Dyes and Pigments 122 (2015) 74–84

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Review

Optimization of polycyclic electron-donors based on julolidinyl structure in push–pull chromophores for second order NLO effects

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ARTICLE INFO

Article history:
Received 6 March 2015
Received in revised form
3 June 2015
Accepted 8 June 2015
Available online 17 June 2015

Keywords:
Nonlinear optics
Electro optics
Chromophore
D–π–A molecule
Optical materials
Electron donor

ABSTRACT

Organic electro-optic (EO) materials have been widely explored and used in the fabrication of microwave photonic devices. Their principal advantages are the follows: lower half-wave voltage, wider bandwidth, lower cost and more convenience of integration. Organic second order nonlinear optical (NLO) chromophores, as the core of the organic EO devices, define the key technological parameters: EO efficiency, long term stability, solubility and optical losses. In the present review article, the use of D–π–A chromophore molecules with polycyclic electron donors based on julolidinyl structure is reported and discussed. Significant improvement of electron donating ability and appropriate isolated effect are shown. Future perspectives of the application of such kind of NLO chromophores are considered.

1. Introduction

Due to low dielectric constants and huge EO (Pockels) coefficients, organic NLO materials have a great potential in wide bandwidth optoelectronic telecommunication systems and sensing such as electronic/photonic integrated circuits, phased array radar, terahertz spectroscopy, etc. [1–3] Recently researchers pay more attention to organic NLO materials possessing large first order hyperpolarizabilities and good optical transparency [4–6]. NLO chromophores can substantially enhance organic NLO parameters with respect to EO activity, solubility, machinability and optical loss [4–7]. In the past decades, a couple of excellent NLO chromophores have been designed and prepared. Some of them possessed large EO coefficients (above 300 pm/V at wavelength of 1310 nm), but their EO activities are far from a theoretical limit. And these materials present a key enabling platform for driving the rapid deployment of high-performance photonic devices [8,9]. Organic EO light modulators are important commercial devices for transmitting and transformation of ultrafast electrical signals into optical signals in fiber-optic telecommunications. They have made a breakthrough in half wave voltage and bandwidth frequency. The bandwidth frequency has reached a magnitude equal to 150 GHz and the half wave voltage has been reduced to below 1 V, which is impossible using traditional inorganic crystals, like lithium niobate [10–13].

However, for practical application in commercial EO devices, it is necessary to achieve more higher first order hyperpolarizability coefficients for the chromophores and to optimize an adverse for strong inter-molecular electrostatic interaction among the polymer-chromophores [14,15], The solution of these problems could greatly improve the performances of organic NLO materials in EO efficiency machinability, long term stability, exploitation time and optical loss.

Push–pull chromophores typically consist of a π-conjugated bridge end-capped with strong electron-donating and accepting groups. They form the well known class of compounds possessing second order NLO properties. In order to optimize their molecular hyperpolarizability described by third-order polar tensors, significant efforts have been focused on modifying of the π-conjugated bridge and the molecular structure of electron acceptors. At the same time, the donor units have remained relatively stable, mostly derived from 4-(dialkylamino)phenyl groups due to their relatively strong electron-donating ability and ease of synthesis and functionalization [16–21]. As the potential of electronic acceptors and

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http://dx.doi.org/10.1016/j.dyepig.2015.06.007
0143-7208/

bridges reaches a peak, researchers concentrate their efforts to optimization of electron donors again.

Recently, polycyclic donors attract an enhanced interest in fabrication of NLO chromophores, which have a great potential in enhancement of the first order hyperpolarizability and reduction of the inter-molecular electrostatic dipole–dipole interaction [22–32]. According to their strong contributions in improving of the EO coefficients and solubility, researchers from University of Washington and Chinese Academy of Sciences have designed and manufactured a couple of excellent NLO chromophores based on tetrahydroquinolinyl or julolidinyl polycyclic donor structures. Following the Table 1, most of the chromophores containing polycyclic donors possess relatively large EO coefficients, first order hyperpolarizability and good thermal stability.

In this review, the principles and application of NLO effects in the titled organic materials will be considered and novel NLO chromophores with multi-cyclic donors will be presented based on their structures and modifying groups.

