

Supplementary Information

Dimethyl phosphorothioate and phosphoroselenoate ionic liquids as solvent media for cellulosic materials

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Experimental details of O,*Se*-dimethylphosphoroselenoate compounds

1-Allyl-3-methylimidazolium O,*Se*-dimethylphosphoroselenoate 1b. 1-Allyl-3-methylimidazolium chloride (10.00 g, 63.04 mmol), sodium *O,Se*-dimethylphosphoroselenoate (13.30 g, 63.04 mmol). Yield: 13.48 g, n_D^{20} : 1.5463, density: 1.299 g/ml.

$\nu_{\max}/\text{cm}^{-1}$: 3138, 3050, 2858, 1645, 1562, 1448, 1424, 1336, 1270, 1240, 1167, 1062, 1046, 995, 940, 736, 675, 623, 536.

$^1\text{H NMR}$ (300 MHz, $\text{DMSO-}d_6$): δ 1.79 (1.83H, d, $J=9.7$ Hz, $\text{P}(\text{SeCH}_3)$), 3.30 (1.9H, d, $J=12.7$ Hz, $\text{P}(\text{OCH}_3)$), 3.88 (2H, s, NCH_3), 4.89 (2H, d, $J=6.0$ Hz, $\text{NCH}_2\text{CH}=\text{CH}_2$), 5.28 (2H, m, $\text{NCH}_2\text{CH}=\text{CH}_2$), 6.01 (1H, m, $\text{NCH}_2\text{CH}=\text{CH}_2$), 7.83 (1H, s, NCHCHN), 7.85 (1H, s, NCHCHN), 9.53 (1H, s, NCHN) ppm.

$^{13}\text{C NMR}$ (75 MHz, $\text{DMSO-}d_6$): δ 3.2 (d, $J=4.5$ Hz, $\text{P}(\text{SeCH}_3)$), 35.7 (NCH_3), 50.6 ($\text{NCH}_2\text{CH}=\text{CH}_2$), 51.5 (d, $J=6.4$ Hz, $\text{P}(\text{OCH}_3)$), 120.0 ($\text{NCH}_2\text{CH}=\text{CH}_2$), 122.3 ($\text{NCH}_2\text{CH}_2\text{CH}_3$), 123.7, (NCHCHN) 131.9, ($\text{NCH}_2\text{CH}=\text{CH}_2$), 136.9 (NCHN) ppm.

1-Butyl-3-methylimidazolium O,*Se*-dimethylphosphoroselenoate 2b. 1-Butyl-3-methylimidazolium chloride (12.08 g, 57.25 mmol), sodium *O,Se*-dimethylphosphoroselenoate (10.00 g, 57.25 mmol). Yield: 13.60 g, n_D^{20} : 1.5267, density: 1.229 g/ml.

$\nu_{\max}/\text{cm}^{-1}$: 3048, 2957, 2932, 2871, 1567, 1463, 1382, 1337, 1270, 1240, 1170, 1048, 901, 736, 654, 624, 535.

$^1\text{H NMR}$ (300 MHz, $\text{DMSO-}d_6$): δ 0.85 (3H, t, $J=7.5$ Hz, $(\text{CH}_2)_3\text{CH}_3$), 1.22 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.75 (3.2H, m, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{P}(\text{SeCH}_3)$), 3.29 (1.3H, d, $J=12.7$ Hz, $\text{P}(\text{OCH}_3)$), 3.87 (3H, s, NCH_3), 4.19 (2H, t, $J=7$ Hz, $\text{NCH}_2\text{-Pr}$), 7.82 (1H, s, NCHCHN), 7.90 (1H, s, NCHCHN), 9.59 (1H, s, NCHN) ppm.

$^{13}\text{C NMR}$ (75 MHz, $\text{DMSO-}d_6$): δ 3.1 (d, $J=4.3$ Hz, $\text{P}(\text{SeCH}_3)$), 13.3 ($(\text{CH}_2)_3\text{CH}_3$), 18.8 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 31.4 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 35.6 (NCH_3), 48.4 ($\text{NCH}_2\text{-Pr}$), 51.4 (d, $J=6.4$ Hz, $\text{P}(\text{OCH}_3)$), 122.3 (NCHCHN), 123.6 (NCHCHN), 136.89 (NCHN) ppm.

1-Methyl-3-propylimidazolium O,*Se*-dimethylphosphoroselenoate 3b. 1-Methyl-3-propylimidazolium chloride (10.00 g, 62.25 mmol), sodium *O,Se*-dimethylphosphoroselenoate (13.13 g, 62.25 mmol). Yield: 12.71 g, n_D^{20} : 1.5326, density: 1.274 g/ml.

