Chapter 2

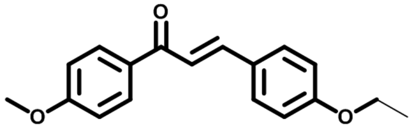
LITERATURE REVIEW

2.1 Introduction:

This chapter reviews the previous research work carried out to explore NLO activity of organic molecules. In this review of the literature, the chalcone derivatives are mainly focused on getting an idea of its extent of optical nonlinearity observed so far. As the luminescent property is also interconnected to NLO activity, few examples of chalcone based luminescent compounds is also incorporated. Besides chalcone based materials, the optical nonlinearity of few other classes of compounds is also discussed.

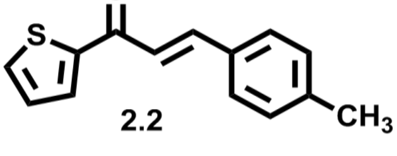
2.2 Review of chalcone based NLO chromophores:

Kitaoka *et al.,* (1990) had synthesized and grown large single crystal of the compound [*(E)-3-(4-ethoxyphenyl)-1-(4-methoxyphenyl)prop-2-en-1-one*], **2.1**. The effective nonlinear optical coefficients (d_{eff}) for type I and type II were estimated to be 3.5 and 5.7 pm/V respectively. For a single shot, the bulk laser damage threshold was over 30 GW/cm^2 against a 1.053 μm laser with 1 ns pulse width, which was higher compared to inorganic crystals like potassium dihydrogen phosphate (KDP) crystal and fused silica. The SHG efficiency, measured by the powder technique, was 8.9 times larger than that of the urea. The chalcone derivative was also found to be chemically stable [1].


2.1

Kitaoka *et al.,* (1991**)** studied the laser properties of the single crystal, **2.2,** thienylchalcone at a wavelength of 1064 nm.

In the material, the cut-off wavelength was 430 nm and the effective nonlinear optical coefficient (d_{eff}) was 7.1pm/V; i.e. 1.7 times as large as that of KTP. The compound **2.2** could be type-1 phase matched for more than 910 nm wavelength of light. It was proposed as a useful nonlinear crystal for generating green and blue lasers [2].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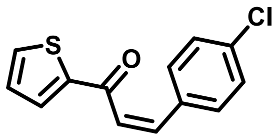
Gandhimathi *et al.,* (2013) synthesized [*(Z)-3-(4-chlorophenyl)-1-(thiophen-2-yl)prop-2-en-1-one*] **(2.3)** and showed that **2.3** had SHG, 2.7 times better than KDP**.** The noncentrosymmetric crystal had moderate birefringent value compared to other organic materials.



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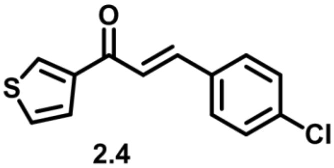
Uchida *et al.,* (1998) determined the crystal structures of several SHG-active chalcone derivatives by X-ray analysis. The phase matching direction of [*l-(3-thienyl)-3-(4-chlorophenyl)-2-propen-l-one*], **2.4** and [*l-(3-thienyl)-3-(4-bromophenyl)-2-propen-l-one*], **2.5** crystal was described based on its molecular packing in the crystal.



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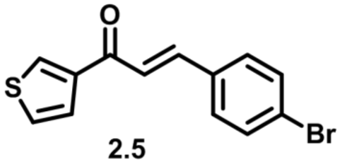
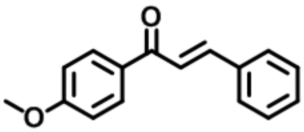


2.5

They found that molecule having large twisting angle tends to possess a small value of SHG, probably because of less conjugated π-electrons [4].

Indira *et al.,* (2002) explored the second harmonic generation conversion efficiency of [*1-(4-methoxyphenyl)-3-(phenyl)-2-propen-1-one*], **2.6** in powder form.



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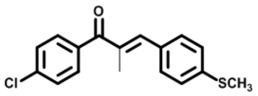
The SHG conversion efficiency was found to be 0.8 times that of urea when measured by powder technique using Nd:YAG laser at was 13 mJ/s [5].

