Supplementary Information to:

π-Stacked and Unstacked Aggregates Formation of A Near-infrared Dye Leading to Characteristic Photophysical Properties

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Contents:

1. Experimental

Materials and mixture samples preparation

3,3'-Diethylthiatricarbocyanine iodide (DTCI) and methanol (Wako Chem.) were used as purchased. DTCI solutions in methanol at [DTCI] = 4.0 x 10^{-4} M and 1.0 x 10^{-4} M were prepared by dissolving 5.45 mg of DTCI (10.00 mmol) in 25 mL and 100 mL of a solvent, and those at [DTCI] = 4.0 x 10^{-5} M, 1.0 x 10^{-5} M, 4.0 x 10^{-6} M and 1.0 x 10^{-6} M were prepared by diluting the 4.0 x 10^{-4} M and 1.0 x 10^{-4} M samples.

Aqueous solution samples of DTCI were prepared by adding DTCI to deionized water at the apparent ratios of 0.1 g/L, 0.5 g/L, 1 g/L, and 2 g/L, rigorously stirring the mixtures for 1 h to facilitate dissolution, and standing them for 30 min; the supernatant liquid part was used for measurements. Because DTCI was only partially soluble in water, accurate concentrations of DTCI in water were determined by dissolving 50 μL for the supernatant solutions made at 0.5 g/L, and 1 g/L, and 2 g/L or 300 μL of the supernatant solution made at 0.1 g/L in 1 mL of MeOH and measuring absorbance spectra of the resulting solution whose methanol content was 95 volume % or 77 volume %. Molar absorptivities of DTCI at 758 nm in pure MeOH follow: ε = 367000 at 1.0 x 10^{-6} M [absorbance 0.037], 330000 at 4.0 x 10^{-6} M [absorbance 0.132], 313160 at 1.0 x 10^{-5} M [absorbance 0.313], 283427 at 4.0 x 10^{-5} M [absorbance 1.13], and 263220 at 1.0 x 10^{-4} M [absorbance 2.63]). Non-linear curve fitting led the following equation:

$$[\text{DTCI}] = 3.509 \times 10^{-5} \times (\text{Absorbance at 758 nm})^{1.083}$$

On the basis of this equation and absorbance values red from Figure S2 along with the dilution ratios led to the concentrations: [DTCI] = 7.2 x 10^{-5} M for 0.1 g/L, 2.0 x 10^{-4} M for 0.5 g/L, 4.8 x 10^{-4} M for 1 g/L, and 8.8 x 10^{-4} M for 2 g/L.

Instrumentation

Circular dichroism (CD) spectra were taken with a JASCO-820 spectrometer. UV-vis absorption spectra were measured with a JASCO V-570 spectrophotometer. Emission spectra were taken on a JASCO FP-8500 fluorescence spectrophotometer.

