Supplementary Information

Reversible formation of multiple stimuli-responsive polymeric materials through processing control of trifunctional amphiphilic molecule

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1. Instrumentation

$^1$H and $^{13}$C NMR spectra were recorded on 400 MHz FT NMR Bruker BioSpin AVANCE III 400 spectrometer or 600 MHz FT NMR Bruker BioSpin AVANCE III 600, where the chemical shifts were determined with respect to tetramethylsilane (TMS), hexamethyldisilane or a residual non-deuterated solvent as an internal standard. DLS measurement was performed with Malvern Zetasizer Nano ZS, where Zetasizer nano series DTS 1060 Folded capillary cell or 10-mm thick quartz cell was used. High resolution electrospay ionization (HR ESI) TOF MS spectra were recorded on Bruker micrOTOF-Q II-S1. MALDI-TOF MS spectrometry was performed in a reflector positive mode with α-cyano-4-hydrocinnamic acid (CHCA) as a matrix on Bruker autoflex speed. UV-Vis spectra were recorded on JASCO V-530 UV-Vis spectrophotometer. Fluorescence spectra were recorded on JASCO FP-6500 spectrophotometer. For the spectroscopic analyses, 1-mm, 5-mm, or 10-mm quartz cuvettes with a teflon screw cap were used, and the samples in the cuvette were under Ar during the analyses. Light irradiation was carried out with Xenon lamps in Asahi Spectra LAX-1000 (for 360 nm, 1000 W) and LAX-110 (for 200–300-nm, 100 W) attached with a band-pass filter.

2. Materials

EtOAc, hexane, and MeOH were purchased from Junsei Chemical Company. Dry methanol and NaHCO$_3$ were purchased from Wako Pure Chemical Industries. 9-Chloromethylanthracene, imidazole, KSAc, Me$_3$N•HCl, sodium hydride (NaH), tetrabutylammonium iodide, tetraethylene glycol, tosyl chloride, and triisopropylsilyl chloride were purchased from Tokyo Chemical Industry. Deuterated solvents were purchased from Acros Organics. Et$_2$O, K$_2$CO$_3$, NaCl, NH$_4$Cl, and anhydrous Na$_2$SO$_4$ were purchased from Nacalai Tesque. Dry Et$_3$N and tetrabutylammonium fluoride (1.0 M in THF) were purchased from Sigma Aldrich. Dry CH$_2$Cl$_2$, dry N,N-dimehylfomamide (DMF), dry tetrahydrofuran
(THF), and dry hexane were purchased from Kanto Chemical and passed through sequential two drying columns on a Glass-Contour system just prior to use. Deionized water (filtered through a 0.22 μm membrane filter, >18.2 MΩ cm) was purified in a Milli-Q system of Millipore. Silica gel column chromatography was carried out with Silica Gel 60 (spherical, neutral, particle size: 63–210 μm) purchased from Kanto Chemical or Chromatorex-Diol silica (MB100-75/200, spherical, neutral, particle size: 110 μm) purchased from Fuji Silysia Chemical. Thin layer chromatography (TLC) was carried out with 60 F254 purchased from Merck or Diol TLC purchased from Fuji Silysia Chemical. Visualization of the developed chromatogram was performed by UV absorbance or I₂.

3. Syntheses

![Chemical structure image]

R = OSi(i-Pr)₃  (2)
= OH  (3)
= OTs  (4)
= SAc  (5)
= SH (AnthTEG3-SH)
1) Synthesis of 3,3-diisopropyl-2-methyl-4,7,10,13-tetraoxa-3-silapentadecan-15-ol

