Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for:

Highly Selective Methanol Adsorption from Dilute Aqueous Solutions Using $Mn_3[Fe(CN)_6]_2$: A Prussian Blue Analog

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This file includes:

Experimental section:

All chemicals are commercially available from Fujifilm Wako Pure chemical Co. (Osaka, Japan).

Preparation of MnHCF:

MnHCF (Manganese hexacyanoferrate) was prepared. Aqueous solution 20 ml of 0.6 mol/L manganese (II) chloride and 20 ml of 0.4 mol/L potassium hexacyanoferrate (III) were mixed in a beaker with stirring for one hour at ambient temperature. Obtained MnHCF precipitation was centrifuged, and the residue was washed with water six-time, and finally collected as white precipitation after being dried under a vacuum overnight.

Screening test for Prussian blue analogs:

All other PBA adsorbents were screened out by batch adsorption test methods. PBA powders were placed into a centrifuged tube with 1000 mg-MeOH/L or 24000 mg-MeOH/L of aqueous methanol and shake for three days. PBA and aqueous methanol were separated by centrifuge to obtain aqueous methanol. Captured aqueous methanol was measured by Gas Chromatography-Mass Spectrometry (GC-MS-QP2010, Shimadzu) and adopted the PBA showed low methanol concentrations in aqueous methanol.

Characterization:

The Scanning electron microscope (SEM) and electron diffraction X-ray spectroscopy (SEM-EDX) were collected on the TM 4000 Plus (Hitachi high tech) The XRD pattern was collected on the D8 advance (Bruker) which uses Cu Kα radiation. The chemical composition charge balance, mass balance, and water content of MnHCF were determined by using SEM-EDX, XRD and Element analysis (C, N, H, 2400 Series II CHNS/O Elemental Analysis, PerkinElmer). BET surface area of MnHCF was obtained using BELSORP-mini and BELSORP-MAX II (Microtrac Bel Inc.). The specific heat capacity (C_p) was measured by DSC7020 (Hitachi high tech).

Adsorption experiment in batch:

Adsorption performance of MnHCF, activated carbon, and zeolite was investigated by batch experiment in Figure 2. PBA powders were placed into a centrifuged tube with aqueous methanol and shake for setting time. PBA and aqueous methanol were separated by centrifuge to obtain aqueous methanol. Captured aqueous methanol was measured by Gas

Chromatography-Mass Spectrometry. Adsorption tests were conducted with n=3. The amount of adsorption was evaluated from the average and standard deviation. Adsorption volume is evaluated based on the weight of the material on a wet base using bellow equation.

$$Adsorption\ capacity = \frac{(C_0 - C_e) \times v}{m_a} \#(S1)$$

Where C_0, C_e, v, and m_a are the initial concentration, the equilibrium methanol concentration, the volume of the methanol solution, and the weight of the adsorbent. In this study, the main target concentration was 1000 mg MeOH/L. Therefore, adsorption isotherm measurements were performed within a concentration range of one order of magnitude above and below this target.

The *K* value:

The equilibrium constant *K* value is derived from the Figure S6. The *K* value can be made dimensionless by converting the adsorbent to volume using the true density of the adsorbent. The *K* value is determined by following equation.

$$K_{eq}^{'} \approx K_D^{'} = \frac{q_e^{'}}{C_e^{'}} \#(S2)$$

where K'_{eq}, K'_D, q'_e, C'_e, are the equilibrium constant[no unit], distribution coefficient [no unit], the equilibrium density (mmol/L), the equilibrium adsorbate concentration (mmol/L).

Adsorption experiment in column:

Adsorption performance of MnHCF was investigated in Figure 3a. Breakthrough curve experiments for adsorption at ambient temperature were carried out by using GC-MS in Figure 3b. The 200 mg of MnHCC powder was placed middle part of the glass tube at middle part between glass wools. The 1000 mg/L of methanol aqueous were flown to the column at a flow rate of 0.5 ml/min controlled by plunger pump via 1/8-inch tubes. Adsorption performance was calculated from the breakthrough curve and corrected blank column experiments using bellow equation.

$$A = \sum_{k=1}^{n} (C_0 - C) t_k \#(S3)$$

where A, n, t_k, C_0, and C are the adsorption capacity of sample, saturated time, measurement time, the initial concentration, and the concentration given from GC-MS. The concentrations of methanol are calculated from the areas of the peak.

