Novel Low Melting Salts with Donor-Acceptor Substituents as Targets for Second-Order Nonlinear Optical Applications

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General methods: All reactions were carried out under nitrogen atmosphere. All the reagents used were purchased from commercial sources and used without further purification. N-arylimidazoles were prepared according to the reported procedure.[1] DMSO and acetonitrile were freshly distilled from CaH2. Acetone were freshly distilled from K2CO3. 1H, 13C and 19F NMR spectra were recorded in CDCl3, DMSO-d6, D2O and Acetone-d6 on a spectrometer operating at 300, 75 and 282.4 MHz, respectively. Chemical shifts are reported in parts per million relative to the appropriate standard: TMS for 1H and CFCl3 for 19F and 13C NMR spectra. Mass spectra were recorded on a Shimadzu LCMS instrument. The IR spectra were recorded on a Shimadzu IR-440 spectrometer. Column chromatography was carried out on silica gel H (10-40 mm). Differential scanning calorimetry (DSC) measurements were performed with a Perkin Elmer Pyris 1 at a scanning rate for both heating and cooling of 10 °C min⁻¹. Thermogravimetric analysis (TGA) measurements were carried out with a TA Q500 by heating samples at 20 °C min⁻¹ from room temperature to 700 °C in a dynamic nitrogen atmosphere. In Hyper-Rayleigh Scattering experiment, we used Nd:YAG laser working at 1064 nm with 8 ns pulses duration and 10 Hz repetition rate.

Quaternization of N-arylimidazoles: N-arylimidazole (1 mmol), 1-chloro-2,4-dinitrobenzene (1.2 mmol) were mixed together in a dry 5 ml sealed tube. To this mixture were added dry CH3CN (0.5 ml). The mixture was heated at 120 °C. After 18 h, the mixture of acetone and dimethyl ether (1:1, 2 ml) was added. The precipitate was filtered and crude product purification was performed by recrystallization with ethanol/dimethyl ether to afford the desired chlorates.
1-(2,4-dinitrophenyl)-3-phenyl-imidazolium chloride (2a): Yield 58%. 1H NMR (D2O, δ): 9.29 (s, 1 H), 8.85 (d, J = 9.0 Hz, 1 H), 8.20 (s, 1 H), 8.18 (d, J = 9.0 Hz, 1 H), 8.04 (s, 1 H), 7.65-7.78 (m, 5 H); IR (KBr): v = 3029, 2878, 2785, 1859, 1549, 1494, 1457, 1350, 1260, 1147, 899, 837, 778, 760, 738, 688, 653, 521 cm⁻¹; MS (ESI, m/z): 311.2 [M-Cl]⁺; Anal. calcd for C15H11ClN4O4: C 51.96, H 3.20, N 16.16; Found: C 52.00, H 3.24, N 16.38.

1-(2,4-dinitrophenyl)-3-p-tolyl-imidazolium chloride (2b): Yield 87%. 1H NMR (D2O, δ): 9.29 (s, 1 H), 8.86 (d, J = 8.4 Hz, 1 H), 8.19 (d, J = 8.4 Hz, 1 H), 8.17 (s, 1 H), 8.04 (s, 1 H), 7.62 (d, J = 8.4 Hz, 2 H), 7.50 (d, J = 8.4 Hz, 2 H), 2.36 (s, 3 H); IR (KBr): v = 3495, 3247, 3167, 3058, 2778, 1983, 1774, 1621, 1508, 1357, 1242, 1067, 956, 911, 815, 739, 651, 624, 523 cm⁻¹; MS (ESI, m/z): 325.2 [M-Cl]⁺; Anal. calcd for C16H13ClN4O4: C 53.27, H 3.63, N 15.53; Found: C 53.16, H 3.68, N 15.31.

1-(2,4-dinitrophenyl)-3-(4-hydroxyphenyl)-imidazolium chloride (2c): 4-(imidazol-1-yl)phenol (4 mmol), 1-chloro-2,4-dinitrobenzene (4.8 mmol) were mixed together in a dry 5 ml sealed tube. To this mixture were added dry CH3CN (2 ml). The mixture was heated at 120 °C. After 48 h, acetonitrile was removed under reduced pressure. The residue was washed with ethanol (3×5 mL) and dried in vacuo. Yield 62%. 1H NMR (DMSO-d6, δ): 10.31 (s, 1 H), 9.08 (d, J = 2.4 Hz, 1 H), 8.93 (dd, J = 8.8 Hz, J = 2.4 Hz, 1 H), 8.51 (s, 1 H), 8.39 (s, 1 H), 8.38 (d, J = 8.8 Hz, 1 H), 7.70 (d, J = 8.9 Hz, 2 H), 7.07 (d, J = 8.9 Hz, 2 H); IR (KBr): v = 3434, 3154, 3127, 2567, 2444, 1969, 1898, 1764, 1621, 1508, 1357, 1242, 1067, 956, 911, 815, 739, 651, 624, 523 cm⁻¹; MS (ESI, m/z): 341.2 [M-Cl]⁺; Anal. calcd for C15H11ClN4O5: C 49.67, H 3.06, N 15.45; Found: C 49.91, H 3.13, N 15.77.

