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D-A-π-D Synthetic approach for thienyl chalcones – NLO – a structure activity study

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ABSTRACT

With the growing interest for organic molecules in Nonlinear Optical (NLO) applications, we have synthesized nine novel thienyl chalcones based on the D-A-π-D design. In order to establish the identity, these have been characterized in detail. Having followed the design based synthetic route, we have focused on two prime criteria for comparison; namely second harmonic generation (SHG) and non-linear absorption. In this work the role of the electron withdrawing groups, electron donating groups and extended conjugation, have been extensively studied vis-à-vis the NLO properties. The change in these properties by virtue of the molecular structure has been elucidated in this work as the structure activity relationship. Optical nonlinearity is studied using ultrafast (100 fs) laser pulses at 800 nm, employing the open aperture Z-scan technique. The compounds exhibit large effective three-photon absorption (3PA) coefficients, in the order of 10^{-28} m^3/W^2. These observations show that these compounds possess potential for application in all-optical limiting and switching devices.

1. Introduction

In the scenario of modern research, nonlinear optical (NLO) studies have assumed unquestionable importance, due to their applications in optical data storage, optical processing, optical computing, sensor protection, optical switching, and various other photonic technologies. Improved research has extended their application in THz wave generators, passive optical limiters, electro-optic modulators, and frequency converters [1–4]. The choice of the material in these applications is based on, response times in picoseconds or less, large nonlinear refractive and/or absorptive coefficients, and broad spectral response [5]. Therefore determination of nonlinear properties and response times of the compounds is decisive [1]. In the process of realizing this goal, organic compounds are chosen primarily due to their large diversity, and the flexibility they offer in the synthesis, strength of electron acceptor or donor groups [6a–d], planarity in the molecule [7], the molecular symmetry, and extended conjugation stretches [8,9]. The susceptibilities of these molecules can be additionally enriched by increasing the length of conjugation. However, these changes result in the consequent decrease of the HOMO-first excited state energy gap [10]. In order to obtain the best from these molecules, researchers have established various strategies to design organic molecules with enhanced nonlinear optical responses. These include synthesis and development of Acceptor-Donor-Acceptor (A-D-A), Donor-Acceptor- Donor (D-A-D), Donor-π- Donor (D-π-D) types of organic systems [2]. Chalcones exhibit intra-molecular charge transfer, and this allows for the use of design-based synthesis achieving the desired results. Molecules with similar structure allow for comparison with focus on the effect of substituents upon the properties under study. The Structure Activity Relation therewith allows to assign the change in the observed phenomena to the specific functional groups on the molecule.

An additional benefit of chalcones is that they have blue-light transmittance, and high propensity to crystallize in non-Centro symmetric structure [11a,b,12]. Chalcones being organic molecules cannot be used right away in applied photonic device applications as they get degraded or bleached when exposed to extreme optical signals [13–15]. In order to overcome this shortcoming, they can be either doped into a polymer matrix or made into a solution [16]. However the polymer matrix is cumbersome to formulate and hence solutions of the compounds were made and the nonlinear

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optical studies were conducted. The solvent of choice must essentially be transparent towards the laser signal, must possess high thermal and photochemical stability [17–20].

Thienyl-chalcones which have a D-A-π-D molecular configuration are related to the class of organic chromophores, chalcones [3]. Apart from their optical properties, they have been used in numerous applications ranging from anti-cancer, radio-protective, cytotoxic [21] and anti-viral activities; as synthons for heterocycles, chemo- protective agents, phase two enzyme inducers, radical scavengers, and catalysts; and in nonlinear optics [22–25]. Thiophene containing polymeric compounds have been investigated, and are found to exhibit good nonlinear optical properties by the effective 3PA process [26]. Owing to the numerous applications of thienyl-chalcones and high nonlinear optical activity [27], in the present work we studied nine chalcones, and report their synthesis, characterization, and nonlinear optical properties. Optical nonlinearity is investigated using the Z-scan technique, employing ultrafast (femtosecond) laser pulses for excitation. The observed effective three-photon absorption and the consequent optical limiting behavior are discussed in detail. Second Harmonic Generation (SHG) of these compounds also has been investigated. Finally, we correlate the observed NLO enhancement to the presence of extended conjugation and different electron pumping and withdrawing groups substituted at different positions in the aromatic ring.

2. Results and discussion

2.1. Characterization

The compounds were synthesized by Claisen-Schmidt condensation [28] and were characterized by UV-vis, IR, ^{1}H NMR, ^{13}C NMR, and MS. The data is reported in Table-S in the supplementary data.

