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Electronic Supplementary Information (ESI)

Photohealable ion gels based on the reversible dimerisation of anthracene

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Experimental

Materials

Tetra-arm poly(ethylene glycol) (tetraPEG, M_n = 40 kDa) was purchased from JenKem technology (TX, USA) and purified by reprecipitation from toluene as a good solvent and *n*-hexane as a poor solvent. 2-Aminoanthracene was purchased from TCI Chemicals (Japan) and was used as received. Triphosgene was purchased from Sigma-Aldrich (MO, USA) and was used as received. All other chemicals were purchased from Wako Pure Chemical Industries (Japan) and were used as received unless stated otherwise.

Synthesis of TetraPEG-Ant

TetraPEG-Ant was synthesised through reaction of the terminal hydroxyl groups of TetraPEG with anthracene isocyanate.[S1] Initially, 2-aminoanthracene was converted into 2-isocyanatoanthracene, as outlined in **Scheme S1a**. More specifically, 2-aminoanthracene (0.205 g, 1.06 mmol) was dispersed in dichloromethane (10 mL) in a round-bottom flask. Triethylamine (0.412 mL, 3.00 mmol) was then added to the dispersion and the flask was cooled in an ice bath. Triphosgene (0.340 g, 1.15 mmol) was subsequently added slowly to the flask, the ice bath was removed, and the reaction was allowed to proceed for 24 h at room temperature. After this time, the obtained solution was filtered and evaporated, and the desired anthracene isocyanate was obtained as a brown solid. Avoiding further purification, this anthracene isocyanate was allowed to react with tetraPEG (**Scheme S1b**) by the addition of a tetraPEG (1.00 g, 0.0250 mmol) solution in dichloroethane (15 mL) to the flask containing the synthesised anthracene isocyanate. Following the subsequent addition of a dibutyltin dilaurate catalyst (0.250 mL, 0.416 mmol), the reaction was allowed to proceed at 50 °C for 14 h. After this time, the reaction mixture was filtered and evaporated, then reprecipitated from tetrahydrofuran (THF) as a good solvent and diethyl ether as a poor solvent. After vacuum drying overnight at 35 °C, the desired tetraPEG-Ant was obtained as a brown powder (0.70 g, 69% yield).

The modification efficiency of anthracene on the polymer terminal of tetraPEG was then estimated by ^{1}H NMR spectroscopy (DRX500, Bruker Biospin, Germany), as outlined in **Fig. S1**. In addition, the polydispersity of the prepared tetraPEG-Ant was calculated by gel permeation chromatography (GPC) (**Fig. S2**), where the GPC column (Tosoh, Japan) was calibrated with polyethylene oxide standards using THF as the eluent.

Preparation of tetraPEG-Ant solutions in ILs

TetraPEG-Ant was dissolved in [C$_2$mim][NTf$_2$] using a conventional cosolvent method. More specifically, the desired masses of tetraPEG-Ant and [C_2mim][NTf_2] were dissolved in THF under stirring. The solvent was then evaporated at 65 °C under stirring, and further drying was carried out under vacuum overnight at 65 °C.

UV-vis spectrophotometry

The UV-vis spectra of tetraPEG-Ant in [C_2mim][NTf_2] were recorded using a UV-2700 UV-vis spectrophotometer (Shimadzu, Japan). For all measurements, the polymer solution was sealed in a quartz cell with an optical path length of 1 mm in an argon-filled glove box. The samples were subjected to UV light irradiation using a UV-LED spot light source (LC-L1V3, Hamamatsu, Japan), with a peak wavelength of 365 ± 5 nm.

