Electronic Supplementary Information (ESI)

Redox-responsive Host-guest System Using Redox-active Pillar[5]arene Containing One Benzoquinone Unit

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Experimental section

Materials. All solvents and reagents were used as supplied. Per-ethylated pillar[5]arene (**H1**), **G**, quinone-**H2** and 2OH-**H2** were synthesized according to the previous papers.[S1-S3]

Measurements. The ^{1}H NMR spectra were recorded at 500 MHz and ^{13}C NMR spectra were recorded at 125 MHz with a JEOL-ECA500 spectrometer.

Determination of association constants.

In quinone-**H2**⊃**G** complex in $CDCl_3$, chemical exchange between uncomplexed and complexed species was fast on an NMR timescale. Thus, NMR titrations were done with solutions which had a constant concentration of **G** (2 mM) and varying concentrations of quinone-**H2**. By the non-linear curve-fitting method,[S4] the association constant K for the host-guest complex between quinone-**H2** and **G** was found to be $K = 28 \pm 1.1\ M^{-1}$.

In 2OH-**H2**⊃**G** complex in $CDCl_3$, chemical exchange between complexed and uncpomlexed species was slow on an NMR timescale. Thus, ^{1}H NMR spectra of mixtures of 2OH-**H2** and **G** in different ratio showed two sets of resonances for complexed and uncomplexed **G**. The association constant for 2OH-**H2**⊃**G** complex was $(4.6 \pm 1.4) \times 10^2\ M^{-1}$, calculated from integrations of complexed (Fig. 2b, pink peak a') and uncomplexed signals (Fig. 2b, pink peak b) of **G**.

Determination of rate constants of the host-guest exchange. The exchange rate constant (k) at a coalescence temperature was estimated by using the approximate expression[S5,6]:

$$\Delta G^{\ddagger} = 8.314 T_c[22.96 + \log(T_c/\delta\nu)]$$

where $\Delta G^{\ddagger}$ is the free energy of activation for the exchange, $\delta\nu$ is the chemical shift difference between the proton signals from complexed and uncomplexed proton protons (Fig. S6, signals g and g'). The coalescence temperature T_c was estimated on the coalescence signal in these proton signals. The extrapolated value of k, which represent rate constant, at 25 ^{o}C was obtained from the Eyring equation:

$$k = k_B T/h \exp(-\Delta G^{\ddagger}/RT)$$

where k_B is the Boltzmann constant, T is the absolute temperature, h is Plank's constant, $\Delta G^{\ddagger}$ is the free energy of activation, and R is the gas constant.

$$k = k_{in} + k_{out} \qquad K = k_{in} / k_{out}$$

In 2OH-**H2**⊃**G** complex, k, k_{in} and k_{out} (25 °C) were 190 s^{-1}, 189 s^{-1} and 1 s^{-1}, respectively.

Reversible redox reaction of H2⊃G complex by alternating addition of oxidant and reductant. To the mixture of 2OH-**H2** (2.5 mM) and **G** (2.5 mM) in a mixture of $CDCl_3$ and CD_3OD ($CDCl_3$: CD_3OD = 9:1), oxidant, tetrabutylammonium periodate (2 equiv. to 2OH-**H3**, 5.0 mM) was added. After 72 h, we checked the complexation by ^1H NMR (Fig 4b). To the mixture, reductant, tetrabutylammonium tetrahydroborate (2.5 mM) was added. After 72 h, we checked the complexation by ^1H NMR (Fig 4c). This redox-switching process was repeated by alternating addition of the oxidant and reductant.

