

Supporting Information

Thermally-Stable, Room-Temperature Ionic Liquids from Amidines and Amines by Adding CS₂. Comparison with CO₂ Adducts

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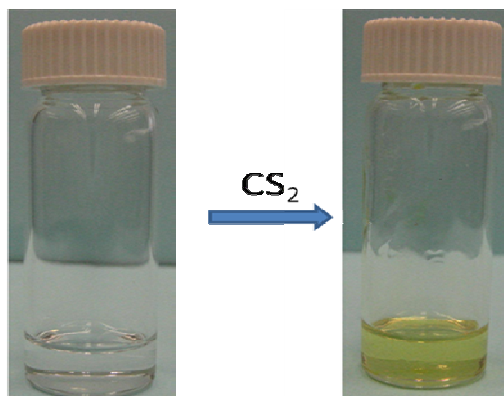


Figure S1. Photos of a 1/1 (mol/mol) **C6**/cyclohexylamine mixture before and after addition of one equivalent of CS_2 .

1. Characterizations of D-A-S RTILs

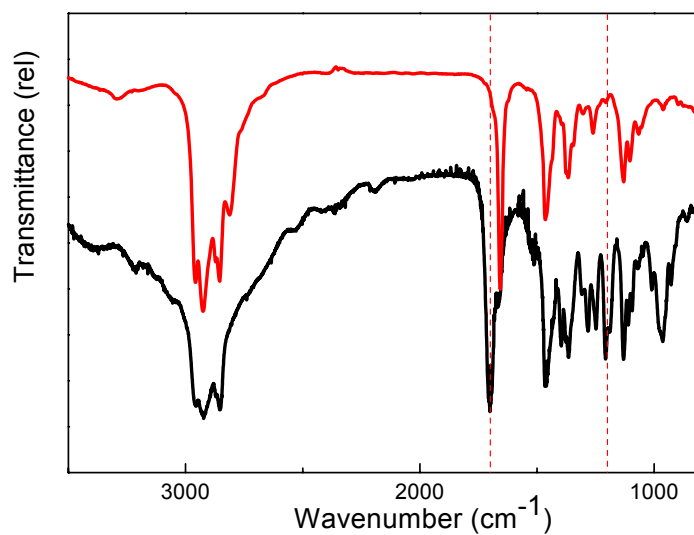


Figure S2(a). FT-IR spectra of **C16**/di-*n*-butylamine (red) and **C16**-di-*n*-butylamine- CS_2 (black).

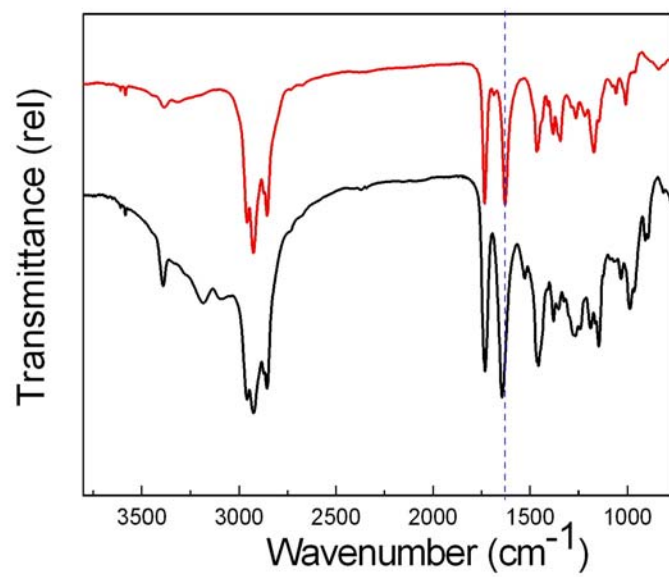


Figure S2(b). FT-IR spectra of **C8/IleC8** (red) and **C8-IleC8-CS₂** (black).

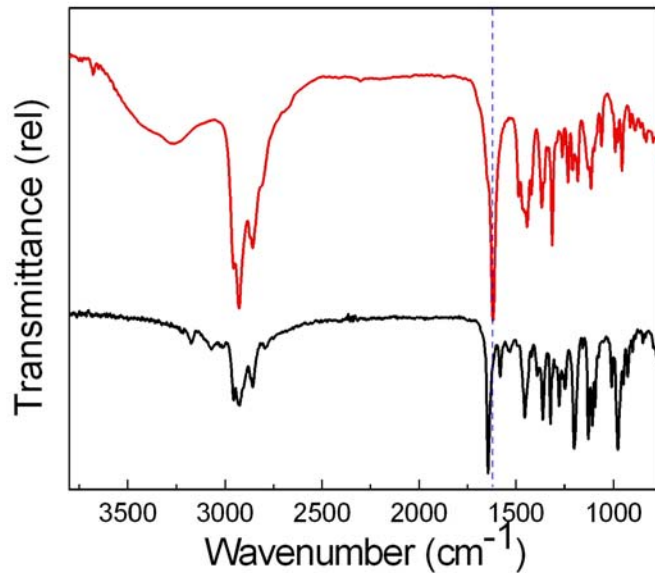


Figure S2(c). FT-IR spectra of **DBU/ di-*n*-butylamine** (red) and **DBU-di-*n*-butylamine-CS₂** (black).