To a dry THF solution (200 mL) of tetraethylene glycol (97.1 g, 0.50 mol) and imidazole (13.6 g, 0.20 mol) was added a dry THF solution (50 mL) of triisopropylsilyl chloride (19.3 g, 0.20 mol) dropwise at 25 °C. After being stirred overnight, to the reaction mixture was added brine (300 mL). The resulting mixture was extracted with Et₂O (500 mL, three times). The collected organic extract was dried over anhydrous Na₂SO₄, and filtered off from insoluble substances. The filtrate was evaporated to dryness under reduced pressure at 30 °C, and the residue was chromatographed on silica gel (Silica Gel 60) with EtOAc/hexane (1/1 v/v) to allow isolation of 3,3-diisopropyl-2-methyl-4,7,10,13-tetraoxa-3-silapentadecan-15-ol (31.1 g, 88.0 mmol) as colorless oil in 89% yield. TLC Rf (Merck 60 F254, EtOAc/hexane = 1/2 v/v): 0.32.

¹H NMR (400 MHz, CDCl₃ containing 0.03% TMS, 22 °C): δ 3.85 (t, J = 7.2 Hz, 2H, TEG), 3.69–3.58 (m, 14H, TEG), 1.11–1.04 (m, 21H, TIPS). HR ESI-TOF MS (MeOH, positive mode): m/z: calculated for C₁₇H₃₈NaO₅Si [M + Na]⁺: 373.2386; found: 373.2369.

2) Synthesis of 3,3-diisopropyl-2-methyl-4,7,10,13-tetraoxa-3-silapentadecan-15-yl 4-methylbenzenesulfonate

To a dry CH₂Cl₂ (200 mL) and Et₃N (30.7 mL, 220 mmol) solution of 3,3-diisopropyl-2-methyl-4,7,10,13-tetraoxa-3-silapentadecan-15-ol (31.1 g, 88.0 mmol) was added Me₃N•HCl (100 mg, 1.05 mmol) and tosyl chloride (20.1 g, 106 mmol) at 25 °C under Ar. After being stirred overnight, to the reaction mixture was added sat. NH₄Cl aq. (200 mL). The resulting mixture was extracted with CH₂Cl₂ (100 mL, three times). The collected organic extract was dried over anhydrous Na₂SO₄, and filtered off from insoluble substances. The filtrate was evaporated to dryness under reduced pressure at 30 °C, and the residue was chromatographed on silica gel (Silica Gel 60) with EtOAc/hexane (2/3 v/v) to allow isolation of 3,3-diisopropyl-2-methyl-4,7,10,13-tetraoxa-3-silapentadecan-15-yl 4-methylbenzenesulfonate (41.7 g, 82.6 mmol) as pale brown oil in 94% yield. TLC Rf (Merck 60 F254, EtOAc/hexane = 2/3 v/v): 0.57. ¹H NMR (400 MHz, CDCl₃ containing 0.03% TMS, 22 °C): δ 7.80 (d, J = 8.4 Hz, 2H,
Ts), 7.34 (d, J = 8.4 Hz, 2H, Ts), 4.16 (t, J = 4.8 Hz, 2H, TsOCH₂), 3.83 (t, J = 5.6 Hz, 2H, SiOCH₂), 3.67–3.56 (m, 12H, TEG), 1.11–1.03 (m, 21H, TIPS). HR ESI-TOF MS (MeOH, positive mode): m/z: calculated for C₂₄H₄₄NaO₇S[Na][M + Na]⁺: 527.2475; found: 527.2462.

3) Synthesis of 2-{(anthracen-9-ylmethoxy)methyl}-2-(hydroxymethyl)propane-1,3-diol (1)

