

The Development of Zwitterionic Second Order Nonlinear Optical Organic Materials

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Introduction

The development of second order nonlinear optical (NLO) organic materials has been an area of intense research over the last 25 years.¹ This has been largely driven by the expectation that next-generation devices in, for example, telecommunications, sensing and computing will contain NLO materials as the active components. These devices will, in turn, underpin the rapidly increasing global photonics industry, which is already worth over \$NZ 800 billion p.a.² Nonetheless, the uptake and commercialization of organic NLO materials has been slow, mainly due to competition from existing inorganic materials as well as issues with the long-term stability of organic compounds when exposed to high intensity light.³ Consequently, there is still a significant quantity of research needed before the widespread deployment of device-quality organic NLO materials is realised,^{4,5} and in particular those that will allow operation at relatively low power levels.⁶ This article describes some of the research that has been undertaken by the Photonics team at IRL on the development of organic NLO chromophores. It includes some theoretical aspects around the design of NLO materials, options for optimizing their response and stability, and outlines the specific approach taken by IRL towards developing our materials.

Fundamental Concepts of Organic NLO Materials

Optical nonlinearity occurs when an external field (either high intensity light or an electric field) is applied to a dielectric medium to produce light that is altered in phase, amplitude or frequency.⁷ In order for a medium to exhibit nonlinearity, the field must be of sufficient strength to overcome any internal electrostatic interactions. As a result, NLO materials need to contain weakly bound or highly polarizable electrons. A straightforward way of viewing NLO materials is to regard them as compounds in which a large change in refractive index can be obtained by applying a field. This, in turn, allows for the development of materials in which it is possible to *control* light as it passes through them, and this is of considerable interest to optics and physics researchers. The magnitude of the NLO effect is defined by the second term of the equations that describe polarisation as a function of the applied electric field; hence the materials are termed *second order*. These equations, or power series, can describe both the molecular (Eq. 1) and macroscopic (Eq. 2) polarization:¹

$$p = \alpha E + \beta EE + \gamma EEE + \dots \quad \dots \text{Eq. 1}$$

$$P = \chi^{(1)}E + \chi^{(2)}EE + \chi^{(3)}EEE + \dots \quad \dots \text{Eq. 2}$$

Equation 1 provides the first hyperpolarizability, β ; it is of particular interest as it is the component we aim to maxi-

mize. Equation 2 contains the second-order susceptibility, $\chi^{(2)}$, a further value that must be maximised. The $\chi^{(2)}$ value is calculated from what is termed *the r_{33} value*, which is the experimentally measured electro-optic coefficient. Not surprisingly, the incorporation of molecules that have high β values into bulk materials (or polymers) results in materials with the highest macroscopic responses [$\chi^{(2)}$]. Furthermore, in order to observe a macroscopic response, it is essential that the bulk material is non-centrosymmetric; for organic compounds this typically means that the dipole moments of the embedded chromophores must be at least partially aligned. This can be achieved by heating a thin film of an NLO material to its glass transition temperature and then applying an electric field of sufficient strength to force the dipole moments into alignment. The larger the dipole moment (μ) of the embedded chromophore, the more efficiently this can be achieved. Consequently, when selecting a molecule as a potential candidate for use in an NLO material, a key requirement is for it to have what is termed a *large figure of merit*; it is the product of the first hyperpolarizability and dipole moment, *i.e.* $\mu \times \beta$ esu, and given as the value $\times 10^{-48}$ esu.

Organic compounds with the highest NLO responses typically contain donor and acceptor groups that are separated by a conjugated polyene spacer, *i.e.* Donor- π -Acceptor. In a push-pull system such as this, the π electrons will almost always be polarized asymmetrically. Furthermore, the degree of polarization of such an NLO molecule in its ground state allows for its classification as either neutral or ionic. This led Marder *et al.* to use the concept of bond length alternation (BLA) in a compound for the classification of NLO chromophores as either left hand side (LHS), right hand side (RHS) or neutral (Fig. 1).⁸ From Fig. 1 it can be seen that there are two opportunities to maximize the first hyperpolarizability, β . By tuning the strength of the donor and acceptor moieties, as well as the length of the conjugated interconnect, it is theoretically possible - although not necessarily easy - to tune the magnitude of BLA within a compound in order to maximize the NLO response. Over the last two decades LHS molecules, those with a positive BLA, have been extensively studied by a number of researchers,^{1,6} whereas negative BLA molecules of the RHS type remain largely unexplored. As a consequence, we decided that focusing on RHS molecules would provide the greatest scope to develop a novel suite of compounds. In taking this approach some of the key considerations were:

- ease of synthesis,
- a unique, and therefore patentable, series of compounds,
- a *building block* synthesis that would allow for easy introduction and modification of the donor, acceptor, and π interconnect components,

- figures of merit greater than $5,000 \times 10^{-48}$ esu and thermal stabilities not less than 230 °C, and
- easy incorporation of functionality to allow for tethering to a polymer backbone (improving solubility) or reducing aggregation.

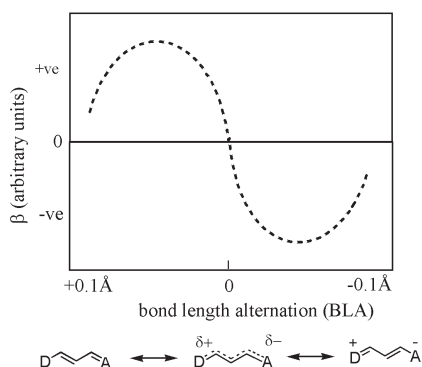


Fig. 1. NLO response (or first order hyperpolarizability) dependence on chromophore bond length alternation; LHS = +ve BLA, RHS = -ve BLA

First Generation NLO Materials

A straightforward method for creating chromophores with zwitterionic ground states is to synthesise molecules that gain in aromatic stabilization energy upon transfer of charge from the donor to the acceptor. Consequently, our initial strategies focussed primarily on the synthesis of planar conjugated molecules with a donor (4-pyridinylidene, 4-quinolinylidene or benzothiazolidinylidene) capable of aromatization and a range of acceptors (Fig. 2).^{9,10} While almost all of the compounds synthesised had respectable figures of merit, it was found that the combination of either a pyridinylidene or quinolinylidene donor with a cyano(dicyanomethylidene)dihydrofuranyl (CDF – see Scheme 1) acceptor led to molecules with the highest NLO responses.¹¹ This class of compounds has become the focus of our research.

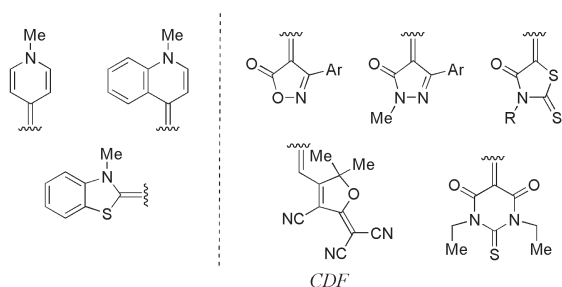
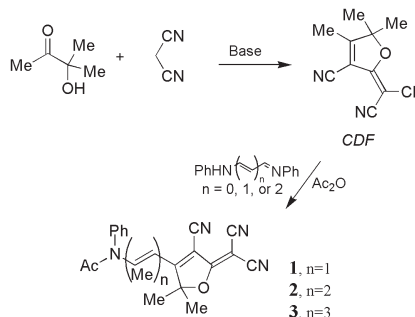


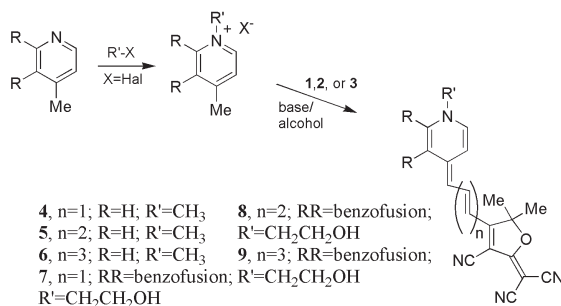
Fig. 2 Some of the donor (left) and acceptor (right) systems studied during our early work.

