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Synthesis and Nonlinear Optical Studies on Organic Compounds in Laser-Deposited Films

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Abstract

Organic semiconductors as active materials in thin-film electronic devices such as alkynes, heterocycles, dyes, ferrocenes, spiranes, or porphyrins, with special geometries and certain electronic molecular parameters, which possess nonlinear optical (NLO) properties and offer several major advantages over their inorganic counterparts, are presented in this chapter. There are a number of simple and versatile techniques that can be employed for the deposition of these important classes of materials. The matrix-assisted pulsed laser evaporation (MAPLE) technique provides advantages with regard to making organic films of different morphologies on different types of substrates. New insights into the crystallization growth mechanisms in MAPLE-deposited conjugated polymer films, which realize the connection between the structure and the carrier transport properties, are discussed herein. Second harmonic generation (SHG) capabilities of the thin films were also investigated.

Keywords: organic synthesis, laser deposition, nonlinear optical properties, thin films

1. Introduction

During the last decades, the nonlinear optical (NLO) materials have gained significant role because of their various applications in medicine, molecular switches, luminescent materials, laser technology, spectroscopic and electrochemical sensors, data storage, microfabrication and imaging, modulation of optical signals, and telecommunication [1–3]. Organic materials are distinguished by the fact that they exhibit strong nonlinear optical (NLO) properties [4–8]. In the last years, researchers have based on the synthesis of the target organic molecules with particular geometries and certain electronic molecular parameters, in order to have the desired nonlinear optic properties [9–31].

The changes of optical properties (absorption coefficient, index of refraction), through the increasing intensity of the input light, led to the discovery of the nonlinear optical phenomenon, second harmonic generation (SHG), detectable only after the improvement of the laser in 1962 [32]. Thus, nonlinear optics developed as a tremendous field of research, especially after the profound understanding of nonlinear optic phenomena (NLO) and the structure-property relations of

chromophores, after the development of different tools to accurately measure and calculate hyperpolarizabilities [33].

Recent literature highlights the increased interest in organic materials in recent decades, as an alternative to their inorganic counterparts, and having several advantages, such as their low cost, low toxicity, ease of solution processability, flexibility for device fabrications [34], and modulation of their optical, electronic, and chemical properties by adapting their molecular structure. Field effect transistors, photovoltaic devices, organic light-emitting diodes (OLEDs), and white light sources for indoor and outdoor lighting are some of the applications of organic materials [33].

The deposition of organic materials in thin films, required for the design of new, successful devices, implied the precise monitoring of their chemical, structural, and morphological properties [35]. The deposition of organic substances in thin films has to meet the requirements of the market: (1) good uniformity of simple or multilayer structures of organic, polymeric, or composite materials—in the electronics industry; (2) thickness control, film uniformity of coating, and good interfacing properties—in OLED polymer applications; (3) conformal coatings required to modify the interior surfaces of porous materials (membranes, foams, textiles) or irregular geometries of surfaces—for optoelectronic and medical devices [36].

Several classes of organic compounds, including conjugated molecules, fullerenes, polymers, perylenes, dyes, and thiophenes, have been studied as materials and investigated for their NLO responses [5]. Conjugated organic polymers with large nonlinear responses correlated with rapid response time have been observed as NLO materials with great expectations [37]. Although organic compounds have been considered as frail, the experiments showed, with the optical damage, threshold for polymeric materials can be greater than 10 GW/cm^2 [37].

Two deposition techniques, physical and chemical, are used in order to obtain *organic thin films* with good quality. For each type, there are several techniques applied. Physical deposition techniques for thin organic films include physical vapor deposition (PVD) [38–42], organic vapor phase deposition (OVPD) [43–45], organic molecular beam deposition (OMBD) [46–51], solvent vapor annealing (SVA) [52–56], self-assembled monolayers (SAMs) [57, 58], inkjet printing [59, 60], pulsed laser deposition (PDL) [61–64], and laser evaporation [65–67] techniques. The chemical methods include solution techniques and gas-phase deposition methods. Techniques that use solutions include Langmuir-Blodgett (LB) [68, 69], spin coating [70, 71], dip coating [72, 73], sol-gel [74, 75], and spray pyrolysis [76]. Chemical vapor deposition (CVD) [77–82] uses the gas phase of organic compounds.

Many articles report the synthesis of the novel organic molecules or polymers with highly active chromophores and superior optical activity, as response to the demand of substances with NLO properties for various applications [83–86].

This chapter refers to synthesis of organic compounds with nonlinear optical properties in one of the techniques mentioned above, laser-deposited films.

2. Nonlinear optical (NLO) response in organic molecules

The optical response is due to a transition of the dipole moment from the ground state to the excited state due to the transition of an electron between frontier orbitals, from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The chemical activity of the molecule and the availability of the internal charge transfer are due to the balance between the redox ability of HOMO (as reducing agent) and LUMO (as oxidizing agent), which

reveals the internal charge transfer responsible for the non linear optical properties. Nonlinear materials are defined as optical media in which the refractive index depends on light intensity [87]. So, the HOMO-LUMO gap energy is involved in molecular electrical transport properties.

The designing and obtaining (synthesis) of the new molecules with high first hyperpolarizability β (theoretical and experimental) is central in discovery of the second-order and higher-order nonlinear optical materials and is quantified by the induced dipole moment under an intense light field E in Eq. (1):

$$\mu_i = \alpha_{ij}E_j + \beta_{ijk}E_jE_k + \gamma_{ijkl}E_jE_kE_l + \dots \quad (1)$$

with μ_i the i th component of the induced dipole moment, E_j the corresponding component of the applied electromagnetic field, and α_{ij} , β_{ijk} , γ_{ijkl} , the components of the linear polarizability, the first hyperpolarizability, and the second hyperpolarizability. In case of an ensemble of molecules, the macroscopic polarization is defined by Eq. (2):

$$P_i = \chi_{ij}^{(1)} E_j + \chi_{ijk}^{(2)} E_jE_k + \chi_{ijkl}^{(3)} E_jE_kE_l + \dots \quad (2)$$

with $\chi_s^{(1), (2), (3)}$ the macroscopic susceptibilities of the first (1), second (2), and third (3) order, which can be directly related to the density of the organic chromophore [88]. Recent advances in chromophore design report some features for classic dipolar organic structures with good nonlinear optic properties [89]: (1) presence of a π -conjugated systems with π electron delocalization, (2) a “push-pull” system, which is a couple donor-acceptor or connected to a system that contributes to the delocalization of the π electrons; (3) presence of a strong electron donor groups (e.g., $-\text{NR}_2$, $-\text{NHR}$, $-\text{OR}$, $-\text{OH}$), and strong electron withdrawing groups (e.g., $-\text{CF}_3$, SO_2CF_3 , $-\text{SO}_3\text{H}$, $-\text{NO}_2$, $-\text{CN}$), positioned at opposite ends of a conjugated molecule in case of dipolar molecules; (4) great values of dipole moment and polarizability; (5) small HOMO-LUMO energy gap; (6) planarity of the molecule for neutral, polar, and zwitterionic resonance structures. Dipole organic molecules have an intrinsic matter: the dipoles prefer to align antiparallel with each other in the solid-state film to nullify the bulk effect. Octupolar molecules, alternative NLO materials, present more advantages compared with dipole molecules [90]: (1) the second harmonic response (SHG) does not depend on the polarization of the incident light because they are more isotropic than the dipolar molecules; (2) β values of the octupoles can be increased by increasing of intramolecular charge transfer; (3) octupoles form noncentrosymmetric crystals; and (4) they are less likely to undergo relaxation due to the lack of ground-state dipole moment.