1-(2,4-dinitrophenyl)-3-(4-methoxyphenyl)-imidazolium chloride (2d): 1-(4-methoxyphenyl)-imidazole (20 mmol), 1-chloro-2,4-dinitrobenzene (22 mmol) were mixed together in a 50 ml tube equipped with a condensor. To this mixture were added dry acetone (15 ml). The mixture was heated at 80 °C. After 8 h, the precipitate was filtered and washed with acetone (3×5 mL). The crude product purification was performed by recrystallization with ethanol/dimethyl ether to afford the mild yellow powder 6.319 g. Yield 84%. 1H NMR (DMSO-d6, δ): 10.41 (s, 1 H), 9.09 (d, J = 2.4 Hz, 1 H), 8.93 (dd, J = 8.8 Hz, J = 2.4 Hz, 1 H), 8.58 (t, J = 1.8 Hz, 1 H), 8.43 (t, J = 1.8 Hz, 1 H), 8.41 (d, J = 8.7 Hz, 2 H), 7.86 (d, J = 9.1 Hz, 2 H), 7.26 (d, J = 9.1 Hz, 2 H), 3.87 (s, 3 H); IR (KBr): v = 3402, 3140, 3021, 2886, 2771, 1849, 1665, 1618, 1508, 1358, 1250, 1078, 1017, 953, 897, 860, 773, 662, 530 cm⁻¹; MS (ESI, m/z): 341.2 [M-Cl]⁺; Anal. calcd for C16H13ClN4O5: C 51.01, H 3.48, N 14.87; Found: C 50.78, H 3.68, N 14.59.

Metathetical reaction of 2 with KPF₆ or LiNTf₂: Salts 2 (1 mmol) was dissolved in a mixture of water and acetone (1:1, 10 mL) and treated with an aqueous solution of LiNTf₂ (1.1 mmol, 5 ml) or KPF₆ (1.1 mmol). After 4 h, acetone was removed at reduced pressure. The precipitate was filtered and washed with water (3×5 mL). The water layer was extracted with CH₂Cl₂ (3×15 mL). The precipitate was dissolved in the combined organic layer, washed with water (3×15 mL) and evaporated in vacuo to give 3 and 4.
1-(2,4-dinitrophenyl)-3-phenyl-imidazolium hexafluorophosphate (3a): Yield 95%.

$^1$H NMR (Acetone-d$_6$, $\delta$): 10.00 (s, 1 H), 9.07 (d, $J = 2.5$ Hz, 1 H), 8.83 (dd, $J = 8.7$ Hz, $J = 2.5$ Hz, 1 H), 8.41 (t, $J = 1.8$ Hz, 1 H), 8.36 (d, $J = 8.7$ Hz, 1 H), 8.29 (t, $J = 1.8$ Hz, 1 H), 7.82 (d, $J = 8.1$ Hz, 2 H), 7.59-7.64 (m, 3 H); 19F NMR (Acetone-d$_6$, $\delta$): $-71.34$ (d, $J = 709.8$ Hz, 6 F); IR (KBr): v = 3148, 3105, 3078, 2877, 1618, 1530, 1409, 1353, 1255, 1117, 1073, 911, 838, 741, 638, 559, 507 cm$^{-1}$; MS (ESI, m/z): 311 [M-PF$_6$]$^+$


1-(2,4-dinitrophenyl)-3-p-tolyl-imidazolium hexafluorophosphate (3b): Yield 92%.

