol suspension as cold trap. Raman spectroscopies were measured by LabRAM HR-800 spectrometer with a semiconductor laser at 785 nm. ^{57}Fe Mössbauer spectroscopy was performed using a ^{57}Co source with a nominal activity of 1.85 GBq. Velocity scale was calibrated as isomer shifts relative to α-Fe. Impedance analyses were performed on powders of samples without modification. The powders (ca. 35 mg) were pressed at 400 kg N for 1 minutes by a standard 5 mm die and sandwiched between two gold electrodes. Measurements were performed using an impedance and gain-phase analyzer (Solartron SI 1260 Impedance/Gain-Phase analyzer) over frequency range 1 Hz–1 MHz with an input voltage amplitude of 30 mV. The measurement cell was filled with nitrogen at atmospheric pressure before recording the measurements. ZView software was used to fit impedance data sets by means of an equivalent circuit simulation to obtain the resistance values.

Synthesis of compounds.

We synthesized all four compounds under the Ar atmosphere. $FeCl_2$ (0.3 mmol) and 4,4’-bipyridyl (0.75 mmol) and dicarboxylates (1.5 mmol) were mixed in DMF (30 mL) and reacted at 150 °C with 50 mL glass vial for two days to have crystalline compounds. {[Fe(isophthalate)(bpy)]$\supset$DMF}$_n$ (FeCID-1$\supset$DMF), {[Fe(3,5-pyridinedicarboxylate)(bpy)] $\supset$DMF}$_n$ (FeCID-2$\supset$DMF), {[Fe(5-NO_2-isophthalte)(bpy)]$\supset$DMF}$_n$ (FeCID-5$\supset$DMF), {[Fe(5-MeO-isophthalate)(bpy)] $\supset$DMF}$_n$ (FeCID-6$\supset$DMF) were characterized by single crystal X-ray diffractions and elemental analyses. Elemental analyses were measured after evacuated four samples at 150 °C for 6 hours to remove solvents. Elemental analysis: calcd (%) for FeCID-1 [Fe(isophthalate)(bpy)]$_n$: C 57.47, H 3.22, N 7.45; found (%) C 57.30, H 3.25, N 7.55. calcd for FeCID-2 [Fe(3,5-pyridinedicarboxylate)(bpy)]$_n$: C 54.14, H 2.94, N 11.14; found (%) C 54.0, H 2.56, N 9.69. calcd (%) for FeCID-5 [Fe(5-NO_2-isophthalte)(bpy)]$_n$: C 51.33, H 2.63, N 9.97; found (%) C 51.06, H 2.68, N 10.16. calcd (%) for FeCID-6 [Fe(5-MeO-isophthalate)(bpy)]$_n$: C 56.18, H 3.47, N 6.90; found (%) C 55.41, H 3.46, N 6.95.

