

Supporting Information for
Transparent and colourless room temperature ionic liquids
having high refractive index over 1.60

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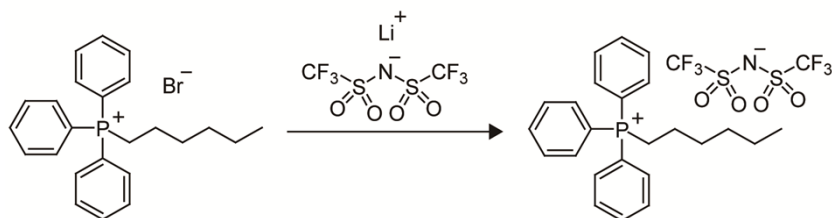
General Procedures. ^1H NMR and ^{13}C NMR spectra were obtained on a JEOL JNM-ECX400 at 400 and 100 MHz in CDCl_3 and DMSO-d_6 , respectively. The thermal properties of the newly designed ionic liquids were measured using a differential scanning calorimeter (DSC-6220, Seiko Instruments). Refractive indices were determined using an Abbe Refractometer (NAR-2T, ATAGO). Kamlet–Taft parameters of these ionic liquids were estimated according to the literature.¹ Elemental analyses were carried out on an Elementar Analytical vario EL3.

1) L. Croehurst, P. R. Mawdsley, J. M. Perez-Arlandis, P. A. Salter and T. Welton, *Phys. Chem. Chem. Phys.*, 2003, **5**, 2790.

Materials. All chemical reagents and solvents were obtained from commercial sources and used without purification.

Synthesis of hexyltriphenylphosphonium bistrifluoromethanesulfonimide

[P_{p,p,p,6}][N(Tf)₂]

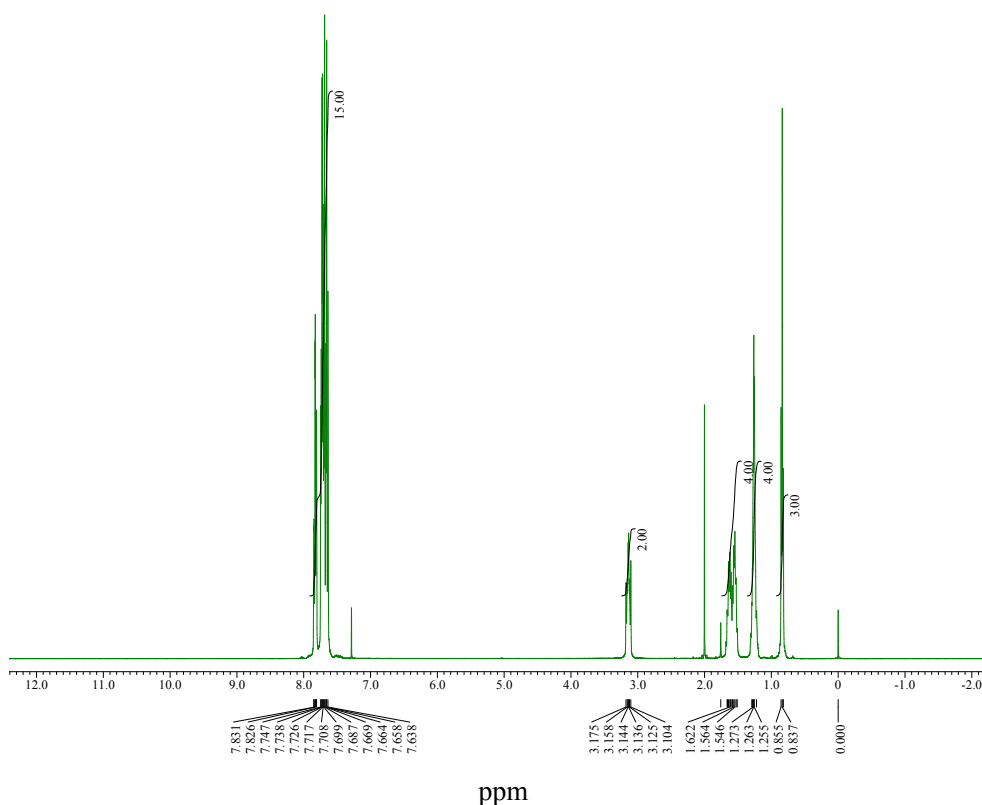


To a solution of hexyltriphenylphosphonium bromide (3.0 g) in water (150 ml) was added a solution of lithium bistrifluoromethanesulfonimide (9.0 g) in water stirring at room temperature. The mixture was stirred at room temperature for 1 day and poured into CH₂Cl₂. The organic phase was separated, dried over MgSO₄, filtered, and the solvent was removed in vacuo. The residue was purified by alumina column (eluent: acetonitrile) to give [P_{p,p,p,6}][N(Tf)₂] as a white solid.