Job plot for a mixture of G and quinone-H2

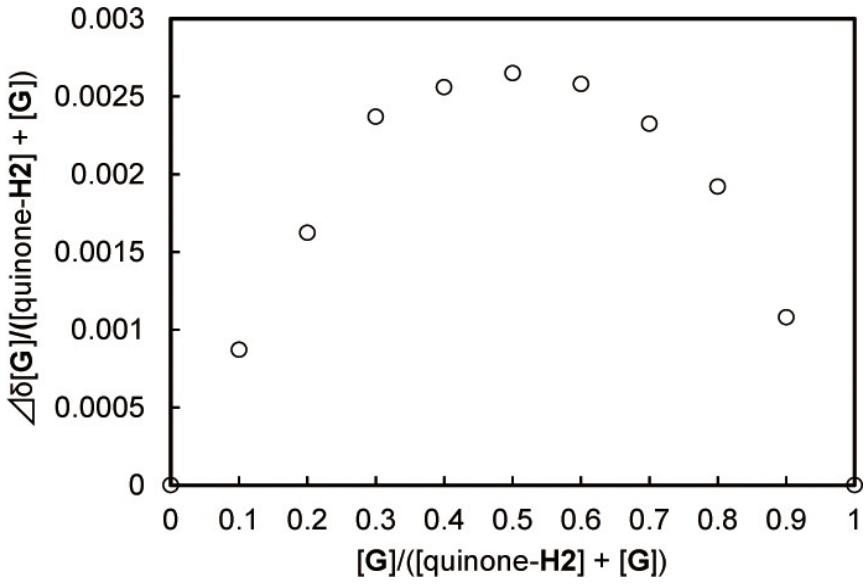
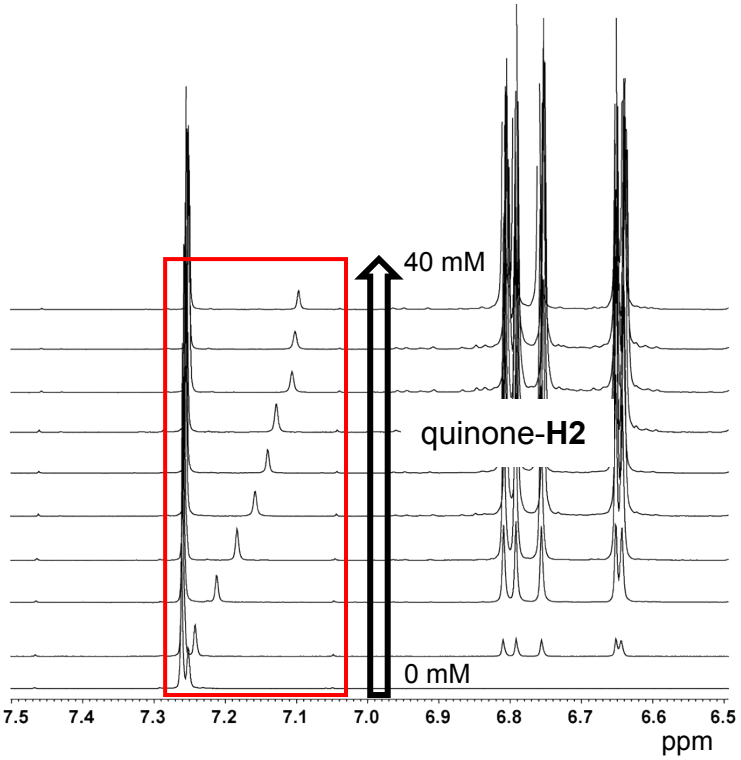
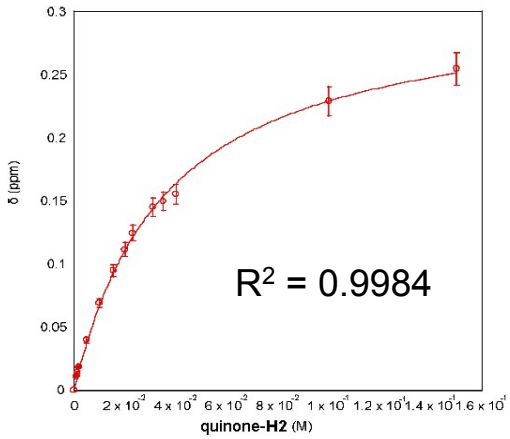


Fig. S1 Job plot between **G** (guest) and quinone-**H2** (host) was collected by plotting the Δδ in chemical shift of the triazole proton signal (Fig. 2d, yellow peak c). Concentration: [**G**] + [quinone-**H2**] = 1 mM. The plot indicates a 1:1 binding between the host and guest.

^{1}H NMR titration of G with quinone-H2 in $CDCl_3$





K_a = (28 ± 1.1) M^{-1} (25 ^oC)

Fig. S2 ^{1}H NMR titration of **G** (Fig. 2d, proton peak c) with quinone-**H2** in $CDCl_3$ at 25 ^{o}C.

