Supporting Information

Interfacial Photocycloaddition Polymerization: A Synthetic Approach for Structurally Functionalized Degradable Polymer Particles from Naturally derived Monomers

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Contents

1. Materials

Glycerin was kindly supplied from Sakamoto Yakuhin Kogyo Co., Ltd. (Osaka, Japan). Cinnamoyl chloride, *o*-nitrocinnamic acid, *m*-nitrocinnamic acid, *p*-nitrocinnamic acid, *p*-nitro cinnamic acid, *p*-methoxy cinnamic acid, 1,5-pentanediol, 2-amino-1,3-propanediol, and limonene were purchased from Tokyo Chemical Industries (Tokyo, Japan). *p*-(Dimethylamino)cinnamic acid, 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC), di-*t*-butyl bicarbonate, trifluoroacetic acid (TFA), triethylamine (TEA), ethyl acetate, toluene, magnesium sulfate (anhydrous), PVA (degree of polymerization: 1000, degree of saponification: 88%), sulforhodamine B, tetrahydrofuran (THF), and *N*,*N*-dimethylformamide (DMF) were purchased from Wako Pure Chemical Co., Ltd. (Osaka, Japan). NHS-fluorescein, 4-dimethylaminopyridine, 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC), pyridine, chloroform, dimethyl sulfoxide (DMSO), ethanol, and sodium hydroxide (NaOH), 4-dimethylaminopyridine (DMAP), hexane, dichloromethane (DCM), methanol, chloroform, acetone, LiCl, HCl, NaOH, were purchased from Nacalai Tesque Co. (Kyoto, Japan). Deionized water was obtained from a Millipore Milli-Q purification system (Merk-Millipore, MA, USA).

2. Apparatus

UV-Vis spectra of photoreactive monomer and polymer species were obtained using a V-560 spectrophotometer (Jasco Ltd., Tokyo, Japan). ^{1}H NMR spectra were measured using a 400 MHz FT-NMR apparatus (JNM-ECX400, FT-NMR system, JEOL Ltd., Tokyo, Japan). A confocal laser-scanning microscope (LSM5 Exciter, Carl Zeiss, Germany) with an excitation wavelength of 543 nm (for Sulforhodamine B) was employed to visualize the particles. Melting points of photoreactive monomers were measured using MP-S3 (Yanaco, Tokyo, Japan). A scanning electron microscope (SEM) images of the hollow particles were obtained by FE-SEM (SU8010, Hitachi High-tech, Tokyo, Japan), in which the dried particles were obtained by freeze-drying process. A homogenizer (POLYTRON PT 1600 E, Kinematica Inc., Bohemia, NY, USA) was used to emulsify the polymer solution into a PVA aqueous solution. Photoirradiation to the polymer particles was carried out using spot-type LED lights.

3. Synthesis of 1,5-Dicinnamoyl Pentane (dCP)

1,5-Pentandiol (2.01 g, 19 mmol), TEA (4.26 g, 42 mmol) were dissolved in THF (10 mL). Cinnamoyl chloride (7.09 g, 43 mmol) dissolved in THF (10 mL) were added slowly to the 1,5-pentandiol solution under stirring in an ice bath. Then, the reaction proceeded overnight at room temperature. The precipitant was removed by the filtration. Then, the solvent was evaporated. The crude product was dissolved in ethyl acetate and washed with pure water thrice. After drying the

ethyl acetate solution using $MgSO_4$, the solvent was evaporated. Finally, the product was purified by recrystallization twice using ethyl acetate as a solvent.
Yield: 2.34 g (33%). Melting point: 43°C

4. Synthesis of Tricinnamoyl Glycerin (tCG)

Glycerin (2.00 g, 22 mmol), TEA (10 mL, 75 mmol) were dissolved in chloroform (20 mL). Cinnamoyl chloride (12.57 g, 75 mmol) dissolved in chloroform (20 mL) were added slowly to the solution under stirring in an ice bath. Then, the reaction proceeded overnight at room temperature. The precipitant was removed by the filtration. Then, the solvent was evaporated. The crude product was dissolved in chloroform and washed with brine thrice. After drying the chloroform solution using $MgSO_4$, the solvent was evaporated. Finally, the product was purified by recrystallization twice using ethyl acetate as a solvent.
Yield: 1.78 g (28%). Melting point: 74°C

5. Preparation of Photoreactive Monomer Particles

Typical procedure is as follows. dCP (21.5 mg, 60 μmol) and tCG (28.5 mg, 60 μmol) were dissolved in chloroform (1 mL). The solution was mixed with PVA aqueous solution (25 mL, 0.067 wt%), then the mixture was treated with homogenizer (16,000 rpm, 5 min). The monomer dispersion was stirred gently to evaporate chloroform slowly.

6. Preparation of Hollow Polymer Particles by Interfacial Photocycloaddition Polymerization

The dispersion containing monomer particles (2 mg/mL, 1 mL) was mixed with PVA aqueous solution (2 mL), then LED light with λ=265 nm (LED_{265}, 4 mW/cm^2) was irradiated to the particle dispersion for the different photoirradiation periods. The photoirradiated particles were separated from the solvent by centrifugation. Then, DMSO (1 mL) was added to the particles. After centrifugation, the supernatant was corrected, and the absorbance derived from the non-reacted monomers/oligomers was measured by UV-Vis. The remained particles were further washed thrice using DMSO. The particles were finally dispersed in PVA aqueous solution.

7. Preparation of Capsule Polymer Particles Containing Sulforhodamine B

The hollow P(dCP-tCG) particles prepared by the interfacial photocycloaddition polymerization with LED_{265} for 16 h (Experimental section 4-4) were separated from the PVA aqueous solution by centrifugation. The particles were incubated in the mixture containing THF (0.9 mL) and DMSO (0.1 mL) dissolving sulforhodamine B (10 mg/mL) for 30 min at room temperature. Then, the particles were separated from the solution by centrifugation, and the PVA aqueous solution

was added to the particles. Then, the particles were washed with the PVA aqueous solutions thrice to remove a free sulforhodamine B.

8. Preparation of Capsule Polymer Particles Containing Limonene

The hollow P(dCP-tCG) particles prepared by the interfacial photocycloaddition polymerization with LED_{265} for 16 h (Experimental section 4-4) were separated from the PVA aqueous solution by centrifugation. The particles were incubated in the mixture containing THF (0.9 mL) and DMSO (0.1 mL) containing limonene (10 mg/mL) for 30 min at room temperature. Then, the particles were separated from the solution by centrifugation, and the PVA aqueous solution was added to the particles. Then, the particles were washed with the PVA aqueous solutions thrice. The particles were added in vials, and the limonene remained outside of the capsules were evaporated at room temperature. After closing vial using septum cap, the fragrance capsules were incubated with or without stirring using stirring bar for 24 h. The gas phase was collected and analyzed by gas chromatography (GC-2030, Shimadzu Corporation, Kyoto, Japan).

9. Photolysis of Hollow Polymer Particles

Typical procedure is as follows. The hollow P(dCP-tCG) particles prepared by the interfacial photocycloaddition polymerization with LED_{265} for 16 h (Experimental section 4-4) were separated from the PVA aqueous solution by centrifugation. The particles were dispersed in DMSO (2 mL). The photoirradiation (λ= 254 nm, 2 mW/cm^2) was performed for various periods (0, 6, 12, 24, 48, 72 h). The transmittance at 600 nm was measured at the different photoirradiation periods. The supernatant corrected by centrifugation was diluted 10 times, and the absorbance derived from cinnamate groups was measured by UV-Vis.

10. Hydrolysis of Hollow P(dCP-tCG) Particles

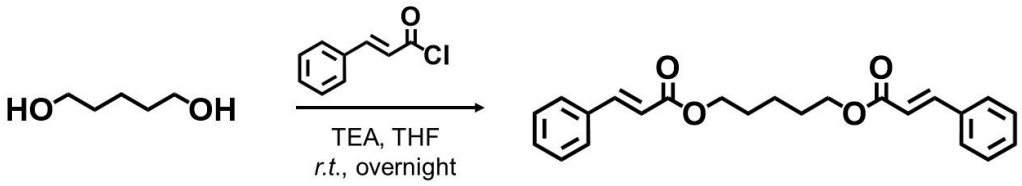
Typical procedure is as follows. The hollow P(dCP-tCG) particles prepared by the interfacial photocrosslinking with LED_{265} for 16 h (Experimental section 4-4) were separated from the PVA aqueous solution by centrifugation. The particles were dispersed in DMSO (6 mL) and 20 mM NaOH aqueous solution (6 mL). The dispersion was incubated for various periods (0 h, 6 h, 1 day, 2 days, 4 days, 6 days, and 8 days) at 40°C. The transmittance at 600 nm was measured at the different photoirradiation periods.

11. Scaled-up Synthesis of Hollow Polymer Particles

dCP (86.4 mg, 240 mmol) and tCG 114.1 mg, 240 mmol) were dissolved in chloroform (4 mL). The solution was mixed with PVA aqueous solution (100 mL, 0.067 wt%), then the mixture was treated with homogenizer (16,000 rpm, 10 min). The monomer dispersion was stirred gently to

evaporate chloroform slowly. The dispersion containing monomer particles (100 mL) was mixed with PVA aqueous solution (200 mL), then LED light with λ=265 nm (LED_{265}, 14 mW/cm^2, 900 mm^2) was irradiated to the particle dispersion for the different photoirradiation periods. The photoirradiated particles were separated from the solvent by centrifugation. Then, DMSO (25 mL) was added to the particles. After centrifugation, the supernatant was corrected, and the absorbance derived from the non-reacted monomers/oligomers was measured by UV-Vis. The remained particles were further washed thrice using DMSO. The particles were finally dispersed in PVA aqueous solution.

12. ^{1}H-NMR and ^{13}C-NMR spectra of dCP



Scheme S1. Synthetic scheme of dCP

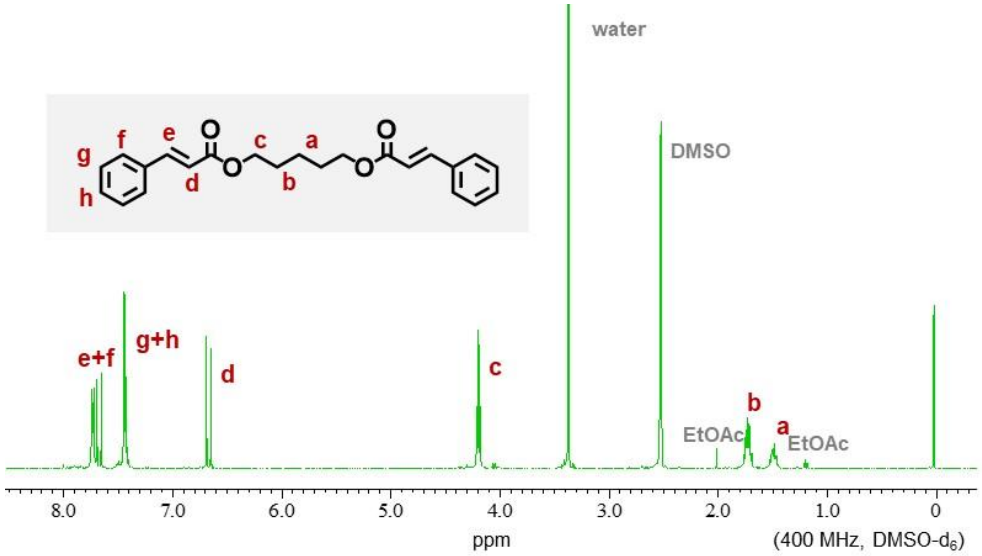


Figure S1. ^{1}H-NMR spectrum of dCP (DMSO-d_6).

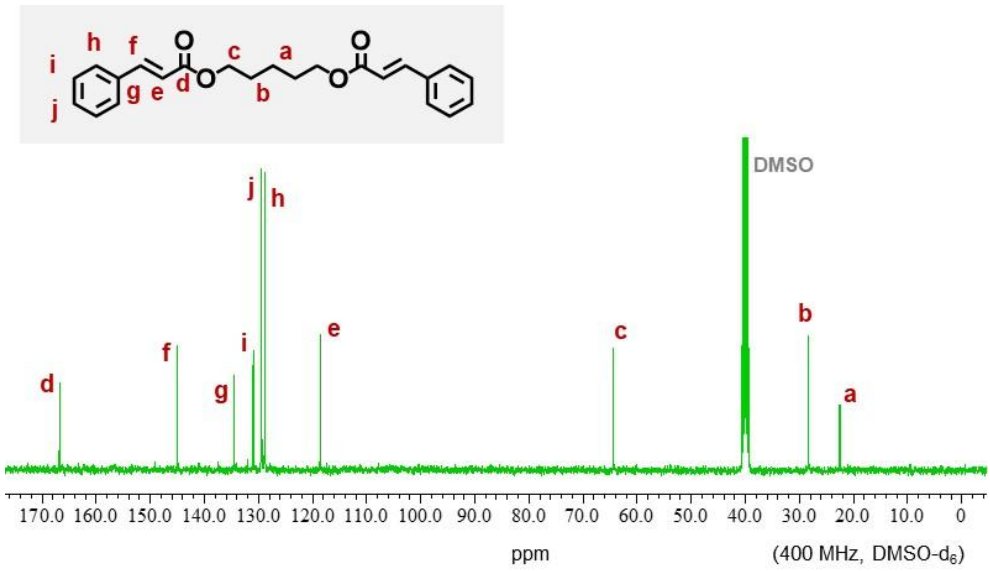
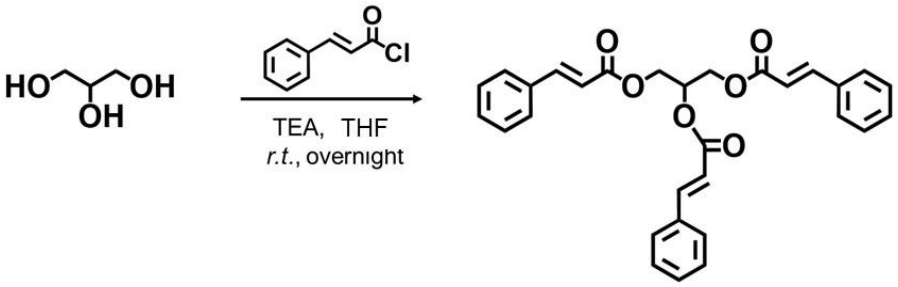


Figure S2. ^{13}C-NMR spectrum of dCP (DMSO-d_6).