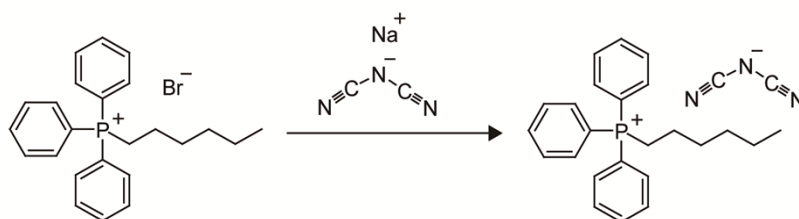
¹H NMR (400 MHz, CDCl₃): δ = 7.85-7.60 (m, 15H), 3.18-3.08 (m, 2H), 1.66-1.51 (m, 4H), 1.29-1.20 (m, 4H), 0.84 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (100MHz, CDCl₃): δ = 135.43, 133.41, 130.79, 118.40, 117.48, 31.03, 30.18, 30.02, 22.50, 22.46, 13.88.

Elemental analysis: Calculated for C₂₆H₂₈F₆NO₄PS₂: C, 49.76; H, 4.50; N, 2.23. Found: C, 49.64; H, 4.59; N, 2.09.



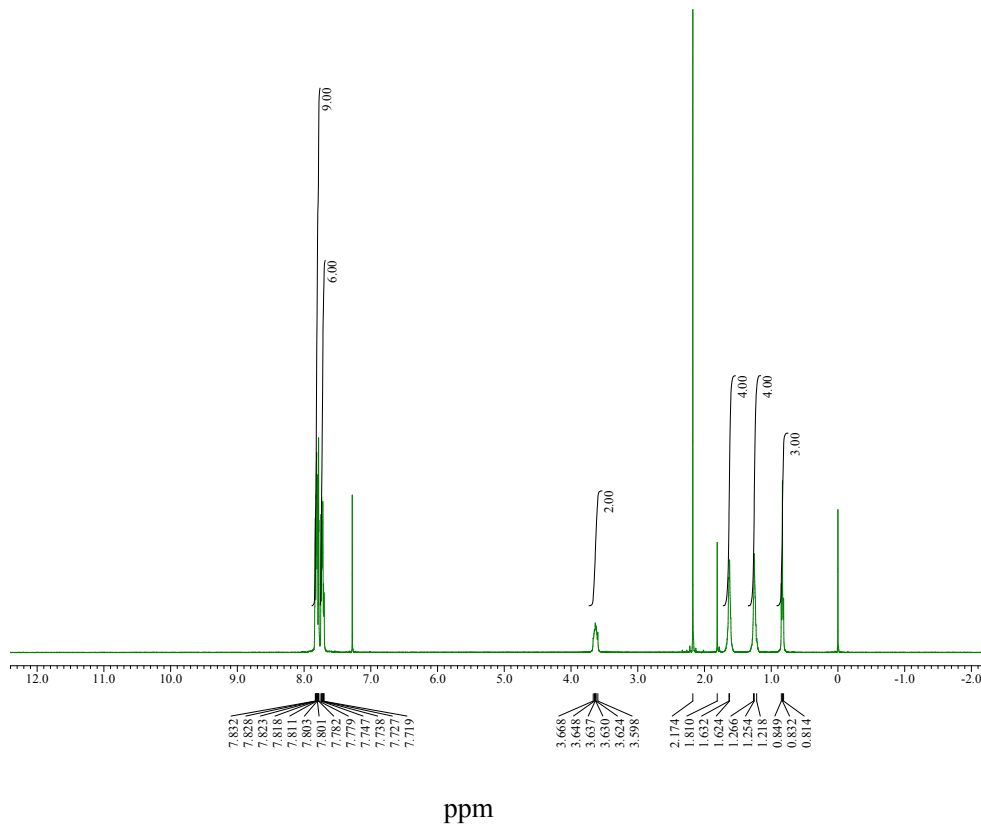
Synthesis of hexyltriphenylphosphonium dicyanamide $[P_{p,p,p,6}][N(CN)_2]$



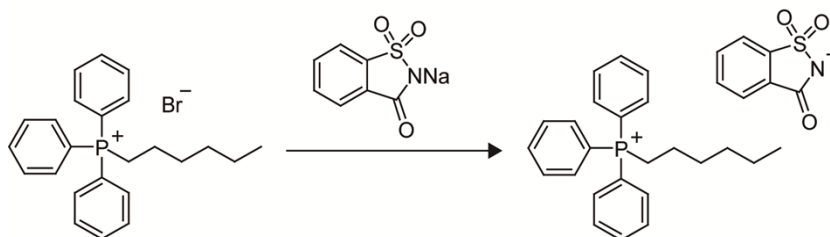
To a solution of hexyltriphenylphosphonium bromide (4.0 g) in CH_2Cl_2 (150 ml) containing a small amount of water was added sodium dicyanamide (0.84 g) stirring at room temperature. The mixture was stirred at room temperature for 1 day. Insoluble was removed by filtration. The obtained solution was concentrated with rotary evaporator and then dried under vacuum at room temperature for 6 h to give $[P_{p,p,p,6}][N(CN)_2]$ as a transparent, colorless liquid.

1H NMR (400 MHz, $CDCl_3$): δ = 7.83-7.80 (m, 9H), 7.78-7.72 (m, 6H), 3.66-3.60 (m, 2H), 1.63-1.62 (m, 4H), 1.27-1.22 (m, 4H), 0.83 (t, J = 7.0 Hz, 3H).