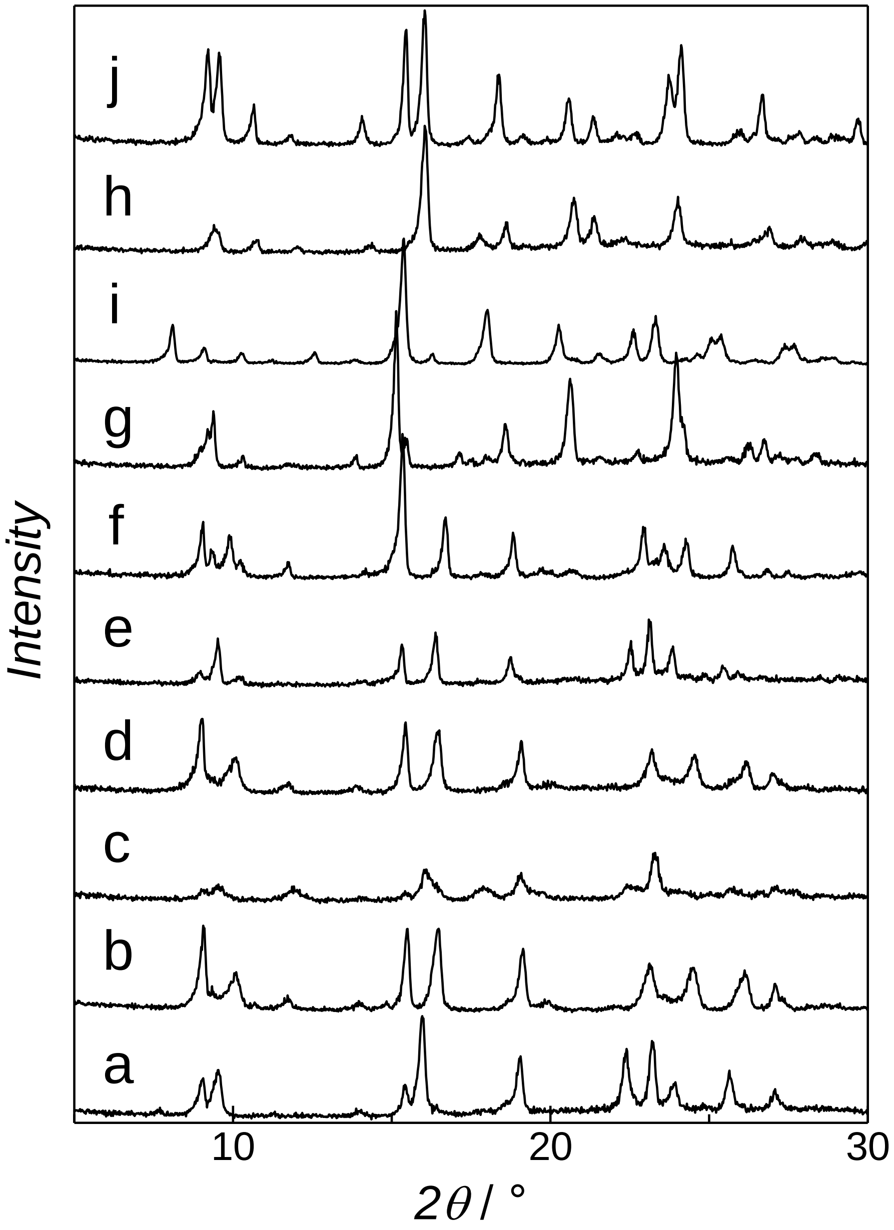


Fig. S1. Powder X-ray diffraction patterns (XRD) of (a) FeCID-1⊃DMF (b) FeCID-1 (c) FeCID-1⊃I (d) FeCID-1 after degassing of accommodated iodine (e) FeCID-2⊃DMF (f) FeCID-2 (g) FeCID-5⊃DMF (h) FeCID-5 (i) FeCID-6⊃DMF (j) FeCID-6.