2. Principles and application of NLO effects in organic materials

2.1. Principles of the NLO effects

The high frequency oscillating electric field of a light causes a space redistribution of the weakly bound valence electron clouds. Such redistribution involves a polarization process which creates an induced charge within the molecule. This microscopic polarization can be expressed as the following power series:

$$P_i = \alpha_{ij}E_j + \beta_{ijk}E_jE_k + \gamma_{ijk}E_jE_kE_i + \cdots \tag{1}$$

Here α is the linear polarizability, β and γ are the first and second molecular hyperpolarizabilities, respectively. The second- and third-order terms (β and γ terms) only exist under the influence of intense electric fields such as a laser light. Furthermore, the even order tensor β, responsible for second-order NLO effects, vanishes in a centrosymmetric molecule.

It is also well established that the macroscopic polarization of a bulk material under the applied strong electric field can be regarded as an averaged sum of the individual molecular polarizations:

$$P = \chi^1E + \chi^2EE + \chi^3EEE + \cdots \tag{2}$$

where χ^2 and χ^3 are the second and third order susceptibility tensors, respectively. The macroscopic susceptibilities are related to the corresponding molecular hyperpolarizability terms β and γ by local field Lorenz field factor and the density of molecules.

$$\chi^{(2)}_{XXX} = N\beta_{XXX}\langle\cos^3\theta\rangle(\text{const}) \tag{3}$$

where N = chromophore number density (molecules/cc); β = molecular first hyperpolarizability, which is determined by the structure of the chromophores; $<\cos^3\theta>$ = acentric order parameter, which is determined by the intermolecular interaction among the chromophores and the poling condition; the constant depends on the dielectric properties of the material lattice and is defined by local electric field. As shown in quation (3), $\chi^{(2)}_{XXX}$ should increase linearly by increasing N, β or the order parameter $<\cos^3\theta>$.

Based on these susceptibilities, many special nonlinear optical effects were derived, such as: Pockels effect (EO effect) described by the third rank polar tensor:

$$r_{33} = -2\chi^2\Big/n^4 \tag{4}$$

The EO effect is a second order NLO process where an external DC or low AC frequency electric field couples with the optical field to change the refractive index of a material. The change of refractive index can be expressed as: $\Delta n = -n^3E(0)/2$; where n is the refractive index with no external electric field, r is the EO coefficient of the material, and $E(0)$ is the applied DC or low frequency electric field. Thus the resulting phase shift $\Delta\varphi$ can be expressed as: $\Delta\varphi = n^3rEL\pi/\lambda$; where L is the coupling length of the applied electric field with incident light. Correspondingly, a phase change of the incident light can be converted to an intensity change in output light using interference effect. As a result, the net outcome is the modulation of light through an externally applied electric field. A half wave modulation voltage can be obtained as: $V_\pi = (\lambda h/n^3rL)$, where h is the distance between the electric field electrodes.

Table 1
Principal parameters of the chromophores considered in this review.

Chromophore	r_{33} (pm/V)	T_d (°C)	T_g (°C)	T_p (°C)	β_{zzz} (10^{-30} esu)	Ref
1	20			105	937	[22]
2	76			105	848	[22]
3	218			135	831	[22,26]
4	72	202		10 above T_g	870	[23]
5	36	244		10 above T_g	124	[24]
6	53	242	110, 137	120, 147	934	[25]
7	266	247	112, 137	122, 147	916	[25]
8	127	219	106, 129	116, 139	925	[25]
9	62		/	/	831	[25]
10	94	238	140	145	800	[27]
11	20	276	140	145	1900	[27]
12	35	239	/	Around T_g	294	[28]
13	52	229	/	Around T_g	262	[28]
14	337				254	[29,30]
15	72				246	[29]
16	86	251		Around T_g	672	[31]
17	128	236		Around T_g	686	[31]
18	98	202		Around T_g	809	[31]

T_d: Thermal decomposition temperature of the NLO chromophores.
T_g: Glass transition temperature of the EO polymers.
T_p: poling temperature of the EO films.