

Supplementary Information

Creation of a polymer backbone in lipid bilayer membrane-based nanotubes

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Instrumentations

Photo-induced polymerization was carried out using Optical Modulex USH-250SC (Ushio Inc. (Japan)) of 0.75 kW power. ¹H NMR (400 MHz) spectra were recorded in CDCl₃ with SiMe₄ as an internal standard on JNM-EX400 (JEOL Ltd. (Japan)). FT-IR spectra were measured in a KBr method with FT/IR-4100 (JASCO Co. (Japan)). UV-Vis and CD spectra were measured with V-560 (JASCO Co.) and J725 (JASCO Co.), respectively. TEM images were observed with JEM-2000X (JEOL Ltd.). DSC thermograms were obtained with DSC 6100 (Seiko Instruments Inc. (Japan)). The aqueous solutions of **g₁₂-Py⁺** with or without styrene (20 mM, 50 μL) were sealed in 70 μL silver pans and scanned between 0 and 70 °C at heating and cooling rate of 2 °C min⁻¹.

Synthesis of L-glutamide-derived amphiphile

Materials

Styrene and divinylbenzene (DVB) were purchased from Wako Pure Chemical Industries, Ltd. (Japan) and purified by filtration through alumina. Irgacure 369 ($\lambda_{\text{max}} = 321$ nm) was purchased from BASF (Japan). Reagent grade and measurement grade solvents were purchased from Nacalai Tesque, Inc. (Japan).

Synthesis of N¹-3-pyridinium propanoyl N²,N³-didodecyl L-glutamine (g₁₂-Py⁺)

g₁₂-Py⁺ was prepared by the previously reported procedure.^[1] mp 181.0-182.0 °C. (Found: C, 62.87; H, 9.69; N, 7.96. C₃₇H₆₇N₄O₃Br requires C, 63.86; H, 9.70; N, 8.05%). $\nu_{\max}/\text{cm}^{-1}$ 3332 and 3302 (N-H), 2918 and 2850 (C-H), 1638 (C=O), 1550 (N-H). δ_{H} (400 MHz; CDCl₃; Me₄Si) 0.86-0.90 (6H, t, -CH₃), 1.26 (36H, br s, -(CH₂)₉-), 1.47 (4H, br, -COCH₂CH₂-), 1.91-2.11 (2H, m, -C*HCH₂-), 2.20-2.35 (2H, m, -C*HCH₂CH₂-), 3.10-3.20 (4H, dt, -COCH₂-), 3.25-3.50 (2H, m, -PyCH₂-), 4.20-4.30 (1H, dt, C*H), 5.18 (2H, t, -PyCH₂CH₂-), 6.84 (1H, t, -NH-), 6.94 (1H, t, -NH-), 8.00-8.10 (2H, t, *m*-PyH), 8.34-8.38 (1H, d, -NH-), 8.43 (1H, t, *p*-PyH), 9.40-9.43 (2H, d, *o*-PyH). MALDI TOF MS: Calcd for C₃₇H₆₇N₄O₃⁺ 615.97, m/z = 615.92.

Intercalation of a polymer backbone into the bilayers

Preparation of lipid bilayer membrane based-nanotubes

g₁₂-Py⁺ (10 mg) was dissolved in 2.5 mL of water, and the mixture was sonicated at 60 °C to be clear. 0.1 mL of methanol solution of a mixture of styrene, DVB (65 : 35 w/w) and Irgacure 369 (5 wt% for monomers) was added to the solution, and the mixture was sonicated in an ice bath for 5 minutes. The obtained solution was diluted with water to 0.5 mM **g₁₂-Py⁺** and kept at 10 °C for an hour. As a reference, 0.1 mL of methanol was used in place of the monomer solution.

Photo-initiated radical polymerization

The solution of a mixture of **g₁₂-Py⁺** and monomers was put into a 1 mm quartz cell, and UV light was irradiated to the solution through a UV cut filter for 2 hours at 10 °C with the ultrahigh-pressure mercury lamp.

Removal of g₁₂-Py⁺ from a polymer backbone

After photo-irradiation, an excess amount of ethanol was added to the aqueous solution. The obtained precipitates were collected by centrifugation, and the extracted **g₁₂-Py⁺** in the supernatant was detected with FT-IR spectroscopy and reversed-phase HPLC. This washing process was repeated until no **g₁₂-Py⁺** was detected in the supernatant.

