Supporting Information

Proton-induced Switching of the Single Molecule Magnetic Properties of a Porphyrin Based Tb^{III} Double-decker Complex

Daisuke Tanaka, Tomoko Inose, Hirofumi Tanaka, Sunri Lee,
Naoto Ishikawa*, Takuji Ogawa*

Department of Chemistry, Graduate School of Science, Osaka University, 1-1 Machikaneyama, Toyonaka, Osaka 560-0043, Japan.

E-mail: iskw@chem.sci.osaka-u.ac.jp, ogawa@chem.sci.osaka-u.ac.jp

General Information.

All chemicals and solvents were of reagent grade and used without further purification. Elemental analyses were performed by a Yanaco CHN CORDER MT-5. Infrared spectra were recorded as KBr pellets on a JASCO FT/IR-460 Plus. UV-visible absorption spectra were recorded with a Shimadzu UV-3150 double-beam spectrophotometer. Mass spectra were recorded on a Shimadzu AXIMA-CFR MALDI-TOF mass spectrometer. Cyclic voltammetric experiments were carried out using a BAS CV-50W voltammetric analyzer. All experiments were conducted in CH_2Cl_2 with 0.10 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. Electrochemical experiments were conducted in a three-component cell consisting of a Pt auxiliary electrode, a non-aqueous reference electrode ($Ag/AgNO_3$), and a Pt working electrode. All electrochemical measurements were referenced by the ferrocene/ferrocenium couple. The ac magnetic susceptibility and hysteresis loop measurements were carried out on a Quantum Design MPMS-XL7AC SQUID magnetometer.

Synthesis of [Tb^{III}H(TPP)$_2$] (1)

Tetraphenylporphyrin (H$_2$TPP) was prepared according to literature procedures.[1] The powder crystalline sample of **1** was prepared by treating Tb^{III}(acac)$_3$·xH$_2$O (0.276 g), H$_2$TPP (0.124 g) in 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 500 μL) at 350 °C for 1.5 h. The obtained residue was purified by passing it through an alumina column (CH$_2$Cl$_2$) to give a dark purple solid (0.174 g, 62.1%). The powder sample for magnetic measurements was obtained by the same procedure. Crystals suitable for single-crystal X-ray crystallography were obtained by recrystallization from CHCl$_3$/MeOH. MALDI-TOF MS (m/z): M$^+$ calcd for C$_{88}$H$_{57}$N$_8$Tb, 1384.4960; found 1385.7; Anal. Calcd for [Tb^{III}H(TPP)$_2$(CH$_2$Cl$_2$)$_2$]: C, 69.50; H, 3.95; Cl, 9.12; N, 7.20; Tb, 10.22. Found C, 69.09; H, 4.02; N, 7.08.

Synthesis of {[Tb^{III}(TPP)$_2$](H-DBU)} (2)

DBU (60 μL, 4x10^{-4} mol) was added to a solution of **1** (9.5 mg, 6.9x10^{-6} mol) in CHCl$_3$ (10 mL). Then, methanol was slowly added to the solution resulting in crystalline powder **2**. Crystals suitable for single-crystal X-ray crystallography and the powder sample for magnetic measurements were obtained by the same procedure. MALDI-TOF MS (m/z): M$^+$ C$_{88}$H$_{56}$N$_8$Tb, 1383.39; found 1385.3; Anal. Calcd for {[Tb^{III}(TPP)$_2$](H-DBU)(CHCl$_3$)$_2$}: C, 66.94; H, 4.26; Cl, 11.97; N, 7.89; Tb, 8.95. Found C, 66.58; H, 4.32; N, 7.83.

Synthesis of {[Tb^{III}(TPP)$_2$](*n*Bu$_4$N)} (3).