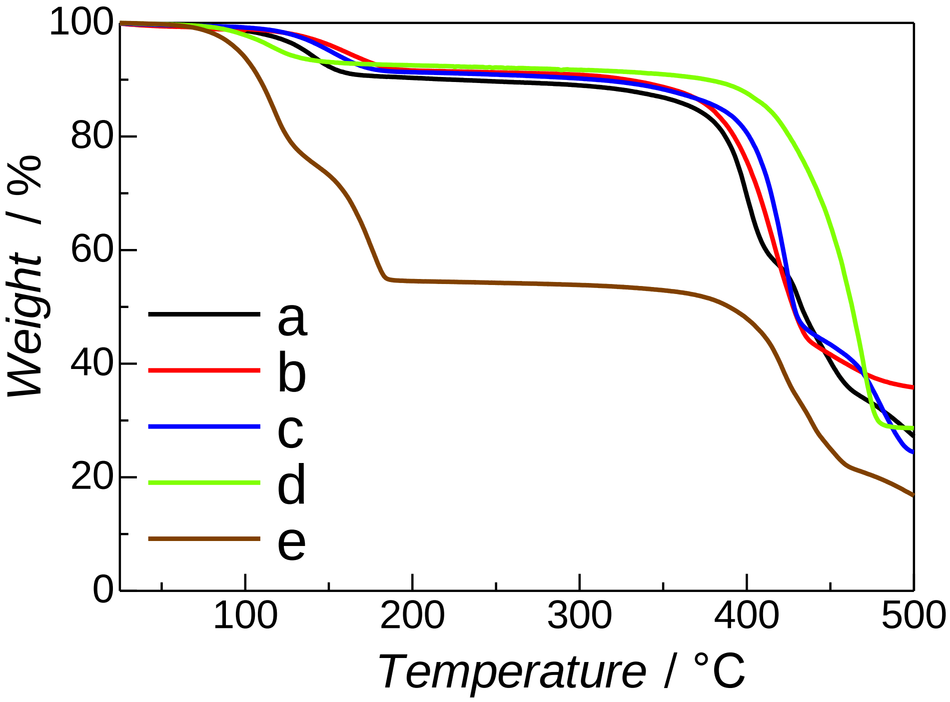


Fig. S2. TGA profiles of (a) FeCID-1⊃DMF (b) FeCID-2⊃DMF (c) FeCID-5⊃DMF (d) FeCID-6⊃DMF (e) FeCID-1⊃I.

Table S1. Parameters of Mössbauer spectra of FeCID-1 and FeCID-1⊃I. Ratio (%) are calculated by the area of each spectrum.

		Ratio (%)	I.S. (mm / s)	Q.S. (mm / s)
FeCID1	Fe(II)HS	100	1.06	2.75
FeCID1⊃1	Fe(II)HS	48.9	1.09	2.05
	Fe(III)HS	51.1	0.37	0.6