Sample preparation for TEM observation

A drop (ca. 20 μl) of the **g₁₂-Py⁺** aqueous solution was mixed with another drop (ca. 20 μl) of an uranyl acetate aqueous solution (1 wt%) on a paraffin film for negative staining. A carbon-coated copper grid was placed on the mixed solution and allowed to stand for 5 min. Excess solution on the

grid was removed by a paper filter. After vacuum drying, the grid was used for TEM observation.

[1] H. Ihara, M. Takafuji, C. Hirayama and D. F. O'Brien, *Langmuir*, 1992, **8**, 1548; V. Gopal, T. K. Prasad, N. M. Rao, M. Takafuji, M. M. Rahman and H. Ihara, *Bioconjug. Chem.*, 2006, **17**, 1530-1536.

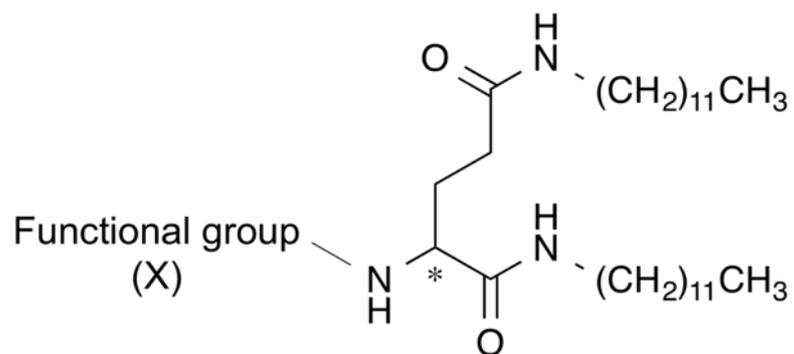


Fig. S1 Base structure of L-glutamic acid-derived compound for creating nanofibrillar aggregates.