$\nu_{\max}/\text{cm}^{-1}$: 3140, 3049, 2963, 2934, 2875, 1567, 1456, 1386, 1337, 1270, 1241, 1172, 1062, 1047, 901, 801, 736, 653, 624, 535.

$^1\text{H NMR}$ (300 MHz, $\text{DMSO-}d_6$): δ 0.80 (3H, t, $J=7.4$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_3$), 1.78 (2H, m, $\text{NCH}_2\text{CH}_2\text{CH}_3$), 1.79 (1.2H, d, $J=9.7$ Hz, $\text{P}(\text{SeCH}_3)$), 3.29 (1.4H, d, $J=12.7$ Hz, $\text{P}(\text{OCH}_3)$), 3.87 (3H, s, NCH_3), 4.16 (2H, t, $J=7.1$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_3$), 7.84 (1H, s, NCHCHN), 7.92 (1H, s, NCHCHN), 9.61 (1H, s, NCHN) ppm.

$^{13}\text{C NMR}$ (75 MHz, $\text{DMSO-}d_6$): δ 3.1 (d, $J=4.5$ Hz, $\text{P}(\text{SeCH}_3)$), 10.4 ($\text{NCH}_2\text{CH}_2\text{CH}_3$), 22.9 ($\text{NCH}_2\text{CH}_2\text{CH}_3$), 35.7 (NCH_3), 50.2 ($\text{NCH}_2\text{CH}_2\text{CH}_3$), 51.4 (d, $J=5.9$ Hz, $\text{P}(\text{OCH}_3)$), 122.3 (NCHCHN), 123.6 (NCHCHN), 136.8 (NCHN) ppm.

1-Benzyl-3-methylimidazolium O,*Se*-dimethylphosphoroselenoate 4b. 1-Benzyl-3-methylimidazolium chloride (1.15 g, 5.51 mmol), sodium *O,Se*-dimethylphosphoroselenoate (1.16 g, 5.51 mmol) were suspended in 25 ml of acetone (differing from the general synthetic procedure) and stirred at room temperature for 15 minutes. Afterwards, the mixture was ultrasonicated for 2 hours, and again stirred at room temperature for 24 hours. The suspension was filtered without the Celite layer, deviant from the general synthetic procedure. The remaining sodium chloride in the filter was very stropy, so it had to be washed seven times with acetone. After the solvent was removed with a rotary evaporator and by means of an oil pump vacuum at 80 °C (oil bath), a colourless viscous liquid was obtained. Yield: 1.17 g, n_D^{20} : 1.5832.

$\nu_{\max}/\text{cm}^{-1}$: 2934, 2832, 1708, 1561, 1497, 1455, 1363, 1334, 1270, 1238, 1181, 1082, 1045, 903, 822, 719, 697, 662, 624, 535.

$^1\text{H NMR}$ (300 MHz, $\text{DMSO-}d_6$): δ 1.80 (1.7H, d, $J=9.6$ Hz, $\text{P}(\text{SeCH}_3)$), 3.30 (1.9H, d, $J=12.8$ Hz, $\text{P}(\text{OCH}_3)$), 3.86 (3H, s, NCH_3), 5.46 (2H, s, NCH_2Ph), 7.40 (5H, m, $\text{CH}_{\text{o,m,p}}$), 7.76 (1H, s, NCHCHN), 7.87 (1H, s, NCHCHN), 9.52 (1H, s, NCHN) ppm.

$^{13}\text{C NMR}$ (75 MHz, $\text{DMSO-}d_6$): δ 3.2 (d, $J=4.2$ Hz, $\text{P}(\text{SeCH}_3)$), 35.8 (NCH_3), 51.4 (d, $J=6.2$ Hz, $\text{P}(\text{OCH}_3)$), 51.7 (NCH_2Ph), 122.3 (NCHCHN), 124.0 (NCHCHN), 128.4 (C_m), 128.7 (C_p), 128.9 (C_o), 135.1 (C_i), 136.9 (NCHN) ppm.

1-(2-Hydroxyethyl)-3-methylimidazolium O,*Se*-dimethylphosphoroselenoate 5b. 1-(2-Hydroxyethyl)-3-methylimidazolium chloride (1.15 g, 7.07 mmol), sodium *O,Se*-dimethylphosphoroselenoate (1.49 g, 7.07 mmol). Yield: 1.77 g, n_D^{20} : 1.5410.

$\nu_{\max}/\text{cm}^{-1}$: 3147, 3093, 2934, 1567, 1449, 1339, 1271, 1223, 1167, 1040, 672, 743, 652, 622, 535.

