Supplementary Material (ESI) for Chemical Communications

Supplementary Material for Chemical Communications

Allosteric binding of anionic guests to a bicyclic host which imitates an action of 'turnstile'

Osamu Hirata, Masayuki Takeuchi* and Seiji Shinkai*

Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan.

E-mail: taketcm@mbox.nc.kyushu-u.ac.jp, seijitcm@mbox.nc.kyushu-u.ac.jp; Fax: +81-92-642-3611

Measurements

All starting materials and solvents were purchased from Tokyo Kasei Organic Chemicals or Wako Organic Chemicals and used as received. The ^{1}H and ^{19}F NMR spectra were recorded either on a Brucker AC 250 (250 MHz) or Brucker DRX 600 (600 MHz) spectrometer. Chemical shifts are reported in ppm downfield from tetramethylsilane as the internal standard. Mass spectral data were obtained using a Perseptive Voyager RP MALDI TOF mass spectrometer and/or a JEOL JMS HX110A high-resolution magnetic sector FAB mass spectrometer. UV-Vis and Fluorescent spectra were recorded with a Shimadzu UV-2500 PC and Hitachi F-4500 spectrophotometer, respectively.

Binding isotherm analysis

Cooperative guest-binding process was analyzed according to the Hill equation: $\log(y/(1-y)) = n\log[\text{guest}] + \log K$, where K , y and n_H are the association constant, the extents of complexation and Hill coefficient, respectively. From the slope and the intercept of the linear plots (Hill plot) one can estimate K and n_H, which are useful as measures of the cooperativity. A higher value of n_H is related to a higher degree of cooperativity. The maximum is equal to the number of binding sites. In the analysis of binding isotherm by Hill plot, we have evaluated the concentration of unbound guest, [guest], by assuming that 100 % 1:2 complex is formed when the chemical shift change is saturated. 1:2 Complex formation was confirmed by Job plot and/or CSI mass spectroscopy.

Measurements

TBA denotes tetra-*n*-butylammonium cation.

