

## **Electronic Supplementary Information**

### **Reversible and Contrasting Changes of the Cloud Point Temperature of Pillar[5]arenes with One Quinone Unit and Tri(ethylene oxide) Chains Induced by Redox Chemistry and Host-Guest Complexation**

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## Experimental section

**Materials.** All solvents and reagents were used as supplied. **1** was synthesized according to the previous paper.<sup>S1</sup>

**Measurements.** The <sup>1</sup>H NMR spectra were recorded at 500 MHz and <sup>13</sup>C NMR spectra were recorded at 125 MHz with a JEOL-ECA500 spectrometer. UV-Vis absorption spectra were recorded with a JASCO V-670. For UV-Vis measurements, one centimeter quartz cuvetts were used. Cloud points were determined by transmission changes (at 650 nm) of the solutions heated at 0.1 °C /min; values of the cloud points were defined as the temperature at which the transmission decreases by 50%.<sup>S2</sup>

**quinone-H2.** To a solution of **1** (7.18 mg, 3.40 mmol) in a mixture of acetonitrile (220 mL) and water (220 mL), [bis(trifluoroacetoxy)iodo]benzene (1.70 g, 3.90 mmol) was added. The mixture was stirred at 25 °C for 48 h. The resulting solution was concentrated under vacuum. The obtained product was dissolved in ethyl acetate and saturated sodium bicarbonate. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration, the filtrate was evaporated to give a red residue. The residue was purified by column chromatography on silica gel with ethyl acetate/methanol = 10/1 as the eluent. The second fraction was a pillar[5]arene containing one benzoquinone unit (quinone-H2, 2.6 g, 1.5 mmol, Yield: 44%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, ppm): δ 6.91, 6.89, 6.84, 6.77, 6.65 (s, 10H, phenyl and benzoquinone), 3.99–4.05, 3.42–3.87 (m, 130H, methylene), 3.31–3.28 (m, 24H, methyl). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz, ppm): δ 188.7, 150.4, 149.9, 149.7, 146.1, 133.5, 130.0, 128.8, 128.7, 124.0, 115.6, 114.9, 71.8, 70.8, 70.7, 70.5, 70.2, 70.0, 68.2, 67.9, 67.6, 58.9, 29.7, 29.2, 28.5, 27.7. HRESIMS: *m/z* calcd for C<sub>91</sub>H<sub>140</sub>NaO<sub>34</sub> [M]<sup>+</sup>: 1799.9124, found 1799.9119.

**Determination of association constants.** The association constants (*K*) of quinone-H2 ⊃ G1 and 2OH-H2 ⊃ G1 complexes were determined by probing the charge-transfer (CT) band of the complex by UV-Vis spectroscopy and employing titration method. Addition of G1 (guest) to an aqueous solution with the same concentration of host resulted in an increase of the intensity of the CT band of the complex. By the non-linear curve-fitting methods, *K* for the complexes in water at 25 °C were determined. The non-linear curve-fitting was based on the equation:<sup>S3</sup>

$$A = (A_{\infty}/[H]_0)(0.5[G]_0 + 1/K) - (0.5[G]_0^2 + (2[G]_0(1/K - [H]_0)) + (1/K + [H]_0)^2)^{0.5})$$

Where  $A$  is the absorption intensity of the CT band at  $[G]_0$ ,  $A_\infty$  is the absorption intensity of the CT band when the guest is completely complexed,  $[H]_0$  is the fixed initial concentration of the host, and  $[G]_0$  is the initial concentration of the guest.

