

Design, Synthesis and Study of Non-Linear Optical Properties of Phenyl Bridged Diphenylamine-*s*-triazine Based Donor-Acceptor Triads Containing Different π -Acceptor Groups

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Novel donor-acceptor triads of starburst D-A-A type incorporating electron deficient triazine moiety as a non-conjugating π -spacer/acceptor with two acceptor/anchoring arms comprising of cyanoacetic acid (DTP-CYA), rhodanine-3-acetic acid (DTP-RHA), barbituric acid (DTP-BA) or thiobarbituric acid (DTP-TBA) linked to triazine core *via* a phenyl bridge have been synthesized. Diphenylamine is used as the donor moiety and the role of the π -spacer on the absorption spectra and other electronic properties were studied. All the compounds were tested for their non-linear optical properties and determined the non-linear absorption coefficient (β) and non-linear refractive index (n_2) in DMF solutions. Improved non-linear optical properties were obtained when compared to the compounds with triazine moiety as a non-conjugating π -spacer/acceptor with rhodanine-3-acetic acid (DTOP-RHA), barbituric acid (DTOP-BA) or thiobarbituric acid (DTOP-TBA) as anchoring/acceptor groups. DTOP series compounds are in the geometry of the molecule where the phenyl π -bridge and the triazine unit are coplanar with the arylidene acceptor unit. The enhanced performance may be due to the structural variants, which expected to improve through bond coupling between the donor and the terminal acceptor parts of the molecules and all compounds show asymmetry in the electron density due to the basic donor-acceptor nature of the structure.

Keywords: Donor acceptor systems, Triazine, Non-linear optics, Optical limiting.

INTRODUCTION

In recent years, dye-sensitized solar cells (DSSCs) have captivated much interest due to their potential advantages like cost effective, flexible and straight forward device fabrication [1-7]. Dye sensitized solar cells based on coordination complexes with heavy metal ions are considered as the most competent device, but cannot be used for large scale applications due to the limited resources and high cost [8-11]. The challenge is open to develop new systems using cost effective materials and promising photoconversion efficiencies. Use of organic D- π -A dyes are one such option with promising results. Most widely studied D- π -A systems include triphenyl amine as the donor and cyanoacrylic acid moiety as acceptor [12-15]. Different π -spacers with planar configuration effectively improve the electron-transportation from donors to acceptors and results in significant change in overall photovoltaic performances [16-

18]. Electron deficient heterocyclic structural units such as thiazole, triazine, cyanovinyl, cyano- and fluoro-substituted phenyl groups, *etc.* have been used as the π bridges in the D- π -A-A systems. They exhibit several advantages over the straight D- π -A systems, with significantly changes the molecular energy levels, absorption characteristics and finally the overall photovoltaic performance [19,20]. 1,3,5-Triazine have been used as a building block for the synthesis of D- π -A-A systems as dyes in DSSCs. Recently, triphenylamine or porphyrins have been used in a similar solar cell design with cyanoacrylic acid as the acceptor as well as the anchoring groups. Herein, a series of dyes where diphenylamine as the donor unit and rhodanine acetic acid, barbituric acid/thiobarbituric acid linked to 1,3,5-triazine as the π -acceptor unit is reported.

In simple valence bond terms when there are two substituents in benzene ring which are *meta* to each other the possibility of conjugation of π -orbitals of one with the other

is not possible due to the absence of resonance form of the benzene ring supporting such conjugation. This gives us the possibility of designing dyes having intramolecular charge transfer states in which donor and acceptor moieties are separated in space and thus increase the length of the charge separation in comparison to directly coupled systems. But such charge separation is useful only when the lifetime of such intramolecular charge separated state is long enough to permit subsequent electron transfer cascade when they are used as dyes and light harvesting systems in photo-voltaic or photo-electrochemical systems. The lifetime of the intramolecular charge transfer (ICT) state depends on the free energy of the back electron transfer regenerating the ground state [21,22].

The molecules of D- π -A-A type triads with 1,3,5-triazine as the first acceptor and as the core bridging π unit is reported [23], these compounds feature an *o*-phenyl flexible linkage of the acceptor/anchoring group on to the diphenylamine-triazine conjugate. This flexibility may lead to a less rigid geometry for the molecule where, the small average donor-acceptor distance of separation may lead to increase through space interaction between the donor and the acceptor moieties. The theoretically calculated optimal geometry for these compounds reveal a smaller distance of separation in these series of compounds. The less rigid structure makes increased non-radiative deactivation of the excited state thus reducing the excited state lifetime and reduced probability of electron transfer between the semiconductor and the dye. The relative orientation and disposition of HOMO and LUMO orbitals also play significant role in the rate of charge separation as well as the rate of back electron transfer within the D-A-A triad under study [24]. This orientation dependence on electron transfer has been studied by Marcus *et al.* [25-29]. Nature adopts proper orientation as a means to effectively reduce the importance of back electron transfer in natural photosynthetic systems [30-32]. Similar results have been reported for synthetic systems, where carefully designed systems with reduced back electron transfer has been reported by Chang *et al.* [33-36].