The third order nonlinear optical properties of chalcone-based compounds enjoyed similar enthusiasm in various research groups, Kiran *et al.,* (2007) observed the exhibition of third order nonlinear optical properties of 1,-3-diaryl-propenones containing 4-methylthiophenyl moieties at 532 nm using the nanosecond single beam z-scan technique. The compounds, **2.7.1**, **2.7.2** and **2.7.5** showed very good optical limiting properties. The variation in π-electron density in these conjugated materials was reported to be responsible for the variation in their third order nonlinear response and the compounds exhibited strong two-photon absorption.



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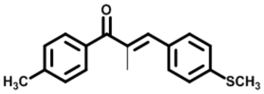

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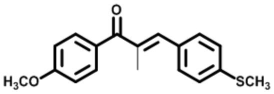

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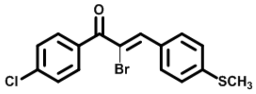

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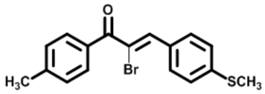

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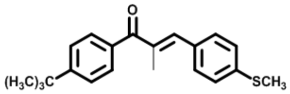

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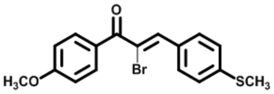

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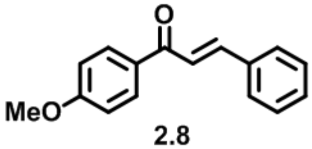
The largest value of the nonlinear refractive index, n_2, was measured for the compound (substituted by a high electron donor), **2.7.5,** was -2.033×10^{-11}esu[6].

Ravindra *et al.,* (2007) investigated the third order nonlinear optical properties of **2.8** [*4ʹ-methoxy chalcone*] and its derivatives. The nonlinear response of these molecules was found to increase with an increase in the electron acceptor strength in $D\!-A\!-A$ type and with the donor strength of the substituted group in donor–acceptor–donor type molecules. The NLO response was found to be of the order of 10^{-13} esu[7].



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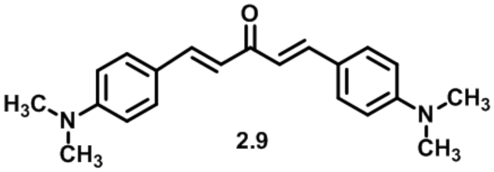
Kiran *et al.,* (2008**)** reported that the bis-chalcone derivative, [*p-(N,N-dimethylamino) dibenzylideneacetone*], **2.9,** on doping in poly(methylmethacrylate), showed third-order nonlinear susceptibility as high as 10^{-12} esu.



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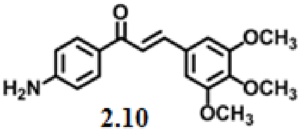
The nonlinear refractive index of the doped polymer was found to be negative. The results show that the compound exhibits strong reverse saturable absorption and a good optical limiting property[8].

Gu *et al.,* (2008) studied optical nonlinearities of *4ʹ substituted 3,4,5-trimethoxy chalcone* derivatives, **2.10, 2.11** and **2.12** in the near infrared region by a single-beam z-scan technique with fs laser pulses, the microscopic second-order hyperpolarizability (γ_R), 2PA cross section σ_{2PA} in chalcone derivatives increases, as the acceptor strength of the molecules increases.



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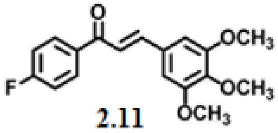

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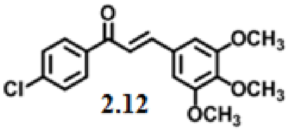

