SUPPORTING INFORMATION

A Reversible Supramolecular Assembly Containing Ionic Interactions and Disulfide Linkages

Xinrong Lin, Guilhem Godeau, and Mark W. Grinstaff

Experimental Section

General Procedure for Thermal Measurements

Thermalgravimetric Analysis (TGA) measurements were performed with TGA Q50. All samples were heated from 20 to 500 ^{o}C at a heating rate of 50 ^{o}C /min. Samples were also tested with Differential Scanning Calorimetry (DSC) at a heating rate of 20 ^{o}C /min and a cooling rate of 10 ^{o}C /min from -100 to 200 ^{o}C. All samples were measured between 5 to 10 mg and scanned for three heat-cool cycles.

General Procedure for Rheological Measurement

About 1 mL of each sample was placed on an AR 1000 Controlled Strain Rheometer from TA Instruments equipped with a Peltier temperature control using a 20 mm diameter parallel aluminum plate. In order to load the sample on the geometry properly, samples were first rolled to pellets then melted on a Peltier heating block at 60 ^{o}C to ensure the sample fully covered the geometry. The gap was set to be 1.0-2.0 mm in all the runs. To minimize the effect of moisture in the air, the experiments were performed in a glove bag filled with nitrogen gas. Prior to each test, a pre-shear was done at shear rate 100 1/s for 10 s to eliminate the physical memory of the sample, followed by a 15 minutes equilibrium step in order for the sample to reach a steady state condition.

Strain amplitude from 0.1 to 10% was determined to lie within the linear viscoelastic region (LVR) via an oscillatory strain sweep at a fixed frequency (1 Hz). Dynamic shear measurements covering 0.628- 628 rad/s were conducted to obtain dynamic viscosity, storage modulus (G'), loss modulus (G") and phase angle. Measurements were typically performed at 25 ^{o}C unless temperature effect was investigated. Oscillatory temperature sweep was conducted from 10 ^{o}C to 95 ^{o}C with increment of 5 ^{o}C and 1 minute equilibrium at each temperature. Strain and frequency were set to be 1.0% and 1 Hz, respectively.

Steady State Flow was conducted at shear rate 0.01-50 1/s from 25 ^{o}C to 95 ^{o}C. The values of the plateaus found at very low shear rates, where the viscosity did not change as the shear rates increase, were taken as the zero shear viscosity at each temperature. A creep-recovery experiment was performed by subjecting the sample to 500 Pa of stress for 8 min. Then the stress was totally removed and the sample was left for deformation recovery for 8 min.

Conductivity Measurement

The conductivity measurements were performed using a Conductivity Meter (K912, Consort) that has a 4-electrode cell to prevent the polarization error and fouling of the electrode. Ionic liquid electrolytes were dried at 100 °C under high-vacuum overnight to remove any trace amount of moisture before testing. Samples were loaded in test tubes sealed with septum stopper in order to maintain N_2 environment. A heat block was used to control the temperature and stirring was maintained during the measurement to promote the homogeneity. A 30-minute equilibration time was used at each temperature.

Synthesis of 6-bromohexyl thioacetate

In a round bottom flask charged with a stir bar and 2.5 g potassium ethanethioate (21.9 mmol) in DMF, 10.7 g 1,6-dibromohexane (43.8 mmol) was added dropwise via syringe. The mixture was stirred at room temperature for 24 hours. The solvent is removed under reduced pressure. The formed oil is dissolved in 100 mL of DCM and washed by 2*30 mL of water and 30 mL of brine. The organic layer is dried on anhydrous $MgSO_4$ and the solvent is removed under reduced pressure. Pure compound are finally obtained after purification on column (from 99/1 to 95/5; cyclohexane/ethyl acetate) (Yield: 61 %). R_f: 0.56 (9/1; Cyclohexane/Ethyl acetate). ^{1}H NMR (400M, $CDCl_3$): 1.31-1.41 (m, 4H); 1.49-1.55 (m, 2H); 1.75-1.83 (m, 2H); 2.26 (s, 3H); 2.80 (t,*J*=8 Hz, 2H); 3.34 (t, *J*=8 Hz, 2H). ^{13}C NMR ($CDCl_3$): 27.6; 27.8; 28.9; 29.3; 30.6; 32.5; 33.7; 195.6. NMR ^{31}P (161 MHz, $CDCl_3$): 31.3. HRMS (m/z): 239.1721

