Electronic Supplementary Information

for

Formation of a supramolecular assembly between a Na\textsuperscript{+}-templated G-quartet and a Ni(II)-porphyrin complex

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Materials and methods. CHCl₃ (Wako Pure Chemical Industries) was purified by distillation over CaH₂. CH₃OH (Wako Pure Chemical Industries) was dried using Mg and I₂. CDCl₃ 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. ¹H 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.

¹H NMR measurements. A mixed solvent of CH₃OH/CDCl₃ (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 H₂OEP and NiOEP upon addition of ¹PG-4-Na⁺ were conducted in mixed solvents of CHCl₃/CH₃OH after stirring for 20 min at every addition of ¹PG-4-Na⁺ at each temperature. Sodium tetraphenylborate was used as the sources of the template cation and the ¹PG-4-Na⁺ solution was prepared from the mixture of ¹PG/NaBPh₄ (4:1 mol/mol) in CH₃OH/CHCl₃ (1:40 v/v). H₂OEP and NiOEP solutions were prepared in CHCl₃ 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 ¹PG (0.21 mM) in CH₃OH/CHCl₃ were monitored with addition of NiOEP solution in CHCl₃ due to the low solubility of ¹PG in CHCl₃. The UV-Vis spectrum of NiOEP upon addition of NaBPh₄ was monitored by adding NaBPh₄ solution (0–106 µM) in CH₃OH/CHCl₃ to the solution of NiOEP (1.1 µM) in CHCl₃. 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 [¹PG-4-Na⁺]ⁿ vs. 1/(A₀–A) (n=1 or 2) to determine formation constants of complexes between ¹PG-4-Na⁺ and NiOEP. Concerning the formation of the 1:1 complex, we assumed the following equilibrium:

\[
¹\text{PG-4-Na}^+ + \text{NiOEP} \rightleftharpoons K \quad ¹\text{PG-4-Na}^+\text{-NiOEP}
\]

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):
\[
\Delta A = \Delta \varepsilon \frac{[G4]_{\text{add}} + [\text{Por}]_0 + \frac{1}{K} - \sqrt{[(G4)_{\text{add}} + [\text{Por}]_0 + \frac{1}{K})^2 - 4[G4]_{\text{add}}[\text{Por}]_0}}{2}
\]  

(1)

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

(2)

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

\[
\begin{align*}
{K_1} \\
{i}^\text{PG-4-Na}^+ + \text{NiOEP} & \rightleftharpoons {i}^\text{PG-4-Na}^+\cdot\text{NiOEP} & \rightleftharpoons (i\text{PG-4-Na}^+)_{2}\cdot\text{NiOEP} \\
\end{align*}
\]

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):

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

(3)

\[
(K = K_1K_2)
\]

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

(4)
**Fig. S1** (a) Spectral change in the course of the addition of $^{1}$PG-4-Na$^{+}$ to the solution of H$_2$OEP (1.6 µM). The baseline was adjusted by subtracting the absorbance of $^{1}$PG-4-Na$^{+}$ at each concentration. (b) A plot of absorbance at 400 nm relative to $[^{1}PG-4-Na^{+}]$ in the corrected absorption spectra depicted in (a).
Fig. S2 Titration curves for temperature-dependent UV-Vis measurements on the adduct formation of iPG-4-Na⁺ with NiOEP. iPG-4-Na⁺ prepared by iPG and NaBPh₄ (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 CH₃OH/CHCl₃. 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 CHCl₃/CH₃OH: (a) spectral change of NiOEP (1.4 µM) by adding ['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 ['PG-4-Na']⁺ with NiOEP at 288 K (■) and at 298 K (○); (c) a plot of 1/(A₀-A) at 393 nm vs. [‘PG-4-Na']⁺² at 298 K; (d) curve fitting for the absorption change at 553 nm observed for the adduct of ['PG-4-Na']⁺ with NiOEP at 288 K (■) and at 298 K (○) at 553 nm; (e) a plot of 1/(A₀-A) vs. [‘PG-4-Na']⁺ at 288 K; (f) a plot of 1/(A₀-A) vs. [‘PG-4-Na']⁺² at 298 K.