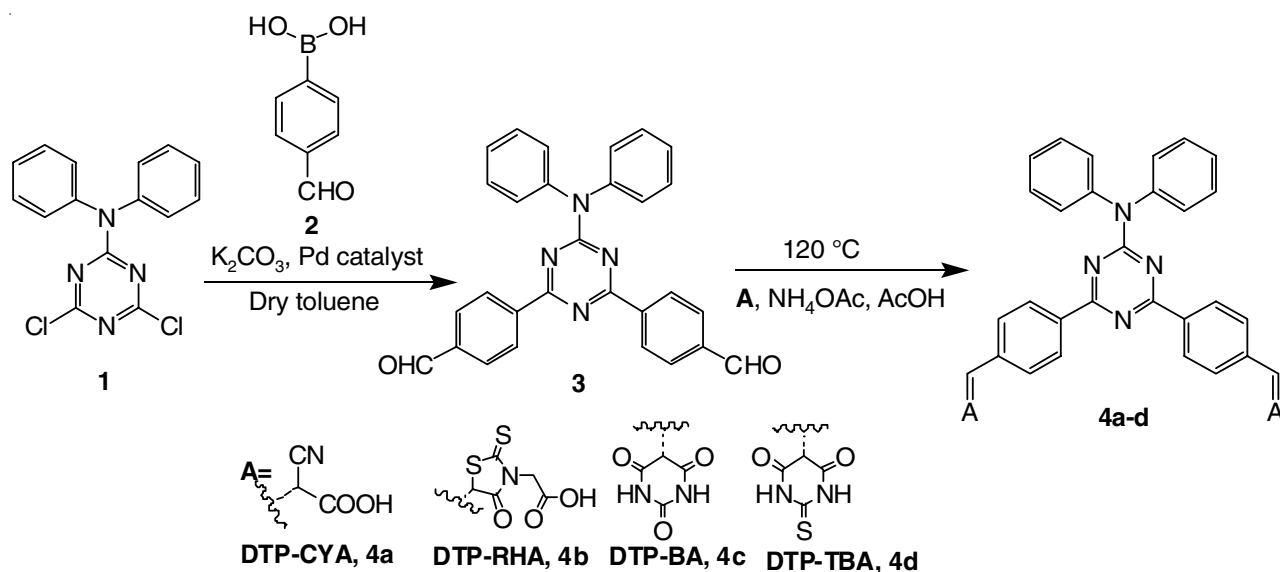
In order to bring better control on the orientation of donor and acceptor groups, a series of new molecules are designed where the bridging *o*-phenyl group was replaced by a phenyl group *via* direct coupling of phenyl and triazine units. The present design is expected to improve through bond coupling between the donor and the terminal acceptor parts of the molecules resulting into a low energy intramolecular charge transfer absorption with high molar extinction coefficient.

EXPERIMENTAL

Diphenylamine-*s*-triazine DPA-T (**1**) was synthesized according to a reported procedure [37].

Synthesis of DPA-T-PH (3): A solution 4-formylboronic acid (**2**, 200 mmol), *tetrakis*(triphenylphosphene)palladium(0) (20 mmol) and K₂CO₃ (10 mmol) and compound **1** (100 mmol) in dichloromethane (50 mL) were stirred under N₂ atmosphere at room temperature for 24 h. The reaction mixture was treated with water (50 mL) and the organic layer was separated and washed with distilled water. The residue obtained was purified by column chromatography on silica gel. Elution with a mixture of (1:20) hexane and dichloromethane gave pale yellow powder of **3** in 60% yield; m.p.: 210 °C (decomp.). FT-IR (KBr, ν_{\max} , cm⁻¹): 3348, 1703, 1584, 1370, 1199, 1108. ¹H NMR (400 MHz, DMSO, δ ppm): 10.10 (m, 2H), 8.48-8.46 (m, 4H), 8.06-8.04 (m, 4H), 7.53-7.48 (m, 8H), 7.40-7.36 (m, 2H). ¹³C NMR (100 MHz, DMSO, δ ppm): 192.92, 169.68, 142.85, 140.87, 138.67, 134.46, 129.70, 129.17, 128.82, 128.33, 127.78, 126.76. ESI m/z: 455.49 (M-1). Anal. calcd. (found) % for C₂₉H₂₀N₄O₂: C, 76.30 (76.10); H, 4.42 (4.22); N, 12.27 (12.17).

General synthesis of DTP-CYA (4a), DTP-RHA (4b), DTP-BA (4c) and DTP-TBA (4d): A mixture of the dialdehyde (**3**, 1 mmol) and cyanoacetic acid/rhodanine-3-acetic acid/barbituric acid/thiobarbituric acid (22 mmol) and ammonium acetate (19 mmol) were dissolved in 0.5 M acetic acid heated at 120 °C for 12 h. After cooling, the precipitated product was washed with chloroform and methanol to remove the unreacted reagents and unwanted compounds (**Scheme-I**).



Scheme-I: Scheme of synthesis of compounds

DTP-CYA (4a): Yellow solid, yield 58%, m.p.: 235 °C (decomp.); FT-IR (KBr, ν_{\max} , cm^{-1}): 3381, 1522, 1370, 1185. ^1H NMR (400 MHz, DMSO, δ ppm): 8.47-8.45 (m, 2H), 8.37-8.32 (m, 2H), 8.17-7.55 (m, 3H), 7.43-7.41 (m, 1H), 3.08-3.06 (m, 2H), ^{13}C NMR (100 MHz, DMSO, δ ppm): 179.43, 148.67, 142.99, 129.08, 129.04, 128.63, 127.82, 118.42, 73.51, 37.78, 22.48. Anal. calcd. (found) % for $\text{C}_{35}\text{H}_{22}\text{N}_6\text{O}_4$: C, 71.18 (71.00); H, 3.75 (3.65); N, 14.23 (14.13).