To a dry DMF suspension (10 mL) of NaH (88 mg, 3.68 mmol; washed with dry hexane twice just prior to use) was added pentaerythritol (2.0 g, 14.7 mmol) and tetrabutylammonium iodide (150 mg, 407 μmol) at 25 °C under Ar, and the mixture was stirred for 1 h. To the resulting mixture was added a dry DMF solution (2.0 mL) of 9-chloromethylanthracene (834 mg, 3.68 mmol). After being stirred overnight at 25 °C, to the reaction mixture was added MeOH (10 mL), which was then vacuumed at 40 °C to remove the solvent. To the residue was added water (20 mL) followed by extraction with EtOAc (20 mL, three times). The collected organic extract was dried over anhydrous Na₂SO₄, and filtered off from insoluble substances. The filtrate was evaporated to dryness under reduced pressure at 30 °C, and the residue was chromatographed on silica gel (Silica Gel 60) with EtOAc/MeOH (100/0 to 90/10 v/v) to allow isolation of 1 (668 mg, 2.05 mmol) as white solid in 56% yield. TLC Rf (Merck 60 F254, EtOAc): 0.20. ¹H NMR (400 MHz, DMSO-d₆, 23 °C): δ 8.62 (s, 1H, anthracene), 8.43 (d, J = 8.8 Hz, 2H, anthracene), 8.10 (d, J = 8.0 Hz, 2H, anthracene), 7.60–7.50 (m, 4H, anthracene), 5.38 (s, 2H, anthracene-CH₂O), 4.21 (t, J = 5.2 Hz, 3H, OH), 3.62 (s, 2H, CH₂C(CH₂OH)₃), 3.35 (s, 6H, C(CH₂OH)₃) ppm. HR ESI-TOF MS (MeOH, positive mode): m/z: calculated for C₂₀H₂₂NaO₄ [Na][M + Na]⁺: 349.1416; found: 349.1418.


To a dry THF suspension (40 mL) of NaH (984 mg, 41.0 mmol; washed with dry hexane twice
just prior to use) was added 3,3-diisopropyl-2-methyl-4,7,10,13-tetraoxa-3-silapentadecan-15-yl 4-methylbenzenesulfonate (8.28 g, 16.4 mmol) at 25 °C under Ar. The mixture was heated to reflux, to which a dry THF solution (40 mL) of 2 (1.34 g, 4.10 mmol) was added dropwise. After being refluxed overnight, the reaction mixture was cooled over an ice bath, followed by addition of water until the mixture turned into a clear solution. The resulting mixture was extracted with EtOAc (80 mL, three times). The collected organic extract was dried over anhydrous Na₂SO₄, and filtered off from insoluble substances. The filtrate was evaporated to dryness under reduced pressure at 30 °C, and the residue was chromatographed on silica gel (Silica Gel 60) with EtOAc/hexane (1/1 v/v) to allow isolation of 2 (4.54 g, 3.42 mmol) as yellow oil in 83% yield. TLC \( R_f \) (Merck 60 F254, EtOAc/hexane = 1/1 v/v): 0.37. \(^1\)H NMR (400 MHz, CDCl₃ containing 0.03% TMS, 22 °C): \( \delta \) 8.44 (s, 1H, anthracene), 8.38 (d, \( J = 4.8 \) Hz, 2H, anthracene), 8.00 (d, \( J = 8.0 \) Hz, 2H, anthracene), 7.54–7.38 (m, 4H, anthracene), 5.40 (s, 2H, anthracene-CH₂O), 3.82 (t, \( J = 5.6 \) Hz, 6H, CH₂OSi), 3.80–3.39 (m, 44H, TEG and CH₂OCH₂C), 3.38 (s, 6H, C(CH₂OTEG-TIPS)₃), 1.09–1.04 (m, 63H, TIPS). HR ESI-TOF MS (MeOH, positive mode): \( m/z \) calculated for C₇₁H₁₃₀NaO₁₆Si₃ [M + Na]⁺: 1345.8564; found: 1345.8554.