$^1$H NMR (Acetone-d$_6$, $\delta$): 9.99 (s, 1 H), 9.07 (d, $J = 2.5$ Hz, 1 H), 8.83 (dd, $J = 8.6$ Hz, $J = 2.5$ Hz, 1 H), 8.38 (t, $J = 1.8$ Hz, 1 H), 8.37 (d, $J = 8.6$ Hz, 1 H), 8.29 (t, $J = 1.8$ Hz, 1 H), 7.69 (d, $J = 8.6$ Hz, 2 H), 7.43 (d, $J = 8.6$ Hz, 2 H), 2.34 (s, 3 H); 19F NMR (Acetone-d$_6$, $\delta$): $-72.57$ (d, $J = 707.3$ Hz, 6 F); IR (KBr): v = 3647, 3151, 3102, 2865, 1612, 1551, 1341, 1244, 1151, 1098, 1071, 882, 736, 642, 557 cm$^{-1}$; MS (ESI, m/z): 325.2 [M-PF$_6$]$^+$; Anal. calcd for C$_{16}$H$_{13}$F$_6$N$_4$O$_4$P: C 40.86, H 2.79, N 11.91; Found: C 41.09, H 2.89, N 12.07.

1-(2,4-dinitrophenyl)-3-(4-hydroxyphenyl)-imidazolium hexafluorophosphate (3c): ionic salts 2c (1 mmol) was dissolved in a mixture of water, methanol and acetone (1:1:1, 15 mL) and treated with an aqueous solution of KPF$_6$ (1.2 mmol, 5 ml). After 12 h, acetone and methanol were removed at reduced pressure. The precipitate was filtered and washed with water (3×5 mL). The water layer was extracted with CH$_2$Cl$_2$ (3×15 mL). The precipitate was dissolved in the combined organic layer, washed with water (3×15 mL) and evaporated in vacuo to give the product. Yield 87%.

$^1$H NMR (Acetone-d$_6$, $\delta$): 9.98 (s, 1 H), 9.19 (d, $J = 2.5$ Hz, 1 H), 8.48 (d, $J = 8.7$ Hz, 1 H), 8.41 (s, 1 H), 8.36 (s, 1 H), 7.75 (d, $J = 8.9$ Hz, 2 H), 7.13 (d, $J = 8.9$ Hz, 2 H); 19F NMR (Acetone-d$_6$, $\delta$): $-72.24$ (d, $J = 707.0$ Hz, 6 F); IR (KBr): v = 3526, 3149, 2881, 1939, 1839, 1809, 1508, 1413, 1365, 1252, 1201, 1174, 1116, 1201, 1174, 1116, 1073, 952, 828, 743, 624 cm$^{-1}$; Anal. calcd for C$_{15}$H$_{11}$F$_6$N$_4$O$_5$P: C 38.15, H 2.35, N 11.86; Found: C 38.38, H 2.41, N 12.09.

1-(2,4-dinitrophenyl)-3-(4-methoxyphenyl)-imidazolium hexafluorophosphate (3d): Yield 94%.

$^1$H NMR (Acetone-d$_6$, $\delta$): 9.99 (s, 1 H), 9.07 (d, $J = 2.5$ Hz, 1 H), 8.41 (s, 1 H), 8.36 (d, $J = 8.7$ Hz, 1 H), 8.33 (d, $J = 1.7$ Hz, 1 H), 7.75 (d, $J = 8.9$ Hz, 2 H), 7.13 (d, $J = 8.9$ Hz, 2 H); 19F NMR (Acetone-d$_6$, $\delta$): $-72.24$ (d, $J = 707.0$ Hz, 6 F); IR (KBr): v = 3526, 3149, 2881, 1939, 1839, 1809, 1508, 1413, 1365, 1252, 1201, 1174, 1116, 1201, 1174, 1116, 1073, 952, 828, 743, 624 cm$^{-1}$; Anal. calcd for C$_{15}$H$_{11}$F$_6$N$_4$O$_5$P: C 38.15, H 2.35, N 11.86; Found: C 38.38, H 2.41, N 12.09.

1-(2,4-dinitrophenyl)-3-(4-methoxyphenyl)-imidazolium bis(trifluoromethylsulfonyl)amide (4a): Yield 88%.

$^1$H NMR (Acetone-d$_6$, $\delta$): 10.06 (s, 1 H), 9.08 (d, $J = 2.5$ Hz, 1 H), 8.84 (dd, $J = 8.7$ Hz, $J = 2.5$ Hz, 1 H), 8.44 (t, $J = 1.7$ Hz, 1 H), 8.40 (d, $J = 8.7$ Hz, 1 H), 8.32 (t, $J = 1.7$ Hz, 1 H), 7.83 (d, $J = 7.9$ Hz, 2 H), 7.58-7.67 (m, 3 H); 19F NMR (Acetone-d$_6$, $\delta$): $-78.76$ (s, 6 F); IR (KBr): v = 3145, 3078, 2963, 2891, 1619, 1536, 1492, 1352, 1262,
1007, 909, 854, 797, 739, 690, 648, 598, 571, 521, 507 cm$^{-1}$; MS (ESI, m/z): 311 [M-NTf$_2$]$^+$; Anal. calcd. for C$_{17}$H$_{11}$F$_6$N$_5$O$_8$S: C 34.52, H 1.87, N 11.84; Found: C 34.58, H 2.11, N 11.52.