Variable temperature ^{1}H NMR spectra of a mixture of quinone-H2 and G in $CDCl_3$

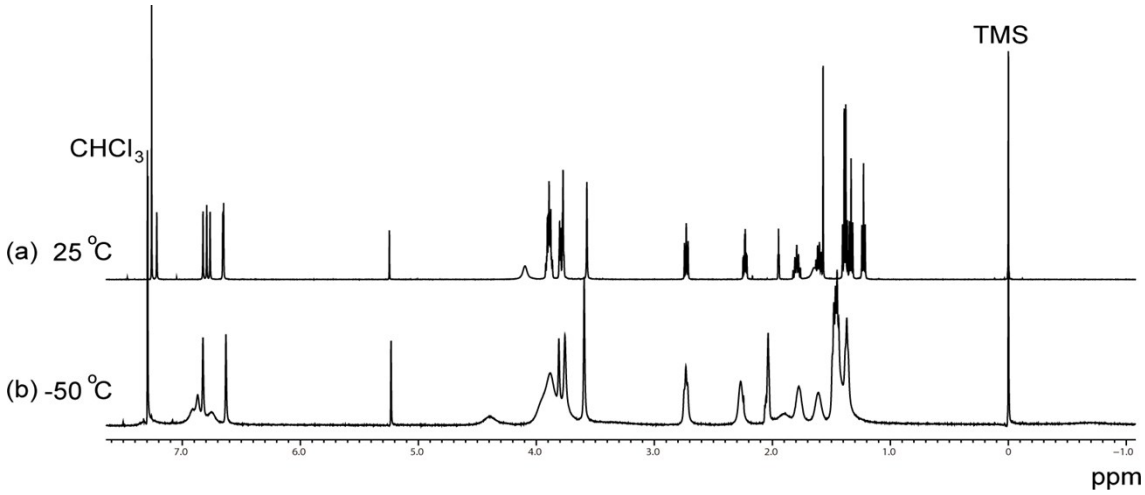


Fig. S3 Variable temperature ^{1}H NMR spectra (5 mM) of a mixture of quinone-**H2** and **G** in $CDCl_3$. The averaged proton signals were observed at –50 ^{o}C, while the signals were largely broadening, indicating that the exchange was still fast on the NMR timescale even at – 50 ^{o}C.

Job plot for a mixture of G and 2OH-H2

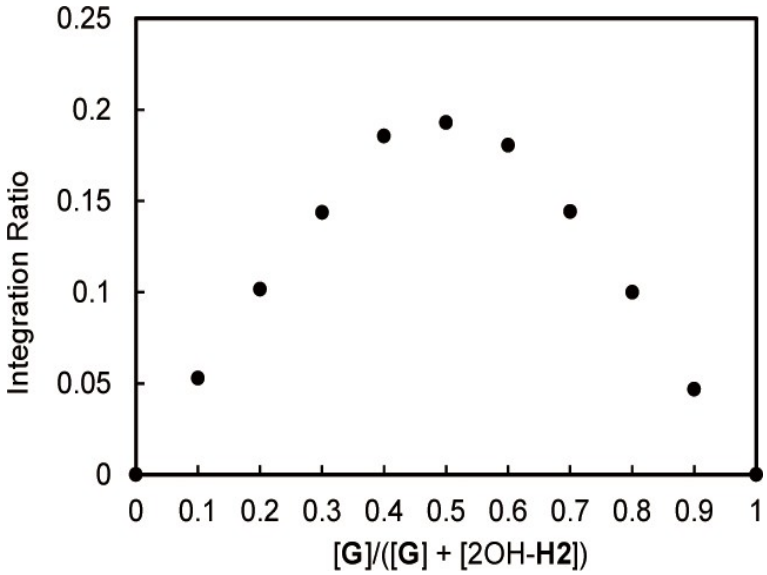


Fig. S4 Job plot between **G** (guest) and 2OH-**H2** (host). The job plot was conducted by varying the mole fractions of the guest and host. Integration ratios between uncomplexed and complexed proton signals (Fig. 2b, pink peaks b and a') were utilized. Concentration: [**G**] + [2OH-**H2**] = 1 mM. The plot indicates a 1:1 binding between the host and guest.