Energy cost calculation:

Energy of methanol adsorption as the energy consumption of the pumps was calculated using bellow equation.

$$Adsorption\ energy\ of\ adsorbent = \frac{t_b \times \Delta p \times Q}{M_{adsorbent}} \#(S4)$$

Where t_b, Δp, Q, $M_{adsorbent}$ are breakthrough time, different pressure, flow rate, and amount of adsorbent.

Table S1. The result of screening test. MnHCF ($Mn_3[Fe(CN)_6]_2$) was adopted as shown highest desorption.

Sample	Methanol uptake from 1000 mg-MeOH/L (mmol-MeOH / g-adsorbent)	Methanol uptake from 24000 mg-MeOH/L (mmol-MeOH / g-adsorbent)
$In_3[Fe(CN)_6]_3$	0.12	1.14
$In[Fe(CN)_6]$	0.08	1.38
$Ni_3[Fe(CN)_6]_2$	0.09	1.25
$Co_3[Fe(CN)_6]_2$	0.07	0.88
$Mn_3[Co(CN)_6]_2$	0.19	1.60
$Mn_3[Fe(CN)_6]_2$	0.31	1.72
$Rb_{0.1}Mn[Fe(CN)_6]_{0.7}$	0.30	1.51
$Ag_{0.1}Mn[Fe(CN)_6]_{0.7}$	0.30	1.61
$Cs_{0.1}Mn[Fe(CN)_6]_{0.7}$	0.30	1.41

Table S2. Methanol isotherm parameters at 25 °C for MnHCF, Activated carbon, and zeolite.

	Langmuir			Freundlich			Redlich-Peterson				Koble-Corrigan			
	$q_{m,L}$	K_L	R^2	K_F	n_F	R^2	K_{RN}	a_{RN}	b_{RN}	R^2	a_{KC}	b_{KC}	n_{KC}	R^2
MnHCF	157.18	0.00007	0.999832	0.286	0.577	0.98943	0.0116	0.000100	0.97	0.98943	0.015	0.00009	0.97	0.999881
Activated Carbon	65.72	0.00004	0.991919	0.077	0.593	0.990718	0.0077	0.024768	0.52	0.993502	0.082	0.00006	0.59	0.990819
Zeolite	8.19	0.00047	0.757003	0.005	0.859	0.948246	0.0018	0.000007	1.21	0.960379	0.008	0.00000	0.80	0.989257

