Supporting Information

Cellulose-stimulated self-assembling solvent for molecular dispersion of cellulose

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Experimental

Materials and Equipment

Triethylamine, 1-bromopentane, 1-bromohexane, 1-bromooctane, 1-bromododecane, and 4-nitroaniline were purchased from Tokyo Chemical Industry Co. Ltd. and used as received. Dimethylsulfoxide was purchased from Kanto Chemical Co., Inc., and used as received. Ethanol, acetonitrile, acetic acid, and aluminium oxide (basic 0.5 μm) were purchased from FUJIFILM Wako Pure Chemical Industries Ltd. and used as received. Amberlite™ IRN78 was purchased from Sigma-Aldrich Co. and used as received. N,N-diethyl-4-nitroaniline was purchased from Apollo Scientific and used as received. 5'-(2,4,6-Triphenylpyridin-1-ium-1-yl)-[1,1':3',1"-terphenyl]-2'-olate was purchased from Angene Chemical and used as received. Avicel® PH-101 was purchased from Sigma-Aldrich Co. and used as received. Filter paper (No.5A, consists of more than 99% purity α-cellulose) was purchased from ADVANTEC and used as received.

Viscosity values were measured using A AND D SV viscometer. UV-vis. spectra were measured using JASCO V-730 spectrometer. Rheology measurements were conducted using Thermo Scientific HAAKE MARS rheometer. Transmission WAXS measurements were conducted using a Rigaku SmartLab XRD equipment.

Synthesis of triethylpentylammonium acetate

Triethylamine (61.33 g, 0.60 mol), 1-bromopentane (83.23 g, 0.54 mol), and acetonitrile (100 g) were added. The mixture was then heated in an oil bath 80 °C for 5.5 h. The acetonitrile was evaporated under reduced pressure to yield triethylpentylammonium bromide (130.09 g, 0.52 mol). Triethylpentylammonium bromide (50.45 g, 0.20 mol) and Amberlite IRN-78 (ion exchange resin, nuclear grade) (150 g) were stirred in ethanol (200 g) at r.t. for 7 h. Following the removal of the ion exchange resin through filtration, acetic acid (12.05 g, 0.20 mol) in ethanol (30 g) was added and stirred at r.t. for 5.5 h. The solvent was then evaporated under reduced pressure to yield triethylpentylammonium acetate (44.97 g, 0.19 mol).

Synthesis of triethylhexylammonium acetate

Triethylamine (61.33 g, 0.60 mol), 1-bromohexane (90.96 g, 0.54 mol), and acetonitrile (100

g) were added. The mixture was then heated in an oil bath 80 °C for 6 h. The acetonitrile was evaporated under reduced pressure to yield triethylhexylammonium bromide (131.13 g, 0.49 mol). Triethylhexylammonium bromide (119.82 g, 0.45 mol) and Amberlite IRN-78 (ion exchange resin, nuclear grade) (400 g) were stirred in ethanol (200 g) at r.t. for 6 h. Following the removal of the ion exchange resin through filtration, acetic acid (27.10 g, 0.45 mol) in ethanol (30 g) was added and stirred at r.t. for 2.5 h. The solvent was then evaporated under reduced pressure to yield triethylhexylammonium acetate (95.00 g, 0.39 mol).

Synthesis of triethyloctylammonium acetate

Triethylamine (67.46 g, 0.66 mol), 1-bromooctane (118.24 g, 0.60 mol), and acetonitrile (100 g) were added. The mixture was then heated in an oil bath 80 °C for 9.5 h. The acetonitrile was evaporated under reduced pressure to yield triethyloctylammonium bromide (143.19 g, 0.49 mol). Triethyloctylammonium bromide (58.86 g, 0.20 mol) and Amberlite IRN-78 (ion exchange resin, nuclear grade) (300 g) were stirred in ethanol (200 g) at room temperature for 7 h. Following the removal of the ion exchange resin through filtration, acetic acid (12.05 g, 0.20 mol) in ethanol (30 g) was added and stirred at room temperature for 7 h. The solvent was then evaporated under reduced pressure to yield triethyloctylammonium acetate (54.31 g, 0.20 mol).

