Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information for

Enhanced Seebeck Coefficient of Thermocells by Heat-Induced Deposition of I_3^-/Hydrophobized α-Cyclodextrin Complexes on Electrode

Hirotaka Inoue,[a] Yimin Liang,[a] Teppei Yamada,*[a,b] Nobuo Kimizuka[1,2]

---

[a] *Division of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Motooka 744, Nishi-ku, Fukuoka 819-0395, Japan.*

[b] *Center for Molecular Systems, Kyushu University.*

Experimental Details

Synthesis of Et$_{18}$-α-CD

α-CD was evacuated at 90 °C for 12 hrs before use. To a stirred solution of α-CD (1.2 g) in dry DMF (50 mL), NaH (6.0 g) was added and stirred for 30 mins. The solution was cooled with an ice bath, and iodoethane (20 mL) was added dropwise and stirred for one day. The reaction was quenched by the addition of MeOH and water. The resulting solution was then extracted with dichloromethane, and the organic layer was dried over Na_2SO_4 and the solvent was removed. After the silica-gel column chromatography with $CHCl_3$ and MeOH (25:1, v/v), a colorless product (0.7 g, 47 %) was obtained. MALDI-TOF-MS: *m/z*: calcd for $C_{72}H_{132}O_{30}$: 1477.8. Found 1500.8 $[M+Na]^+$ ^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 5.06-5.05 (d, 6H), 4.08-4.04 (dd, 6H), 3.92-3.89 (dd, 6H), 3.81-3.46 (m, 54H), 3.26-3.23 (dd, 6H), 1.27-1.16 (m, 54H). Elemental analysis calcd (found) % for $C_{72}H_{132}O_{30}$: C 58.52 (58.34); H 9.00 (8.89).

Turbidity measurement

The turbidity of these solutions was measured by using a UV-vis spectrometer (V670, JASCO). Aqueous solutions of I_3^- (2.5 mM) and I^- (10 mM) containing 0.5 mM of α-CD or Et$_{18}$-α-CD (0.5 mM) were prepared and put into 1 cm quartz cells. The cell temperature was set at 10-60 °C with the heating and cooling rate of 0.5 ºC min^{-1}. The transmittance of the aqueous specimens was measured at a fixed wavelength of 800 nm, where the solution has no absorption peak.

Temperature dependence of UV-vis spectroscopy

Various-temperature UV-vis spectroscopy was executed with a UV-vis spectrometer (V670, JASCO) in the wavelength between 200 and 800 nm at varying temperatures from 10 ºC to 50 ºC with a temperature increment of 5 ºC. Spectral measurements were conducted for aqueous solutions containing I_3^- (2.5 mM), I^- (10 mM), and Et$_{18}$-α-CD (0.5 mM) in 0.1 mm quartz cells.

Various-temperature DLS measurement

DLS measurement was executed by ZetaSizer Nano ZS (Malvern), equipped with He–Ne laser (λ = 633 nm).

Raman spectroscopy

The solution of I_3^- (2.5 mM) and I^- (10 mM) with Et$_{18}$-α-CD (0.5 mM) in water was heated at above 50 ºC. The resultant precipitation was collected by filtration at 50 ºC. Raman spectrum was recorded by Raman spectrometer (Jasco NRS 3100KK) equipped with YAG laser (532 nm).

Thermo-electric measurement

Thermo-electric measurements were conducted for an aqueous solution of I_3^- (2.5 mM), I^- (10 mM) and Et_{18}-α-CD (0.5 mM) dissolved in water (40 mL) by using an H-shaped cell. The temperature of one side of the cell was fixed at ca. 19.5 °C. The temperature of the other side was changed by using a temperature-controlled water bath. The temperature of both sides of the cell was monitored by a couple of thermocouples (TM201, AS ONE). Pt wires are used as electrodes, and the voltage in between was recorded by a source meter 2401 (Keithley).

Cyclic voltammetry at various temperature

Cyclic voltammetry was executed for the aqueous solution of I_3^- (2.5 mM), I^- (10 mM), Et_{18}-α-CD (0.5 mM) and KNO_3 (100 mM) with ALS 620 (BAS) under N_2 atmosphere. The solution without Et_{18}-α-CD was used as control.