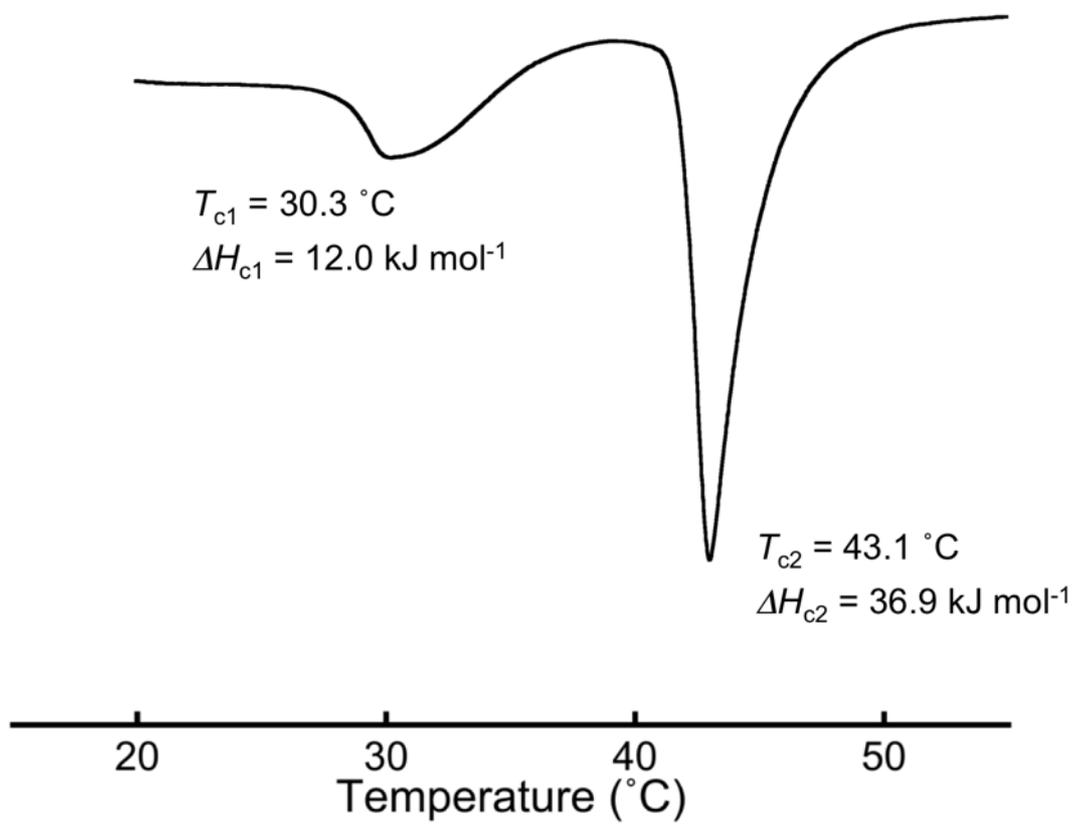


Fig. S2 DSC thermogram of aqueous solution of $g_{12}\text{-Py}^+$. [$g_{12}\text{-Py}^+$] = 20 mM.

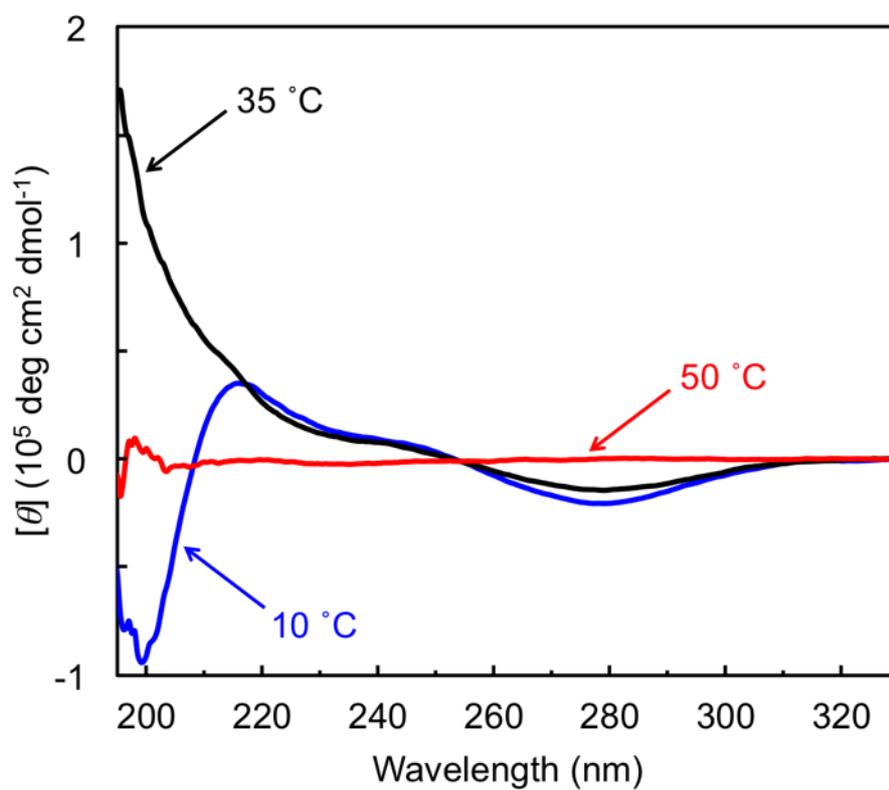


Fig. S3 CD spectra of 0.5 mM of g_{12} -Py⁺ in water at 10 °C (blue line), 35 °C (black line) and 50 °C (red line).