3. Synthesis of the compounds with NLO properties

In the last decades, literature reveals some classes of organic compounds suitable for organic electronic devices, such as organic photovoltaics (OPVs) and organic thin-film transistors (OTFTs), which possess certain characteristics, such as high molecular hyperpolarizability coefficients (β), special geometry, and in most cases, small HOMO-LUMO energy gaps [25–27]. Among these classes of organic compounds, there are highlighting fullerenes, perylenes, thiophene compounds, polymers, and dyes.

Furthermore, the polymers represent one of the most used classes of substances in pulsed laser deposition (PLD), but also in the other methods for preparing thin films. Organic compounds with nonlinear optical properties and

organic compounds reported in laser deposition (PLD) will be presented in the following two sections.

3.1 Synthesis of the nonlinear optical fullerenes

Canulescu group [91] studied thin films of fullerenes (C_{60}) **1** deposited onto silicon using matrix-assisted pulsed laser evaporation (MAPLE). MALDI analysis showed that a dominant transfer of intact C_{60} molecules onto a silicon wafer is realized when the laser fluence is carefully selected, for example, below a threshold of $\sim 1.5 \text{ J cm}^{-2}$. Labrunie et al. synthesized triphenylamine-based push-pull σ - C_{60} dyad, as photoactive molecular material for single-component organic solar cells, using a copper(I)-catalyzed 1,3-dipolar Huisgen cycloaddition under strict anaerobic conditions, leading to the selective formation of a 1,2,3-triazole ring and affording fullerene **2** in 80% yield (see **Figure 1**).

Thin films of **2**, prepared by spin coating of a CHCl_3 solution, highlight the ambipolar semiconducting behavior and also very good electron-transporting properties for fullerene **2** [92]. Kim et al. synthesized new fullerene **3** soluble in ethanol/water solvent mixtures and implemented these materials to fabricate polymer solar cells (PSCs) using environmentally friendly solvents [93]. The results of this paper provide important guidelines for the design of aqueous-electroactive materials having high carrier mobilities suitable to achieve very efficient eco-PSCs.

Kamanina highlights that there are two reasons for the importance of fullerenes: their unique energy levels and high value of electron affinity energy (0.65–0.7 eV). This value is larger than the one for most dyes and organic molecules with intramolecular acceptor fragment and can stimulate the efficient intermolecular charge transfer complex formation in the fullerene-doped organic conjugated materials [94].

Although fullerene acceptors were the predominant choice in the acceptor materials for two decades, the limited tunability of electronic properties and weak absorption of fullerene derivatives in visible range prevent further development of organic solar [95]. Therefore, other classes of organic molecules have been researched to obtain the desired properties of the electronic materials.

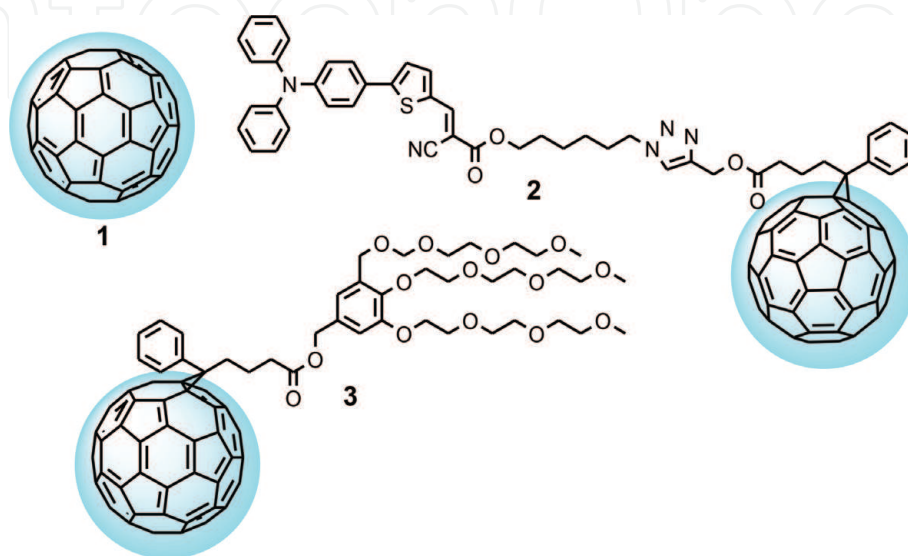


Figure 1.
Fullerenes with NLO properties [91–93].

3.2 Synthesis of the nonlinear optical perylenes

Perylene compound **4** was synthesized by a catalyzed heteroarylation reaction by McAfee et al. [83]. The geometry of perylene **4** exhibits planes of diketopyrrolopyrrole and perylene diimide at one dihedral angle too high for a good π -orbital overlapping, which determines HOMO-LUMO orbitals on specific atoms, supposition confirmed by TDDFT calculations at B3LYP/6-31G(d,p) level of theory. Optical, electronic, and self-assembly properties of the thin films of perylene **4** fabricated by solvent vapor annealing (SVA) recommended this compound as suitable for organic solar cells (OSCs) (see **Figure 2**).

Perylene diimides (PDIs) are a new class of nonfullerene electron acceptors for organic solar cells with many attracting features, like low cost; significant thermal, chemical, and light stability; good electron-accepting ability; and excellent electron mobility [96]. Carlotti et al. investigated PDI dimers as nonfullerene electron acceptors [96] for organic solar cells. Two isomers **5** and **6** have planar and twisted geometries, which determined very diverse spectral and photophysical properties (see **Figure 3**). Theoretical calculations and also the experimental time-resolved investigation confirm isomers **5** and **6** show charge transfer following light excitation.

