



Original article

Improved the optical nonlinearity of carbazole based chromophores via molecular engineering: A DFT approach

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ABSTRACT

The present investigation was based on designing of carbazole based derivatives (**DTCFD1–DTCFD8**) having D1- π -D2- π -A architecture from **DTCFR**, upon substituting acceptor motifs for nonlinear optical (NLO) materials. M06-2X/6-311G(d,p) level was accomplished to explore the optoelectronic behavior of designed compounds. The UV–Vis, density of states (DOS), natural bond orbitals (NBOs), transition density matrix (TDM) and frontier molecular orbitals (FMOs) analyses were executed to comprehend the nonlinear optical properties of above-mentioned compounds. The FMO analysis showed **DTCFD7** as having the lowest energy gap at 3.734 eV among the derivatives, indicating its potential for efficient charge transfer. The overall decreasing order of band gaps was observed: **DTCFR** > **DTCFD5** > **DTCFD3** > **DTCFD1** > **DTCFD2** > **DTCFD4** > **DTCFD6** > **DTCFD7**. UV–Visible analysis exploited that **DTCFD7** displayed distinctive absorption characteristics. In the gas phase, it exhibited a λ_{max} of 494.927 nm, while in the dichloromethane it showed a significantly higher λ_{max} of 516.515 nm, then all other derivatives. All the derivatives exhibited greater values of linear polarizability [$\langle\alpha\rangle=1.633\text{--}1.786 \times 10^{-22}$ esu], first hyperpolarizability ($\beta_{tot} = 3.690\text{--}6.549 \times 10^{-28}$ esu) and second hyperpolarizability ($\gamma_{tot} = 4.825\text{--}7.229 \times 10^{-33}$ esu) as compared to the reference molecule. Furthermore, NLO analysis revealed that the highest β_{tot} (6.549×10^{-28} esu) and γ_{tot} (7.229×10^{-33} esu) was exhibited by **DTCFD7** and **DTCFD1**, respectively, then other derivatives. Moreover, a comparative study with standard urea and para-nitroaniline (p-NA), exhibited effective NLO properties in current study compounds. In light of the comprehensive findings, this study concludes that the designed compounds may be considered as effective NLO materials.

1. Introduction

Over the past few decades, NLO materials have attained great importance due to their potential applications *i.e.*, frequency mixing, electro-optic variation, optical parametric oscillation and optical bistability (Eaton, 1991; Nicoud, 1988). This rapid progress in optics, characterized by high speed and scalability, has paved the way for the emergence of photonic systems capable of performing a diverse range of functions through optical means (Muhammad et al., 2018). To achieve

this, the manufacturing of novel optical materials with improved performance is crucial. The NLO materials have emerged as key performers in enabling optical and photonic advancements (Janjua et al., 2009). Among different kinds of NLO materials, organic materials are superior to their inorganic analogue in terms of synthesis, crystal manufacture, faster rate of optical nonlinearities, high second harmonic generation (SHG) proficiency and formation of comparably low power laser-driven NLO system (Jordan et al., 2003; Kitazawa et al., 1994). The extended conjugation within structural framework allows these compounds to