$^1\text{H NMR}$ (300 MHz, $\text{DMSO-}d_6$): δ 1.81 (2.4H, d, $J=9.7$ Hz, $\text{P}(\text{SeCH}_3)$), 3.30 (2.5H, d, $J=12.7$ Hz, $\text{P}(\text{OCH}_3)$), 3.69 (2H, t, $J=4.9$ Hz, $\text{NCH}_2\text{CH}_2\text{OH}$), 3.86 (3H, s, NCH_3), 4.23 (2H, t, $J=5.0$ Hz, $\text{NCH}_2\text{CH}_2\text{OH}$), 7.71 (1H, s, NCHCHN), 7.76 (1H, s, NCHCHN), 9.23 (1H, s, NCHN) ppm.

$^{13}\text{C NMR}$ (75 MHz, $\text{DMSO-}d_6$): δ 3.2 (d, $J=4.3$ Hz, $\text{P}(\text{SeCH}_3)$), 35.6 (NCH_3), 51.5 (d, $J=5.7$ Hz, $\text{P}(\text{OCH}_3)$), 51.5 ($\text{NCH}_2\text{CH}_2\text{OH}$), 59.4 ($\text{NCH}_2\text{CH}_2\text{OH}$), 122.7 (NCHCHN), 123.3 (NCHCHN), 137.0 (NCHN) ppm.

1-Allyl-3-butylimidazolium O,*Se*-dimethylphosphoroselenoate 7b. 1-Allyl-3-butylimidazolium chloride (4.59 g, 22.9 mmol), sodium *O,Se*-dimethylphosphoroselenoate (4.82 g, 22.9 mmol). Yield: 6.08 g, n_D^{20} : 1.5281, density: 1.21 g/ml.

$\nu_{\max}/\text{cm}^{-1}$: 3048, 2958, 2932, 2871, 1561, 1462, 1270, 1240, 1166, 1049, 994, 940, 735, 629, 535.

$^1\text{H NMR}$ (300 MHz, $\text{DMSO-}d_6$): δ 0.86 (3H, t, $J=7.4$ Hz, $(\text{CH}_2)_3\text{CH}_3$), 1.22 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.76 (2H, m,

$\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.79 (1.76H, d, $J=96$ Hz, $\text{P}(\text{SeCH}_3)$), 3.29 (1.7H, d, $J=12.6$ Hz, $\text{P}(\text{OCH}_3)$), 4.21 (2H, t, $J=7.1$ Hz, $\text{NCH}_2\text{-Pr}$), 4.89 (2H, d, $J=5.7$ Hz, $\text{NCH}_2\text{CH}=\text{CH}_2$), 5.30 (2H, m, $\text{NCH}_2\text{CH}=\text{CH}_2$), 6.05 (1H, m, $\text{NCH}_2\text{CH}=\text{CH}_2$), 7.83 (1H, s, NCHCHN), 7.94 (1H, s, NCHCHN), 9.62 (1H, s, NCHN) ppm.

^{13}C NMR (75 MHz, $\text{DMSO-}d_6$): δ 3.1 (d, $J=4.1$ Hz, $\text{P}(\text{SeCH}_3)$), 13.3 ($(\text{CH}_2)_3\text{CH}_3$), 18.8 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 31.4 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 48.5 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 50.7 ($\text{NCH}_2\text{CH}=\text{CH}_2$), 51.4 (d, $J=5.9$ Hz, $\text{P}(\text{OCH}_3)$), 120.0 ($\text{NCH}_2\text{CH}=\text{CH}_2$), 122.5 ($\text{NCH}_2\text{CH}_2\text{CH}_3$), 122.6 (NCHCHN), 131.9 ($\text{NCH}_2\text{CH}=\text{CH}_2$), 136.4 (NCHN) ppm.

1-Butyl-3-methylpyridinium *O*,*Se*-dimethylphosphoroselenoate 8b. 1-Butyl-3-methylpyridinium chloride (10.00 g, 53.85 mmol), sodium *O*,*Se*-dimethylphosphoroselenoate (11.36 g, 53.85 mmol). Yield: 15.19 g, n_D^{20} : 1.5502, density: 1.256 g/ml.

$\square_{\text{max}}/\text{cm}^{-1}$: 3010, 2957, 2931, 2872, 1633, 1505, 1465, 1505, 1465, 1384, 1269, 1242, 1158, 1048, 919, 814, 733, 690, 532.

^1H NMR (300 MHz, $\text{DMSO-}d_6$): δ 0.88 (3H, t, $J=7.4$ Hz, $(\text{CH}_2)_3\text{CH}_3$), 1.27 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.79 (1.7H, d, $J=9.5$ Hz, $\text{P}(\text{SeCH}_3)$), 1.88 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.50 (3H, s, CCH_3), 3.29 (1.9H, d, $J=12.7$ Hz, $\text{P}(\text{OCH}_3)$), 4.61 (2H, t, $J=7.3$ Hz, $\text{NCH}_2\text{-Pr}$), 8.06 (1H, t, $J=6.9$ Hz, NCHCHCHC), 8.47 (1H, d, $J=7.9$ Hz, NCHCHCHC), 9.09 (1H, d, 5.5 Hz, NCHCHCHC), 9.21 (1H, s, NCHC) ppm.