Synthesis of (6- acetylthio) hexyl) tributylphosphonium bromide

An oven-dried round bottom flask was charged with a stir bar and 2.0 g 6-bromohexyl thioacetate (8.4 mmol) in glove box. 1.7 g $P(Bu)_3$ (8.4 mmol) was added via a syringe. Then, the vessel was sealed with septum and moved out from the glove box, and stirred at 80 °C for 24 hours. After reaction, the mixture was concentrated under vacuum to afford the crude product (yield: 92%). R_f: 0.61 (9/1; DCM/Methanol). ^{1}H NMR ($CDCl_3$): 0.91 (t, *J*=6 Hz, 9H); 1.34-1.61 (m, 20H); 2.26 (s, 3H); 2.32-2.46 (m, 8H); 2.78 (t, *J*=6 Hz, 3H). ^{13}C NMR ($CDCl_3$): 13.3; 13.4; 18.3; 18.6; 19.3; 19.5; 21.4; 21.5; 23.6; 23.9; 24.1; 26.7; 27.7; 28.0; 28.5; 28.9; 29.7; 30.0; 30.5; 195.7. ^{31}P NMR ($CDCl_3$): 32.7. HRMS (m/z): 361.5235

Synthesis of tributyl (6-mercaptohexyl) phosphonium bromide

In a round bottomed flask 4.4 g of compound *(6- acetylthio) hexyl) tributylphosphonium bromide* (10 mmol) are dissolved in 50 mL of methanol and 50 mL of 0.2 M HBr methanol solution are added. Dean-stark apparatus and refregerent are adapted and the mixture is heated 2 h at 95 °C The solvant is removed under reduced pressure. 3.88 g of compound are obtained after purification on column (95/5, DCM/Methanol). Yield: 97 %. R_f: 0.58 (9/1; DCM/Methanol) ^{1}H NMR ($CDCl_3$): 0.97 (t, *J*=6 Hz, 9H); 1.41-1.85 (m, 20H); 2.37-2.58 (m, 10H). ^{13}C NMR ($CDCl_3$): 13.5; 13.6; 18.6; 18.9; 19.5; 19.8; 21.7;

21.8; 23.7; 23.8; 24.0; 24.4; 27.0; 27.5; 28.2; 30.0; 30.3; 33.4. ^{31}P NMR ($CDCl_3$): 32.7. HRMS (m/z): 319.1816

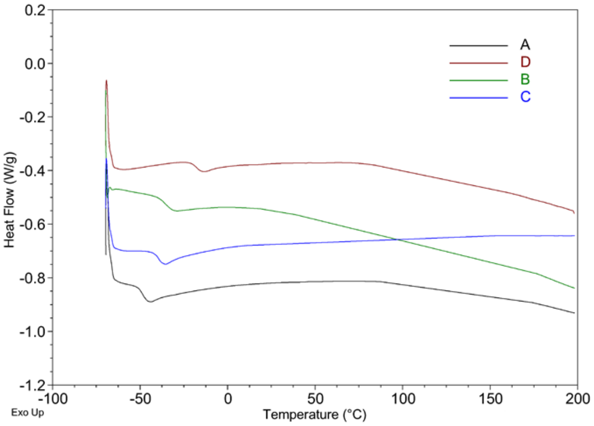

Figure SI1. Glass transition temperatures of the ionic liquids (ILs) and ILs with EDTA: **A**: disulfide-diphosphonium/EDTA assembly (i.e., the network); **B**: thiol-monophosphonium/EDTA mixture; **C**: disulfide diphosphonium IL; and **D**: thiol monophosphonium IL.