## <sup>1</sup>H and <sup>13</sup>C NMR spectra of quinone-H2

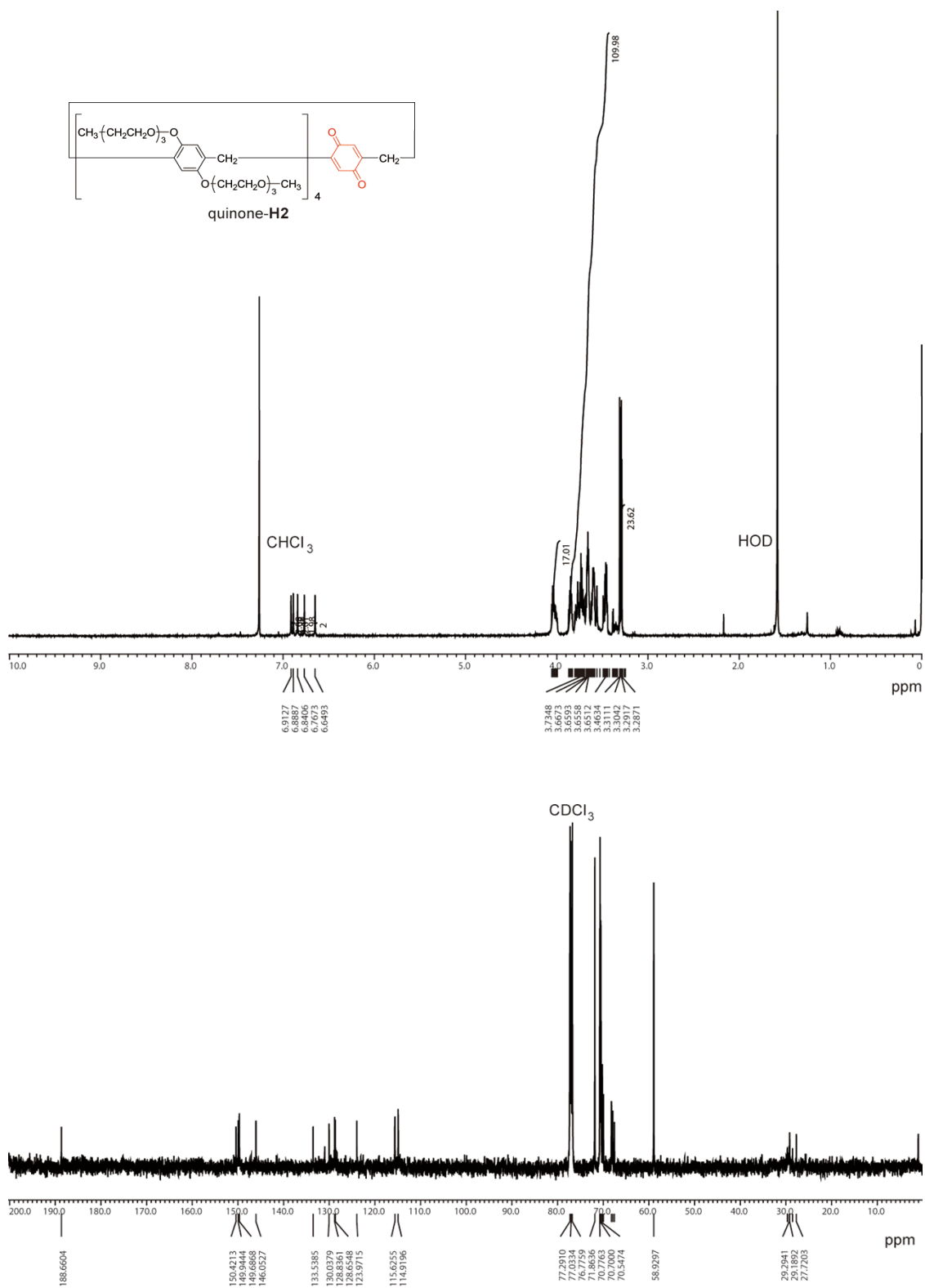
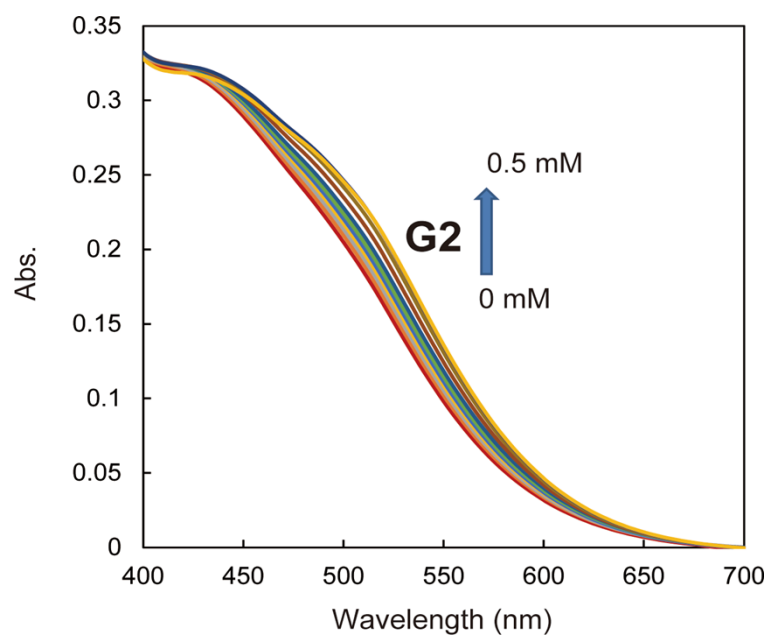