13. [1]H-NMR and [13]C-NMR spectra of tCG



Scheme S2. Synthetic scheme of tCG

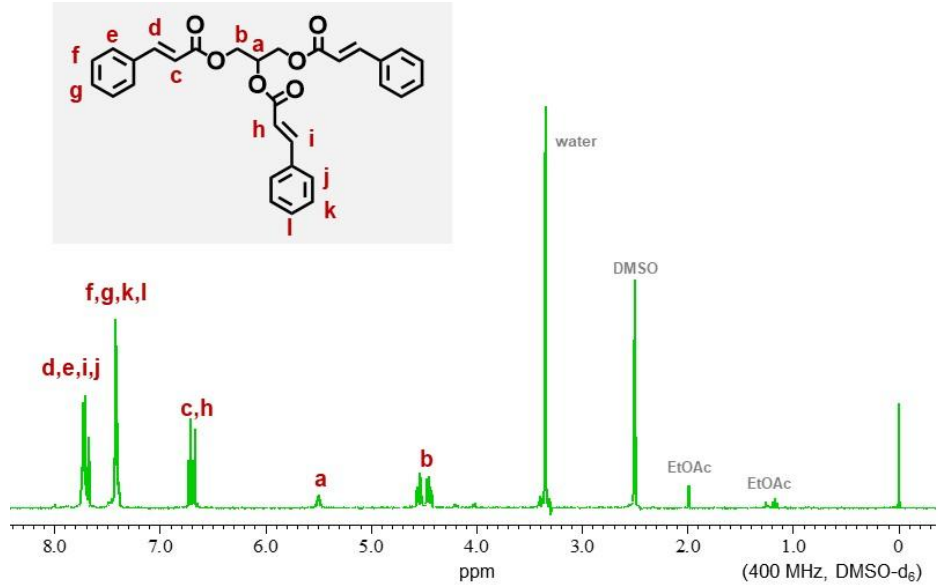


Figure S3. [1]H-NMR spectrum of tCG (DMSO-d_6).

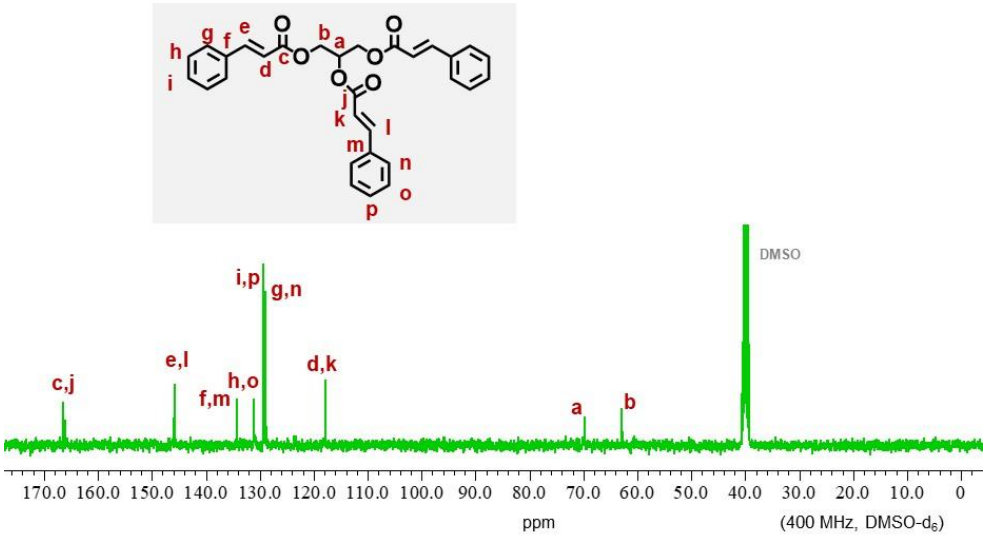


Figure S4. [13]C-NMR spectrum of tCG (DMSO-d_6).

14. UV-Vis spectrum of dCP

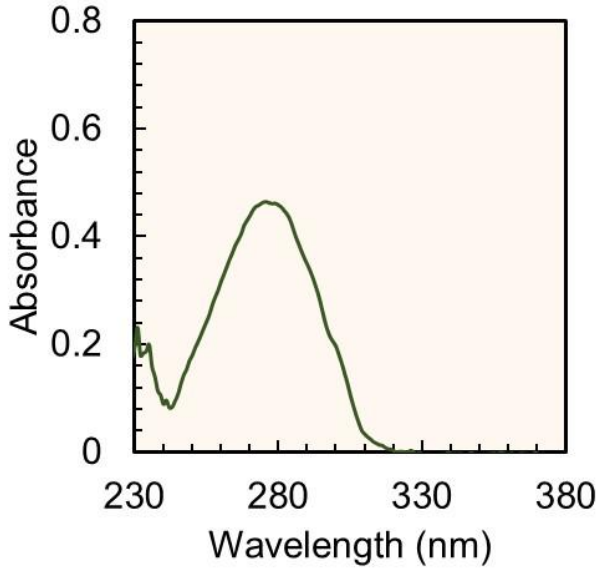


Figure S5. UV–Vis spectrum of 10 μM solutions of dCP in dioxane.

15. UV-Vis spectrum of tCG

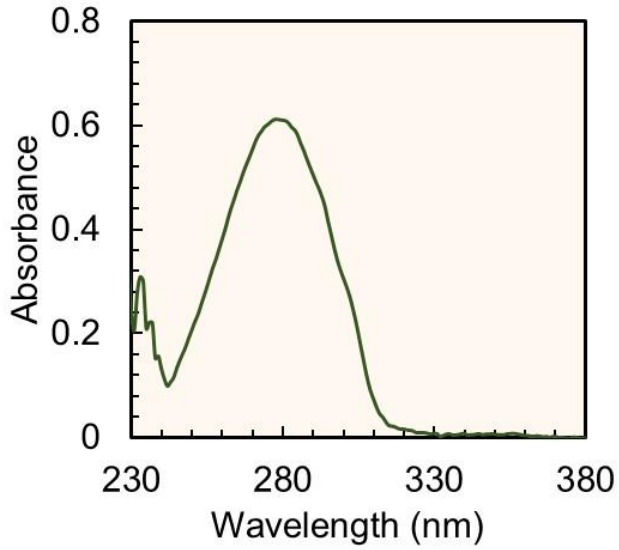


Figure S6. UV–Vis spectrum of 10 μM solutions of tCG in dioxane.

16. <u>Monomer Particles Prepared with Ethyl Acetate.</u>

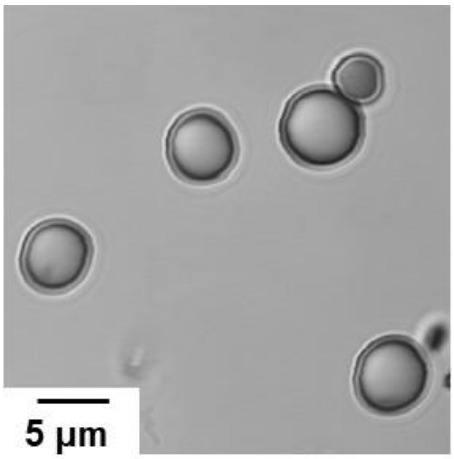


Figure S7. Optical microscope image of monomer particles prepared by solvent evaporation with ethyl acetate as an organic solvent.

17. <u>Preparation of Monomer Particles from High Concentration of Monomer/Chroroform Droplets</u>

dCP (43.1 mg, 118 μmol) and tCG (57.2 mg, 119 μmol) were dissolved in chloroform (2 mL), where monomer concentration in droplet was approximately 5 vol%. The solution was mixed with PVA aqueous solution (10 mL, 0.067 wt%), then the mixture was treated with homogenizer (16,000 rpm, 2.5 min), where the monomer/chloroform droplet concentration in the dispersion is 16.7 vol%. The monomer dispersion was stirred gently to evaporate chloroform slowly.

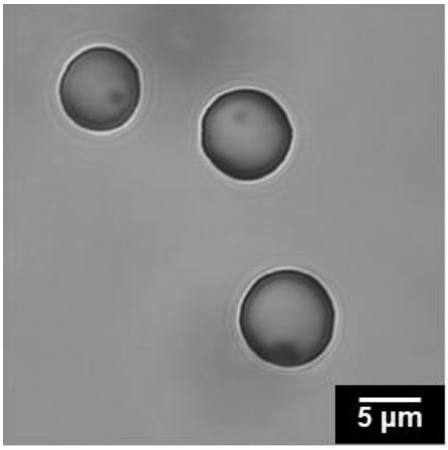


Figure S8. Optical microscope image of the monomer particles. The monomer particles were prepared through the high-solid-content monomer/chloroform droplets dispersion (~16.7 vol%).

18. <u>Preparation of Monomer Particles with High Solid Contents</u>

dCP (108.8 mg, 0.30 mmol) and tCG (142.2 mg, 0.30 mmol) were dissolved in chloroform (0.2 mL). The solution was mixed with PVA aqueous solution (2.5 mL, 0.067 wt%), then the mixture was treated with homogenizer (16,000 rpm, 0.5 min). The monomer dispersion was stirred gently to evaporate chloroform slowly. The final monomer solid content in the dispersion is approximately 10 wt%.

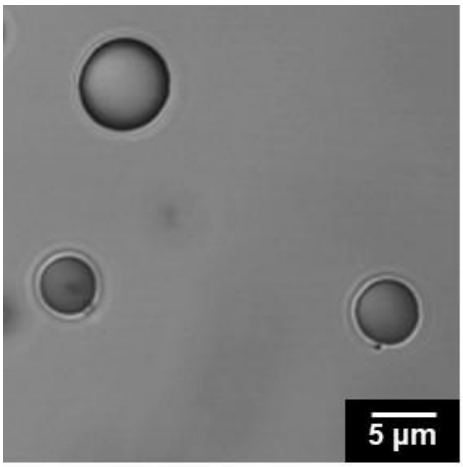


Figure S9. Optical microscope image of the monomer particles. The final monomer solid content in the dispersion is approximately 10 wt%.

19. <u>Effect of Photoirradiation</u>

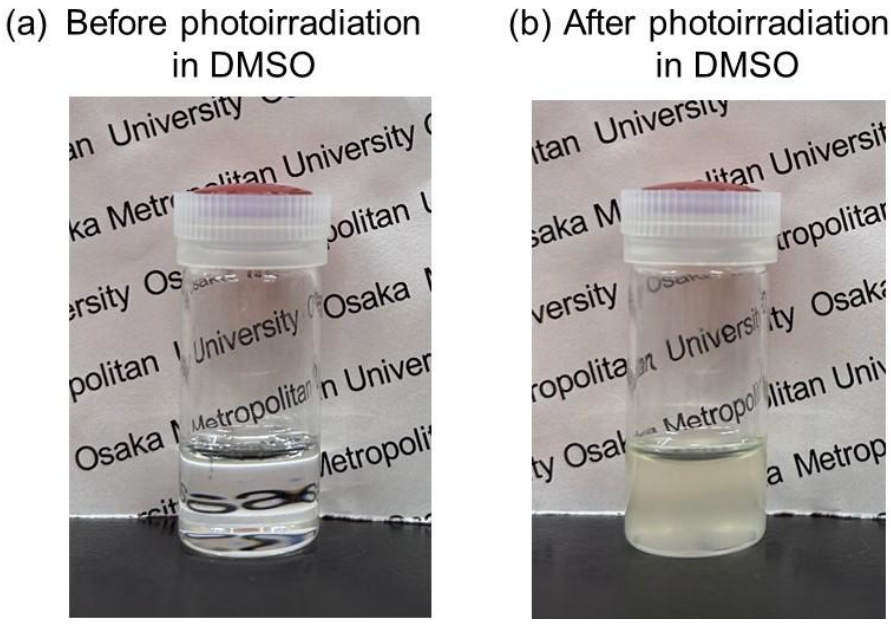
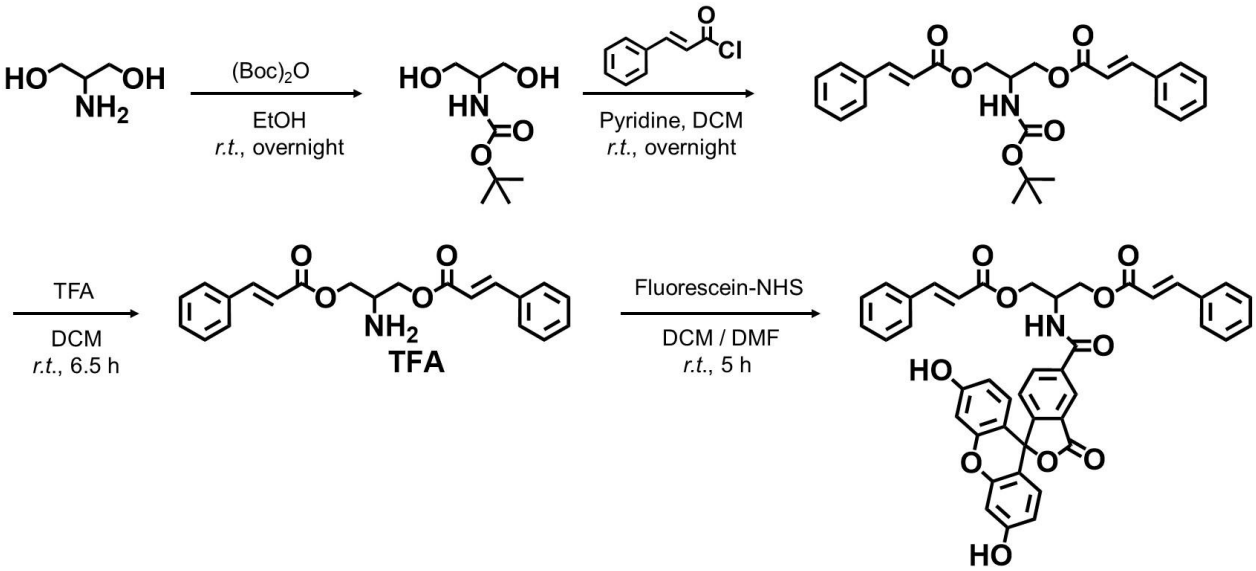


Figure S10. Photographs showing monomer particle dispersions before (a) and after (b) photoirradiation following the addition of DMSO as a good solvent.

