



Spectroscopic, DFT and Z-scan supported investigation of dicyanoisophorone based push-pull NLOphoric styryl dyes

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ABSTRACT

The dicyanoisophorone acceptor based NLOphores with Intramolecular Charge Transfer (ICT) character are newly synthesised, characterised and explored for linear and non linear optical (NLO) property investigation. Strong ICT character of these D- π -A styryl NLOphores is established with support of emission solvatochromism, polarity functions and Generalised Mulliken Hush (GMH) analysis. First, second and third order polarizability of these NLOphores is investigated by spectroscopic and TDDFT computational approach using CAM/B3LYP-6-311 + g (d, p) method. BLA and BOA values of these chromophores are evaluated from ground and excited state optimized geometries and found that the respective structures are approaching towards cyanine limit. Third order nonlinear susceptibility ($\chi^{(3)}$) along with nonlinear absorption coefficient (β) and nonlinear refraction (n_2) are evaluated for these NLOphores using Z-scan experiment. All four chromophores exhibit large polarization anisotropy ($\Delta\alpha$), first order hyperpolarizability (β_0), second order hyperpolarizability (γ) and third order nonlinear susceptibility ($\chi^{(3)}$). TGA analysis proved these NLOphores are stable up to 320 °C and hence can be used in device fabrication.

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1. Introduction

Though inorganic molecules are prominently making count as NLO materials [1–4], organic molecules have advantages of being potential NLOphores by virtues of freedom of design, easy synthesis and comparative large nonlinear optical susceptibility [5–9]. Also their polarizability is of purely electronic origin making the response times extremely fast as it is limited only by the electronic phase relaxation time of a few tens of femtosecond [10]. Particularly organic molecules of D- π -A framework with push-pull type arrangement are known to perturb the π -electron delocalization of the locally excited state (LE) attained by the absorption which can promote intra-molecular charge transfer (ICT) and such phenomena are more prominent in polar solvents [11–14]. The high NLO responses of such push-pull organic π -systems is intrinsically related to ICT at excited states [15–17]. Organic molecules containing D- π -A linkage offer design flexibility and broad ranges of

conversion efficiencies. For chromophores to exhibit large hyperpolarizability the design and synthesis is a necessary step in the optimisation of molecule based materials for NLO applications [18]. Electronic structure with strong donor separated from strong acceptor by length of π -conjugation path is an ideal framework for ICT phenomenon at excited state [19–21]. Such molecules have electron transfer or electron separation between the strong electron donor and the accepting group like cyanoethoxycarbonylvinylene, dicyanovinylene, cyanobenzthiazovinylnes and 2-(1-phenylethylidene)malononitrile, which provide the class of compounds with highly anisotropic structures and results in interesting photophysical and electrochemical properties [22,23].

Dicyanoisophorone chromophores aided with strong donors are highly promising NLOphores [24,25] and have been demonstrated to provide efficient photochromic response in materials for holographic-optical data storage [26] [27], in organic photorefractive materials [28]. Further to possess photorefractive properties, the material should exhibit good optical nonlinearity along with photoconductivity [29]. The isophorone moiety was chosen as a conjugation bridge in designing the NLOphores because a polyene-based chromophore exhibits a larger dipole moment and polarizability anisotropy than an aromatic ring [30], since the more

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efficient charge transfer may occur along the polyene conjugation than the benzene bridge [29]. The rigidification of the π -linker also gives rise to an improved molar absorption coefficient at the maximum absorption wavelength [31]. In this case isophorone is a configurationally locked ployene (CLP) system which is very promising for achieving highly polar and forming acentric structure to obtain large optical nonlinearities [32]. When a strong electron-donor and strong electron-acceptor (here it is dicyanovinyl group) are incorporated at both the ends of the isophorone CLP structure, the extensive charge transfer is able to occur along a π -conjugated bridge, which is expected to possess the large polarizability anisotropy ($\Delta\alpha$) and dipole moment (μ) to NLOphore [29]. Consequently such systems are characterised by large β -responses and dicyanoisophorone based NLOphores have a promise of good photorefractive material [29].

Further the molecular polarizability and hyperpolarizability are greatly influenced by the degree of ground-state polarization or charge separation [33]. The charge separation in the ground state can be controlled by altering the strength of the donor and acceptor and/or by extending the π -conjugated path [34]. Now acceptor and π -linker are fixed so we have chosen four different strong donor moieties. The effects of altering the chemical structure in such a way were evaluated by Oudar's two level model [35].