^{13}C NMR (75 MHz, $\text{DMSO-}d_6$): δ 3.1 (d, $J=4.6$ Hz, $\text{P}(\text{SeCH}_3)$), 13.3 ($(\text{CH}_2)_3\text{CH}_3$), 17.8 (CCH_3), 18.7 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 32.7 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 51.4 (d, $J=6.2$ Hz, $\text{P}(\text{OCH}_3)$), 60.2 ($\text{NCH}_2\text{-Pr}$), 127.3 (NCHCHCHC), 138.7 (NCHC), 142.1 (NCHCHCHC), 144.4 (NCHCHCHC), 145.7 (NCHC) ppm.

1-Methyl-1-propylpyrrolidinium *O*,*Se*-dimethylphosphoroselenoate 9b. 1-Methyl-1-propylpyrrolidinium chloride (7.76 g, 47.4 mmol), sodium *O*,*Se*-dimethylphosphoroselenoate (10.00 g, 47.40 mmol). Yield: 9.20 g, mp: 40-46°C.

$\square_{\text{max}}/\text{cm}^{-1}$: 3004, 2962, 2877, 1459, 1270, 1246, 1049, 1006, 976, 943, 905, 731, 532.

^1H NMR (300 MHz, $\text{DMSO-}d_6$): δ 0.87 (3H, t, $J=7.3$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_3$), 1.69 (2H, m, $\text{NCH}_2\text{CH}_2\text{CH}_3$), 1.78 (2.2H, d, $J=9.5$ Hz, $\text{P}(\text{SeCH}_3)$), 2.05 (4H, s, CH_2), 3.00 (3H, s, NCH_3), 3.27 (2.6H, d, $J=12.7$ Hz, $\text{P}(\text{OCH}_3)$), 3.32 (2H, m, $\text{NCH}_2\text{CH}_2\text{CH}_3$), 3.49 (4H, broad s, NCH_2) ppm.

^{13}C NMR (75 MHz, $\text{DMSO-}d_6$): δ 3.1 (d, $J=4.5$ Hz, $\text{P}(\text{SeCH}_3)$), 10.7 ($\text{NCH}_2\text{CH}_2\text{CH}_3$), 16.6 ($\text{NCH}_2\text{CH}_2\text{CH}_3$), 21.1 (2C, CH_2), 47.3 (NCH_3), 51.3 (d, $J=6.0$ Hz, $\text{P}(\text{OCH}_3)$), 63.3 (2C, NCH_2), 64.3 (NCH_2) ppm.

4-Ethyl-4-methylmorpholinium *O*,*Se*-dimethylphosphoroselenoate 10b.

4-Ethyl-4-methylmorpholinium chloride (8.07 g, 48.7 mmol), sodium *O*,*Se*-dimethylphosphoroselenoate (10.28 g, 48.74 mmol). Yield: 11.87 g.

$\square_{\text{max}}/\text{cm}^{-1}$: 2972, 2881, 1462, 1303, 1270, 1242, 1183, 1130, 1108, 1090, 1045, 953, 883, 847, 815, 732, 622, 533.

^1H NMR (300 MHz, $\text{DMSO-}d_6$): δ 1.22 (3H, t, $J=7.0$ Hz, NCH_2CH_3), 1.78 (1.2H, d, $J=9.5$ Hz, $\text{P}(\text{SeCH}_3)$), 3.14 (3H, s, NCH_3), 3.27 (1.4H, d, $J=12.6$ Hz, $\text{P}(\text{OCH}_3)$), 3.44 (4H, s, $\text{N}(\text{CH}_2\text{CH}_2)_2\text{O}$), 3.58 (2H, q, $J=7.2$ Hz, NCH_2CH_3), 3.89 (4H, s, $\text{N}(\text{CH}_2\text{CH}_2)_2\text{O}$) ppm.

^{13}C NMR (75 MHz, $\text{DMSO-}d_6$): δ 3.2 (d, $J=4.4$ Hz, $\text{P}(\text{SeCH}_3)$), 6.9 (NCH_2CH_3), 45.2 (NCH_3), 51.6 (d, $J=5.8$ Hz, $\text{P}(\text{OCH}_3)$), 58.4 (2C, $\text{N}(\text{CH}_2\text{CH}_2)_2\text{O}$), 59.2 (NCH_2CH_3), 59.8 (2C, $\text{N}(\text{CH}_2\text{CH}_2)_2\text{O}$) ppm.