2. Absorbance Spectra of DTCI in methanol

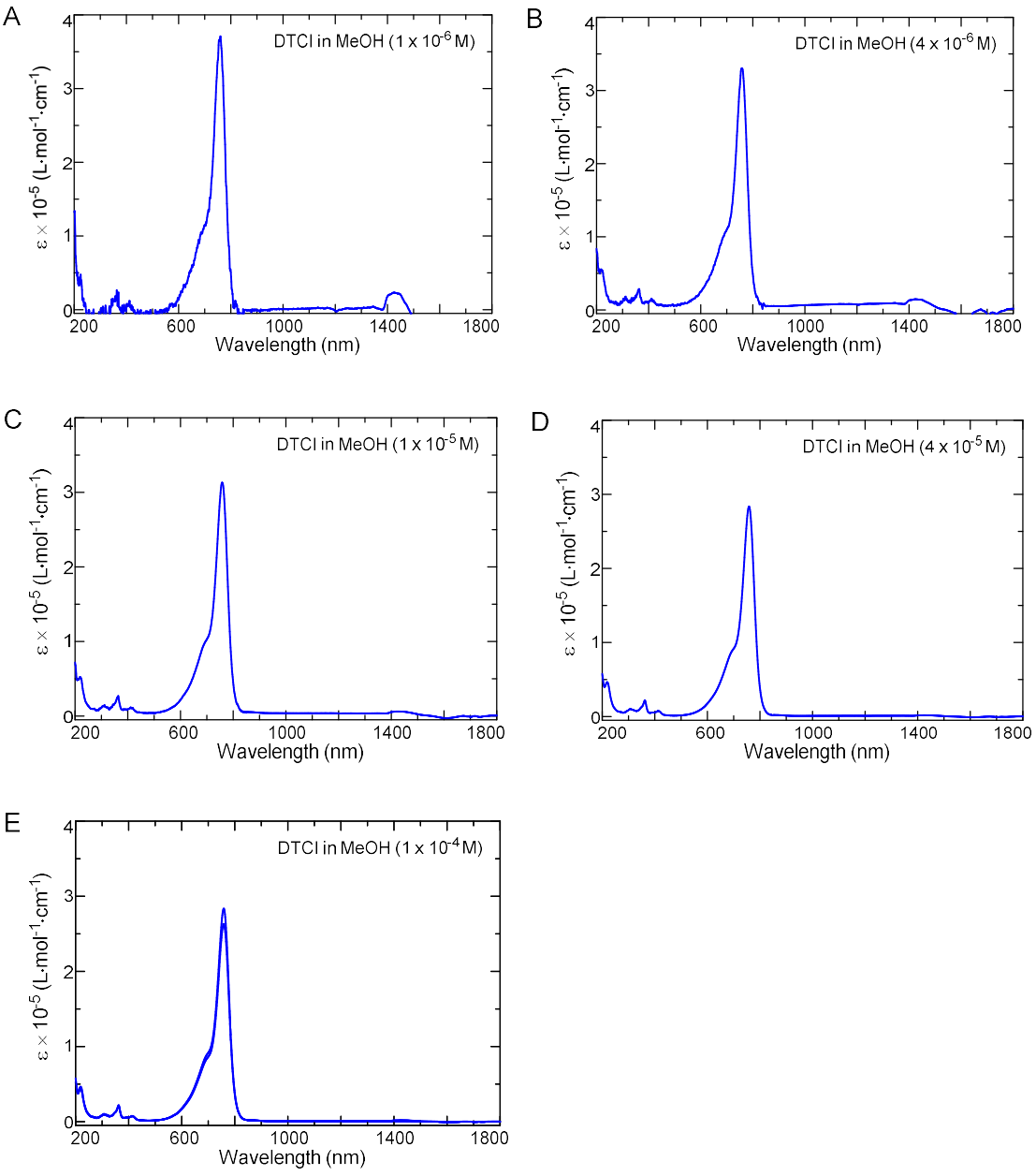

Figure S1. Absorbance spectra of DTCI in methanol at 1.0 x 10^{-6} M (A), 4.0 x 10^{-6} M (B), 1.0 x 10^{-5} M (C), 4.0 x 10^{-5} M (D), and 1.0 x 10^{-4} M (D) [room temperature, 1-mm cell].