DTP-RHA (4b): Yellow solid, yield 58%, m.p.: 245 °C; FT-IR (KBr, ν_{\max} , cm^{-1}): 3320, 2355, 1592, 1322, 1188, 1105. ^1H NMR (400 MHz, DMSO, δ ppm): 8.40-8.38 (m, 2H), 7.98-7.88 (m, 2H), 7.79-7.77 (m, 4H), 7.84-7.48 (m, 8H), 7.40-7.36 (m, 2H), 4.62 (m, 6H). ^{13}C NMR (100 MHz, DMSO, δ ppm): 169.19, 166.46, 129.11, 128.9, 127.74, 124.17. Anal. calcd. (found) % for $\text{C}_{39}\text{H}_{26}\text{N}_6\text{O}_6\text{S}_4$: C, 58.34 (58.30); H, 3.26 (3.20); N, 10.47 (10.40); S, 15.97 (15.88).

DTP-BA (4c): Yellow solid, yield 58%; m.p.: 224 °C; FT-IR (KBr, ν_{\max} , cm^{-1}): 3185, 2350, 1671, 1520, 1390, 1209, 1209. ^1H NMR (400 MHz, DMSO, δ ppm): 11.42 (s, 1H), 11.26 (s, 1H), 8.32-8.30 (m, 3H), 8.10-8.08 (m, 2H), 7.51-7.36 (m, 5H). ^{13}C NMR (100 MHz, DMSO, δ ppm): 163.07, 153.15, 150.15, 136.55, 132.60, 129.10, 127.78, 127.48. Anal. calcd. (found) % for $\text{C}_{37}\text{H}_{24}\text{N}_8\text{O}_6$: C, 65.68 (65.58); H, 3.58 (3.50); N, 16.56 (16.50).

DTP-TBA (4d): Yellow solid; yield 58%; m.p.: 250 °C (decomp.) FT-IR (KBr, ν_{\max} , cm^{-1}): 3320, 2360, 1623, 1572, 1514, 1396, 1198, 1115. ^1H NMR (400 MHz, DMSO, δ ppm): 12.49 (s, 1H), 12.36 (s, 1H), 8.35-8.23 (m, 3H), 8.18-8.08 (m, 2H), 7.54-7.48 (m, 5H). Anal. calcd. (found) % for $\text{C}_{37}\text{H}_{24}\text{N}_8\text{O}_4\text{S}_2$: C, 62.70 (62.60); H, 3.41 (3.35); N, 15.81 (15.79); S, 9.05 (9.00).

RESULTS AND DISCUSSION

Photophysical properties: All the synthesized compounds have poor solubility in methanol, chloroform and acetonitrile and good solubility in DMF and DMSO. The absorption spectra of DTP-CYA, DTP-RHA, DTP-BA and DTP-TBA were recorded in DMF and show characteristic intramolecular charge transfer (ICT) absorption band at 322, 388, 345 and 380 nm, respectively. The onset of absorption for these compounds extends up to 450 nm except for DTP-CYA which ends at 400 nm (Fig. 1). The diffuse reflectance spectra of all the compounds in the powder form showed broad absorption maximum peaking at 400 nm and the onset of absorption extending to 500 nm for DTP-CYA, 600 nm for DTP-RHA and DTP-BA. In the case of DTP-TBA, this absorption extends upto 650 nm (Fig. 2). This red shift could be due to the stacking arrangement that facilitate intramolecular charge transfer [38]. Nanocrystalline TiO_2 thin films were made from a paste of TiO_2 and annealed at 500 °C for 0.5 h in a muffle furnace. The dye coated TiO_2 thin films were prepared by immersing these thin films in respective dye solutions in DMF for 24 h followed by washing successively with fresh DMF, water and ethanol. The air dried dye coated thin films showed light yellow to light orange colour and diffuse reflectance spectra obtained are presented in Fig. 3. DTP-RHA showed a red shifted and broad absorption spectrum and DTP-BA and DTP-TBA showed

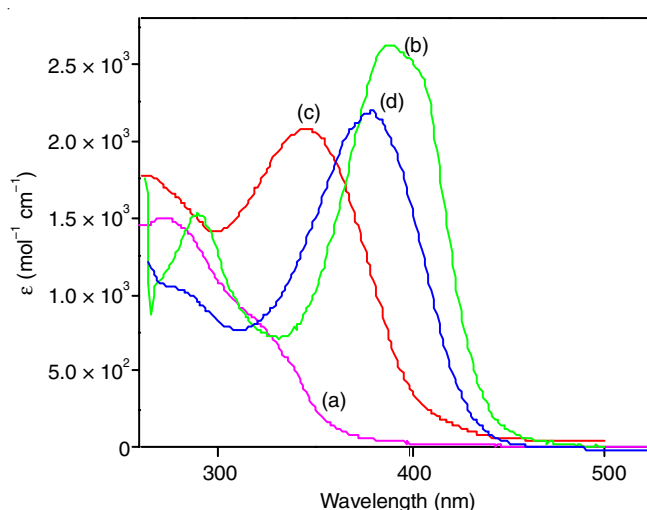


Fig. 1. Absorption spectra of DTP-CYA (a) DTP-RHA (b) DTP-BA (c) and DTP-TBA (d) in DMF