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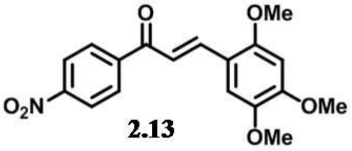
The synthesized molecules belonged to $D-A-A$ type structures. The 3,4,5-trimethoxy group attached at one end acts as a donor, the oxygen of the carbonyl group is located in the center, and the fluorine or chlorine or amino group is attached to the other end of the molecules. For $D-A-A$ type molecules, the charge transfer is from end to end of the molecule. The observed enrichment in the nonlinear response was because of the electron accepting ability of the groups present in the molecule. The amino group in **2.10** (5.79 × 10^{-33}esu) acts as a strong electron acceptor compared to both chlorine in **2.12** and fluorine in **2.11** (2.62 × 10^{-33} esu). The charge transfer was more effective in **2.10**. And it exhibits higher nonlinear response than both **2.12** (4.01 × 10^{-33}esu) and **2.11**. The inductive effect of chlorine is stronger compared to fluorine, the charge transfer in **2.12** is stronger than that in **2.11**. So, **2.12** exhibited a higher nonlinear response than **2.11** [9].



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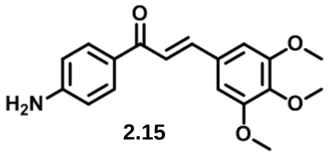
Gu *et al.,* (2009) reported very high order nonlinearity in the compound [*2,4,5-trimethoxy-4′-nitrochalcone*], **2.13** in the near infrared region, with z-scans with fs laser pulses, The compounds possesses $D-\pi-A$ type structure. Although, third-order nonlinearity was dominant at low laser intensity, both the third- and fifth-order nonlinearities are observable at excitation intensity exceeding a critical value. The 2,4,5-trimethoxy phenyl moiety acts as a donor at one end, the C=O bond acts as the electron-withdrawing group in the center, and the nitro group is an acceptor at the other end of the molecule [10].

Ravindra *et al.,* (2009) synthesized single crystals of a chalcone co-crystal of **2.15/2.16** (0.972/0.028); the powder second harmonic generation (SHG) efficiency of this chalcone co-crystal was 7 times than that of urea. The large SHG efficiency observed was mainly due to the unidirectional, head-to-tail,



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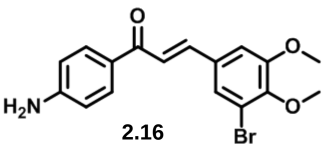

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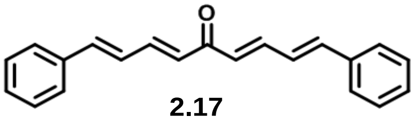
alignment of molecular dipoles, in which the dipole moment of each molecule adds to establish a net polarization. This alignment was facilitated through N–H· · ·O hydrogen bond interactions.

This molecule also showed third-order NLO response and good optical limiting property with 8 ns laser pulses at 532 nm. The mechanism for optical limiting in this chalcone was attributed to two-photon induced excited state absorption leading to reverse saturable absorption. They observed that the substitution of a strong electron donor group at the phenylene group was more effective rather than at the benzoyl group. Increasing the number of donor methoxy groups at the phenylene group was not effective rather a single methoxy group was enough in enhancing NLO properties. The structure–property relationship in this chalcone and related compounds was discussed based on the experimental results and semi-empirical hyperpolarizability calculations [11].

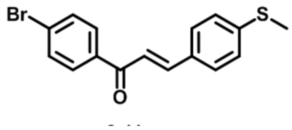
Bhadauria *et al.,* (2011**)** prepared dicinnamalacetone (**2.17**) where two benzene moieties are linked with -C=O group via conjugated alternate single and double



2.17

C-H bonds. The SHG power of **2.17** was approximately twice of urea. Their experimental data suggested that the charge transfer in molecules enhances the SHG property [12].

D’silva *et al.*, (2011) synthesized chalcone cocrystal with **2.18** & **2.19** (**2.18**/**2.19** = 0.66/0.44) and performed a z-scan experiment with a picosecond (ps) at a wavelength of 800 nm. $ß_{\mathrm{eff}} = 5 \times 10^{-12}$ cm W^{-1} and $n_2 = 3.257 \times 10^{-14}$ esu was derived from the single beam z-scan technique.