The original synthesis of these new chromophores is shown in Scheme 1.¹¹ The CDF acceptor is readily available from condensation of excess malononitrile with an α,α -disubstituted methyl ketone (in this case 3-hydroxy-3-methylbutanone).¹² The acceptor is then reacted with the appropriate dialdehyde bisanil in acetic anhydride to give the corresponding (*oligo*)amido dihydrofurans **1-3**. These can then be condensed with either an *N*-substituted 4-methylpyridinium or a 4-methylquinolinium salt to give the final chromophores **4-9** (Scheme 2). A significant advantage of this approach is that compounds such as **1-9** almost always precipitate from the crude reaction

mixture. Simple filtration and washing typically gives a product suitable for immediate use. If necessary the compounds can be further purified by recrystallization. A further advantage of this approach is that it achieves our aim of developing a *building block* approach. For example, it is easy to change the donor group (or indeed the substituent on the donor N atom), the length of the interconnect or the nature of the alkyl substituents on the acceptor.



Scheme 1. Synthesis of the basic acceptor unit.



Scheme 2. Synthesis of first generation NLO materials with aromatisable donors and CDF acceptor

The linear and nonlinear optical properties of compounds **4-9** are summarised in Table 1. It can be seen that these compounds are very solvatochromic, with changes in the measured absorption maxima of up to 155 nm in the spectra from polar (methanol) to non-polar solvents (pyridine). This reflects the fact that the molecules are much more zwitterionic in character in polar solvents compared with a non-polar solvent where the neutral form will dominate (Fig. 3). It is also notable that increasing the number of carbon atoms in the conjugated interconnect from three to five to seven carbon leads to a steady increase in the observed NLO response. Increasing the conjugation length reduces the HOMO-LUMO gap, which accounts for the large β values seen for compounds such as **6** and **9**.

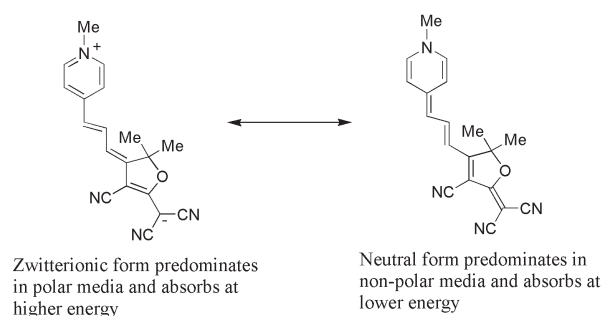


Fig. 3. Canonical forms of compound **4**.

While it would appear that compounds **7-9** with quinoline donors have greater NLO responses compared to their pyridine analogues, the situation is, in fact, far more

Table 1. Calculated and experimental linear and nonlinear optical properties of first generation chromophores 4-9.

Compound	λ_{\max} (nm) DMF ($\log_{10}\epsilon$)	λ_{\max} (nm) MeOH	λ_{\max} (nm) pyridine	μ^a (calc.)/ 10^{-18} esu	β (exp.)/ 10^{-30} esu DMSO	$\mu_{\text{(calc.)}}\beta_{\text{(exp.)}}$ / 10^{-48} esu	T_d ($^{\circ}$ C)
4	570 (4.86)	564	600	17.7	250	4,425	294
5	600 (4.78)	592	670	17.9	660	11,815	283
6	615 (4.76)	595	685	17.8	920	16,375	254
7	660 (5.00)	654	682	15.5	790	12,245	308
8	735 (4.88)	724	782	12.7	1,270	16,130	271
9	735 (4.70)	705	860	13.8	1,660	22,910	262

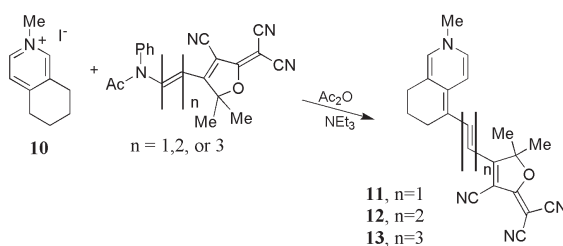
^aMOPAC (CS Chem3D pro, Cambridge soft) AM1 level using the precise keyword. Poor solubility prevented measurement of the dipole moment of any of the compounds.