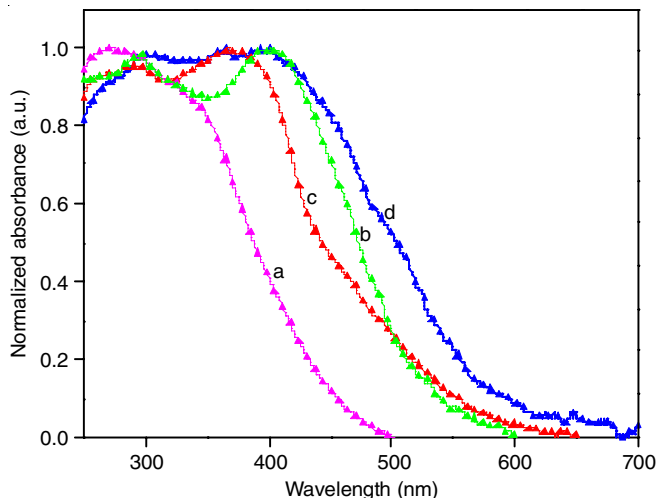


Fig. 2. Diffuse reflectance spectra of DTP-CYA (a) DTP-RHA (b) DTP-BA (c) and DTP-TBA (d) in powder form

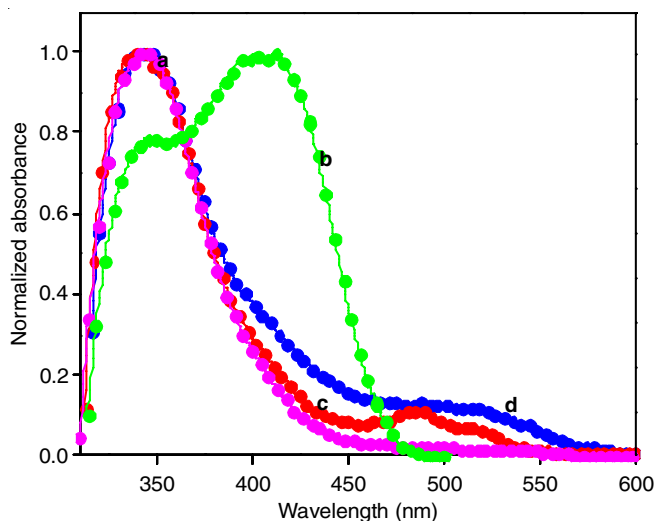


Fig. 3. Diffuse reflectance spectra of DTP-CYA (a) DTP-RHA (b) DTP-BA (c) and DTP-TBA (d) adsorbed on TiO_2 thin film

an additional weak band at 415 nm and 520 nm, respectively. The singlet excited state energy ($E_{0,0}$) of these compounds was calculated from onset absorption using eqn. 1 [39]:

$$\text{HOMO} = \frac{1242}{\lambda_{\text{onset}}} \quad (1)$$

The absorption spectral properties of all the compounds are summarized in Table-1. In comparison to *o*-phenyl bridged compounds, DTP-RHA and DTP-TBA showed a red shift of 26 nm and 5 nm, respectively. This shows that direct coupling of phenyl bridge between the triazine and acceptor moieties led enhanced electronic coupling between the donor and acceptor groups. Whereas, DTP-BA showed a blue shift of 9 nm in comparison to *o*-phenyl bridged dye (vide supra).

Compound	$\lambda_{\text{max}}^{\text{(Abs)}} \text{ (nm)}$	$\lambda_{\text{onset}} \text{ (nm)}$	$\epsilon_{\text{max}} \text{ (mol}^{-1} \text{ cm}^{-1})$	$E_{0,0} \text{ (eV)}$
DTP-CYA	276, 322 (sh)	372	2.8×10^4 1.5×10^4	3.45
DTP-RHA	388	465	1.6×10^4	2.85
DTP-BA	345	439	6.9×10^3	3.07
DTP-TBA	380	456	2.3×10^4	2.87

Electrochemical properties: The oxidation potentials of these compounds were determined from the square wave voltammograms (Fig. 4). They exhibit characteristic oxidation potentials at 1.25, 1.26, 1.13 and 1.23 V, respectively vs. NHE. The results are summarized in Table-2. These values lie at a higher potential than the redox potential of electrolytes I^-/I_3^- and $\text{Br}^-/\text{Br}_3^-$, the common redox couples used in the construction of DSSCs. The energy gap between the redox couple and oxidation potential of the compound is significant in determining the current as well as the fill factor. For the compounds used in the present study, this energy gap is very large for I^-/I_3^- electrolyte whereas, for the electrolyte $\text{Br}^-/\text{Br}_3^-$, the gap is 0.16, 0.17, 0.04 and 0.14 V respectively, for DTP-CYA, DTP-