5) Synthesis of 14-\{(anthracen-9-ylmethoxy)methyl\}-14-(13-hydroxy-2,5,8,11-tetraoxatridecyl)-3,6,9,12,16,19,22,25-octaoxaheptacosane-1,27-diol (3)

To a dry THF solution (70 mL) of 3 (4.58 g, 3.46 mmol) was added 1.0 M tetrabutylammonium fluoride in THF (13.8 mL) at 25 °C under Ar. After being stirred for 1 h, to the reaction mixture was added water (100 mL). The resulting mixture was extracted with EtOAc (100 mL, three times). The collected organic extract was dried over anhydrous Na₂SO₄, and filtered off from insoluble substances. The filtrate was evaporated to dryness under reduced pressure at 30 °C, and the residue was chromatographed on silica gel (Chromatorex-Diol silica) with EtOAc/MeOH (9/1 v/v) to allow isolation of 3 (1.69 g, 1.98 mmol) as yellow oil in 57% yield. TLC \( R_f \) (Merck 60 F254, EtOAc/MeOH = 9/1 v/v): 0.10. \(^1\)H NMR (400 MHz, CDCl₃
containing 0.03% TMS, 22 °C): δ 8.44 (s, 1H, anthracene), 8.39 (d, J = 8.8 Hz, 2H, anthracene), 8.00 (d, J = 8.0 Hz, 2H, anthracene), 7.54–7.44 (m, 4H, anthracene), 5.40 (s, 2H, anthracene-CH₂O), 3.69 (t, J = 5.6 Hz, 6H, C₃H₆OH), 3.68–3.46 (m, 44H, TEG and CH₂OC₃H₂C), 3.39 (s, 6H, C(CH₂OTEG)₃), 2.98 (br, 3H, OH). HR ESI-TOF MS (MeOH, positive mode): m/z: calculated for C₄₄H₇₀NaO₁₆ [M + Na]+: 877.4562; found: 877.4539.

6) Synthesis of 14-[(anthracen-9-ylmethoxy)methyl]-14-(13-tosyloxy-2,5,8,11-tetraoxatridecyl)-3,6,9,12,16,19,22,25-octaoxaheptacosane-1,27-diyl bis(4-methylbenzene-sulfonate) (4)

To a dry CH₂Cl₂ (20 mL) and Et₃N (0.80 mL, 4.8 mmol) solution of 4 (1.03 g, 1.20 mmol) was added Me₃N•HCl (10 mg, 0.105 mmol) and tosyl chloride (1.37 g, 7.20 mmol) at 25 °C under Ar. After being stirred for 1 h, to the reaction mixture was added water (50 mL). The resulting mixture was extracted with EtOAc (50 mL, three times). The collected organic extract was dried over anhydrous Na₂SO₄, and filtered off from insoluble substances. The filtrate was evaporated to dryness under reduced pressure at 30 °C, and the residue was chromatographed on silica gel (Silica Gel 60) with EtOAc/MeOH (100/0 to 95/5 v/v) to allow isolation of 4 (1.46 g, 1.10 mmol) as yellow oil in 92% yield. TLC Rf (Merck 60 F254, EtOAc/MeOH = 95/5 v/v): 0.17. ¹H NMR (400 MHz, CDCl₃ containing 0.03% TMS, 22 °C): δ 8.44 (s, 1H, anthracene), 8.37 (d, J = 9.2 Hz, 2H, anthracene), 8.00 (d, J = 8.0 Hz, 2H, anthracene), 7.78 (d, J = 8.4 Hz, 6H, Ts), 7.54–7.43 (m, 4H, anthracene), 7.31 (d, J = 8.4 Hz, 6H, Ts), 5.39 (s, 2H, anthracene-CH₂O), 3.65 (t, J = 3.6 Hz, 6H, CH₂OTs), 3.64–3.44 (m, 44H, TEG and CH₂OCH₂C), 3.37 (s, 6H, C(CH₂OTEG)₃), 2.42 (s, 9H, Ts). HR ESI-TOF MS (MeOH, positive mode): m/z: calculated for C₆₅H₸₈KO₂₂S₃ [M + K]+: 1355.4566; found: 1355.4541.