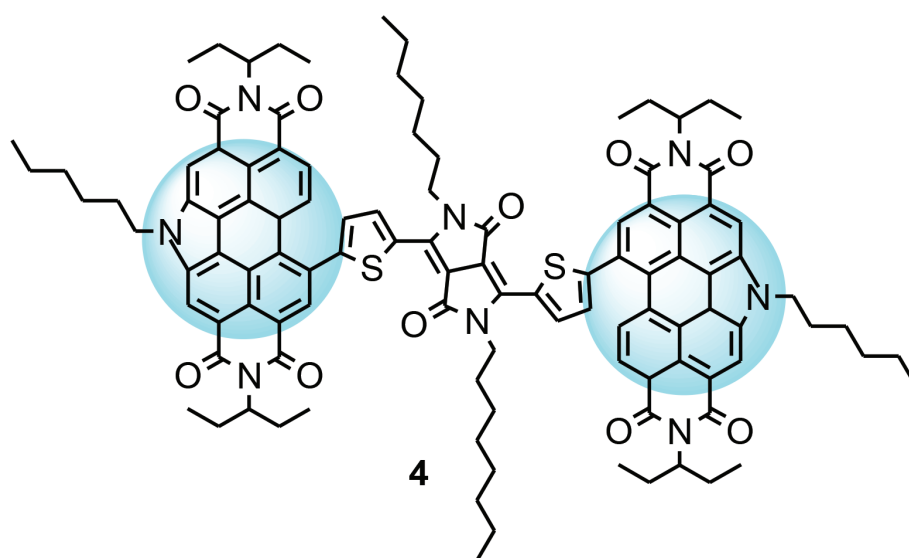


Figure 2.
 Perylene **4** with NLO properties [83].

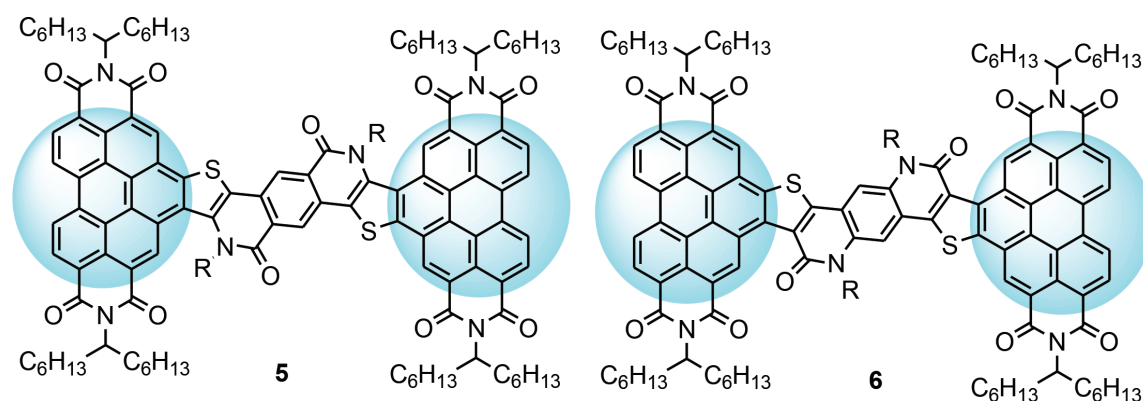


Figure 3.
 Perylene isomers **5** and **6** [96].

3.3 Synthesis of the nonlinear optical thiophene compounds

Small-molecule semiconductors with an A-D-A core structure (D is an electron-rich unit and A is an electron-deficient unit) function as an electron donor or electron acceptor in organic photovoltaic cell devices [97].

Thiophenes are one of the most studied heterocyclic compounds for D- π -A systems due to their relatively low resonance energies, the facile and cheap preparation of chromophores with high stabilities, and good nonlinearities [98]. The hyperpolarizabilities β of derivatives **7–9** were measured using hyper-Rayleigh scattering, and also the solvatochromic behavior of these thiophenes was investigated [99] (see **Figure 4**). A series of formyl-5-aryl-2,2'-bithiophenes **10** were synthesized by Herbivo et al. through two methods: Vilsmeier-Haack-Arnold reaction or through Suzuki coupling as precursors for NLO materials [100]. Raposo et al. synthesized two series of donor-acceptor conjugated heterocyclic azo-thienylpyrroles **11–12**. Thienylpyrroles **11** have largest first-order hyperpolarizabilities ($\beta = 460\text{--}660 \times 10^{-30}$ esu, T convention) [101]. Two series of novel push-pull 1-(4-(thiophen-2-yl)phenyl)-1H-pyrroles **13–14**, reported by Castro et al., were studied considering the electron-accepting moieties linked at the arylthiophene bridge or to the pyrrole heterocycle, which plays the role of donor group. Thiophene ring with functionalized thiobarbituric acid derivative **14** shows the largest first hyperpolarizability ($\beta = 2480 \times 10^{-30}$ esu) [102]. Batista et al. developed a series of thienylpyrrolyl with π -conjugated system attached to functionalized benzimidazole heterocycles **15–16** [103]. The new chromophores possess excellent solvatochromic properties and good molecular optical nonlinearities. By condensation of 5,6-phenanthroline-dione with formyl-thiophene derivatives in the presence of ammonium acetate in glacial acetic acid, oligothieryl-imidazophenanthroline compounds **17–18** were synthesized by Batista et al. These *p*-conjugated compounds possessed good values of β hyperpolarizabilities and solvatochromic properties [104]. Liu et al. synthesized isomers **19** and **20** [97], very similar in chemical structure, differing only in the substitution position of the alkyl groups attached to their conjugated cores, two novel small molecule photovoltaic materials, by implying a Knoevenagel reaction and investigated their photovoltaic properties by blending each of them with a polymer donor and a fullerene acceptor. Compounds present similar optical absorption spectra in solution and molecular energy levels in

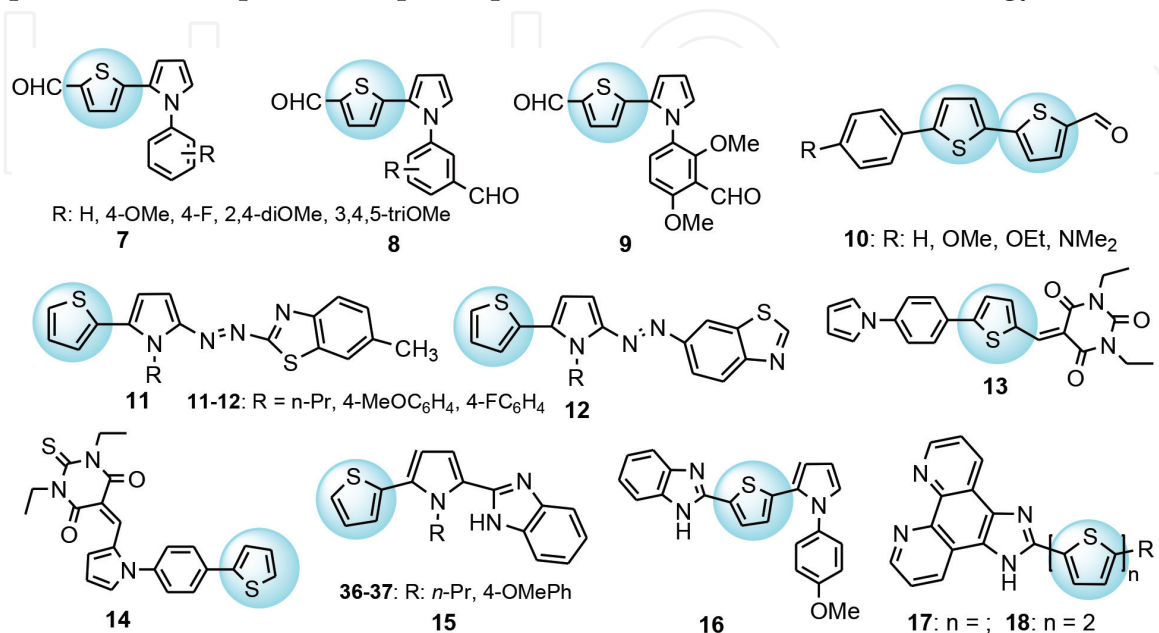


Figure 4. Thienyl compounds with nonlinear optical properties [97–104].