20. Synthesis Scheme of Fluorescein-labeled Dicinnamoyl Serinol (Fluorescein-dCS)



Scheme S3. Synthetic scheme of Fluorescein-labeled dicinnamoyl serinol (Fluorescein-dCS).

21. Synthesis of *N*-Boc Serinol

Serinol (5.00 g, 55 mmol) was dissolved in ethanol (40 mL). Di-*tert*-butyl dicarbonate (12.00 g, 55 mmol) dissolved in ethanol (40 mL) was added slowly to the solution under stirring at room temperature. Then, the reaction proceeded overnight at room temperature. After evaporation, the product was obtained. Yield: 10.29 g (98%).

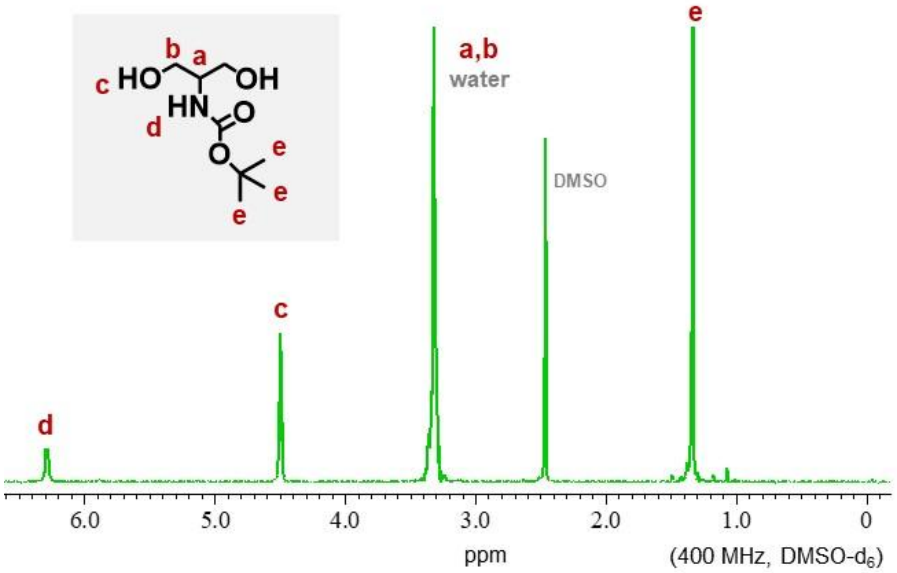


Figure S11. ^{1}H-NMR spectrum of *N*-Boc Serinol (DMSO-d_6).

22. Synthesis of Dicinnamoyl *N*-Boc-Serinol (*N*-Boc dCS)

N-Boc-serinol (10.49 g, 55 mmol) and pyridine (11.52 mL, 143 mmol) were dissolved in DCM (80 mL). Cinnamoyl chloride (24.20 g, 145 mmol) dissolved in DCM (20 mL) was added slowly to the solution under stirring in an ice bath. Then, the reaction proceeded overnight at room temperature. The precipitant was removed by the filtration. Then, the solvent was evaporated. The crude product was dissolved in dichloromethane and washed with brine thrice. After drying the chloroform solution using $MgSO_4$, the solvent was evaporated. Finally, the product was purified by washing with ethyl acetate, and the product was dried in vacuo. Yield: 5.14 g (21%)

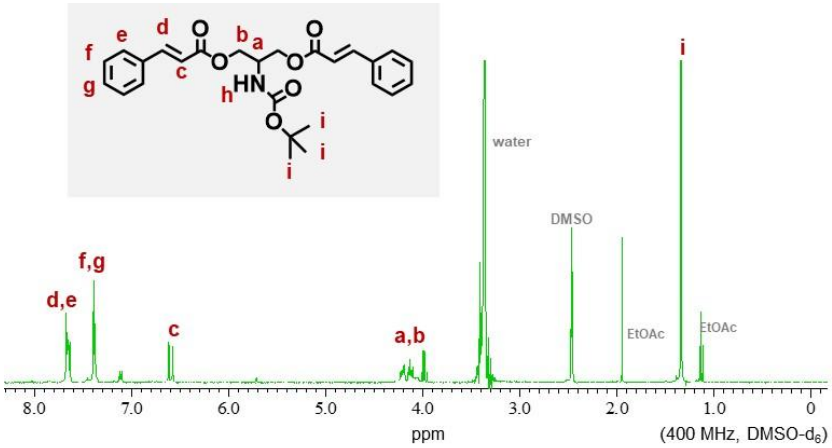


Figure S12. ^{1}H-NMR spectrum of *N*-Boc dCS (DMSO-d_6).

23. Synthesis of Dicinnamoyl Serinol (dCS)

N-Boc-serinol dicinnamate (5.00 g, 11 mmol) was dissolved in DCM (100 mL). TFA (100 mL) was added slowly to the solution. The reaction proceeded for 6.5 h at room temperature. Then, the product was obtained by evaporation. Yield: 5.16 g (100%)

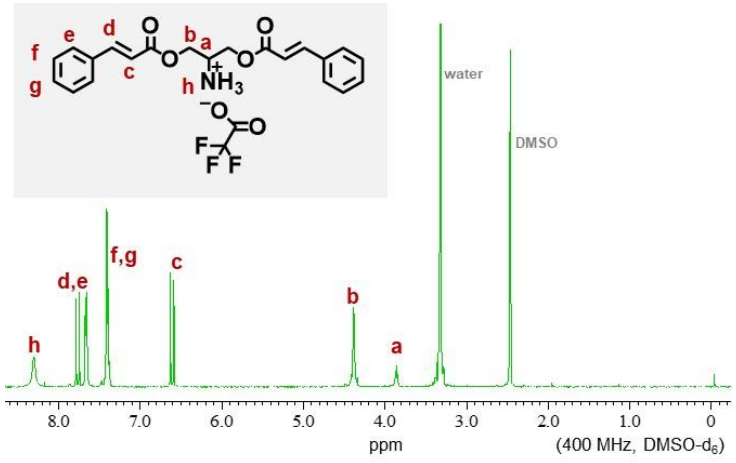


Figure S13. ^{1}H-NMR spectrum of dCS (DMSO-d_6).

24. <u>Synthesis of Fluorescein-labeled Dicinnamoyl Serinol (Fluorescein-dCS)</u>

Serinol dicinnamate TFA salt (18.8 mg, 42.3 µmol) and TEA (8.9 µL) were dissolved in DCM (1 mL). Fluorescein-NHS (24 mg, 51 µmol) dissolved in DCM (3 mL) was added slowly to the solution. The reaction proceeded for 16 h at room temperature. Then, DMF (1.5 mL) was added to the solution and the reaction proceeded for 5 h at room temperature. The product was washed with brine thrice. After drying the solution using $MgSO_4$, the solvent was evaporated. Finally, the product was purified by recrystallization using ethyl acetate and hexane.

Yield: 6.1 mg (20%)

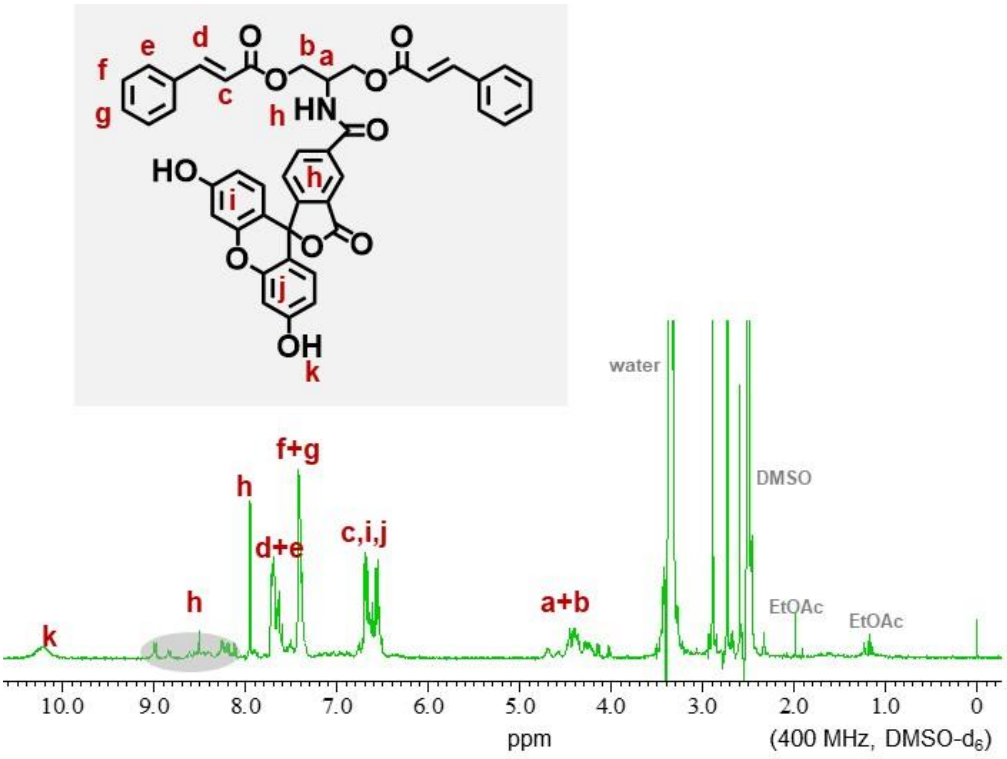


Figure S14. ^{1}H-NMR spectrum of Fluorescein dCS (DMSO-d_6).

25. <u>Effect of Photoirradiation Time</u>

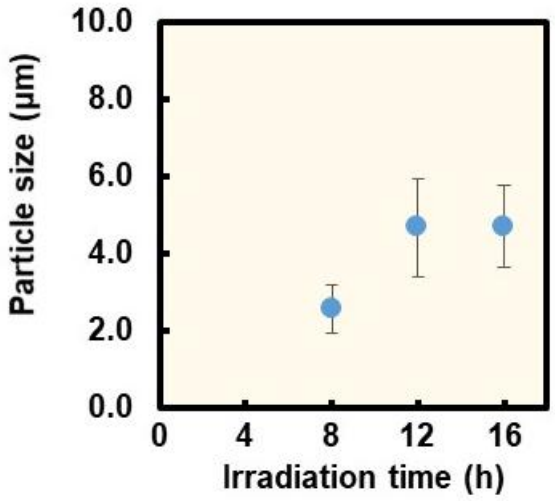


Figure S15. Effect of photoirradiation time for number-average particle size of the P(dCP-tCG) hollow particles prepared by the interfacial photocycloaddition polymerization.

26. <u>Interfacial Photocycloaddition Polymerization of tCG</u>

tCG (57 mg, 120 mmol) were dissolved in chloroform (1 mL). The solution was mixed with PVA aqueous solution (25 mL, 0.067 wt%), then the mixture was treated with homogenizer (16,000 rpm, 5 min). The monomer dispersion was stirred gently to evaporate chloroform slowly. The dispersion containing monomer particles (2 mg/mL, 1 mL) was mixed with PVA aqueous solution (2 mL), then LED light with λ=265 nm (LED_{265}, 4 mW/cm^2) was irradiated to the particle dispersion for the different photoirradiation periods. The photoirradiated particles were seperatred from the solvent by centrifugation. The remained particles were further washed thrice using DMSO. The particles were finally dispersed in PVA aqueous solution. SEM images of the PtCG particles were obtained by FE-SEM (SU8010, Hitachi High-tech, Tokyo, Japan). The particles were freeze-dried, and the sample was observed after platinum coating.