To a dry DMF (27 mL) solution of 5 (1.07 g, 0.81 mmol) was added KSAc (0.83 g, 7.29 mmol) at 25 °C under Ar. After being stirred overnight at 80 °C, the reaction mixture was vacuumed to remove DMF at 40 °C. To the resulting mixture was added water (30 mL) followed by extraction with EtOAc (30 mL, three times). The collected organic extract was dried over anhydrous Na₂SO₄, and filtered off from insoluble substances. The filtrate was evaporated to dryness under reduced pressure at 30 °C, and the residue was chromatographed on silica gel (Silica Gel 60) with EtOAc to allow isolation of 5 (0.57 g, 0.54 mmol) as brown oil in 67% yield. TLC Rf (Merck 60 F254, EtOAc): 0.37. ¹H NMR (400 MHz, CDCl₃ containing 0.03% TMS, 22 °C): δ 8.45 (s, 1H, anthracene), 8.38 (d, J = 8.8 Hz, 2H, anthracene), 8.01 (d, J = 8.4 Hz, 2H, anthracene), 7.55–7.44 (m, 4H, anthracene), 5.40 (s, 2H, anthracene-CH₂O), 3.67–3.45 (m, TEG and CH₂OC₂H₂C), 3.38 (s, 6H, C(CH₂OTEG)₃), 3.07 (t, J = 6.6 Hz, 6H, CH₂SAc), 2.32 (s, 9H, Ac). HR ESI-TOF MS (MeOH, positive mode): m/z: calculated for C₅₀H₇₆NaO₁₆S₃ [M + Na]⁺: 1051.4193; found: 1051.4180.

8) Synthesis of 14-{(anthracen-9-ylmethoxy)methyl}-14-(13-mercapto-2,5,8,11-tetraoxatridecyl)-3,6,9,12,16,19,22,25-octaoxaheptacosane-1,27-dithiol (AnthTEG3-SH)

To a dry MeOH (5 mL) solution of 6 (25.7 mg, 50 μmol) was added K₂CO₃ (27.6 mg, 0.20 mmol) at 25 °C under Ar. After being stirred for 1 h, to the reaction mixture was added water (10 mL). The resulting mixture was extracted with EtOAc (10 mL, three times). The collected organic extract was dried over anhydrous Na₂SO₄, and filtered off from insoluble substances. The filtrate was evaporated to dryness under reduced pressure at 30 °C, and the residue was chromatographed on silica gel (Silica Gel 60) with EtOAc/MeOH (9/1 v/v) to allow isolation of AnthTEG3-SH (20.3 mg, 22 μmol) as yellow oil in 90% yield. TLC Rf (Merck 60 F254, EtOAc/MeOH = 9/1 v/v): 0.60. ¹H NMR (600 MHz, CDCl₃ containing 0.03% TMS, 25 °C): δ 8.40 (s, 1H, anthracene), 8.35 (d, J = 9.0 Hz, 2H, anthracene), 7.96 (d, J = 8.4 Hz, 2H, anthracene), 7.49–7.41 (m, 4H, anthracene), 5.37 (s, 2H, anthracene-CH₂O), 3.67–3.36 (m, TEG and CH₂OCH₂C), 3.36 (s, 6H, C(CH₂OTEG)₃), 2.66 (q, J = 7.8 Hz, 6H, CH₂SAc), 1.57
(t, $J = 8.4$ Hz, 3H, SH). HR ESI-TOF MS (MeOH, positive mode): $m/z$: calculated for C$_{44}$H$_{70}$NaO$_{13}$S$_3$ [M + Na]$^+$: 925.3876; found: 925.3756.

4. **Oxidation procedure to prepare AnthTEG3-SS$^{20}$ and AnthTEG3-SS$^{70}$**

Aqueous solution of AnthTEG3-SH (0.25 mM) was prepared in a round-bottom flask with a magnetic stirrer bar under Ar. After the temperature of the solution was stabilized at 20 °C or 70 °C with gentle stirring, Ar was removed by vacuuming followed by filling the flask with O$_2$. 
5. **Schematic figures of stimuli-responsive systems of this study**

**Dispersed Condition in Water (nm-Scale Materials)**

- Anthracene Unit: Self-assembling and Photo-responsive Unit
- TEG Chains: Thermo-responsive Units
- SH Groups: Radio-responsive Units