3. Absorbance Spectra of DTCI in methanol containing water

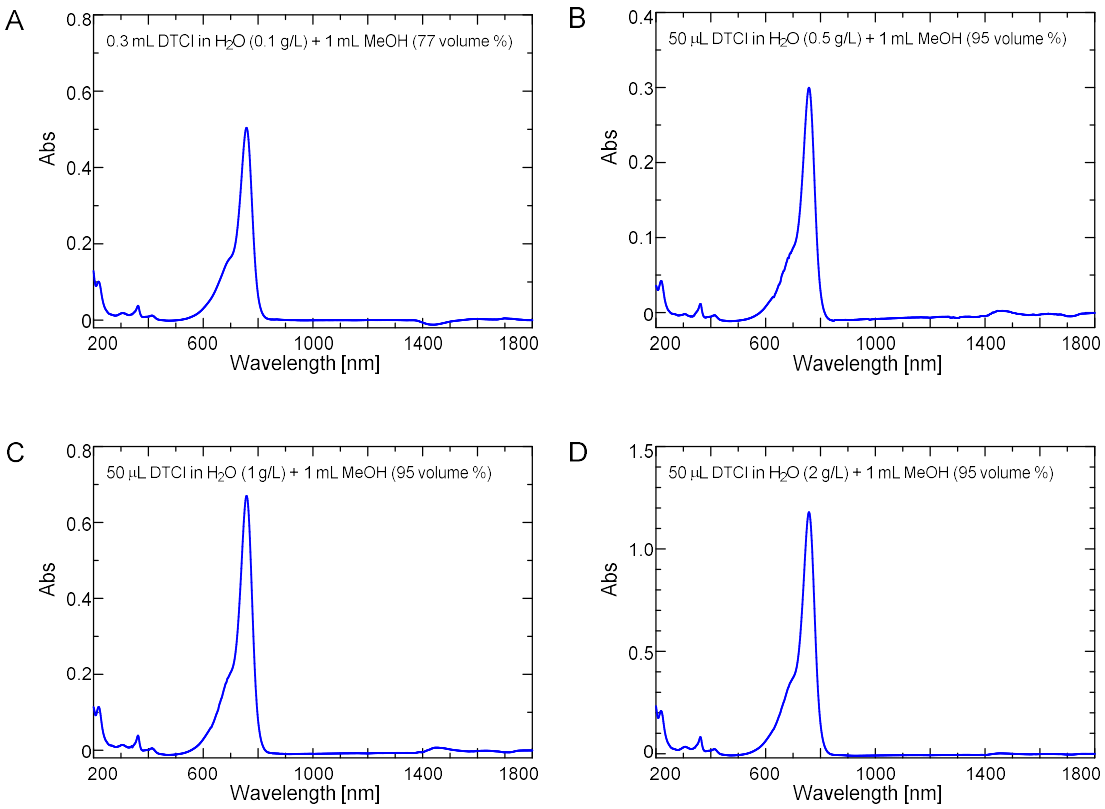

Figure S2. Absorbance spectra of DTCI in methanol containing water. The samples were prepared by dissolving supernatant water solution prepared at a ratio of DTCI and water of 0.1 g/L (A), 0.5 g/L (B), 1 g/L (C), and 2 g/L (D) [room temperature, 1-mm cell]. See Experimental text for further details.

4. Fluorescence and excitation spectra of DTCI in methanol and in water measured through front-face illumination in a triangular cell or a in a square cell set diagonally to the incident light beam