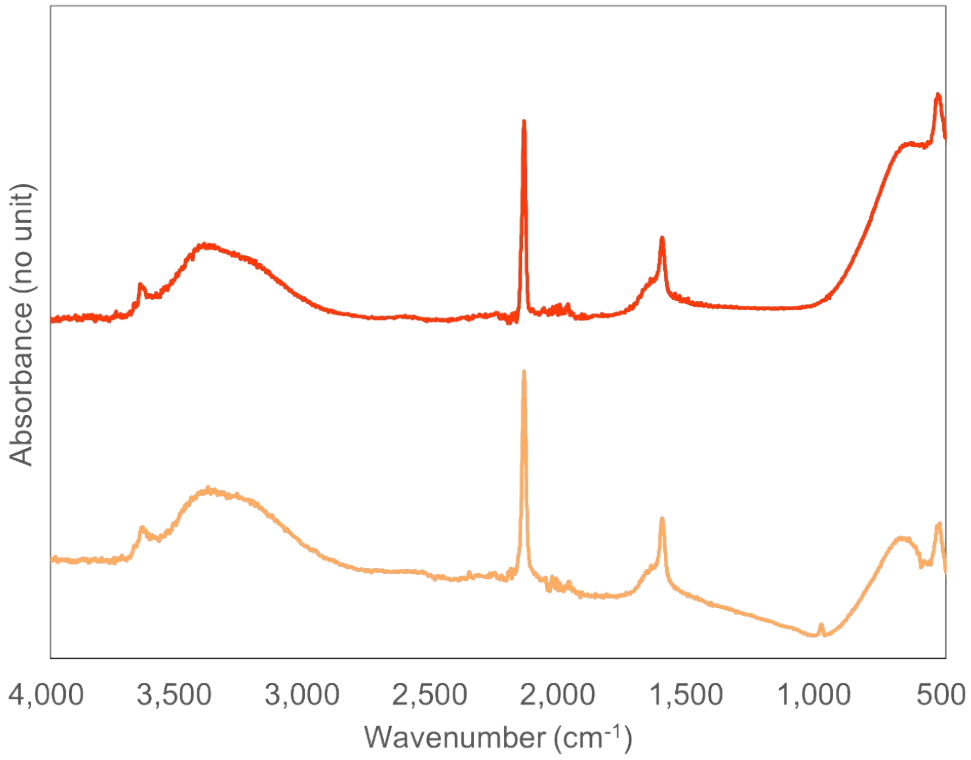

Figure S1. IR spectra of MnHCF for before adsorption (red line), and after adsorption (orange line). All spectra are normalized a peak at 2100 cm^{-1}.

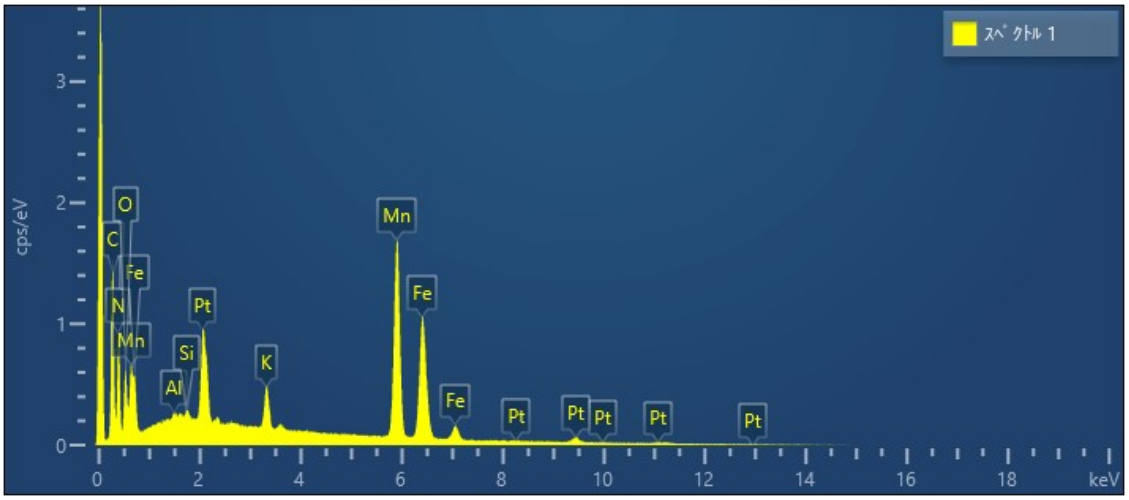

Figure S2. SEM-EDS spectra of MnHCF. Pt is derived Pt coating by spattering.