complex. This is because the relationship between various donors (and acceptors) and the measured first hyperpolarizability is solvent dependant.¹³ Consequently, strictly speaking, the trend observed here is only valid for values obtained in media of similar polarity to DMSO. Given that all of the first generation chromophores were thermally stable ($T_d > 250$ $^{\circ}$ C) and that a number of them have figures of merit above $10,000 \times 10^{-48}$ esu, it was decided to modify them further in order to optimise their performance.

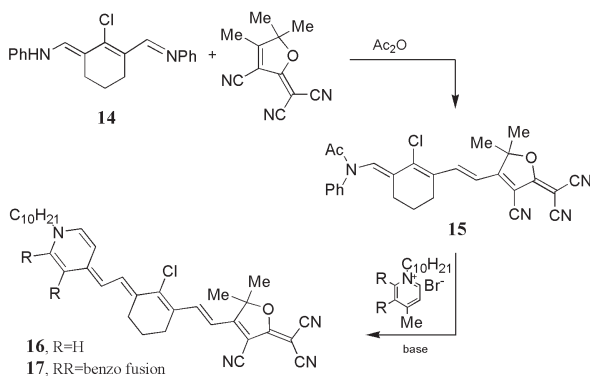
Second Generation NLO Materials

A number of methods have been used previously to enhance the NLO response of organic compounds. These include ring-locking of the chromophore backbone,¹⁴ incorporation of donor/acceptor groups onto the conjugated interconnect,¹⁵ development of multi-chromophore macromolecular systems,¹⁶ and induction of a very large twist angle (*ca.* 89 $^{\circ}$) between the donor and acceptor units in zwitterionic chromophores.¹⁷ Using our initial methodology, we saw an opportunity to introduce ring-locking into our molecules to enhance rigidity and planarity via modification of either the donor unit or the conjugated interconnect. This should also improve the thermal and photochemical stabilities due to buttressing of the structure. Therefore, following the method of Scheme 2 but replacing 4-methylpyridine methiodide by its tetrahydroisoquinoline analogue **10**, we were able to prepare the ring-locked chromophores **11-13** (Scheme 3).¹⁸ As was the case for the earlier compounds, the final products readily precipitated from solution and were isolated essentially pure by filtering and washing. A second iteration using the cyclic bisanil **14** gave precursor **15**, which in turn afforded ring-locked compounds **16** and **17** (Scheme 4).

Whilst it would have been interesting to couple the tetrahydroisoquinoline donor **10** to **15** to give a double ring-locked system, all attempts to carry this out were unsuccessful. The properties of the second generation chromophores are summarised in Table 2. Not only are the decomposition temperatures of the new compounds about 15 $^{\circ}$ C higher, but also the β values of **11-13** are *ca.* 50% higher than that of parents **4-6**, respectively. While it is logical to assume this stems from the improved pla-



Scheme 3. Synthesis of chromophores containing a tetrahydroisoquinolinyl donor.



Scheme 4. Synthesis of chromophores with ring locking in the conjugated interconnect.

narity of the molecular skeleton,¹⁴ it has been shown that ring-locked compounds may be less planar due to steric interactions between the ring methylene groups and the protons of the polyenic conjugated system.¹⁹ This twisting (*ca.* 30 $^{\circ}$) leads to a reduction in the dipole moment by around 50%. However, given that the extinction coefficients and calculated dipole moments (and planarities) of **11-13** are essentially identical to **4-6** it is unlikely that is occurring.

In the case of compounds **16** and **17**, it was not possible to obtain data for the first hyperpolarizability using DMSO or DMF as solvent; only in THF could data be obtained. Compound **16** (pyridinylidene donor) has a respectable response of $1,000 \times 10^{-30}$ esu but **17**, with the quinolinylidene donor, has a β value of only 350×10^{-30} esu. This serves to emphasise that the response obtained with a given donor is heavily dependent on the polarity of the solvent. This is due to how the various donors determine

Table 2. Calculated and experimental linear and nonlinear optical properties of ring-locked chromophores **11-13**, **16**, and **17**.

