Syntheses of NLO diamino chromophores containing imidazole and thiophene rings as conjugation linkage

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Three nonlinear optical chromophores bearing diamino groups have been synthesised, in which imidazole and thiophene rings were employed as elongated conjugation bridges.

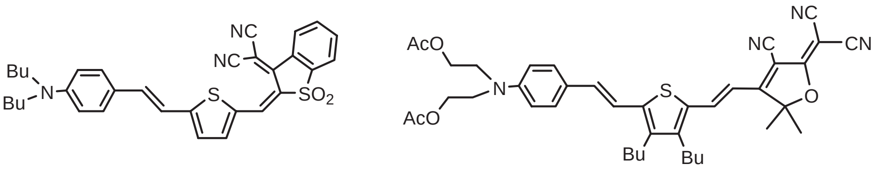
Keywords: imidazole, nonlinear optics, chromophores, first hyperpolarisability

Organic molecules with large first hyperpolarisabilities (β) have attracted considerable attention over the last 20 years for their potential applications in optical data storage, telecommunications and optical signal processing.[1,2] It is already well known that molecules containing electron–donor and electron–acceptor groups linked by a large conjugated framework possess large values of β.[3] Molecular nonlinearities can be significantly enhanced by increasing the donor and acceptor strength or the length of the conjugation pathway.[4] For example, compounds 1 and 2 shown in Scheme 1, represent the highest value of $\mu_g\beta_0$ (510.8×10^{-48}/esu, 800.4×10^{-48}/esu).[5]

Although significant progress has achieved in the design and syntheses of such one dimensional dipole chromophores,[6,7] in order to make a useful device, NLO chromophores must be incorporated into a fabric version, such as poled polymers, LB films, self-assembled or crystal environments, *etc*. Among these, chemical incorporation of chromophores into a polymer backbone is probably the most important choice. Thus the NLO chromophores that bear reactive groups and can be covalently banded into a suitable molecular structure are greatly demanded. Up to now, only a few such chromophores have been reported,[8] and there exists a need to explore and develop such reactive chromophores with efficient nonlinearities, desired transparency and high thermal stabilities. Here we report the synthesis of three imidazole-based diamino chromophores, which can be used to form high *T*g NLO polymers such as polyureas and polyimides.

Our approach to the design of superior nonlinear optical chromophores was based on the use of the electron rich imidazole ring. The conjugation pathway was further extended, by using thiophene, olefin and benzene groups. Two aminophenyl groups were introduced into the 4- and 5-positions of the imidazole ring. Amino groups were used as an electron-donor and a nitro group was used as an electron–acceptor. The designed chromophores are shown in Scheme 2.

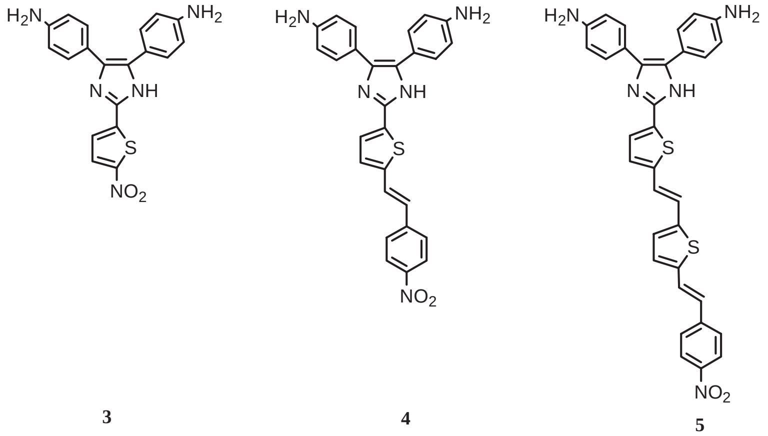
The syntheses of chromophores **3, 4** and **5** are summarised in Scheme 3. Wadsworth–Emmons reaction of aldehyde **7** with *p*-nitrophosphonate **8**[9] (prepared by the Michaelis–Arbuzov reaction using benzyl chloride and trimethyl phosphite, followed by nitration to introduce the nitro group in the *para* position.) gave product **9** in high yield. Vilsmeier–Haack formylation reaction of **9** formed aldehyde **10** with a small amount of isomer. Again Wadsworth–Emmons reaction of **10** with thiophenyl-