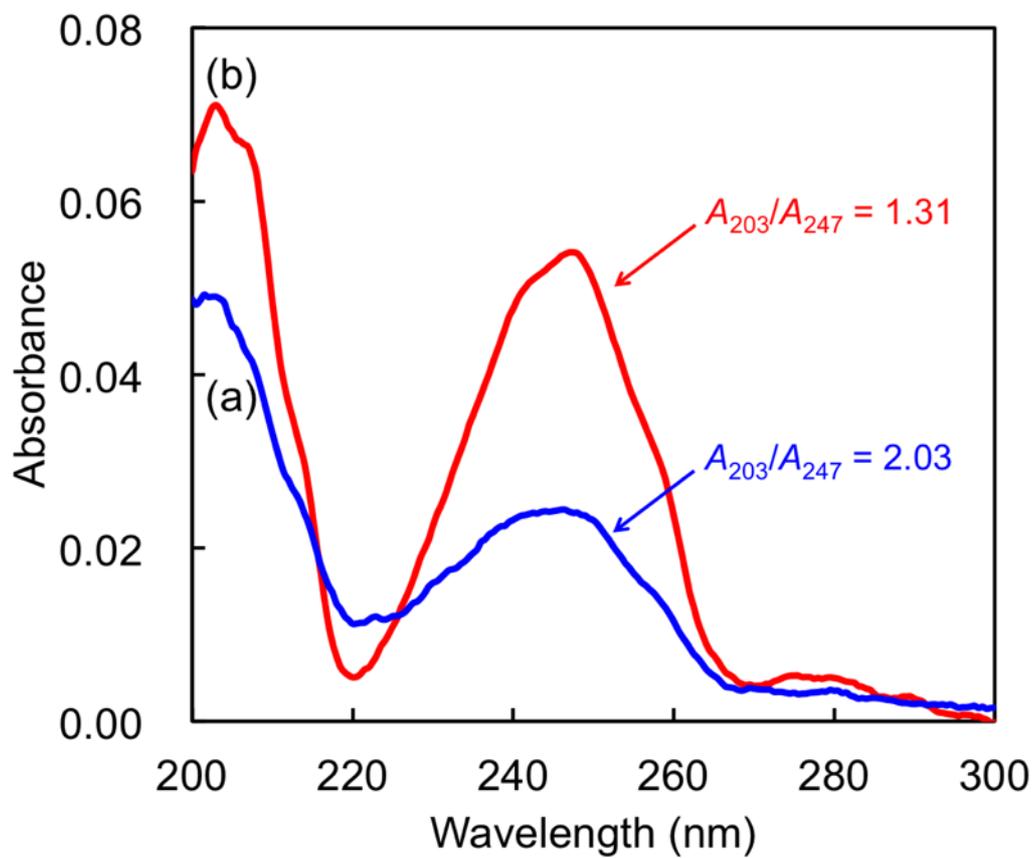


Fig. S4 (a) UV spectrum of styrene (0.02 mM) in water; (b) UV spectrum of styrene (0.67 mM) in $g_{12}\text{-Py}^+$ aqueous solution. $[g_{12}\text{-Py}^+] = 0.5$ mM, styrene/ $g_{12}\text{-Py}^+ = 1$ (w/w).