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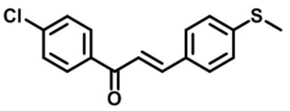

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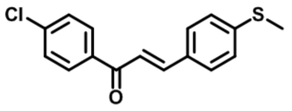
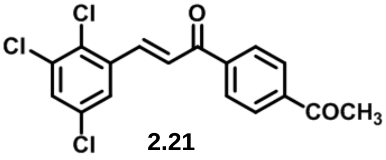


2.20

In the molecular structure of this chalcone co-crystal, the para position of benzoyl ring consisted of electron donating −Br and −Cl groups. But electron donating strength of the $-SCH_3$ group is greater than −Cl and −Br. The co-crystal with Br/Cl and SCH_3 at the ends and an electron acceptor carbonyl (C=O) group in the middle formed a donor-π-acceptor-π-donor ($D - \pi - A - \pi - D$) system, where charge transfer took place from the donor ends to the acceptor at the middle of the molecule. The charge transfer to the carbonyl group was more effective from the donor attached to the phenylene group, rather than the benzoyl group. This charge transfer was responsible for the NLO property[13].

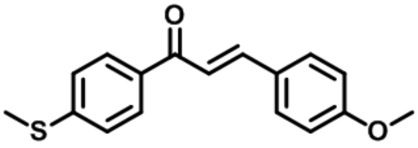


2.21

Kumar *et al.*, (2011) prepared a single crystal of **2.21** *[(E)-1-(4-methoxyphenyl)-3-(2,3,5-trichlorophenyl)prop-2-en-1-one*] which belonged to the monoclinic system with a space group of *Cc*. They studied second harmonic generation test with Kurtz powder technique. The crystal was hard and NLO active. The SHG efficiency was three times than that of urea, which originated from its structural features. The crystal had good thermal stability and could be suitable for device application, with$D - A - D$architectural arrangement; the $C_6H_2(Cl)_3$ acted as a donor group due to its mesomeric electron releasing behavior and the carbonyl group (−C=O) present at the middle of the molecule acted as an electron accepting group. So, in this case the charge transfer took place from the ends of the molecule to the center. This ensured the electronic delocalization within the molecule, different polarization and therefore optical non-linearity.

Moreover, in addition to the C-H---O hydrogen bond interactions, weak C-H---π bond (benzene ring as π center) intermolecular interactions was present in the crystal lattice, which made the crystal align the in head-to-tail fashion within the solid-state structure. Such interactions facilitated to extend the molecular charge transfer within the supramolecular dominion which in turn extended delocalization both in the ground state &in the excited state resulting in enhanced of SHG efficiency [14].

Kumar *et al.,* (2012**)** synthesized sulfur-containing compound [*1-(4-methylthiophenyl)-3-(4-methoxyphenyl)prop-2-en-1-one*], **2.22** with crystal of space group *Pna21*. Importantly, the compound **2.22** was found to be transparent in the entire visible region. The chalcone derivative exhibited optical nonlinearity (NLO) and its second order NLO efficiency was 3.15 times to that of urea. The conversion efficiency for SHG depended on the power of the fundamental beam, field-gain coefficient, size of the crystal, and minimum beam waist [15].



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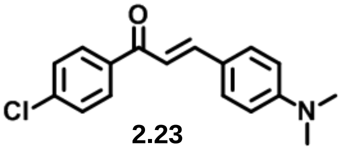
Janardhana *et al.,* (2013) synthesized **2.23** [*1-(4-chlorophenyl)-3-(4-dimethylaminophenyl)prop-2-en-1-one*], The compound crystallizes in the monoclinic space group *P2₁/c*. The coefficient of nonlinear refraction (γ) of the compound was found to be negative as revealed by the signature of closed aperture z-scan data, (γ) was found to be-1.89 × 10^{-20} m^2V^{-2} & *ß* was found to be 0.58 × 10^{-20} m^2V^{-2} [16-20].



