Electronic Supplementary Information

for

Formation of a supramolecular assembly between a Na^+-templated G-quartet and a Ni(II)-porphyrin complex

Yuji Inui,[a] Shunichi Fukuzumi*[a, b] and Takahiko Kojima*[c]

[a] *Department of Material and Life Science, Graduate School of Engineering, Osaka University and ALCA (JST), 2-1 Yamada-oka, Suita, Osaka 565-0871, Japan*

[b] *Department of Bioinspired Science, Ewha Womans University, Seoul 120-750, Korea*

[c] *Department of Chemistry, Graduate School of Pure and Applied Sciences, University of Tsukuba,1-1-1 Tennoudai, Tsukuba, Ibaraki 305-8571, Japan*

Materials and methods. $CHCl_3$ (Wako Pure Chemical Industries) was purified by distillation over CaH_2. CH_3OH (Wako Pure Chemical Industries) was dried using Mg and I_2. $CDCl_3$ was purchased from Cambridge Isotope Laboratories, Inc.. Other chemicals and solvents were purchased from Wako Pure Chemical Industries and Tokyo Chemical Industries and were used as received. 9-isopropylguanine was synthesized according to the literature method (see the reference 9 in the text). Octaethylporphinatonickel(II) (NiOEP) was synthesized by a literature method (see the references 11 and 13).

Apparatus. ^{1}H NMR spectra were measured on a JEOL JNM-AL300 spectrometer. UV–Vis absorption spectra were recorded on a SHIMAZU UV2450. ESI-MS measurements were made on an Applied Biosystems QStar Pulsar i (ESI-TOF; positive mode) spectrometer.

^{1}H NMR measurements. A mixed solvent of $CH_3OH/CDCl_3$ (1:60 v/v) was used for measurements and chemical shifts were determined relative to an internal standard (TMS). NMR measurements at 283 K was made on a sample containing 9-isopropylguanine (9.9 mM), sodium tetraphenylborate (2.5 mM) and NiOEP (1.3 mM) after incubating for over 3 minutes at certain temperature.

UV-Vis titration to determine the equilibrium constants. UV-Vis spectroscopic titrations of H_2OEP and NiOEP upon addition of ^{i}PG-4-Na^+ were conducted in mixed solvents of $CHCl_3/CH_3OH$ after stirring for 20 min at every addition of ^{i}PG-4-Na^+ at each temperature. Sodium tetraphenylborate was used as the sources of the template cation and the ^{i}PG-4-Na^+ solution was prepared from the mixture of ^{i}PG/$NaBPh_4$ (4:1 mol/mol) in $CH_3OH/CHCl_3$ (1:40 v/v). H_2OEP and NiOEP solutions were prepared in $CHCl_3$ for every measurement. In order to determine K values (see below), absorbance at 393 nm due to the Soret band of NiOEP was monitored. The UV-Vis spectra of ^{i}PG (0.21 mM) in $CH_3OH/CHCl_3$ were monitored with addition of NiOEP solution in $CHCl_3$ due to the low solubility of ^{i}PG in $CHCl_3$. The UV-Vis spectrum of NiOEP upon addition of $NaBPh_4$ was monitored by adding $NaBPh_4$ solution (0–106 μM) in $CH_3OH/CHCl_3$ to the solution of NiOEP (1.1 μM) in $CHCl_3$. Their absorption coefficients were used for the comparison (Fig. S2).