Elemental analysis: Calculated for $C_{26}H_{28}N_3P$: C, 75.52; H, 6.83; N, 10.16. Found: C, 75.17; H, 6.74; N, 10.33.



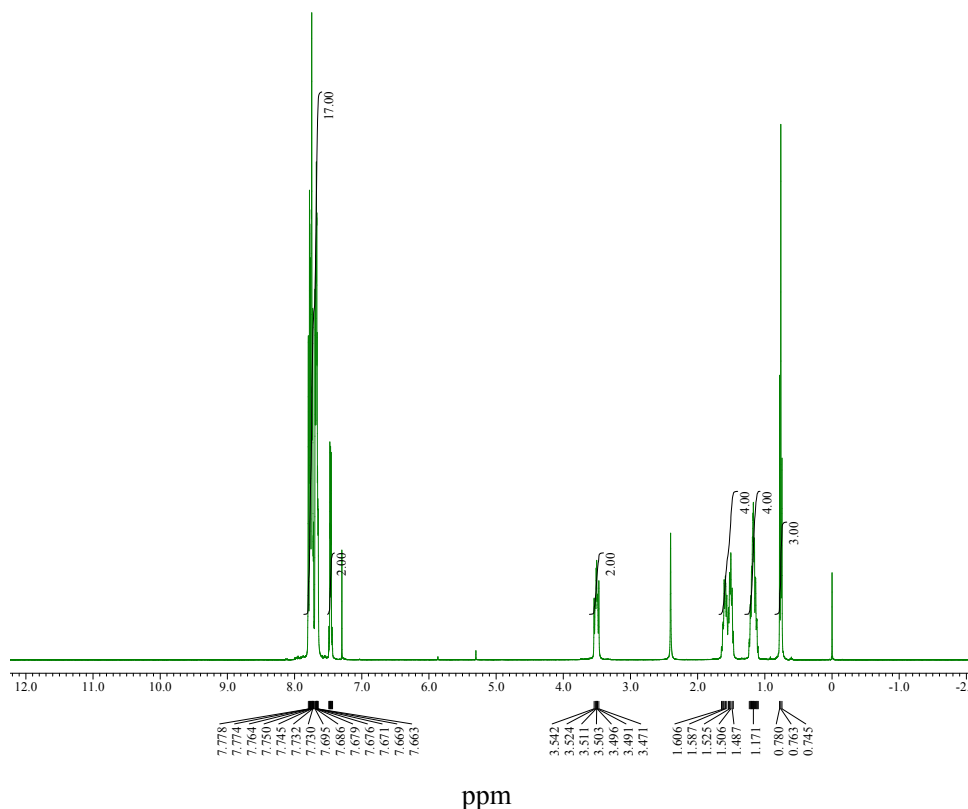
Synthesis of hexyltriphenylphosphonium saccharinate [$P_{p,p,p,6}$][Sac]



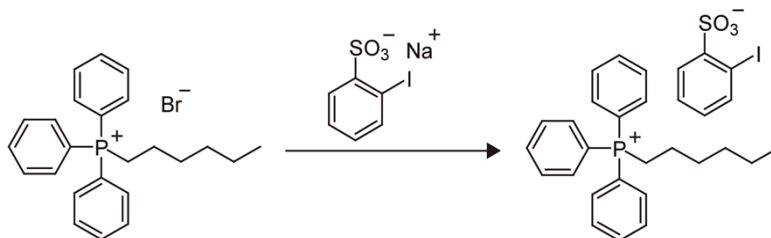
To a solution of hexyltriphenylphosphonium bromide (5.5 g) in CH_2Cl_2 (150 ml) containing a small amount of water was added sodium saccharin (3.7 g) stirring at room temperature. The mixture was stirred at room temperature for 1 day. The mixture was poured into water and the organic phase was separated, dried over MgSO_4 , filtered. The solvent was removed with rotary evaporator and then dried under vacuum at room temperature for 6 h to give [$P_{p,p,p,6}$][Sac] as a transparent liquid.

^1H NMR (400 MHz, CDCl_3): δ = 7.78-7.66 (m, 17H), 7.49-7.43 (m, 2H), 3.54-3.47 (m, 2H), 1.65-1.47 (m, 4H), 1.23-1.10 (m, 4H), 0.76 (t, J = 7.0 Hz, 3H).

Elemental analysis: Calculated for $\text{C}_{31}\text{H}_{32}\text{NO}_3\text{PS}$: C, 70.30; H, 6.09; N, 2.64. Found: C, 70.35; H, 6.08; N, 2.79.