A solution of **1** (32.6 mg, 2.4×10^{-5} mol), *n*Bu$_4$NBr (9.3 mg, 2.4×10^{-5} mol) and triethylamine (1 mL, 7.2×10^{-3} mol) in acetone (10 mL) was evaporated and the dark purple precipitate of **3** was recrystallized in Acetone/Methanol. MALDI-TOF MS (m/z): M$^+$ C$_{88}$H$_{56}$N$_8$Tb, 1383.39; found 1385.3; Anal. Calcd for {[Tb^{III}(TPP)$_2$](*n*Bu$_4$N)(H$_2$O)}: C, 75.94; H, 5.76; Cl, 11.97; N, 7.66; Tb, 9.66. Found C, 75.82; H, 5.49; N, 7.79.

Single Crystal X-ray Diffraction.

X-ray structure determination was conducted on a Rigaku VariMax RAPID / FR-E system with $\mathrm{Mo}_{K\alpha}$ radiation. In all cases, the structure was solved by direct methods (SHELXS-97)[2] and refined by full-matrix least-squares techniques on F^2 (SHELXL-97).[3]

Crystal data for **1**, C92 H61 Cl12 N8 Tb, M_r = 1862.81, monoclinic, space group $P2_1/c$, (#14), a = 16.0300(5) Å, b = 17.0927(5) Å, c = 30.0170(8) Å, β = 91.7771(8), V = 8220.6(4) Å^3, Z = 4, T = 150 K. ρ_{calcd} = 1.505 g/cm^3, $\mu(\mathrm{Mo}_{K\alpha})$ = 1.304 cm^{-1}, $2\theta_{\max}$ = 50˚, λ(MoKα) = 0.71075 Å, 62010 reflections measured, 14442 unique, 9945 > 2σ(I) were used to refine 1010 parameters, 12 restraints, $R(R_w)$ = 0.0800 (0.2367), GOF = 1.034.

Crystal data for **2**, C99 H75 Cl6 N10 Tb, M_r = 1776.31, tetragonal, space group $I4/mmm$, (#139), a = 14.6111(12) Å, c = 19.3957(16) Å, V = 4140.7(6) Å^3, Z = 2, T = 150 K. ρ_{calcd} = 1.425 g/cm^3, $\mu(\mathrm{Mo}_{K\alpha})$ = 1.104 cm^{-1}, $2\theta_{\max}$ = 55˚, λ(MoKα) = 0.71075 Å, 20354 reflections measured, 1377 unique, 1376 > 2σ(I) were used to refine 114 parameters, 6 restraints, $R(R_w)$ = 0.0373 (0.1074), GOF = 1.125.

We obtained a non-disordered model of **2** in the space group of $I/422$. However, in the non-disorderd model, inter-molecular distance is too short and unreasonable inter-atom distance was found (H-H distance is 1.42Å). To avoid such unexplainable crowding, we employed the disordered model.

(1) Lindsey, J. S.; Schreiman, I. C.; Hsu, H. C.; Kearney, P. C.; Marguerettaz, A. M. *J Org Chem* **1987**, *52*, 827.
(2) Sheldrick, G. M. *SHELXS-97*, Universität-Gottingen, 1997
(3) Sheldrick, G. M. *SHELXL-97*, Universität-Gottingen, 1997.