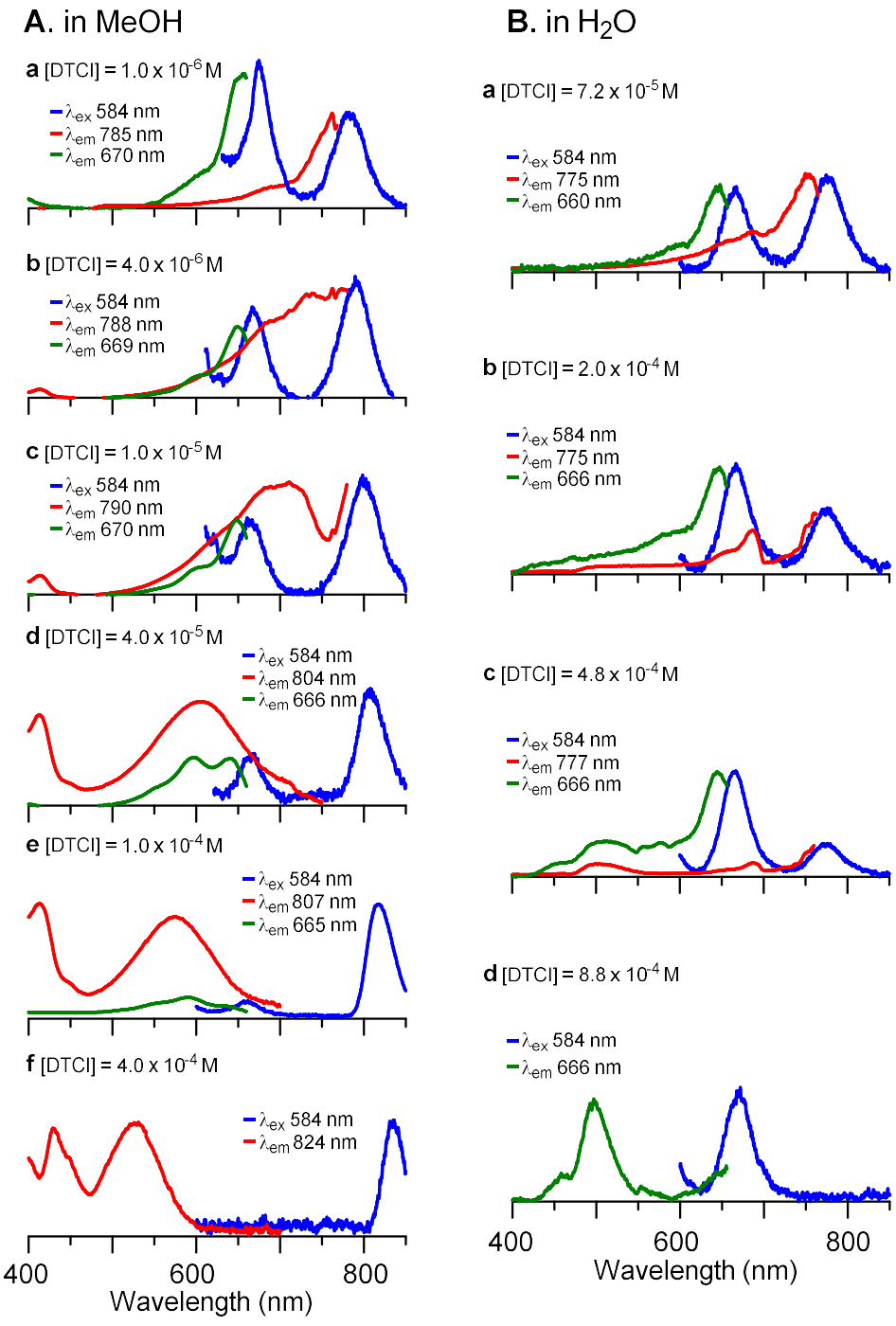

Figure S3. Emission (blue) and excitation (red and green) spectra of DTCI in methanol (A) and in water (B) measured through front-face illumination: [DTCI] a= 1.0 x 10^{-6} M (a), 4.0 x 10^{-6} M (b), 1.0 x 10^{-5} M (c), 4.0 x 10^{-5} M (d), 1.0 x 10^{-4} M (e), and 4.0 x 10^{-4} M (f) in A and 7.2 x 10^{-5} M (a), 2.0 x 10^{-4} M (b), 4.8 x 10^{-4} M (c), and 8.8 x 10^{-4} M (d) in B. Excitation wavelengths for fluorescence emission spectra (λ_{ex}) and monitoring wavelengths for excitation spectra (λ_{em}) are indicated above relevant spectra [room temperature, 10-mm cell].