Compound	λ_{\max} (nm) DMF ($\log_{10}\epsilon$)	λ_{\max} (nm) MeOH	λ_{\max} (nm) Pyridine	μ^a (calc.)/ 10^{-18} esu	β (exp.)/ 10^{-30} esu DMSO	$\mu_{\text{calc.}}\beta_{\text{exp.}}$ / 10^{-48} esu	T_d ($^{\circ}\text{C}$)
11	573 (4.79)	564	602	17.1	400	4,425	310
12	598 (4.71)	586	657	17.2	1070	11,815	301
13	611 (4.77)	590	670	17.2	1110	16,375	265
16	637 (4.55)	622	700	17.1	1000 ^b	17,100	308
17	739 (4.71)	715	878	16.8	350 ^b	5,880	277

^aMOPAC (CS Chem3D pro, Cambridge soft) AM1 level using the precise keyword. ^bMeasured in THF.

where the chromophores sit on the hyperpolarizability vs BLA curve shown in Fig. 1, combined with the effect of solvent polarity on BLA in the ground state structure.^{13,18}

Aggregation: a Significant Challenge

The NLO compounds we have developed ultimately are to be used in polymer systems, which have dielectric constants (ϵ) of 1-7. Thus, it is necessary to study their behaviour in environments similar to these. This is particularly important because the asymmetric distribution of electrons in a compound typically leads to intermolecular interactions between neighboring molecules in both solution and/or the solid state. This phenomenon is very common in the cyanine and merocyanine dyes and is termed *aggregation* or *self-association*. Aggregation of chromophores causes the shape of their UV spectra to deviate from normal and results in the appearance of extra bands (or shoulders). The position of these shoulders depends on the type of the aggregation present, *e.g.* H (hypsochromic) or J (named after Jelly)²⁰ aggregation. H-aggregation has shoulders that appear on the high energy side of the main absorption band whereas J-aggregation has them on the low energy side. Organic chromophores with highly polar, *i.e.* zwitterionic, ground states often exhibit poor solubilities and tend to readily form aggregates.²¹ This can be seen from the various absorption spectra of **18**, which is a basic chromophore with a $\text{C}_{10}\text{H}_{21}$ substituent attached to improve solubility (see Fig. 4).¹⁸ The spectrum of **18** in DMF, THF and CHCl_3 (ϵ : 38, 7.5 and 4.8, respectively) each displays a single symmetrical absorption band that

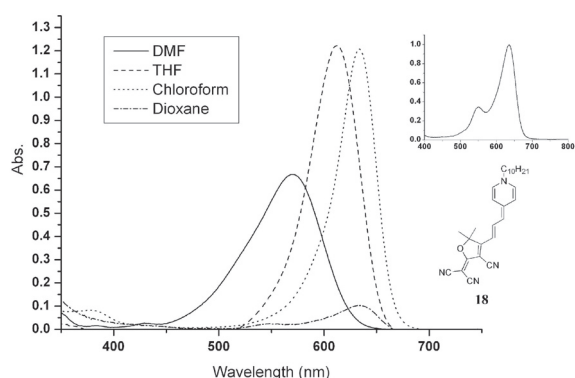


Fig. 4. UV-Vis absorption spectra of C10-containing chromophore **18**, in a range of solvents and (inset) in a host-guest thin film – 10% loading in amorphous polycarbonate.