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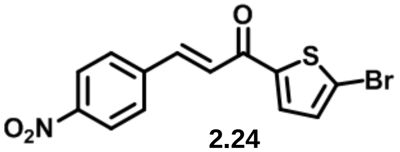
Prabhu *et al.,* (2013**)** synthesized a new nonlinear optical (NLO) organic material [*1-(5-bromothiophen-2-yl)-3-(4-nitrophenyl) prop-2-en-1-one*], **2.24.**



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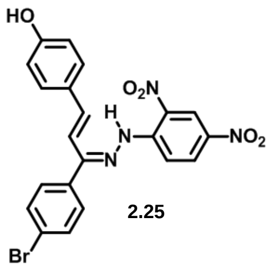
The crystal system was *triclinic* with a noncentrosymmetric space group *P1*. SHG efficiency of the crystal, determined by powder technique using Nd:YAG laser, was four times that of urea.

The Bromine substituted on thiophene ring at one end acted as a strong electron donor and a nitro group on aryl ring at the other end as strong electron acceptor thereby enhancing nonlinearity [21].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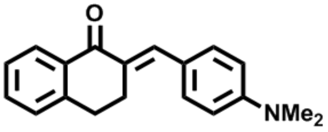
Janardhana *et al.,* (2013) synthesized chalcone based NLO material, [*4-{(1E, 3Z)-3-(4-bromo phenyl]-3-[2-(2, 4-dinitrophenyl) hydrazinylidene] prop-1-en-1-yl}phenol*], **2.25** and studied their nonlinear absorption using a z-scan technique with 7 ns laser .The nonlinear absorption originated from 2PA (two-photon absorption) or 2PA assisted excited state absorption [22].

2.3 Chalcone-based luminescent materials:

Kamalakshi *et al.,* (2010) studied the photoluminescence property of chalcone derivative **2.26** and **2.27**. Fluorescence in chalcone arrives from extensive conjugation. When chalcones having donor and acceptor groups are excited, internal charge transfer takes place in it.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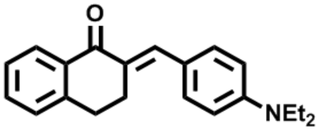
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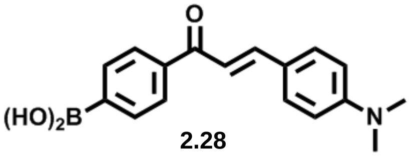
Chalcone-based fluorescent materials have extensive use in liquid crystal display, photorefractive polymers, and fluorescence probes for sensing DNA or metal ions and to observe cell membrane penetration. Fluorescence emission (recorded at absorption maxima) for **2.26** (λ_{max}= 269,406 nm), **2.27** (λ_{max}= 244,341 nm) showed charge-transfer emission spectra. N,N-dialkyl group is a donor and carbonyl group is an acceptor. So, **2.26** & **2.27** form a donor-acceptor complex when excited with UV light. **2.27** showed more intense emission than **2.26** as donating character of ethyl group is larger than a methyl group [23].

DiCesare *et al.,* (2002) synthesized [*(E)-(4-(3-(4-(dimethylamino)phenyl)acryloyl)phenyl)boronic acid*], **2.28,** a chalcone based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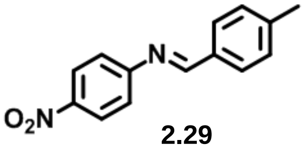
fluorescent probe for sugar signaling based on the ICT mechanism probes. Long-wavelength probes are highly desirable for biochemical analysis to decrease the interference of the autofluorescence background of biological samples. In addition, it was demonstrated that the boronic acid group does not have to be directly involved in the charge transfer [24].

2.4 Review of NLO chromophores other than chalcone: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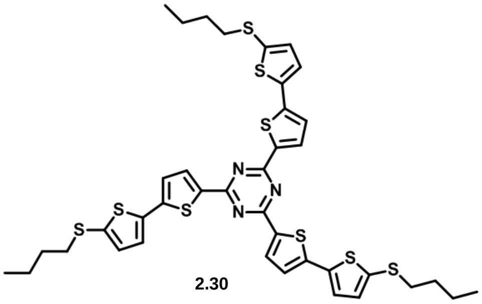
Bailey *et al.,* (1993**)** identified by the powder technique that the organic crystal *4-nitro-4'-methylbenzylidene aniline* (**2.29**) as a promising nonlinear optical material. Large single crystals of dimensions 5x3x1 cm^3 were also grown. It showed very high second harmonic intensity, 16 times that of urea [25].

