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New class of imidazoles incorporated with thiophenevinyl conjugation pathway for robust nonlinear optical chromophores

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Abstract—A new series of thermally stable heterocyclic imidazole-based nonlinear optical chromophores has been developed. These chromophores possess a thiophene based stilbene conjugation pathway with a nitro acceptor group attached to the phenyl end. This feature leads to robust chromophores with high thermal stability and enhanced molecular nonlinearity © 2001 Elsevier Science Ltd. All rights reserved.

In order to be compatible with existing semiconductor processing technology, organic nonlinear optical (NLO) chromophores for device application are required to be highly thermally stable for sustaining the processing and operating temperatures.[1] Heterocyclic imidazole based NLO chromophores have received increasing interest due to their excellent thermal stability in guest–host systems, and good miscibility with high performance polymers.[2] The imidazole ring is easily tailored to accommodate functional groups,[3] which allows the covalent incorporation of the NLO chromophores into polyimides leading to NLO side chain polymers.[3] Owing to synthetic challenge, most of the NLO imidazoles developed so far only possess short conjugation pathways (spacers) such as phenyl.[4,5] No report has appeared yet about NLO imidazoles with long conjugation pathways.

Extension of conjugation pathways is desirable to enhance molecular nonlinearity. Jen and co-workers also revealed that molecular nonlinearity can be further improved when thiophene is used in the conjugation pathways.[6] However, simple annexation of conjugation pathways often leads to a compromise of thermal stability and solubility. In particular, when a nitro group is used as an acceptor, it is likely that a direct placement of the nitro group on the thiophenyl end will severely compromise thermal stability.[5] This has prompted us to design a new system, which possesses thiophene in a long conjugation pathway, but at the same time to have nitro groups attached to phenyl instead of thiophenyl. The new class of NLO imidazoles has been found to possess improved molecular nonlinearity, high thermal stability, and excellent solubility.

The general route for the preparation of new chromophores **13**–**16** is developed according to Scheme 1. The key development is the aldehydes **9**–**12**, which are versatile precursors which could lead to a variety of imidazole-based NLO chromophores.[7] Condensation of 2-formylthiophene with benzil derivatives in the presence of ammonium acetate led to the formation of the imidazole **1**–**4** in a yield from 70 to 87%. *N*-methylation was achieved by the treatment of **1**–**4** with iodomethane in the presence of potassium carbonate to give **5**–**8** with a yield from 65 to 90%. It was found that the exact 1:1 ratio of iodomethane to imidazoles **1**–**4** was needed, and even slightly excessive MeI would lead to the formation of salts. For example, treatment of **3** with 1.2 equiv. iodomethane gave **17** exclusively (Scheme 2). The aldehydes **9**–**12** were prepared by the treatment of **5**–**8** with *n*-butyl lithium at low temperature in situ, followed by the addition of anhydrous DMF. Yields are moderate to good with **9** of 68%, **10** of 40%, **11** of 75% and **12** of 53%. The direct formulation of **1**–**4** using 1–3 equiv. *n*-butyl lithium had been attempted, and in no case had any of the corresponding aldehydes been obtained, suggesting the *N*-methylation