Synthesis of dodecyltriethylammonium acetate

Triethylamine (61.33 g, 0.60 mol), 1-bromododecane (137.34 g, 0.54 mol), and acetonitrile (100 g) were added. The mixture was then heated in an oil bath 80 °C for 17 h. The acetonitrile was evaporated under reduced pressure to yield dodecyltriethylammonium bromide (190.91 g, 0.54 mol). Dodecyltriethylammonium bromide (70.09 g, 0.20 mol) and Amberlite IRN-78 (ion exchange resin, nuclear grade) (190 g) were stirred in ethanol (200 g) at room temperature for 7 h. Following the removal of the ion exchange resin through filtration, acetic acid (12.05 g, 0.20 mol) in ethanol (30 g) was added and stirred at room temperature for 7 h. The solvent was then evaporated under reduced pressure to yield triethyloctylammonium acetate (60.89 g, 0.18 mol).

Evaluation of physical state of ionic liquids at room temperature

The resulting quaternary ammonium acetate was dried to a moisture content of less than 1 wt% and then left to stand overnight at room temperature. The physical state was visually determined at room temperature.

Viscosity

The viscosity of the neat quaternary ammonium acetate and the mixed solvent of quaternary ammonium acetate/DMSO (3/7, w/w) was determined by using an A AND D vibration viscometer at

room temperature.

Kamlet-Taft *β* value

The *β* values of Kamlet-Taft parameters was measured according to the literature.[1]

Cellulose solubility

Mixed solvents of quaternary ammonium acetate/DMSO = 3/7, by weight, were prepared. Avicel® PH-101 was added to the mixed solvents, and the cellulose solubility was evaluated at 85°C. Cellulose dissolution was visually confirmed 10 minutes after adding cellulose. The test was carried out on different batches at different concentrations of 2.5 wt% each.

Rheology

Cellulose solutions were prepared with 5wt% of ADVANTEC filter paper (No.5A). The measurements were conducted using a Thermo Scientific HAAKE MARS rheometer, equipped with a 25 mm parallel plate. A volume of 0.5 mL of the cellulose solution was dispensed onto the lower plate, which was maintained at 80 °C, using a needleless syringe. Subsequently, the upper plate was elevated to create 1 mm gap. The experiment was repeated twice at a strain of $\gamma = 0.5$, a frequency of $f = 30$ to 0.03 Hz.

The sample solutions have the following shear history: three times shear rate-dependent viscosity measurement of the shear rate ranging from 1/s to 100/s over a period of 60 seconds, followed immediately by another sweep, ranging from 100/s to 1/s, also over a period of 60 seconds (Figure S1); and three times strain-dispersion dynamic viscoelasticity measurements at a frequency of $f = 1$ Hz, a strain of $\gamma = 0.01$ to 100.

Regenerated cellulose films

Cellulose solutions were prepared with 5 wt% of ADVANTEC filter paper (No.5A). A thin layer of the cellulose solution with a thickness of 300 μm was prepared using a bar coater and the solution was coagulated in water at room temperature and dried overnight at 23°C, 50.5%RH.

Transmission WAXS

The measurements were conducted using a Rigaku SmartLab. The film sample was irradiated with X-rays at an X-ray wavelength of 0.154 nm, a camera length of 24.94 mm, and an exposure time of 1 h/sample. The environment surrounding the sample cell was set to atmospheric pressure and room temperature. The degree of crystallinity was determined by analyzing the WAXS profile, which was obtained by averaging the measured two-dimensional WAXS pattern (diffraction

angle of 6-32°, azimuth angle of 0-360° or 60-120°). The degree of crystallinity of the regenerated cellulose film was calculated in accordance with the literature.[2]