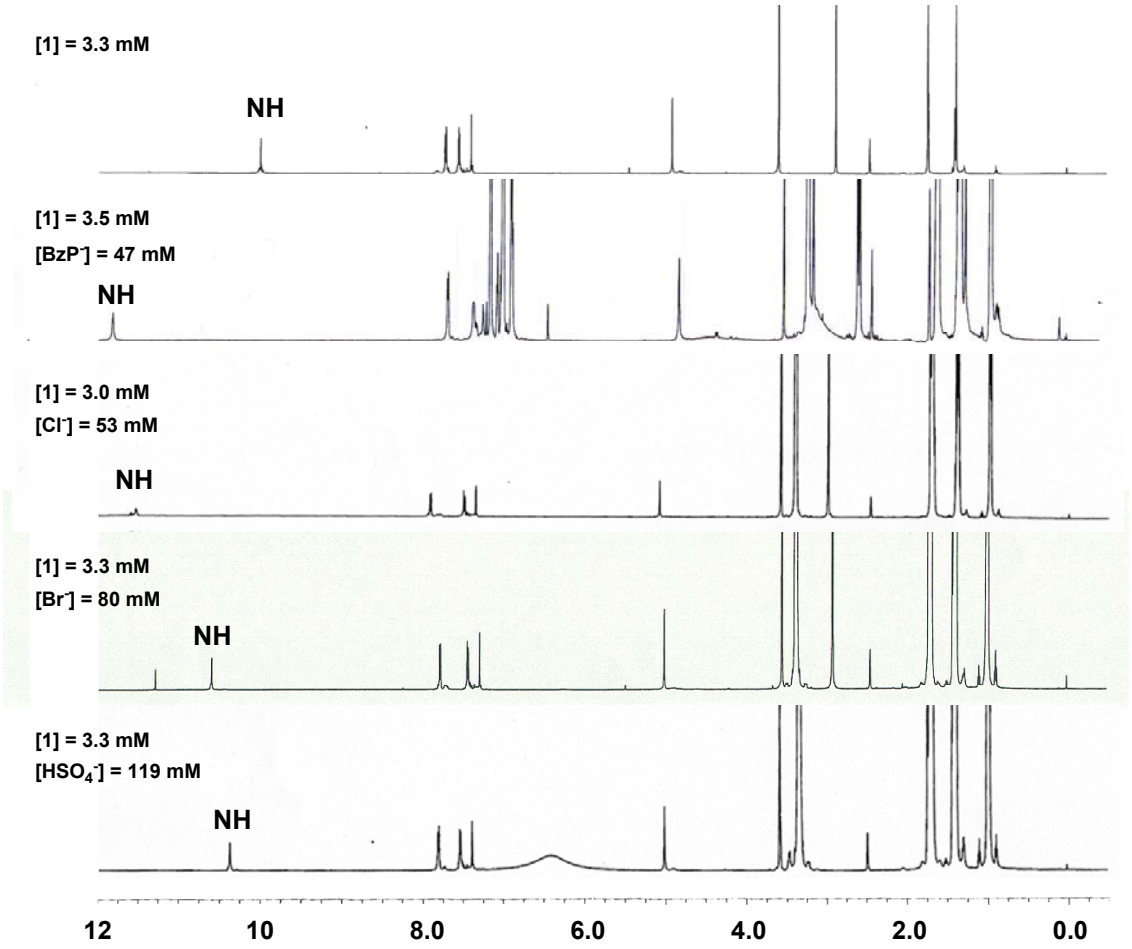


Fig. S1 ^{1}H NMR spectra (600 MHz) of **1** (3.3 mM) in THF-d_8/DMSO-d_6 (5/1, v/v) upon addition of anions at 25 °C.