1 **2**

$\mu_g\beta_0 = 510.8\times10^{-48}$/esu $\mu_g\beta_0 = 800.4\times10^{-48}$/esu

Scheme 1



3 **4** **5**

Scheme 2

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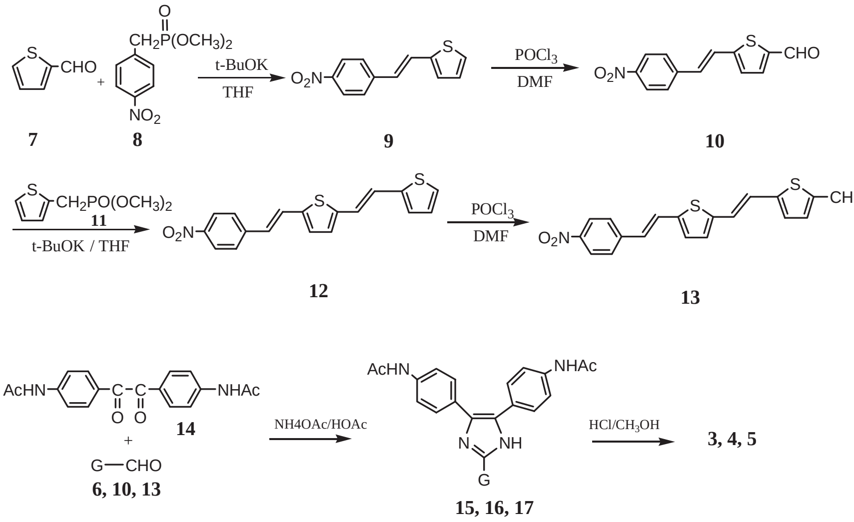

Scheme 3

Table 1 Characterisation data of chromophores

Chromophore	λ_{max} (nm)	μ_g (D)	$\beta_0/10^{-30}$ (esu)	$\mu_g\beta_0/10^{-48}$ (esu)	$\mu_g\beta_0/MW^a$	T_d (°C)
3	419	8.57	22.52	193.1	0.512	286
4	435	9.11	44.56	405.8	0.848	279
5	463	9.10	101.9	927.3	1.587	268

^{a}Figure of Merit(FOM).

phosphonate **11** gave product **12,** followed by Vilsmeier-Haack formylation reaction to afford the aldehyde **13**.

To form the imidazole ring, condensation of aldehydes with benzil in the presence of ammonium acetate in glacial acetic acid solution is employed as a general method. Previously, in a preparation of a lophin-type compounds, Marks and co-workers reported the use of 4,4'-diphthalimidobenzil as a starting dicarbonyl compound.[10] The condensation product was further hydrazinolysed to afford the target diamino product. Since the use of the bulky phthaloyl group as a protecting amino group could result in poor solubility of the substrates and due to the harsh reaction conditions for hydrazinolysis, the chromophores were produced in poor overall yield. Here we simply use the acetyl group as the protecting group, as it can be removed under mild conditions. Thus, reaction of **14**[11] with aldehyde **6** (5-nitro-thiophene-2-carbaldehyde), **10** and **13** in the presence of ammonium acetate in glacial acetic acid solution afforded the acetyl-protected diamino chromophores **15**, **16** and **17** , which were further treated with HCl/MeOH to give chromophores **3,** **4** and **5**, respectively.

The electrostatic first hyperpolarisabilitie β_0 and the ground state dipole moment μ_g of the three chromophores have been calculated by employing the semi-empirical AM1/FF (finite field) calculations.[12] Their characterisation data including $\mu_g\beta_0$, maximum absorption wavelength λ_{max} in THF and thermal decomposition temperature T_d are collected in Table 1.