MD simulation

As in the previous report, a crystal model of cellulose Iβ (30 molecular chains × 20 glucose residues, shown in Figure A) was constructed using synchrotron X-ray diffraction data.[3] A nick site equivalent to two glucose residues was introduced in the center of the molecular chain on the (200) crystal surface. The cellulose crystal model was positioned within a periodic boundary box, and a solution of quaternary ammonium acetate/DMSO (3/7, w/w) was introduced in its immediate vicinity. In this instance, the IL was either $[N_{2,2,2,5}]$OAc or $[N_{2,2,2,8}]$OAc, with 1,500 ion pairs established. For the constructed system, structural optimization calculations and molecular dynamics (MD) simulations of the equilibration process with heating (0.1 K/ps) were conducted. The MD simulations were conducted to investigate the dissolution of cellulose at a constant temperature of 160 °C and pressure of 1 bar for a duration of 3.5 μs. In the experiment, cellulose was dissolved at 85 °C; however, due to the high computational cost, calculations were performed at elevated temperatures. Subsequently, the temperature was decreased at a rate of 0.1 K/ps, and MD simulations were performed at a constant temperature (80 °C) and pressure (1 bar) for 2.4 μs to investigate the state of dissolution of cellulose.

The cellulose was described using the GLYCAM06 force field, while the quaternary ammonium acetate and DMSO were modelled using the generalized AMBER force field (GAFF). The SHAKE option was employed, and the integration step was set to 0.2 fs. The MD simulations were conducted using the PMEMD and PMEMD.cuda modules of the AMBER20 and AmberTools21 software packages, respectively. The MD trajectories were analyzed using the cpptraj module, and the resulting data were visualized using PyMOL 2.5.0 for the generation of molecular graphics.
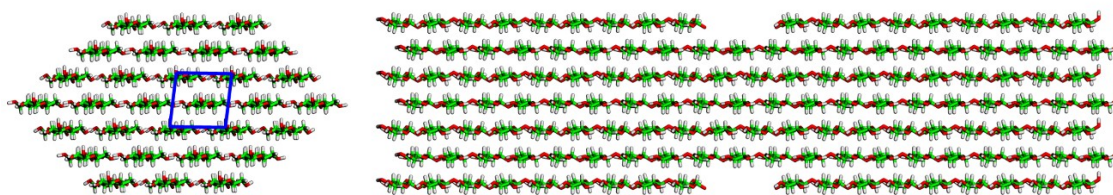