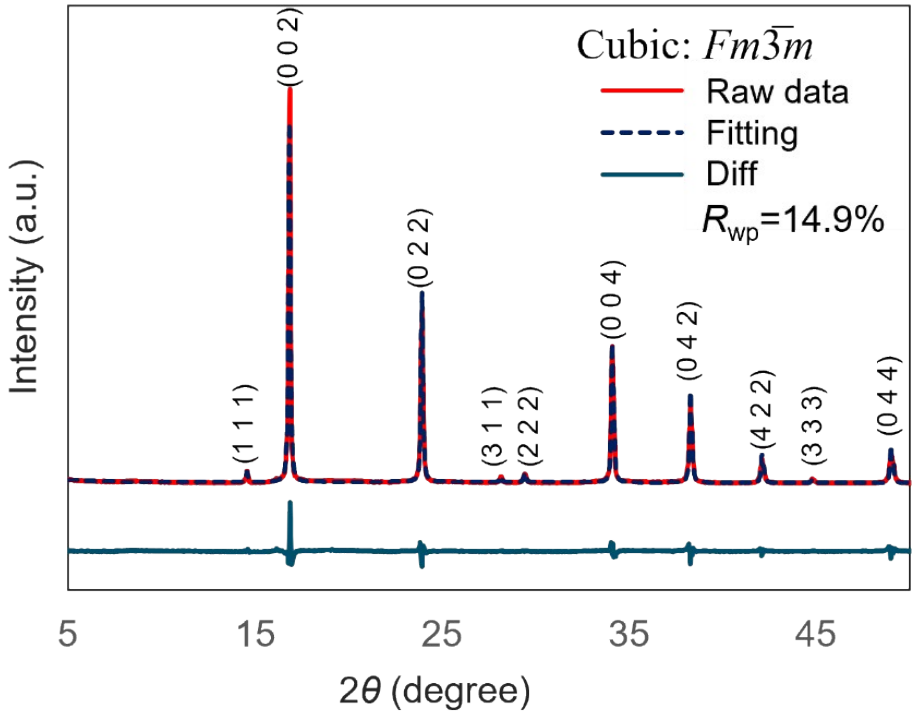

Figure S3. The XRD patterns of MnHCF. Relative factors: R_{wp} = 14.9%, R_p = 10.0%, R_e = 4.16%.

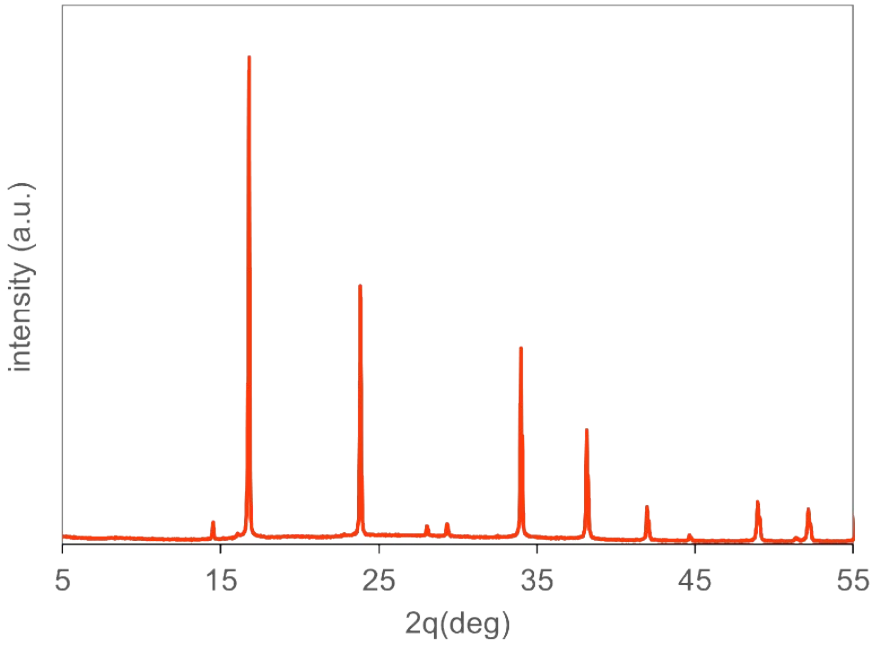

Figure S4. (a) The XRD patterns of MnHCF after methanol adsorbed. No difference with before methanol adsorbed.