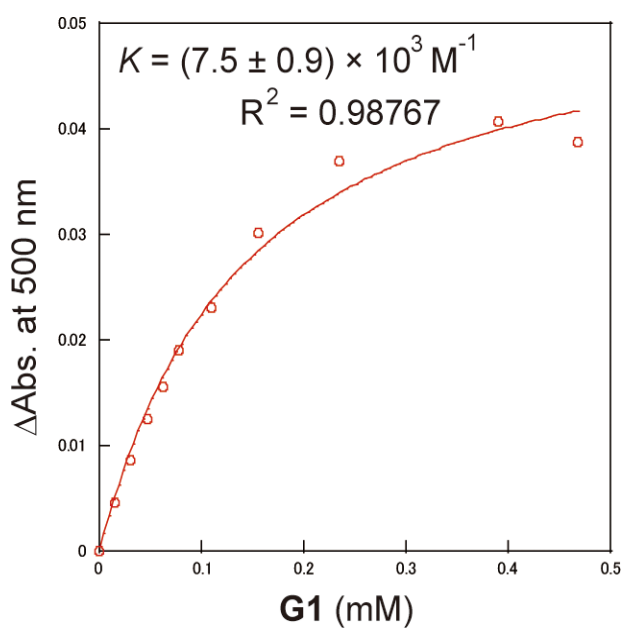
Fig. S1 <sup>1</sup>H and <sup>13</sup>C NMR spectra of quinone-H2 in CDCl<sub>3</sub> at 25 °C.

## UV-vis spectra and titration of quinone-H2 with G1

(a)