4-Ethyl-4-methylmorpholinium chloride [6343-87-9]. 3 ml of hydrochloric acid (37 %, 97.92 mmol) were added to a solution of 4-ethyl-4-methylmorpholinium methyl carbonate [947601-93-6] in methanol (50 w/w-%, 20.00 g, 48.72 mmol) and stirred at room temperature. As soon as the gas evolution had ceased, the mixture was heated to 100 °C by means of an oil bath and stirred for an additional hour. Subsequently, all volatile compounds were removed by means of a rotary vane oil pump. The residual gelatinous paste was dissolved in 30 ml of acetonitrile and dried again by applying vacuum. Yield 7.93 g (47.8 mmol, 98.3 %). The product was immediately subjected to metathesis to give the respective *O*,*S*-dimethylphosphorothioate and *O*,*Se*-dimethylphosphoroselenoate ILs.

Thermogravimetric analysis:

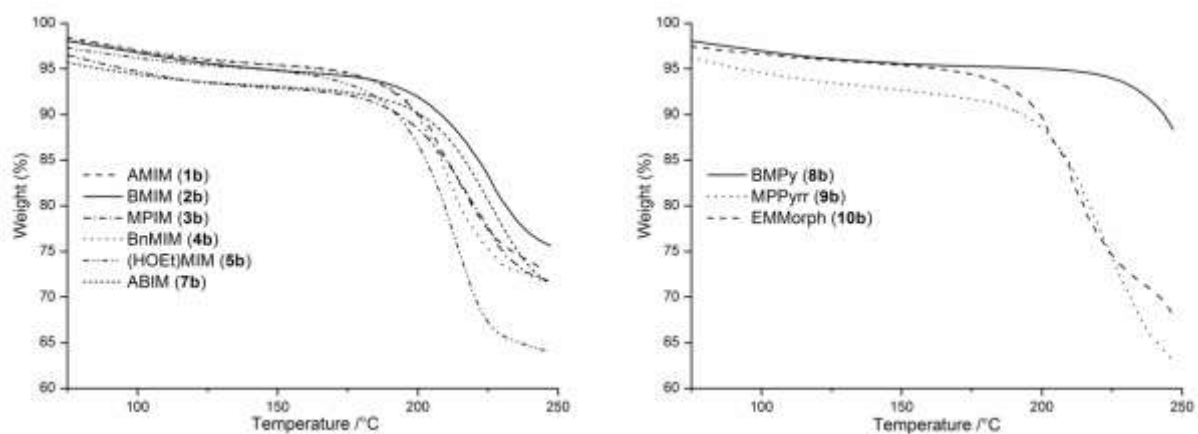


Fig. S1 Thermogravimetric analysis (TGA) of imidazolium (left) and non-imidazolium (right) *O*,*Se*-dimethylphosphoroselenoate (dmpSe)-ILs.

Moisture sorption analysis:

The left figure shows the weight change as a function of time upon stepwise in- and decrease of relative humidity (r.H.). The right figure depicts the same data as sorption isotherm (the X indicates that the system did not reach the equilibrium state within the measurement interval).

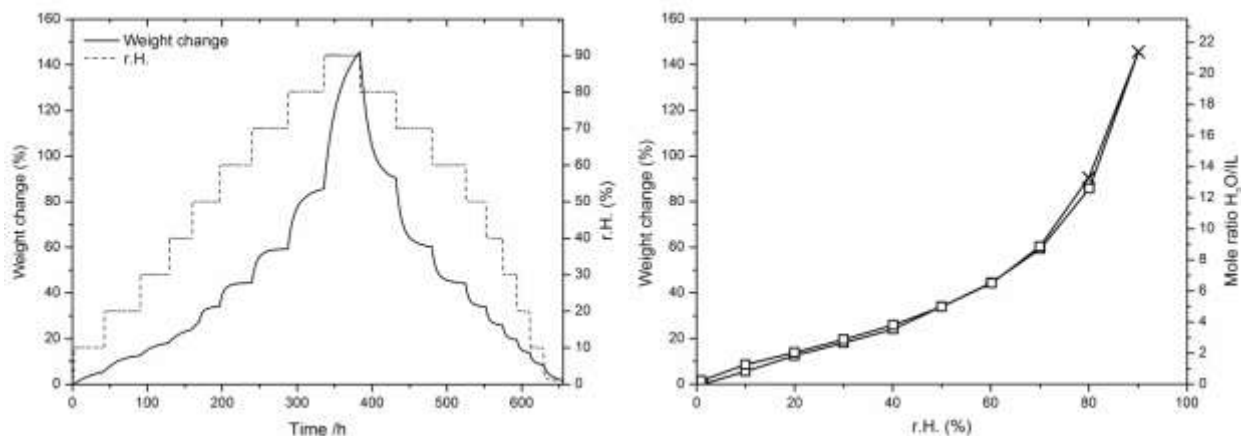


Fig. S2 1-Allyl-3-methylimidazolium *O,S*-dimethylphosphorothioate AMIM dmpt (**1a**).