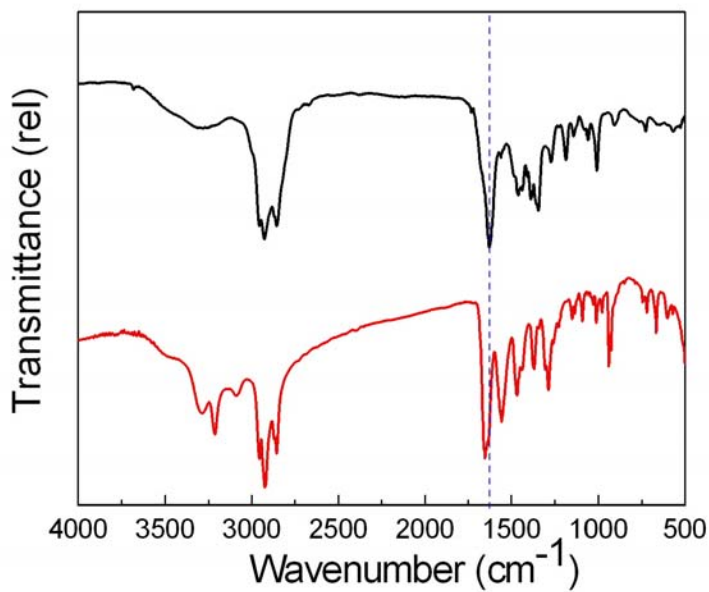


Figure S2(d). FT-IR spectra of **C6/octylamine** (black) and **C6-octylamine-CS₂** (red).

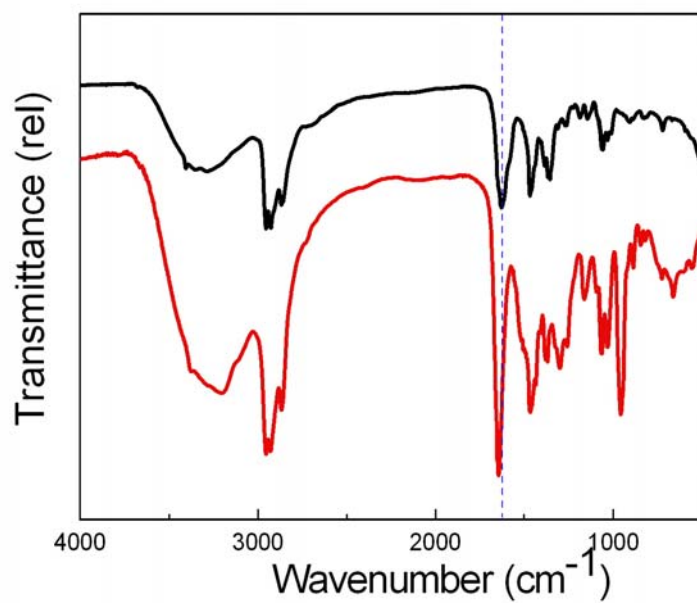


Figure S2(e). FT-IR spectra of **C6/LeuOH** (black) and **C6-LeuOH-CS₂** (red).

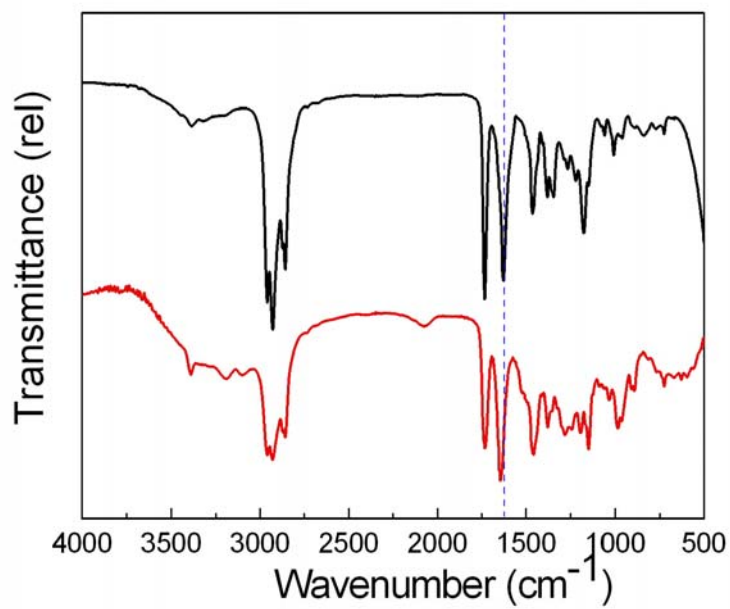


Figure S2(f). FT-IR spectra of **C6/IleC8** (black) and **C6-IleC8-CS₂** (red).

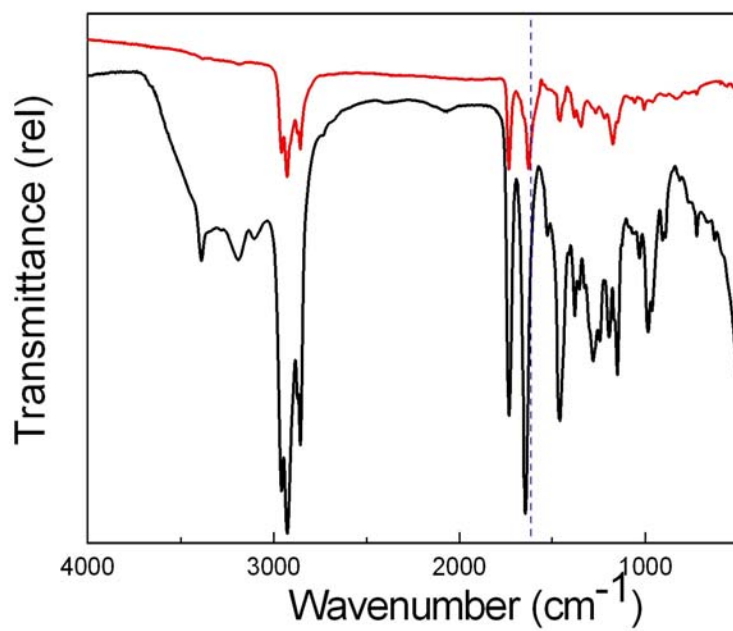


Figure S2(g). FT-IR spectra of **C4/IleC8** (red) and **C4-IleC8-CS₂** (black).