Analysis of titration curves of the adduct formation. Data obtained from temperature-dependent UV-Vis measurements were analyzed by curve fitting for plots of $[^i\mathrm{PG\text{-}4\text{-}Na}^+]^{-n}$ *vs*. $1/(A_0\text{-}A)$ (n=1 or 2) to determine formation constants of complexes between ^{i}PG-4-Na^+ and NiOEP. Concerning the formation of the 1:1 complex, we assumed the following equilibrium:

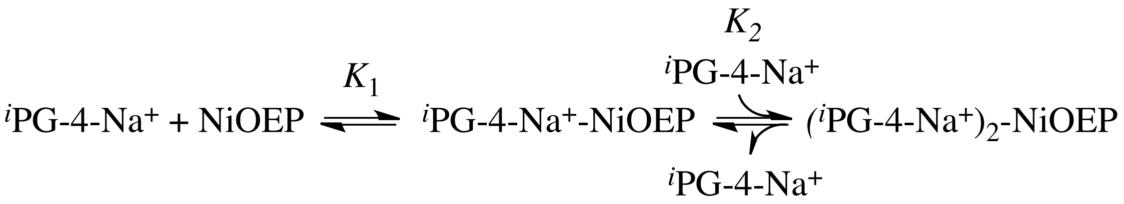
$$^{i}\mathrm{PG\text{-}4\text{-}Na^{+}} + \mathrm{NiOEP} \xrightleftharpoons{K} {}^{i}\mathrm{PG\text{-}4\text{-}Na^{+}\text{-}NiOEP}$$

Curve-fitting was made to estimate the formation constants of the 1:1 complex on the basis of following equation (1) for the plots in Fig. 2(b), Fig. S3(b), and Fig. S3(d) at 288 K and equation (2) for the plots in Fig. 5 and Fig. S3(e):

$$\Delta A = \Delta\varepsilon \frac{[\mathrm{G4}]_{\mathrm{add}} + [\mathrm{Por}]_0 + {}^{1}\!/_{K} - \sqrt{([\mathrm{G4}]_{\mathrm{add}} + [\mathrm{Por}]_0 + {}^{1}\!/_{K})^2 - 4[\mathrm{G4}]_{\mathrm{add}}[\mathrm{Por}]_0}}{2} \tag{1}$$

$$\frac{1}{\Delta A} = \left(\frac{1}{\Delta\varepsilon K[\mathrm{G4}]_{\mathrm{add}}} + \frac{1}{\Delta\varepsilon}\right)\left(\frac{1}{[\mathrm{Por}]_0}\right) \tag{2}$$

As for the formation constant of the 2:1 complex between ^{i}PG-4-Na$^+$ and NiOEP, we assumed the following equilibrium:



$${}^{i}\mathrm{PG\text{-}4\text{-}Na^+} + \mathrm{NiOEP} \overset{K_1}{\rightleftharpoons} {}^{i}\mathrm{PG\text{-}4\text{-}Na^+\text{-}NiOEP} \underset{{}^{i}\mathrm{PG\text{-}4\text{-}Na^+}}{\overset{\overset{K_2}{{}^{i}\mathrm{PG\text{-}4\text{-}Na^+}}}{\rightleftharpoons}} ({}^{i}\mathrm{PG\text{-}4\text{-}Na^+})_2\mathrm{\text{-}NiOEP}$$

The calculation of the formation constant for the 2:1 complex was made on the basis of following equation (3) for the plots in Fig. S3(b) and Fig. S3(d) at 298 K and equation (4) for the plots in Fig. S3(c) and Fig. S3(f):

$$[\mathrm{G4}]_{\mathrm{add}} = 2({}^{\Delta A}\!/_{\Delta\varepsilon}) + \sqrt{\frac{({}^{\Delta A}\!/_{\Delta\varepsilon})}{K([\mathrm{Por}]_0 - ({}^{\Delta A}\!/_{\Delta\varepsilon}))}} \tag{3}$$

$$(K = K_1K_2)$$

$$\frac{1}{\Delta A} = \left(\frac{1}{\Delta\varepsilon K[\mathrm{G4}]_{\mathrm{add}}^2} + \frac{1}{\Delta\varepsilon}\right)\left(\frac{1}{[\mathrm{Por}]_0}\right) \tag{4}$$