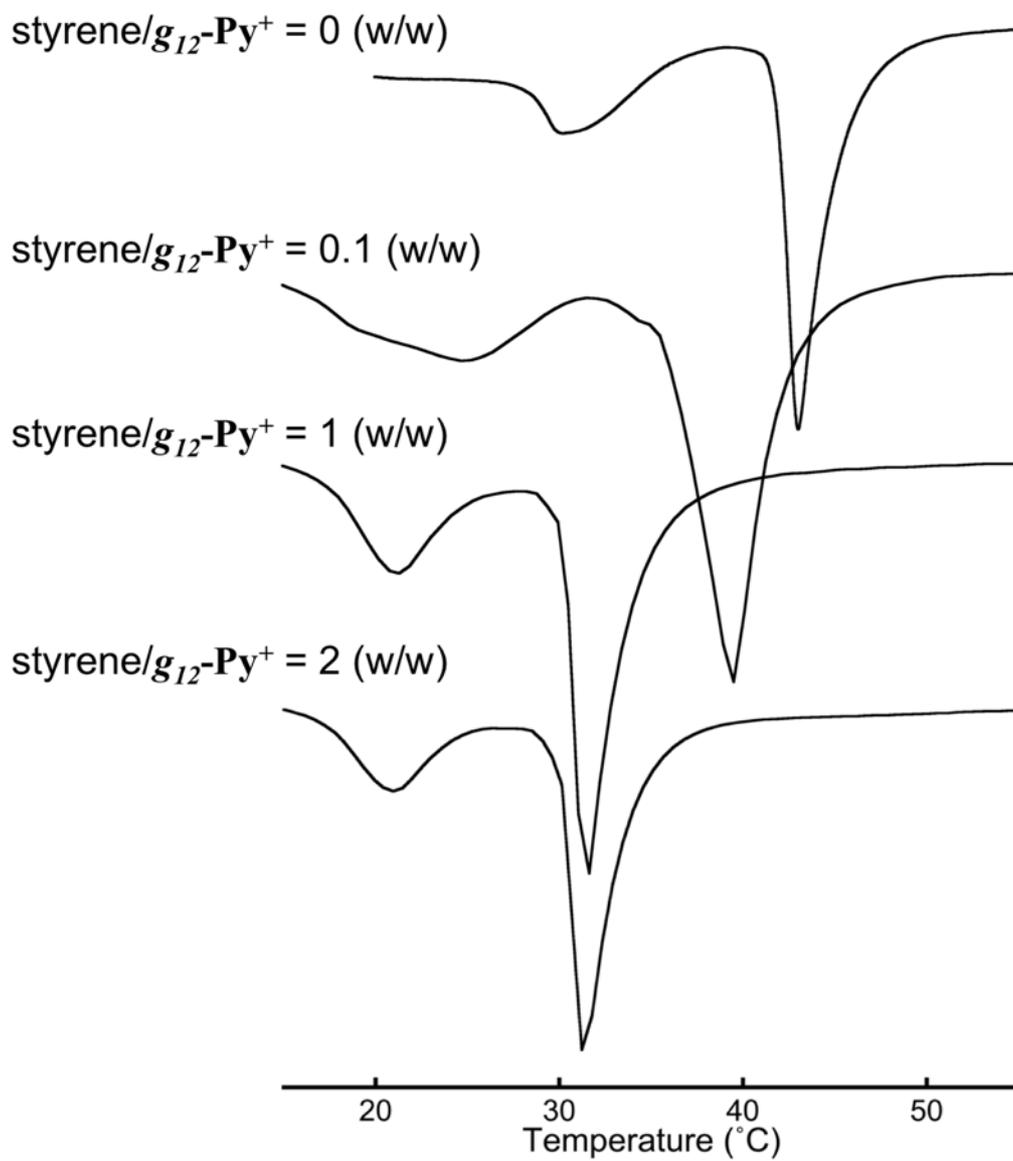


Figure S5 DSC thermograms of aqueous solutions of $g_{12}\text{-Py}^+$ with styrene. $[g_{12}\text{-Py}^+] = 20$ mM, styrene/ $g_{12}\text{-Py}^+ = 0, 0.1, 1,$ and 2 (w/w).

