Optical Materials 85 (2018) 18–25

Contents lists available at ScienceDirect

Optical Materials

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

Donor-acceptor substituted thiophene dyes for enhanced nonlinear optical limiting

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ARTICLE INFO

Keywords:
Thiophene dyes
Nonlinear optics
Z-Scan
Two-photon absorption
Optical limiting

ABSTRACT

Designed, synthesized and characterized here two thiophene dyes 3-(4-(diethylamino)phenyl)-2-(thiophen-2-yl) acrylonitrile (**ET**), 3-(4-(diphenylamino)phenyl)-2-(thiophen-2-yl)acrylonitrile (**PT**) along with their -CHO substituted derivatives 3-(4-(diethylamino)phenyl)-2-(5-formylthiophen-2-yl)acrylonitrile (**ET-CHO**) and 3-(4-((4-formylphenyl) (phenyl)amino)phenyl)-2-(5-formylthiophen-2-yl)acrylonitrile (**PT-2CHO**) for optoelectronic devices towards protecting human eyes and optical sensors, as well as for stabilizing light sources in optical communications. Using the open aperture Z-scan method in tandem with linear absorption spectroscopy, emission spectroscopy and density functional theory (DFT) calculations, the nonlinear absorption and optical limiting behavior under nanosecond (5 ns) Nd: YAG laser excitation at 532 nm wavelength was demonstrated. The observed nonlinearity in all the samples was found to be arising from two-photon absorption process. The DFT calculations at a B3LYP/6-31G(d) level for the geometry optimization have shown that the HOMO levels of ET and PT dyes are delocalized throughout the molecule, while for ET-CHO and PT-2CHO dyes, they occupy all over the molecule except -CHO group present on thiophene ring. Also, LUMO levels are delocalized through the aromatic bridge and shift towards thiophene ring for all dyes. This change in the band structure has tuned the effective nonlinear absorption coefficients (β_{eff}) and PT-CHO possesses a maximum value of $\beta_{eff} = 2.9 \times 10^{-11}$ m/W. The excellent optical limiting performance of these chromophores makes them useful in photonic or optoelectronic devices for protecting human eyes and optical sensors, as well as for stabilizing light sources in optical communications.

1. Introduction

With the development of laser technology, much interest in the development of optical limiting material has been made among researchers working on optical materials. Devices for protection to human eyes and solid-state sensors from intense laser beam damages are sought. For the past two decades, a lot of explorations in the field of nonlinear optics were done in order to find a good optical limiting material which transmits low-intensity lights and blocks high-intensity beams when it crosses a limiting value called limiting threshold. Though previously researchers relied on inorganic materials for finding out better NLO activity due to their high mechanical strength, environmental stability, non-toxicity and usability in high power applications [1–3], the organic materials have overpowered inorganic materials because of their high optical nonlinearity, architectural flexibility, ultrafast response and versatile ability to tune the optical properties through structural modifications [4–6]. Most importantly molecular tailorability is utilized to achieve desired band structure in various types of organic compounds which have been investigated for their second and third order NLO properties. These include tetraphenylene, porphyrin, pentacene, dimenthine cyanine, polyaniline-porphyrin, chalcones and stilbazolium compounds [7–12] and many more.

The enhanced NLO response of organic chromophores could be mainly attributed to effective tuning and alteration of intermolecular and intramolecular interactions through molecular engineering. In particular the intramolecular charge transfer between strong donor and acceptor groups aids in enhancing hyperpolarizabilities at the molecular level. The conjugated structure based compounds facilitates electron transfer between the donor and acceptor groups, causing

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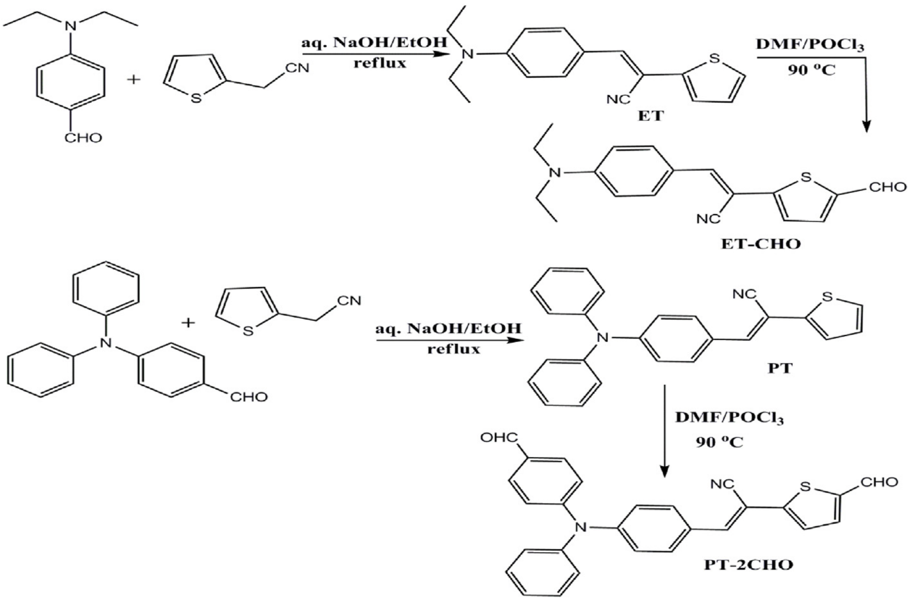
https://doi.org/10.1016/j.optmat.2018.08.004
Received 20 February 2018; Received in revised form 5 June 2018; Accepted 5 August 2018