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exhibit appealing NLO designs, leading to promising intra-molecular charge transfer (ICT) phenomena (Khalid et al., 2023). Fullerenes (3-D conjugated cage like molecules) can exhibit an outstanding NLO response due to their extended π -conjugated network and delocalization of charges (Guldi, 2000; He and Li, 2011). However, they still have some defects such as: high production cost, insufficient light absorption in the visible region, problem in tuning of energy level and instability (Wadsworth et al., 2019; Rodriguez et al., 2016; Numbury, 2022). Now a days, non-fullerene (NF) based compounds have gained a lot of concentration of researchers due to flexibility in their chemical structures, tunable band gaps, easy to synthesize and planar structure (Cheng et al., 2018; Arshad et al., 2022; Adnan et al., 2021; Doust Mohammadi et al., 2023; Undiandeye et al., 2022). On the basis of appreciable stability, fully conjugated structure, strong electron accepting capability, electron transport ability and huge electronic delocalization NF-based compounds have replaced the classic fullerene compounds (Duan et al., 2019; Sun et al., 2015; Khalid et al., 2022). Hence, a number of NF-based molecules are reported in the past few decades to explore their significant optical and electronic characteristics and extensive absorption spectra with reduced energy gap (Zhang et al., 2018; Zhang and Li, 2020). Modification of organic materials through the incorporation of acceptor units has been recognized as an effective strategy for enhancing charge transfer capacity and improving the optical response (Khalid et al., 2022; Rafiq et al., 2022). Moreover, the conjugated compounds comprise of a framework comprehending conjugated π -electrons, conjugated π -bridge is interconnected to two terminal units with electron donor (D) and electron acceptor (A) nature, respectively (Abraham et al., 2009; Khalid et al., 2020). The "A" part pull out electronic charge from "D" through conjugated π -spacer as a result the π -electrons of the framework become polarized giving rise to a significant molecular dipole moment which describes a charge transfer (CT) axis nearly parallel to the chain axis of the conjugated system (Nalwa and Miyata, 1996; Bosshard et al., 2020; Hadi et al., 2023). The main strategy of utilizing electron donating and accepting species is to polarize the π -electron system of organic materials is noteworthy for progressing the NLO chromophores owing large molecular nonlinearity, good thermal stability, enhanced solubility and process capability (Eaton, 1991; Numbury, 2022; Prasad and Williams, 1991). The electronic charge easily transfers from donor to acceptor moiety via π -spacer generating large dipole moment (μ_{tot}) which helps to attain large average linear polarizability (α), first hyperpolarizability (β_{tot}) and second hyperpolarizability (γ_{tot}) (Prasad and Williams, 1991; Janjua, 2017). Additionally, few structural properties such as D-A relative position and extended conjugation length can also switch the NLO properties (Tan et al., 2016; Kimoto and Tajima, 2012). Hence, it is imperative to say that donor- π -acceptor architecture builds remarkable NLO responses as it has a strong push-pull mechanism which improve the transfer of electronic charge density in a molecule (Khalid et al., 2022; Broo and Zerner, 1995; Castro et al., 2016). Moreover, D-A parts of molecules are connected to one another through π -linker electron bridges as D- π -A. The behavior of the donor-acceptor moieties along with π -spacer length have been evaluated in the development of D- π -A compound. The π -bond structure of NLO organic materials frequently exhibits delocalization of the electronic charge. Interestingly, the charge transfer is correlated with the initial hyperpolarizabilities (β_{tot}) (Mahmood et al., 2014). The D1- π -D2- π -A architecture introduces an additional donor moiety (D1) between the main donor and acceptor units, forming a push-pull conjugated system. This design aims to enhance the delocalization of π -electrons, leading to improved charge transfer and ultimately enhancing the NLO response (Mustafa et al., 2023; Haq et al., 2023). Carbazole (donor unit) is an inflexible planar aromatic compound with high luminescent efficacy, varied energy gap and a flexible molecule capable of structural alterations. Due to these characteristics, carbazole plays a crucial role in electroluminescence and optoelectronic materials, thin film transistors, metal sensors and photoconductors (Kimoto and Tajima, 2012; Tsai et al., 2009; Khalid et al., 2022; Khalid et al., 2023;