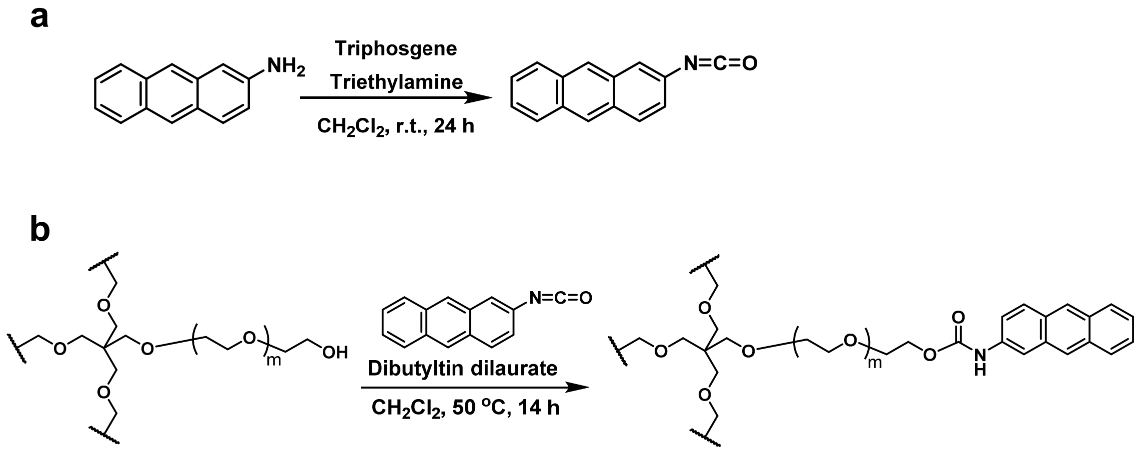
Rheological measurements

Rheological measurements were carried out for the prepared tetraPEG-Ant ion gels using an Anton Paar Physica MCR 102 instrument (Anton Paar, Austria) equipped with a standard cell for UV irradiation (P-PTD200/GL) under a flow of argon. A parallel plate geometry with a diameter of 12.5 mm and a gap spacing of ~0.2 mm was employed for all measurements.

Tensile tests

Tensile tests were conducted for rectangular-shaped 10 wt% tetraPEG-Ant ion gels with a thickness of 1 mm. More specifically, a 10 wt% solution of tetraPEG-Ant in $[C_2mim][NTf_2]$ was transferred into a rectangular-shaped silicon rubber mould. Following UV light irradiation at room temperature overnight, the desired ion gel sheets were obtained through the photodimerisation-induced chemical crosslinking of tetraPEG-Ant in the IL. Tensile tests were performed on a Shimadzu EZ-LX instrument (Shimadzu, Japan) with a 10 N load cell at a strain rate of 1 cm $\mathrm{min^{-1}}$ at room temperature. For the photo-healing test, the ion gel sheet was cut into two pieces using a sharp blade. The cut surfaces were re-contacted and heated to 150 °C for 10 h, followed by UV irradiation at room temperature overnight.