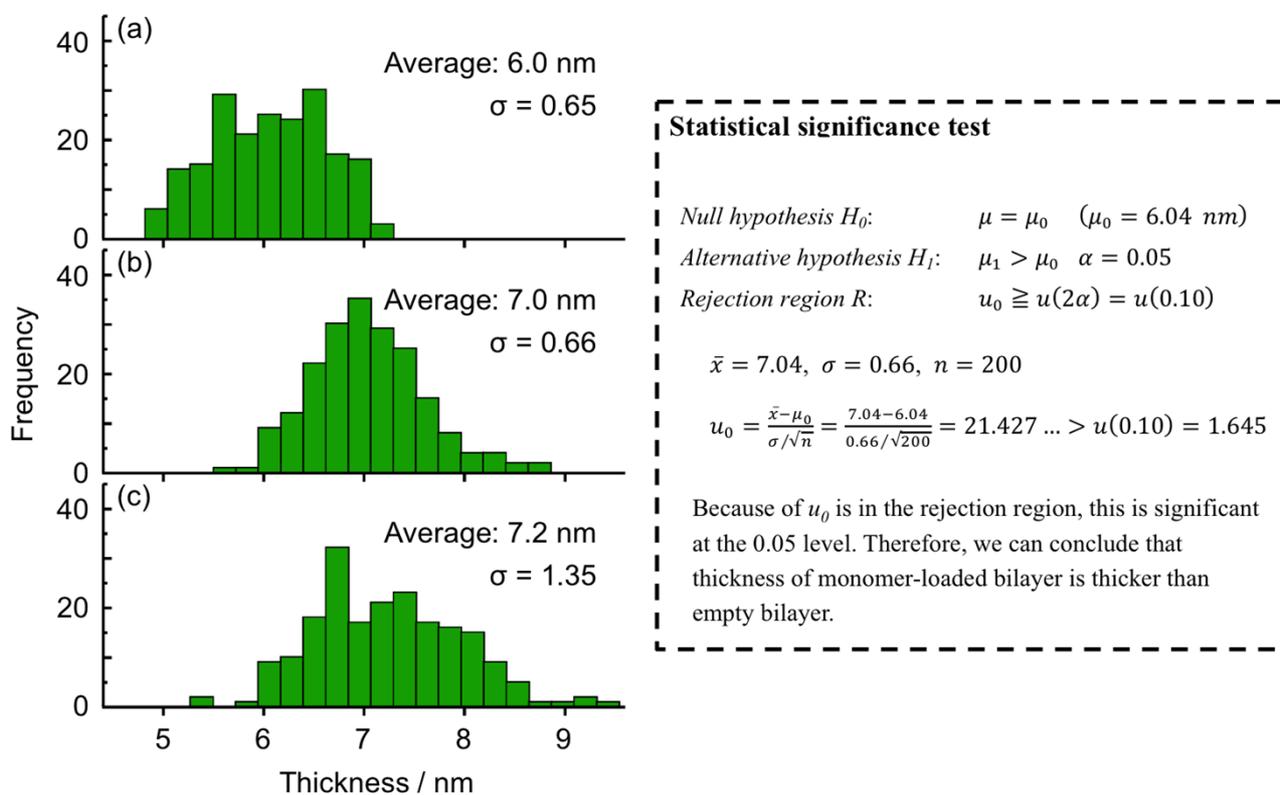


Fig. S6 Thickness distribution of $g_{12}\text{-Py}^+$ aggregates: (a) without monomer, (b) with styrene (100 wt% for $g_{12}\text{-Py}^+$) and (c) with polymerized styrene-DVB (65 wt% and 35 wt% for $g_{12}\text{-Py}^+$). $[g_{12}\text{-Py}^+] = 0.5 \text{ mM}$, monomer/ $g_{12}\text{-Py}^+ = 1$ (w/w).