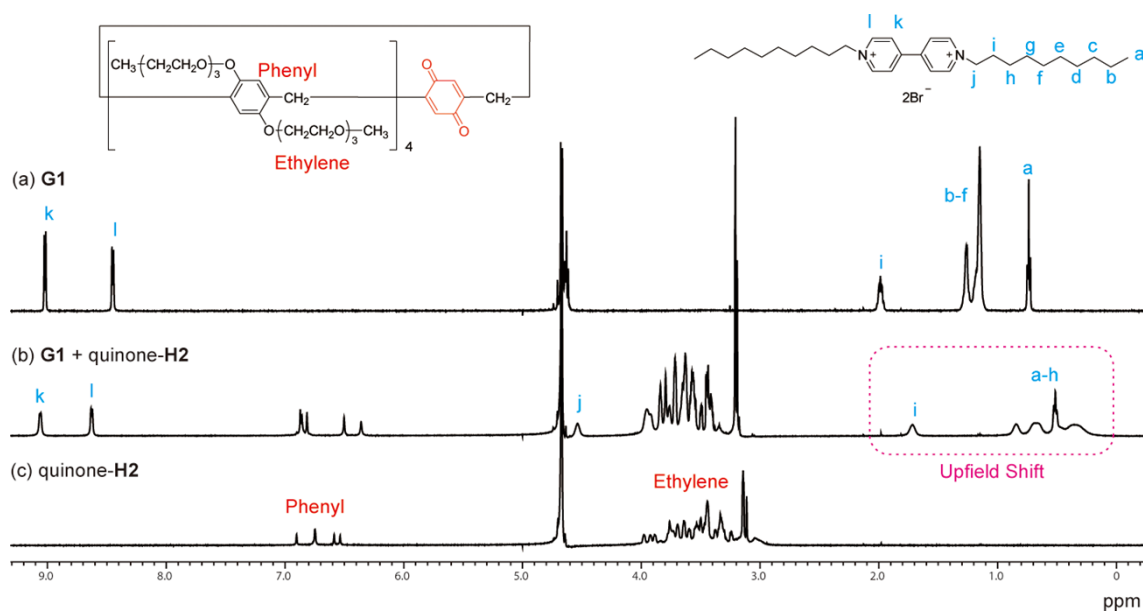


(b)



**Fig. S2** (a) UV-Vis spectra and (b) titration of quinone-H2 (0.50 mM) with G1 in aqueous media at 25 °C.

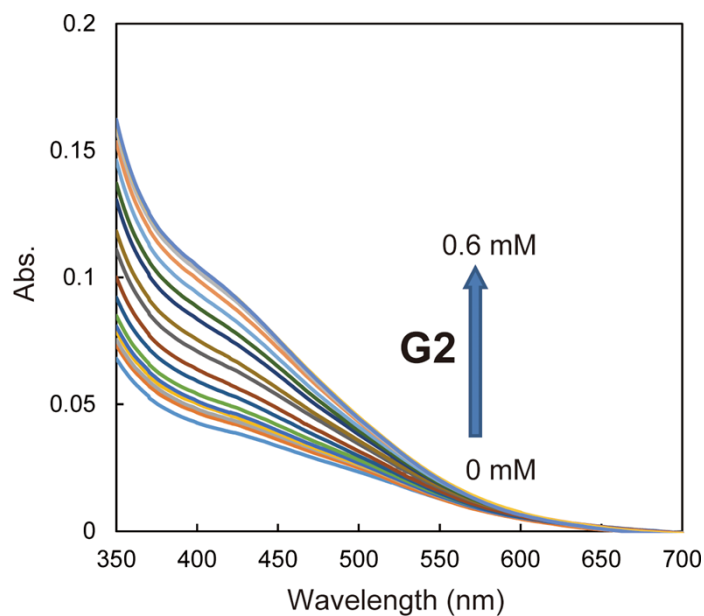
## $^1\text{H}$ NMR spectra for a mixture of quinone-H2 and G1



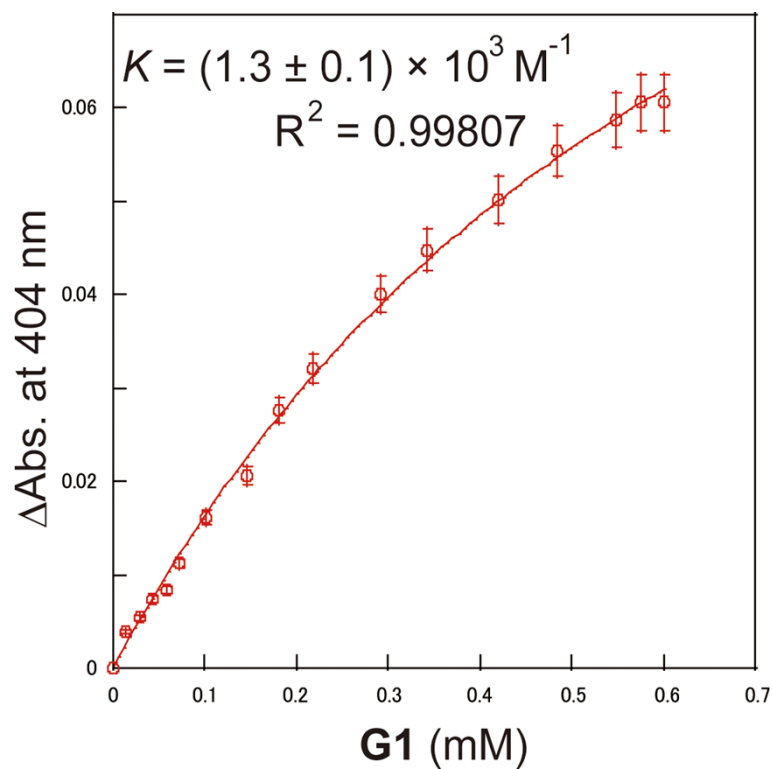
**Fig. S3**  $^1\text{H}$  NMR spectra (2 mM, 25 °C) of (a) **G1**, (b) a mixture of **G1** and quinone-**H2** and (c) quinone-**H2**.

