Electronic Supplementary Information (ESI)

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 CaH_2. Acetone were freshly distilled from K_2CO_3. ^1H, ^{13}C and ^{19}F NMR spectra were recorded in $CDCl_3$, DMSO-d_6, D_2O and Acetone-d_6 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 $CFCl_3$ for ^{19}F and ^{13}C 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 $^oC\ min^{-1}$. Thermogravimetric analysis (TGA) measurements were carried out with a TA Q500 by heating samples at 20 $^oC\ min^{-1}$ from room temperature to 700 ^oC 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 CH_3CN (0.5 ml). The mixture was heated at 120 ^oC. 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 H. Zhang, Q. Cai, D. Ma, *J. Org. Chem.* 2005, **70**, 5164.

1-(2,4-dinitrophenyl)-3-phenyl-imidazolium chloride (2a): Yield 58%. ^{1}H NMR (D_2O, 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, 1607, 1549, 1494, 1457, 1350, 1260, 1147, 1085, 899, 837, 778, 760, 738, 688, 653, 521 cm^{-1}; MS (ESI, m/z): 311.2 $[M\text{-}Cl]^+$; Anal. calcd for $C_{15}H_{11}ClN_4O_4$: 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%. ^{1}H NMR (D_2O, 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 $[M\text{-}Cl]^+$; Anal. calcd for $C_{16}H_{13}ClN_4O_4$: 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 CH_3CN (2 ml). The mixture was heated at 120 ^oC. After 48 h, acetonitrile was removed under reduced pressure. The residue was washed with ethanol (3×5 mL) and dried in vacuo. Yield 62%. ^{1}H NMR (DMSO-d_6, 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, 1450, 1358, 1280, 1225, 1150, 1069, 952, 906, 865, 845, 746, 684, 642, 627, 549, 524 cm^{-1}; Anal. calcd for $C_{15}H_{11}ClN_4O_5$: 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 ^oC. 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%. ^{1}H NMR (DMSO-d_6, δ): 10.41 (s, 1 H), 9.09 (d, 1 H, *J* = 2.4 Hz), 8.95 (dd, *J* = 8.7 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, 2 H, *J* = 9.1 Hz), 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 $[M\text{-}Cl]^+$; Anal. calcd for $C_{16}H_{13}ClN_4O_5$: C 51.01, H 3.48, N 14.87; Found: C 50.78, H 3.68, N 14.59.

Metathetical reaction of 2 with KPF_6 or $LiNTf_2$: Salts **2** (1 mmol) was dissolved in a mixture of water and acetone (1:1, 10 mL) and treated with an aqueous solution of $LiNTf_2$ (1.1 mmol, 5 ml) or KPF_6 (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 CH_2Cl_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 **3** and **4**.

1-(2,4-dinitrophenyl)-3-phenyl-imidazolium hexafluorophosphate (3a): Yield 95%. ^{1}H NMR (Acetone-d_6, δ): 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); ^{19}F NMR (Acetone-d_6, δ): −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, 691, 638, 559, 507 cm^{-1}; MS (ESI, m/z): 311 $[M\text{-}PF_6]^+$ Anal. calcd for $C_{15}H_{11}F_6N_4O_4P$: C 39.49, H 2.43, N 12.28; Found: C 39.64, H 2.53, N 12.26.

1-(2,4-dinitrophenyl)-3-p-tolyl-imidazolium hexafluorophosphate (3b): Yield 92%. ^{1}H NMR (Acetone-d_6, δ): 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); ^{19}F NMR (Acetone-d_6, δ): −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 $[M\text{-}PF_6]^+$; Anal. calcd for $C_{16}H_{13}F_6N_4O_4P$: 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_2Cl_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, δ): 9.98 (s, 1 H), 9.19 (d, *J* = 2.5 Hz, 1 H), 8.95 (dd, *J* = 8.7 Hz, *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); ^{19}F NMR (Acetone-d_6, δ): −72.24 (d, *J* = 707.0 Hz, 6 F); IR (KBr): v = 3526, 3149, 2881, 1939, 1839, 1809, 1624, 1508, 1454, 1413, 1365, 1252, 1201, 1174, 1116, 1201, 1174, 1116, 1073, 952, 828, 743, 624 cm^{-1}; Anal. calcd for $C_{15}H_{11}F_6N_4O_5P$: 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, δ): 9.92 (s, 1 H), 9.07 (d, *J* = 2.6 Hz, 1 H), 8.83 (dd, *J* = 8.7 Hz, *J* = 2.6 Hz, 1 H), 8.36 (d, *J* = 8.7 Hz, 1 H), 8.33 (d, *J* = 1.7 Hz, 1 H), 8.26 (d, *J* = 1.7 Hz, 1 H), 7.73 (d, *J* = 9.0 Hz, 2 H), 7.13 (d, *J* = 9.0 Hz, 2 H), 3.80 (s, 3 H); ^{19}F NMR (Acetone-d_6, δ): −71.34 (d, *J* = 706.7 Hz, 6 F); IR (KBr): v = 3173, 2942, 2879, 2851, 1885, 1620, 1582, 1460, 1345, 1256, 1185, 1073, 1017, 962, 866, 732, 694, 638, 559 cm^{-1}; Anal. calcd for $C_{16}H_{13}F_6N_4O_5P$: C 39.52, H 2.69, N 11.52; Found: C 39.50, H 2.58, N 11.51.