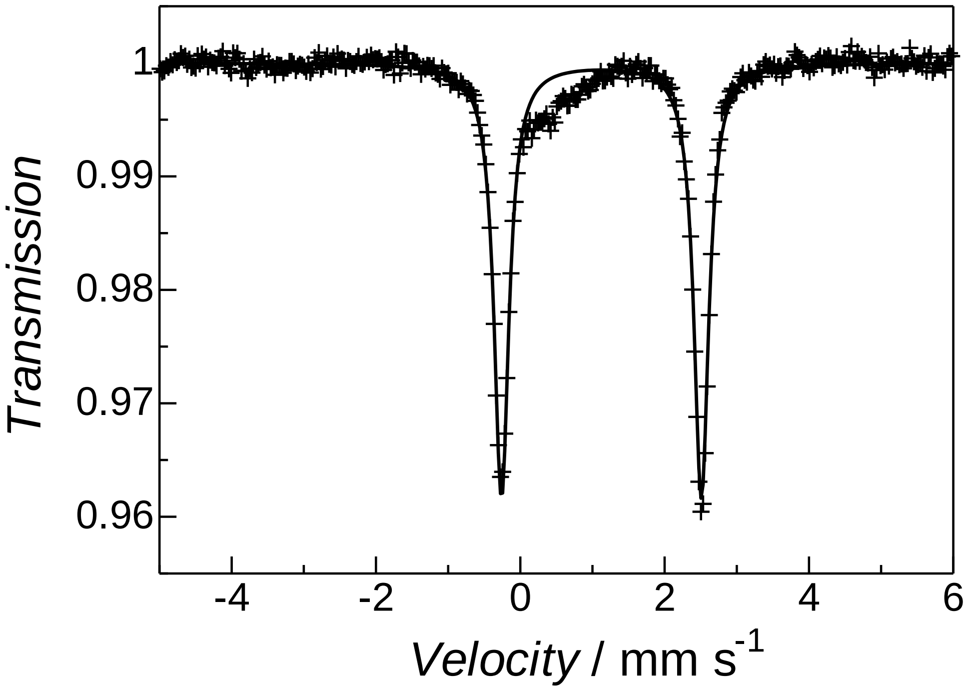
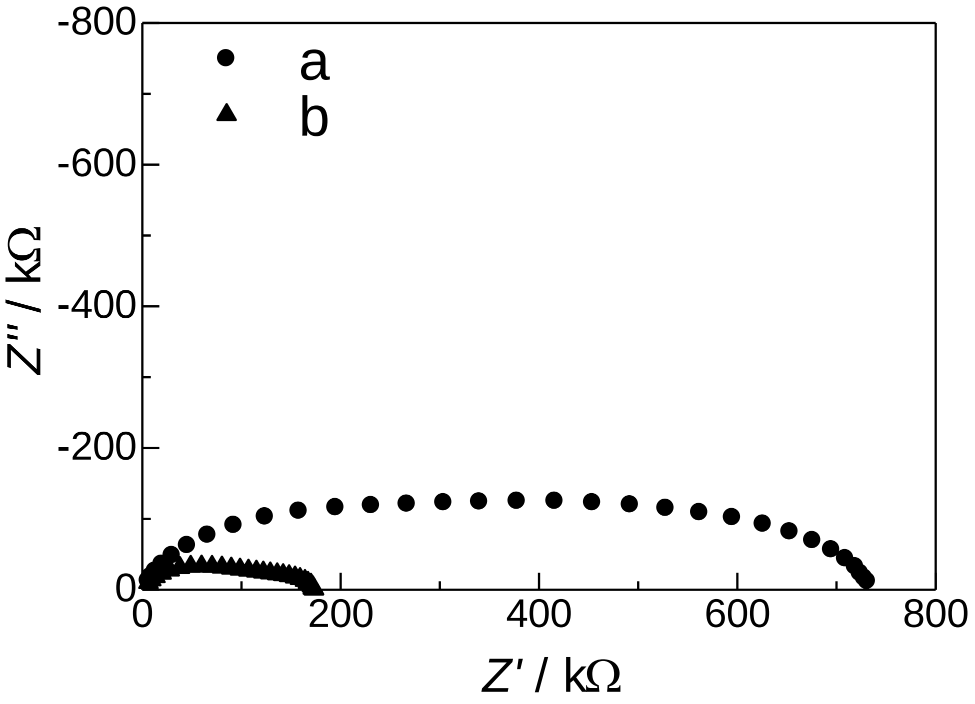


Fig. S3. Mössbauer spectra of FeCID-1 after degassing of accommodated iodine.