It is found that extending the conjugation pathway by a thiophene ring resulted in greatly enhanced charge transfer properties and nonlinear responses, although the thermal stability was slightly decreased. Chromophore **5** has a very high value of $\mu_g\beta_0$: 927.3×10^{-48} esu, which is larger than that of the previously reported chromophore **2** (800.4×10^{-48} esu).

In summary, a novel series of diamino imidazole-type chromophores has been synthesised. They can be used as monomers to form high T_g polymers for nonlinear optical applications.

Experimental

Synthesis of **9:** To a 1:1 mixture of the aldehyde **7** (3.26g, 0.0291 mol) and the *p*-nitrophosphonate **8** (7.13g, 0.0291 mol) in THF solution was added equivalent potassium *t*-butoxide (3.26g, 0.0291mol). The resultant mixture was stirred at room temperature for 3 h. After filtration, and removal of the solvent, the crude product was purified by recrystallisation from ethyl acetate and the pure product (5.78g) was obtained as bright yellow crystals. Yield : 86%. m.p. 168–170 °C . ^1H NMR(DMSO-d_6) δ (ppm) 8.22 (d, 2H, *J* = 9.5 Hz), 7.58 (d, 2H), 7.18 (d, 4H, *J* = 9.5 Hz), 7.42 (d, 1H, *J* = 16.4 Hz), 7.32–7.20 (m, 3H), 6.95 (d, 1H, *J* = 16.4 Hz). ^{13}C NMR (DMSO-d_6) δ (ppm) 146.7, 143.5, 141.7, 128.0, 127.9, 126.5, 126.2, 126.1, 125.7, 124.1. *m/z* (EI): 231(M^+). Anal. Calcd. for $C_{12}H_9NO_2S$: C, 62.34 H, 3.91; N, 6.06. Found: C, 62.23; H, 3.91; N, 5.94.

Synthesis of **10:** Phosphorus oxychloride (0.768 g, 5 mmol) was added dropwise at 0 °C to DMF (2 ml). The mixture was stirred at 0°C for 1 h and then at room temperature for 30 min. To the resulting solution was then added compound **9** (1.155 g, 5 mmol) at once. This reaction mixture was heated to 80–90 °C and maintained at this temperature for 6 h. After cooling, the mixture was poured into water (50 ml). The yellow solid was collected by filtration, washed with water and recrystallised from ethyl acetate to give **10** (1.15 g, yield: 54.2%. m.p. 132–134 °C. IR (KBr) cm^{-1}: 3042, 2900, 1645, 1534, 1503, 1438, 1330,1218, 942, 652. ^1H NMR(DMSO-d_6) δ (ppm) 9.90 (s, 1H), 8.25 (d, 2H, *J* = 8.5 Hz), 8.01 (d, 1H, *J* =3.8 Hz), 7.86 (d, 2H, *J* = 8.5 Hz), 7.79 (d, 1H, *J* = 16.0 Hz), 7.52 (d, 1H, *J* = 3.8 Hz), 7.42 (d, 1H, *J* = 16.0 Hz). ^{13}C NMR (DMSO-d_6), δ(ppm) 182.7, 136.9, 133.6, 133.3, 129.1,128.9, 128.2, 127.6, 127.5, 125.5, 125.0. *m/z* (EI): 259 (M^+). Anal. Calcd. for $C_{13}H_9NO_3S$: C, 60.21; H, 3.51; N, 5.40. Found: C, 60.48; H, 3.97; N, 5.39.