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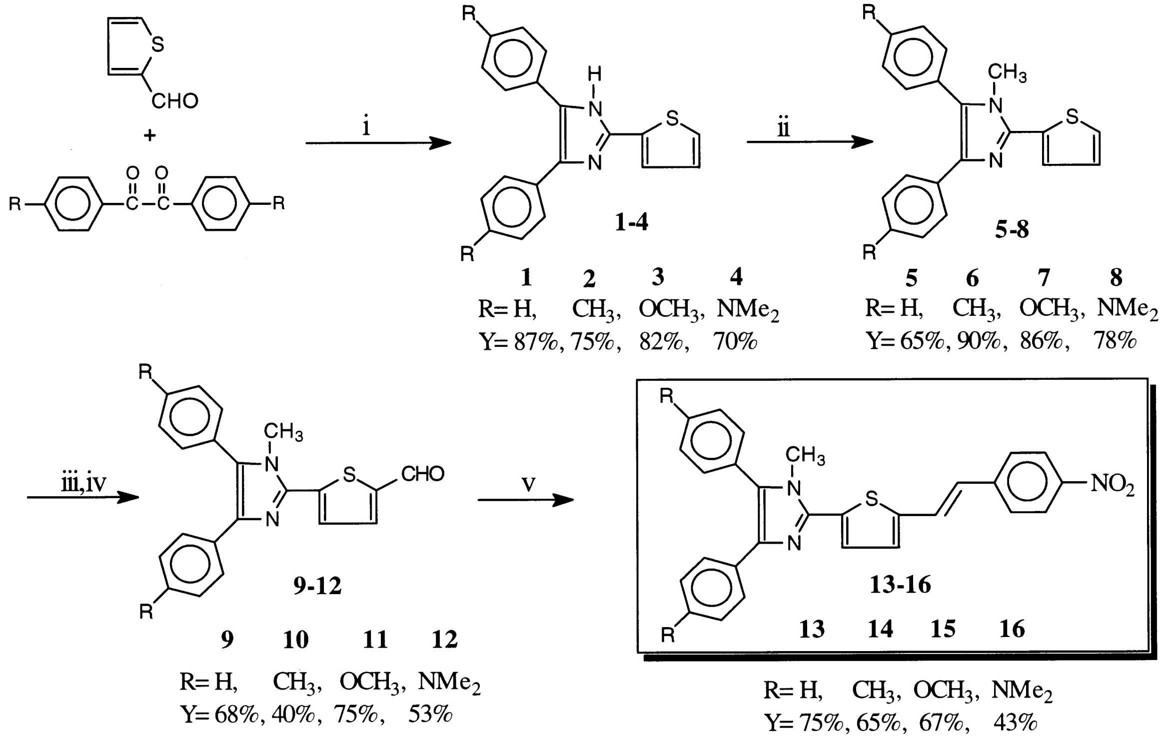
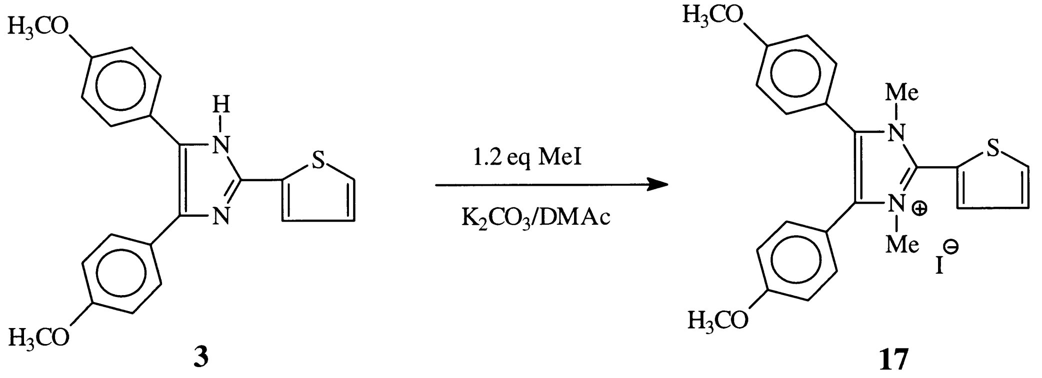
of **1**–**4** is very necessary for the successful formulation in the next step.

The new NLO chromophores **13**–**16** were initially prepared by the condensation of the aldehydes **9**–**12** with 4-nitrophenylacetic acid, but with less satisfactory yield and more time-consuming separation due to several undesirable by-products. It was found that the reaction of a Wittig reagent with **9**–**12** in the presence of potassium *tert*-butoxide generated the chromophores in moderate to good yield (**13**, 75%; **14**, 65%; **15**, 67%; **16**, 43%). The reaction was promoted by 15-crown-5 in methylene chloride. The use of 18-crown-6 led to a similar result of the yield.

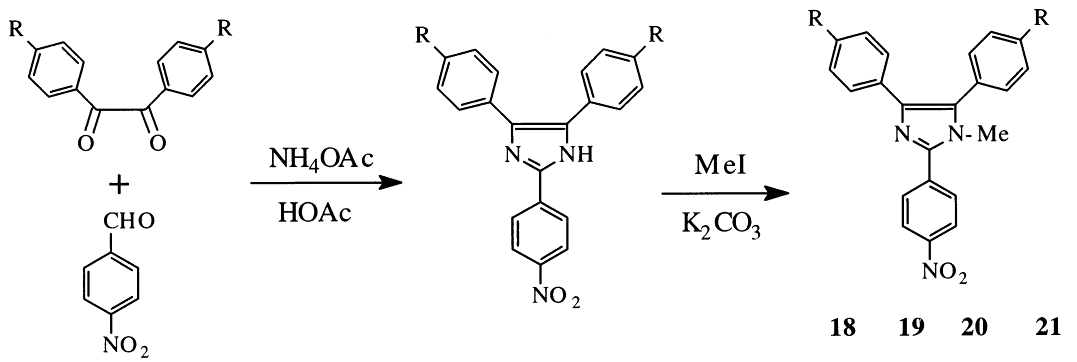
Chromophores **18**–**21** have been prepared which bear identical donors and acceptors to those in **13**–**16** but without thiophenevinyl units. The comparison has been made to manifest the contribution of thiophenevinyl conjugation in **13**–**16**. The synthesis started with the direct condensation of benzil derivatives and 4-nitrobenaldehyde in the presence of ammonium acetate, followed by *N*-methylation by iodomethane in the presence of potassium carbonate (Scheme 3). The chromophore **20** absorbs at 399 nm and **21** at 443 nm. Compared with **20**, the chromophore **15** has a red shift of 37 nm while **16** is red shifted by 20 nm relative to **21**. These large shifts clearly indicate that the present system with larger delocalized conjugation pathway facilitates charge transfer from donors to acceptors, leading to more effective D–A chromophores. In addition, the transparency of chromophores **13**–**16** in the visible region has also been determined. The chromophore **13** is transparent from 550 nm while **14**, **15** and **16** are transparent from 560, 570, and 650 nm, respectively.