1-(2,4-dinitrophenyl)-3-p-tolyl-imidazolium bis(trifluoromethylsulfonyl)amide (4b): Yield 90%. $^1$H NMR (Acetone-d$_6$, $\delta$): 10.14 (t, $J = 1.7$ Hz, 1 H), 9.20 (d, $J = 2.4$ Hz, 1 H), 8.96 (dd, $J = 8.8$ Hz, $J = 2.4$ Hz, 1 H), 8.52 (t, $J = 1.8$ Hz, 1 H), 8.51 (d, $J = 8.8$ Hz, 1 H), 8.43 (t, $J = 1.8$ Hz, 1 H), 7.82 (d, $J = 8.5$ Hz, 2 H), 7.56 (d, $J = 8.5$ Hz, 2 H), 2.47 (s, 3 H); $^{19}$F NMR (Acetone-d$_6$, $\delta$): $-79.90$ (s, 6 F); IR (KBr): $v = 3130, 3080, 2877, 1906, 1729, 1621, 1547, 1514, 1356, 1265, 1205, 1125, 1049, 951, 912, 868, 819, 790, 740, 687, 650, 570, 509$ cm$^{-1}$; Anal. calcd for C$_{18}$H$_{13}$F$_6$N$_5$O$_8$S$_2$: C 35.71, H 2.16, N 11.57; Found: C 35.86, H 2.11, N 11.56.

1-(2,4-dinitrophenyl)-3-(4-methoxyphenyl)-imidazolium bis(trifluoromethylsulfonyl)amide (4d): Yield 91%. $^1$H NMR (Acetone-d$_6$, $\delta$): 9.94 (s, 1 H), 9.07 (d, $J = 2.5$ Hz, 1 H), 8.82 (dd, $J = 8.7$ Hz, $J = 2.5$ Hz, 1 H), 8.37 (d, $J = 8.7$ Hz, 1 H), 8.34 (s, 1 H), 8.27 (s, 1 H), 7.73 (d, $J = 9.0$ Hz, 2 H), 7.13 (d, $J = 9.0$ Hz, 2 H), 3.79 (s, 3 H); $^{19}$F NMR (Acetone-d$_6$, $\delta$): $-78.76$ (s, 6 F); IR (KBr): $v = 3146, 3022, 2963, 2884, 2983, 2563, 2066, 1935, 1624, 1503, 1366, 1019, 901, 734, 659, 515$ cm$^{-1}$; Anal. calcd for C$_{18}$H$_{13}$F$_6$N$_5$O$_9$S$_2$: C 34.79, H 2.11, N 11.27; Found: C 34.74, H 2.31, N 11.14.
X-ray Crystallography

X-ray diffraction data were collected using Bruker APEX CCD diffractometers.

Table 1. Hydrogen bonds for 3d [Å and °]

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<th>D-H...A</th>
<th>d(D-H)</th>
<th>d(H...A)</th>
<th>d(D...A)</th>
<th>∠ (DHA)</th>
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<tr>
<td>C(3)-H(3)...F(3)#1</td>
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<td>2.59</td>
<td>3.341(5)</td>
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<tr>
<td>C(5)-H(5)...F(2)#2</td>
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<td>2.55</td>
<td>3.127(5)</td>
<td>120.2</td>
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<tr>
<td>C(12)-H(12)...F(4)#3</td>
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<td>2.47</td>
<td>3.331(5)</td>
<td>154.1</td>
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<tr>
<td>C(15)-H(15)...F(2)</td>
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<td>2.83</td>
<td>3.491(5)</td>
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<tr>
<td>C(1)-H(1)...F(5)</td>
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<tr>
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<tr>
<td>C(1)-H(1)...F(2)</td>
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<td>2.51</td>
<td>3.429(5)</td>
<td>169.4</td>
</tr>
</tbody>
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#1 x, -y+1/2, z-1/2   #2 -x+1, -y, -z   #3 x+1, y, z
Fig. 1 Packing diagram of 3d