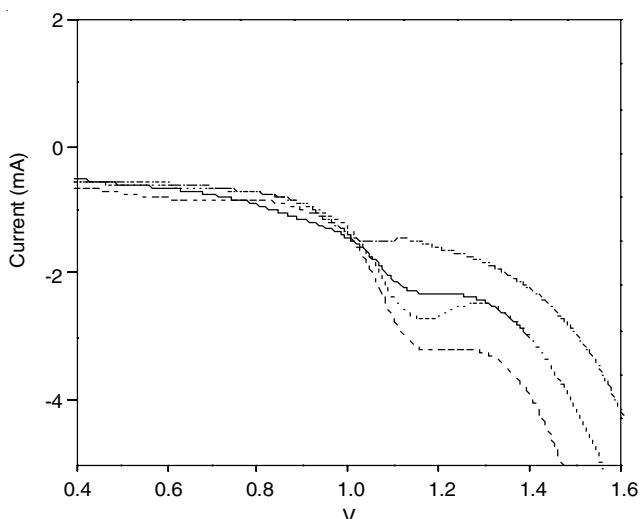


Fig. 4. Square wave voltammograms obtained for compounds DTP-CYA (····), DTP-RHA (—), DTP-BA (---) and DTP-TBA (-·-·) in DMF

TABLE-2
ELECTROCHEMICAL PROPERTIES OF DTP-CYA, DTP-RHA, DTP-BA AND DTP-TBA IN DMF

Compound	$E_{\text{onset}}^{\text{a}}$ (V) in DMF	$E_{\text{onset}}^{\text{(ox)}}$ vs. $E_{\text{FOC}}^{\text{b}}$ (V)	$E_{\text{(S+/S)}}^{\text{c}}$ vs. NHE (V)	LUMO vs. NHE (V)	$^{\text{d}}E_{\text{gap}}$ (V)
DTP-CYA	1.16	1.05	1.25	-2.2	-1.70
DTP-RHA	1.17	1.06	1.26	-1.59	-1.15
DTP-BA	1.04	0.93	1.13	-1.94	-1.44
DTP-TBA	1.14	1.03	1.23	-1.64	-1.03

^aObserved reduction potential in DMF, ^b $E_{\text{FOC}} = -0.11 \text{ V vs. Ag/AgCl}$. ^cThe ground-state oxidation potentials $E_{\text{(S+/S)}}$ (HOMO) were measured in DMF containing 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte using a glassy carbon working electrode, a Pt counter electrode and a Ag/AgCl reference electrode. ^dE gap is the energy gap between LUMO of the compound and the conduction band level of TiO_2 (-0.5 V vs. NHE).

RHA, DTP-BA and DTP-TBA. This energy gap makes the regeneration of the oxidized form of the compound thermodynamically favourable during the cell operation (Fig. 5) [40]. Too high an energy gap may also be detrimental to efficient functioning of the cell as inverted region effect can reduce the rate of regeneration of the dye [41-43]. The values of HOMO energy levels of these compounds referenced to NHE were calculated from the oxidation potentials of these compounds. The values are comparable to that observed for *o*-phenyl bridged compounds except for DTP-BA. In this case, the oxidation potential is less positive. The LUMO energy level was determined by adding the respective singlet state energies obtained from the onset of absorption spectra of respective compounds. Estimations of HOMO and LUMO energies against vacuum continuum were also been made and the calculated values are presented in Table-3.

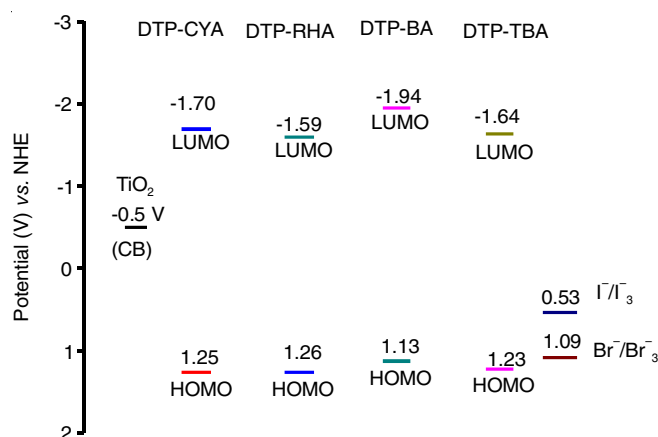


Fig. 5. Schematic energy level diagram for a DSSC based on dyes coated nanocrystalline TiO_2 film on conducting FTO

Theoretical study: The optimized geometry of the compounds as well as the frontier orbitals and their energies are computed by density functional theory (DFT) with B3LYP exchange-correlation functional [44,45] and 6-31+G(d) basis set. The stationary points are characterized by frequency calculation. To include the effects of solvation, the polarization continuum model (PCM) for DMF has been used in the calculations. All calculations were performed with the GAUSSIAN 09 quan-

TABLE-3
COMPARISON OF THEORETICAL AND EXPERIMENTAL
ORBITAL ENERGIES OF DTP-CYA, DTP-RHA,
DTP-BA AND DTP-TBA [Ref. 46,47]

Compounds	Experimental		Theoretical	
	^a HOMO (IP) (eV)	^b LUMO (EA) (eV)	HOMO (eV)	LUMO (eV)
DTP-CYA	-6.05	-2.61	-6.29	-3.30
DTP-RHA	-6.06	-3.21	-6.30	-3.56
DTP-BA	-5.93	-2.86	-6.29	-3.43
DTP-TBA	-6.03	-3.16	-6.24	-3.28

