NLOphoric multichromophoric auxiliary methoxy aided triphenylamine D-π-A chromophores — Spectroscopic and computational studies

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ABSTRACT

Molecules containing methoxy supported triphenylamine as strong electron-donor and dicyanovinyl as electron-acceptor groups interacting via isophorone as a configurationally locked polyene π-conjugated bridge are studied for their nonlinear optical properties. The photophysical study of examined chromophores in non-polar and polar solvents suggest that they exhibit strong emission solvatochromism and significant charge transfer characteristics supported by Lippert-Mataga plots and Generalised Mulliken Hush analysis. Linear and nonlinear optical properties as well as electronic properties measured by spectroscopic methods and cyclic voltametry and supported by DFT calculation were used to elucidate the structure property relationships. All three chromophores exhibit very high thermal stabilities with the decomposition temperatures higher than 340°C. The vibrational motions play very important role in determining the overall NLO response styryl chromophores which was established by DFT study. Dye 3 with maximum nonlinear optical susceptibility among three D-π-A systems proves that the multi-branched push-pull chromophores exhibit a higher third order nonlinear susceptibility and justifies the design strategy.

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1. Introduction

Non linear optical (NLO) materials have wide applications in areas ranging from medicine to optical information processing, integrated optics, sensor protectors, data storage, optical power limiting, optical communications served by inorganic and organic NLOphores[1–5]. Organic NLOphores have purely electronic origin of their polarizability and extremely fast response time combined with ease of custom tailored design and easy incorporation into fabrication matrix compared to inorganic counterparts. NLOphoric organic materials should posses a wide optical window around the visible region, chemical and thermal stability, asymmetric charge distribution over the electron rich (donor) and deficient (acceptor) linked by π-conjugation framework and a high damage threshold. These molecular property oriented requirements can be

approached by strategic molecular design[6]. The strength of donor(D) and acceptor(A) substituents, the type and distance between the D and A moieties, and the symmetry of the molecules would have significant effects on their NLO properties which can be tuned by choosing proper ones over the extensive range of functional units [7–10]. Intrinsic NLO properties of organic push-pull type systems are mainly governed by the extent of ICT, which is a consequence of the D-A interaction[11]. In contrast to ordinary linear D-π -A molecules, branched molecules with multiple D-π -A arrangements exhibit enhanced ICT character[12–15]. All the three i.e. D, A and π-bridge are the integrated parts of NLOphoric D-π—A system and strategic optimisation of this system could enhance the ICT character which leads to maximise the NLO response of the system along with the enhancement of the two photon absorption (TPA) cross section area [11].

For device application the NLOphoric material should possess high electrooptic (EO) activity which can be achieved by higher quadratic hyperpolarizability ($\mu\beta$) and strong ICT character[16–18]. Triphenyamine derived molecules have shown very good NLO

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response because of their multifunctional properties[19–24]. They exhibit a low oxidation potential, which makes them attractive as hole-transport layers in organic light emitting diodes[25,26]. Triphenylamine derived dyes are expected to exhibit good laser photostability [27,28]. Further to achieve high thermochemical stability triphenylamine donors are preferred over their alkyl analogues and lone pair of electrons on central nitrogen can be easily delocalized over the chromophoric system for efficient charge transfer. In case of application in photonic devices the organic NLOphores undergo the polarization process which cause strong intermolecular electrostatic interactions between highly polarizable chromophores to reduce the performance efficiency[29]. Multichromophoric framework can overcome this problem by the relieving dipole interactions because of the steric isolation[30,31]. This design strategy provides enough space for each chromophoric unit to orientate efficiently which could result into enhanced NLO performance of material[29,32]. Adhering to this strategy we have studied branched D-π-A system based on triphenylamine as a donor. Incorporating heteroatom-groups into the donor moiety of NLOphore could dramatically enhance the conjugation of the π-electron networks and the ICT character, which could further influence the NLO response [33–37]. Further, loosely bound excess electrons on the donor play a crucial role in obtaining a large static first hyperpolarizability (β_0) of solvated electrons system [38,39]. In this context triphenylamine with multiple auxiliary methoxy donors are chosen for the role of donor moiety in design strategy. Dicyanovinyl is one of the most successful strong acceptor utilised for D-π-A NLOphoric systems[40,41], which was a primitive choice for high NLO response. Further D-π-A type push-pull chromophores with dicyanovinyl as a strong acceptor and isophorone as a π-spacer are showing very high electrooptic (EO) coefficient when used as NLOphore in polymer EO devices. Such chromophore with ring locked π-bridge has a strong electron transfer ability and thermal stability. Due to such large isolated groups that are introduced to the electron acceptor, the chromophores polarization efficiency is greatly improved [42]. Hence have extended the dicyanovinyl moiety as a dicyanoisophorone which could also serve as a π-linker between D and A[43]. Generally phenyl rings are avoided as a linker since they reduce NLO efficiency on the cost of stability[44]. Configurationally locked polyene (CLP) systems are good alternative since configurationally locked π-conjugation results into reduced *cis*-trans isomerisation leads to increased steric protection to improve the stability of chromophores the other way [45]. The CLP system can prevent the dipole −dipole interaction between chromophores. Considering all these decisive factors and functional role of each moiety we have designed three multichromophoric D- π-A dyes viz.**1**, **2** and **3**.