a solid film. Compound **19** forms an ordered lamellar packed structure with compact π - π stacking, whereas **20** shows only a weak π - π stacking effect in solid film. Also, the authors correlate chemical structure of the A-D-A semiconductors with their aggregation structure in solid state and their electron-donating and electron-accepting properties in OPV devices (see **Figure 5**). Zhu et al. synthesized the fused-ring electron acceptors **21** and **22** with a naphtho[1,2-b,5,6-b']dithiophene core and alkoxy side chains using a Stille reaction between an organotin compound and ethyl 2-bromothiophene-3-carboxylate [105]. It was found that change in the side chains affects electronic, optical, charge transport and morphological properties of these analogues. Compound **22** exhibits a narrower bandgap, redshifted absorption spectra, and higher electron mobility compared with **21**. The introduction of alkoxy side chains in fused-ring electron acceptors appears to be a promising approach to enhance absorption and electron mobility and therefore efficiencies in organic solar cells. Dai et al. synthesize fused-ring electron acceptors **23–24** using a Suzuki reaction and found that extending the core size leads to upshift of the energy levels, enhancement of molecular packing, higher electron mobility, more balanced-charged transport, and reduced bimolecular charge recombination (**Figure 6**).

3.4 Synthesis of the nonlinear optical dyes

Raposo et al. reported the synthesis of the 2,2'-bithiophene-conjugated dyes **25**, using the Friedel-Crafts and the Lawesson reactions. The compounds **25** have proved promising NLO chromophores (see **Figure 7**), exhibiting β_0 values of 2.5–4 times higher than that of 4-nitroaniline [106]. Also, azo-dyes **26** possessed great values of molecular hyperpolarizability β_0 [107]. Marinescu et al. synthesized by azo-coupling reactions a series of pyrazole-5-ones **27–30**, which possessed only hydrazo tautomers and torsional structures, correlated with their NLO properties and the efficiency of compounds was assessed by the relationship between high β_{tot} and low HOMO-LUMO energy gap [89]. Liu et al. synthesized porphyrin dyes **31** by [2+2] click reaction, with very good yields and small energy gaps HOMO-LUMO for each compound, and demonstrated that click moieties affected the third-order nonlinear optical responses [108] (see **Figure 8**).

Pascal et al. obtained the push-pull dyes **33–34** with tricyanofuran acceptor linked to donors of various strengths, by two consecutive condensations, and investigated their second-order nonlinear optical properties [109]. It was found that a high intrinsic hyperpolarizability coupled with a high static dipolar moment results in excellent $\mu\beta$ values for polymethine dyes containing pyran, thiopyran,

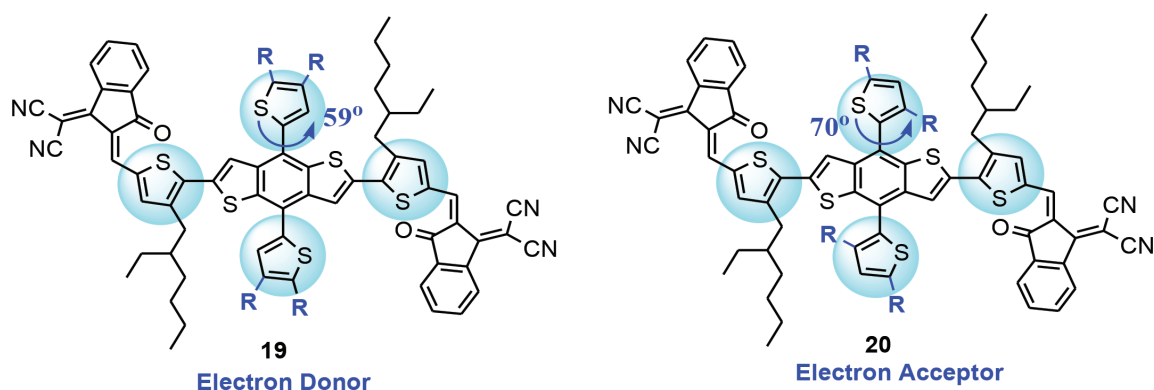


Figure 5.
 Small-molecule semiconductors based on an A-D-A structure [96].

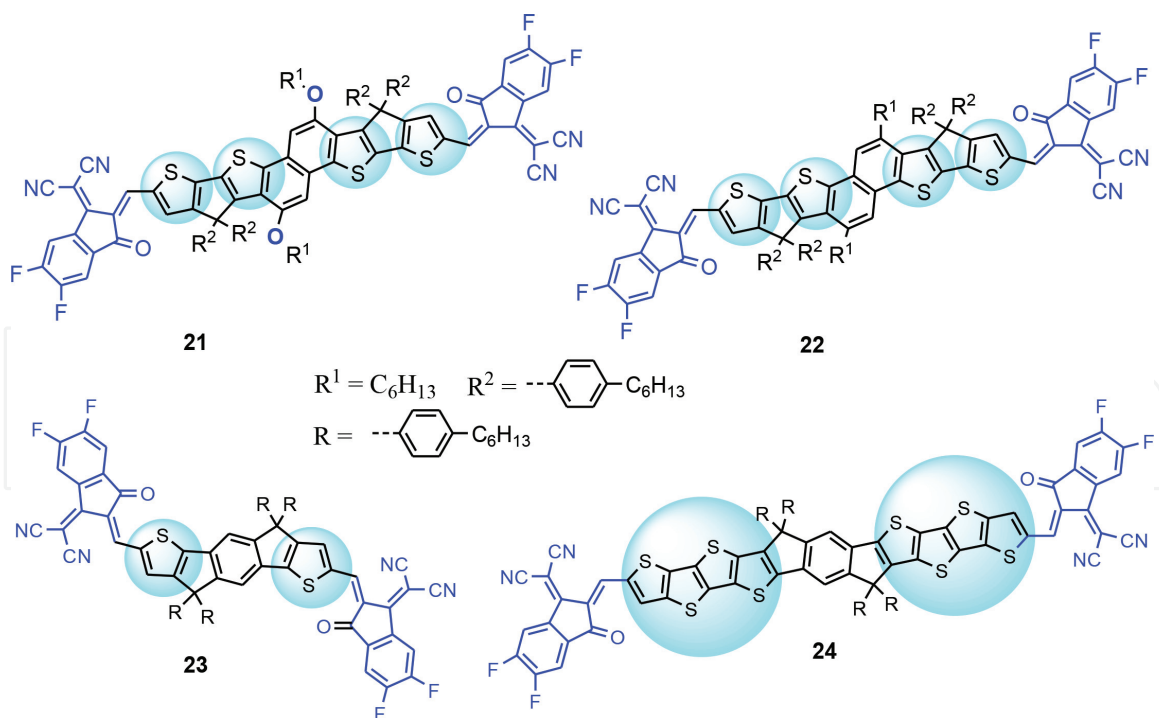


Figure 6.
Chemical structure of fused-ring electron acceptor **21–24** [104, 105].