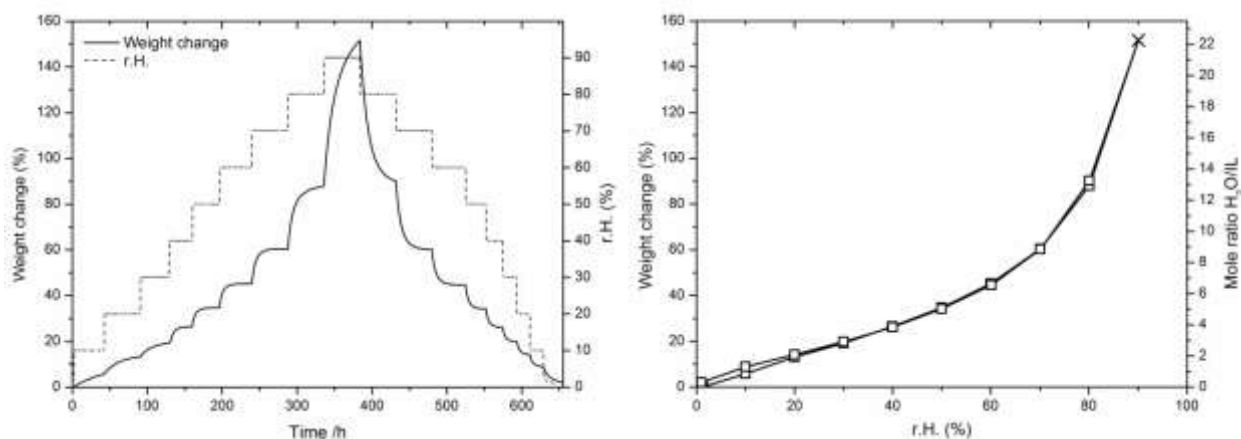


Fig. S3 1-Methyl-3-propylimidazolium *O,S*-dimethylphosphorothioate MPIM dmpt (**3a**).

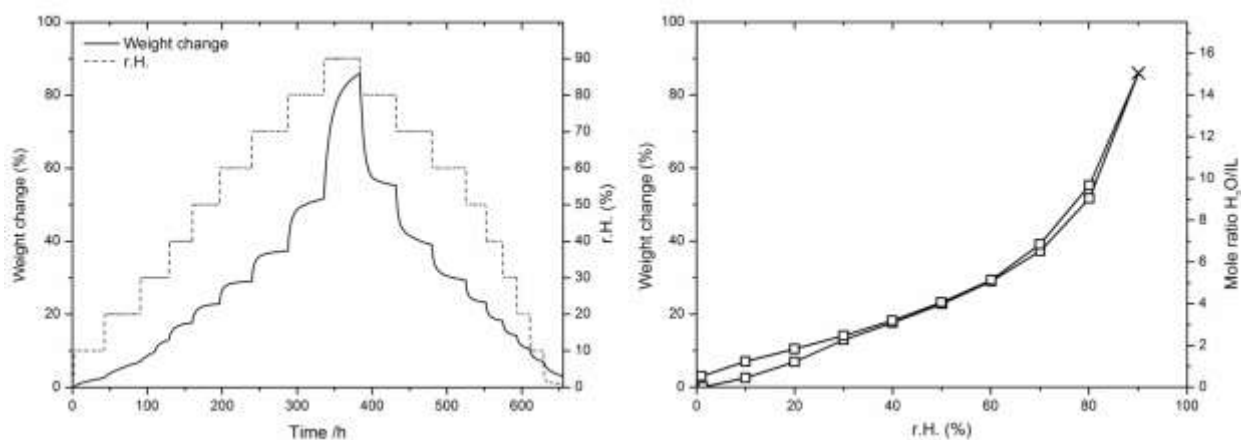


Fig. S4 1-Benzyl-3-methylimidazolium *O,S*-dimethylphosphorothioate BnMIM dmpt (**4a**).