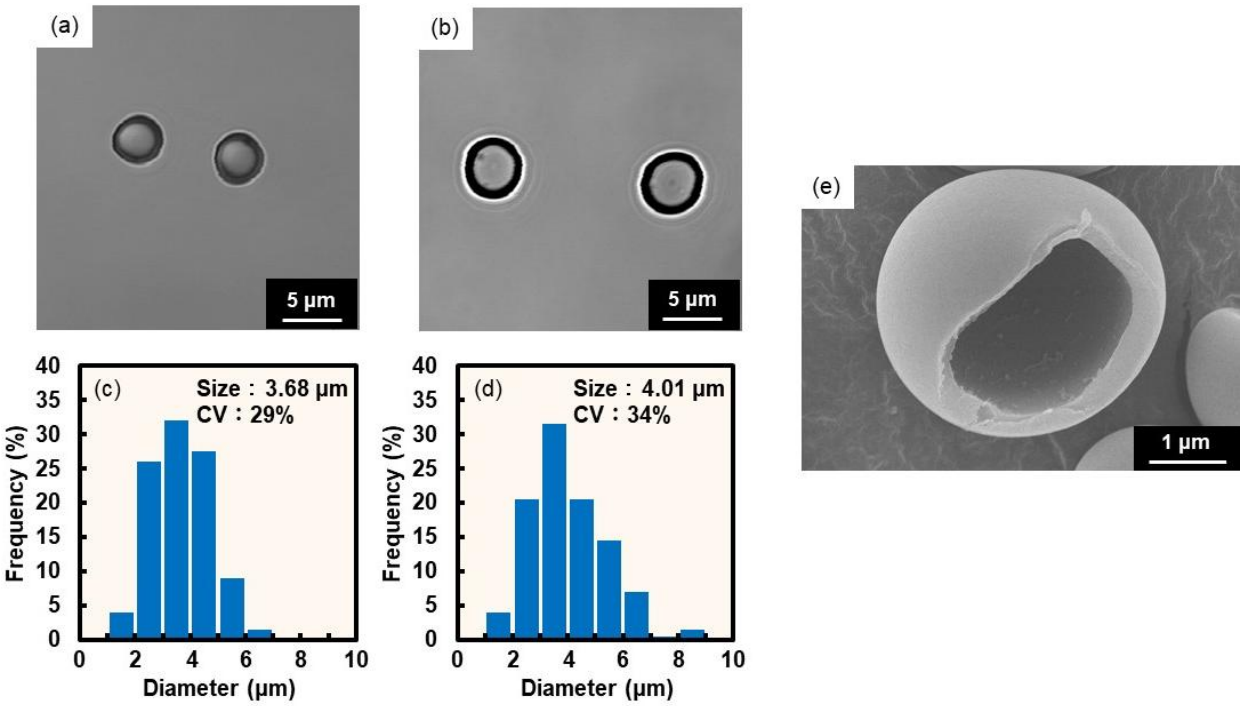


Figure S16. Optical microscope images (a, b) and particle size distributions (c, d) of tCG particles as a starting materials (a, c) and hollow PtCG particles obtained by the interfacial photocycloaddition polymerization (b, d). Sccaning microscope microscope image of the obtained hollow particles (e).

27. Interfacial Photocycloaddition Polymerization of dCP

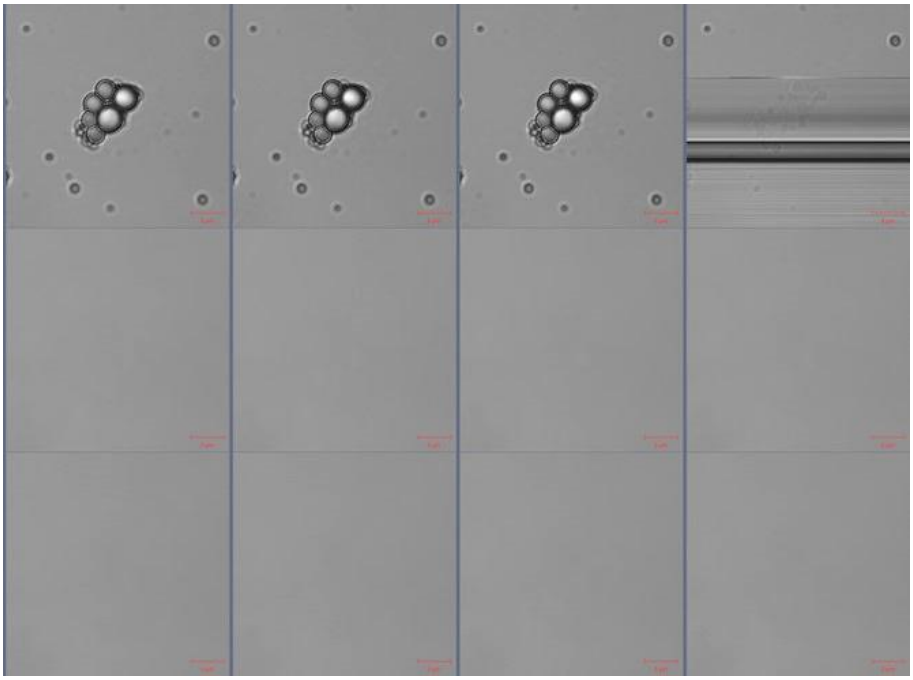


Figure S17. A series of optical microscope images showing the washing process of photoirradiated dCP particles using LED_{265} for 16 h.

28. Interfacial Photocycloaddition Polymerization of dCP and tCG with Different Wavelength.

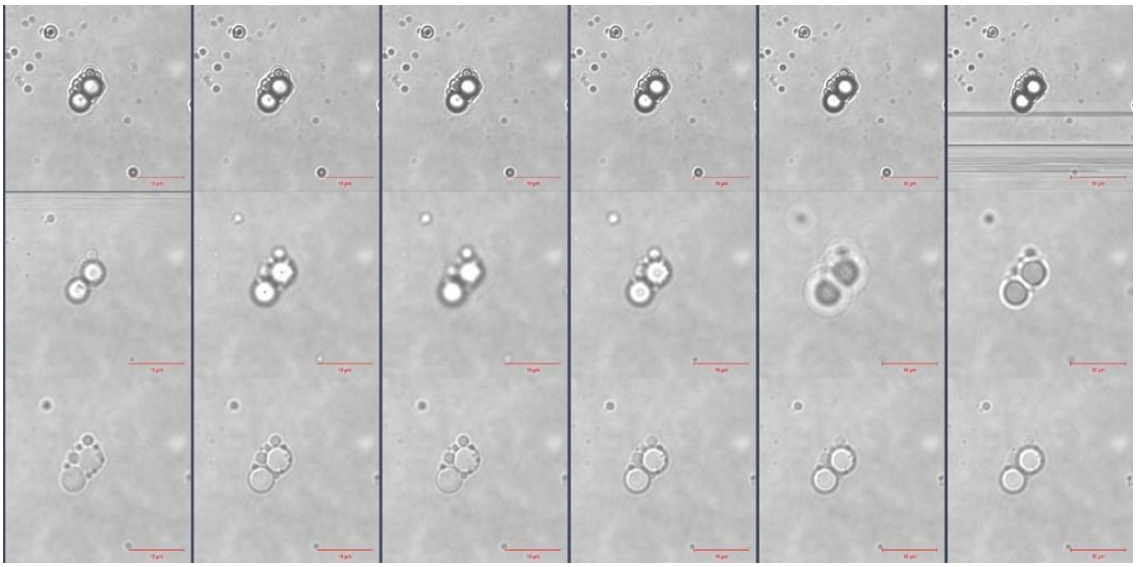


Figure S18. A series of optical microscope images showing the washing process of photoirradiated dCP/tCG particles using LED_{310} for 16 h.

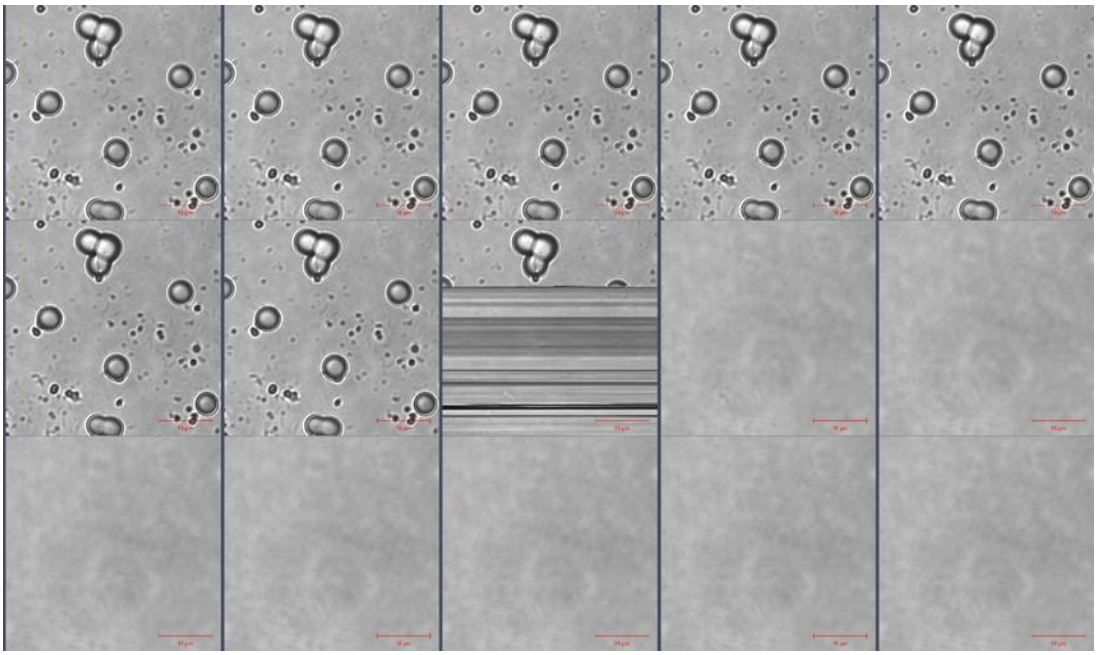


Figure S19. A series of optical microscope images showing the washing process of photoirradiated dCP/tCG particles using LED_{365} for 16 h.

29. Encapsulation Stability of P(dCP-tCG) Capsules Particles

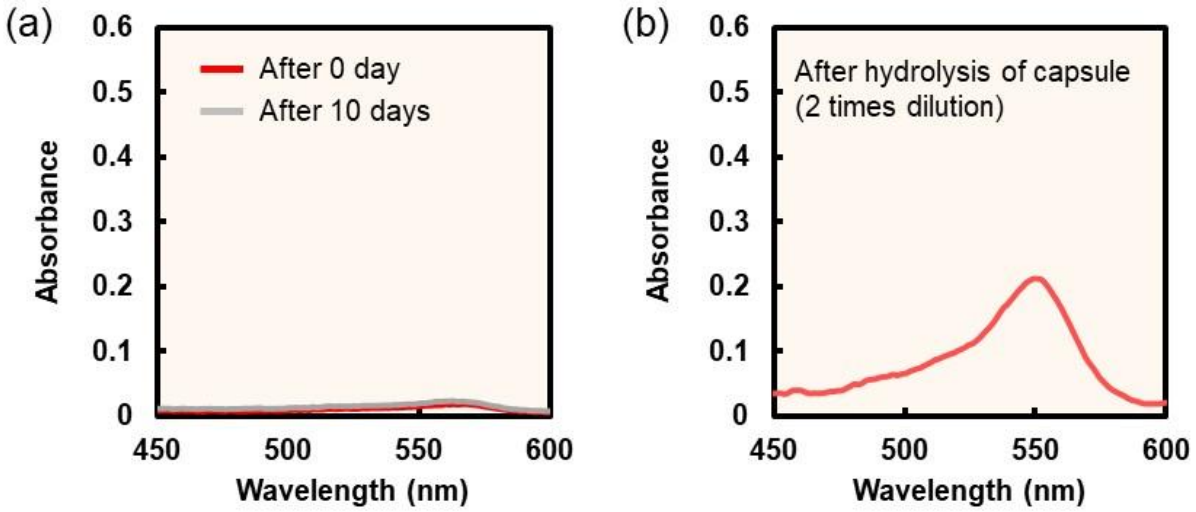


Figure S20. UV-Vis spectra derived from sulforhodamine B leaked from the P(dCP-tCG) capsules after 0 and 10 days (a). UV-Vis spectra derived from Sulforhodamine B completely released from the P(dCP-tCG) capsules by hydrolysis after 10 days (b).

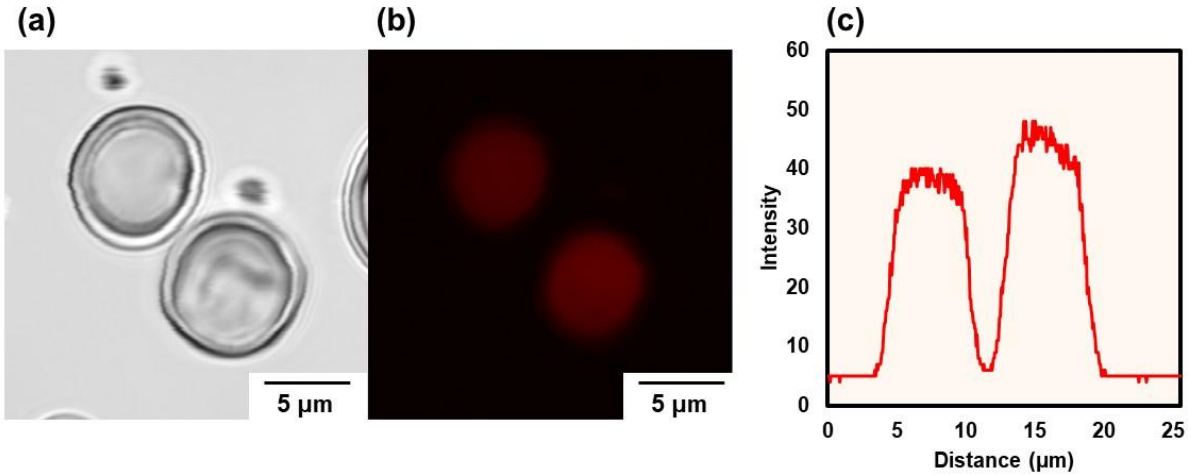


Figure S21. Bright field (a) and confocal laser scanning microscopy image (b) of sulforhodamine B encapsulated P(dCP-tCG) particles after storage for three months. Line profile of the fluorescent intensity of the confocal laser scanning microscopy image of sulforhodamine encapsulated P(dCP-tCG) particles (c).