Fig. A Native cellulose crystal model (30 molecular chains × 20 glucose residues) used for MD simulations. The *ab*-projection with the corresponding unit cells (left) and the *ac*-projection (right).
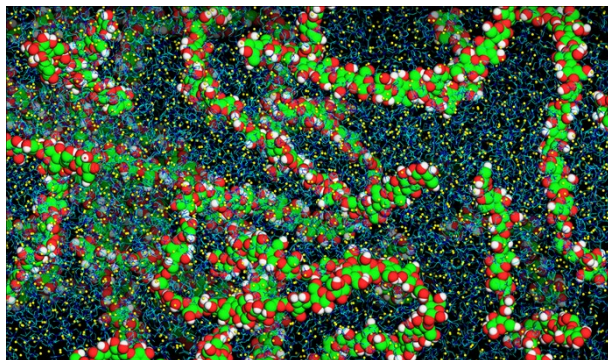
Fig. S1 Cellulose dissolved in 1-allyl-3-methylimidazolium chloride. green/red/white spheres: cellulose, blue sticks: 1-allyl-3-methylimidazolium cation, yellow spheres: chloride anion
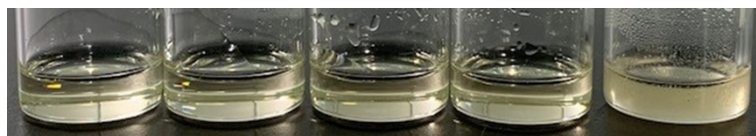
Fig. S2 Photograph of [N$_{2,2,2,6}$]OAc/DMSO (= 3/7, w/w)/cellulose solutions. Cellulose concentrations are 5, 7.5, 10, 12.5, and 15 wt% (from left to right, 5–12.5 wt%: soluble, 15 wt% insoluble).
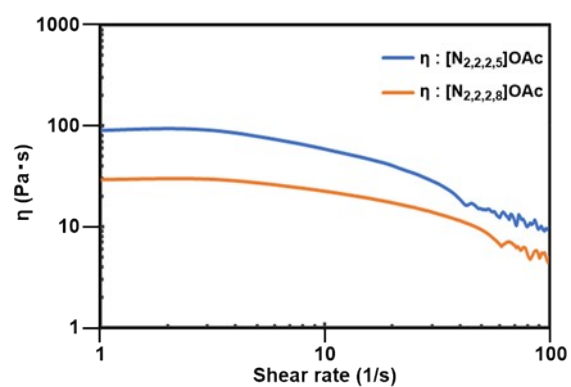
Fig. S3 Shear rate-dependent viscosity in rotational mode of the $[N_{2,2,2,5}]$OAc and $[N_{2,2,2,8}]$OAc solutions with 5 wt% cellulose at 80 °C
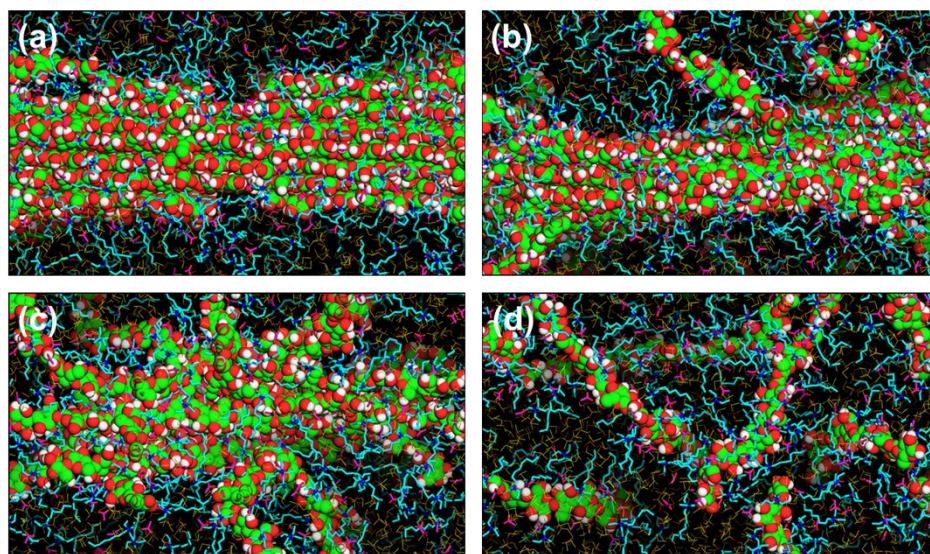
Fig. S4 Time course of cellulose dissolution in [$N_{2,2,2,8}$]OAc, (a) 0.05 μs, (b) 1 μs, (c) 2.5 μs, (d) 3.5 μs. green/red/white spheres: cellulose, blue sticks: [$N_{2,2,2,8}$]cation, pink sticks: acetate anion, yellow sticks: DMSO
