

## Non-linear Optical Response of Triphenylamine Dyes with D-A- $\pi$ -A Structure

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In this study, we have designed new triphenylamine dyes with D-A- $\pi$ -A structure and calculated their electro-optical and non-linear properties. Computational techniques were used to study the effect of additional acceptor in  $\pi$ -conjugated systems on absorption spectra and non-linear properties. All the dyes show absorbance in visible region. During theoretical examination polarizability ( $\alpha$ ), hyperpolarizability ( $\beta$ ) and electronic transitions were calculated. Results indicated that the selection of appropriate lengths of conjugated bridges in dye is very important to design high efficiency dyes. This theoretical frame work would be useful to design other organic dyes.

**Keywords:** Organic dyes, Polarizability, Hyperpolarizability, DFT.

### INTRODUCTION

In previous years, scientific community use organic compounds extensively for non-optical applications due to their easy synthesis and fabrication. Versatile structural feathers of organic compounds are very helpful to modify the chemical structures and properties to obtain desired non-linear optical (NLO) response [1]. Organic compounds show good nonlinear optical properties due to delocalized electrons. The non-linear optical (NLO) properties of materials are determined by the non-linear optical properties of the basic molecules. This criterion provides benefit to model the organic compounds with high non-linear optical properties [2-6]. To model and design high response non-linear optical materials, suitable donor- $\pi$ -spacer-acceptor (D- $\pi$ -A) systems are needed whose properties can be changed by structural modifications. In this fashion, substitution plays a vital rule in the modification of the conjugation and hereafter the non-linear optical activity [7-11].

The structure-property relationship through experimental as well as theoretical investigations provides appropriate information for the designing of novel non-linear optical materials. This type of studies help to find effect of the strengths of donor and acceptor groups and nature as well as the extent of the  $\pi$ -conjugation in nonlinear optical response function such as polarizability and hyperpolarizability.

According to the two-level model, suitable combination of the donor-acceptor groups provides high non-linear optical

response [12,13]. Further enhancement can be obtained by the selection of optimal length of conjugation [13,14].

Many efforts devoted for the designing of metal free organic dyes. In D- $\pi$ -A format both electron-donating (D) and electron-accepting (A) groups linked by a  $\pi$ -conjugated bridge exhibiting broad and intense absorption spectra, have been proposed as being one of the most promising organic dye sensitizers [15-19]. It has been reported that incorporation of additional acceptor facilitates electron transfer from the light absorbing donor side to the anchoring acceptor side and have a diverse effect on the photovoltaic performance in the D-A- $\pi$ -A system [20-22].

In the present study, we designed efficient dye sensitizers using triphenylamine as an electron donor (D), a cyanoacrylic acid moiety as an electron acceptor (A) and different  $\pi$ -spacers. Quantum chemical calculations were performed to calculate the non-linear optical properties and absorption spectra of dyes. It is hoped that this work would facilitate the future experimental studies to design new efficient organic dyes. This study will also provide a spring board to experimentalists for the synthesis of more efficient non-linear optical compounds.

### COMPUTATIONAL METHODS

Gaussian 09 program package was used for all the calculations [23] and structures of dyes were optimized in gas phase using B3LYP functional [23] and 6-31+G\* basis set [23]. A tight SCF convergence criteria ( $10^{-8}$  a.u.) and integration grid of  $10^{-8}$  were used for all calculations. Frequency calculations

have been performed on the optimized geometry to verify the nature of the computed geometries. The lack of imaginary values in the wave numbers calculations indicated the successful geometry optimization.

Conventional exchange-correlation functionals are not good for the simulation of absorption spectra especially for compounds with significant charge-transfer (CT) character [24,25]. Therefore, selection of suitable functional is very important to describe the absorption spectroscopy of organic dyes with D- $\pi$ -A structure.

For a reasonable computational effort, state of the art DFT/TDDFT computational methodologies provide reasonable results and reproduce well the optical properties of various organic dyes [26-29]. We first examined the effect of the functionals and basis set on  $\lambda_{\max}$  of reference dye. CAM-B3LYP/6-31+G\* is best methodology that produced result comparable to experimental value. This methodology is used to simulate the UV/visible spectra of designed dyes.

Coulomb-attenuating method CAM-B3LYP functional, which is long-range corrected form of B3LYP was used to calculate absorption spectra of designed dyes [30]. Success of this functional for determination of transition energies for a series of organic dyes is already proven [30].