Van't Hoff plot of a mixture of G and 2OH-H2 in $CDCl_3$

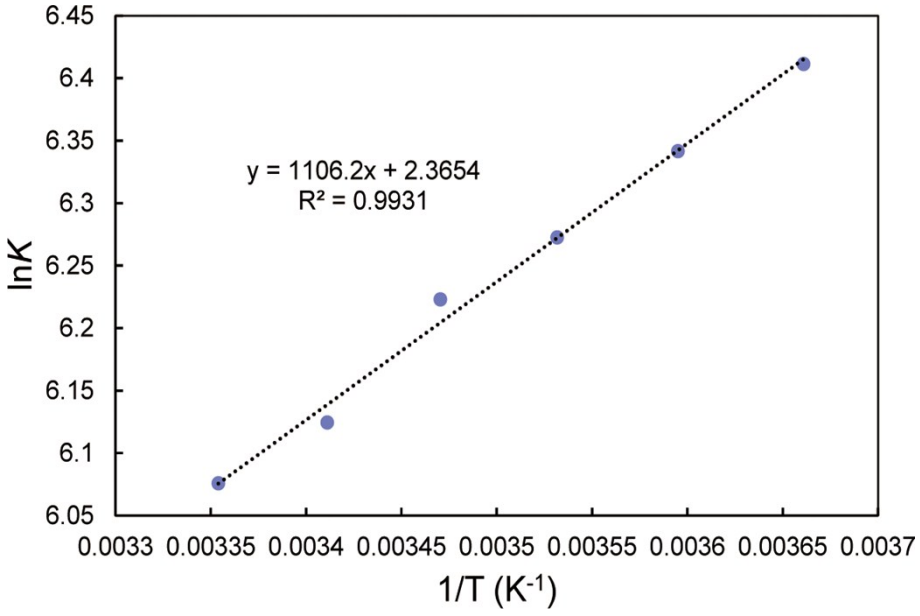


Fig. S5 van't Hoff plots for a mixture of **G** and 2OH-**H2**. From the van't Hoff plots, ΔH, ΔS and ΔG_{298} were calculated to be -9.20 $kJmol^{-1}$, 19.7 $JK^{-1}mol^{-1}$, and -14.6 $kJmol^{-1}$, respectively.

Variable temperature ^{1}H NMR spectra of a mixture of G and 2OH-H2 in $CDCl_3$

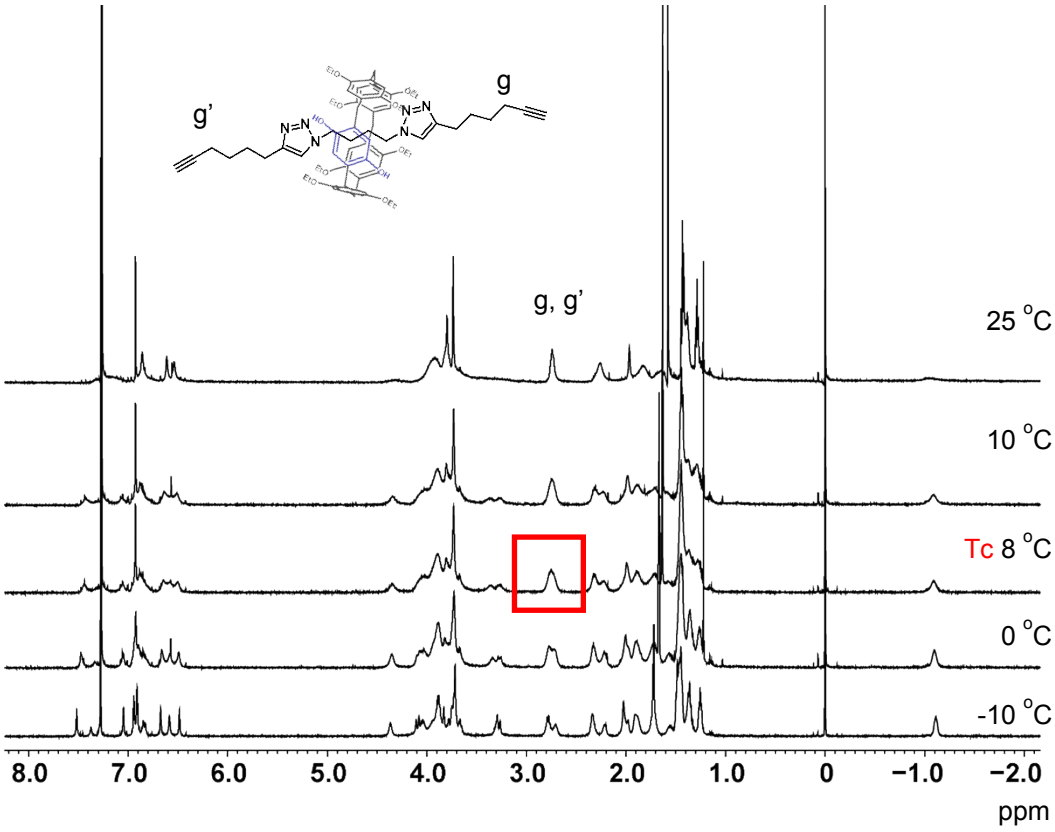


Fig. S6 Variable-temperature ^{1}H NMR spectra ($CDCl_3$) of a mixture of **G** and 2OH-**H2** in $CDCl_3$. The coalescence of the sets of the signals of from **G** was observed at 8 °C. From the coalescence temperature (T_c = 8 °C), the rate constant (k) at 298 K was calculated to be 1.9 × 10^2 s^{-1}.

References

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