Novel low-melting salts with donor–acceptor substituents as targets for second-order nonlinear optical applications†

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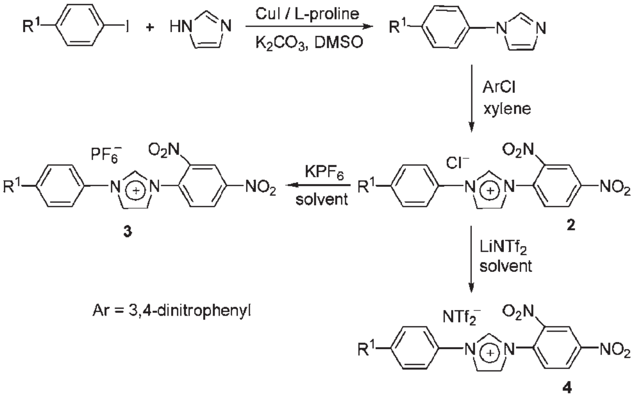
We synthesized several novel low-melting ionic salts with donor–acceptor substituents and investigated their possible applications as second-order nonlinear optical materials.

Organic nonlinear optical (NLO) materials have attracted considerable attention due to their potential applications in optical communication, data manipulation and information processing.[1] The main advantages of organic NLO materials as compared with inorganic ones are their larger first hyperpolarizabilities (β), shorter response time, lower dielectric constant and better synthetic flexibility.[2] Molecules of such materials generally possess a large dissymmetric delocalized π-electron system with a donor π-conjugated bridge acceptor (D–π–A) structure. Current research activities are mainly focused on optimizing the combination of donor and acceptor, increasing conjugation length and improving molecular planarity.[3] However, widespread practical applications of organic NLO materials still suffer from their low thermal stability and poor processability.[4]

The past few years have witnessed a growing interest in ionic liquids composed entirely of organic cations and organic or inorganic anions.[5] They are salts with low melting points (below 100 °C, often even lower than room temperature), which have been widely used as alternative solvents in green chemistry due to their unique physicochemical properties such as negligible vapor pressure, large liquid ranges and environmental benignancy. Most importantly, their properties could be fine-tuned by choosing suitable combination of cation and anion.[6] It is possible to design an ionic liquid for a specific application by the modification of the substituents on the cation or anion. Recently, novel ionic liquids have been designed and synthesized for materials application such as energetic density materials,[7] magnetorheological fluids,[8] liquid crystals,[9] and so on.[10] Compared with the existing non-ionic materials, these ionic analogues demonstrated an improved melt-processability resulting from the low melting point and high thermal stability of ionic liquid. Owing to these characteristics, we reasoned that ionic liquids might be designed and synthesized according to the structural requirements of organic NLO materials. Our earlier experiences[11] in ionic liquids prompted us to investigate the synthesis of novel low-melting salts with donor–acceptor substituents and their potential applications in nonlinear optics.

Imidazolium is one of the most frequently used cations in the development of new ionic liquids because of its reported stability to degradation.[12] Imidazolium cations containing a conjugated aromatic core were then chosen for study. Coupling reaction of imidazole and aryl iodides was carried out according to the method of Ma and co-workers[13] to afford the corresponding *N*-arylated products. Reaction with 1.2 equiv. of 1-chloro-2,4-dinitrobenzene at 120 °C led to the quaternized salts **2a–d** in good yields (Scheme 1). Subsequent metathetical reactions with potassium hexafluorophosphate (KPF_6) or lithium bis(trifluoromethanesulfonyl)amide ($LiNTf_2$) resulted in the formation of **3** and **4**, which were fully characterized by NMR, IR, MS and elemental analysis. The structure of **3d** was further confirmed by single-crystal X-ray diffraction analysis as shown in Fig. 1.‡

Melting points determined by differential scanning calorimetry (DSC) are given in Table 1. It can be seen that the anion exhibits a strong influence on the melting point. With the same cations, the respective melting points decreased greatly on changing the anion from Cl^- to PF_6^- and NTf_2^- (Table 1). Salts **4b** and **4d** have T_m of <100 °C and therefore may be considered ionic liquids (entries 10–11). While most of the chlorides decomposed before melting, the corresponding hexafluorophosphates or bis(trifluoromethanesulfonyl)amides have excellent thermal



Scheme 1 General synthetic routes to **2**, **3** and **4**.