The absorption spectra of the dyes were simulated by TD-DFT. Solvent effect (acetone) was undertaken using conductor-like polarizable continuum model (CPCM) [31].

Average polarizability ( $\alpha$ ) is determined using following formula [32]:

$$\alpha = 1/3 (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (1)$$

Ten components ( $\beta_{xxx}$ ,  $\beta_{xxy}$ ,  $\beta_{xyy}$ ,  $\beta_{yyy}$ ,  $\beta_{xxz}$ ,  $\beta_{xyz}$ ,  $\beta_{yyz}$ ,  $\beta_{xzz}$ ,  $\beta_{yzz}$  and  $\beta_{zzz}$ ) present in Gaussian 09W output file. First hyperpolarizability ( $\beta_{tot}$ ) is calculated using following formula [32]:

$$\beta_{tot} = \left[ (\beta_{xxx} + \beta_{xxy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{xyy} + \beta_{yyz})^2 + (\beta_{zzz} + \beta_{xzz} + \beta_{yzz})^2 \right]^{1/2} \quad (2)$$

## RESULTS AND DISCUSSION

In this study, we have presented the results of theoretical designing of efficient sensitizers for dye sensitized solar cells. Designed dyes consist of triphenylamine as donor, cyanoacrylic acid as electron acceptor, different acceptor and  $\pi$ -spacer in middle. Structures of dyes are given in Fig. 1. DFT and TDDFT calculations were performed to shed light on how two donor moieties influence the non-linear optical properties. Key parameters *e.g.*, (i) polarizability ( $\alpha$ ), (ii) hyperpolarizability ( $\beta$ ), (iii) absorption wave length and (iv) light harvesting efficiency (LHE) were calculated.

**Non-linear optical properties:** Non-linear optical materials have many technical applications like laser science, optoelectronics and optical signal processing. Understanding of nonlinear optical properties is very important in the designing of materials for signal processing, communication technology, optical memory devices and optical switches. The strength of optical response depends upon the electrical properties of the whole material, which for molecules depends on the polarizability ( $\alpha$ , linear response) and hyperpolarizabilities ( $\beta$ ,  $\gamma$ , *etc.* nonlinear responses). Therefore, these properties should be measured in order to assess the non-linear optical potential of molecules.

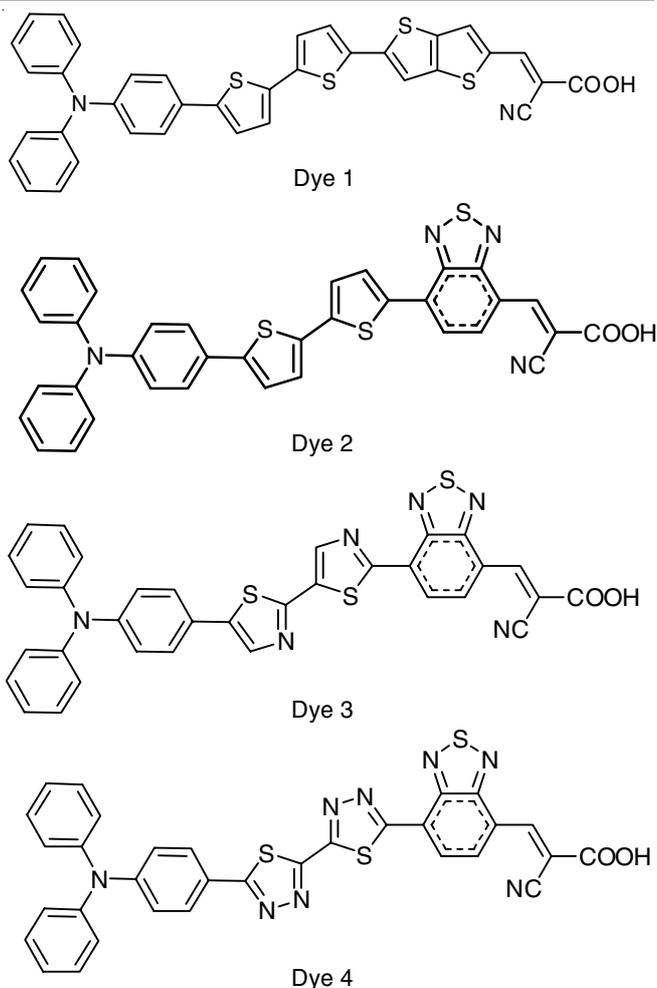


Fig. 1. Structures of studied dyes

Values of average polarizability and major contributing tensors of four dyes are given in Table-1. Order of average polarizability of four dyes was: Dye 2 > Dye 1 > Dye 3 > Dye 4.