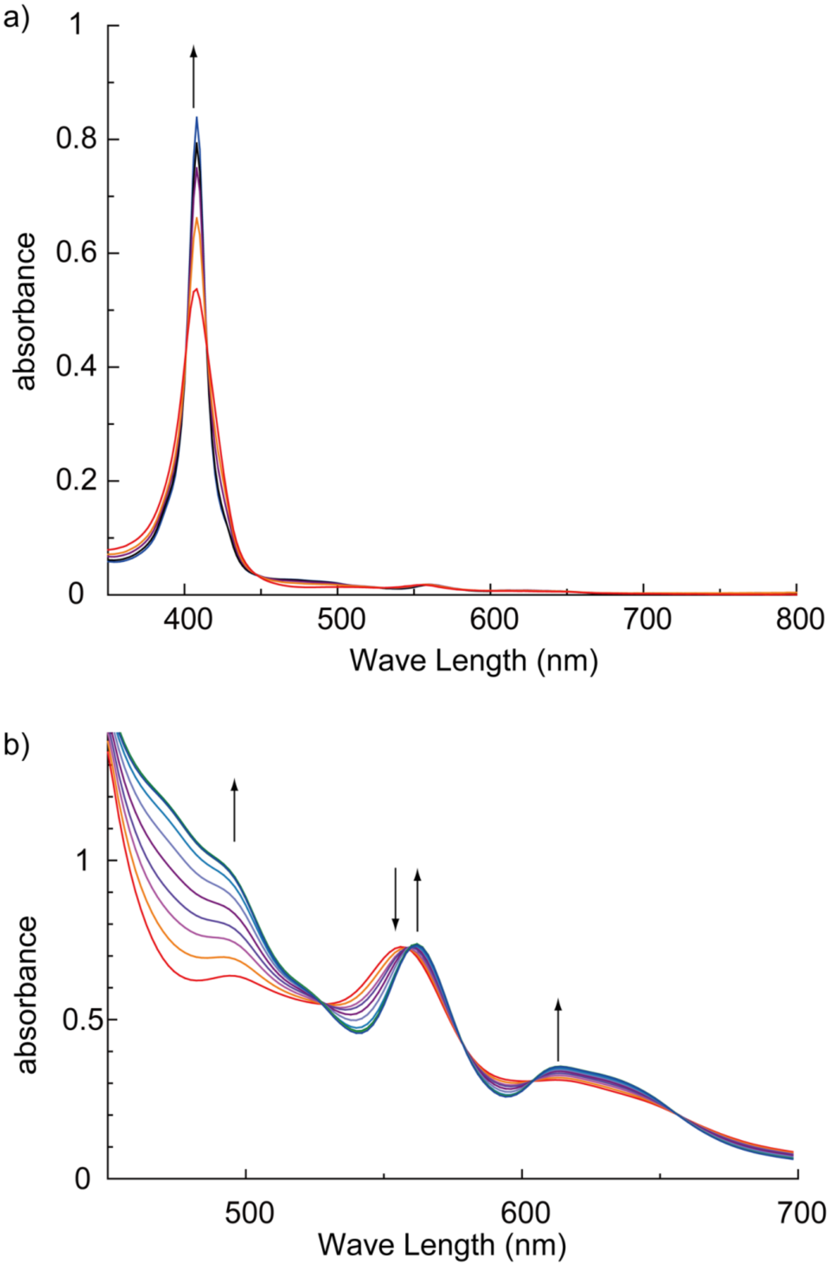

Figure S1. UV-visible spectral changes of **1** during a titration with DBU in CH_2Cl_2. The original concentration of **1** is (a) 1.87×10^{-6} M, and (b) 8.26×10^{-5} M.

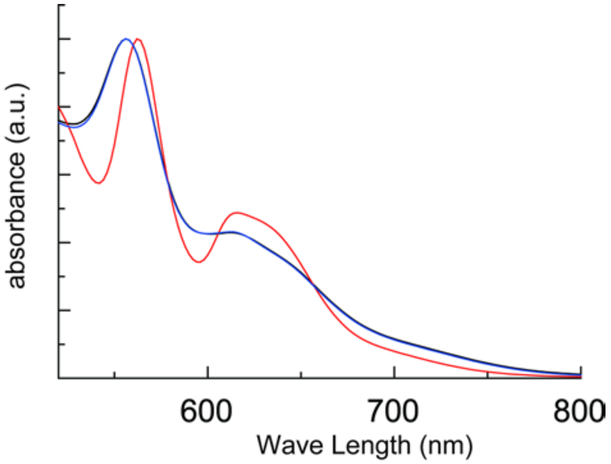

Figure S2. UV-visible spectra of **1** (black), **2** (red) and **2** re-protonated with acetic acid (blue) in CH_2Cl_2. The absorbances are normalized to the maximum peaks. The original absorption peak of **1** reappears upon adding acetic acid to the solution of anion complex, **2**.