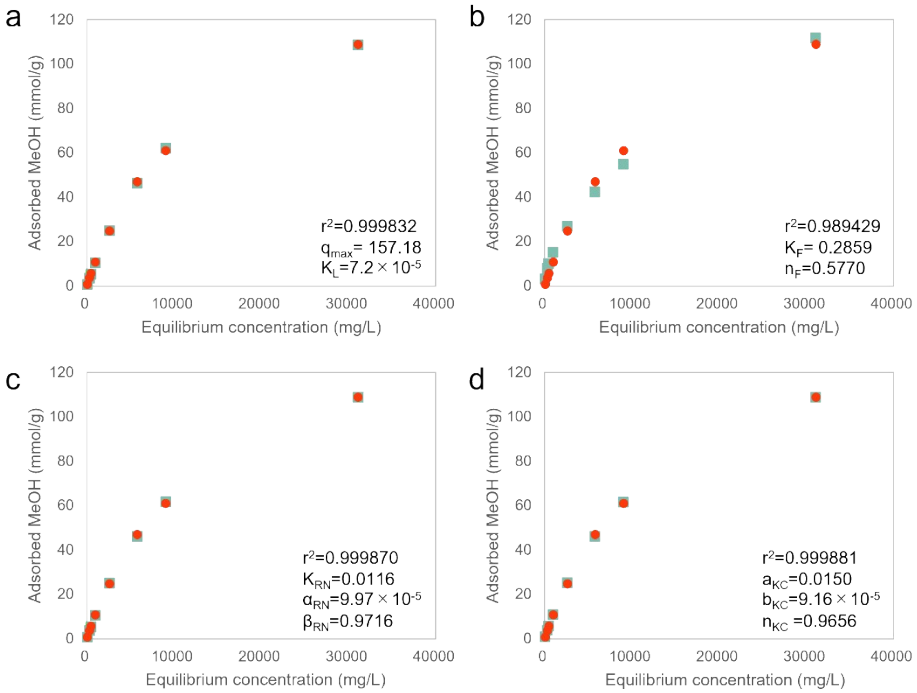

Figure S5. (a) MnHCF adsorption isotherms at 25°C and fitted with each adsorption model; Langmuir, Freundlich, Redlich-Peterson, Koble-Corrigan. The coefficients of determination indicate agreement with Koble-Corrigan, Redlich-Peterson, Langmuir, and Freundlich, in that order.

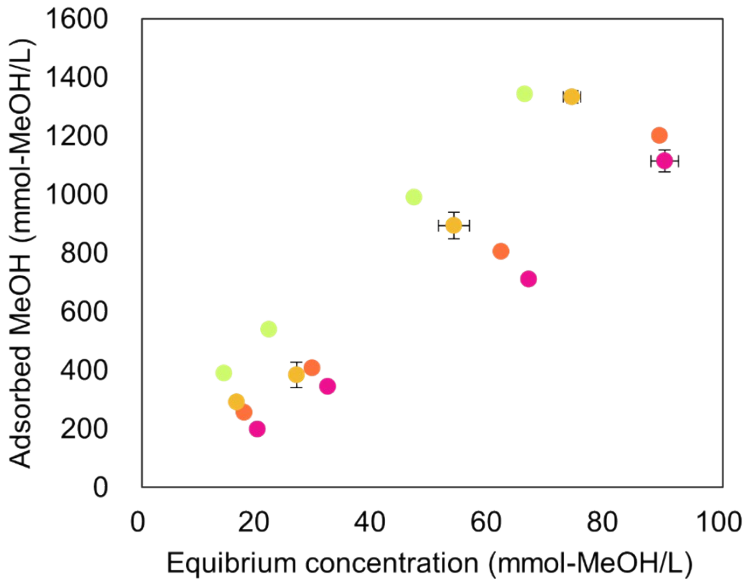

Figure S6. Temperature dependence of methanol adsorption isotherms at 10 (green), 25 (yellow), 40 (orange), and 55 °C (pink). The unit of Y-axis was converted from mmol/g to mmol/L.