TABLE-1  
DIPOLE POLARIZABILITIES AND  
MAJOR CONTRIBUTING TENSORS (a.u.)

| Dye | $\alpha_{xx}$ | $\alpha_{yy}$ | $\alpha_{zz}$ | $\alpha$ |
|-----|---------------|---------------|---------------|----------|
| 1   | 1580.22       | 478.19        | 208.38        | 755.60   |
| 2   | 1650.48       | 493.63        | 202.90        | 782.34   |
| 3   | 1504.50       | 486.03        | 197.56        | 729.36   |
| 4   | 1288.42       | 458.35        | 214.45        | 653.74   |

Polarizability is dominantly determined by the x or y-direction transition. For example, the expression of dipole polarizability (x direction) is described in the following equation:

$$\alpha_{xx} \propto \frac{(M_x^{gm})^2}{E_{gm}} \quad (3)$$

where  $M_x^{gm}$  is transition moment between the ground and  $m^{\text{th}}$  excited state and  $E_{gm}$  is transition energy. From eqn. 3, we can observe that the  $\alpha$  value is directly proportional to the square of the transition moment and is inversely proportional to the transition energy. Generally dye with a high value of  $M_x^{gm}$  will have a larger  $\alpha$  value.

Second order polarizability ( $\beta$ ) is the measure of the non-linear optical response of materials.  $\beta$  is associated with the intramolecular charge transfer (ICT), resulting from the movement of electrons from electron donor to electron acceptor through  $\pi$ -conjugated system. The interaction of electronic density with an external electric field changes the dipole moment and second order non-linear optical activity [33].

Hyperpolarizabilities were calculated by using CAM-B3LYP functional. The computed  $\beta_{\text{tot}}$  values and major contributing tensor of Dyes 1-4 are given in Table-2. Order  $\beta_{\text{tot}}$  of four dyes is: Dye 2 > Dye 3 > Dye 4 > Dye 1.

TABLE-2  
SECOND-ORDER POLARIZABILITIES ( $\beta_{\text{tot}}$ ) AND  
MAJOR CONTRIBUTING TENSORS (a.u.)

| Dye | $\beta_{\text{xxx}}$ | $\beta_{\text{xyy}}$ | $\beta_{\text{yyx}}$ | $\beta_{\text{xxz}}$ | $\beta_{\text{tot}}$ |
|-----|----------------------|----------------------|----------------------|----------------------|----------------------|
| 1   | 141157.67            | 657.32               | 1384.42              | 502.54               | 142621.78            |
| 2   | 224725.11            | 42.98                | -1193.48             | 400.77               | 223428.05            |
| 3   | -223005.11           | 404.41               | 1157.72              | 274.71               | 221737.97            |
| 4   | 172816.03            | -123.42              | 1033.08              | 151.43               | 173967.44            |

**UV-visible spectra of dyes:** TD-DFT calculations were performed at CAM-B3LYP/6-31+G\* level using C-PCM in acetone to gain insight into the excited states giving rise to the absorption spectra. During TD-DFT calculations the 10 lowest singlet-singlet transitions were studied.

The computed maximum absorption wavelengths ( $\lambda_{\text{max}}$ ), oscillator strengths ( $f$ ) and nature of the transitions are summarized in Table-3. All the dyes show absorbance in visible region (Fig. 2).