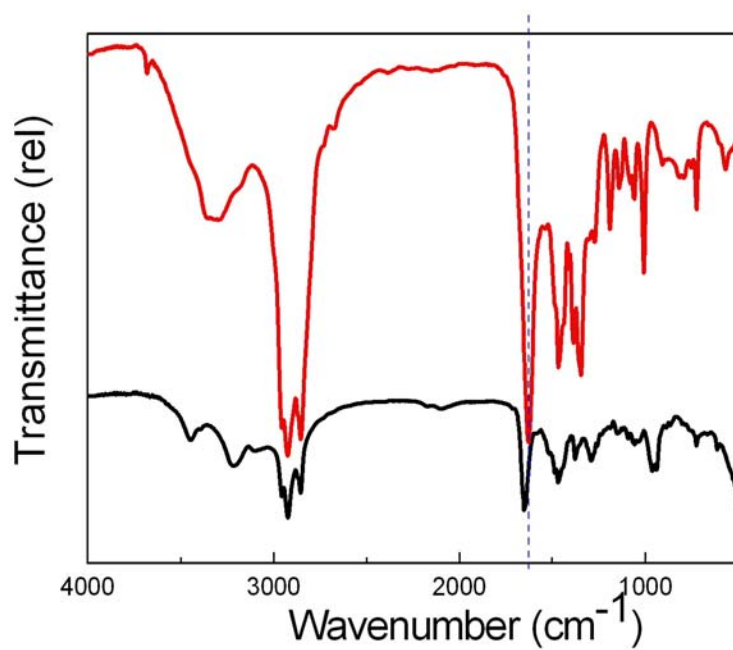


Figure S2(h). FT-IR spectra of **C8/octylamine** (red) and **C8-octylamine-CS₂** (black).

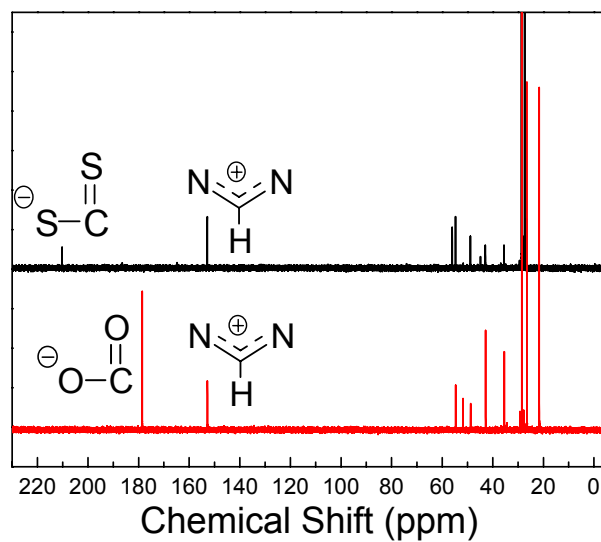
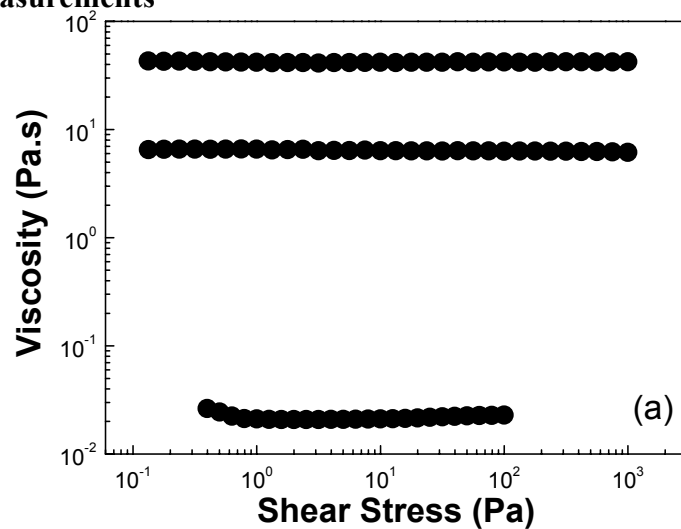


Figure S3. ^{13}C NMR of **tC4**-*t*-butylamine- CS_2 in D_2O (black) and **tC4**-*t*-butylamine- CS_2 after treatment with acetic acid (red) in D_2O .

2. Viscosity Measurements



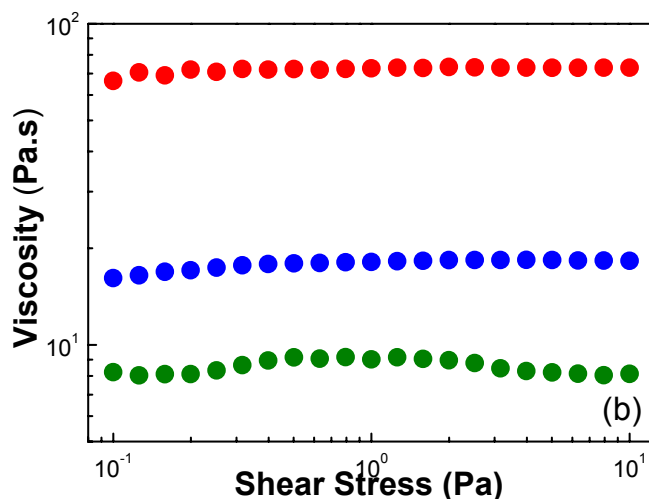


Figure S4. (a) Viscosities (Pa·s) at 25 °C of **C8-LeuOH-CS₂**, **C8-LeuOH-CO₂** and **C8/LeuOH** (from top to bottom) as a function of shear stress (Pa). (b) Viscosities (Pa·s) of **C8-IleC8-CS₂** at (from top to bottom) 25, 35, and 45 °C.