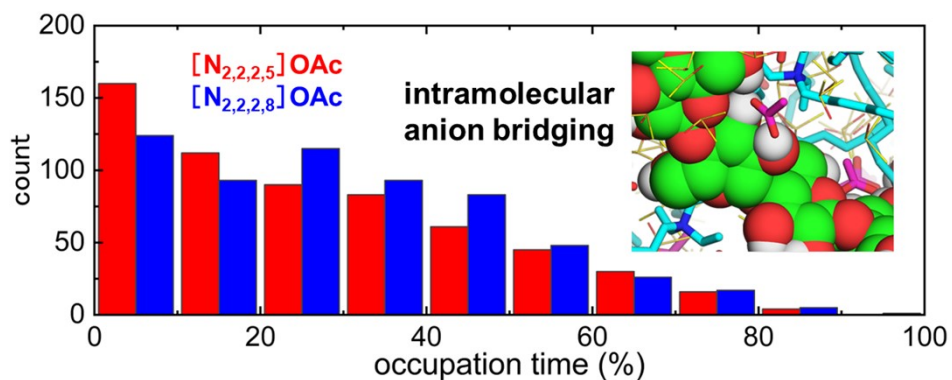
Fig. S5 Anion bridging formation within and between cellulose molecules (distribution of time occupancy rates for anion bridging formation obtained from the MD trajectory analysis of the final 0.5 µs at 80°C) green/red/white spheres: cellulose, blue sticks: [$N_{2,2,2,8}$]cation, pink sticks: acetate anion, yellow sticks: DMSO
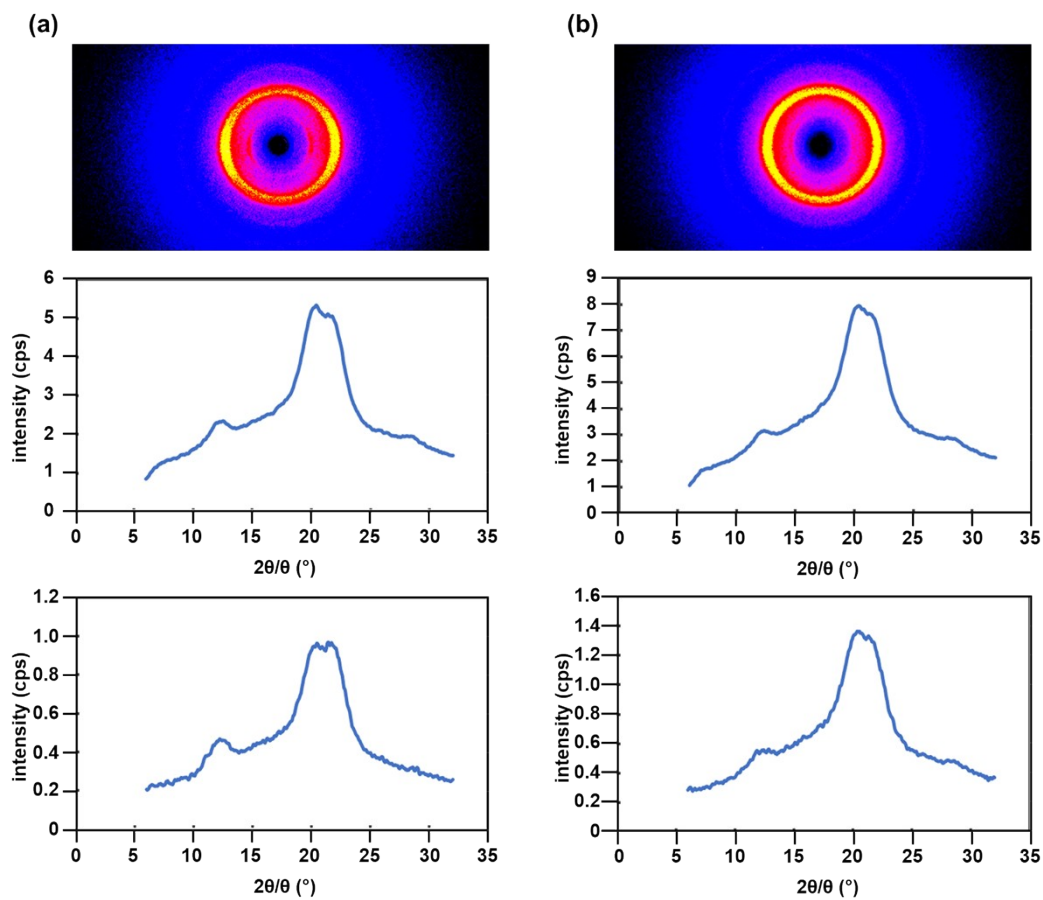
Fig. S6 WAXS profile, 2D pattern (top), and 1D profile (center, bottom) (diffraction angle $2\theta = 6\text{–}32°$, azimuth angle $\beta = 0\text{–}360°$, center; $60\text{–}120°$; bottom) of regenerated cellulose film from (a) $[N_{2,2,2,5}]$OAc/cellulose solution and (b) $[N_{2,2,2,8}]$OAc/cellulose solution.

References

(1) M. J. Kamlet, *et al.*, *J. Am. Chem. Soc.*, 1976, **98**, 377-383.

(2) A. Isogai, *et al.*, *Sen'i Gakkaishi*, 1990, **46**, 324-329.

(3) Y. Nishiyama, *et al.*, *J. Am. Chem. Soc.*, 2002, **124**, 9074-9082.