^aIonization potential: IP = -4.8 - (E_{onset} (ox) - E_{FOC}); ^bElectron affinity: EA - E_{0,0} = IP

tum chemistry package. The optimized geometry along with the frontier orbital representation and their respective energies against vacuum continuum is given in Fig. 6. Contrary to our expectation, the orbital coefficients of the HOMO for all compounds were found to be delocalized over the triazine core which is one of the acceptor units. Similar result was obtained in the case of *o*-phenyl bridged compounds. Delocalization of HOMO over the triazine has a profound effect in the lowering of HOMO energies as well as on the observed oxidation potential of all the compounds in comparison to the HOMO of diphenylamine (-5.8 eV or 1 V vs. NHE). Both electrochemical and theoretical data suggests that they are difficult to oxidize in comparison to diphenylamine. The LUMO calculated for these series of compounds show extensive delocalization over two arms of the compounds bearing acceptor groups. This extended delocalization has led to the stabilization of the respective LUMOs in the case of DTP-RHA and DTP-TBA. All the compounds show better directionality of charge transfer on the electronic excitation as the HOMO and LUMO are localized on different regions of the molecule. For DTP-RHA and DTP-TBA, the theoretically calculated energy levels are in good agreement with the experimental values obtained from electrochemical measurements.

Non-linear optical properties: All the synthesized compounds show asymmetry in the electron density due to the basic donor-acceptor nature of the structure. This is further confirmed by the DFT calculations. One important difference between the DTOP series and the present compounds is in the geometry of the molecule where the phenyl π -bridge and the triazine unit are coplanar with the arylidne acceptor unit. Moreover, the molecule is more rigid and the difference in the electron distribution between the HOMO and LUMO is not as pronounced as it is seen in the DTOP series.

Fig. 6 shows the HOMO and LUMO orbitals of these compounds. In all the compounds, the HOMO is centered on the diphenylamine and the triazine core. The LUMO is delocalized over the phenyl bridge and two acceptor moieties. These molecules were tested for their Non-linear optical behaviour by Z-scan technique using 532 nm second harmonic of an Nd-YAG laser with a pulse width of 7 ns. A ~1 mM solution in DMF was used for the experiment [48]. No appreciable optical damages were observed after the Z-scan measurements.

Experimentally, the non-linear behaviour is manifested in the observation of reverse saturable absorption (RSA), two photon absorption (TPA) and saturable absorption (SA) depending on the variation (increase or decrease) in transmission of the sample as a function of intensity of the laser. For a molecule, decreased transmittance or increase in the light absorption for a given laser light due to an enhanced light absorption property of the excited state in comparison to the ground state is the result of TPA and RSA with increasing laser intensity [49]. The DTP-RHA and DTP-BA showed RSA closer to the focus *i.e.* decreased transmittance as the excited state absorption become dominant. DTP-TBA however, showed SA behaviour, *i.e.* increased transmittance closer to the focus. This is because, the excitation wavelength 532 nm was at the edge of the ground state absorption by these molecules at lower fluences the molecules gets excited and may not have sufficient time to

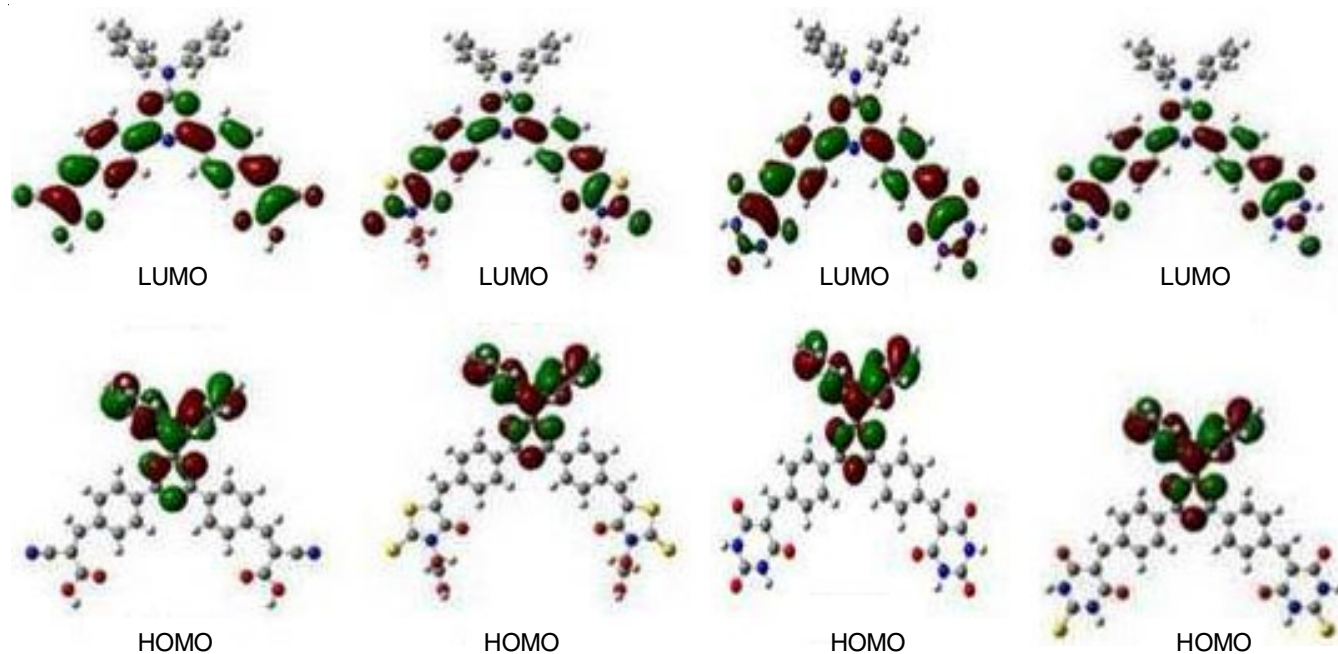


Fig. 6. Optimized geometries of the computed using DFT theory at the B3LYP/6-31G + (d) level