Scheme S1. Synthetic scheme for preparation of the tetraPEG-Ant



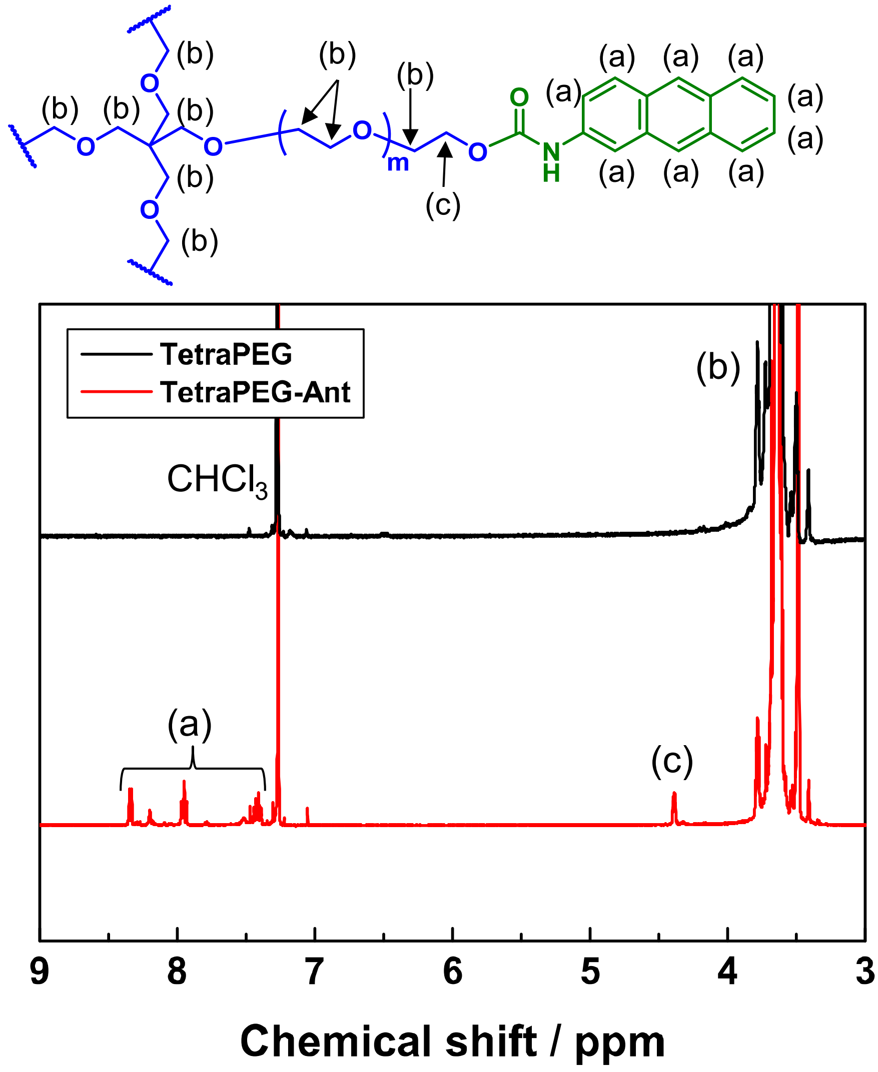


Fig. S1 ^{1}H NMR spectra for the tetraPEG precursor (upper, black) and tetraPEG-Ant (lower, red) (recorded in CDCl$_3$).

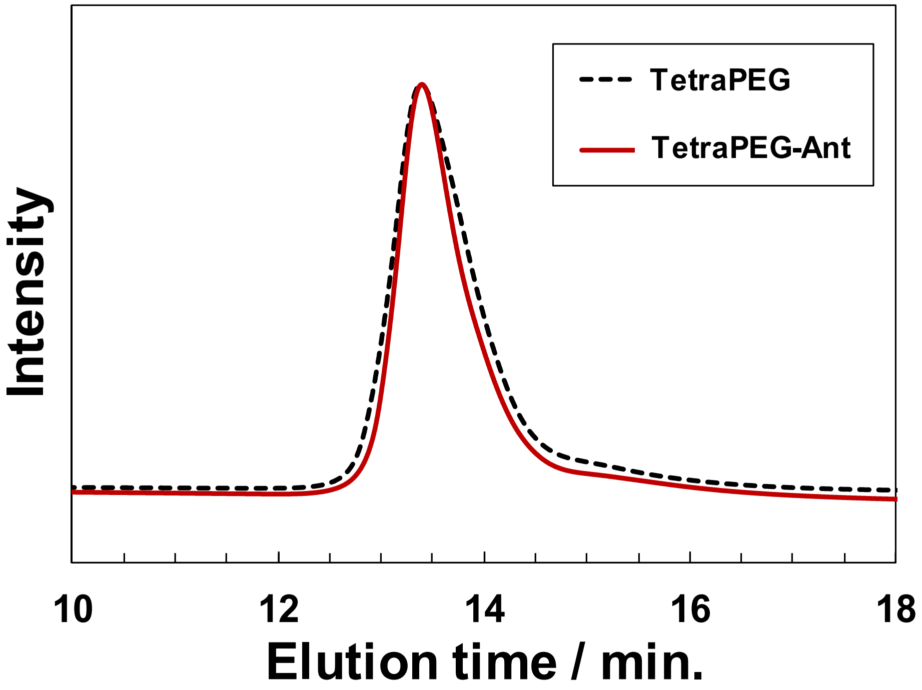
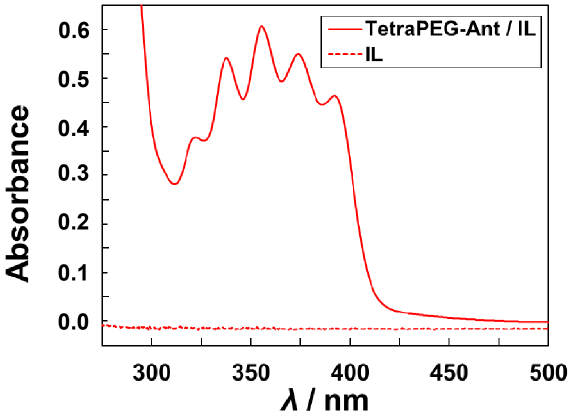
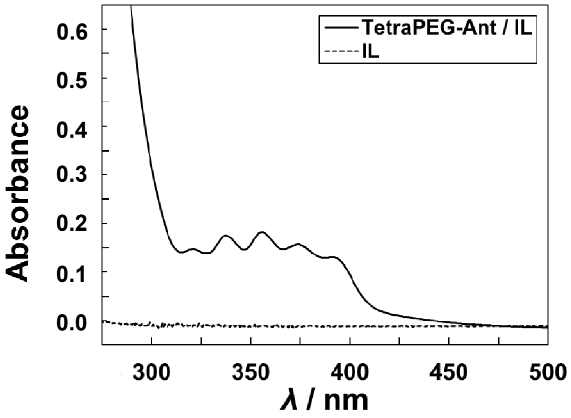