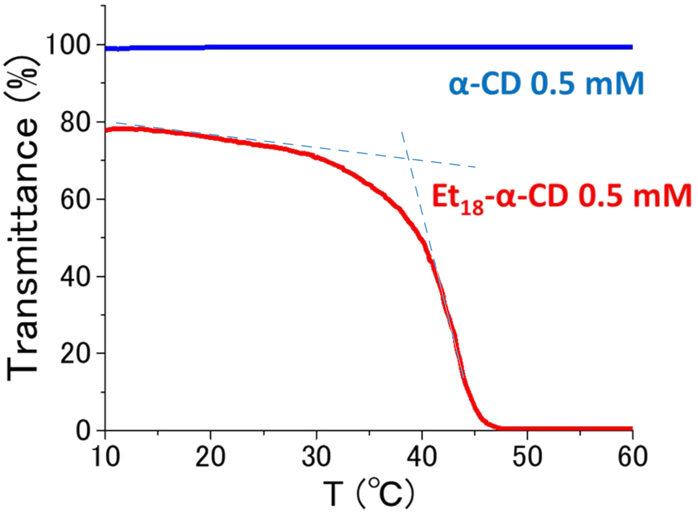

Figure S1. Temperature dependence of the transmittance at 800 nm measured for the aqueous solution of Et_{18}-α-CD with 2.5 mM of I_3^-. The transmittance of α-CD alone is shown in comparison. $[I_3^-] = 2.5$ mM, $[I^-] = 10$ mM, [α-CD] or [Et_{18}-α-CD] = 0.5 mM, λ = 800 nm.

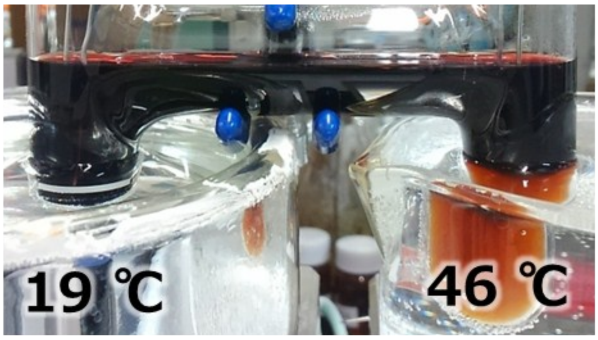

Figure S2. Photograph of thermocell.

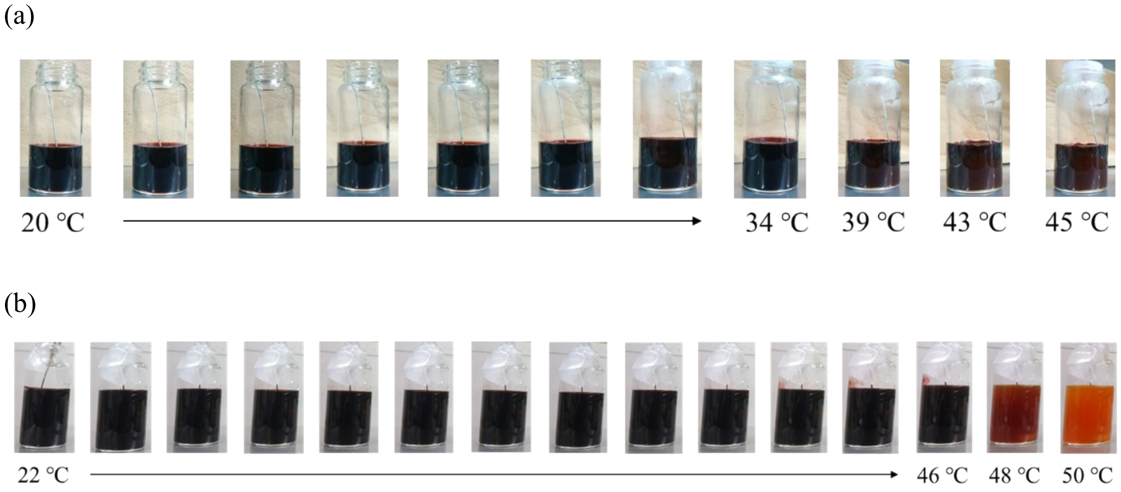

Figure S3. Photographs of aqueous solutions of I^- (10 mM), I_3^- (2.5 mM) and Et_{18}-α-CD (0.5 mM) at various temperature (a) with the addition of 100 mM of KNO_3 (b) without KNO_3.