5. Temperature effects on absorbance spectra in MeOH

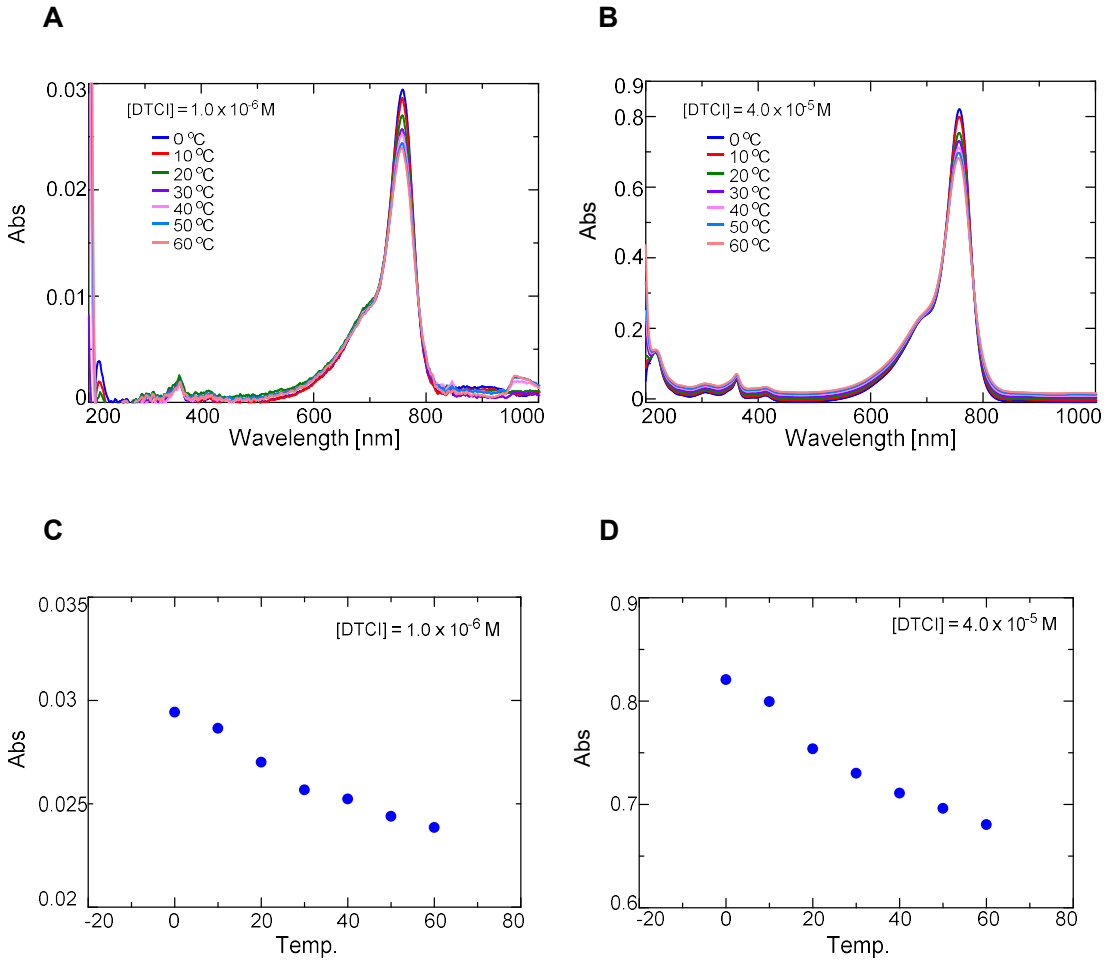

Figure S4. Absorbance spectra of DTCI in methanol at [DTCI] = 1.0 x 10^{-6} M (A) and 4.0 x 10^{-5} M (B) measured at different temperatures and relations between absorbance at 758 nm and temperature at 1.0 x 10^{-6} M (C) and 4.0 x 10^{-5} M (D).

