

Materials science communication

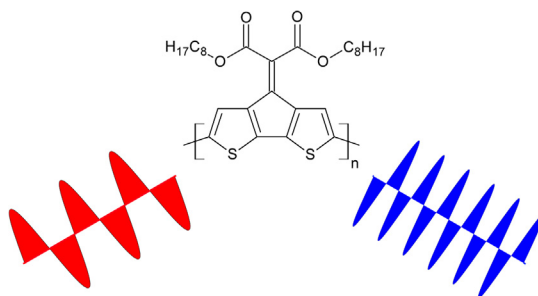
Optical second harmonic generation in a low-bandgap polymer

Stefaan Vandendriessche^{a,*}, Pieter Willot^b, Ventsislav K. Valev^c, Guy Koeckelberghs^b, Thierry Verbiest^a^a Molecular Imaging and Photonics, KU Leuven, Celestijnenlaan 200D – Box 2425, 3001 Heverlee, Belgium^b Polymer Chemistry and Materials, KU Leuven, Celestijnenlaan 200F – Box 2404, 3001 Heverlee, Belgium^c Nanophotonics Centre, Cavendish Laboratory, University of Cambridge, Cambridge CB3 0HE, United Kingdom

HIGHLIGHTS

- We characterize optical second harmonic generation in a low-bandgap polymer (PCPDT).
- PCPDT displays unexpectedly large nonlinear optical susceptibilities.
- PCPDT has a very low absorption in the relevant wavelength region.
- We demonstrate favorable thermal and temporal stability of the material.
- We show the promise of low-bandgap polymers for nonlinear optical devices.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 17 June 2013

Received in revised form

24 March 2014

Accepted 2 June 2014

Available online 20 June 2014

Keywords:

Optical properties

Polymers

Thin films

Non-crystalline materials

Electronic materials

ABSTRACT

Recently, much research has been performed on developing low-bandgap polymers for e.g. harvesting solar energy. In the quest to improve these properties, little attention has been paid to their nonlinear optical properties, despite their interesting linear optical spectra and structural similarities to certain nonlinear optically active compounds. We characterized the optical second harmonic generation of corona poled films of poly(cyclopenta[2,1-*b*;3,4-*b'*] dithiophen-4-ylidenedioctylmalonate). The unexpectedly large nonlinear optical susceptibilities and the thermal and temporal stability of the material compare favorably to other novel nonlinear optical materials despite the lack of a donor-acceptor dye. Additionally, the polymer displays a very low absorption in the relevant wavelength region. These results demonstrate the promise of these materials for nonlinear optical devices.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The promising properties of low-bandgap polymers for applications such as solar cells have attracted much recent research [1–5]. These new polymers provide many advantages over classical

materials, including their light weight, low cost and easy processability.

Low-bandgap polymers have been designed to achieve high power conversion efficiencies, but despite their conjugation and superficial similarity to certain nonlinear optical materials, no effort has been made to characterize their second order nonlinear optical response. Nonlinear optical processes occur when intense light fields, such as a laser, interact with matter. At these high electrical fields, the classical linear polarization equations are no longer sufficient to describe the response of the material, and

* Corresponding author. Tel.: +32 16 3 27154.

E-mail address: stefaan.vandendriessche@chem.kuleuven.be (S. Vandendriessche).

higher order terms need to be invoked. This can be written macroscopically (using the Einstein summation convention) as

$$P = P_0 + \chi_{ij}^{(1)} E_j + \chi_{ijk}^{(2)} E_j E_k + \chi_{ijkl}^{(3)} E_j E_k E_l + \dots \quad (1)$$

where P is the induced polarization, P_0 is the equilibrium polarization, E_j is the electric field in the j direction and $\chi_{ij}^{(1)}$, $\chi_{ijk}^{(2)}$, $\chi_{ijkl}^{(3)}$ are the first, second and third order polarizability. They affect the efficiency of materials in nonlinear optical devices such as electro-optical modulators, [6] high-speed optical switches [7,8] and data storage [9]. In molecules, they are determined by the molecular higher order polarizabilities α , β , γ and the arrangement of the individual nonlinear optical active moieties in the material. $\chi_{ijk}^{(2)}$, a second order tensor consisting of 27 elements, determines the efficiency of optical second harmonic generation (SHG), where two photons of frequency ω combine to form one photon of double frequency, 2ω . For efficient SHG to occur, in addition to large molecular hyperpolarizabilities β , it is also important that the molecules are not arranged in a centrosymmetric fashion [10]. To achieve this, the molecules must be oriented, which is achieved by substrate-induced ordering or by electric field-poling. For such poled films there are three independent components within the electrical dipole approximation contributing to SHG, [11] $\chi_{xxz}^{(2)}$, $\chi_{zxx}^{(2)}$ and $\chi_{zzz}^{(2)}$.