Fig. S2 GPC traces for the tetraPEG precursor and for tetraPEG-Ant. The polydispersity indices of tetraPEG and tetraPEG-Ant were calculated to be 1.42 and 1.36, respectively.

(a) Before UV



(b) UV 360 min



(c) Heat 180 min

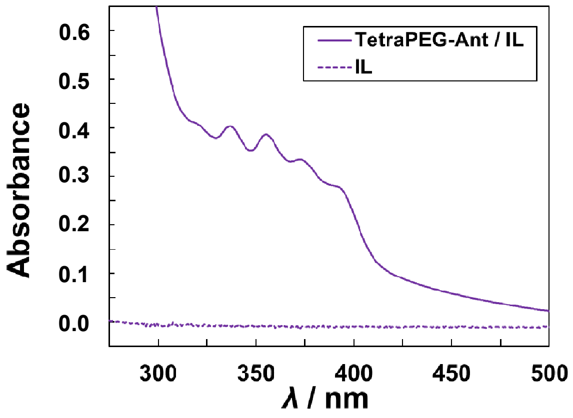


Fig. S3 UV−vis spectra for a 1 wt% tetraPEG-Ant solution in [C$_2$mim][NTf$_2$] (solid line) and pure [C$_2$mim][NTf$_2$] (dotted line) (a) before UV irradiation, (b) after UV irradiation for 360 min, and (c) after heating at 150 °C for 180 min following UV irradiation.