relax to the ground state leading to an increased transmittance. Such behaviour is common to many substances. As evident from the solid lines in Fig. 7a-c, theoretical fit to the two photon absorption theory showed very good correlation. This shows that TPA is the main mechanism involved in the non-linear absorption process for all these molecules. The non-linear absorption coefficient (β) was determined by fitting the data obtained from the open aperture measurements to eqn. 3. The results are tabulated in Table-4. The β value obtained for DTP-BA is high compared to other two compounds.

$$T_z = \frac{C}{q_0\sqrt{\pi}} \int_{-\infty}^{\infty} \ln(1 + q_0 e^{-t^2}) dt \quad (3)$$

where $q_0(z,r,t) = bI_0(t) L_{\text{eff}}$ and $L_{\text{eff}} = (1 + e^{-\alpha})/\alpha$ is the effective thickness of linear absorption coefficient α , I_0 is the irradiance at focus. The non-linear refractive index and non-linear susceptibility of NLO active materials at high laser fluences can also be measured by the Z-scan technique. Here, the transmittance is measured by varying the laser spot size at the plane of a finite aperture detector combination and is called the closed aperture method. The NLO active material will act as a thin

lens with varying focal length as it moves along the optical axis of the Z-scan set-up. The transmission data obtained in the open aperture Z-scan is sensitive to non-linear absorption only and the closed aperture scan involves both non-linear refraction and absorption effects. In order to exclude the non-linear absorption effects the closed aperture data obtained were divided by the corresponding open aperture data. Fig. 8a-c show the normalized transmission data obtained for DTP-RHA, DTP-BA and DTP-TBA respectively in the closed aperture scan. The Non-linear transmittance $T(z)$ is related to on-axis non-linear phase shift ($\Delta\phi_0$) and the ratio z/z_0 . This relation is given by eqn. 4 [50]:

$$T(z) = 1 - \frac{4x\Delta\phi_0}{(x^2 + 9)(x^2 + 1)} \quad (4)$$

Typical peak valley pattern due to non-linear refraction was observed for all the compounds and indicative of a negative NLR index due to self-defocusing (Fig. 7a-c). The data were fitted to eqn. 3, and the non-linear phase shift ($\Delta\phi_0$) is determined. The non-linear refractive index (n_2), the real ($\text{Re } \chi^3$) and the imaginary part ($\text{Im } \chi^3$) and thus the non-linear suscep-

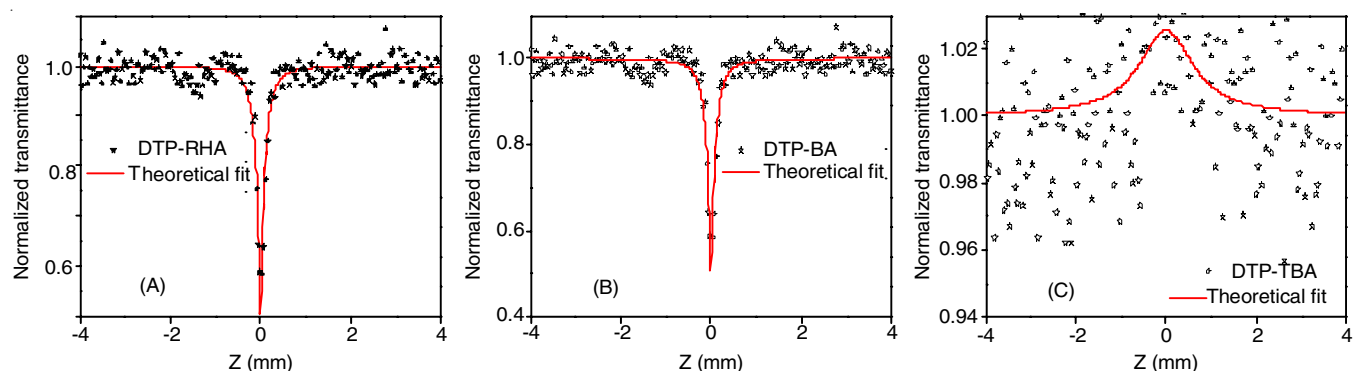


Fig. 7. Open aperture profile of the DTP-RHA (A), DTP-BA (B) and DTP-TBA (C) in DMF ($\sim 4 \times 10^{-4}$ M)