3. UV-vis spectroscopic measurements

An aliquot of a methanol solution of **DAPNE**¹ was transferred into a sample vial and the methanol was removed by blowing N₂ gas over it. Then, an aliquot of the solvent of interest was added and stirred until the solid completely dissolved. The concentrations of **DAPNE** were 2.4 mM. The absorption spectra were recorded in a 1 mm path length quartz cuvette. The wavelength maxima are collected in Table S1.

Table S1. Absorption maxima (λ_{max} , nm) of 2.4 mM **DAPNE** in various solvents² and RTILs.³

solvent	λ_{max} (nm)
n-heptane	393
n-decane	396
C8/Hexylamine	423
C8/LeuOH	424
Toluene	425
THF	427
Acetone	433
C8-Hexylamine-CO ₂	438
C8-Hexylamine-CS ₂	440
C8-ValOH-CO ₂	443
C8-LeuOH-CS ₂	444
DMF	446
DMSO	456

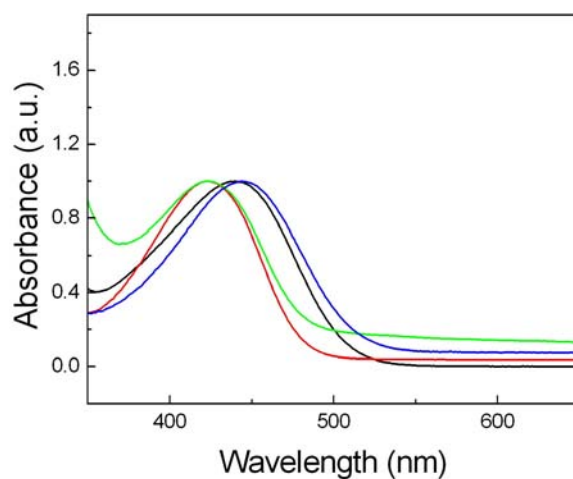


Figure S5. UV-vis absorption spectra of DAPNE in **C8**/hexylamine (red), **C8/LeuOH** (green), **C8**-hexylamine-CS₂ (black), and **C8-LeuOH**-CS₂ (blue).

4. Density measurements:⁴

Densities were measured by a method that yields only approximate values. For the purpose that they were used, to construct Walden plots, the values obtained are adequate. An aliquot of C4-hexylamine-CS₂ was weighed in a 1.00 mL volumetric flask that was filled to the mark initially at room temperature. The flask was heated in stages to progressively higher temperatures in a GC oven and equilibrated at each temperature for 15 min before the excess volume from thermal expansion was removed rapidly by syringe and the flask was reweighed. Because the density changes are small over the temperature range investigated (Figure S6), the probable experimental errors have little effect on the overall conclusions derived from them.

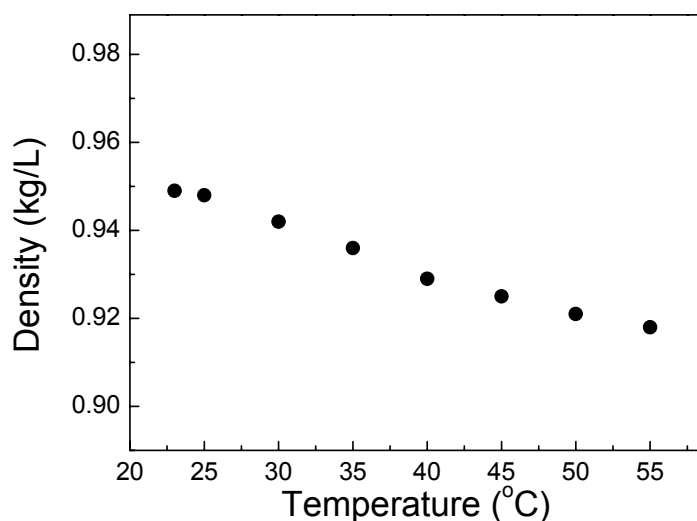


Figure S6. Density of C4-hexylamine-CS₂ at different temperatures.

5. Conductivity and viscosity measurements

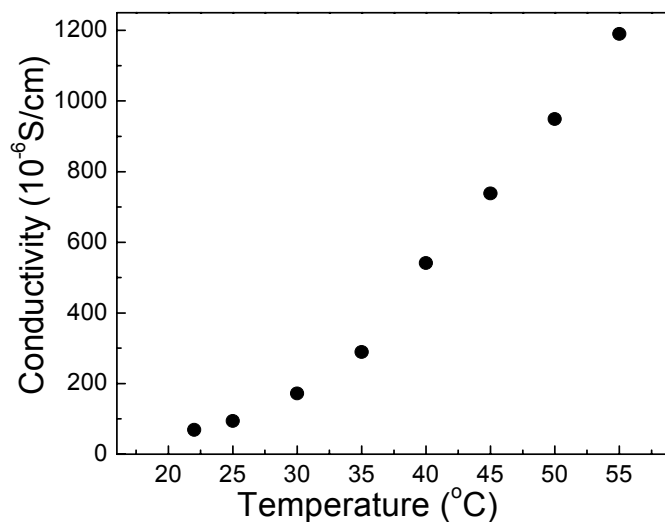


Figure S7. Conductivities of neat C4-hexylamine-CS₂ at various temperatures.