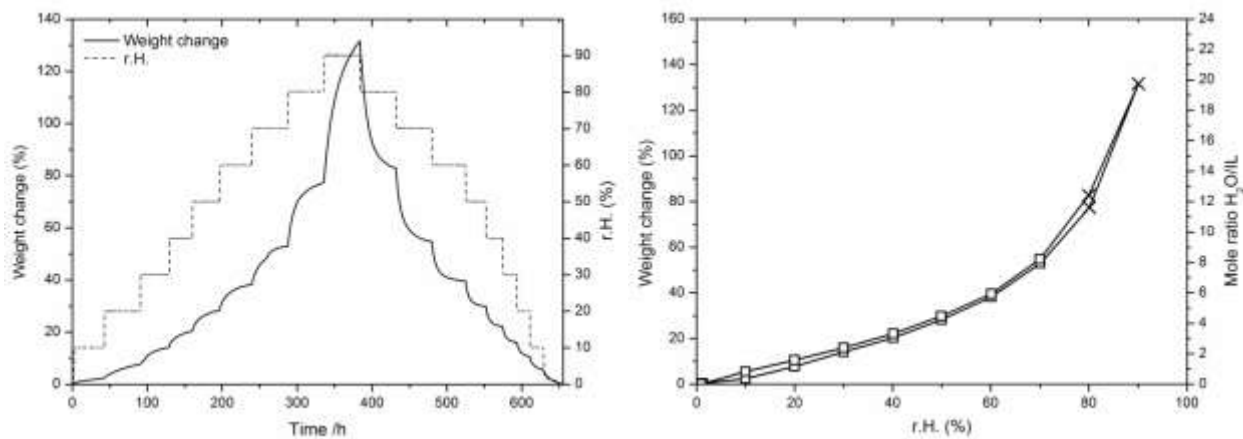


Fig. S5 1-(2-Hydroxyethyl)-3-methylimidazolium *O,S*-dimethylphosphorothioate (HOEt)MIM dmpt (**5a**).

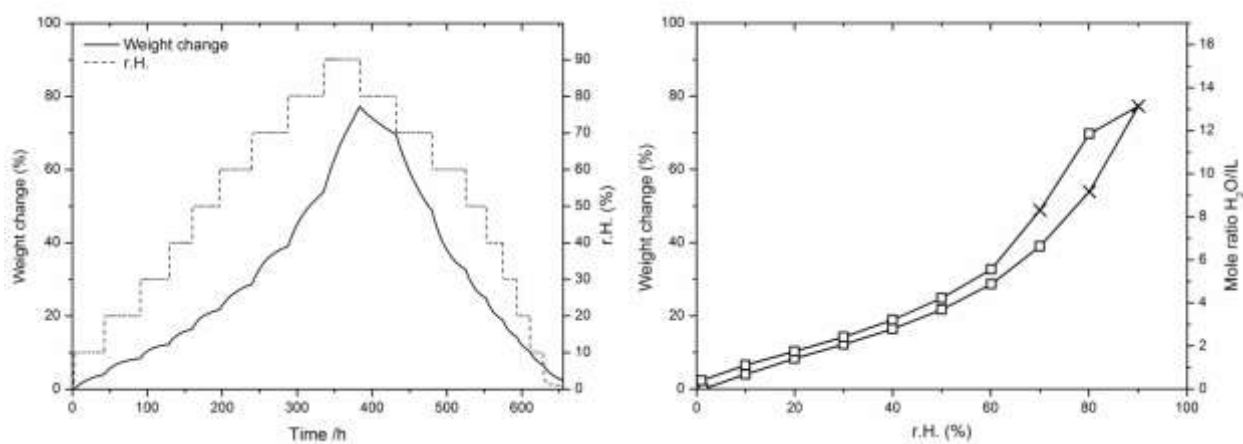


Fig. S6 1-Allyl-3-butylimidazolium *O,S*-dimethylphosphorothioate ABIM dmpt (**7a**).