$$\beta \propto \frac{\mu_{ge}\Delta\mu_{ge}}{(\Delta E_{eg})^3}$$

In the above mentioned four NLOphores dye-1 and 3 have para N, N-di(substituted) ethyl phenyl donors in which the substituents on ethyl ends are -CN and -COOMe groups respectively. Effect of such non conjugated electron accepting groups (-CN and -COOMe) on NLO properties is studied here. The compounds with dispersive excess electrons, open a new perspective to the design strategies of NLO molecular materials [36] and in this context pyrene is one of the most promising nonlinear functional electron rich building blocks [37]. The dye-2 is having pyrene as electron donor with no aliphatic substitution and is expected to have large hyperpolarizability. Therefore it has a potential as an optoelectronic material [38]. While in dye-4 donor part is not rigid like pyrene but it has di phenyl substituted imidazole core in conjugation with the acceptor. Introduction of such additional N atoms in the donor moiety of chromophores could dramatically increase the donor strength and length of conjugation influencing the molecular hyperpolarizability [39–41]. Also five-membered heterocycles are useful to strengthen the thermal and chemical robustness of NLO materials [42,43]. Further such donors could impart remarkable third order optical nonlinearity to chromophores [38].

In order to determine the linear and NLO properties of compounds 1 to 4, a comprehensive investigation was conducted by a combination of spectroscopic techniques and computational approach. All four dyes show significant emission solvatochromism. Being charge transfer chromophores their charge transfer properties are evaluated using different solvent polarity functions. The second order hyperpolarizabilities were determined experimentally by Z-scan technique. The real and imaginary part of third order nonlinear susceptibility ($X^{(3)}$) along with nonlinear absorption coefficient and nonlinear refraction were evaluated for all the dyes. Molecular linear and non linear optical properties are governed by bond length alternation (BLA) and bond order alternation (BOA). Since little change in BLA and/or BOA values significantly affects the NLO properties [44], we have calculated BLA and BOA using DFT and TDDFT optimized geometries of chromophores. The non linear optical performance of molecules depends on efficiency of charge transfer in D- π -A system by the virtue of D-A distance and coupling strength. For four NLOphores Generalised Mulliken Hush (GMH)

analysis accounted the coupling strength H_{DA} between ground state and charge transfer excited state [45].

2. Experimental

2.1. Material and spectroscopic methods

All the reagents were procured from SD Fine Chemicals (Mumbai) and were used without further purification. Laboratory reagent grade solvents were purchased from Rankem, Mumbai. The reactions were monitored by TLC using on 0.25 mm EMerck silica gel 60 F₂₅₄ precoated plates, which were visualized using UV light (254 nm and 344 nm). Melting points were measured on standard melting point apparatus from Sunder Industrial Products, Mumbai and are uncorrected. Proton and Carbon NMR spectra were recorded on Varian 500 MHz instrument using TMS as an internal standard. The absorption spectra of the compounds were recorded on a Perkin-Elmer Lambda 25 UV–Visible spectrophotometer and emission spectra were recorded on Varian Inc. Cary Eclipse spectrofluorometer. The TGA was carried out on Perkin Elmer STA 6000 instrument with a heating rate of 10 °C/min under the protection of nitrogen. Cyclic voltammetric data were measured on an Autolab instrument using a conventional three-electrode cell with Pt metal as the working electrode, Pt gauze as the counter-electrode, and Ag/AgNO₃ as the reference electrode at a scan rate of 100 mV/s. The 0.1 M tetrabutylammonium hexa-fluorophosphate (NBu₄PF₆) in dichloromethane as the electrolyte.

2.2. Z-scan experimental

By the Z-scan technique both nonlinear absorption (β) coefficient and nonlinear refractive index (n_2) were simultaneously measured for dye-1 to 4 samples that were liquid solutions of DMSO, ethanol and methanol. In the Z-scan experiment, a laser beam was focused to a minimum waist at the focal point which corresponds to the value of $Z = 0$, where Z is the propagation direction (Z axis) of the beam. A sample is then made to move along the path of the beam, with variations of the incident beam intensity resulting in distortion and changes in transmittance of the beam which were probed by two detectors, open-aperture and closed-aperture detectors. For all dye solutions the Z-scan measurement was performed at 0.3 mM concentration using 532 nm Nd:YAG laser having 5ns pulses at a repetition rate of 10 Hz. Analysis of the results obtained for samples, to determine the microscopic parameters β , n_2 and $X^{(3)}$.

2.3. Computational details

For hyperpolarizability computation Density functional theory (DFT) is generally used for many large conjugated organic NLOphores [46]. The synthesised D- π -A styryl systems are expected to show significant charge transfer character and the lack of exact exchange in typical DFT functionals often leads to underestimation of charge-transfer energies [47]. So the appropriate functional in computational strategy to calculate the molecular hyperpolarizability is highly demanding. This can be provided either by the choice of hybrid functional which uses a fixed amount of exchange at all inerelectronic distances or a long-range corrected (LC) functional which uses a larger fraction of generalised gradient approximation (GGA) DFT exchange at short range and larger fraction of exact exchange at long range inerelectronic distances [48–50]. To eliminate the problem of delocalization error for estimation of molecular hyperpolarizabilities, it is recommended that the use of hybrid GGA functionals in combination with a percentage of the local exchange replaced by the exact HF [51]. Following this

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