Their linear and nonlinear properties are extensively investigated by spectroscopic, Z-Scan and theoretical methods. Polarity of medium plays crucial role towards the NLO response of highly polarizable chromophores so we have did spectroscopic NLO investigation of these chromophores in solvents of different polarity ranging from non polar to polar [46].

Further the solvent dependence of the hyperpolarizability is due to the solvent induced changes in the excitation energy to the CT state, the transition dipole moment, and the dipole moment difference between ground and excited state which is explained by the two-state model[47,48]. Spectroscopic results are compared with the computational values. Overall designing strategy of these NLOphores resulted into significant NLO response evident from their dipole moment, polarizability, and hyperpolarizability values. Thermal stability study of chromophores was done by thermogravimetric analysis (TGA). All chromophores show the decomposition temperature above 320°C, which justifies the design strategy.

2. Methods

2.1. Computational details

The NLO properties take into account the charge transfer transitions; hence an appropriate computational method should be able to predict both optical transitions and the hyperpolarizability with maximum accuracy. Density functional theory (DFT) method is the choice for understanding charge transfer characteristics of many large conjugated organic NLOphores [40]. In our case for three dyes D-π-A systems are expected to show significant charge transfer character and the lack of exact exchange in typical DFT functionals often results into underestimation of charge-transfer energies [49]. The embodiment of exact functional in computational strategy to calculate the molecular hyperpolarizability with precision can be the solution. This can be addressed either by the choice of hybrid functional which uses a fixed amount of exchange at all interelectronic 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 interelectronic distances [50–52]. For reliable estimation of molecular hyperpolarizability, to eliminate the problem of delocalization error it is recommended that the use of hybrid GGA functionals in combination with a percentage of the local exchange replaced by the exact HF[53]. In that context we incorporated the range separated CAM-B3LYP hybrid functional which uses 19% (short range) to 65% (long range) Hartree-Fock exchange which estimates the NLO values more appropriately as compared to B3LYP and BHandHLYP (uses fix 50% HF exchange) functionals [54]. Since solute-solvent interactions play crucial role in the determination of molecular electronic properties, the direct and indirect solvent effect must be included in the treatment when computing the hyperpolarizabilities of the NLOphores[55]. Polarization Continuum Model (PCM) was employed to account for the bulk solvent effect in calculation of electronic as well as structural properties[54,56]. Seven solvents of varying polarity were used and mentioned in discussion section.

All the DFT and TDDFT computations were performed using Gaussian 09 program [57] and the results were visualized with Gauss View 5.0 [58]. The ground-state geometries of the styryl dyes were optimized in gas and different solvents using DFT applying the B3LYP functional and the 6-31G(d) basis set for all the atoms [59–61]. The vibrational frequencies of the optimized structures were calculated using the same method for verification whether the optimized structures correspond to local minima on the potential energy surface. All the computations in solvents were carried out using the Polarizable Continuum Model (PCM)[62].

2.2. Materials and experimental 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 F$_{254}$ 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. Emission quantum yields were obtained by using Rhodamine-B ($\phi = 0.97$ in ethanol) as reference.

The TGA was determined by Perkin Elmer STA 6000 instrument