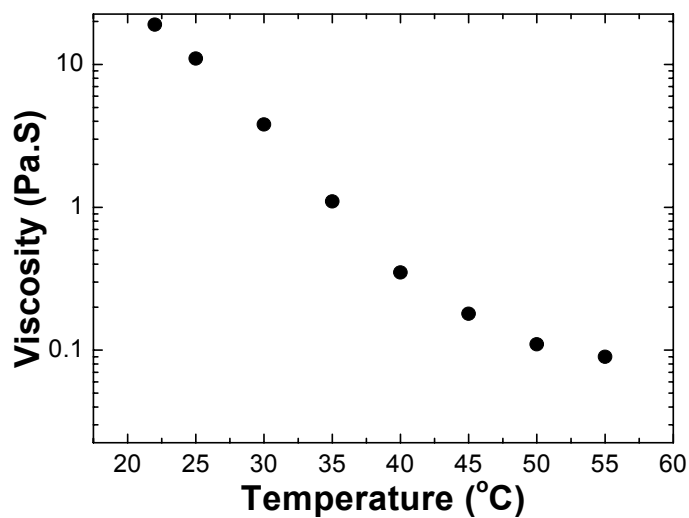


Figure S8. Viscosities of neat C4-hexylamine-CS₂ at various temperatures.

Table S2. Physicochemical properties of some D-A-S RTILs at room temperature, including density (ρ), viscosity (η), and conductivity (σ).

D-A-S	ρ (kg/L)	η (Pa·s)	σ (10 ⁻⁶ S/cm)
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C4 -hexylamine-CS ₂	0.952	9	75
C6 -hexylamine-CS ₂	0.958	23	64
C8 -hexylamine-CS ₂	0.966	63	39

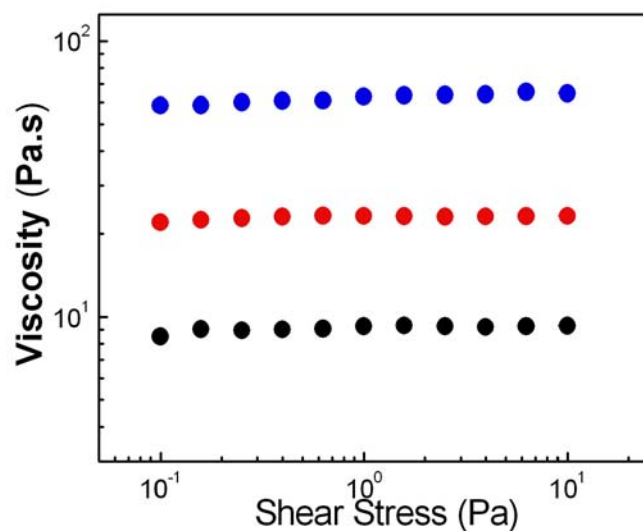


Figure S9. Viscosities (Pa.s) of samples as a function of shear stress (Pa) at 25 °C. From bottom to top: **C4**-hexylamine-CS₂ (black), **C6**-hexylamine-CS₂ (red), and **C4**-hexylamine-CS₂ (blue).

6. Thermolyses.

General procedure for synthesis of tC4-t-butylamine-CS₂ and separation of its thermolysis products. CS₂ liquid (1 mole equivalent) was added slowly to a stirred chloroform solution containing equal molar amounts of **tC4** and *tert*-butylamine, in a round bottom flask. The flask was placed in an ice-water bath during the CS₂ addition (*Warning*: CS₂ is a toxic liquid that should be handled carefully in a well ventilated area.) to dissipate the heat from the exothermic reaction. The mixture was stirred for 1 h at room temperature. Then, the temperature was raised to 120 °C for 2 h. The products were separated by column chromatography (silica gel; 3:1 and 2:1 hexanes:ethyl acetate as eluants) and were identified spectroscopically, using literature assignments for comparison; the literature citations are noted after the name of each compound;

the spectroscopic data below are for the isolated products. Before separation by column, the data from the NMR of the mixture indicated a molar ratio of 58:42 *N-tert-Butyl-N',N'-dimethylthiourea* (**VIII**):*N,N'-Di-tert-butylthiourea* (**IX**).

*Tert-butyl isothiocyanate*⁵ (**V**): a liquid, C₅H₉NS. ¹H NMR (400MHz, CDCl₃) δ = 1.37 (9H, s, C(CH₃)₃); ¹³C NMR (100MHz, CDCl₃) δ = 131 (C=S), 57 (C(CH₃)₃), 30.7 (C(CH₃)₃); IR (thin film) ν = 2981, 2081, 1975, 1368, 1207 cm⁻¹; MS (EI) m/z (%) 115.

*Tert-butyl thioformamide*⁶ (**VI**): a liquid, C₅H₁₁NS. ¹H NMR (400MHz, CDCl₃) δ = 1.36 (9H, s, C(CH₃)₃), 7.6-8.0 (1H, br, s, NH), 9.25-9.28 (1H, d, J=7.8Hz, CH); ¹³C NMR (100MHz, CDCl₃) δ = 187.7 (C=S), 55.8 (C(CH₃)₃), 29.8 (C(CH₃)₃); IR (thin film) ν = 1567, 1369, 1041 cm⁻¹; MS m/z (M⁺) 117.

*N,N-Dimethyl thioformamide*⁷ (**VII**): a liquid, C₃H₇NS. ¹H NMR (400MHz, CDCl₃) δ = 3.27-3.29 (6H, d, J=4.6 Hz, N(CH₃)₂), 9.2 (1H, s, CH); ¹³C NMR (100MHz, CDCl₃) δ = 188.2 (C=S), 45.3 (N(CH₃)₂), 37.2 (N(CH₃)₂); IR (thin film) ν = 1540, 1397, 1130, 1040 cm⁻¹; MS m/z (M⁺) 89.