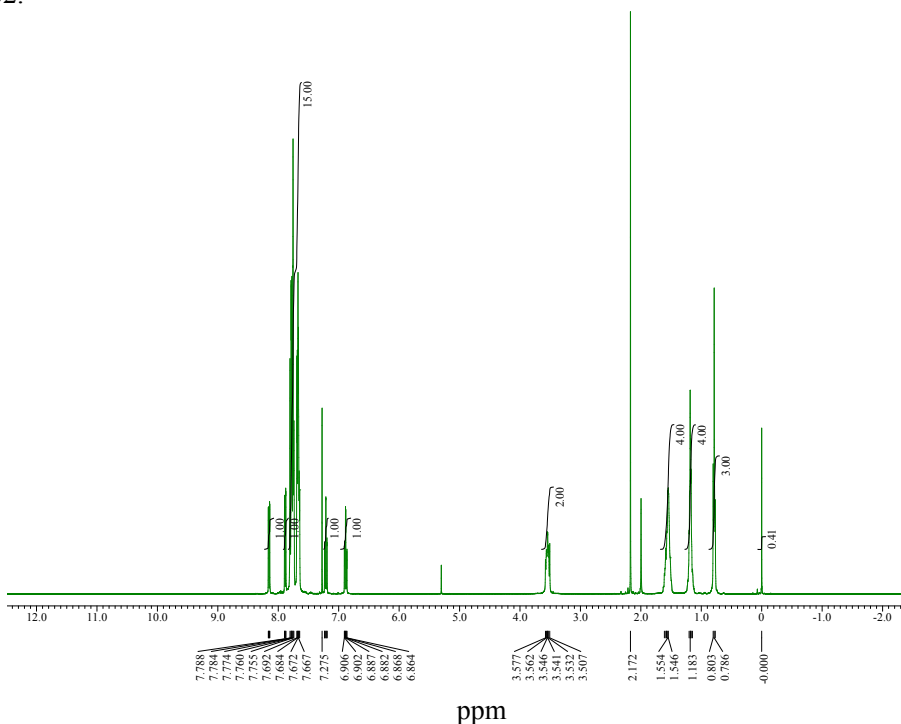
Synthesis of hexyltriphenylphosphonium 2-iodobenzenesulfonate [P_{p,p,p,6}][Bz-I-SO₃]



To a suspended solution of hexyltriphenylphosphonium bromide (3.0 g) in ethanol (300 ml) was added silver(I) oxide (1.95 g) stirring at room temperature. The mixture was stirred at room temperature for 1 day and then filtered through a plug of celite. The obtained solution was neutralized with 2-iodobenzenesulfonic acid dehydrate. The solution was concentrated with rotary evaporator. The residue was purified by silica column (eluent: CHCl₃:MeOH = 9:1) to give [P_{p,p,p,6}][Bz-I-SO₃] as a transparent liquid.

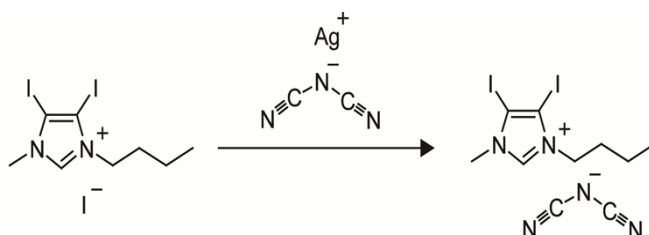
¹H NMR (400 MHz, CDCl₃): δ = 8.16-8.14 (m, 1H), 7.90-7.87 (m, 1H), 7.81-7.65 (m, 15H), 7.23-7.19 (m, 1H), 6.91-6.86 (m, 1H), 3.56-3.49 (m, 2H), 1.61-1.51 (m, 4H), 1.20-1.15 (m, 4H), 0.76 (t, *J* = 7.0 Hz, 3H).

Elemental analysis: Calculated for C₃₀H₃₂IO₃PS: C, 57.15; H, 5.12; N, 0. Found: C, 56.86; H, 5.44; N, 0.02.



Synthesis of 4,5-diiodo-1-butyl-3-methylimidazolium dicyanamide

[BmImI₂][N(CN)₂]