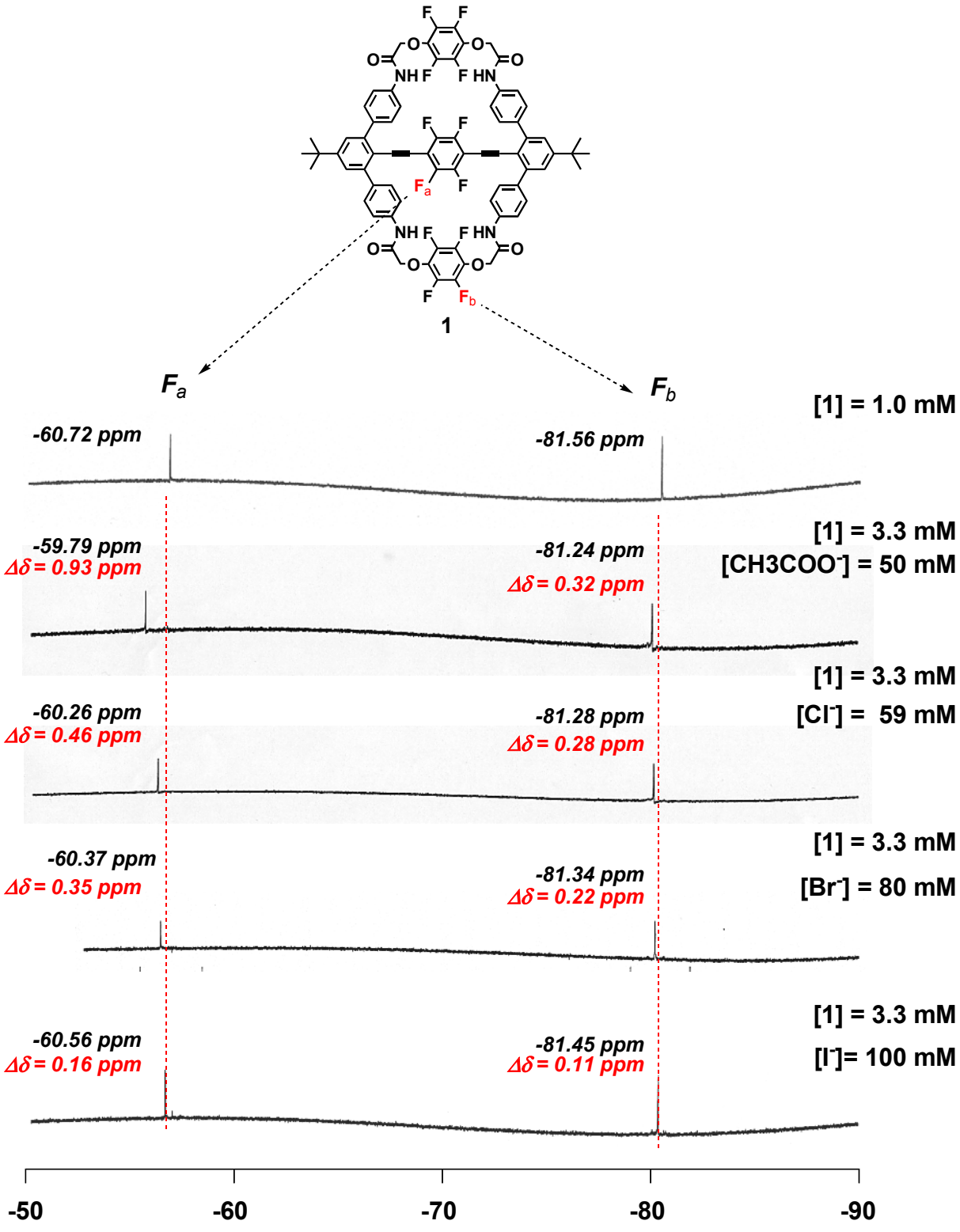


Fig. S2 ^{19}F NMR spectra (500 MHz) of **1** (3.3 mM) in THF-d_8/DMSO-d_6 (5/1, v/v) upon addition of anions at 25 °C (TFA as an external standard).