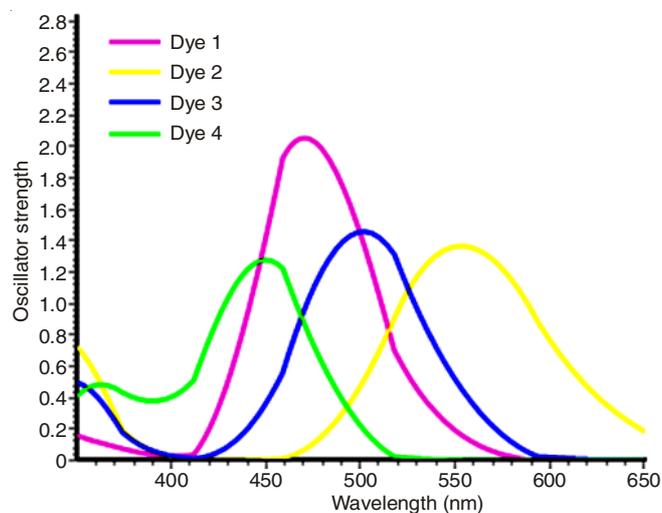


Fig. 2. Simulated absorption spectra of dyes

Light harvesting efficiency (LHE) is another factor relates to efficiency of the dyes. The light harvesting efficiency is the fraction of photons absorbed by the dye at a particular wave-