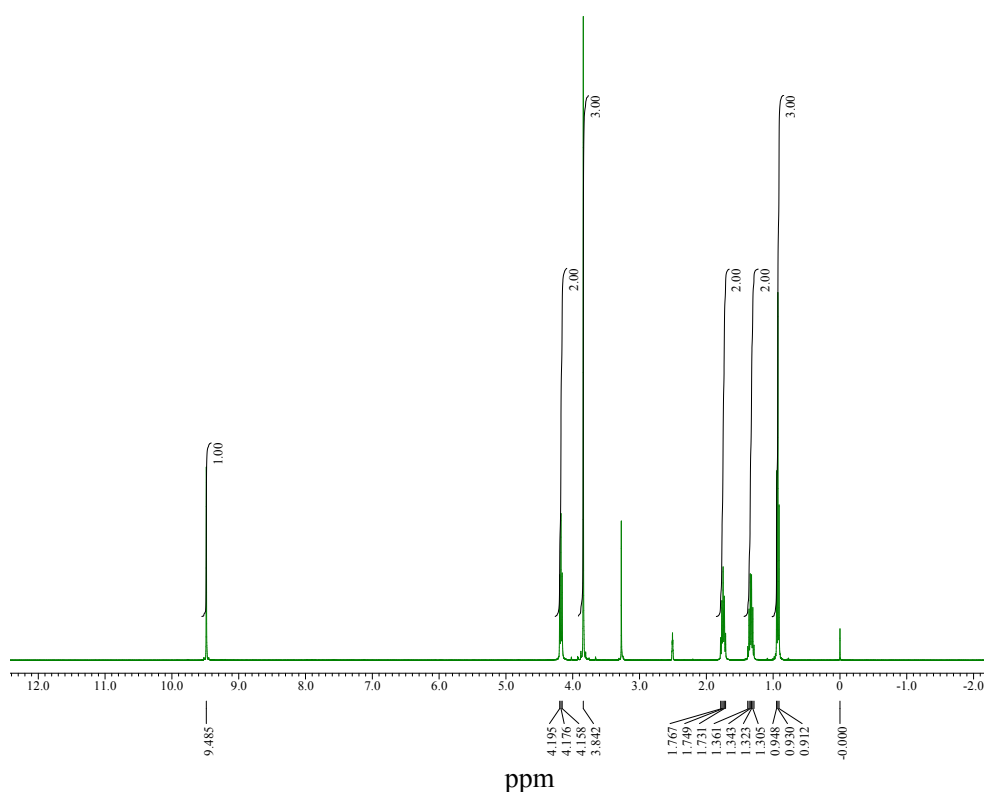


To a suspended solution of 4,5-diiodo-1-butyl-3-methylimidazolium iodide (2.0 g) in EtOH was added dropwise a solution of silver dicyanamide (0.91 g) in EtOH. The mixture was stirred at room temperature for 1 day. Insoluble was removed by filtration. The obtained solution was concentrated with rotary evaporator and then dried under vacuum at room temperature for 6 h. The obtained residue was washed with water three times to give [BmimI₂][N(CN)₂] as a white solid.

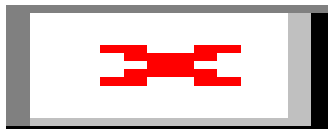
¹H NMR (400 MHz, DMSO-d₆): δ = 9.48 (s, 1H), 4.18 (t, *J* = 7.4 Hz, 2H), 3.84 (s, 3H), 1.77-1.73 (m, 2H), 1.34-1.30 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (100MHz, DMSO-d₆): δ = 141.16, 119.59, 94.69, 92.87, 52.03, 31.52, 19.21, 13.85.

Elemental analysis: Calculated for C₁₀H₁₃I₂N₅: C, 26.28; H, 2.87; N, 15.32. Found: C, 26.18; H, 2.92; N, 15.53.



Synthesis of 4,5-diiodo-1-butyl-3-methylimidazolium bistrifluoromethane sulfonimide [BmImI₂][N(Tf)₂]

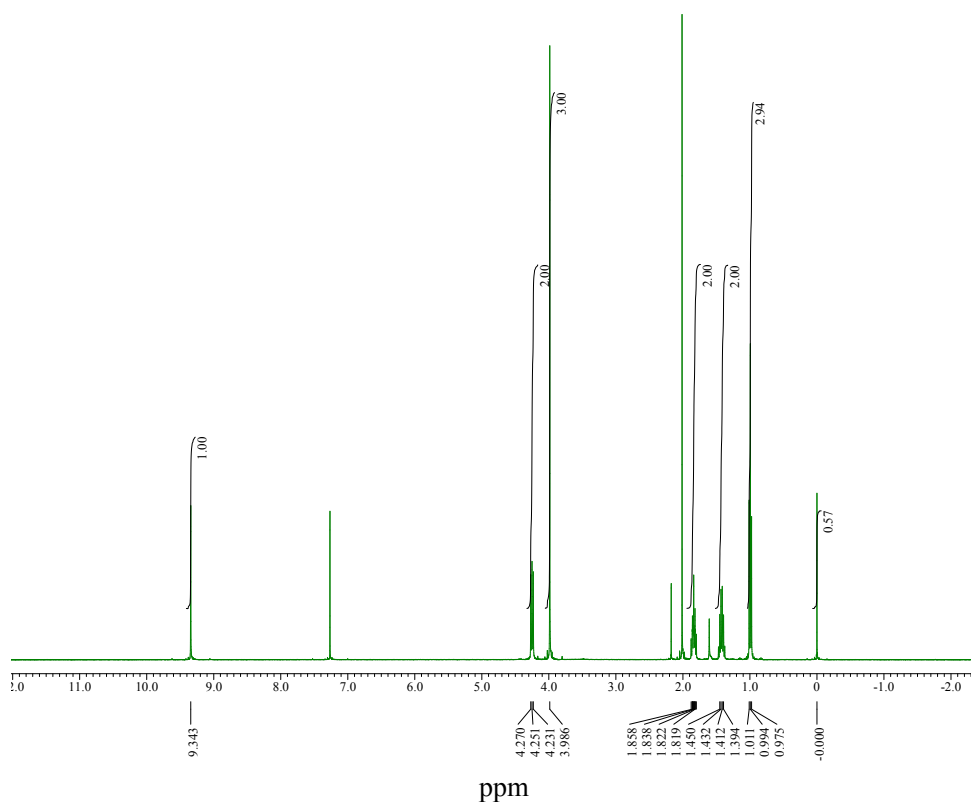


To a suspended solution of 4,5-diiodo-1-butyl-3-methylimidazolium iodide (2.0 g) in MeOH/CH₂Cl₂ (150 ml) was added lithium bistrifluoromethanesulfonimide (9.98 g) stirring at room temperature. The mixture was stirred at room temperature. After 1 day of stirring, the mixture was concentrated with rotary evaporator and poured into water and extracted with CH₂Cl₂. The organic phase was washed with water three times. The obtained organic phase was concentrated with rotary evaporator and then dried under vacuum at room temperature. The residue was purified by alumina column (eluent: acetonitrile) to give [BmImI₂][N(Tf)₂] as a transparent colorless liquid.