1-(2,4-dinitrophenyl)-3-phenyl-imidazolium bis(trifluoromethylsulfonyl)amide (4a): Yield 88%. ^{1}H NMR (Acetone-d_6, δ): 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); ^{19}F NMR (Acetone-d_6, δ): −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 $[M\text{-}NTf_2]^+$; Anal. calcd. for $C_{17}H_{11}F_6N_5O_8S$: 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%. ^1H NMR (Acetone-d_6, δ): 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, δ): −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 $C_{18}H_{13}F_6N_5O_8S_2$: 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(trifluoromethylsulfony-l)amide (4d): Yield 91%. ^1H NMR (Acetone-d_6, δ): 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, δ): −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 $C_{18}H_{13}F_6N_5O_9S_2$: 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 °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	∠ (DHA)
C(3)-H(3)...F(3)$^{\#1}$	0.93	2.59	3.341(5)	138.2
C(5)-H(5)...F(2)$^{\#2}$	0.93	2.55	3.127(5)	120.2
C(12)-H(12)...F(4)$^{\#3}$	0.93	2.47	3.331(5)	154.1
C(15)-H(15)...F(2)	0.93	2.83	3.491(5)	129.3
C(1)-H(1)...F(5)	0.93	2.53	3.278(5)	138.1
C(1)-H(1)...F(3)	0.93	2.66	3.307(5)	127.3
C(1)-H(1)...F(2)	0.93	2.51	3.429(5)	169.4

#1 x, -y+1/2, z-1/2 **#2 -x+1, -y, -z** **#3 x+1, y, z**

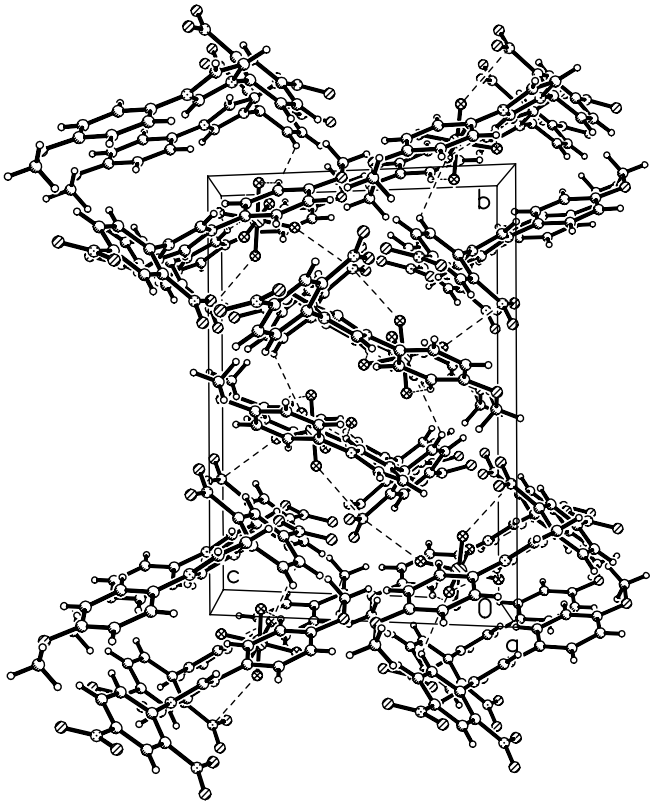

Fig. 1 Packing digram of **3d**