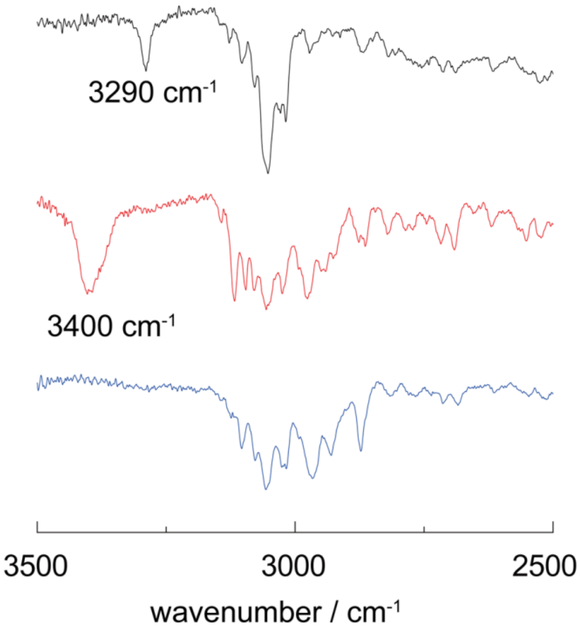

Figure S3. IR spectra of **1** (black), **2** (red), and **3** (blue). The peaks between 2900 and 3150 cm^{-1} are due to C-H stretching of TPP and organic cation. The peaks at 3290 cm^{-1} and 3400 cm^{-1} are from N-H stretching of TPP and $[H\text{-}DBU]^+$, respectively.

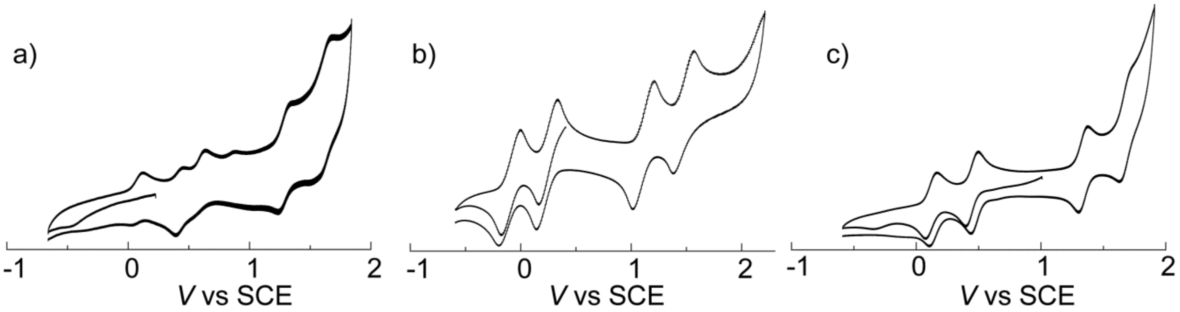

Figure S4. Cyclic voltammograms of (a) **1** in CH_2Cl_2, (b) **2** in CH_2Cl_2, and (c) **3** in CH_2Cl_2 recorded at room temperature (0.10 M *n*-Bu_4NPF_6, scan rate = 0.10 V/s).