2.1.1. Linear optical properties

UV–vis absorption spectra for all the compounds is shown in Fig. 1 and the λ_{max} values are reported in Table 1. All the compounds were found to have two absorption maxima. The λ_{max} values for theseα, β-unsaturated carbonyl compounds can be attributed to the $\pi\,\pi^*$ transition of the carbonyl group. The spectra can be interpreted by taking the substitutions into consideration comparing with a non-substituted one i.e. T-CHL-B whose λ_{max} value stands at 320 nm. The λ_{max} value for the compound T-CHL-NDM at 428 nm is the highest among the others, due to the conjugation by the electron pumping nature of the N,N-dimethyl amino group. This is followed by T-CHL-SM, T-CHL-OH, and T-CHL-OM with λ_{max} values of about 363 nm, 356 nm, and 349 nm respectively. In all these compounds the absorption increases with increasing capacity of donating electrons. Due to the increase in the conjugation between both the rings, the λ_{max} value for T-CHL-2T stands at 352 nm. Due to the nature of the isopropyl group, which is a good electron donating group, T-CHL-ISO has a λ_{max} value of 331 nm. Whereas the λ_{max} value for T-CHL- Cl is 323 nm.

2.1.2. FT-IR, NMR, & Mass spectra

In the FT-IR spectrum of T-CHL-B the $\nu_{C=O}$ is observed at 1650 cm^{-1} which is characteristic of chalcones [29]. The frequency of this band decreased as the electron donating nature of the substituent on the benzene ring increased and the lowest value of 1630 cm^{-1} is seen in the case of T-CHL-NDM due to the powerful electron donating ability of —N(Me)$_2$ [30]. The pmr spectra of these compounds were completely analyzed and the data is given in Table-S. Proton H-1 which is highly deshielded is observed at ~ δ7.80–8.14 as a double doublet with an ortho and meta coupling (J = 3.6–4.0 Hz and 0.8–1.2 Hz). H-2 is seen as a double doublet at δ7.17–7.34 with two ortho couplings (J = 4.8–5.2 and 3.6–4.0 Hz). H-3 signal appeared at ~ δ7.66–7.94 as a dd (J = 4.8–5.2 and

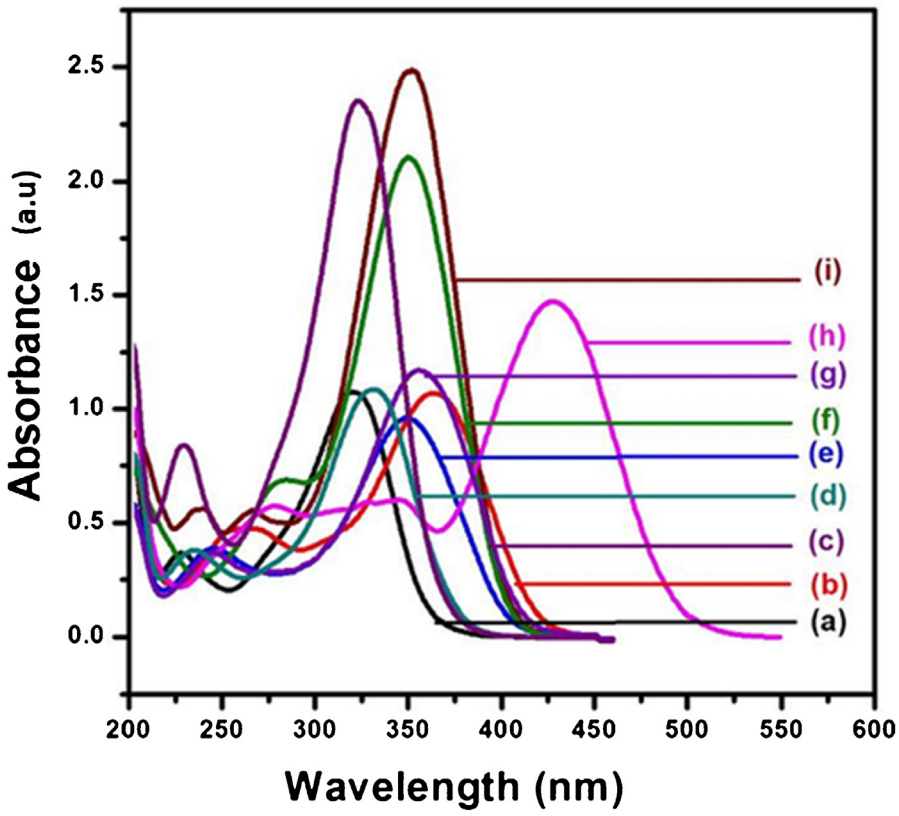

Fig. 1. UV–vis absorption plot: a) T-CHL-B, b) T-CHL- SM, c) T-CHL-ClB, d) T-CHL-ISO, e) T-CHL-OM, f) T-CHL-2T, g) T-CHL-OH, h) T-CHL-NDM, i) T-CHL-CAN.