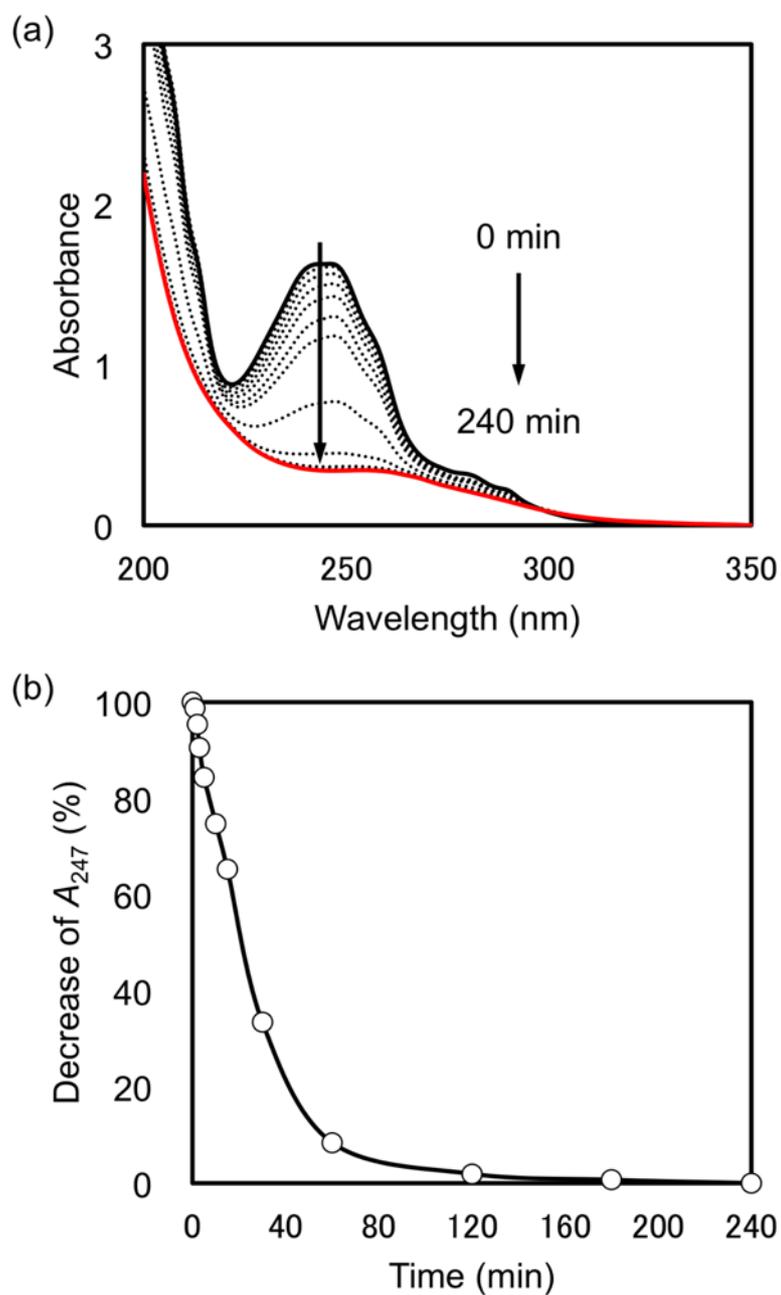


Figure S7 a) UV-vis spectral changes of a styrene-DVB (65:35 w/w) mixture in the presence of $g_{12}\text{-Py}^+$ nanotubes under photoirradiation at 10 °C. b) Decreasing rate of absorbance at 247 nm (A_{247}) during photoirradiation. $[g_{12}\text{-Py}^+] = 0.5 \text{ mM}$, monomer/ $g_{12}\text{-Py}^+ = 1$ (w/w).

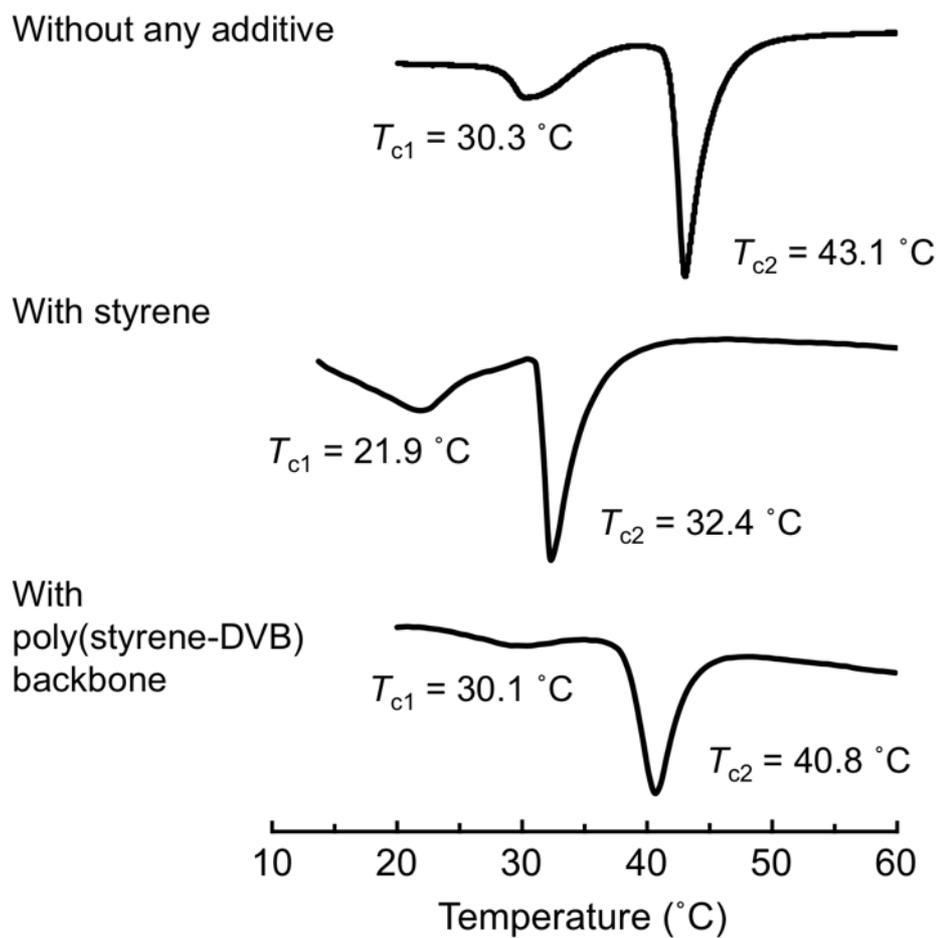


Figure S8 DSC thermograms of aqueous solutions of $g_{12}\text{-Py}^+$ (a) without any additive, (b) with styrene and (c) with poly(styrene-DVB) backbone . $[g_{12}\text{-Py}^+] = 20\text{ mM}$, monomer/ $g_{12}\text{-Py}^+ = 1$ (w/w).