

A new donor–acceptor type conjugative poly{2-[4-(1-cyanoethenyl)phenyl]-3-(3,4-didodecyloxythiophen-2-yl)prop-2-enenitrile}: Synthesis and NLO studies

Pramod Kumar Hegde^a, A. Vasudeva Adhikari^{a,*}, M.G. Manjunatha^a,
C.S. Suchand Sandeep^b, Reji Philip^b

^a Department of Chemistry, National Institute of Technology Karnataka, Surathkal, Mangalore 575 025, India

^b Light and Matter Physics Group, Raman Research Institute, C. V. Raman Avenue, Sadashiva Nagar, Bangalore 560 080, India

ARTICLE INFO

Article history:

Received 3 September 2009

Received in revised form 24 May 2010

Accepted 9 June 2010

Keywords:

Conjugated polymer

Cyanophenylenevinylene

3,4-Didodecyloxythiophene

NLO

Saturable absorption

ABSTRACT

This research article describes a technique to synthesize a new donor–acceptor type conjugated polymer carrying cyanophenylenevinylene and 3,4-didodecyloxy thiophene moieties, as an effective optical limiting material. It also includes the evaluation of its linear and nonlinear optical properties and electrochemical studies. The new polymer, viz., poly{2-[4-(1-cyanoethenyl)phenyl]-3-(3,4-didodecyloxythiophen-2-yl)prop-2-enenitrile} (**P1**) has been synthesized starting from 2,2'-sulfanediylidiacetic acid and diethyl ethanedioate through multistep reactions. In the final step, the polymerization was brought about by Knoevenagel condensation. The newly synthesized intermediate, monomer and the polymer (**P1**) have been characterized by different spectroscopic techniques followed by elemental analysis. Its optical and electrochemical properties are investigated by UV–vis, fluorescence spectroscopy and cyclic voltammetric studies, respectively. The red colored polymer has a well defined structure, good thermal stability and a band gap of 1.78 eV. It emits green fluorescence both in solution and in film state. The third-order nonlinear optical property (NLO) of the polymer was studied by the Z-scan technique. The measurements were performed at 532 nm with 5 ns laser pulses using samples in solution form. An absorptive nonlinearity of the optical limiting type was found in this polymer, which is due to the combined action of saturable absorption and excited state absorption processes. These studies revealed that polymer **P1** is a promising material for optical limiting applications.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

During the past 10 years there has been considerable progress in the design of organic materials for optical power limiting. Among the new materials, the more promising are reverse saturable absorbers (RSA), which derive their limiting capability from the photo-generation of highly absorbing charge states. Interestingly, new approaches have been followed for designing new molecules with large two-photon cross-sections which gives access to highly absorbing charge states. Extensive literature survey reveals that over the past few years many research groups have addressed the problem of photo-generated charge state formation in conjugated polymers [1,2].

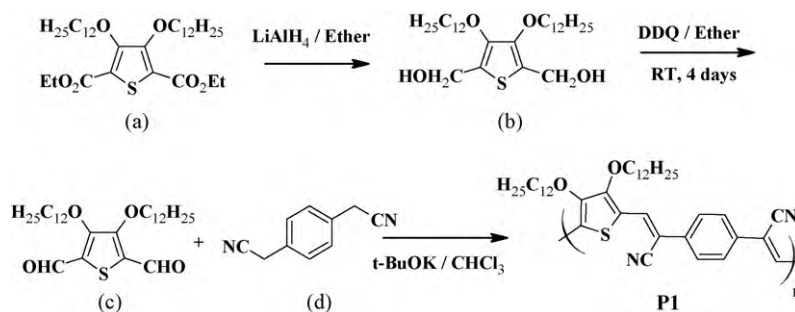
While two-photon absorption has been studied for a number of years, detailed structure–property relationships which might per-

mit the design of new chromophores with enhanced two-photon cross-sections have been lacking [3–5]. However, in the recent past a few groups have attempted to address the requirement of such design paradigms. Among them, Reinhardt et al. have projected some important design parameters and proposed a series of general rules for increasing the molecular two-photon cross-sections in the new targets. According to them (i) the presence of extended conjugation length, (ii) change in the identity of the conjugated bridge, (iii) increase in the π -donor strength, (iv) incorporation of more polarizable double bonds and (v) increase in the planarity of the polymer backbone, would lead to rise in two-photon absorption characteristics of the molecules.

Thiophene based polymers are currently under active investigations for third-order NLO properties due to their easy processability, chemical stability, readiness of functionalities, good film forming characteristics, solubility, optical transparency and adequate mechanical strength [6–12]. According to the recent reports [13–15], in polythiophenes nonlinear optical properties can be synthetically tuned by introducing electron releasing and electron accepting segments in the polymer chain, which would result in

* Corresponding author. Tel.: +91 8242474046; fax: +91 8242474033.

E-mail addresses: avadhikari123@yahoo.co.in, avchem@nitk.ac.in (A.V. Adhikari).



Scheme 1. Synthetic route for the preparation of polymer **P1**.

improved delocalization in the molecule and hence the enhancement of their NLO properties. According to these reports, donor and acceptor groups along the polymer backbone would be a promising molecular design for enhancing the third-order NLO properties.