*N-tert-Butyl-N',N'-dimethylthiourea*⁸ (**VIII**): a white solid, mp 85-88 °C (no reported lit value); C₇H₁₆N₂S. ¹H NMR (400MHz, CDCl₃) δ = 1.54 (9H, s, C(CH₃)₃), 3.21 (6H, s, N(CH₃)₂) 5.1-5.3 (1H, br, s, NH); ¹³C NMR (100MHz, CDCl₃) δ = 181.2 (C=S), 56.0 (C(CH₃)₃), 29.7 (C(CH₃)₃); IR (ATR) ν = 1548, 1393, 1346, 1131, 1050 cm⁻¹; MS m/z (M⁺) 160.

*N,N'-Di-tert-butylthiourea*⁹ (**IX**): a white solid, mp 128-130 °C (lit.⁹ mp 131-132 °C); C₉H₂₀N₂S. ¹H NMR (400 MHz, CDCl₃) δ = 1.48 (18H, s, C(CH₃)₃), 5.7-5.8 (2H, br, NH); ¹³C NMR (100MHz, CDCl₃) δ = 180.2 (C=S), 54.0 (N(CH₃)₂); IR (ATR) ν = 3300, 1540, 1320, 1210 cm⁻¹. MS m/z (M⁺) 188.

Procedures for identification of dimethylamine and t-butylamine upon thermolyses of

tC4-t-butylamine-CS₂. A HCl/D₂O solution was prepared by bubbling HCl gas (generated by dropping sulfuric acid into hydrochloric acid and passed through a Drierite tube) into D₂O in a round-bottom flask. Then, the vapor from thermolysis of ***tC4-t-butylamine-CS₂*** was introduced into the HCl/D₂O solution that had been cooled in an ice-water bath. The peaks characteristic of the hydrochloride salts of dimethylamine and *t*-butylamine were found in the ¹H NMR and ¹³C NMR spectra.

*Dimethylammonium chloride*¹⁰: ¹H NMR (400 MHz, CDCl₃) δ = 2.88 (6H, s, N(CH₃)₂); ¹³C NMR (100 MHz, CDCl₃) δ = 32.6 (N(CH₃)₂).

*Tert-butylammonium chloride*¹¹: ¹H NMR (400 MHz, CDCl₃) δ = 1.10 (9H, s, C(CH₃)₃); ¹³C NMR (100 MHz, CDCl₃) δ = 26.5 (C(CH₃)₃), 48.8 (C(CH₃)₃).

7. TGA curves of some representative D-A-S RTILs

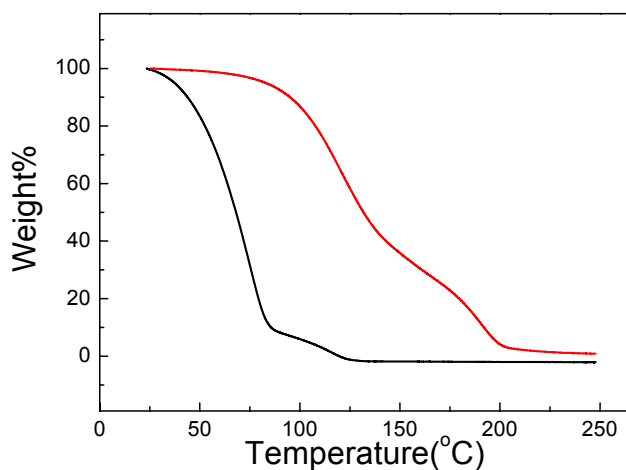


Figure S10 (a). TGA curves of **C4**/octylamine (black) and **C4**-octylamine-CS₂ (red).

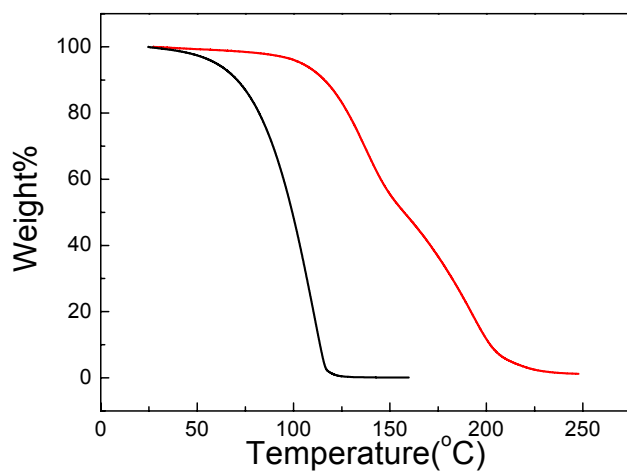


Figure S10 (b). TGA curves of **C8/ProOH** (black) and **C8-ProOH-CS₂** (red).