Scheme 1. i: $NH_4OAc/HOAc$, 120°C; ii: MeI/K_2CO_3, 55°C; iii: BuLi/THF, −78°C to 0°C; iv: DMF; v: 15-crown-5/*t*-BuOK/CH_2Cl_2/1,4-$O_2NC_6H_4$-CH_2PPh_3Br.



Scheme 2.



18 **19** **20** **21**

R = H, Me, OCH_3, NMe_2

Y = 72%, 87%, 83%, 75%

Scheme 3.

Table 1. EFISH data for second-order nonlinear properties of **13**–**16** and **18**–**21**[a]

Chromophores	$\mu\beta$ (10^{-48})esu	Chromophores	$\mu\beta$ (10^{-48})esu	$\Delta(\mu\beta)$ (10^{-48})esu
13	370	**18**	100	270
14	945	**19**	145	800
15	475	**20**	130	345
16	590	**21**	360	230

[a] $\mu\beta$ @ 1907 nm using a quartz reference ($d_{11}=0.277$ pm/V).

Table 2. Electronic absorption and thermal properties of **13**–**16**

Chromophores	λ_{max} (nm)[8]	ε ($M^{-1}cm^{-1}$)	$\lambda_{cut\ off}$ (nm)	T_d(°C)	T_5(°C)	T_m (°C)[9]
13	426	3.05×10^4	550	340	317	213
14	432	3.43×10^4	560	320	316	236
15	436	3.04×10^4	570	332	337	119
16	463	4.32×10^4	650	242	251	242

The second-order nonlinear optical properties of the two series of chromophores have been evaluated by $\mu\beta$, the scalar product of the dipole moment (μ) and the molecular first-order hyperpolarizability (β). The values of $\mu\beta$ for both series as determined by electric field-induced second-harmonic generation (EFISH) at a fundamental wavelength of 1907 nm[10,11] are listed in Table 1. While both series show second-order nonlinear optical properties, the one with the longer conjugation pathway was found to have much enhanced properties. The chromophores **18**–**21** exhibited $\mu\beta$s in the range of 100 to 360×10^{-48} esu. In marked contrast, the chromophores **13**–**16** showed significantly larger $\mu\beta$s which range from 370 to 945×10^{-48} esu. The parallel comparison was made between **13** and **18**, **14** and **19**, **15** and **20**, and **16** and **21,** revealing that the $\mu\beta$ value of **13** is 3.7 times that of **18**, and so is the value of **15** compared to that of **20**. The $\mu\beta$ value of **16** is 1.6 times that of **21** while the value of **14** is 6.5 times that of **19**. If we characterize the contribution of the conjugation pathways (series **18**–**21** vs series **13**–**16**) in terms of the difference in $\mu\beta$ values we see that the contribution of the thiophenylvinyl conjugation pathway ranges from 230 to 800×10^{-48} esu. The largest difference of 800×10^{-48} esu was found between compounds **14** and **19**.

Thermal stability for this new series of chromophores has been evaluated by means of differential scan calorimetry (DSC) and thermogravimetric analysis (TGA). The onset decomposition temperature, T_d, at a heating rate of 10°C min^{-1} in air is obtained from DSC by the intercept of the positive slope of the decomposition peak with the baseline, and a 5% weight loss temperature, T_5, is obtained from TGA with the same heating rate of 10°C min^{-1} in air (Table 2). All the chromophores except **16** exhibit high thermal stability with the onset decomposition temperatures at or higher than 320°C. These chromophores also show 5% weight loss at 316°C or higher. The most impressive chromophore is **15** which does not start decomposition until 332°C, and just loses 5% weight up to 337°C. The overall thermal stability remains high in spite of present expansion of conjugation pathway designed for high nonlinearity. In addition, all the new chromophores are soluble in common organic solvents such as THF, chloroform and DMF. Therefore, the addition of thiophenevinyl to the conjugation pathway and the attachment of the nitro acceptor to the phenyl end lead to enhanced nonlinearity without compromising thermal stability and solubility.

In summary, a new class of heterocyclic imidazole based NLO chromophores has been developed. The new chromophores possess large conjugation pathway to facilitate charge transfer and enhance nonlinearity. They also exhibit high thermal stability, excellent solubility, and good transparency.

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7. Other types of chromophores from the aldehydes **9**–**12** are being developed and will be reported in due course.
8. Concentration used in this study is in the range of 10^{-5} M/L in chloroform.
9. Melting point (Tm) is obtained in DSC run at a heating rate of 10°C min^{-1} in air.
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