Figure S1: Schematic figures of the stimuli-responsive systems of this study (top) in a dispersed condition in water and (bottom) in the neat condition.
6. $^1$H NMR spectra of AnthTEG3-SH

**Figure S2** $^1$H NMR spectra of AnthTEG3-SH (1.0 mM) in the mixtures of THF-$d_8$ and D$_2$O at 20 °C. THF-$d_8$/D$_2$O (v/v) = a) 100/0, b) 90/10, c) 80/20, and d) 50/50.
7. Solvent dependency of AnthTEG3-SH

The fluorescence intensity of AnthTEG3-SH in THF/water = 75/25 was higher than that in THF, while the UV-vis absorption intensity decreased upon addition of water. UV-vis absorption and fluorescence spectra of AnthTEG3-SH (250 μM) in THF/water = 80/20 were measured, which showed nearly overlapping spectra with those in THF/water = 75/25 (Fig. S2). Here, \(^1\)H NMR spectrum of AnthTEG3-SH (1.0 mM) in THF-d$_8$/D$_2$O = 80/20 showed relatively well-resolved signals, suggesting that large portion of the molecules is dispersed in this solvent system (Fig. S5). Therefore, it is likely that the spectral differences of AnthTEG3-SH in THF and in THF/water = 75/25 essentially correspond to the different solvent polarity rather than aggregation formation, where the solvent polarity change would influence the excited state of AnthTEG3-SH to increase the quantum yield of fluorescence.

Figure S3  a) UV-vis absorption and b) fluorescence spectra (excitation at 370 nm) of AnthTEG3-SH (250 μM) in a mixture of THF and water at variable mixing ratios.
8. Concentration dependency of AnthTEG3-SH

Figure S4  a) UV-vis absorption and b) fluorescence spectra (excitation at 370 nm) of AnthTEG3-SH at 20 °C at different concentrations (black: 250 μM, blue: 25 μM, red: 2.5 μM) in water.
9. DLS analysis of AnthTEG3-SH in THF

**Figure S5**  DLS profile of AnthTEG3-SH in THF (250 μM) at 20 °C. The number denotes mean hydrodynamic diameter.
Figure S6  Variable temperature $^{13}$C NMR spectra of AnthTEG3-SH (4.0 mM) in the mixture of THF-$d_8$ and D$_2$O (90/10 v/v) at a) 20, b) 40, c) 60, and d) 80 °C, where the region of the signals assigned to the carbons at the TEG chains is displayed.
11. TEM of AnthTEG3-SH, AnthTEG3-SS\textsuperscript{20} and AnthTEG3-SS\textsuperscript{70}

![TEM images](image)

**Figure S7** Cast TEM of a) AnthTEG3-SH, b) AnthTEG3-SS\textsuperscript{20} and c) AnthTEG3-SS\textsuperscript{70} stained with RuO\textsubscript{4}. The samples in water at 70 °C were rapidly casted on grids followed by staining. Scale bars: 200 nm.
12. UV-vis absorption and fluorescence spectra of AnthTEG3-SH

**Figure S8**  (a) UV-vis absorption and (b) fluorescence spectra (excitation at 370 nm) of AnthTEG3-SH (250 µM) upon heating from 20 to 70 °C. Blue: 20 °C, light blue: 30 °C, green: 40 °C, orange: 50 °C, pink: 60 °C, and red: 70 °C. The arrows denote the direction of the spectral changes. The numbers denote wavelengths of the peak tops.
13. MALDI-TOF MS spectra of AnthTEG3-SS$^{20}$ and AnthTEG3-SS$^{70}$

**Figure S9** MALDI-TOF MS spectra of a) AnthTEG3-SS$^{20}$ and b) AnthTEG3-SS$^{70}$ measured in a linear mode with α-cyano-4-hydrocinnamic acid as a matrix.
Figure S10  GPC chromatograms of a) AnthTEG3-SH, b) AnthTEG3-SS$^{20}$ and c) AnthTEG3-SS$^{70}$. Column: Asahipak GF-7M HQ (Shodex), absorption at 385 nm, THF, 0.6 mL min$^{-1}$, 25 °C.