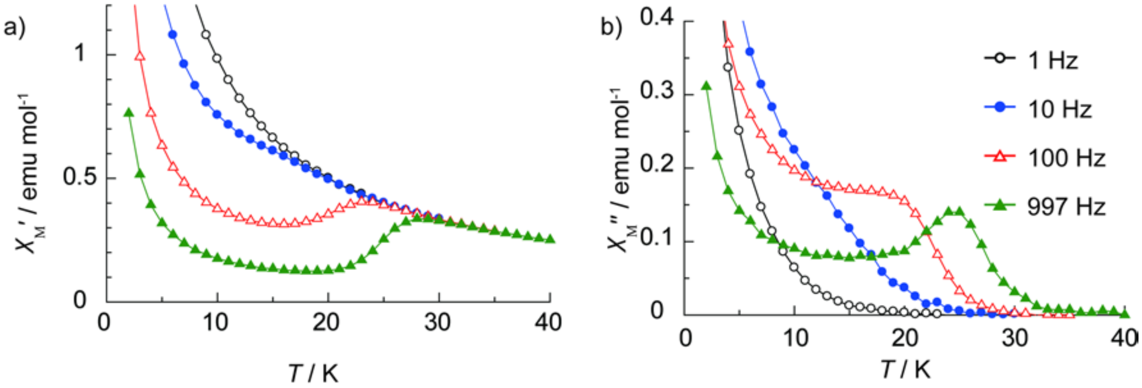

Figure S5. Acsusceptibility of **3** measured in zero dc magnetic field with a 3.9 G ac field oscillating at the indicated frequencies. Plots of (a) in-phase (χ_M') and (b) out-of-phase (χ_M'') against temperature .

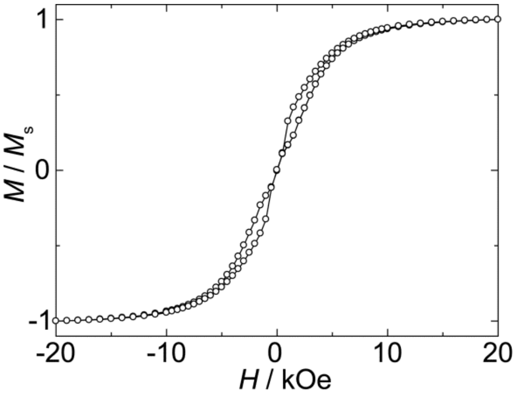

Figure S6. Hysteresis loop for **2** at 1.8 K.