By applying the design concept proposed by Reinhardt et al., we have designed a new donor–acceptor type conjugative polythiophene wherein cyanophenylenevinylene moiety is incorporated in between 3,4-didodecyloxy substituted thiophene moieties in the polymer backbone. It is expected that the new polymer would show enhanced molecular two-photon cross-sections and hence exhibit better *reverse saturable absorption* properties. In this paper, we describe the synthesis and characterization of hitherto unknown polymer containing 3,4-didodecyloxythiophene group as an electron rich n-type segment, cyano-vinylene moiety as electron deficient p-type segment and phenyl ring, as a conjugative spacer as well as a conjugated bridge in the chain. Further, it has been predicted that the introduction of cyanophenylenevinylene moiety reduces the lowest unoccupied molecular orbital (LUMO) level which is expected to increase the linear and nonlinear optical responses [16]. The paper also describes the measurement of nonlinear optical absorption of the polymer using the open aperture Z-scan technique, employing 5 ns laser pulses at 532 nm from a frequency-doubled Nd:YAG laser.

2. Experimental

2.1. Materials

Diethyl 3,4-didodecyloxythiophene-2,5-dicarboxylate (**a**) was synthesized according to the reported literature procedure [17–19]. Dimethylformamide and acetonitrile were dried over CaH_2 . 2,2'-Sulfanediyl diacetic acid, diethyl ethanedioate, n-bromoalkanes, lithium aluminium hydride, dichlorodicyanoquinone (DDQ) and tetrabutylammonium perchlorate (TBAPC) were purchased from Lanchester (UK) and were used as received. 1,4-Phenylene diacetonitrile was purchased from Aldrich and it was used as received. All the solvents and reagents were of analytical grade. They were purchased commercially and used without further purification.

2.2. Instrumentation

Infrared spectrum of all intermediate compounds and the polymer was recorded on a Nicolet Avatar 5700 FTIR (Thermo Electron Corporation). The UV–vis and fluorescence emission spectra of the polymer were measured in GBC Cintra 101 UV-visible and Perkin–Elmer LS55 spectrophotometers respectively. ^1H NMR spectra were obtained with AMX 400 MHz FT-NMR spectrophotometer using TMS/solvent signal as internal reference. Mass spectra were recorded on a Jeol SX-102 (FAB) Mass Spectrometer. Elemental analysis was performed on a Flash EA1112 CHNS analyzer (Thermo Electron Corporation). The electrochemical study

of the polymer was carried out using a AUTOLAB PGSTAT30 electrochemical analyzer. Cyclic voltammogram was recorded using a three-electrode cell system, with glassy carbon button as working electrode, a platinum wire as counter electrode and an Ag/AgCl electrode as the reference electrode. Molecular weight of the polymer was determined on WATERS make gel permeation chromatography (GPC) using polystyrene standards in THF solvent. The thermal stability of the polymer was studied by SII-EXSTAR6000-TG/DTA6300 thermogravimetric analyzer.

2.3. Z-scan measurements

The Z-scan is a well known experimental technique developed by Sheik-Bahae et al. [20] for measuring the nonlinear optical refraction and absorption coefficients of material. The “open aperture” Z-scan is used for nonlinear absorption coefficient measurements. In this technique a Gaussian laser beam is used for molecular excitation, and its propagation direction is taken as the z-axis. The beam is focused using a convex lens, and the focal point is taken at $z=0$. The experiment is done by placing the sample in the beam at different positions with respect to the focus (different values of z), and measuring the corresponding transmissions. The beam will have maximum energy density at the focus, which will symmetrically reduce towards either side of it, for the positive and negative values of z . Thus the sample experiences different laser intensity at each z position. A graph drawn between the z position and sample transmission is known as the open aperture Z-scan curve. From this curve, the nonlinear absorption parameters of the sample can be calculated.

The second harmonic output from a Q-switched pulsed Nd:YAG laser (MiniLite, Continuum) was used for the measurements. The laser pulses had a nominal width of 5 ns, and energy of 190 μJ . Pulse-to-pulse energy fluctuation was less than 2%. The laser beam had a Gaussian spatial intensity profile. The sample was taken in a 1 mm cuvette. The transmission of the sample at each point was measured by means of two pyroelectric energy probes (Rj7620, Laser Probe Inc.). One energy probe monitored the input energy, while the other monitored the transmitted energy through the sample. The pulses were fired in the “single shot” mode, allowing sufficient time between successive pulses to avoid accumulative thermal effects in the sample.

2.4. Synthesis of polymer, **P1**

The polymer, **P1** was synthesized from 3,4-didodecyloxythiophene 2,5-carboxylate following the reaction sequence as described in Scheme 1.

2.4.1. Preparation of

(3,4-didodecyloxythiophene-2,5-diyl)dimethanol (**b**)

To a clear solution of 0.5 g (0.0008 mol) of diethyl 3,4-didodecyloxythiophene-2,5-dicarboxylate (**a**) in 10 mL of dry

Download English Version:

<https://daneshyari.com/en/article/1442404>

Download Persian Version:

<https://daneshyari.com/article/1442404>

[Daneshyari.com](https://daneshyari.com)