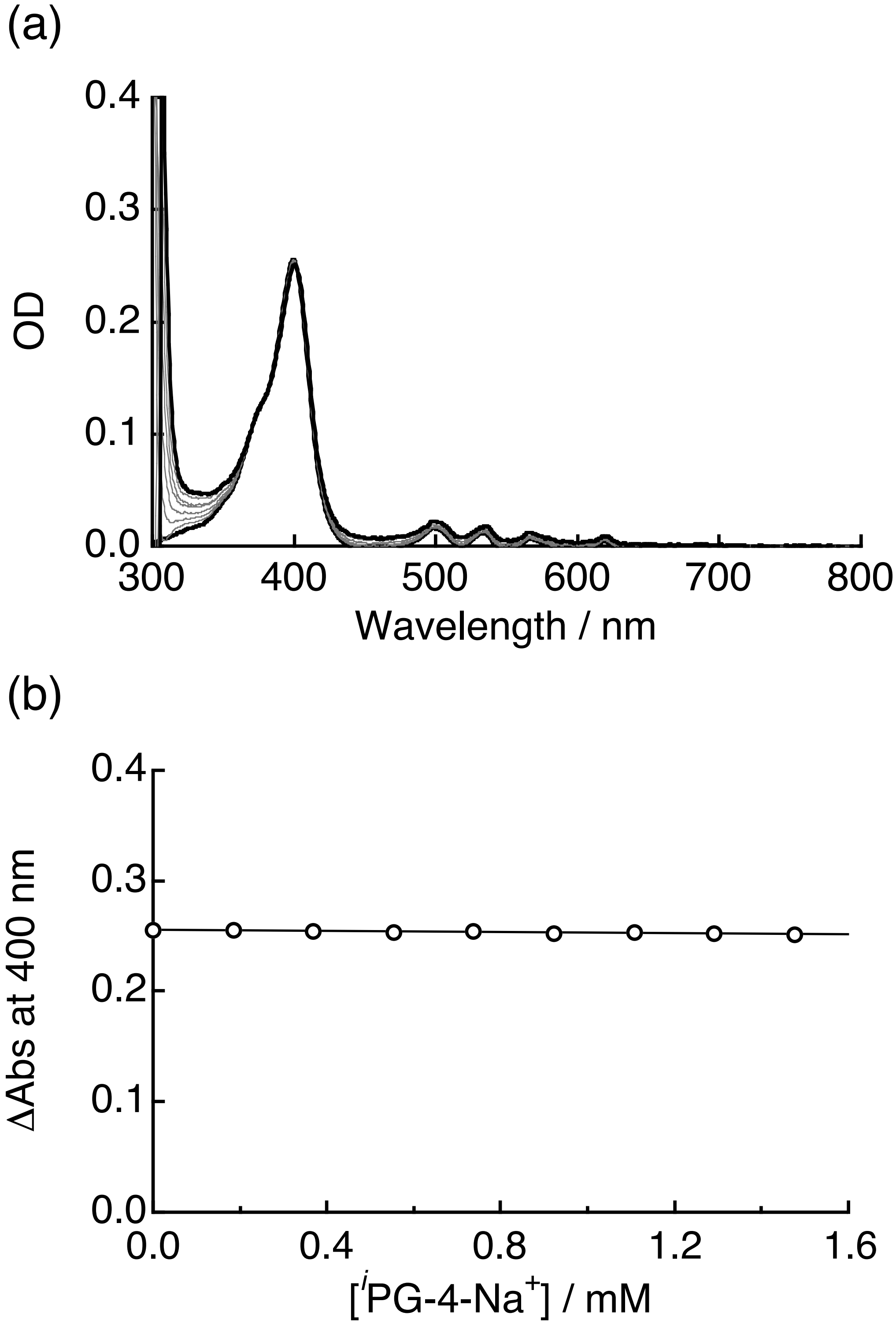


Fig. S1 (a) Spectral change in the course of the addition of ^{i}PG-4-Na$^+$ to the solution of H_2OEP (1.6 μM). The baseline was adjusted by subtracting the absorbance of ^{i}PG-4-Na$^+$ at each concentration. (b) A plot of absorbance at 400 nm relative to [^{i}PG-4-Na$^+$] in the corrected absorption spectra depicted in (a).