6. Temperature effects on absorbance spectra in H_2O

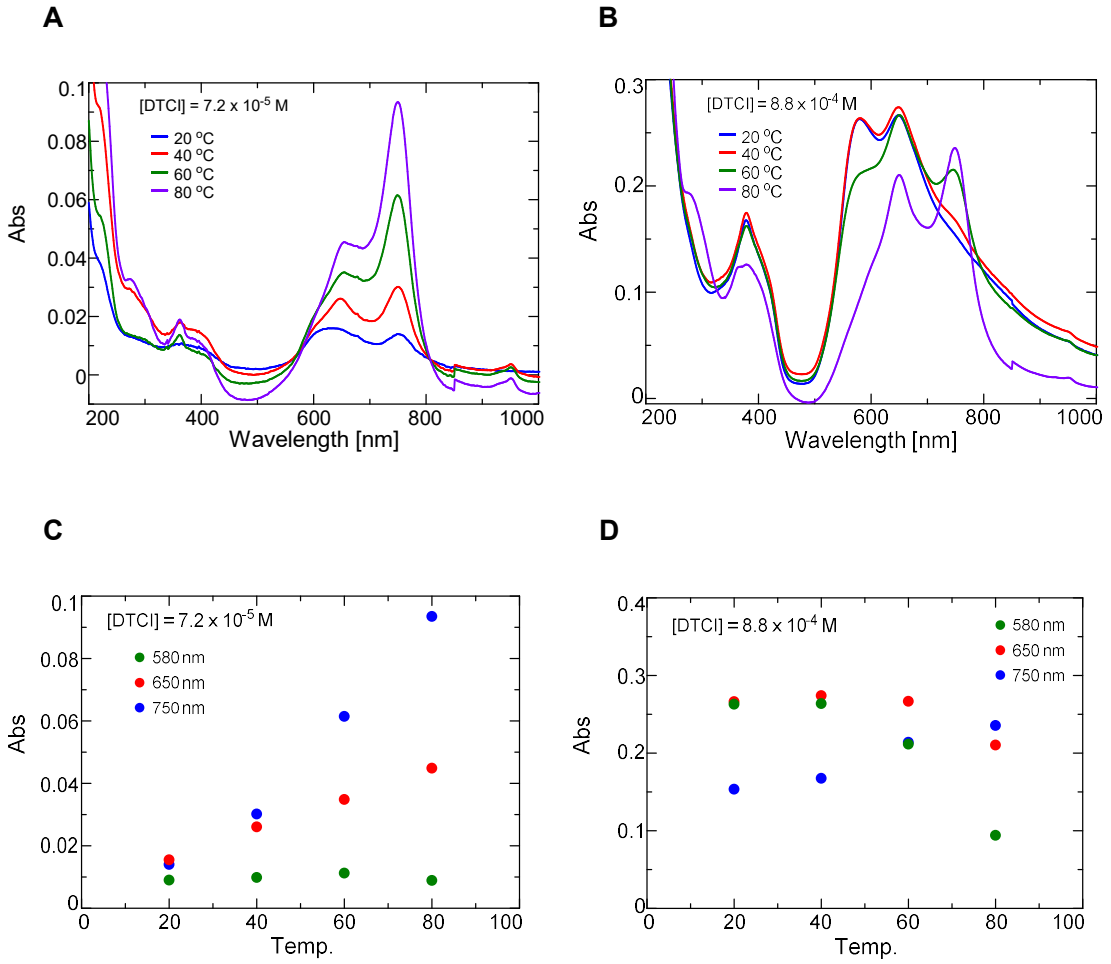

Figure S5. Absorbance spectra of DTCI in methanol at [DTCI] = 7.2 x 10^{-5} M (A) and 8.8 x 10^{-4} M (B) measured at different temperatures and relations of absorbances at 580 nm, 650 nm, and 750 nm and temperature at 7.2 x 10^{-5} M (C) and 8.8 x 10^{-4} M (D).

7. Temperature effects on NMR spectra

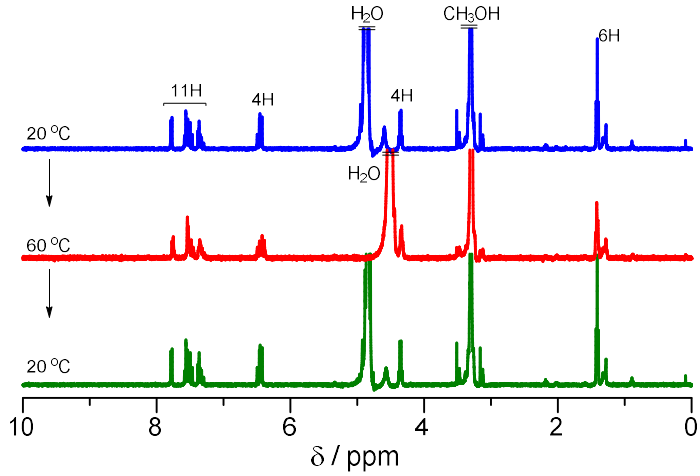

Figure S6. ^{1}H NMR spectra of DTCI taken at different temperatures in CD_3OD at [DTCI] = 4.0 x 10^{-4} M.

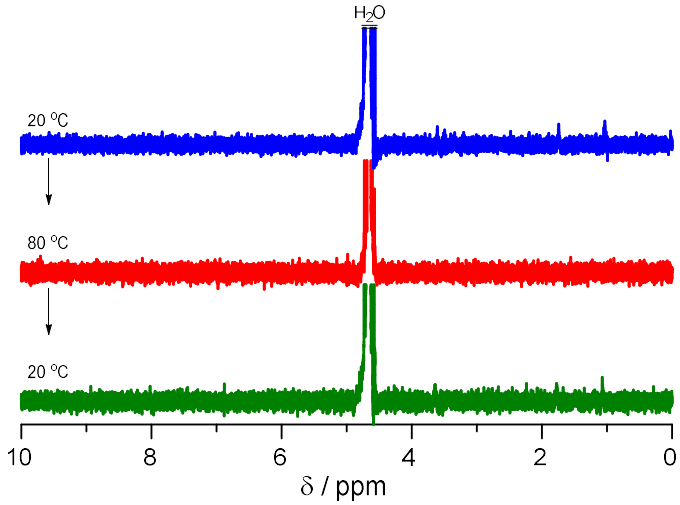

Figure S7. ^{1}H NMR spectra of DTCI taken at different temperatures in D_2O at [DTCI] = 8.8 x 10^{-4} M.