Scheme 1. Molecular Structures and Synthetic procedure of ET, ET-CHO, PT, and PT-2CHO.

efficient π-electrons delocalization and hence high nonlinearity [13,14]. In general, with this donor-π-bridge-acceptor (D-π-A) construction, it is easy to design new dye structures, extend the absorption spectra, adjust the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) levels and complete the intramolecular charge separation. When a dye absorbs light, intramolecular charge transfer occurs from accepting subunit (A) to donating subunit (D) through the π-bridge. The intermolecular interaction like hydrogen bonding favors head to the tail alignment of molecules that leads to the formation of noncentrosymmetric crystal structures which ultimately results in an efficient second harmonic generation [15]. Multiphoton absorption (MPA) is the simultaneous absorption of more than one photon by the same molecule, which provides a means to access an electronically excited state by absorption of lower energy photons when compared to the corresponding one-photon induced transition. The two-photon absorption (TPA) process is a third-order nonlinear optical process that requires high excitation powers and/or systems with high third-order susceptibility coefficients and also it has a much lower transition rate compared to one-photon absorption. However, through rational molecular design, the molecular TPA cross-section can be enhanced by orders of magnitude [16]. Optical power limiting, two-photon upconversion lasing, two-photon fluorescence excitation microscopy, three-dimensional optical data storage, photodynamic therapy, and 3D micro/nano-fabrication, are among the areas where exploitation of the MPA phenomenon has led to significant technological developments [17–23].

It is known that molecules with a large TPA often possess an extended π-conjugation system and strong electron acceptors or donors, which are related to the extent of intramolecular charge-transfer upon photoexcitation [24]. An optimized NLO chromophore is expected to possess an extended conjugated system and a large dipole moment difference between excited state and ground state electronic configuration (charge asymmetry). This charge asymmetry can be achieved by introducing different functional groups substituted in the molecule. The presence of appropriate strong electron donor and strong acceptor groups can improve the polarizability in either or both ground and excited electronic states leading to large molecular hyperpolarizabilities and good crystallizability. The extensive delocalization of π-electrons which favours easier polarizability is achieved by the presence of strong electron donor (D) and strong acceptor (A) groups with a π-electron bridge in between [25]. The presence of appropriate donor and acceptor undoubtedly enhances the nonlinear absorption, but the coplanarity of the molecule plays a key role in enhancing the extent of conjugation, which in turn improves the polarizability of the molecule. Accordingly in this article, design and synthesize of two thiophene dyes 3-(4-(diethylamino)phenyl)-2-(thiophen-2-yl)acrylonitrile (**ET**), 3-(4-(diphenylamino)phenyl)-2-(thiophen-2-yl)acrylonitrile (**PT**) along with their -CHO substituted derivatives 3-(4-(diethylamino)phenyl)-2-(5-formylthiophen-2-yl)acrylonitrile (**ET-CHO**) and 3-(4-((4-formylphenyl) (phenyl)amino)phenyl)-2-(5-formylthiophen-2-yl)acrylonitrile (**PT-2CHO**) for nonlinear optical investigations is reported in detail.

1.1. Materials and photo-physical measurements

Thiophene-2-acetonitrile (Sigma-Aldrich) and 4-diethylaminobenzaldehyde (Alfa Aesar), were purchased and used without further purification. Phosphorus oxychloride ($POCl_3$) and *N, N*-dimethylformamide (DMF) were purchased from Merck. ^{1}H and ^{13}C NMR spectra were obtained on Bruker 500 MHz NMR Spectrometer using tetramethylsilane as an internal standard for the structural conformation of the synthesized variants. High-resolution mass spectra were obtained by ESI (Orbitrap mass spectrometer). Elemental analysis was performed with a Vario EL III elemental analyzer. The FT-IR spectra were obtained with a Thermo Scientific Nicolet iS5 FT-IR Spectrometer. All reactions were monitored by using TLC plates. All chromatographic separations were carried out on silica gel (60–130 mesh). Absorption and fluorescence spectra were measured in ethanol solution on a T90 + UV–Vis spectrometer and Shimadzu RF-5301 PC spectrofluorophotometer respectively.

1.2. Synthesis

The molecular structures and followed synthetic procedure of ET, ET-CHO, PT, and PT-2CHO are shown in Scheme 1.

1.2.1. Synthesis of 3-(4-(diethylamino)phenyl)-2-(thiophen-2-yl)acrylonitrile (ET)

4-diethylaminobenzaldehyde (2 g, 11.3 mmol) and thiophene-2-acetonitrile (1.44 mL, 13.6 mmol) were taken in a two neck round bottom flask containing 30 mL freshly distilled ethanol. 6 M NaOH (0.1 mL) was added to this reaction mixture at room temperature and