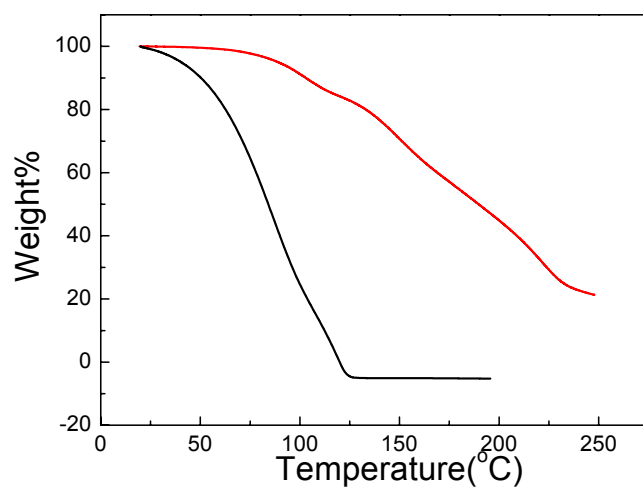
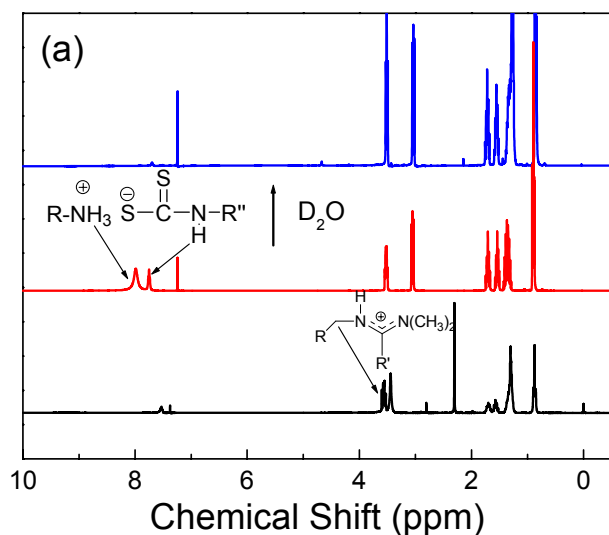


Figure S10 (c). TGA curves of **C8/octylamine** (black) and **C8-octylamine-CS₂** (red).

8. Transformation from ammonium dithiocarbamates to amidinium dithiocarbamates.

CS₂ liquid (0.16 g and 21 mmol) was added slowly to a round-bottom flask containing a

stirred solution of 0.43 g (42 mmol) *n*-hexylamine in 2 mL chloroform-*d*. The solution was stirred for 30 min at room temperature in a dry atmosphere. ^1H and ^{13}C NMR spectra of a sample were recorded and shown to be the ammonium dithiocarbamate (Figure S11a). Then, 0.71 g (42 mmol) C6 amidine and 0.16 g (21 mmol) CS_2 were added. After another 30 min of stirring, ^1H and ^{13}C NMR (Figure S11b) of an aliquot were recorded. They demonstrated that the product was the amidinium dithiocarbamate without any detectable amount of ammonium dithiocarbamate.



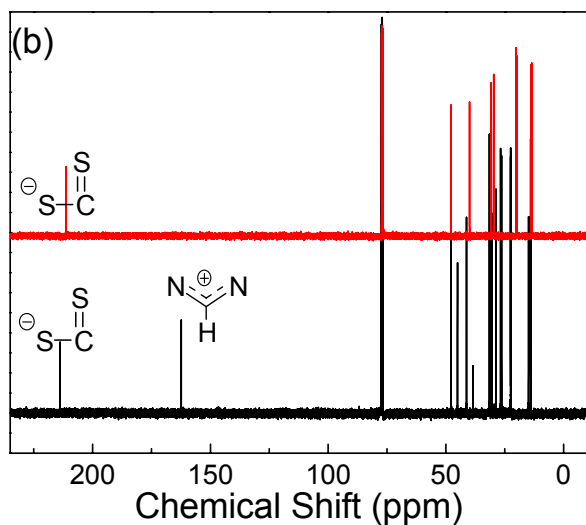


Figure S11. (a) ^1H NMR spectra in CDCl_3 of *n*-hexylamine- CS_2 before (red) and after (black) adding 1.0 equivalent **C6** and 0.5 equivalent CS_2 . The blue spectrum was obtained by adding one drop of D_2O to the *n*-hexylamine- CS_2 in CDCl_3 sample as a means to verify the locations of the N—H peaks in the red spectrum. (b) ^{13}C NMR spectra in CDCl_3 of *n*-hexylamine- CS_2 before (red) and after (black) adding 1.0 equivalent **C6** and 0.5 equivalent CS_2 . The concentrations are lower than described above.

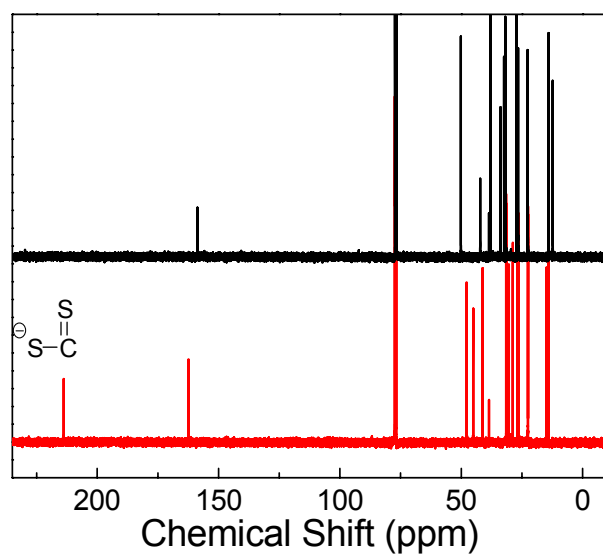
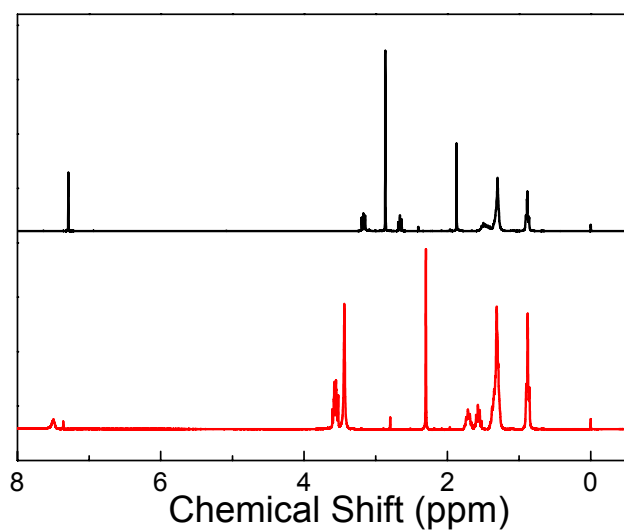


Figure S12. ^1H (a) and ^{13}C (b) NMR spectra in CDCl_3 of **C6**/*n*-hexylamine (black) and **C6**-*n*-hexylamine- CS_2 (red).