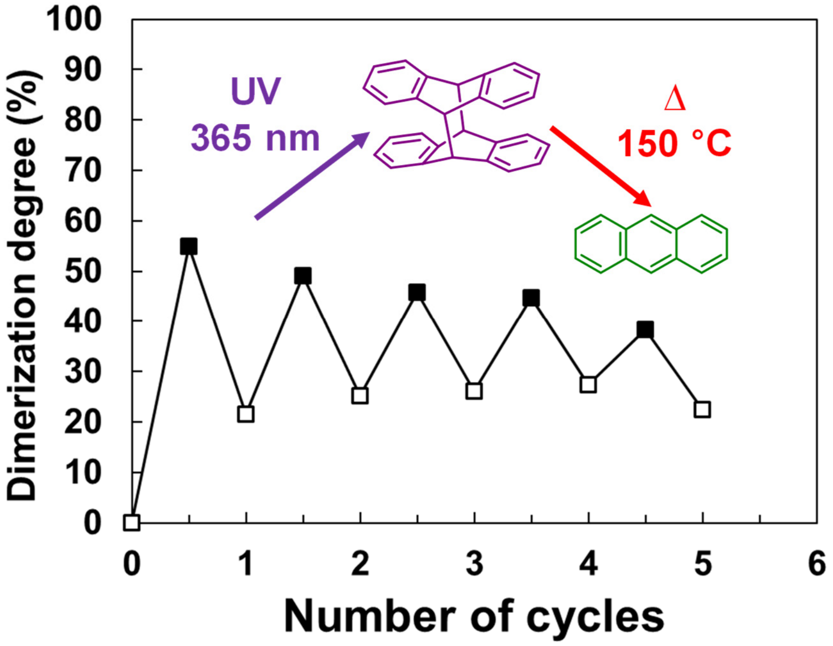


Fig. S4 Reversibility in the dimerisation degree over five cycles of UV irradiation (365 nm, 180 min) and heating (150 °C, 120 min) for a 1 wt% solution of tetraPEG-Ant in [C_2mim][NTf_2].

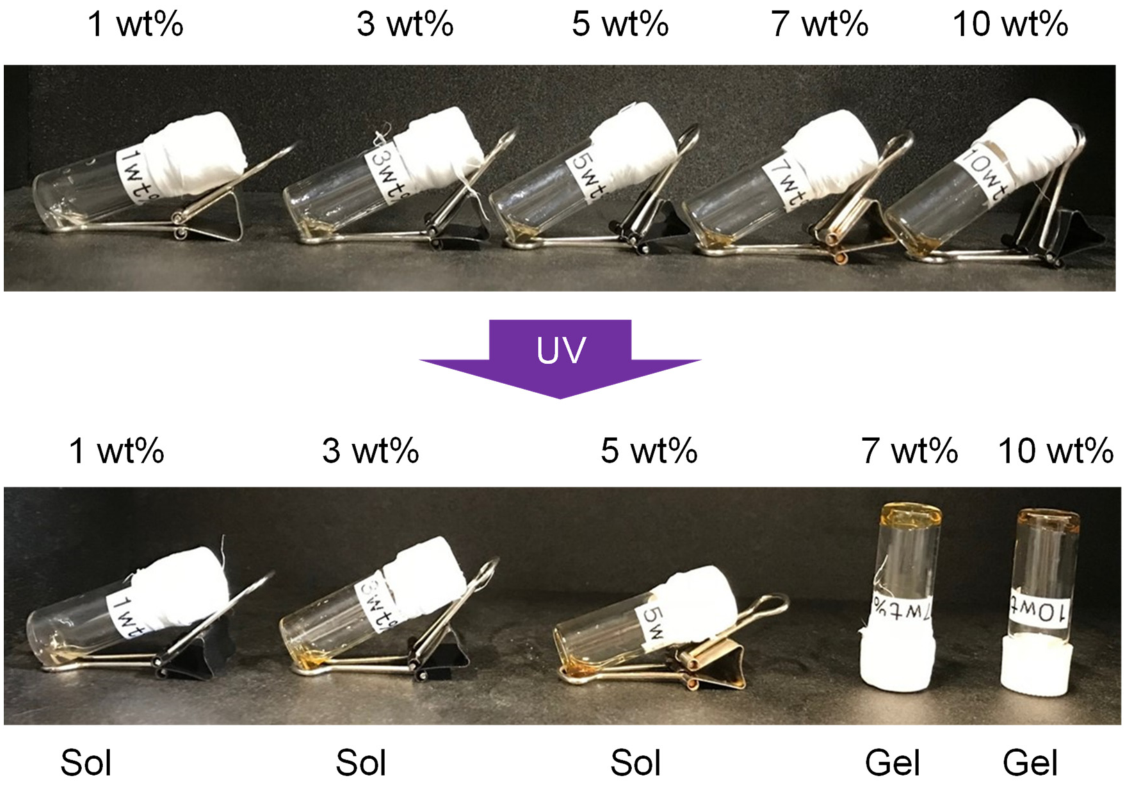
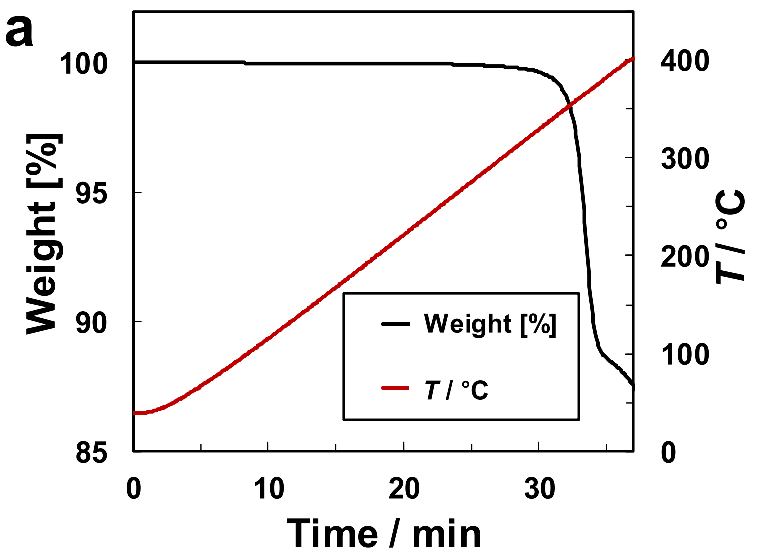