TABLE-4
NON-LINEAR OPTICAL PROPERTIES OF THE DTP-CYA, DTP-RHA, DTP-BA AND DTP-TBA

Compounds	Non-linear absorption coefficient (δ , mW^{-1})	σ_2 (GW)	Non-linear refractive index (n_2 , esu)	Imaginary part of non-linear susceptibility ($\text{Im } \chi^3$, esu)	Real part of non-linear susceptibility ($\text{Re } \chi^3$, esu)	Non-linear susceptibility (χ^3 , esu)	Optical limiting threshold (GW/cm^2)
DTP-RHA	0.8×10^{-10}	4026	-0.73×10^{-10}	0.17×10^{-11}	-1.09×10^{-11}	1.10×10^{-11}	0.6
DTP-BA	7.6×10^{-10}	45581	-2.78×10^{-10}	1.64×10^{-11}	-4.10×10^{-11}	4.35×10^{-11}	1.7
DTP-TBA	0.3×10^{-10}	2618	-0.60×10^{-10}	0.06×10^{-11}	-0.92×10^{-11}	0.92×10^{-11}	—

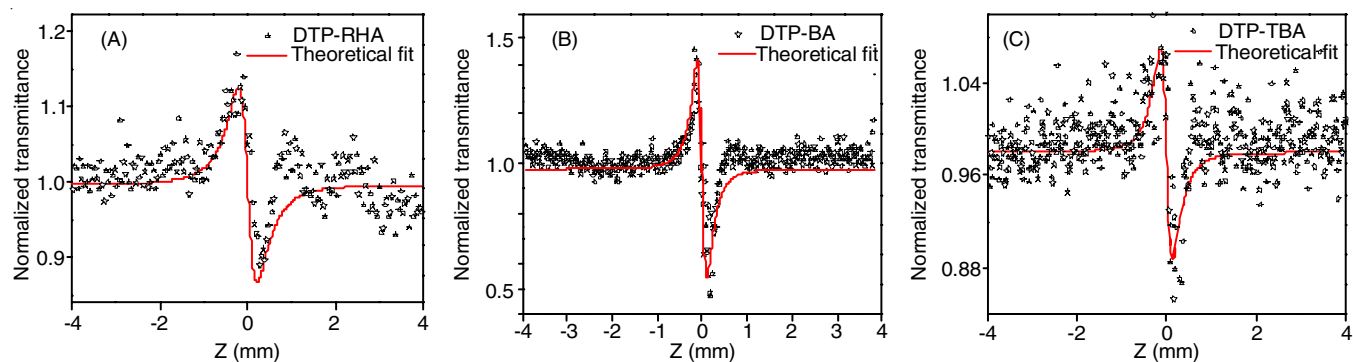


Fig. 8. Closed aperture Z-scan profile of the DTP-RHA (A), DTP-BA (B) and DTP-TBA (C) DMF ($\sim 4 \times 10^{-4}$ M)

tibility χ^3 were determined by using the following set of eqns. 5-10:

$$\chi^{(3)} = \text{Re}\chi^{(3)} + i\text{Im}\chi^{(3)} \quad (5)$$

$$\text{Im}\chi^{(3)} = n_0^2 c^2 \frac{\beta}{240\omega\pi^2} \quad (6)$$

$$\Delta n_0 = \frac{\Delta\phi_0}{\text{KL}_{\text{eff}}} \quad (7)$$

$$\gamma = \frac{\Delta n_0}{I_0} \quad (8)$$

$$n_{2(\text{esu})} = \frac{cn_0}{40\pi} \gamma \quad (9)$$

$$\text{Re}\chi^{(3)} = \frac{n_0 n_{2(\text{esu})}}{3\pi} \quad (10)$$

where γ = the molecular cubic hyperpolarizability of compounds and k = wave vector. The calculated values of non-linear absorption coefficient (β), the non-linear refraction index (n_2), the third order susceptibility (χ^3), molecular cubic hyperpolarizability (σ_2) are listed in Table-4. Among the three donor-acceptor systems studied, DTP-BA shows the highest NLO activity but an order less than the DTOP-BA. This may be due to the lesser asymmetry in the electron density of the excited state in this category of molecules.

Optical limiting property: Since all the studied molecules show third order non-linear optical properties, these are suitable systems for optical limiting applications. The transmittance of a material with higher light intensities is termed as the optical limiting property [51]. Among the three donor-acceptor systems studied, DTP-RHA showed the best optical limiting behaviour. A plot of normalized transmittance against the input intensity is given in Fig. 9. The optical limiting threshold of DTP-BA was estimated as 1.7G W/cm².

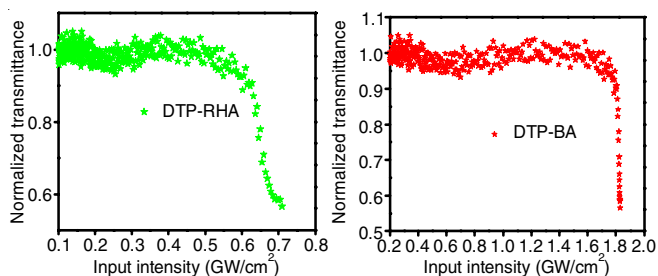


Fig. 9. Optical limiting profile of DTP-RHA and DTP-BA

Conclusion

Three tripodal novel starburst D-A-A systems with 1,3,5-triazine core as the non-conjugating spacer/acceptor with two arms having cyanoacetic acid (DTP-CYA), rhodanine-3-acetic acid (DTP-RHA), barbituric acid (DTP-BA) or thiobarbituric acid (DTP-TBA) as anchoring acceptor groups were designed and synthesized. The electrochemical, photophysical studies and theoretical studies were conducted. The synthesized molecules have also showed very good NLO properties. Among

the three donor-acceptor systems studied DTP-BA shows the highest NLO activity but an order less than the DTOP-BA.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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