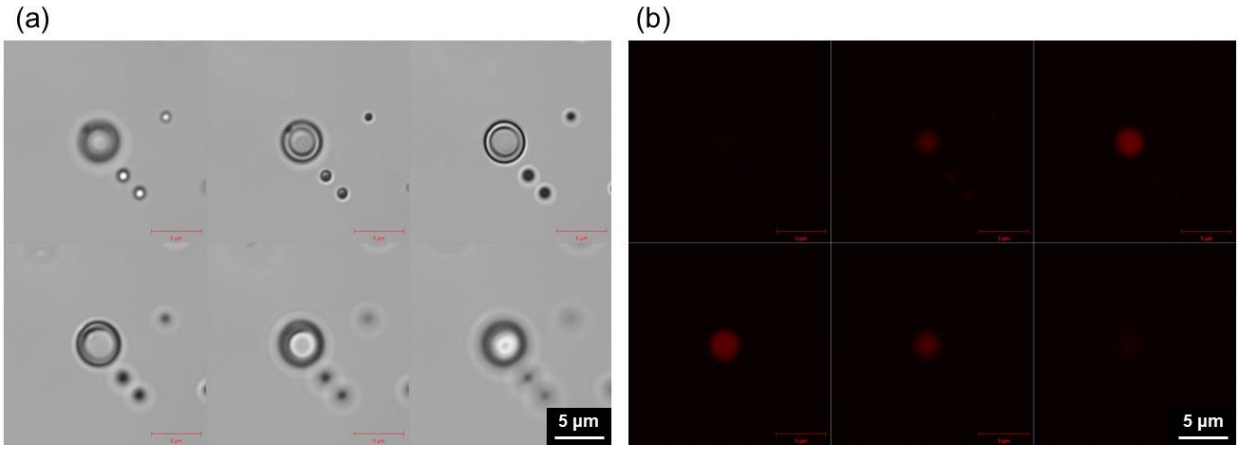


Figure S22. Confocal laser scanning micrographs (z-stack images) of P(dCP-tCG) capsule particles containing sulforhodamine B after storage for three months. Interval of Z-stack images is 1 µm. Left: Bright image and right: Fluorescence image.

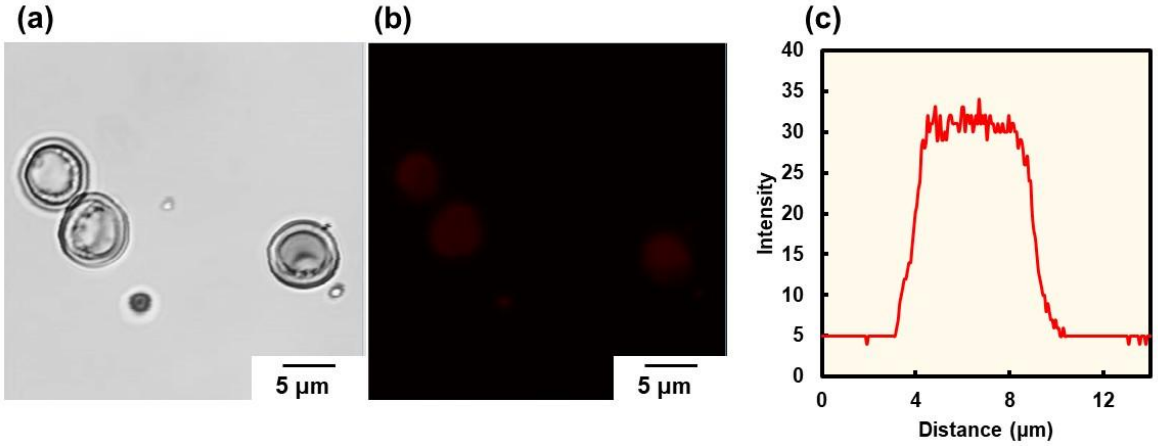


Figure S23. Bright field (a) and confocal laser scanning microscopy image (b) of sulforhodamine B encapsulated P(dCP-tCG) particles after storage for 13 months. Line profile of the fluorescent intensity of the confocal laser scanning microscopy image of sulforhodamine encapsulated P(dCP-tCG) particles (c).

30. SEM Image of Destroyed Capsule Particles

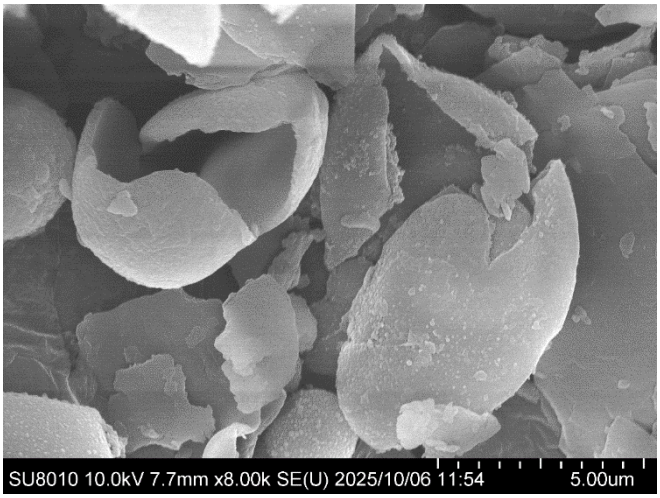


Figure S24. SEM image of P(dCP-tCG) capsule particles physically destroyed by a stirring bar in the dried state for fragrance release.

31. Fragrance Capsules with Higher Limonene Concentration

The hollow P(dCP-tCG) particles prepared by the interfacial photocycloaddition polymerization with LED_{265} for 16 h (Experimental section 4-4) were separated from the PVA aqueous solution by centrifugation. The particles were incubated in the mixture containing limonene (0.9 mL) and acetone (0.1 mL) for 30 min at room temperature. Then, the particles were separated from the solution by centrifugation, and the PVA aqueous solution was added to the particles. Then, the particles were washed with the PVA aqueous solutions thrice. The particles were added in vials, and the limonene remained outside of the capsules were evaporated at room temperature. After addition of water (10 μL) and closing vial using septum cap, the fragrance capsules were incubated with stirring using stirring bar for 24 h. The gas phase was collected and analyzed by gas chromatography (GC-2030, Shimadzu Corporation, Kyoto, Japan).

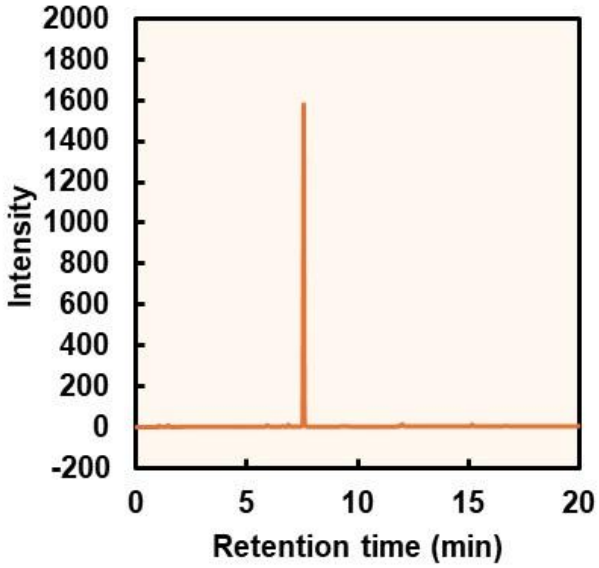


Figure S25. GC chromatograph of limonene-encapsulated polymer capsules stored with stirring; the limonene capsules were prepared using an encapsulation solution with high limonene concentration (~90 vol%).

32. MALDI-TOF-MS Spectrum of Degraded P(dCP-tCG) Hollow Particles by Photolysis

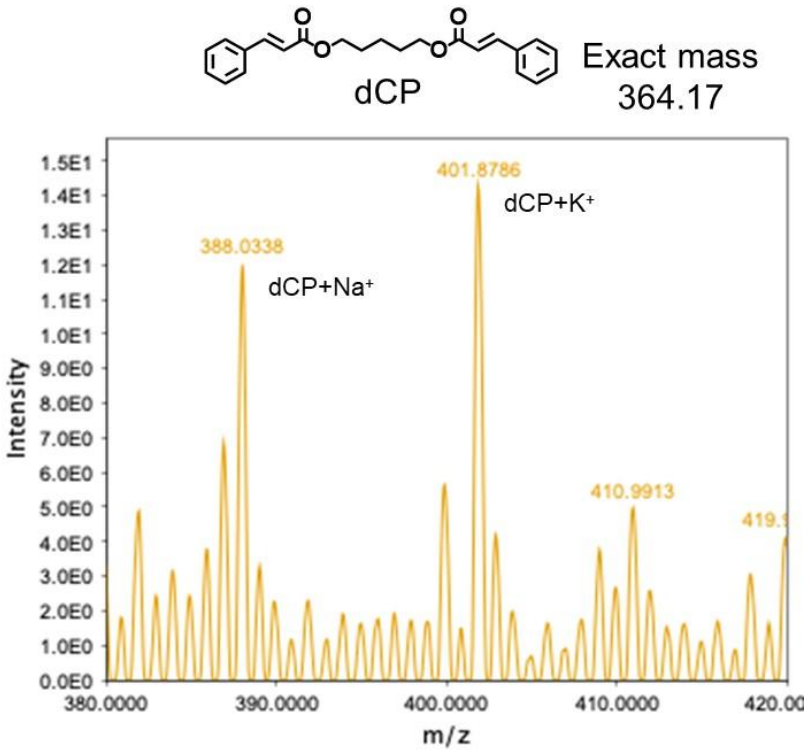


Figure S26. MALDI-TOF-MS spectrum of the degraded P(dCP-tCG) hollow particles by photolysis with λ=254 nm irradiation. The re-generated dCP can be detected.

33. ^{1}H-NMR Spectrum of Hydrolyzed P(dCP-tCG) Hollow Particles

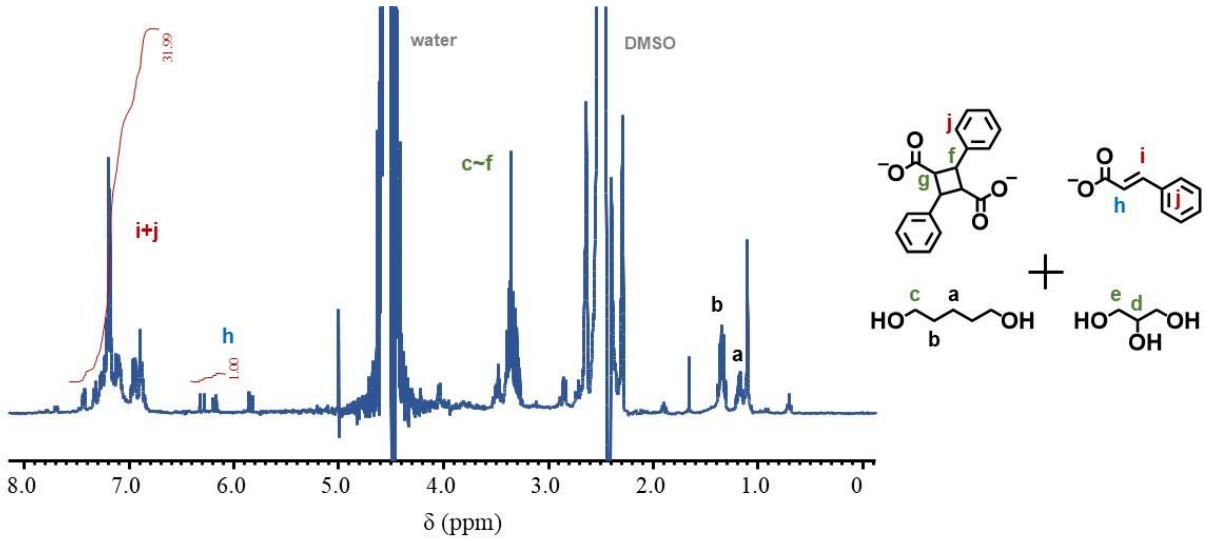
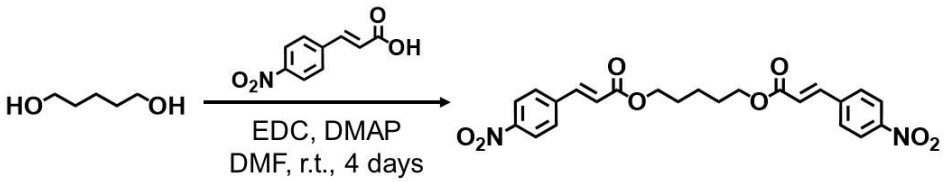


Figure S27. ^{1}H-NMR spectrum of hydrolyzed P(dCP-tCG) hollow particles with NaOD/D_2O/DMSO-d_6.

34. Synthesis of 1,5-Di(*p*-nitro cinnamoyl) Pentane (d*NO*$_2$CP)

1,5-Pentanediol (1.05 g, 10 mmol), *p*-nitro cinnamic acid (4.26 g, 22 mmol), EDC (4.80 g, 25 mmol), and DMAP (0.61 g, 4.5 mmol) were dissolved in DMF (80 mL). The reaction proceeded for four days at room temperature. The solvent was evaporated. The crude product was dissolved in chloroform and washed with brine thrice. After drying the chloroform solution using $MgSO_4$, the solvent was evaporated. Finally, the product was purified by recrystallization twice using ethyl acetate as a solvent. Yield: 2.36 g (52%). Melting point: 130°C.



Scheme S4. Synthetic scheme of d*NO*$_2$CP.