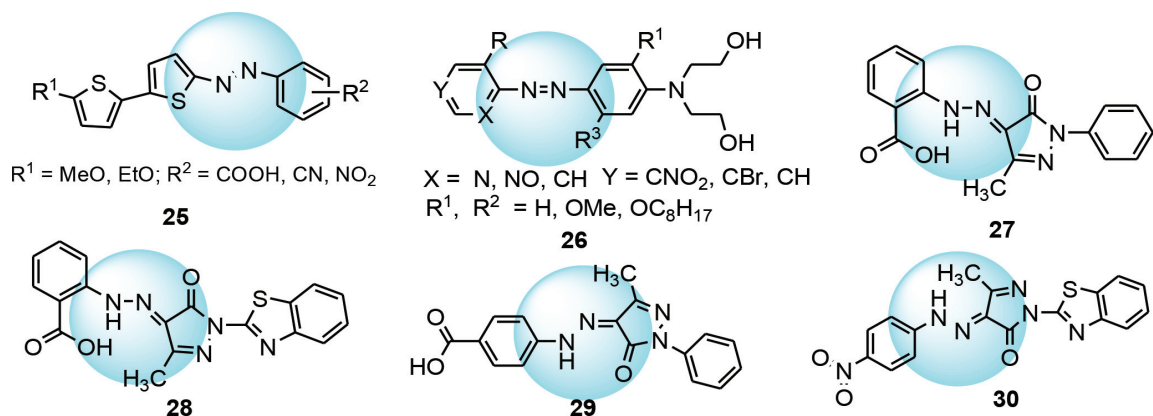


Figure 7.
Azo-dyes as NLO chromophores **25–30** [89, 106, 107].

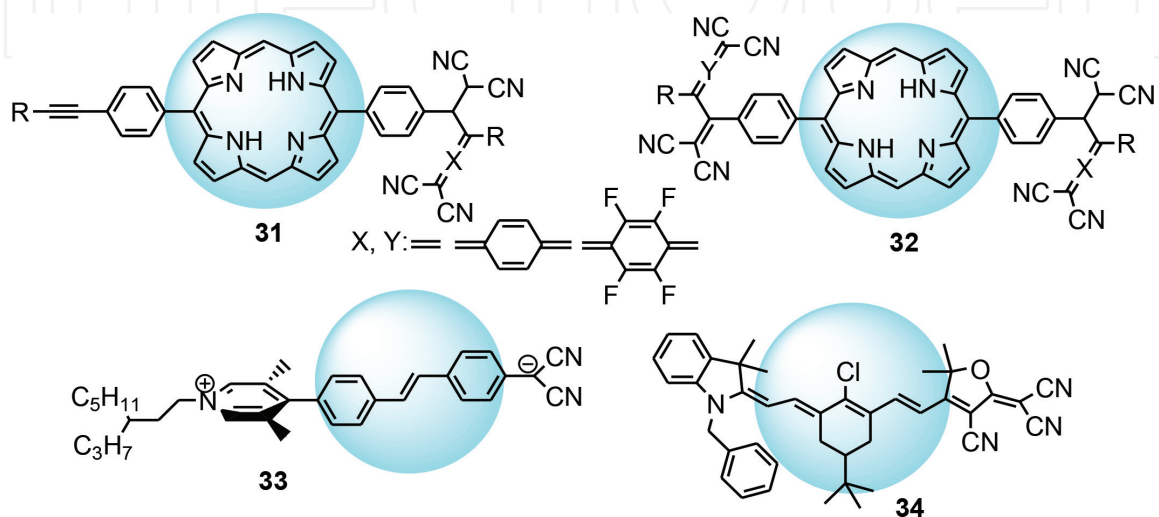


Figure 8.
Porphyrins **31–32** and push-pull polymethine dyes **33–34** [108, 109].

selenopyran, and benzoindoline moieties, and therefore, these dyes are promising for electro-optical modulation.

3.5 Synthesis of the polymers with nonlinear optical properties

A review of all the compounds deposited by MAPLE, including organics, with their applications was carried out by Caricato et al. [33]. Consequently, here we point out the newest structures reported in the literature with the most notable nonlinear optical properties mentioned.

Mariano et al. combine spin coating with the MAPLE technique, to realize polymeric multilayered thin films using three polymers 35–37 [110] (see **Figure 9**). This is the first white light-emitting diode produced by multilayer polymeric thin films reported in literature [110]. Constantinescu et al. reported fabrication of thin solid layers of poly(3,3''-didodecyl-quaterthiophene) 38 by MAPLE, on silicon and quartz substrates and studied films with different thicknesses, morphologies, and optical properties [111]. Thin films of polyvinyl chloride 39, polyacrylic acid 40, and polyaniline 41 with potential use in optoelectronic were reported by Constantinescu et al. [112]. Thin films of the blue-emitting poly(9,9-dioctylfluorene) 42 deposited by MAPLE have been investigated at different laser fluence values and at different laser repetition rate. Authors reported that at high laser fluence (450 mJ/cm^2), the dioctylfluorene surface showed large bubbles presenting the intrinsic blue emission. At smooth surfaces, it can be observed that green emission becomes predominant [110].

Recent works reported new conjugated copolymers with different donor (D)-acceptor (A) motifs (see **Figure 10**) for optoelectronic devices [113]. Authors synthesized a series of four DAA copolymers 43–46 (see **Figure 11**) with thiophene donors and isoindigo-based acceptors and compared the optoelectronic properties of these four copolymers with those of the analogous. It was found that “increasing the number of acceptors in the polymer repeat unit decreased the LUMO energy of the polymer and increased the electron mobility” [113]. The authors studied the influence of acceptor length and planarity on the optoelectronic properties of donor-acceptor systems for the copolymers 43–46 with thiophene donors and isoindigo acceptors and formulated that changing the number of acceptors in the