Synthesis of **12:** Similar to the synthesis of **9**. yield 81%, m.p. 241–243 °C. IR (KBr) cm^{-1}: 3400, 2914, 1650, 1582, 1500, 1434, 1327, 1100. ^1H NMR($CDCl_3$) δ ((ppm) 8.23 (d, 2H, *J* = 9.6 Hz), 7.57 (d, 2H, *J* = 9.6 Hz), 7.34 (d, 1H, *J* =15.9 Hz), 7.22 (d, 1H, *J* = 5.9Hz), 7.10–7.00 (m, 5H), 6.96 (d, 1H, *J* = 5.9 Hz), 6.88(d, 1H, *J* = 15.9 Hz). ^{13}C NMR (DMSO-d_6), δ(ppm) 181.6, 144.1, 139.5, 142.7, 140.8, 129.2, 127.6, 126.9, 126.6, 126.3, 126.0, 125.4, 124.8, 124.0, 122.4, 120.9. *m/z* (EI): 339 (M^+). Anal. Calcd. for $C_{18}H_{13}NO_2S_2$: C, 63.70; H, 3.86; N, 4.13. Found: C, 63.52; H, 3.94; N, 4.46.

Synthesis of **13:** Similar to the synthesis of **10**. yield 34%, m.p. 178–180 °C. IR (KBr) cm^{-1}: 3400, 2900, 1652, 1579, 1500, 1438, 1334, 1100, 940. ^1H NMR($CDCl_3$) δ ((ppm) 9.86 (s, 1H), 8.24 (d, 2H, *J* = 8.5 Hz), 7.94 (d, 1H, *J* = 3.5 Hz), 7.89 (d, 1H, *J* =15.8 Hz), 7.83 (d, 2H, *J* = 8.5Hz), 7.79 (d, 1H, *J* = 3.5 Hz), 7.70 (d, 1H, *J* = 3.5 Hz), 7.50 (d, 1H, *J* = 14.5 Hz). 7.31 (d, 1H, *J* = 4.5 Hz), 7.11 (d, 1H, *J* = 15.8 Hz). 7.20 (d, 1H, *J* = 3.5 Hz). *m/z* (EI): 367 (M^+). Anal. Calcd. for $C_{19}H_{13}NO_3S_2$: C, 62.1; H, 3.57; N, 3.81. Found: C, 61.74; H, 3.92; N, 3.97.

General procedure of the syntheses of imidazole derivatives **15–17** *from aldehydes* **6, 10, 13**

A mixture of the benzil **14** and aldehyde (1:1), ammonium acetate (10 eq.) in glacial acetic acid was stirred at 110 °C for 2 h under nitrogen. After cooling, the resulting homogeneous solution was poured over crushed ice. The precipitate was collected by filtration and washed with cold water, then dried under vacuum. The crude product was recrystallised from ethyl acetate to afford the imidazole derivatives.

Compound **15:** Yield 85%. m.p. >300 ^{o}C. IR (KBr) cm^{-1}: 3400, 1660, 1594, 1515, 1435, 1400, 1314, 1224, 830. ^{1}H NMR (DMSO-d_6) δ (ppm) 12.55 (s, 1H), 10.05 (s, 1H), 9.95 (s, 1H); 8.16 (d, 1H), 7.67 (d, 1H), 7.60–7.40 (m, 8H), 2.00 (s, 6H). ^{13}C NMR (DMSO-d_6) δ (ppm) 168.6, 149.0, 141.9, 139.6, 139.0, 131.7, 129.6, 129.1, 127.8, 127.7, 123.2, 119.3, 24.2. *m/z* (FAB): 461 (M^+). Anal. Calcd. For $C_{23}H_{19}N_5O_4{\bullet}H_2O$: C, 55.60; H, 4.62; N, 14.13. Found: C, 56.27, H, 4.61; N, 14.13.

Compound **16**: Yield: 79%. m.p. >300 ^{o}C. IR (KBr) cm^{-1}: 3400, 1657, 1580, 1515, 1435, 1400, 1327, 1100, 830. ^{1}H NMR (DMSO-d_6) δ (ppm) 12.81 (s, 1H), 10.08 (s, 1H), 9.94 (s, 1H); 8.22 (d, 2H, *J* = 8.6 Hz), 7.83 (d, 2H, *J* = 8.6 Hz), 7.62 (d, 1H, *J* = 3.4 Hz), 7.30 (d, 1H, *J* = 16.0 Hz), 7.32 (d, 1H, *J* = 3.4 Hz), 7.5–7.38 (m, 8H), 7.13 (d, 1H, *J* = 16.0 Hz). ^{13}C NMR (DMSO-d_6) δ (ppm) 168.8, 145.7, 143.4, 141.0, 140.4, 138.3, 138.2, 133.8, 130.6, 129.4, 127.7, 126.7, 126.2, 125.4, 118.6. *m/z* (FAB): 564 (M^+). Anal. Calcd. For $C_{31}H_{25}N_5O_4S\langle$: C, 66.06; H, 4.47; N, 12.43. Found: C, 66.45, H, 4.92; N, 12.46.