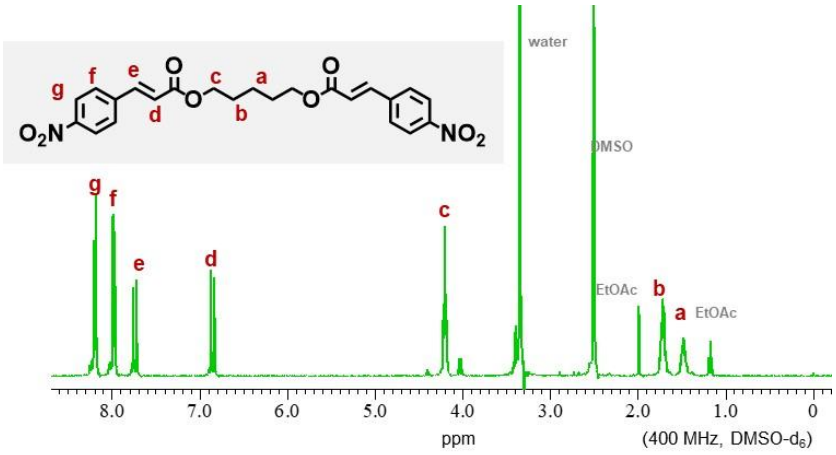


Figure S28 ^{1}H-NMR spectrum of d*NO*$_2$CP(DMSO-d_6).

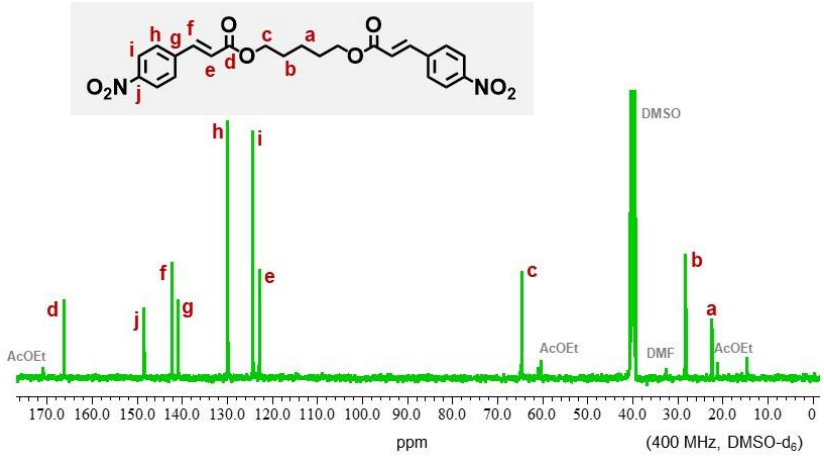
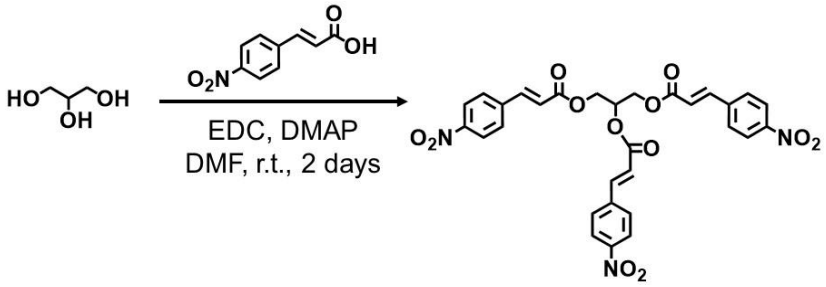


Figure S29. ^{13}C-NMR spectrum of d*NO*$_2$CP(DMSO-d_6).

35. Synthesis of Tri(*p*-nitro cinnamoyl) Glycerol (t*NO*$_2$CG)

Glycerin (0.574 g, 6.23 mmol), *p*-nitro cinnamic acid (3.95 g, 20.5 mmol), EDC (4.31 g, 22.5 mmol), and DMAP (0.40 g, 3.27 mmol) were dissolved in DMF (80 mL). Then, the reaction proceeded for two days at room temperature. The solvent was evaporated. The crude product was dissolved in chloroform and washed with brine thrice. After drying the chloroform solution using $MgSO_4$, the solvent was evaporated. Finally, the product was purified by recrystallization using ethyl acetate as a solvent. Yield: 0.944 g (25%). Melting point: 141°C.



Scheme S5. Synthetic scheme of t*NO*$_2$CG.

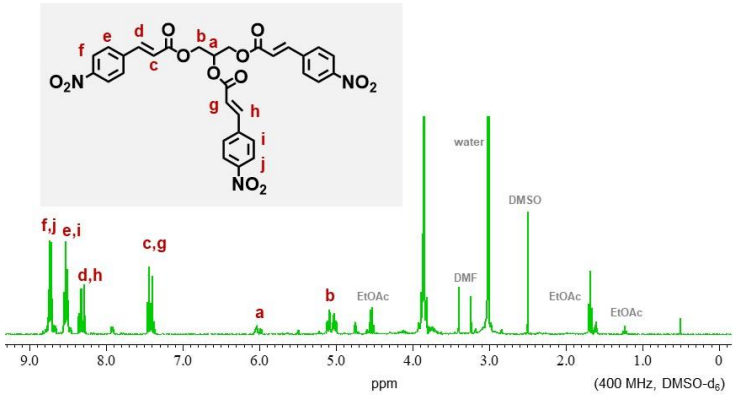


Figure S30. ^{1}H-NMR spectrum of t*NO*$_2$CG(DMSO-d_6).

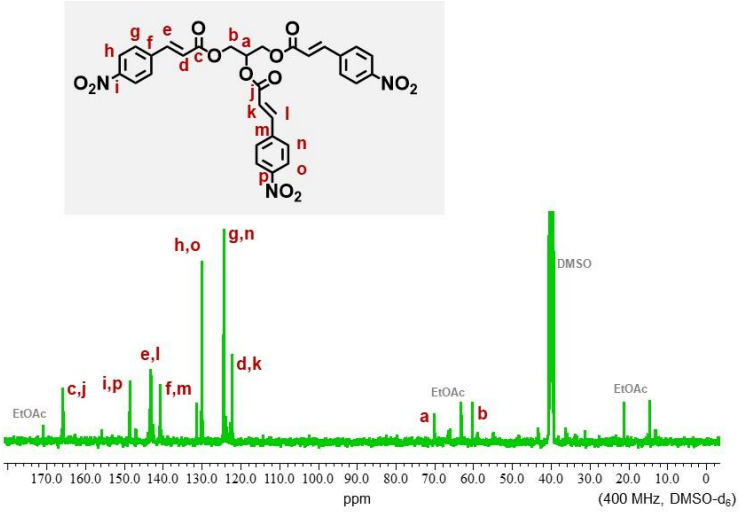
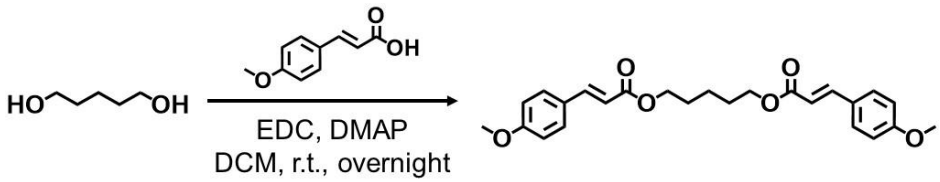


Figure S31. ^{13}C-NMR spectrum of t*NO*$_2$CG(DMSO-d_6).

36. <u>Synthesis of 1,5-Di(*p*-methoxy cinnamoyl) Pentane (d*OMe*CP)</u>

1,5-Pentanediol (0.501 g, 4.81 mmol), *p*-methoxy cinnamic acid (2.06 g, 11.6 mmol), EDC (2.30 g, 12.0 mmol), and DMAP (1.05 g, 8.59 mmol) were dissolved in DCM (80 mL). The reaction proceeded overnight at room temperature. The crude product was dissolved in chloroform and washed with brine thrice. After drying the chloroform solution using $MgSO_4$, the solvent was evaporated. Finally, the product was purified by recrystallization twice using ethyl acetate as a solvent. Yield: 0.48 g (23%). Melting point: 74°C.



Scheme S6. Synthetic scheme of d*OMe*CP.

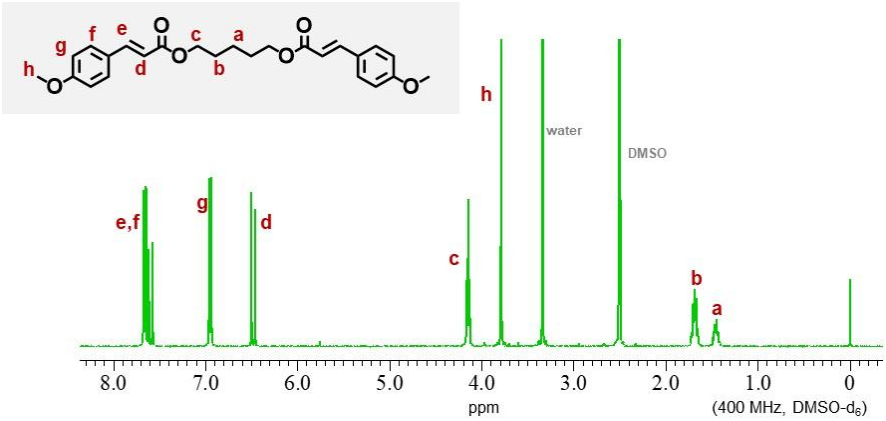


Figure S32. ^{1}H-NMR spectrum of d*OMe*CP(DMSO-d_6).

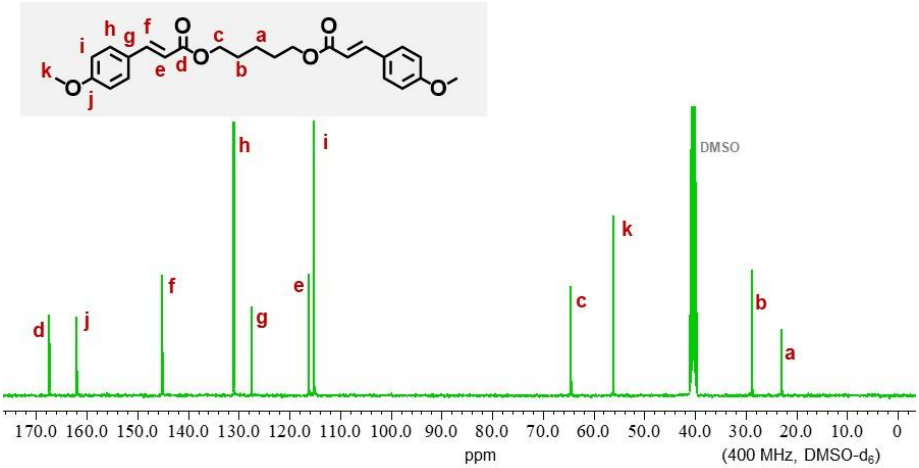
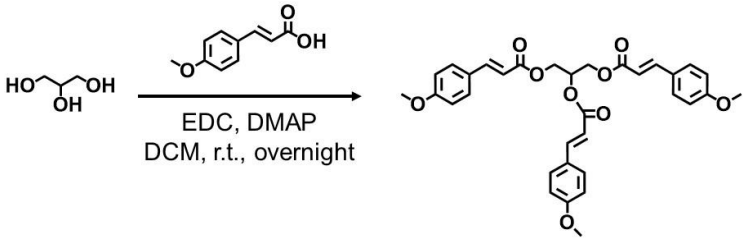


Figure S33. ^{13}C-NMR spectrum of d*OMe*CP(DMSO-d_6).

37. <u>Synthesis of Tri(*p*-methoxy cinnamoyl) Glycerol (t*OMe*CG)</u>

Glycerin (0.397 g, 4.31 mmol), *p*-methoxy cinnamic acid (2.69 g, 15.1 mmol), EDC (2.98 g, 15.5 mmol), and DMAP (1.04 g, 8.49 mmol) were dissolved in dichloromethane (80 mL). Then, the reaction proceeded overnight at room temperature. The crude product was washed with brine thrice. After drying the solution using $MgSO_4$, the solvent was evaporated. Finally, the product was purified by recrystallization using ethyl acetate as a solvent.

Yield: 0.845 g (34%). Melting point: 112°C.



Scheme S7. Synthetic scheme of t*OMe*CG.

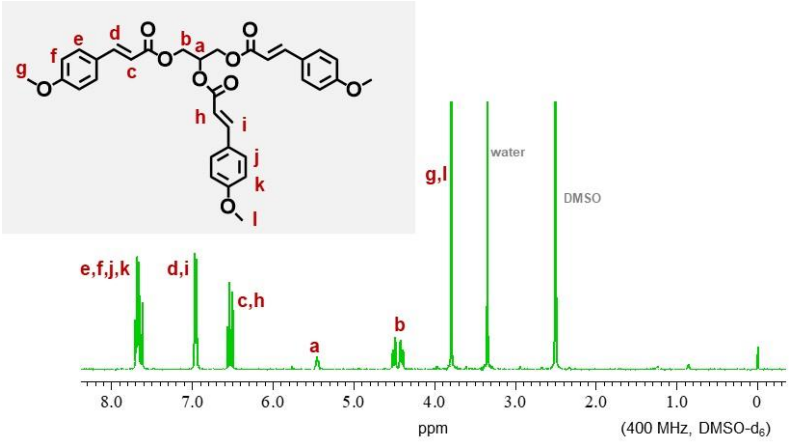


Figure S34. ^{1}H-NMR spectrum of t*OMe*CG (DMSO-d_6).