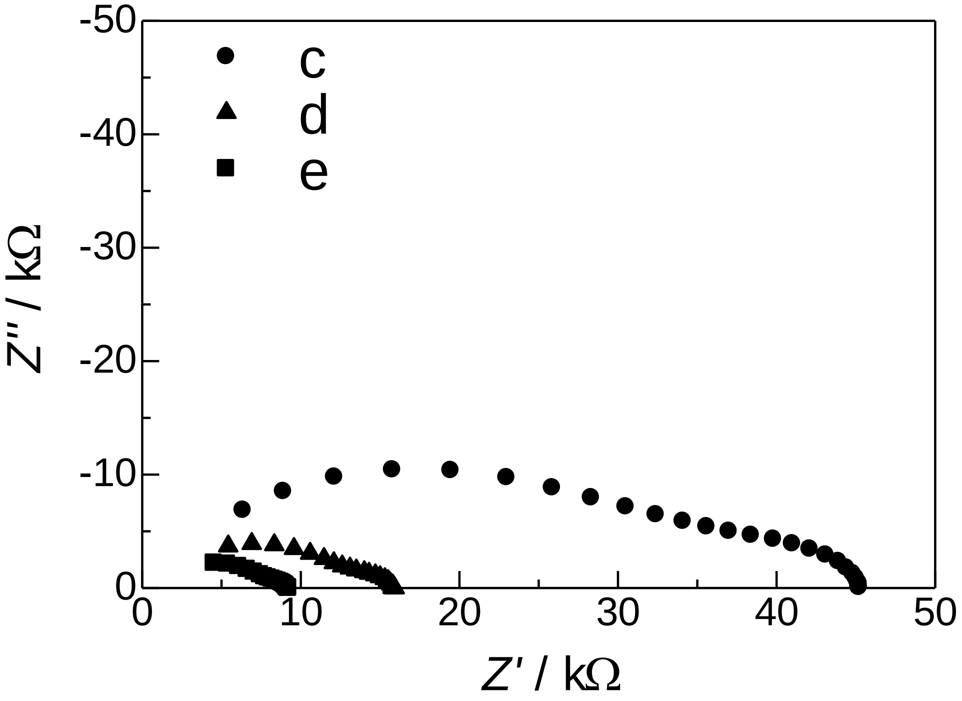


Fig. S4. Impedance spectra of FeCID-1⊃I from (a) 25 °C (a) 50 °C (a) 75 °C (a) 100 °C under N_2 atmosphere.

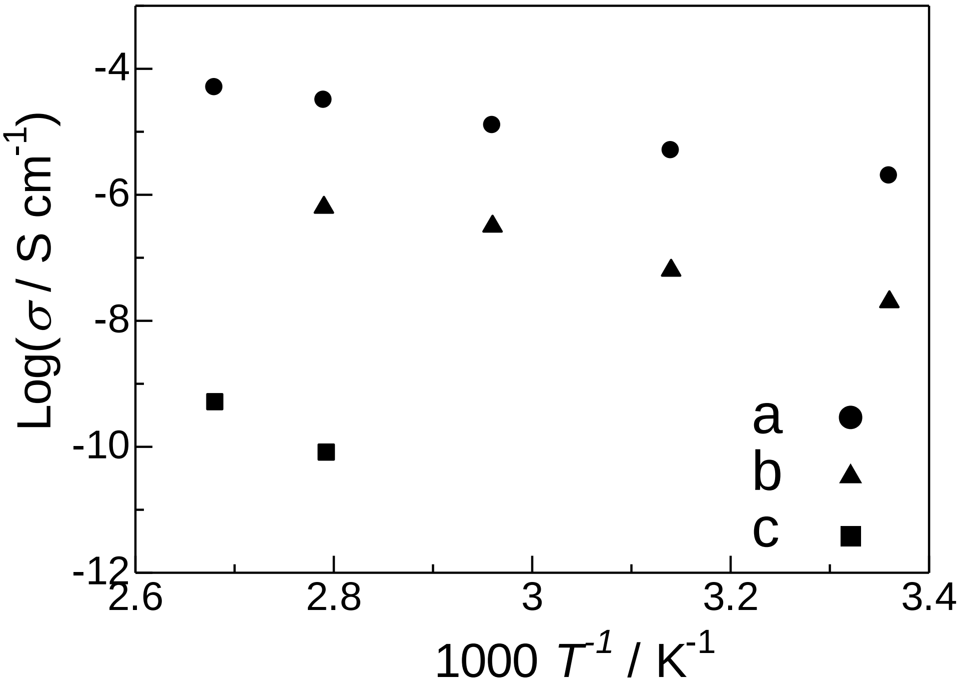


Fig. S5. Arrhenius plots of (a) FeCID-1⊃I (b) FeCID-1⊃0.3I (c) FeCID-1.