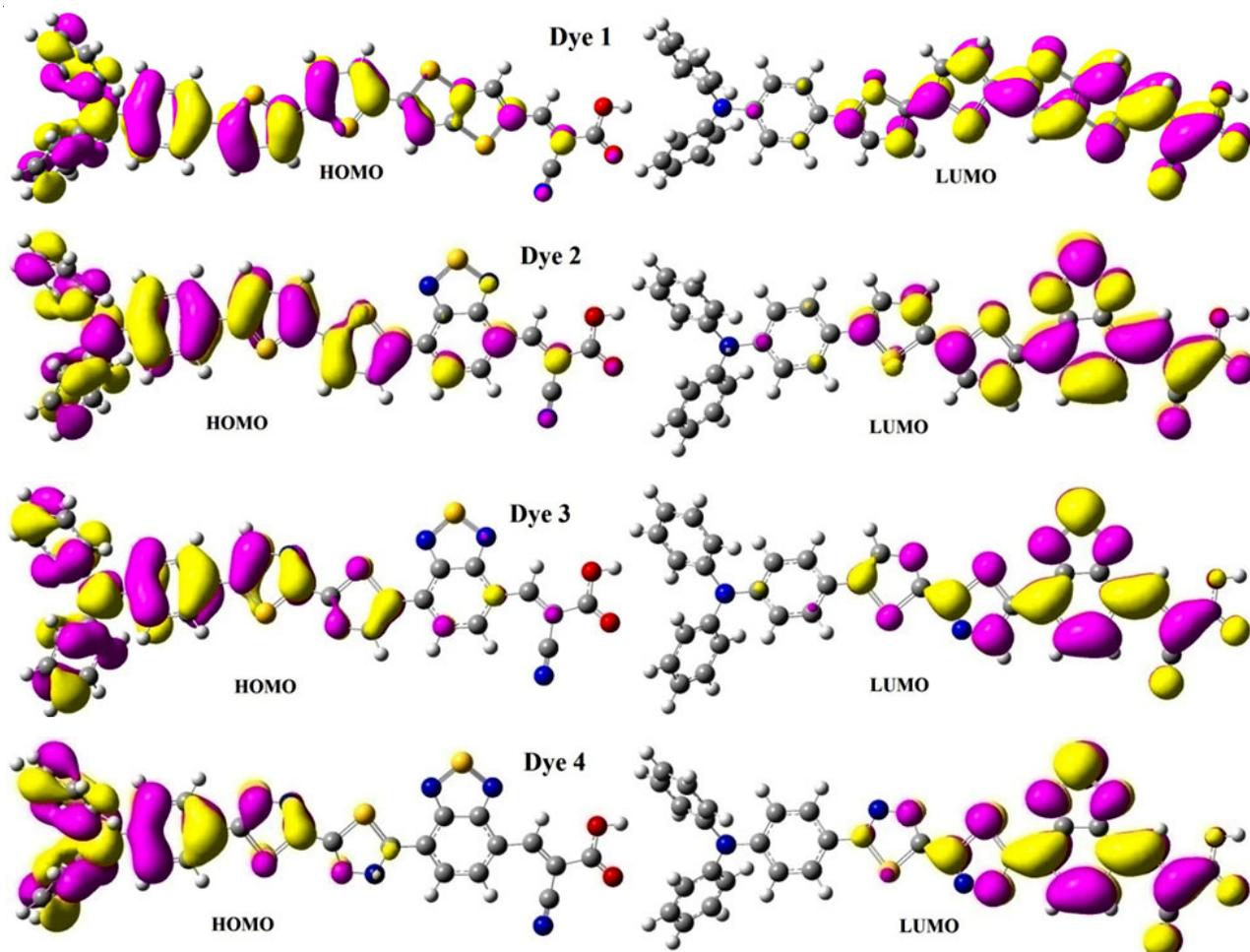


Fig. 3. HOMO and LUMO of studied dyes

TABLE-3  
COMPUTED MAXIMUM ABSORPTION WAVELENGTHS ( $\lambda_{\max}$ , nm), TRANSITION ENERGY ( $E_{\text{gm}}$ , eV), OSCILLATOR STRENGTHS (f), LIGHT HARVESTING EFFICIENCY (LHE), TRANSITION MOMENT ( $M_x^{\text{gm}}$ , a.u.) AND TRANSITION NATURES OF DYES

| Dye | $\lambda_{\max}$ | $E_{\text{gm}}$ | f     | LHE   | $M_x^{\text{gm}}$ | Main configurations* |
|-----|------------------|-----------------|-------|-------|-------------------|----------------------|
| 1   | 474.17           | 2.710           | 2.362 | 0.996 | 2.90              | H→L (51 %)           |
| 2   | 552.65           | 2.243           | 1.631 | 0.977 | 3.89              | H→L (60 %)           |
| 3   | 496.72           | 2.496           | 1.693 | 0.980 | 2.34              | H→L (46 %)           |
| 4   | 445.21           | 2.584           | 1.442 | 0.964 | 2.70              | H→L (54 %)           |

\*H, H-1 and L stand for HOMO, HOMO-1 and LUMO, respectively.

length. The broader the absorbing ranges to sunlight of the dye-loaded electrode, the wider the light harvesting efficiency spectrum. Values of light harvesting efficiency of the dyes should be as high as possible to maximize the photocurrent response. The light harvesting efficiency can be expressed as [34]:

$$\text{Light harvesting efficiency} = 1 - 10^{-f} \quad (4)$$

where f is oscillator strength. In spectroscopy, oscillator strength is a dimensionless quantity that expresses the probability of absorption or emission of electromagnetic radiation in transitions between energy of an atom or molecule.

Values of light harvesting efficiency are given in Table-3. The HOMOs and LUMOs are shown in Fig. 3. For all dyes HOMO are on donor while LUMO are on acceptor. This situation is indicating favourable charge transfer from donor to acceptor.

To know the origin of second-order non-linear optical properties of the studied compounds, a good explanation of a structure-property relationship is required. From the sum-over-states (SOS) approach, a two-state model associated between  $\beta$  and a low-lying charge-transfer transition has been documented [35]. In the static case, the following model expression is employed to estimate  $\beta_{\text{CT}}$ :

$$\beta_{\text{CT}} \propto \frac{\Delta\mu_{\text{gm}} f_{\text{gm}}}{E_{\text{gm}}^3} \quad (5)$$

where  $\Delta\mu_{\text{gm}}$  is the change of dipole moment between the ground and  $m^{\text{th}}$  excited state,  $f_{\text{gm}}$  is the oscillator strength of the transition from the ground state (g) to the  $m^{\text{th}}$  excited state (m) and  $E_{\text{gm}}$  is transition energy.

Therefore, good non-linear optical material must possess a low-energy charge-transfer excited state with large oscillator strength. The most favourable combination of these factors can provide a larger  $\beta$  value. All the studied systems possess the same general framework and thus there is not much difference in the value. That's why is considered as constant. Therefore, the first hyperpolarizabilities for our studied systems are mainly proportional to  $f_{\text{gm}}$  and inversely proportional to the cube of  $E_{\text{gm}}$ . The low transition energy results in the large  $\beta$ . The order of transition energy was opposite to the order of hyperpolarizability. Order of transition energy is: Dye 1 > Dye 4 > Dye 3 > Dye 2, whereas the non-linear optical response found in following order: Dye 2 > Dye 3 > Dye 4 > Dye 1.

## Conclusion

In this study, theoretical designing of triphenylamine dyes containing additional acceptor group with  $\pi$ -spacer was reported. All the dyes show absorbance in visible region. Polari-

zability and hyperpolarizability of all the dyes were higher. It is hoped that this work will be helpful for the designing of the organic dyes with target properties to improve the performance in opto-electronics.

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