General procedure for the syntheses of chromophores **3–5** *from* **15–17.**

A solution of **15–17** in methanol with concentrated hydrochloric acid was refluxed for 30 min. After cooling to room temperature, the resulting yellow solution was poured over crushed ice. The precipitate was filtered and dissolved in water. To this aqueous solution was added ammonia liquor dropwise to the pH 10~11. The thus formed precipitate was collected by filtration and washed with cold water, and then dried under vacuum. Flash column chromatography was performed to afford the pure chromophores **3–5** correspondingly.

Chromophore **3:** Yield 92%. m.p. >300 ^{o}C. IR (KBr) cm^{-1}: 3400, 1615, 1512, 1340, 1312, 1215, 1087, 825. ^{1}H NMR (DMSO-d_6) δ (ppm) 12.95 (s, 1H), 8.21 (d, 1H, *J* = 8.6 Hz), 7.18 (d, 1H, *J* = 5.6 Hz) 6.60 (d, 4H, *J* = 5.6 Hz), 5.36 (s, 4H, *J* = 9.0Hz. ^{13}C NMR (DMSO-d_6) δ (ppm) 155.4, 143.9, 140.7, 132.2, 130.6, 129.3, 125.8, 120.8, 113.0, 103.4. *m/z* (EI): 377 (M^+). Anal. Calcd. For $C_{19}H_{15}N_5O_2S$: C, 60.45; H, 4.01; N, 18.54. Found: C, 60.28; H, 4.45; N, 18.36.

Chromophore **4:** Yield 89.4%. m.p. >300 ^{o}C. IR (KBr) cm^{-1}: 3400, 1608, 1576, 1500, 1435, 1325, 1172, 1100, 825. ^{1}H NMR (DMSO-d_6) δ (ppm) 12.25 (s, 1H), 8.21 (d, 2H, *J* = 8.6 Hz), 7.82 (d, 2H, *J* = 8.6 Hz) 7.66 (d, 1H, *J* = 16.4 Hz), 7.60 (d, 1H, *J* = 3.8 Hz), 7.30 (d, 1H, *J* = 3.8 Hz), 7.20 (d, 4H, *J* = 8.5 Hz). 7.14 (d, 1H, *J* = 16.4 Hz) 6.58 (d, 4H, *J* = 8.5 Hz). ^{13}C NMR (DMSO-d_6) δ (ppm) 146.0, 143.7, 142.9, 141.3, 140.7, 133.4, 130.1, 128.6, 128.4, 128.1, 127.7, 127.1, 126.6, 125.6, 124.6, 124.0, 118.9. HR-MS (M^+). Anal. Calcd. For $C_{27}H_{21}N_5O_2S{\bullet}$: 479.1417, Found: 479.1410

Chromophore **5:** Crude **17** was directly used without further purification. m.p. >300 ^{o}C. IR (KBr) cm^{-1}: 3400, 2900, 1610, 1580, 1500, 1435, 1328, 1152, 1100, 940, 714. ^{1}H NMR (DMSO-d_6) δ (ppm) 12.25 (s, 1H), 8.20 (d, 2H, *J* = 8.6 Hz), 7.81 (d, 2H, *J* = 8.6 Hz) 7.80–7.21(m), 7.20 (d, 4H, *J* = 9.0 Hz), 6.58 (d, 4H, *J* = 9.0 Hz). HR-MS (M^+). Anal. Calcd. For $C_{33}H_{25}N_5O_2S_2$: 588.1522, Found: 588.1530

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