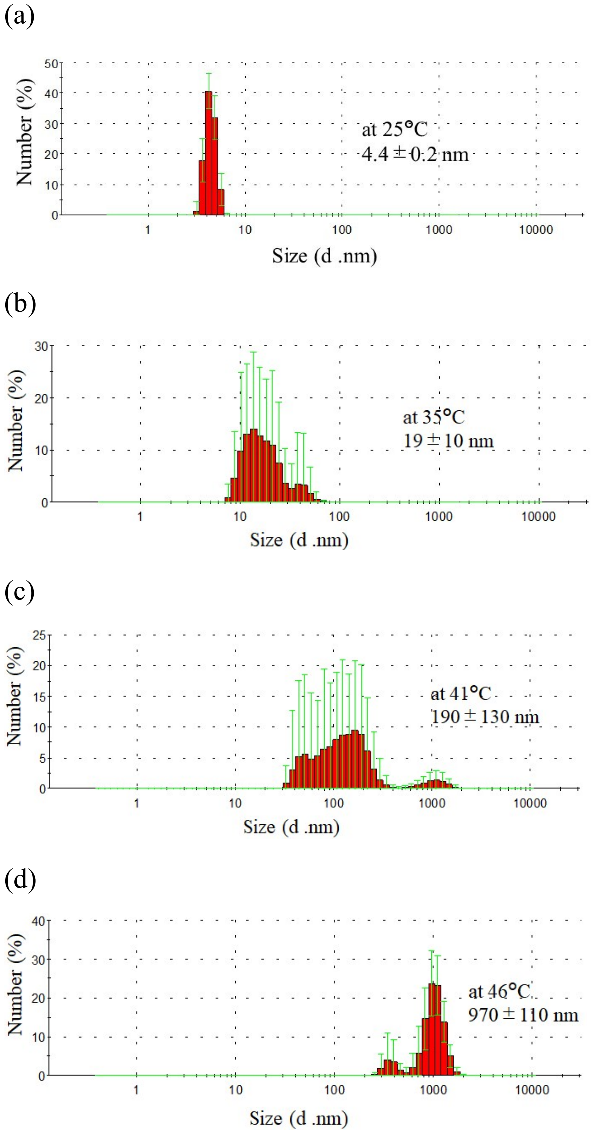

Figure S4. Results of DLS measurement of Et_{18}-α-CD and I_3^- solution with varied temperature. $[I_3^-] = 2.5$ mM, $[I^-] = 10$ mM, $[Et_{18}\text{-}\alpha\text{-CD}] = 0.5$ mM.

The sample was stood for at least 10 mins before measurements, and large aggregate could locate at the bottom of the quartz cell and may have been missed.

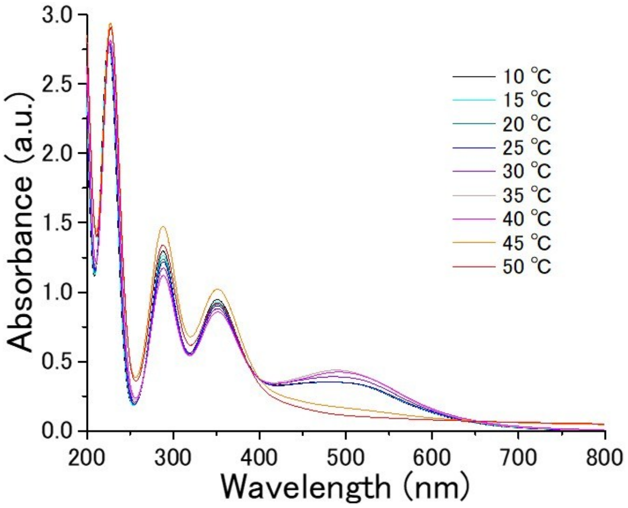

Figure S5. UV-vis spectra of Et$_{18}$-α-CD and polyiodide at varied temperature. [I_3^-] = 2.5 mM, [I^-] = 10 mM, [Et$_{18}$-α-CD] = 0.5 mM.

