Electronic Supplementary Information (ESI)

Paramagnetism Enhancement by *in situ* Electrochemical Hole Doping into Prussian Blue Thin Film

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Determination of the Fe^{III}/Fe^{II} ratio in the intact PB film by XPS

The Fe2*p* photoelectron spectrum of PB film on the ITO substrate was shown in Fig. S2, where the background due to inelastic scattering of higher-energy electrons is subtracted by Tougaard's method.¹ The spectrum was deconvoluted into six components assuming the Doniach-Sunjic peak-shape function² taking asymmetry into account. The peaks originating in low-spin Fe^{III} ions are accompanied with remarkable shake-up satellites due to large final-state effect characteristic of open-shell systems. Two set of peaks with a separation of ~5 eV corresponding to Fe^{II} and Fe^{III} ions were easily recognized just like in the spectra recorded for soluble PB KFe^{III}[Fe^{III}(CN)₆] ·H₂O by Wertheim and Rosencwaig.³ Peak areas of different valence ions were compared to give Fe^{II2} $p_{3/2}$: Fe^{III2} $p_{3/2} \sim 1.0 : 2.0$ and Fe^{II2} $p_{1/2} : Fe^{III2}p_{1/2} \sim 1.0 : 1.9$, suggesting Fe^{III}-richer composition of the PB film rather than the ratio expected for the ideal insoluble bulk PB, Fe^{II} : Fe^{III} ~ 3 : 4.

Cyclic voltammogram of the intact PB film

Cyclic voltammogram of the intact PB film in 0.1 mol L⁻¹ KCl aqueous solution was shown in Fig. S4a. Two sets of peaks were observed at around +0.15 V and +0.86 V vs Ag/AgCl, which were assigned to the redox of high-spin iron sites with N₆ coordination environment (Fe^{III}/Fe^{II}) and the oxidation of low-spin iron sites with C₆ coordination environment ([Fe^{III}(CN)₆]⁴⁻/[Fe^{III}(CN)₆]³⁻), respectively.⁴⁻⁶ The amount of charge Q_{CV} involved in the total redox reactions of the PB film was obtained by the integration of the current with respect to time, giving ~19 mC (200 nmol) (Fig. S4b). Q_{CV} showed a remarkable disagreement with the amounts of Fe atoms in a PB film estimated by ICP-AES (~500 nmol) (Table S1), suggesting that the redox reactions involved in the CV process do not correspond to the full conversion of ideal compositions.

Conversion of the raw SQUID signal to the induced magnetization $\Delta M(V_{DC})$

In a SQUID magnetometer, the uniform linear motion of the sample through a pick-up coil generates the raw SQUID voltage (V) as a function of the sample position (x):⁷

 $V(x) = X(1) + X(2) \cdot x + X(3) \cdot \{2[R^2 + (x + X(4))^2]^{-32} - [R^2 + (A + x + X(4))^2]^{-32} - [R^2 + (-A + x + X(4))^2]^{-32}\}, (1)$ where *R* is the longitudinal radius (R = 0.97 cm), A is the longitudinal coil separation (A = 1.519 cm), and X(i)'s are adjustable parameters. Among them, X(3) is the peak height proportional to the longitudinal magnetic moment *M* of the sample,

$$M(\text{emu}) = X(3) \cdot f_{\text{reg}} / (f_{\text{cal}} \cdot f_{\text{sens}} \cdot f_{\text{cor}}),$$
⁽²⁾

where f_{reg} is the longitudinal regression factor, f_{cal} is the SQUID calibration factor, f_{sens} is the sensitivity factor, and f_{cor} is the correction factor.

After subtraction of the raw SQUID voltage curve of the device without DC bias voltage from the ones with non-zero DC bias voltage, the difference curves $\Delta V(V_{DC})$ were fitted to eq. (1) providing X(3) values corresponding to the magnetization by hole injection into PB-film. DC bias dependence of $\Delta M(V_{DC})$ thus obtained is plotted in Fig. 4.



Fig. S1 Schematic diagram of fabrication of PB-film electrolysis cells.



Fig. S2 XRD patterns of PB films on the ITO substrate with CuK α radiation (λ = 1.5405 Å).



Fig. S3 Fe2*p* photoelectron spectrum of a PB film on the ITO substrate.

	3 PB films		1 PB film (average)	
	K ⁺ / ppm	Fe ^{II, III} / ppm	K ⁺ / nmol	Fe ^{II, III} / nmol
PB-solution1 ¹	1.57	4.53	268	541
PB-solution2 ¹	1.34	3.75	228	447

Table S1 Concentrations of K^+ and $Fe^{II, III}$ ions in PB film on the ITO substrate.

¹ Three intact PB thin-films on ITO substrate each are dissolved in PB-solution1 and 2(20 mL).



Fig. S4 (a) Cyclic voltammogram of the intact PB film in a 0.1 M KCl aqueous solution; (b) the amounts of charge (Q) obtained by current integration is plotted against potential(E).



Fig. S5 Photograph of the PB-film electrolysis cell after a bias-cycled UV/Vis absorption measurement (see Fig. 2c). Complete recovery to blue film was prevented by bubble generation.



Fig. S6 Photograph of the PB-film electrolysis cell fabricated using materials of insufficient dehydration. About 8 min after the bias $V_{DC} = +3.0$ V was applied.



Fig. S7 (a) UV/Vis absorption spectra of PB-film electrolysis cell under $V_{DC} = +3.0$ V; (b) Time evolution of UV/Vis absorption bands of PB-film electrolysis cell under $V_{DC} = +3.0$ V at 751 and 394 nm; (c) Recovery of UV/Vis absorption spectra after short circuit of PB-film electrolysis cell.



Fig. S8 Photographs of PB-film electrolysis cell (a) before electrolysis and (b) about 20 min after applying $V_{\rm DC} = +3.0 \ {\rm V}$



Fig S9 Temperature dependence of magnetization of PB-film electrolysis cell under DC bias V_{DC} of 0 to +3.2 V on the PB-film side.



Fig S10 DC bias dependence of Néel temperature T_N of PB-film electrolysis cell under DC bias V_{DC} of 0 to +3.2 V on the PB-film side with 1000 Oe magnetic field. $T_N(V_{DC})$ are defined as *T*-values of x-intercept of the tangent line at inflection point of the rapid increase of magnetization difference ΔM as shown in Fig. 3.



Fig. S11 (a) The sample position dependence of the raw induced voltage applying $V_{DC} = 4.0$ V and $V_{DC} = 0$ V; (b) The difference of raw induced voltage applying $V_{DC} = 4.0$ V and $V_{DC} = 0$ V. Pink curve is the best-fit to the response function in eq. (1).

Reference

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