## UV-vis spectra and titration of 2OH-H2 with G1

(a)

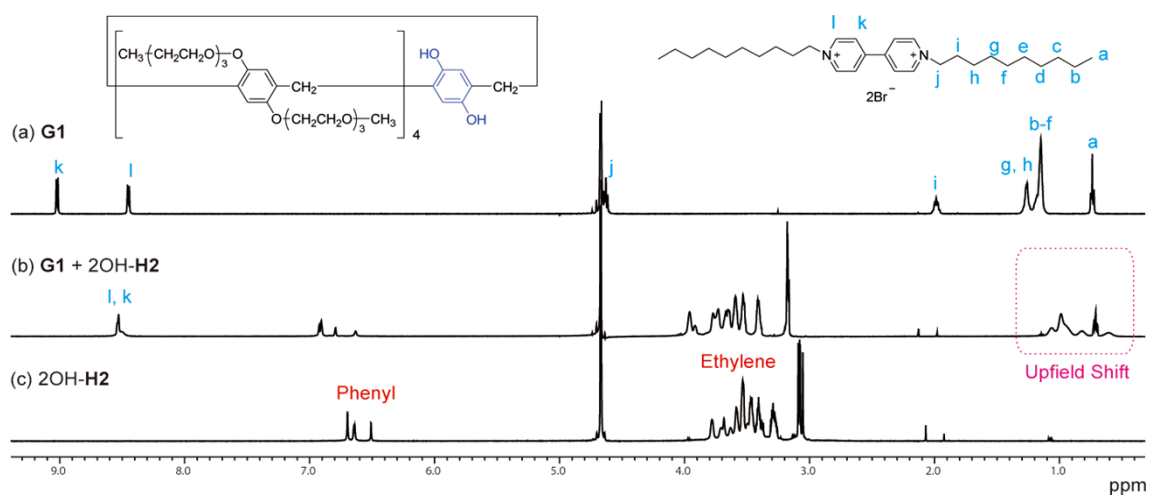


(b)



**Fig. S4** (a) UV-Vis spectra and (b) titration of 2OH-H2 (0.50 mM) with G1 in aqueous media at 25 °C.

## $^1\text{H}$ NMR spectra for a mixture of 2OH-H2 and G1



**Fig. S5**  $^1\text{H}$  NMR spectra (2 mM, 25 °C) of (a) **G1**, (b) a mixture of **G1** and **2OH-H2** and (c) **2OH-H2**.



## References

- S1. T. Ogoshi, R. Shiga and T. Yamagishi, *J. Am. Chem. Soc.*, 2012, **134**, 4577.  
S2. M. Munteanu, S. W. Choi and H. Ritter, *Macromolecules*, 2009, **42**, 3887.  
S3. P. R. Ashton, R. Ballardini, V. Balzani, M. Bělohradský, M. T. Gandolfi, D. Philp, L. Prodi, F. M. Raymo, M. V. Reddington, N. Spencer, J. F. Stoddart, M. Venturi, D. J. Williams, *J. Am. Chem. Soc.*, 1996, **118**, 4931.