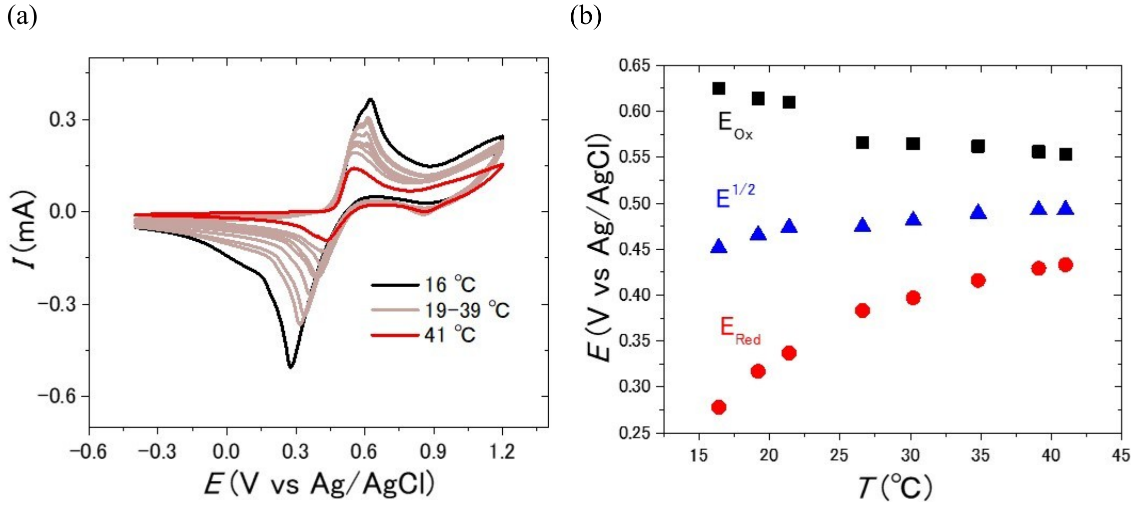

Figure S6. (a) Variable-temperature cyclic voltammograms of I^- (10 mM) and I_3^- (2.5 mM) without Et$_{18}$-α-CD. 100 mM of KNO_3 was added for supporting electrolyte. (b) A plot of the peak potentials of oxidation and reduction reactions at various temperatures. $E_{1/2}$ was also plotted and the slope was estimated to be ca. 1.0 mV/K. Considering the temperature effect of the reference electrode (ca. 0.2 mV/K),[1] the Seebeck coefficient of the electrolyte was estimated to be ca. 0.8 mV/K, which is roughly in good agreement with the reported value.[2]

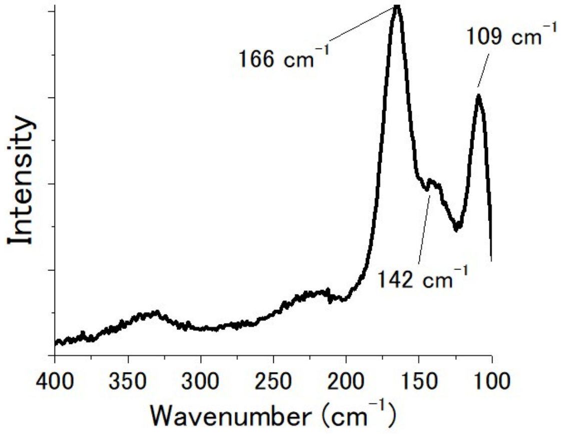

Figure S7. Raman spectrum of the precipitate obtained from the solution of I_3^- (2.5 mM) I^- (10 mM) and Et_{18}-α-CD (0.5 mM) at 45 °C. The precipitate shows three Raman peaks, which are assigned to those of symmetric (109 cm^{-1}) and asymmetric (109 cm^{-1}) stretching of I_3^-, and stretching of $I_2 \ldots I^-$ (166 cm^{-1}) according to the previous report of the encapsulated I_3^- anion into Me_{18}-α-CD[3]

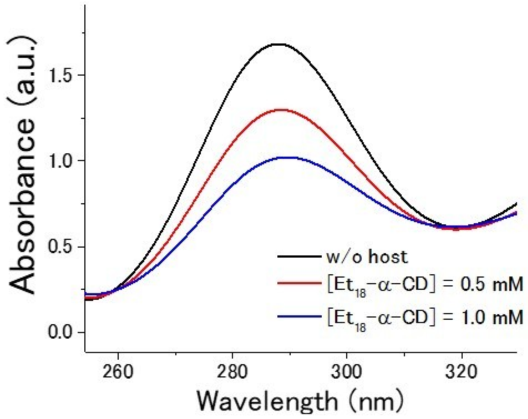

Figure S8. UV-vis spectra of KI (12.5 mM), I_2 (2.5 mM) and various amount of Et_{18}-α-CD in the water at ambient temperature.

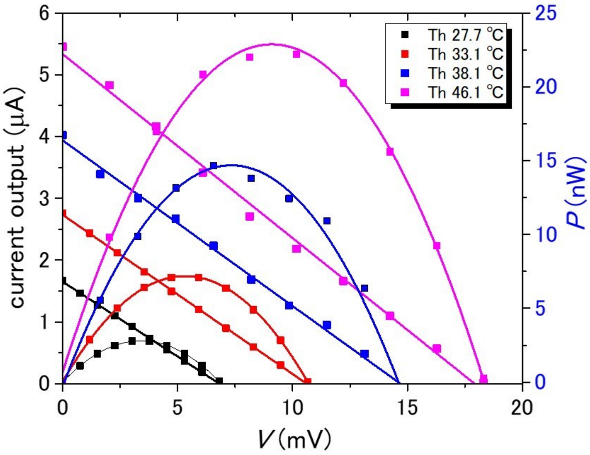

Figure S9. (a) I–V and P–V plots of a thermocell without a host at various temperatures at the hot electrode side. The temperature at the cold side was fixed at ca. 19.5 °C.