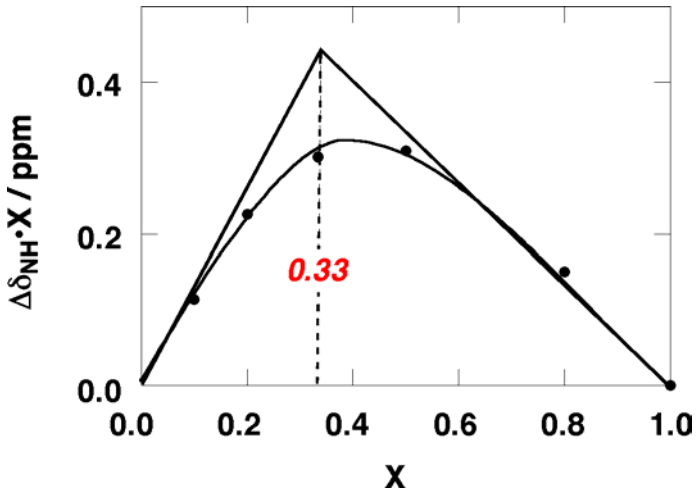
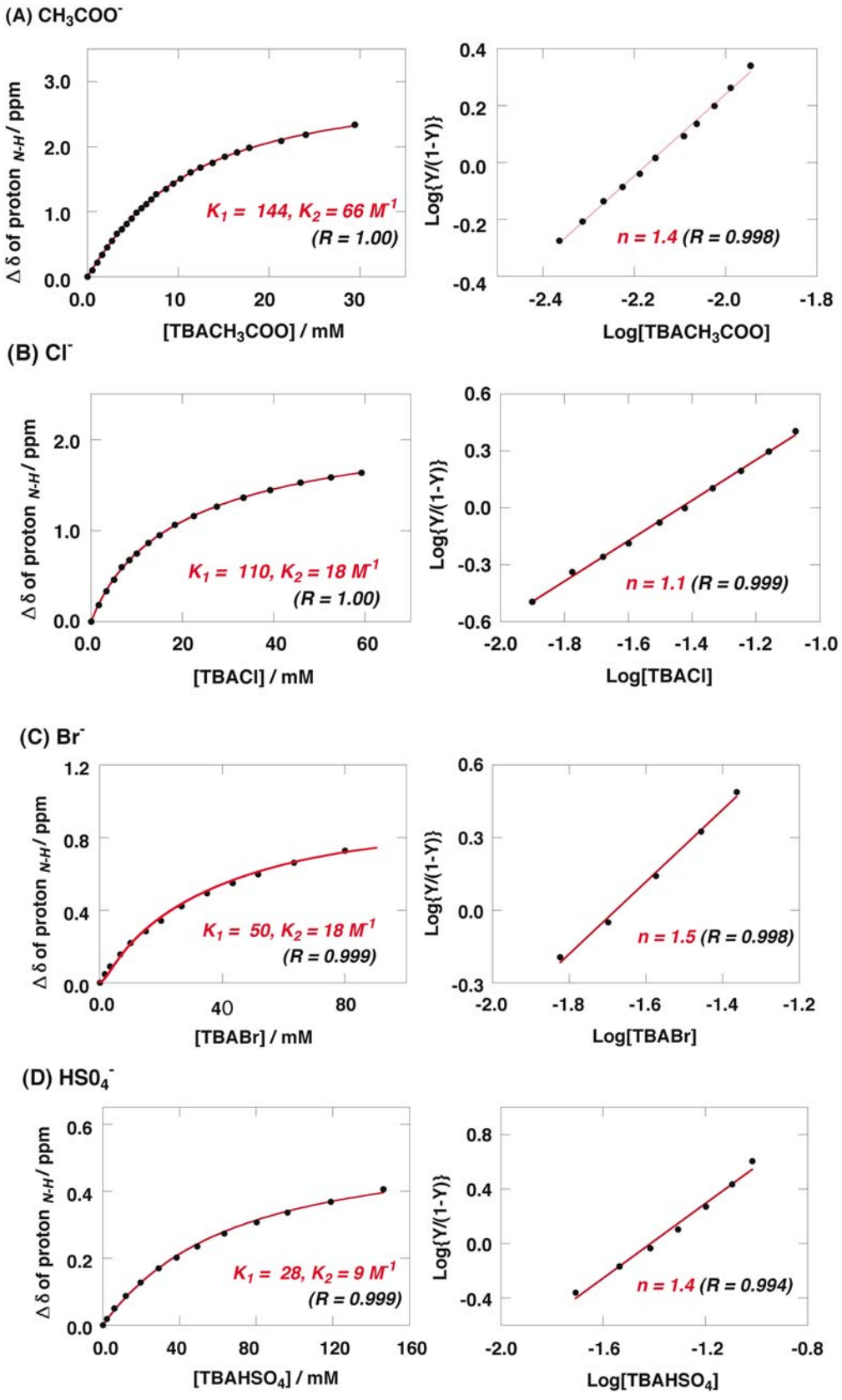


Fig. S3 Job plot : 25 °C, THF-d_8/DMSO-d_6 = 5/1 (v/v), X =[**1**]/([**1**] + [$TBACH_3COO$]), [**1**] + [$TBACH_3COO$] = 3.0 mM (constant).



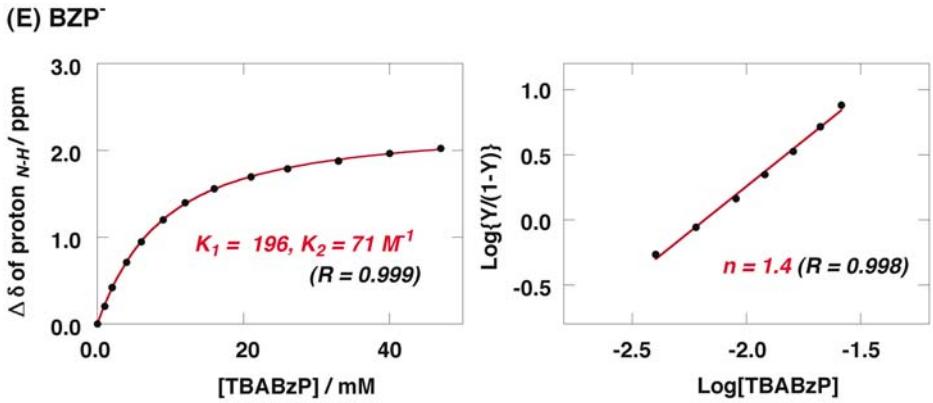


Fig. S4 Plots of $\Delta\delta_{NH}$ of **1** as a function of added anion (left) and Hill plot for each anion (right). The solid line is the theoretical curve obtained from a nonlinear least-squares method and Hill plot. R values in the parentheses denote a correlation coefficient.