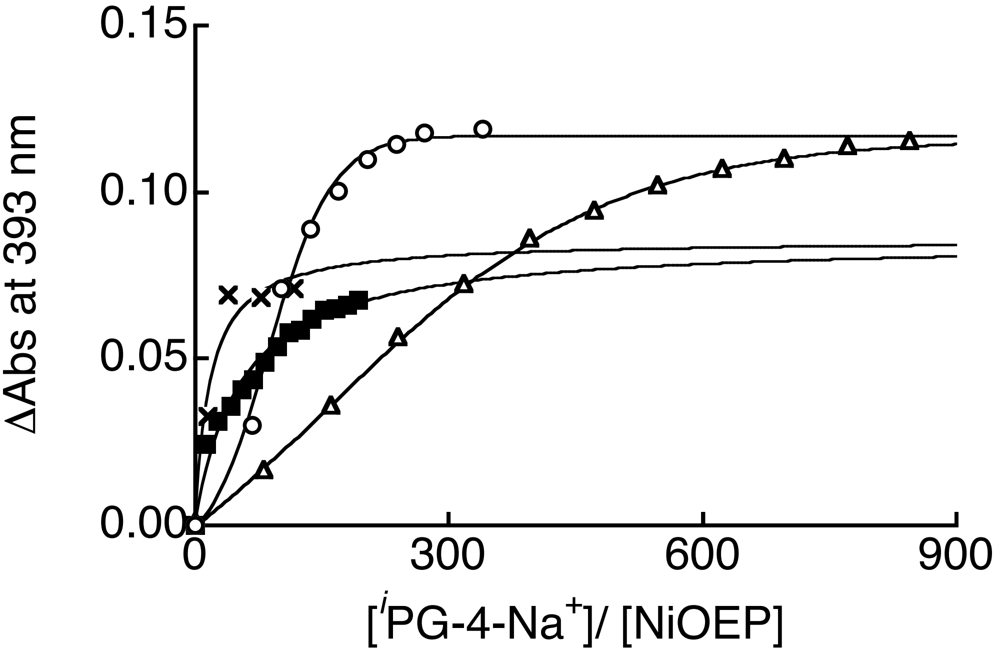


Fig. S2 Titration curves for temperature-dependent UV-Vis measurements on the adduct formation of ^{i}PG-4-Na$^+$ with NiOEP. ^{i}PG-4-Na$^+$ prepared by ^{i}PG and NaBPh$_4$ (4:1 mol/mol) was added to the NiOEP (1.4 μM) at 283 K (–×–), 288K (–■–), 293 K (–△–) and 298 K (–○–) in the mixed solvent of $CH_3OH/CHCl_3$. At 293 K, NiOEP (1.6 μM) solution was prepared and then the absorbance at 393 nm of NiOEP was normalized by the ratio of the concentration of NiOEP (Abs. (393 nm) × 1.4/1.6).