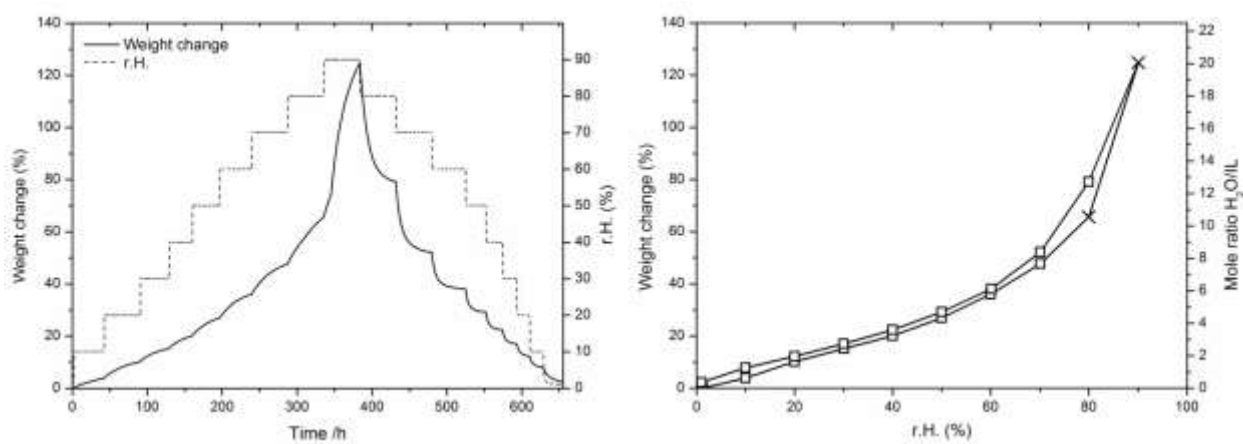


Fig. S7 1-Butyl-3-methylpyridinium *O,S*-dimethylphosphorothioate BMPy dmpt (**8a**).

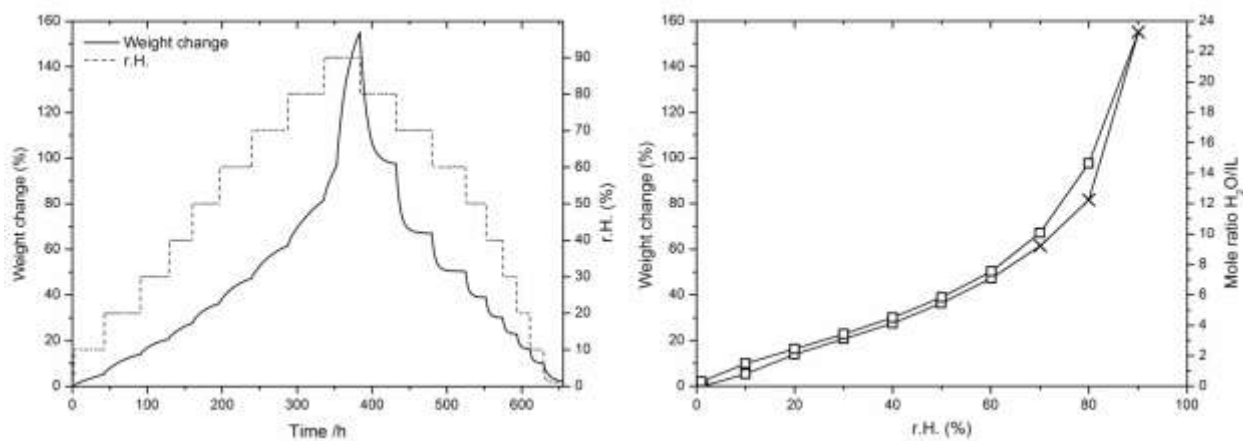


Fig. S8 1-Methyl-1-propylpyrrolidinium *O,S*-dimethylphosphorothioate MPPyrr dmpt (**9a**).

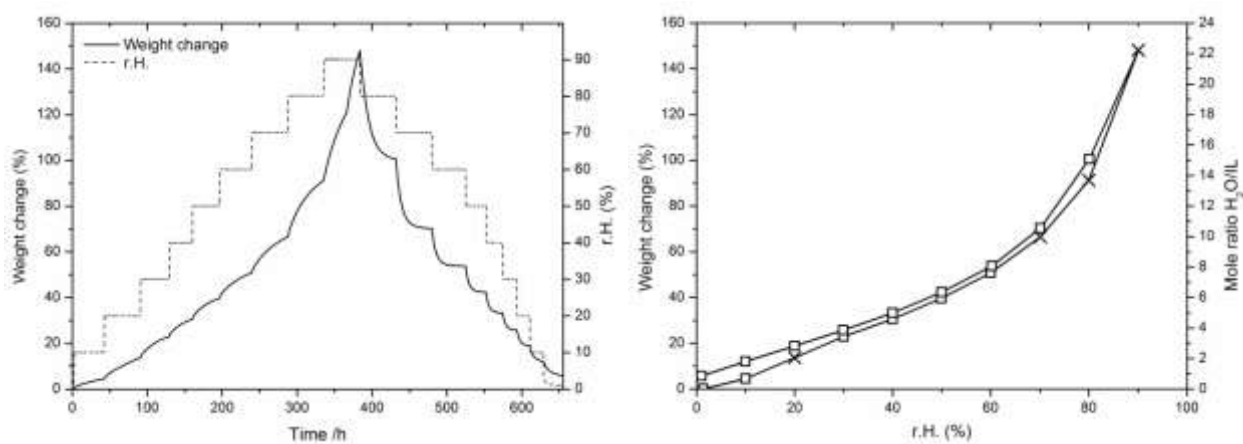


Fig. S9 1-Ethyl-1-methylmorpholinium *O,S*-dimethylphosphorothioate EMMorph dmpt (**10a**).