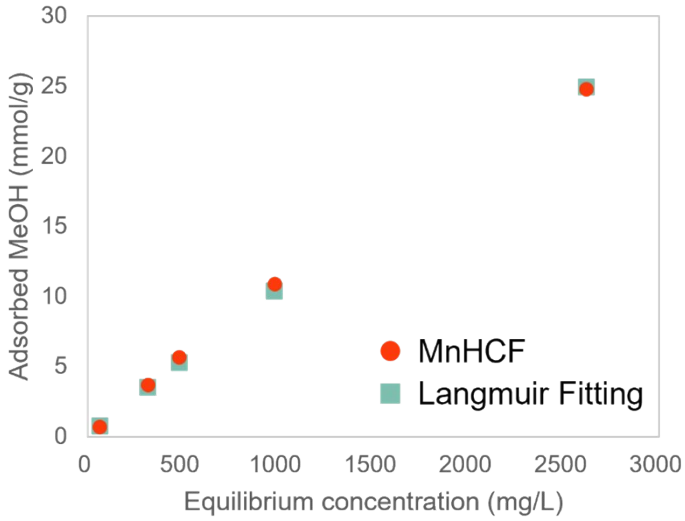

Figure S7. Langmuir fitting of MnHCF focusing on low concentrations from Figure S5a.

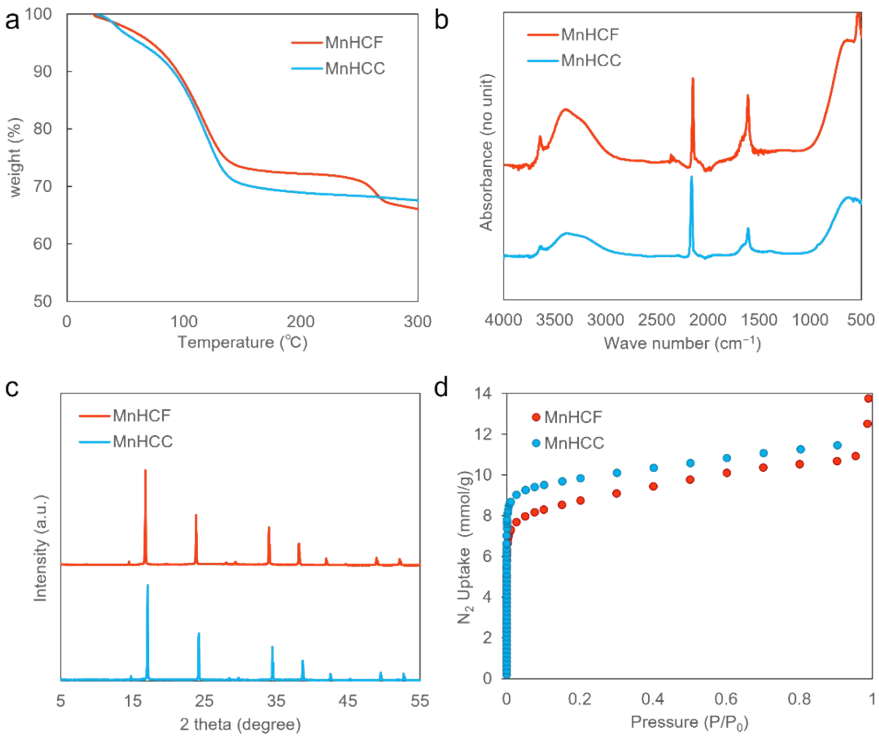

Figure S8. Comparison of MnHCF (red curve) and MnHCC (blue curve) Characterization. Comparison using (a) TG curves, (b) IR spectra, (c) XRD spectra, and (d) nitrogen adsorption isotherms. The MnHCFs and MnHCCs did not exhibit significant structural differences. MnHCF possesses defective sites indicative of methanol coordination bonds at the Mn^{2+} open metal sites. MnHCF has a lattice size of 10.5 Å, which is wider than that of MnCC (10.4 Å). The slightly larger lattice is thought to affect the adsorption of methanol.