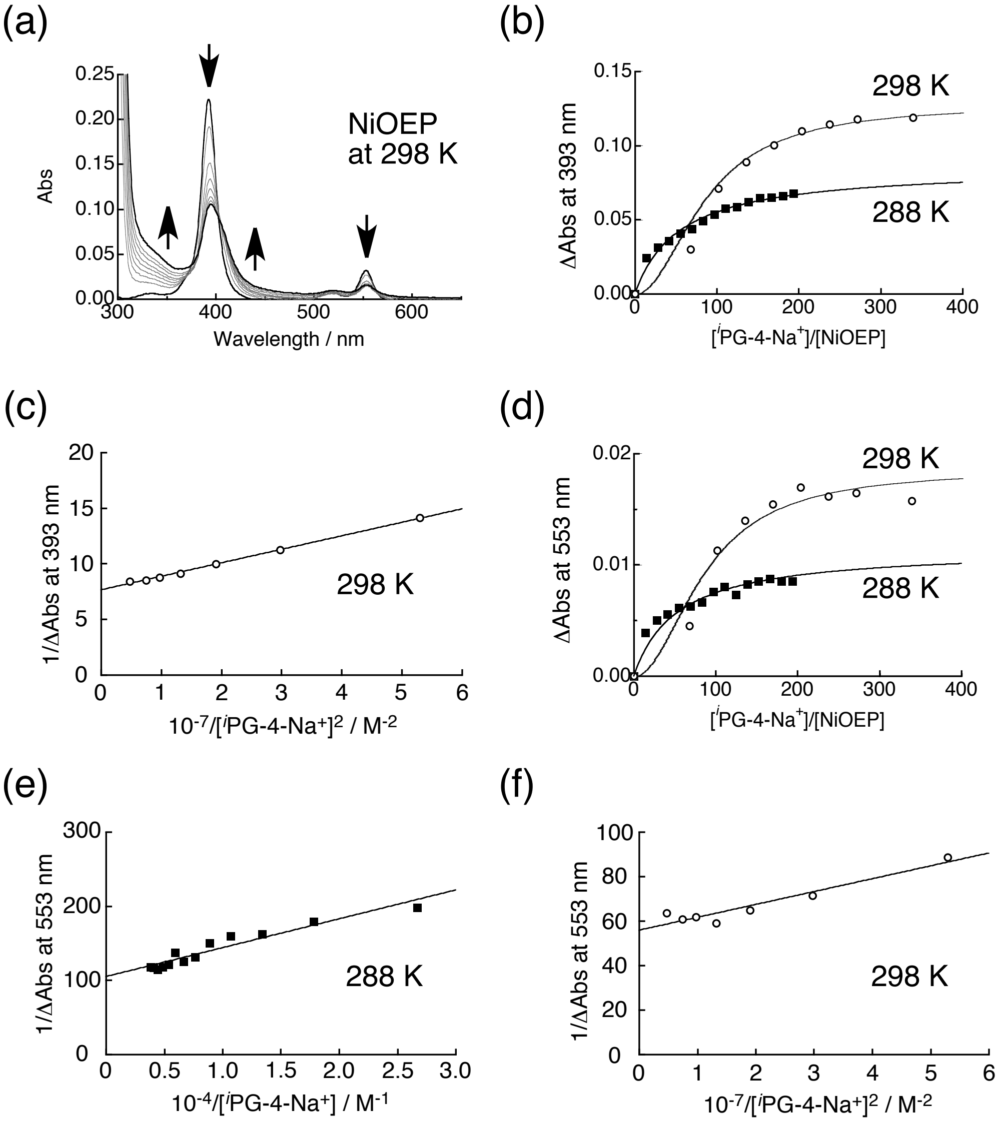


Fig. S3 Analysis of the UV-Vis spectral change for the adduct formation in $CHCl_3/CH_3OH$: (a) spectral change of NiOEP (1.4 μM) by adding ^{i}PG-4-Na$^+$ (0 to 0.46 mM) at 298 K; (b) curve fitting for the absorption change at 393 nm observed for the adduct of ^{i}PG-4-Na$^+$ with NiOEP at 288 K (■) and at 298 K (○); (c) a plot of $1/(A_0\text{-}A)$ at 393 nm *vs*. [^{i}PG-4-Na$^+$]$^{-2}$ at 298 K; (d) curve fitting for the absorption change at 553 nm observed for the adduct of ^{i}PG-4-Na$^+$ with NiOEP at 288 K (■) and at 298 K (○) at 553 nm; (e) a plot of $1/(A_0\text{-}A)$ *vs*. [^{i}PG-4-Na$^+$]$^{-1}$ at 288 K; (f) a plot of $1/(A_0\text{-}A)$ *vs*. [^{i}PG-4-Na$^+$]$^{-2}$ at 298 K.