Fig. S5 Photographic images of the gelation test for solutions of tetraPEG-Ant in [C_2mim][NTf_2] at different polymer concentrations. Irradiation was achieved using UV light at a wavelength of 365 nm overnight at room temperature.



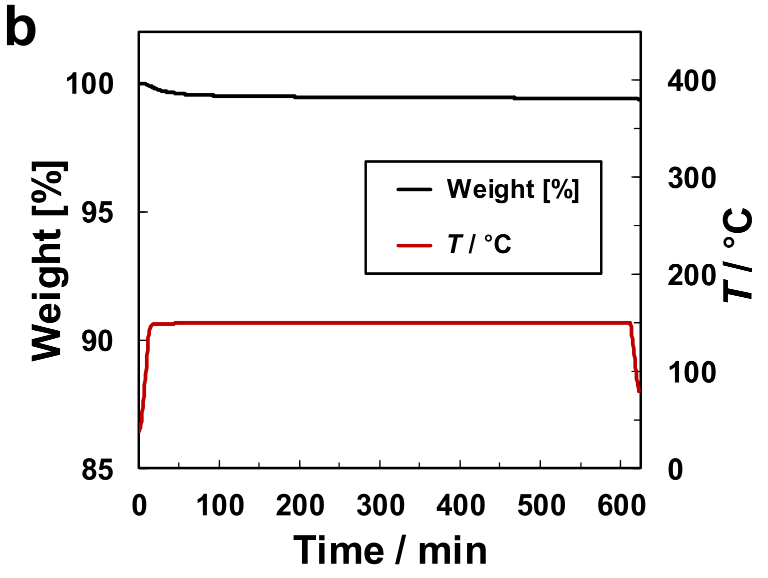


Fig. S6 TGA curves for a 10 wt% tetraPEG-Ant ion gel under a nitrogen atmosphere (a) at a heating rate of 10 °C/min, and (b) at a constant temperature of 150 °C for 10 h.

Supporting Reference

S1 F. Biedermann, E. A. Appel, J. del Barrio, T. Gruendling, C. Barner-Kowollik and O. A. Scherman, *Macromolecules*, 2011, **44**, 4828–4835.