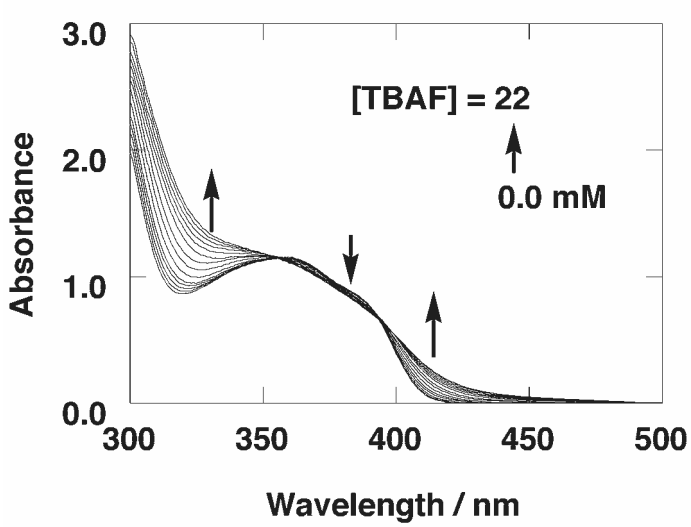


Fig S5 UV-Vis spectral changes of **1** (30 μM) in THF/DMSO (5/1, v/v) upon addition of fluoride anion (0.0 ~ 22 mM) at 25°C.

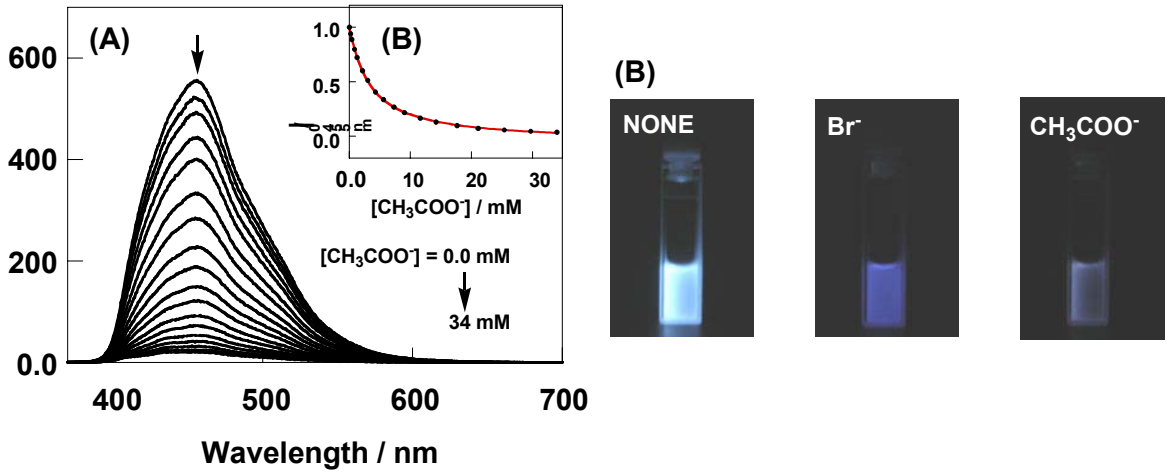


Fig. S6 (A) Emission spectral changes of **1** (10 μM) upon addition of acetate in THF/DMSO = 5/1 (v/v) at 25 °C (excitation wavelength 360 nm), (B) emission colour changes observed from samples of **1** with bromide or acetate. From left to right: **1**, **1**•(bromide)$_2$, **1**•(acetate)$_2$.