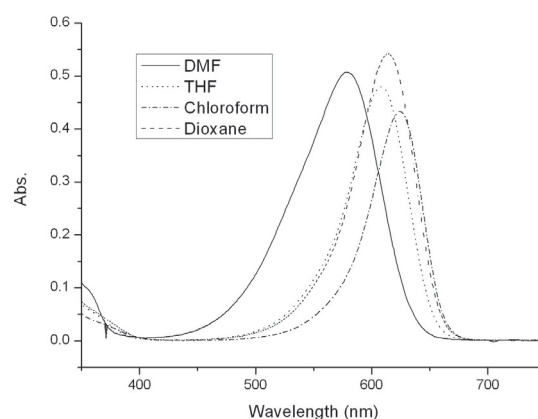
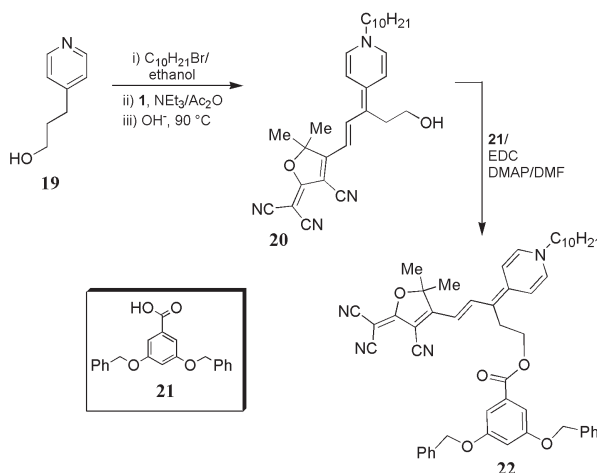


Fig. 5. UV-Vis absorption spectra of **22** in different solvents.

indicates no aggregation to be present. However, when the spectrum is obtained in dioxane ($\epsilon = 2.2$) the extinction coefficient drops and a high energy shoulder becomes evident especially in the thin film (see Fig. 4 inset) – this is indicative of significant aggregation. This is a potential pitfall when considering usage in NLO materials as it indicates that they may not be capable of incorporation into a host polymer at high loadings. Furthermore, the presence of significant aggregation will also lower the overall poling efficiency of the final NLO material as well as increase the propensity for relaxation of the aligned dipoles post-poling. This will result in a gradual decline over time of the observed macroscopic response.



Scheme 5. Synthetic route to chromophores with bulky groups attached to the interconnect.

As a result of these observations, further structural modifications to the active chromophores were needed to minimise aggregation. The inclusion of bulky, *arene-rich* substituents has been shown to be very effective in reducing aggregation and increasing the observed NLO response.²² In particular, the inclusion of substituents that give the chromophore a more oblate (or disc shaped) structure are known to be the most effective. Consequently, we decided to synthesise some new compounds with bulky groups attached to the conjugated interconnect (Scheme 5). Once again the building block approach allows for easy introduction of a new component, in this case 4-pyridinylpropanol (**19**) in place of 4-methylpyridine. This provides ready access to **20**, which has a free alcohol group to which a range of substituents can be tethered. By way of example, coupling **20** with 3,5-dibenzoyloxybenzoic acid (**21**) affords the bulky group-containing ester **22**.²³ A comparison of the UV-Vis absorption spectra of **18** (Fig. 4) and **22** (Fig. 5) shows the effectiveness of incorporating the bulky substituent. The spectra of **22** in all the solvents we have used give similar extinction coefficients and are free of shoulders. This, therefore, confirms that incorporating bulky groups onto the conjugated interconnects of our compounds provides a valid strategy for mitigating aggregation.

Future Directions

A number of the compounds described herein have been subjected to further study, especially to examine their photochemical stability and to determine their macroscopic NLO response (r_{33} value). Our molecules are quite robust on exposure to high intensity visible laser light. *e.g.* 633 nm, and their lifetimes are significantly increased when oxygen is absent.²⁴ Further studies to examine the usefulness of including additives such as anti-oxidants, *e.g.* β -carotene, are underway. More significantly, host-guest thin films containing these compounds have measured r_{33} values of over 300 pm/V.²⁵ This is approximately 10 times higher than the value found for the benchmark inorganic material lithium niobate (32 pm/V). Although the response slowly decays to around 50 pm/V over several weeks, this is not unexpected as we have yet to freeze the chromophores in place following poling using methods such as polymer cross-linking. We have also explored the covalent attachment of chromophores to the thermally robust polyimide backbones.²⁶ Another important step will be to modify the chromophores to improve solubility further. This will allow us to increase the number density of the chromophores in polymer matrices, which should, in theory, allow us access to materials with even higher macroscopic nonlinearities.

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