Supporting Information

**Space Size Dependent Transformation of Tetrphenylethylene Carboxylate Aggregates by Ice-Confinement**

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Figure S1 NMR spectra for TPA-COOH and TPAC.

Figure S2 Absorption spectrum of 14 μM TPEC in 2 M sucrose and tris buffer

Figure S3 Freezing point depression curve for the sucrose/water system.
   Estimation of the freezing point depression curve in the subeutectic temperature range.

Figure S4 Relationship between $l$ and $V_{FCS}$. Estimation of the relationship $l$ vs $V_{FCS}$.
   Derivation of the relationship $l$ vs $V_{FCS}$.

Figure S5 Fluorescence spectrum of 14 μM TPEC in tris buffer.

Figure S6 Fluorescence spectrum of TPEC crystal.

Figure S7 Temperature change of fluorescence spectra of TPEC in 2 M sucrose solution.

Figure S8 Excitation spectra of TPEC in the FCS at various $T$
Figure S9 Repeated measurements of fluorescence spectra between −6 °C and −21 °C.

Figure S10 Fluorescence spectra of TPEC in the FCS for $c_{suc}^{ini} = 50$ mM.

Figure S11 Fluorescence spectra of TPEC in the FCS for $c_{suc}^{ini} = 100$ mM.

Figure S12 Fluorescence spectra of TPEC in the FCS for $c_{suc}^{ini} = 150$ mM.
Figure S1 NMR spectra for TPA-COOH (top) and TPAC (bottom) dissolved in CDCl₃.

TPA-COOH: δ 8.34 (s, 0.1H), 7.72 (d, J = 8.5 Hz, 2H), 7.18-6.99 (m, 18H).

TPA-COONa: δ 7.57 (d, J = 8.3 Hz, 2H), 7.15-6.85 (m, 18H). Peaks of δ=2.2-3.4 originate from solvents, water, CHCl₃, and acetone.
Figure S2 Absorption spectrum of 14 μM TPEC in 2 M sucrose (black) and tris buffer (red) at room temperature.
Figure S3 Freezing point depression curve for the sucrose/water system. The solid curve is fitted to the data reported in the literature (ref. 35 in the main text). The broken curve is extrapolated from the data above the eutectic point ($T_{eu}$).

The freezing point depression curve below $T_{eu}$ is represented by the following relationship between the sucrose concentration ($c_{suc}$) and temperature ($T$).

$$c_{suc} = -3.26 \times 10^{-6} T^5 - 1.72 \times 10^{-4} T^4 - 3.92 \times 10^{-3} T^3 - 5.22 \times 10^{-2} T^2 - 0.485 T$$
Figure S4 Relationship between $l$ and $V_{\text{FCS}}$. The size of the FCS space was calculated from data reported in the literature in the following way.

From the data shown in our previous paper (ref. 25 in the main text), there is a linear relationship between $l$ (m) and $c_{\text{suc}}^{\text{ini}}$ (M) at $-4 \, ^\circ\text{C}$.

$$l = 2.39 \times 10^{-5} \frac{c_{\text{suc}}^{\text{ini}}}{c_{\text{suc}}} \quad (1)$$

The volume of the FCS ($V_{\text{FCS}}^{\text{rel}}$) relative to a unit volume of the original solution before freezing is given by

$$V_{\text{FCS}}^{\text{rel}} = \frac{c_{\text{suc}}^{\text{ini}}}{c_{\text{suc}}} \quad (2)$$
Using $c_{\text{suc}}^{\text{FCS}} (=1.315 \text{ M})$ at $-4^\circ \text{C}$, this equation can be rewritten as:

$$l = 3.15 \times 10^{-5} \ V_{\text{FCS}}^{\text{rel}} \quad (3)$$

Since the freezing depression curve gives $c_{\text{suc}}^{\text{FCS}}$ at a given temperature, we can extend Equation (3) to any temperature and relate $l$ with $V_{\text{FCS}}^{\text{rel}}$. Figure S2 shows the linear relationship between $l$ and $V_{\text{FCS}}^{\text{rel}}$ under the conditions employed in this work.
Figure S5 Fluorescence spectrum of 14 μM TPEC in tris buffer excited at 320 nm.
Figure S6 Fluorescence spectrum of TPEC crystal excited at 320 nm.
Figure S7 Temperature change of fluorescence spectra of 14 μM TPEC in 2 M sucrose solution excited at 320 nm.
Figure S8 Excitation spectra of TPEC in the FCS monitored at 460 nm at various $T$ (black: $-6 \, ^\circ C$, light blue: $-9 \, ^\circ C$, red: $-12 \, ^\circ C$, green: $-15 \, ^\circ C$, purple: $-18 \, ^\circ C$, brown: $-21 \, ^\circ C$). $c_{\text{suc}}^{\text{ini}} = 10 \, \text{mM}$. 
Figure S9 Repeated measurements of fluorescence spectra between −6 °C and −21 °C. 

\(c_{\text{suc}}^{\text{ini}} = 10 \text{ mM} \) (the same condition as Figure 4 in the main text). Order of measurements: 1 at −6 °C, 2 at −21 °C, 3 at −6 °C, and 4 at −21 °C.
Figure S10 Fluorescence spectra of TPEC in the FCS excited at 320 nm at various $T$
(black: $-6 \, ^\circ C$, light blue: $-9 \, ^\circ C$, red: $-12 \, ^\circ C$, green: $-15 \, ^\circ C$, purple: $-18 \, ^\circ C$, brown: $-21 \, ^\circ C$). $c_{\text{suc}}^{\text{ini}} = 50 \, \text{mM}$.
Figure S11 Fluorescence spectra of TPEC in the FCS excited at 320 nm at various $T$.

(black: $-6^\circ\text{C}$, light blue: $-9^\circ\text{C}$, red: $-12^\circ\text{C}$, green: $-15^\circ\text{C}$, purple: $-18^\circ\text{C}$, brown: $-21^\circ\text{C}$). $c^{\text{ini}}_{\text{suc}} = 100$ mM.
Figure S12 Fluorescence spectra of TPEC in the FCS excited at 320 nm at various $T$.