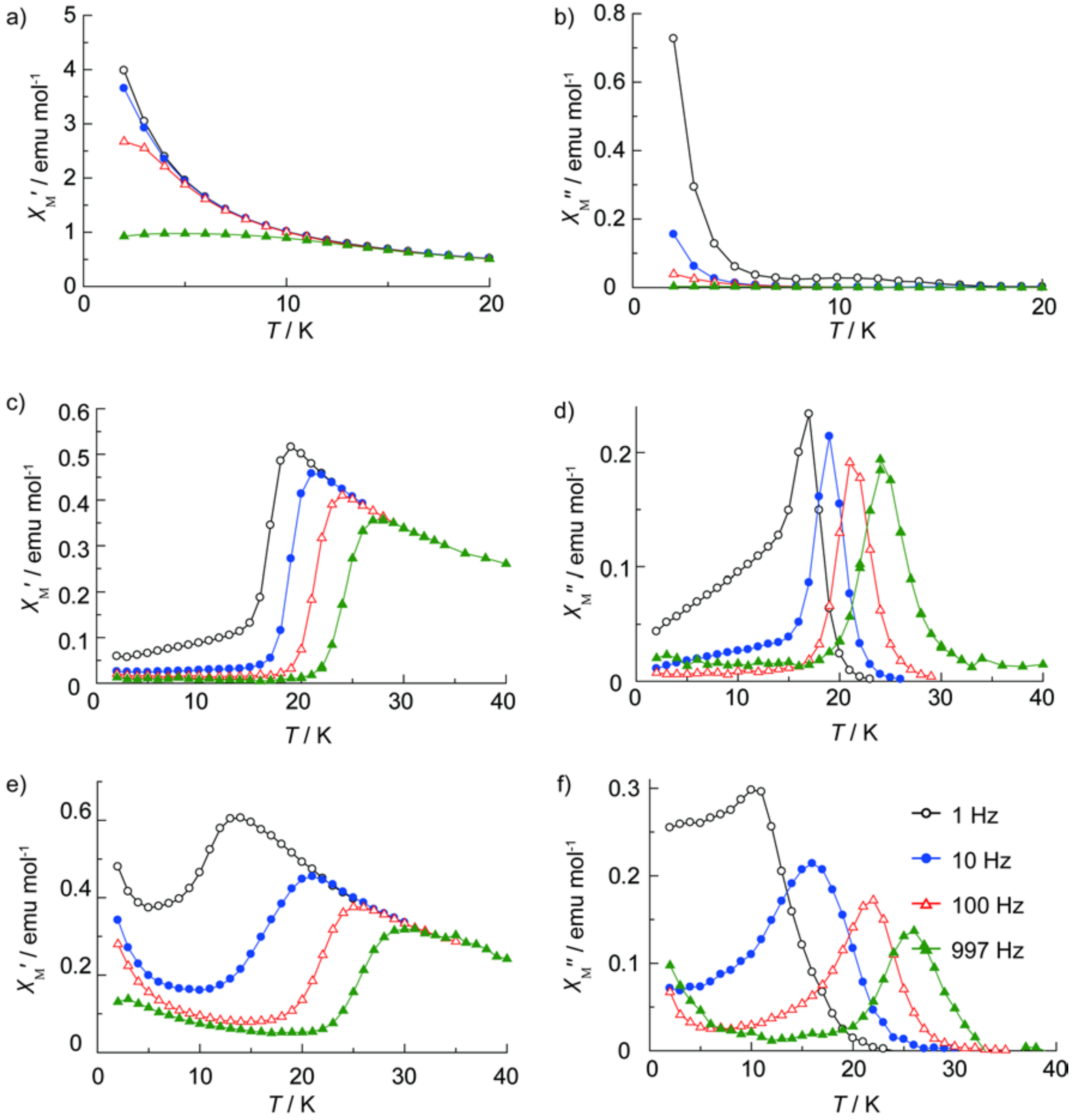

Figure S7. ACsusceptibility measured in 2000 Oe dc magnetic field with a 3.9 G ac field oscillating at the indicated frequencies. Plots of (a) in-phase (χ_{M}') and (b) out-of-phase (χ_{M}'') against temperature *T* for a powder sample of **1**, plots of (c) χ_{M}' and (d) χ_{M}''’ against *T* for a powder sample of **2**, and plots of (e) χ_{M}' and (f) χ_{M}''’ against *T* for a powder sample of **3**.

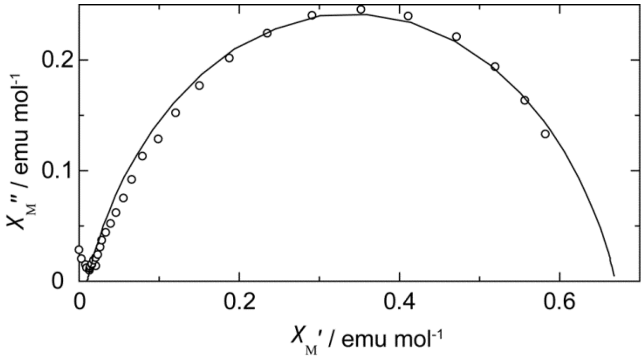

Figure S8. The Argand diagram at 16 K under 2000 Oe for **2**. The solid line represents the least-squares fit obtained with a generalized Debye model with α = 0.19.

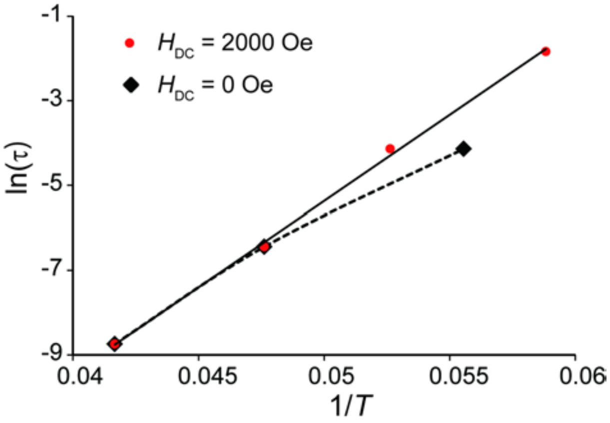

Figure S9. The relaxation time (*τ*) of **2** under represented dc magnetic field. Black line represents the least-square fit of the data under 2000 Oe dc field to Arrhenius equation.