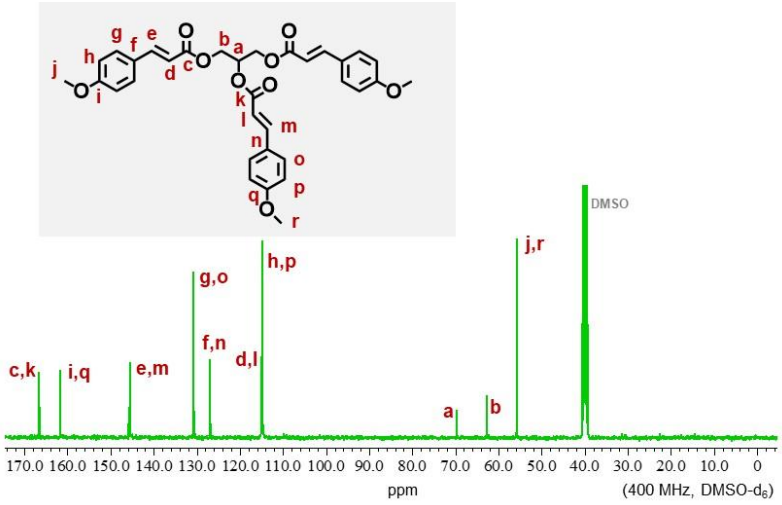
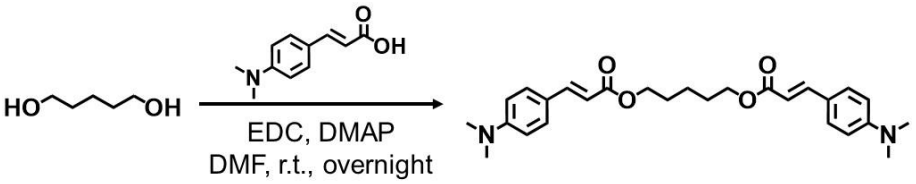


Figure S35. ^{13}C-NMR spectrum of t*OMe*CG (DMSO-d_6).

38. Synthesis of 1,5-Di(*p*-dimethylamino cinnamoyl) Pentane (d*NMe*$_2$CP)

1,5-Pentanediol (0.255 g, 2.45 mmol), *p*-dimethylamino cinnamic acid (1.03 g, 5.39 mmol), EDC (1.18 g, 6.13 mmol), and DMAP (0.151 g, 1.23 mmol) were dissolved in DMF (40 mL). The reaction proceeded overnight at room temperature. After evaporation of the solvent, the crude product was dissolved in chloroform and washed with brine thrice. After drying the solution using $MgSO_4$, the solvent was evaporated. Finally, the product was purified by recrystallization using methanol as a solvent. Yield: 0.305 g (28%). Melting point: 79°C.



Scheme S8. Synthetic scheme of d*NMe*$_2$CP.

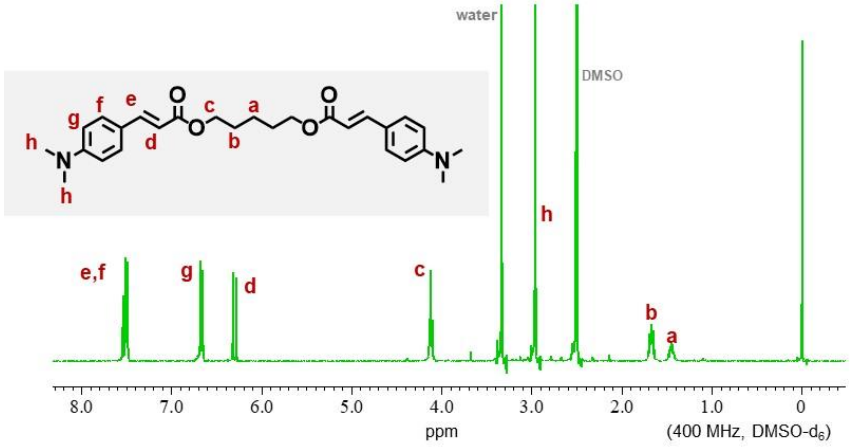


Figure S36. ^{1}H-NMR spectrum of d*NMe*$_2$CP (DMSO-d_6).

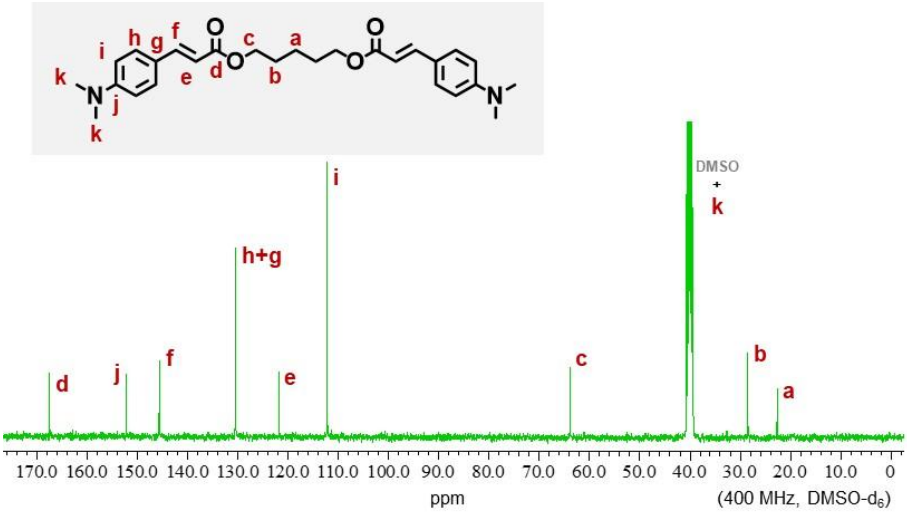
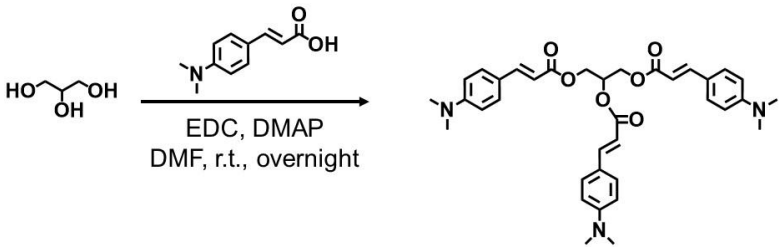


Figure S37. ^{13}C-NMR spectrum of d*NMe*$_2$CP (DMSO-d_6).

39. Synthesis of Tri(*p*-dimethylamino cinnamoyl) Glycerol (t*NMe*$_2$CG)

Glycerin (0.220 g, 2.39 mmol), *p*-dimethylamino cinnamic acid (1.51 g, 7.89 mmol), EDC (1.66 g, 8.64 mmol), and DMAP (0.152 g, 1.24 mmol) were dissolved in DMF (60 mL). Then, the reaction proceeded overnight at room temperature. After evaporation of the solvent, the crude product was dissolved in chloroform and washed with brine thrice. After drying using $MgSO_4$, the solvent was evaporated. Finally, the product was purified by recrystalization using methanol as a solvent.Yield: 0.135 g (9.2%). Melting point: 170°C.



Scheme S9. Synthetic scheme of t*NMe*$_2$CG.

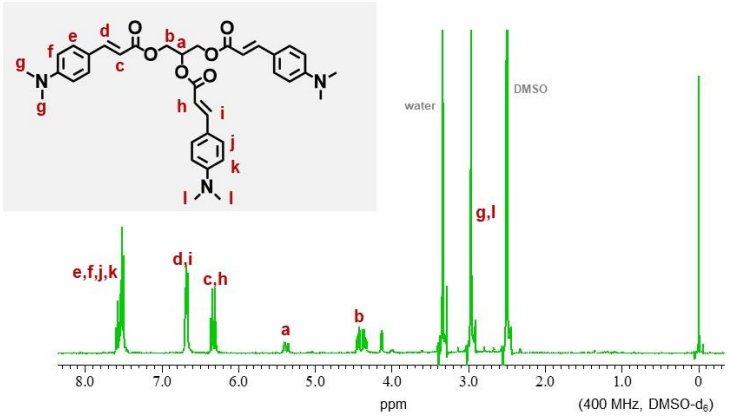


Figure S38. ^{1}H-NMR spectrum of t*NMe*$_2$CG (DMSO-d_6).

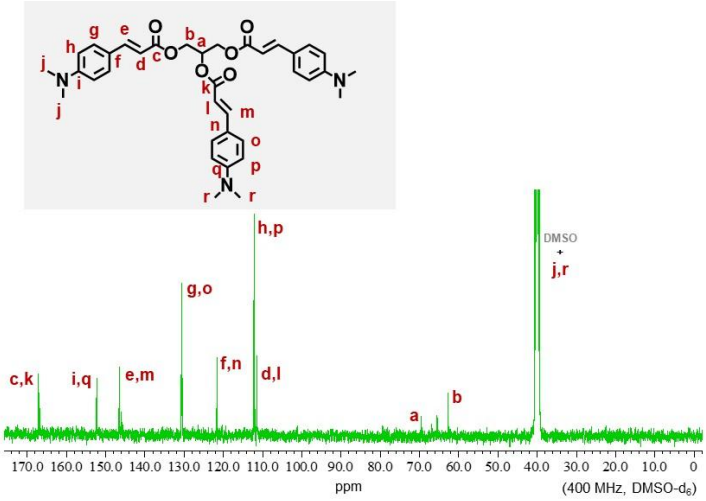


Figure S39. ^{13}C-NMR spectrum of t*NMe*$_2$CG (DMSO-d_6).

40. <u>UV-Vis spectra of Substituted tCG</u>

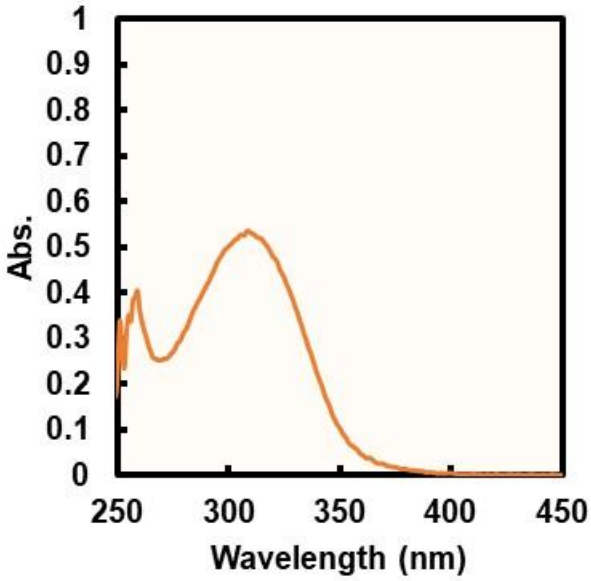


Figure S40. UV-Vis spectrum of t*NO*$_2$CG (10 µM) in DMSO.

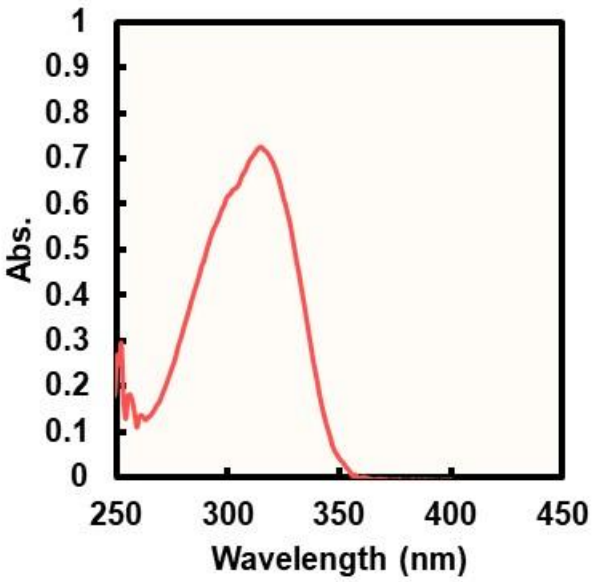


Figure S41. UV-Vis spectrum of t*OMe*CG (10 µM) in DMSO.

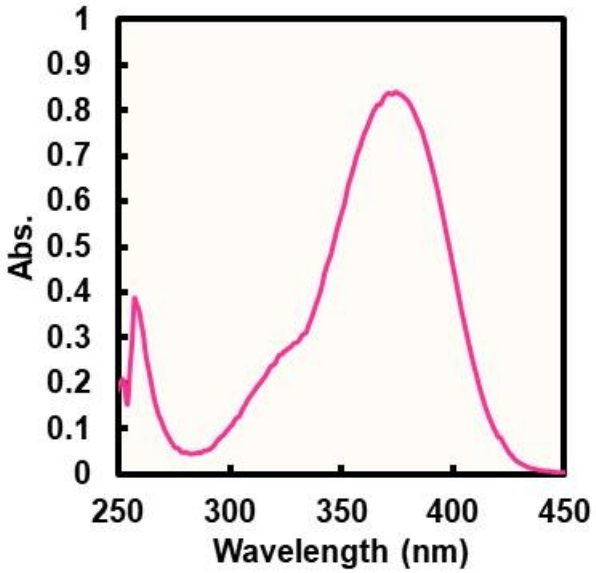


Figure S42. UV-Vis spectrum of t*NMe*$_2$CG (10 µM) in DMSO.

41. Interfacial Photocycloaddition Polymerization of d*OMe*CP and t*OMe*CG with LED_{365}.

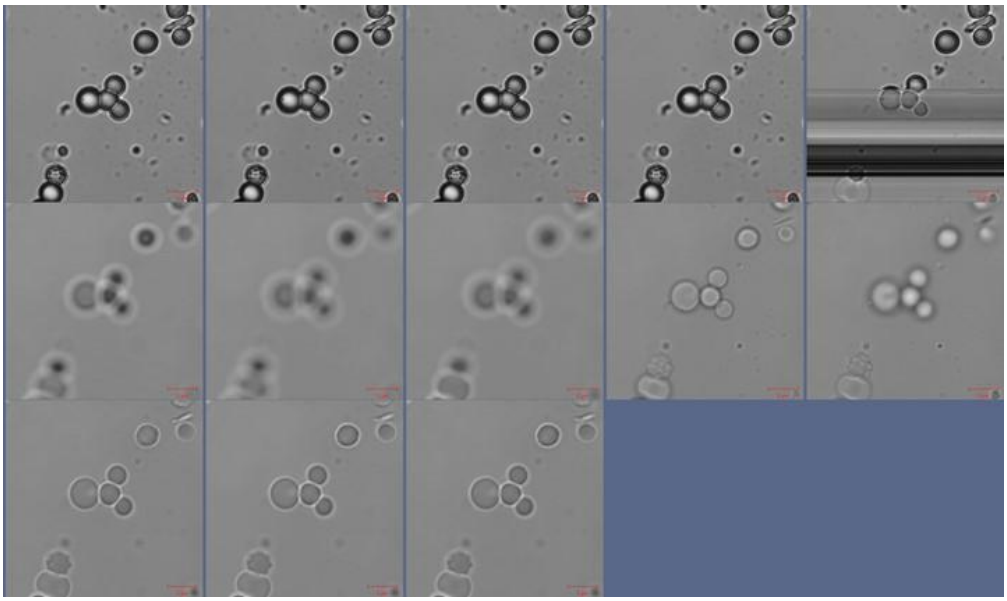


Figure S43. A series of optical microscope images showing the washing process of photoirradiated d*OMe*CP/t*OMe*CG particles using LED_{365} for 16 h.