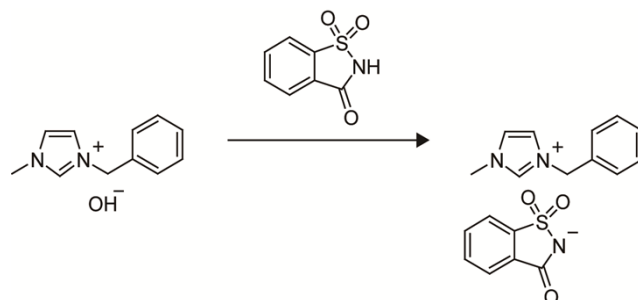
¹H NMR (400 MHz, CDCl₃): δ = 9.34 (s, 1H), 4.25 (t, *J* = 7.8 Hz, 2H), 3.99 (s, 3H), 1.88-1.80 (m, 2H), 1.45-1.39 (m, 2H), 0.99 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (100MHz, CDCl₃): δ= 141.07, 121.42, 90.69, 89.07, 53.29, 40.02, 31.84, 19.40, 13.37.

Elemental analysis: Calculated for C₁₀H₁₃F₆I₂N₃O₄S₂: C, 17.90; H, 1.95; N, 6.26. Found: C, 17.85; H, 2.00; N, 6.28.



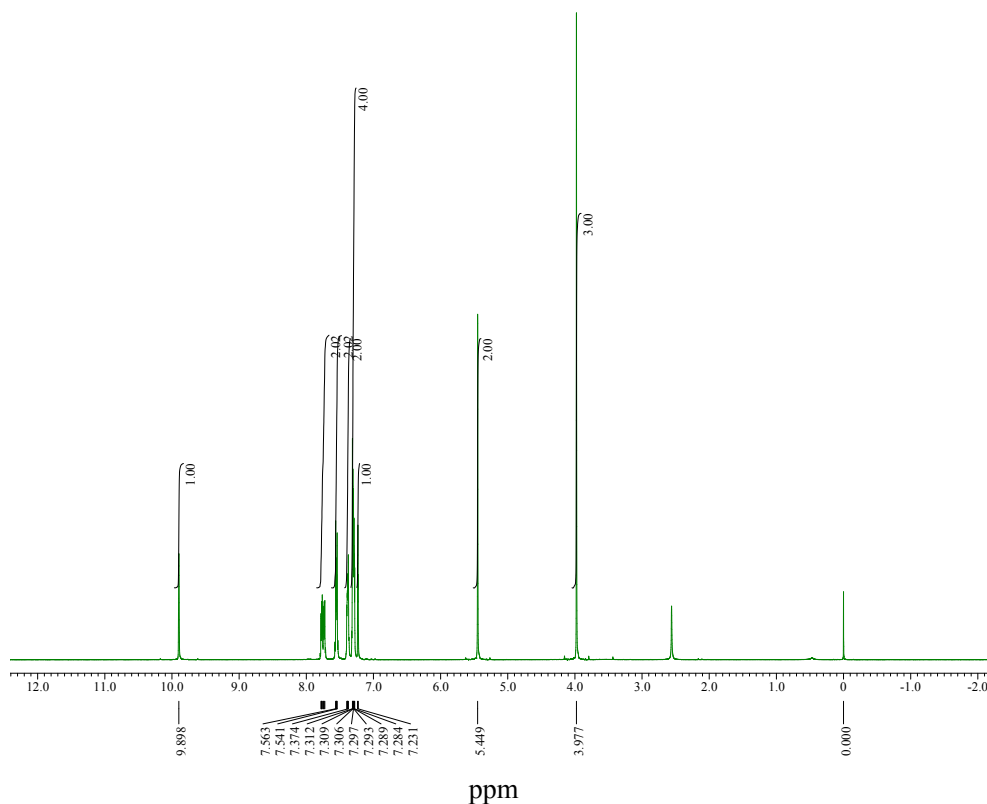
Synthesis of 1-benzyl-3-methylimidazolium saccharinate [BzmIm][Sac]



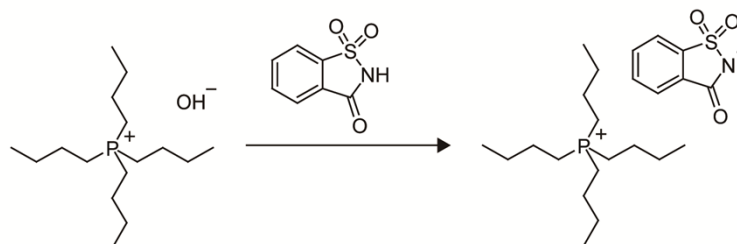
To a solution of 1-benzyl-3-methylimidazolium hydroxide (0.0210 mol) in H₂O (300 ml) was added saccharin (3.85 g, 0.0210 mol) stirring at room temperature. The mixture was stirred at room temperature for 1 day. The obtained solution was concentrated with rotary evaporator and then dried under vacuum at room temperature for 6 h to give [BzmIm][Sac] as a transparent colorless liquid.