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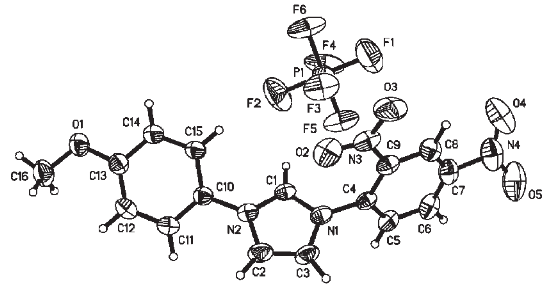

Fig. 1 Single-crystal X-ray crystal structure of **3d**.

Table 1 Thermal properties of **2**, **3** and **4**

Entry	Compd.	R^1	$T_m{}^a/°C$	$T_d{}^b/°C$
1	**2a**	H	—^{c}	253.8
2	**2b**	CH_3	—^{c}	231.5
3	**2c**	OH	—^{c}	228.9
4	**2d**	OCH_3	—^{c}	223.6
5	**3a**	H	203.2	314.8
6	**3b**	CH_3	161.3	323.3
7	**3c**	OH	215.3	277.3
8	**3d**	OCH_3	159.4	297.2
9	**4a**	H	109.3	404.6
10	**4b**	CH_3	69.6	375.8
11	**4d**	OCH_3	82.3	368.2

^{a} Melting point. ^{b} Thermal decomposition temperature. ^{c} Decomposed before melting.

stabilities even at around 300 °C as determined by thermogravimetric analysis (TGA) (entries 5–11).

With these low-melting salts in hand, the second-order nonlinearities were then evaluated using a hyper-Rayleigh scattering[14] (HRS) measurement as shown in Table 2. The first hyperpolarizabilities of these compounds were all larger than those of PNA (4-nitroaniline), which indicated that they might become better second-order NLO materials than PNA derivatives. The relationship between the structure and the hyperpolarizabilities could be clearly observed. On the one hand, the anion has a certain influence on the hyperpolarizability. For a given substituent on the phenyl ring, changing the anion PF_6^- in **3a–c** to NTf_2^- in **4a–d** led to some decrease in the second-order NLO properties. On the other hand, comparison of hyperpolarizabilities of the ionic salts containing differently substituted cations with the same anion clearly illustrates the influence of the substituents. For example, with hexafluorophosphate (PF_6^-) as the anion, on variation of the substituents from methyl (**3b**) to hydroxyl (**3c**), the value of β (10^{-30} esu) increased from 176 to 214 (entries 2–3). A similar tendency can also be observed from **4a** to **4d** with NTf_2^- as the anion. These results indicated that these ionic salts could possess larger hyperpolarizabilities with stronger electron-donating ability of the substituent on the phenyl ring.

Table 2 The second-order nonlinearities of **3** and **4**

Entry	Compd.	R^1	$\beta^a/10^{-30}$ esu	$\beta_0{}^b/10^{-30}$ esu
1	**3a**	H	158	119
2	**3b**	CH_3	176	133
3	**3c**	OH	214	161
4	**4a**	H	135	102
5	**4b**	CH_3	140	105
6	**4d**	OCH_3	151	114

^{a} Measured in THF relative to PNA ($\beta_{PNA} = 21.4 \times 10^{-30}$ esu) at 1064 nm, the error is ±10%. ^{b} Calculated using the two-level model.[15]

In conclusion, we have successfully achieved the synthesis of several novel low-melting salts with donor–acceptor substituents. Some of the salts fall into the ionic liquid class ($T_m < 100$ °C). We have explored the possible application of ionic liquids as second-order nonlinear optical materials. Most of them exhibit excellent properties including good NLO effect, high thermal stability and low melting point, which may be useful for nonlinear optical applications.

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Notes and references

‡ *Crystal data* for **3d**: $C_{16}H_{13}F_6N_4O_5P$, $M = 486.26$, monoclinic, space group $P2_1/c$, $a = 11.1474(10)$, $b = 16.3515(15)$, $c = 12.3412(11)$ Å, $V = 2024.6(3)$ Å^3, $T = 293(2)$ K, $Z = 4$, μ(Mo-Kα) = 0.228 mm^{-1}, $R1 = 0.0755$, $wR2 = 0.2264$ ($I > 2\sigma(I)$); $R1 = 0.1069$, $wR2 = 0.2522$ (all data). CCDC 682525.

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