In the GPC analyses, the oxidized samples showed no signals at the elution volume corresponding to AnthTEG3-SH (9.7 mL) indicating almost full conversion of AnthTEG3-SH to oligomers and polymers. Compared to AnthTEG3-SS$^{20}$, AnthTEG3-SS$^{70}$ showed signals at small elution volumes (8 to 9 mL) with larger ratios, suggesting larger contents of longer oligomers/polymers in AnthTEG3-SS$^{70}$ than in AnthTEG3-SS$^{20}$. 
15. UV-vis absorption and fluorescence spectra of AnthTEG3-SS$^{20}$ and AnthTEG3-SS$^{70}$

Figure S11  a,c) UV-vis absorption and b,d) fluorescence spectra (excitation at 370 nm) of a,b) AnthTEG3-SS$^{20}$ and c,d) AnthTEG3-SS$^{70}$ in water (250 µM) upon heating from 20 to 70 °C. The arrows denote direction of the spectral change. The numbers denote wavelength of the peak tops.
16. DLS analyses of AnthTEG3-SH obtained by reduction of AnthTEG3-SS$_{20}$

**Figure S12** DLS profiles of AnthTEG3-SH after the reduction of AnthTEG3-SS$_{20}$ with NaBH$_4$ in water (250 μM) at a) 20 °C, b) 50 °C, c) 70 °C, and d) 20 °C after cooling. The numbers denote mean hydrodynamic diameters.
17. DLS analyses of AnthTEG3-SH obtained by reduction of AnthTEG3-SS\textsuperscript{70}

Figure S13  DLS profiles of AnthTEG3-SH after the reduction of AnthTEG3-SS\textsuperscript{70} with NaBH\textsubscript{4} in water (250 μM) at a) 20 °C, b) 50 °C, c) 70 °C, and d) 20 °C after cooling. The numbers denote mean hydrodynamic diameters.
18. Diffuse reflectance and fluorescence spectra of AnthTEG3-SS\textsuperscript{70}-film

Figure S14  a) Diffuse reflectance and b) fluorescence spectra (excitation at 370 nm) of AnthTEG3-SS\textsuperscript{70}-film (Polymer D, black lines) prior to and (blue lines) after 360-nm light irradiation for 6 min at 25 °C.  c) UV-vis absorption spectra of (blue solid line) the irradiated side with 360-nm light for 6 min and (black solid line) the non-irradiated side of AnthTEG3-SS\textsuperscript{70}-film (Polymer D) at 25 °C.
19. Diffuse reflectance spectra of AnthTEG3-SS\textsuperscript{20}-film

![Diffuse reflectance spectra](image)

**Figure S15** Diffuse reflectance spectra of (blue solid line) the irradiated side with 360-nm light for 6 min and (black solid line) the non-irradiated side of AnthTEG3-SS\textsuperscript{20}-film (*Polymer C*) at 25 °C.
20. IR spectra of AnthTEG3-SS\textsuperscript{20}.film and AnthTEG3-SS\textsuperscript{70}.film

**Figure S16**  IR spectra of a) AnthTEG3-SS\textsuperscript{20}.film (Polymer C) and b) AnthTEG3-SS\textsuperscript{70}.film (Polymer D) at 25 °C (black solid line) prior to the photo-irradiation, after 360-nm photo-irradiation under Ar for (red solid line) 1, (orange solid line) 3 and (blue solid line) 6 min. IR spectra of the non-irradiated sides of the a) AnthTEG3-SS\textsuperscript{20}.film (Polymer C) and b) AnthTEG3-SS\textsuperscript{70}.film (Polymer D) after the photo-irradiation process are shown as black dashed lines.