¹H NMR (400 MHz, DMSO-d₆): δ = 9.90 (s, 1H), 7.77-7.69 (m, 2H), 7.55-7.50 (m, 2H), 7.38-7.34 (m, 2H), 7.30-7.25 (m, 4H), 7.21-7.20 (m, 1H), 5.45 (s, 2H), 3.98 (s, 3H).

Elemental analysis: Calculated for C₁₈H₁₇N₃O₃S: C, 60.83; H, 4.82; N, 11.82. Found: C, 60.35; H, 5.21; N, 11.84.



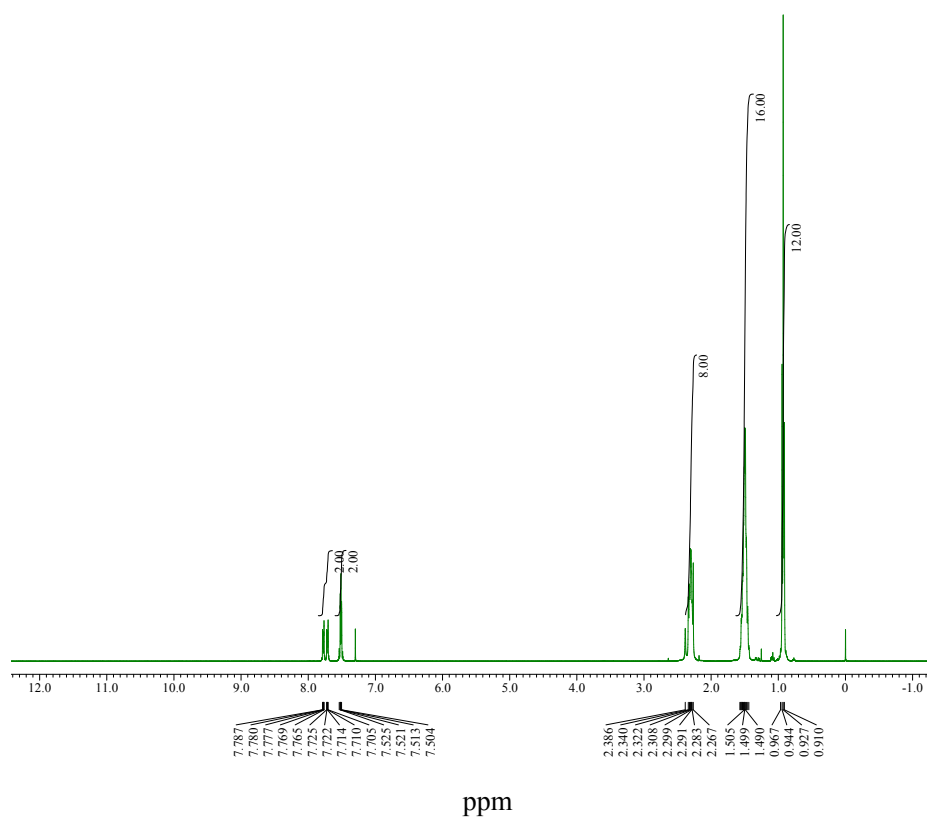
Synthesis of tetrabutylphosphonium saccharinate [P_{4,4,4,4}][Sac]



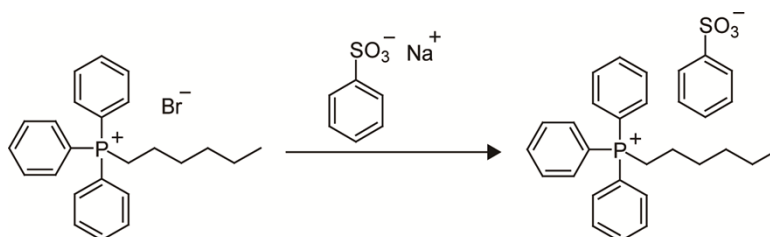
To a solution of tetrabutylphosphonium hydroxide (0.0109 mol) in H₂O (150 ml) was added saccharin (3.0 g, 0.0109 mol) stirring at room temperature. The mixture was stirred at room temperature for 1 day. The obtained solution was concentrated with rotary evaporator and then dried under vacuum at room temperature for 6 h to give [P_{4,4,4,4}][Sac] as a transparent colorless liquid.

¹H NMR (400 MHz, CDCl₃): δ = 7.79-7.70 (m, 2H), 7.52-7.50 (m, 2H), 2.38-2.17 (m, 8H), 1.50-1.49 (m, 16H), 0.93 (t, *J* = 6.8 Hz, 12H).

Elemental analysis: Calculated for C₂₃H₄₀NO₃PS: C, 62.55; H, 9.13; N, 3.17. Found: C, 62.34; H, 8.89; N, 3.34.