Ch´eriouxet *al.,*(1999) reported the synthesis of the first octupolar polymer and two new octupolar thiophene-based molecules, [*2,4,6-tris(5'-(butylthio)-[2,2'-bithiophen]-5-yl)-1,3,5-triazine*], **2.30** and [*2,4,6-tris(5'-(allylthio)-[2,2'-bithiophen]-5-yl)-1,3,5-triazine*], **2.31**. These compounds exhibited off-resonant third-order NLO properties. No modification with respect to the nature of the substituent has been detected on the nonlinear refractive index and on the linear and two-photon absorption properties [27].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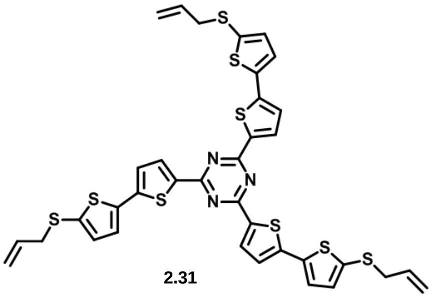
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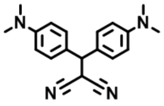
May *et al.,* (2007) theoretically considered nine carbonitriles (**2.32-2.40)** derivatives and showed that a push-pull system was important in the design of third-order nonlinear optically active compounds. By using donors and acceptors to reduce the HOMO-LUMO gap, they substantially increased the off-resonant third-order polarizabilities and demonstrated the most efficient optical nonlinearities both in terms of the absolute third-order polarizabilities and in terms of their proximity to the theoretical limit.



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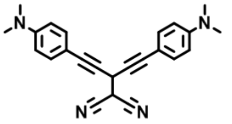

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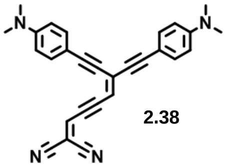
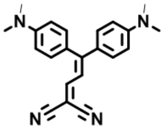


2.38



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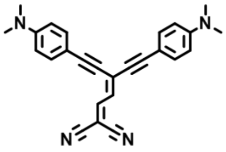

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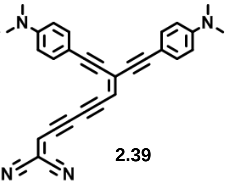

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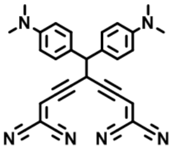
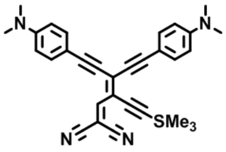
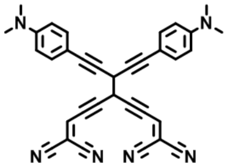


2.34



2.37

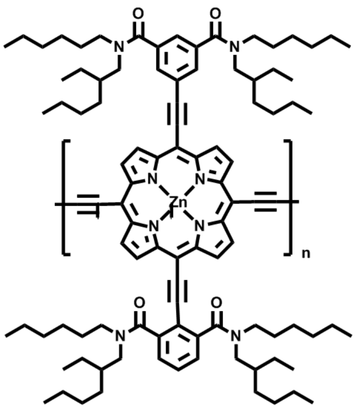


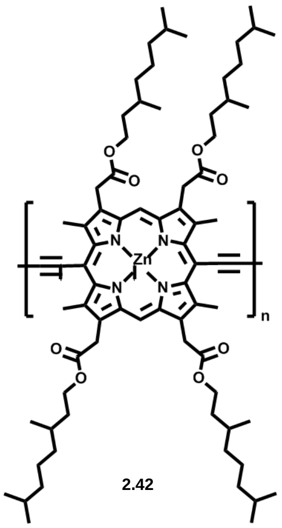
2.40

The observed variation in the nonlinearity of the compounds mostly aroused from a change in their transition dipole moments. In the study, the extreme point was not achieved, where the size of the conjugated system becomes too large to support a good transition dipole moment between the HOMO and LUMO states. The possibility to increase the specific third-order polarizability by the expansion of the conjugated system prevailed [28].