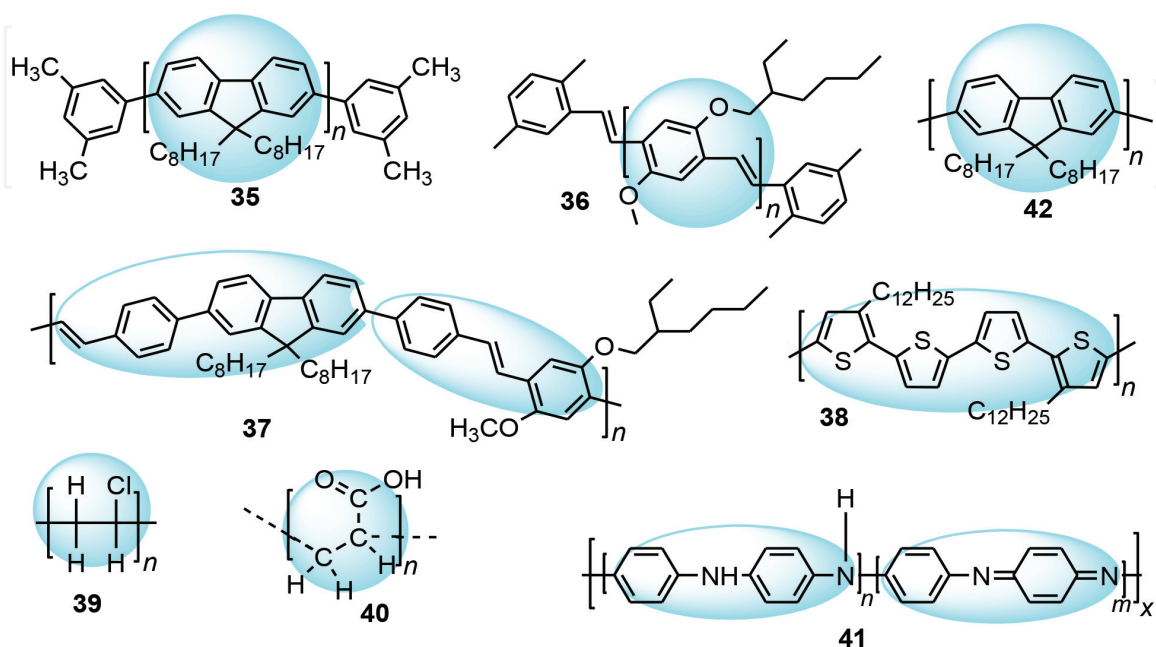
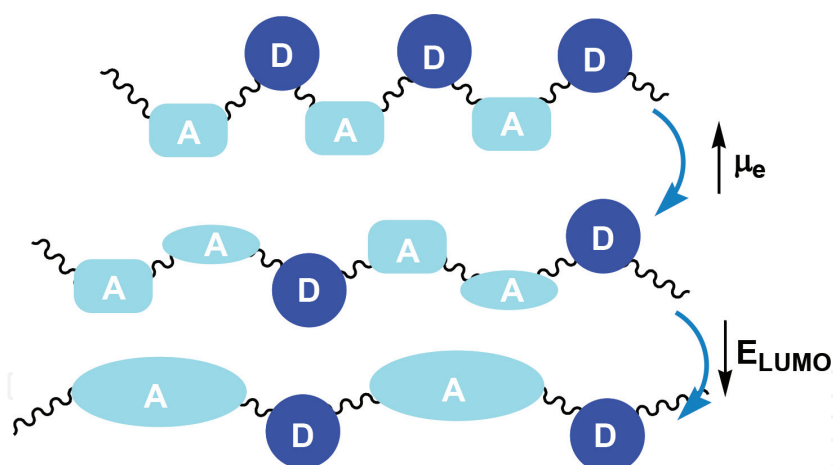
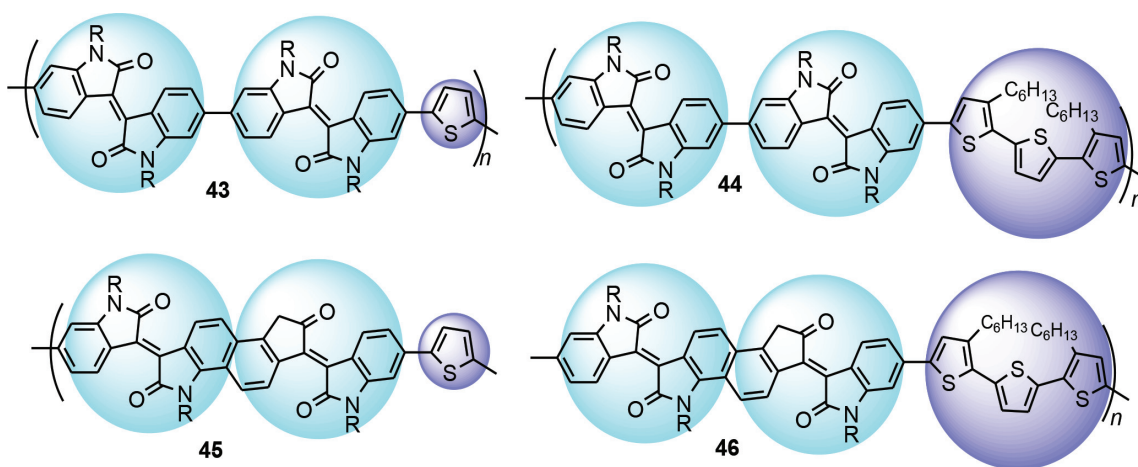


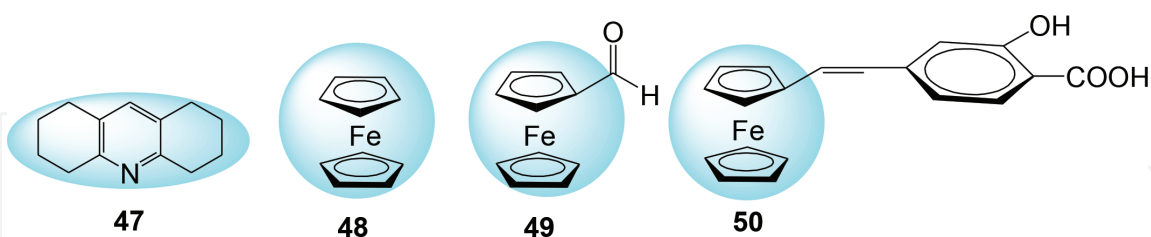
Figure 9.
 Polymers deposited by MAPLE technique [110–112].

**Figure 10.**

Donor (D)-acceptor (A) motifs along with magnetic moment and LUMO energy variations [113].

**Figure 11.**

Structures of DAA copolymers isindigo-based acceptors and thiophene donors 43–46 [113].

**Figure 12.**

Structures of compounds 47–50 with NLO properties.

polymer repeat unit is a key strategy that could be used to obtain donor-acceptor systems with fine properties and better materials.

3.6 Synthesis of other classes of organic compounds with NLO properties

Other classes of heterocyclic compounds were reported to have nonlinear optical properties, and some of them are presented below. 1,2,3,4,5,6,7,8-Octahydroacridine (OHA) **47** (see **Figure 12**) thin films grown by matrix-assisted pulsed laser evaporation (MAPLE) showed the SHG (second harmonic generation) signal of the conformational asymmetry of OHA and therefore the nonlinear optical applications of it [114]. Matei et al. studied the morphology and optical properties of ferrocene **48** thin films grown by MAPLE technique, films that were further used in

two-photon absorption investigations, showing that the compound has SHG capabilities [115]. Nonlinear optical properties of ferrocene carboxaldehyde **49** thin films grown by matrix-assisted pulsed laser evaporation (MAPLE) were studied by Constantinescu et al. [116] using two-photon absorption investigations. The experiment revealed that the ferrocene **49** thin films deposited by MAPLE have second harmonic generation capabilities improved compared to simple ferrocene, with better applications in optoelectronics. 4-(Ferrocenylmethylimino)-2-hydroxybenzoic acid **50** was synthesized by a Schiff reaction, and deposited thin films of it with controlled thickness were fabricated by matrix-assisted pulsed laser evaporation (MAPLE), on quartz and silicon substrates [117].