Synthesis of hexyltriphenylphosphonium benzenesulfonate [$P_{p,p,p,6}$][Bz-SO₃]

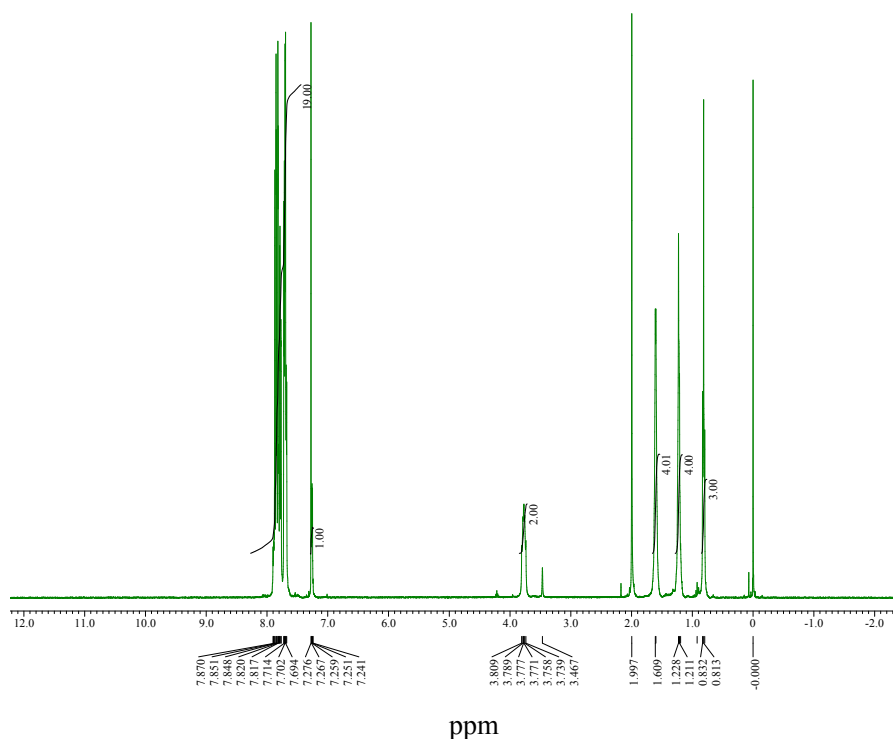


To a solution of hexyltriphenylphosphonium bromide (3.0 g) in water (150 ml) was added a solution of sodium benzenesulfonate (6.0 g) in water stirring at room temperature. The mixture was stirred at room temperature for 1 day. The mixture was poured into CH₂Cl₂ and the organic phase was separated, dried over MgSO₄, filtered. The residue was purified by silica column (eluent: CH₂Cl₂:MeOH = 9:1) to give [$P_{p,p,p,6}$][Bz-SO₃] as a transparent colorless liquid.

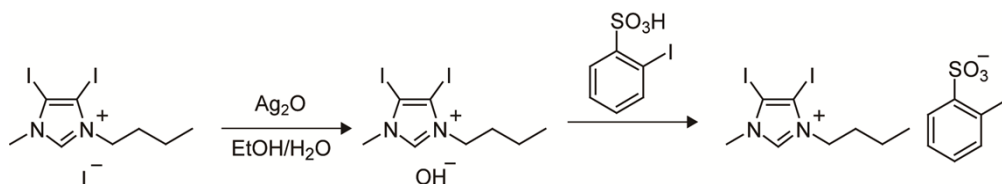
¹H NMR (400 MHz, CDCl₃): δ = 7.90-7.63 (m, 19H), 7.25-7.24 (m, 1H), 3.81-3.74 (m, 2H), 1.68-1.52 (m, 4H), 1.30-1.11 (m, 4H), 0.81 (t, *J* = 7.0 Hz, 3H).

¹³C NMR (100MHz, CDCl₃): δ= 134.98, 133.81, 130.60, 130.47, 127.73, 126.31, 119.06, 118.21, 31.41, 30.22 22.67, 22.33, 22.18, 14.05.

Elemental analysis: Calculated for C₃₀H₃₃O₃PS: C, 71.40; H, 6.59; N, 0. Found: C, 71.70; H, 7.19; N, 0.



Synthesis of 4,5-diiodo-1-butyl-3-methylimidazolium 2-iodobenzenesulfonate
[BmImI₂][Bz-I-SO₃]



To a suspended solution of 4,5-diiodo-1-butyl-3-methylimidazolium iodide (1.5 g) in ethanol (800 ml) was added silver(I) oxide (0.71 g) stirring at room temperature. The mixture was stirred at room temperature for 1 day and then filtered through a plug of celite. The obtained solution was neutralized with 2-iodobenzenesulfonic acid dehydrate. The solution was concentrated with rotary evaporator. The slightly yellowish compound was stirred in acetonitrile with activated carbon for 48 h to decolorize and then filtered through an alumina pad. The solution was concentrated with rotary evaporator. The residue was purified by silica column (eluent: CHCl₃:MeOH = 9:1) to give [BmImI₂][Bz-I-SO₃] as a white solid.

¹H NMR (400 MHz, DMSO-d₆): δ = 9.52 (s, 1H), 7.92-7.87 (m, 2H), 7.36-7.32 (m, 1H), 7.02-6.98 (m, 1H), 4.16 (t, *J* = 7.2 Hz, 2H), 3.83 (s, 3H), 1.74-1.68 (m, 2H), 1.35-1.26 (m, 2H), 0.91 (t, *J* = 7.6 Hz, 3H).

Elemental analysis: Calculated for C₁₄H₁₇I₃N₂O₃S: C, 24.95; H, 2.54; N, 4.16. Found: C, 24.90; H, 2.54; N, 4.28.