To be applicable in nonlinear optical devices the material must display low losses in the relevant wavelength range, as well as good thermal and temporal stability under high incident laser power. Low absorption in the relevant wavelength range is beneficial for these requirements.

We investigated the second harmonic generation in a low-bandgap polymer, poly(cyclopenta[2,1-*b*;3,4-*b'*] dithiophen-4-ylidenedioctylmalonate) (PCPDT) (Fig. 1). PCPDT is known to be amorphous, not displaying any form of order. It also does not contain a typical donor-acceptor system associated with a high nonlinear optical response. Nonetheless, we observed second harmonic generation in thin films of PCPDT.

2. Experimental

SHG measurements were performed as described by Vandendriessche et al. [12] A Ti:sapphire laser (800 nm) emitted pulses of approximately 100 fs with a repetition rate of 82 MHz. The generated beam was polarized by a motorized half-wave plate followed by a motorized Glan-laser polarizer. Subsequently, the beam passed through a motorized quarter-wave plate, and an RG650 filter filtered the beam to exclude 400 nm light generated before the sample. The filtered beam was focused by lenses with a focal length of 10 cm on the sample. The transmitted beam was filtered by an FB400-40 bandpass filter, followed by a BG39 filter to exclude both possible fluorescence and 800 nm light from the laser, allowing only the second harmonic light to pass through a motorized analyzer. A photomultiplier tube cooled to -15 °C collected this light, and after

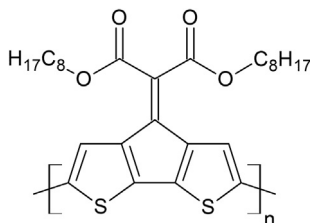


Fig. 1. Poly(cyclopenta[2,1-*b*;3,4-*b'*] dithiophen-4-ylidenedioctylmalonate) was designed as a low-bandgap material for application in organic electronics.

preamplification, an SR400 gated photon counter processed the signal. In order to perform the temperature-dependent measurements, the detection optics were placed at 90° and the measurement was performed in reflection with the sample mounted on a heating stage. Measurements were performed at the four principle polarizer-analyzer configurations.

PCPDT was synthesized as described by Willot et al. [2] A solution of PCPDT in CHCl_3 (typically 4 mg mL^{-1}) was spincoated at 2000 rpm on a glass slide coated with ITO. The resulting films, approximately 200 nm thick, were isotropic in the plane of the sample. The films were corona poled in an electric field of 8 kV, with the corona wire placed approximately 8 cm over the sample. Because the polymer does not show a T_g , [2] 140 °C was chosen as a poling temperature as an optimum between thermal mobility and degradation. The poled films displayed a $C_{\infty v}$ symmetry, and their thickness was characterized by AFM measurements.

3. Results and discussion

By using different input and output polarizations and a quartz reference we were able to determine all nonlinear susceptibility components [13] of a corona poled thin film of PCPDT (Table 1).

The obtained values compare favorably to other novel materials [14–16]. The ratio of χ_{zzz}/χ_{xxz} is larger than the expected value of 3 for poled films [17]. This can be attributed to the breakdown of the low electric field strength assumption used to derive this ratio, inequality of refractive indices for fundamental and second harmonic light or the fact that the molecular hyperpolarizability of PCPDT is expected to contain more than one component.

In addition to the high absolute value of the second-order susceptibility, PCPDT displays many other advantages over alternative novel materials. A key property is the very low absorption of the polymer films at both the fundamental and second harmonic wavelength employed (Fig. 2). This is an advantage for applications, as the low absorption allows for thicker films, less optical losses and less absorption-related damage [18]. Additionally, the nonlinear-active optical moiety is present in the backbone of the polymer, conferring improved tensile and mechanical properties over side-chain nonlinear-active optical moieties [11,19]. In the presence of a large electric field the polymer itself orients along the electric field, possibly by distortion of the orientation of the individual monomer units, in contrast to traditional donor-acceptor substituted polymers where the side-chain dyes orient. While the associated large motion required for poling can increase the necessary poling temperature, this type of polymer is more stable over time as the low temperature relaxation is much smaller (Fig. 3).

PCPDT exhibits good thermal stability (Fig. 4). Heating the thin films past the poling temperature causes a loss of poling order. A decrease in second-harmonic generation is observed until approximately 150 °C, at which temperature the film is no longer poled due to thermal relaxation. From this temperature on a stable, residual response is observed.

Table 1

The components of the second-order susceptibility ($\chi^{(2)}$) of a corona poled thin film of PCPDT.

Component of $\chi^{(2)}$	Magnitude (pm V^{-1})
$\chi_{xxz}^{(2)}$	1.95
$\chi_{zxx}^{(2)}$	2.65
$\chi_{zzz}^{(2)}$	9.85

Download English Version:

<https://daneshyari.com/en/article/1521803>

Download Persian Version:

<https://daneshyari.com/article/1521803>

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