4. Matrix-assisted pulsed laser evaporation

The main method used to obtain thin laser films is matrix-assisted pulsed laser evaporation (MAPLE). Most organic compounds deposited by matrix-assisted pulsed laser evaporation reported so far are polymers, so they are very important for this chapter. There are three important advantages of the MAPLE technique compared to solution cast techniques: (1) the control of thickness; (2) possibility to deposit multilayers; and (3) fabrication of thin films on nonplanar substrates with good surface coverage [110].

The fact that method pulsed laser ablation is not convenient for the deposition of soft materials (almost all polymers, proteins, and other materials are chemically and/or thermally modified or destroyed) has led to the invention of a new improved method to remove these limitations. Two researchers McGill and Chrisey gave birth to matrix-assisted pulsed laser evaporation (MAPLE) technique [33] in order to deposit thin and uniform films of polymers and carbohydrates. The new method is suitable for the deposition of the complex organic materials, such as polymers, bioorganic molecules, and coordination compounds [118]. Fabrication of thin films from such materials is very important for new devices with many applications, including light-emitting diodes (LEDs) [110], field-effect transistors, sensors, photovoltaic devices, and white light sources for indoor and outdoor lighting [13, 110, 114, 115].

Three steps are necessary in the MAPLE technique:

1. dissolving the substance (solute) of interest in a volatile solvent (matrix) to form a diluted homogeneous solution (concentration of the order of 1 wt%);
2. freezing the solution at the temperature of the liquid nitrogen; and
3. placing the solution in the vacuum chamber to act as a target for laser-assisted deposition and irradiation of the frozen solution with a pulsed laser beam.

Matrix-assisted pulsed laser evaporation deposition of the desirable molecules is effectuated in a light manner, which implied the passing of the condensed phase to the gas phase. A low kinetic energy is implied in MAPLE process, in advantage to laser ablation with a high level of kinetic energy [110].

In the MAPLE method, the laser pulse energy is absorbed by the solvent and converted into thermal and kinetic energy, enabling the solvent to evaporate and carry in the gas phase the solute molecules onto the deposition substrate where they adhere as a thin film. A very volatile solvent is required to be pumped during the flight from target to substrate, and thus, the deposited film is made up of the dissolved material only.

Most of the laser energy is absorbed by the volatile matrix, not the dissolved molecules, which minimize the photochemical decomposition of the precursor solution. In addition, the use of low fluences prevents or reduces thermal damage and decomposition of molecules, so deposition can take place at low fluctuations ($0.05\text{--}0.5\text{ J/cm}^2$) compared to conventional pulsed laser deposition (PLD) (typically few J/cm^2).

Particularly important in this technique is the choice of solvent because it has a great impact on the deposition of organic matter, it can interact with the dissolved substance, it can lead to the production of secondary products from it, or it can be present in the deposited films [33]. The role of solvent in MAPLE technique is central; we can say that the solvent (1) must dissolve the solute without interacting with it; (2) has to be volatile; (3) must absorb laser radiation; and (4) must transport the dissolved substance from the target to the substrate.

The experimental setup of MAPLE deposition technique for thin-film fabrication is showed in **Figure 13**. The solution concentration must be of 0.1–2.0% (mass) because of the hard laser interaction with the frozen solid. The solvent is desirable to have a freezing point as high as possible. Only the solvent (also named matrix) absorbed the radiation when the laser reaches the target, so the matrix evaporates, the “solid” is ablated, and only the material’s molecules are deposited on the substrate [119].

4.1 Investigation of NLO properties

4.1.1 Parameters of NLO properties

Interactions of electromagnetic fields in various media produce new fields changed in frequency, phase, amplitude, or other characteristics of the incident fields resulting nonlinear optical (NLO) properties [89]. The parameter used to evaluate the NLO susceptibility is the total hyperpolarizability (β_{tot}), meaning that a compound with large β_{tot} value is predicted to be a potential NLO active one and vice versa [11]. Literature shows that experimental determination of the β_{tot} value and therefore the NLO susceptibility is an expensive and laborious process, which led to using the quantum mechanical calculations including the DFT methods for the designing of NLO materials. The mean polarizability α , the total static dipole

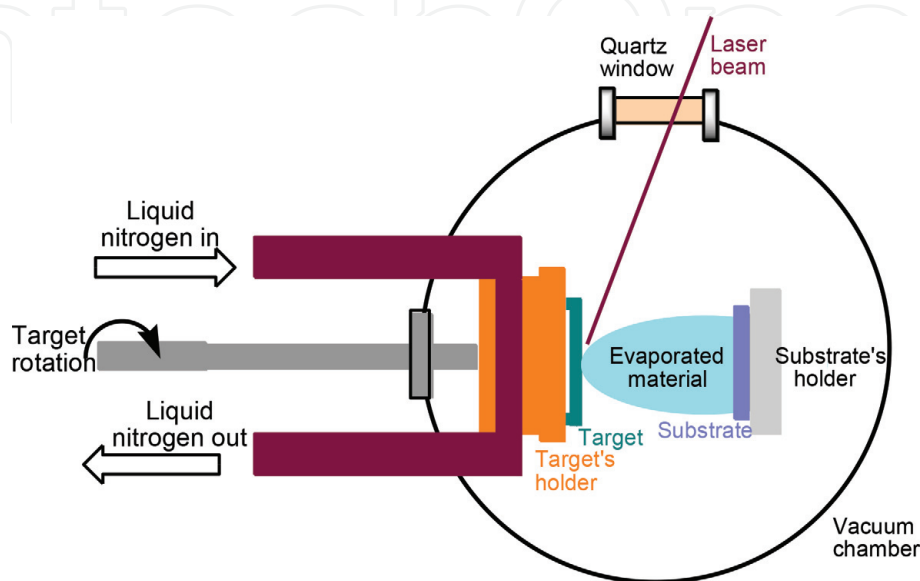


Figure 13.
Scheme of the MAPLE setup [119].

moment μ_{tot} , the quadrupole moment Q , and the mean first polarizability β_{tot} may be calculated by using DFT theory. The x, y, z components are defined as follows:

$$\alpha_{tot} = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3} \quad (3)$$

$$\mu_{tot} = \left(\mu_x^2 + \mu_y^2 + \mu_z^2 \right)^{1/2} \quad (4)$$

$$Q_{tot} = \left(q_x^3 + q_y^3 + q_z^3 \right)^{1/3} \quad (5)$$

$$\beta_{tot} = \sqrt{\left(\beta_x^2 + \beta_y^2 + \beta_z^2 \right)} \quad (6)$$

$$\beta_j = \beta_{iii} + \frac{1}{3} \sum_{i \neq j} \left(\beta_{ijj} + \beta_{jij} + \beta_{jji} \right) \quad (7)$$

Therefore:

$$\beta_{tot} = \sqrt{\left(\beta_{xxx} + \beta_{xyy} + \beta_{xzz} \right)^2 + \left(\beta_{yyy} + \beta_{yzz} + \beta_{yxx} \right)^2 + \left(\beta_{zzz} + \beta_{zxx} + \beta_{zyy} \right)^2} \quad (8)$$

The larger hyperpolarizability value of one component over the other components means that the electronic charge delocalization is larger in that direction [11]. There are a lot of factors that contribute to enhance the NLO properties of the compounds, which are cumulated with the prospective β_{tot} calculated values [3].