9. NMR spectra of D/A and D-A-S

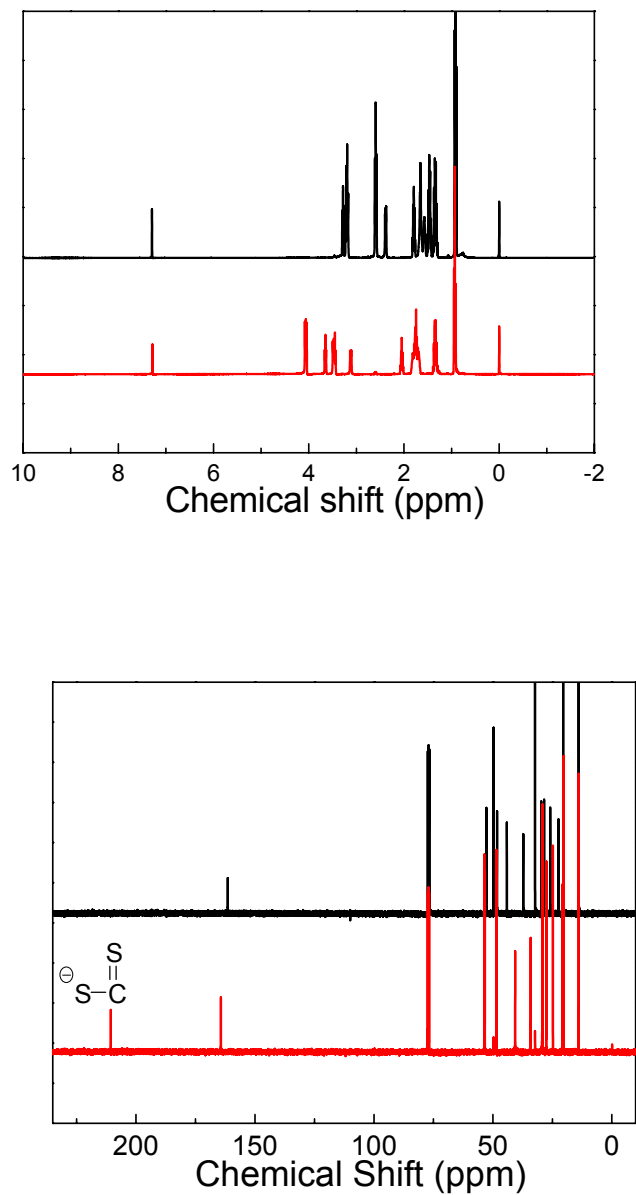


Figure S13. ^1H (a) and ^{13}C (b) NMR spectra in CDCl_3 of **DBU**/di-*n*-butylamine (black) and **DBU**-di-*n*-butylamine- CS_2 (red).

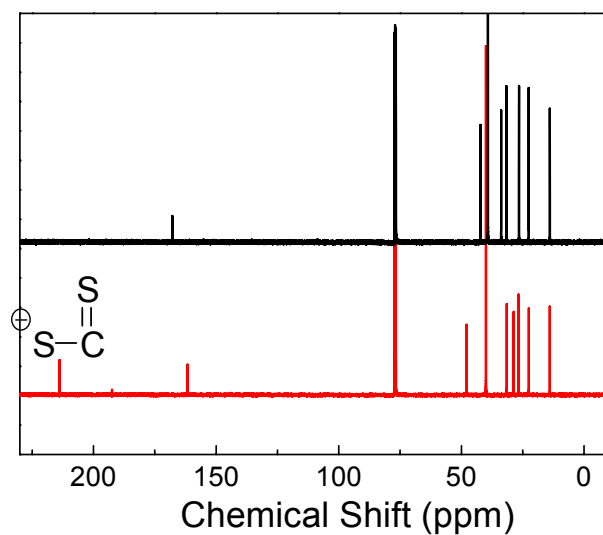
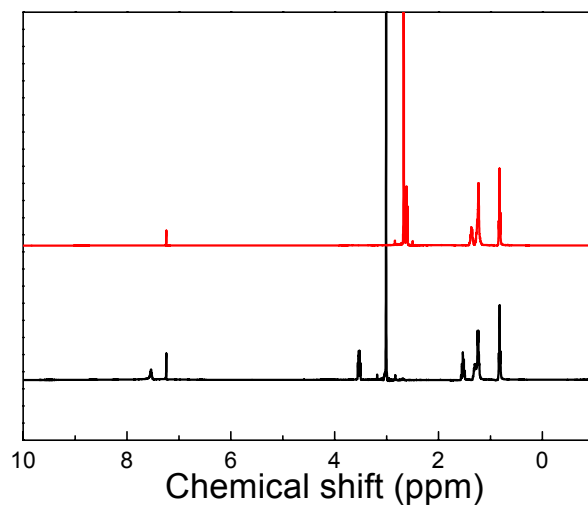


Figure S14. ^1H (a) and ^{13}C (b) NMR spectra in CDCl_3 of **TMG**/*n*-hexylamine (black) and **TMG**-*n*-hexylamine- CS_2 (red).

(1) (a) Reichardt, C. *Chem. Soc. Rev.* **1992**, *21*, 147–153. (b) Reichardt, C. *Chem. Rev.* **1994**, *94*,

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