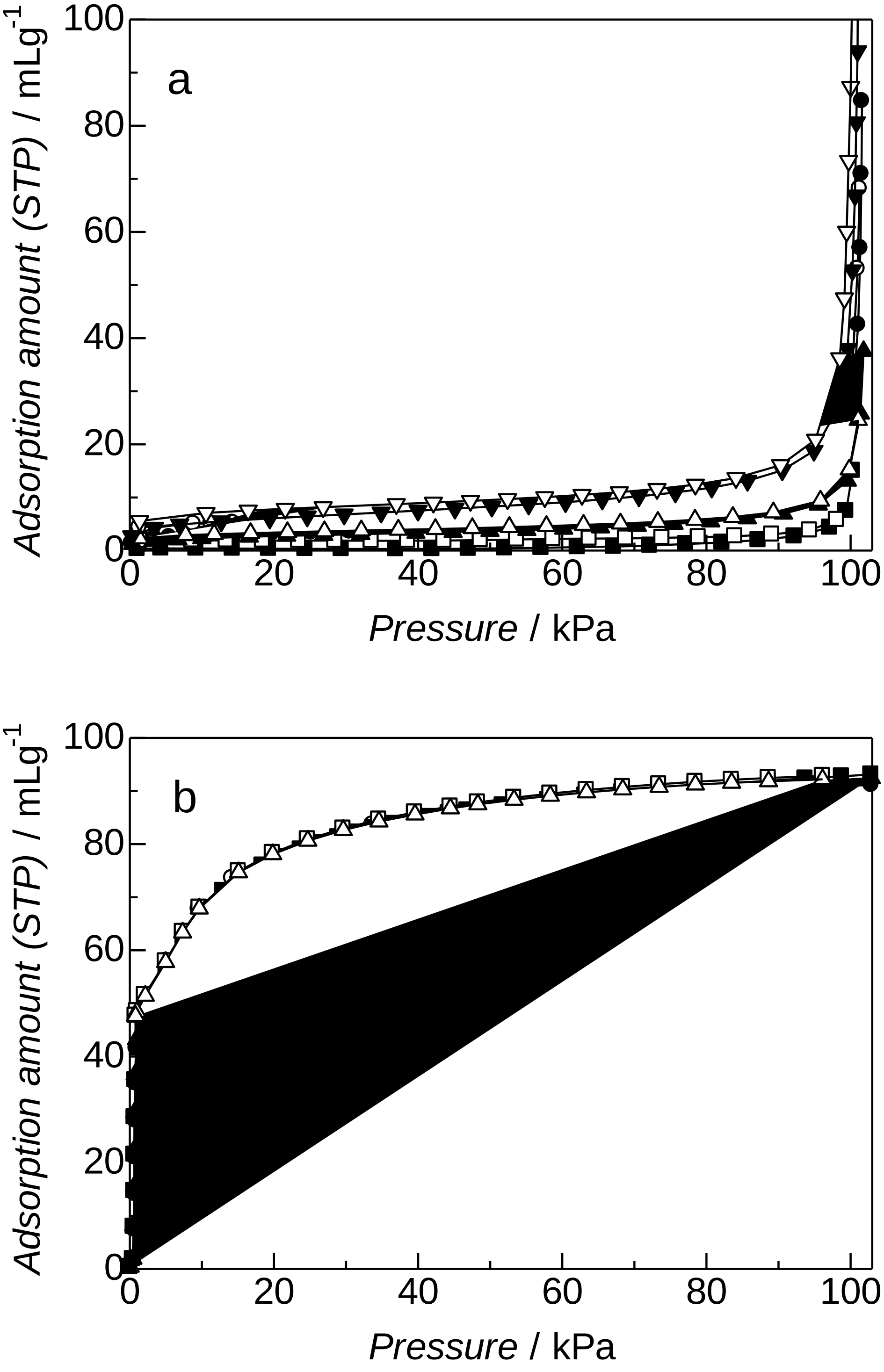


Fig. S6. (a) N_2 adsorption and desorption isotherms of FeCID-1 (●) FeCID-2 (■) FeCID-5 (▲) FeCID-6 (▼) at 77 K. (b) CO_2 adsorption and desorption isotherms of FeCID-5 at 195 K three times. (●) 1st (■) 2nd (▲) 3rd, and adsorption (solid) and desorption (open), respectively.