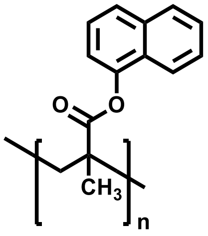
Screen *et al.*, (2001**)** synthesized soluble conjugatedporphyrin polymer. Electron absorption spectroscopy shows that thin films of **2.41** have lower resonant third-order NLO susceptibility than porphyrin polymer **2.42**. Closed z-scan measurements indicated that the off-resonance real susceptibility, at 1064 nm, was exceptionally large for both polymers ($\chi^{(3)}_R = -2 \times 10^{-16}$ m^2 V^{-2}). Open z-scan measurements at 1064 nm, demonstrated that the two polymers exhibited similar nonlinear absorption at this wavelength (*ß* = 1 cm GW^{-1}).

The extended two-dimensional conjugation in **2.41**, compared to **2.42**, did not result in increased optical nonlinearity. The observation revealed that 1D π-systems generally have higher nonlinearities per π-electron than 2D π-systems [29, 30].


2.41

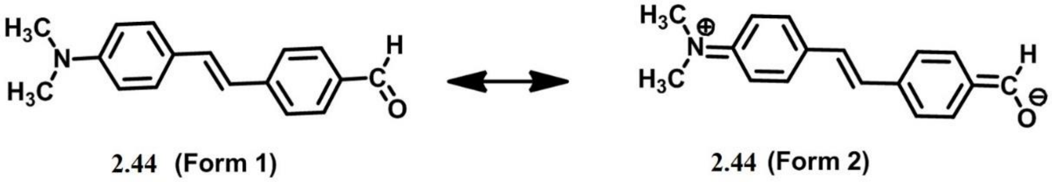

2.42

Hassan *et al.,* 2013 studied the nonlinearities of **2.43** [*Poly (1-naphthyl methacrylate)*] with a continuous wave (CW) 532-nm laser beam and evaluated the nonlinear refractive index n_2 in the order of 10^{-7} cm^2/W in chloroform solution.


2.43

The increase of absorption coefficient directed the polymer to absorb an increased amount of laser power by the solution, which resulted in monotonic enhancement of heat production and alsothe thermal nonlinear refractive index. The decreased thermal conductivity lead to a local accumulation of resultant heat via the absorption; hence the thermal effects were boosted up [31]. Kogej *et al.,* (1998) on the basis of correlated quantum-chemical calculations looked into the structure–TPA property relationships for *4-dimethylamino-4*$^{/}$*-formylstilbene,* (**2.44**), a stilbene backbone end-capped with donor and acceptor groups. The degree of ground-state polarization in **2.44** depended on the relative contributions of the neutral-aromatic-like resonance **form 1** and the charge-separated zwitterionic-quinoid-like **form 2**.

These relationships provide strategies to design dyes with large TPA cross-sections for fundamental photon wavelengths in the range of 0.6–1.0 mm.



Following the results, two strategies were suggested to increase TPA in donor–acceptor stilbenes and other structures related to it. Few of them were, by optimizing donor–acceptor strength, with thepolarity of the medium used and the nature of the conjugated segment under study [26].

2.5 Conclusion:

Based on the detailed review of the literature the following design strategy of NLO chromophore was found useful. An alkene-bridge is usually more efficient link than an alkyne-bridge which is due to a greater degree of conjugation inherent in ethylene-linked π systems.

Dialkyl and diaryl donors have been found more effective than oxygen based donors; phenoxide is the strongest of them.

$D-\pi-D$ and $D-\pi-A-\pi-D$ are generally more effective than $A-\pi-A$ and $A-\pi-D-\pi-A$.

Conjugation Signature (Sc) is the measure of effective conjugation length. For fully conjugated systems, $Sc \propto N_e^4$ (N_e is the number of π electrons), for systems containing of a set of small uncoupled chromophoric units $Sc \propto N_e$. For oligomers, $Sc \propto N_e^k$, integer k varies from 1 to 4. As N_e increases in a series of linear oligomers, k shifts from 4 to 1.

Rigid conformations of π bridge systems are more effective than flexible ones.

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