42. Interfacial Photocycloaddition Polymerization of d*NMe_2*CP and t*NMe_2*CG with LED_{410}.

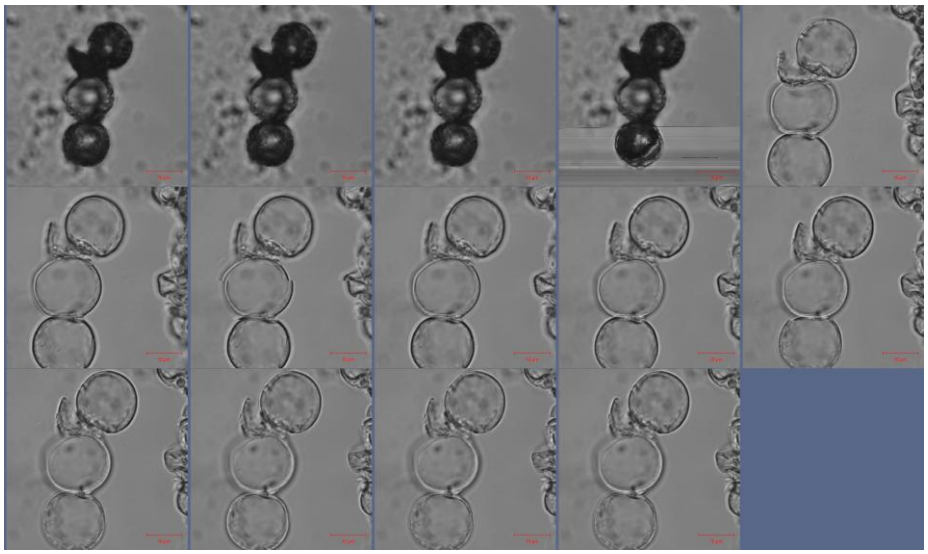


Figure S44. A series of optical microscope images showing the washing process of photoirradiated d*NMe_2*CP/t*NMe_2*CG particles using LED_{410} for 16 h.

43. Interfacial Photocycloaddition Polymerizationof d*NMe*$_2$CP and t*NMe*$_2$CG with LED$_{465}$.

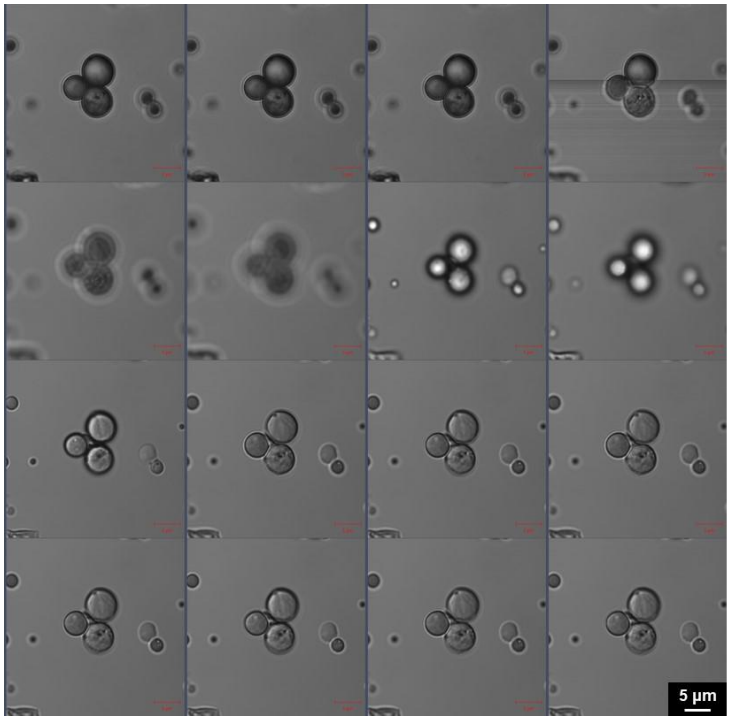


Figure S45. A series of optical microscope images showing the washing process of photoirradiated d*NMe*$_2$CP/t*NMe*$_2$CG particles using LED$_{465}$ for 16 h.

44. <u>Capsule Particles Prepared by Interfacial Photopolymerization with Substituted dCP and tCG</u>

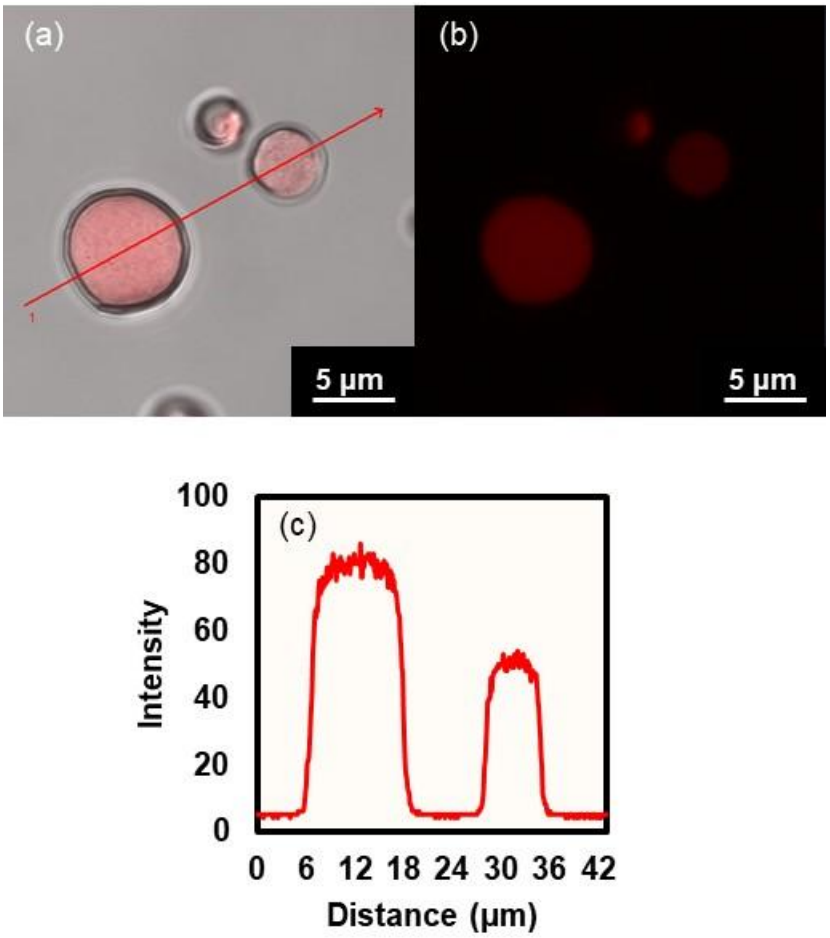


Figure S46. Bright field (a) and confocal laser scanning microscopy image (b) of sulforhodamine B encapsulated P(dNO_2CP-tNO_2CG) particles. Line profile of the fluorescent intensity of the confocal laser scanning microscopy image (right) of sulforhodamine B encapsulated P(dNO_2CP-tNO_2CG) particles (c).

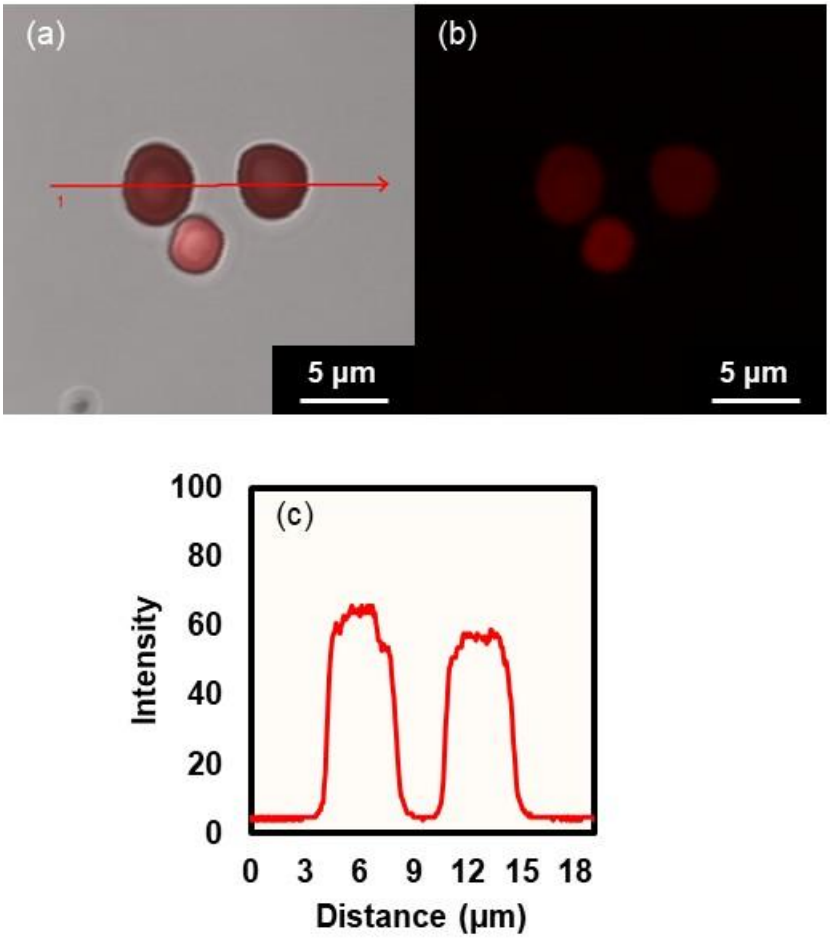


Figure S47. Bright field (a) and confocal laser scanning microscopy image (b) of sulforhodamine B encapsulated P(d*OMe*CP-t*OMe*CG) particles. Line profile of the fluorescent intensity of the confocal laser scanning microscopy image (right) of sulforhodamine B encapsulated P(d*OMe*CP-t*OMe*CG) particles (c).

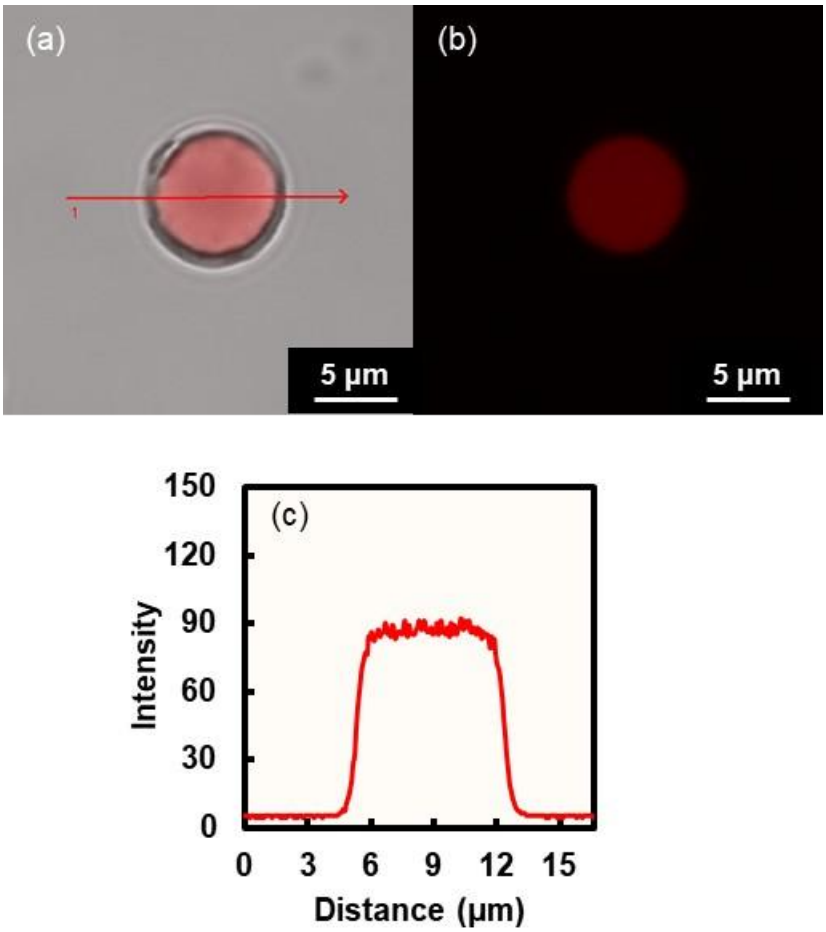


Figure S48. Bright field (a) and confocal laser scanning microscopy image (b) of sulforhodamine B encapsulated P(d*NMe*$_2$CP-t*NMe*$_2$CG) particles. Line profile of the fluorescent intensity of the confocal laser scanning microscopy image (right) of sulforhodamine B encapsulated P(d*NMe*$_2$CP-t*NMe*$_2$CG) particles (c).