4.1.2 Experimental determination of second harmonic generation (SHG) in thin films

Experimental setup used to investigate the SHG behavior [117] in thin-film samples is represented in **Figure 14**. The component parts of the system used for the determination of second harmonic generation (SHG) are a sapphire laser ("Tsunami," from Spectra-Physics; 780 nm, 60–100 fs pulse duration, 80 MHz repetition rate); an optical system made of a half-wave plate and a Glan-Taylor polarizing prism that allows the variation of beam intensity; a microscope's objective is to focus the laser beam onto the thin-film samples and collect the emitted SHG radiation. A dichroic mirror (DM) separated the excitation radiation, and the SHG intensity is measured by a camera spectrograph [117].

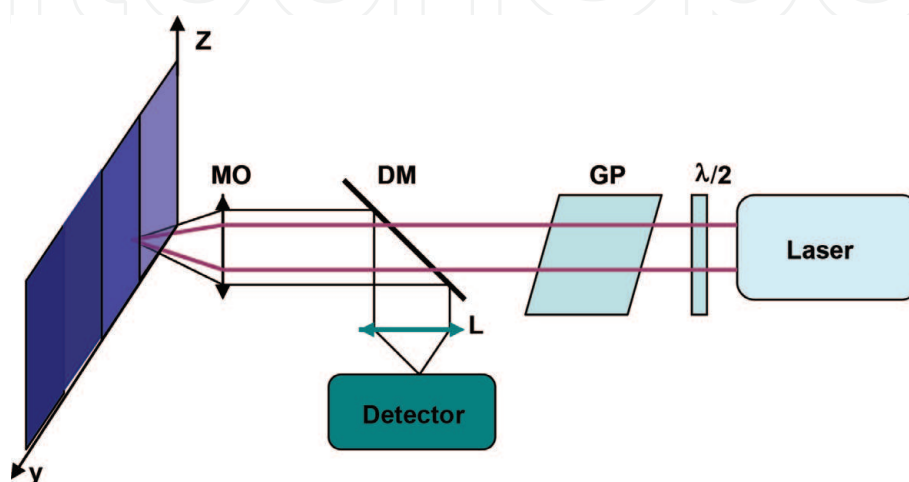


Figure 14.
 Experimental setup for determining second harmonic generation.

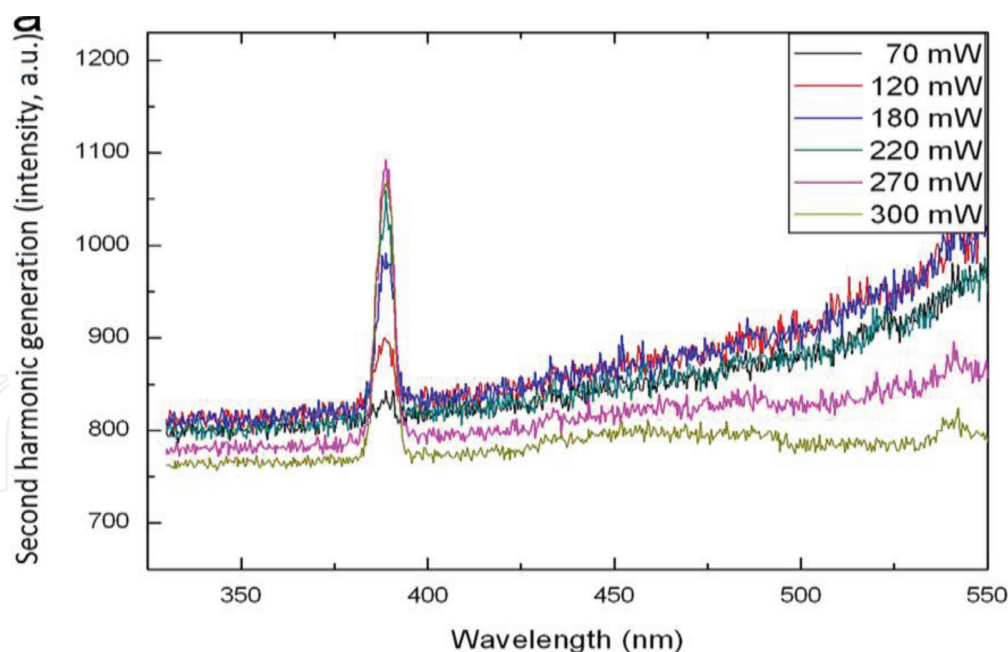


Figure 15.

The SHG experimental spectra of MAPLE-grown OHA thin films (adapted with the permission from reference [114]).

The experimental second harmonic generation of MAPLE-grown 1,2,3,4,5,6,7,8-octahydroacridine (OHA) **47** using laser fluence 0.3 J/cm^2 , laser spot 2 mm^2 , and 40,000 pulses, on Si substrates, under fs-laser irradiation at 788 nm wavelength is represented in **Figure 15** [114]. In this case, the presence of the SHG signal is related to the conformational asymmetry of the OHA molecule.

5. Conclusions

The synthesis of the most important classes of the nonlinear optical organic compounds, fullerenes, perylenes, thiophene, azo-dyes, thienenes, polymers, and other compounds, along with the techniques employed for the deposition of these compounds, was presented. For the synthesis of the new compounds with nonlinear optical applications, important reactions, like Stille, Suzuki, Knoevenagel, Huisgen, Vilsmeier-Haack-Arnold, click, were employed.

Among the simpler and more sophisticated techniques, the matrix-assisted pulsed laser evaporation (MAPLE) technique that permits making organic films with different morphologies, on different types of substrates, is the main method used to obtain thin laser films, with three basic advantages: the control of thickness; possibility to deposit multilayers; and fabrication of thin films on nonplanar substrates with good surface coverage. Crystallization growth mechanisms in MAPLE-deposited conjugated polymer films that determine specific structure, therefore the carrier transport properties, were discussed in relation with second harmonic generation (SHG) behavior of the thin films.

Organic compounds are cheap, low toxicity, ease of solution processability; therefore, their applications as NLO materials are growing.

Conflict of interest

The author has no conflict of interest to declare.

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