Shafiq et al., 2023). A classic conjugated carbazole based compound consist of donor- π -acceptor network having carbazole as a powerful donor joined through a π -conjugated system to powerful acceptor (Khalid et al., 2022; Gupta et al., 2011; Mahmood et al., 2015). Moreover, due to the introduction of electron-withdrawing groups (-NO₂, -CN, -Cl and -Br substituents) over the acceptor moieties extended π -conjugation enhances which results in improved NLO response (Nazeer et al., 2020; Sheppard, 1967). Literature is flooded with numerous reports in which NF compounds with donor-acceptor, donor- π -spacer-acceptor, donor- π -linker-acceptor- π -linker-donor, acceptor- π -spacer-donor- π -spacer-acceptor, donor- π - π -acceptor, donor-acceptor- π -acceptor and donor-donor- π -acceptor configuration (Khalid et al., 2023; Khalid et al., 2022; Khalid et al., 2020; Bhattacharya et al., 2019) exhibited excellent NLO behaviour. These arrangements constitute a push-pull architecture results in reduction of HOMO- LUMO energy bandgap, increases electronic charge distribution and shifts the absorption towards longer wavelength results in larger NLO behavior (Abraham et al., 2009; Panneerselvam et al., 2017) Therefore, keeping in view the above-mentioned qualities, here, we have designed a novel series of seven strong push-pull D1- π -D2- π -A type derivatives (DTCFD1-DTCFD7) from A- π -D- π -A configured reference (DTCFR) (Liao et al., 2021) To the best of our knowledge, NLO characteristics of reference and designed compounds (chromophores with carbazole and thieno [3,2-*b*] thiophene with powerful electron withdrawing units: push-pull framework) have not been reported yet. Therefore, an NLO investigation of these D1- π -D2- π -A type species was conducted in this research paper. The DFT and TD-DFT computations for afore-mentioned chromophores are conducted to perform FMOs, DOS, GRPs, UV-Vis study, NBOs, TDMs, binding energy (E_b) and NLO analyses in dichloromethane (DCM) solvent. It is expected that tailored compounds DTCFD1-DTCFD7 would play a significant role in NLO domain. We anticipated that this investigation might be a facilitator for experimental researchers, physicists and chemists for the synthesis and designing of chemical compounds with astonishing NLO properties.

2. Computational procedure

The DFT analysis was executed at M06-2X/6-311G(d,p) (Zhao and Truhlar, 2008; Raghavachari et al., 1989) method to study the NLO properties of DTCFR and DTCFD1-DTCFD7 having D1- π -D2- π -A configuration. Accompanying with this, time dependent-DFT investigation was achieved to examine the FMOs and UV-Vis analyses by applying the abovementioned functional/basis set. All the quantum chemical calculations for current study were accomplished in dichloromethane solvent by utilizing Gaussian 09 program (Frisch and Clemente, 2009). The effect of solvent was investigated with the aid of conductor-like polarizable continuum model (CPCM) (Kromann et al., 2018). Global reactivity parameters (GRPs) were computed through FMOs findings to determine the reactivity and stability of designed compounds. The NBOs was computed by using 6.0 NBO package (Glendening et al., 2013) to evaluate the charge transfer interaction in entitled compounds. To interpret the data from the output files, Gauss View (Dennington et al., 2008), Avogadro (Hanwell et al., 2012), Chemcraft (Zhurko and Zhurko, 2009), PyMOLyze 2.0 (N.M. O'boyle, A. L. Tenderholt, K.M. Langner, , 2008), Origin 8.0 (Lima et al., 2020) and Multiwfn 3.7 (Lu and Chen, 2012) were used. Eqs. (1)–(4) were used to compute the linear and nonlinear properties of DTCFR and DTCFD1-DTCFD7 molecules (Kraus, 1956; Nackaerts et al., 1979; Dirac et al., 1930; Kurtz and Perry, 1968; Keldysh, 2023).

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \quad (1)$$

$$\langle \alpha \rangle = 1/3(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (2)$$

$$\beta_{tot} = [\beta_x^2 + \beta_y^2 + \beta_z^2]^{1/2}$$

Where, $\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$, $\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yzz}$ and $\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz}$ (3)

$$\gamma_{tot} = \sqrt{\gamma_x^2 + \gamma_y^2 + \gamma_z^2} \quad (4)$$

Where $\gamma_i = \frac{1}{15} \sum_j (\gamma_{iji} + \gamma_{ijj} + \gamma_{ijj})$ $i, j = \{x, y, z\}$

3. Results and discussion

This research concentrates on exploration of NLO properties of newly designed carbazole based NF molecules with push-pull architecture (Scheme 1). The synthesized DTC-T-F-R compound with A- π -D- π -A configuration is utilized as parent chromophore for current study (Liao et al., 2021). The hydrocarbon chain named *n*-octyl (-C₈H₁₇) group on DTC-T-F-R compound is replaced with methyl (-CH₃) group at donor fragment to reduce the computational cost as long alkyl chain has not significant effect on NLO properties. After these structural modification in parent chromophore (DTC-T-F-R), the new reference molecule namely DTCFR was designed as represented in Fig. 1. The chromophore DTCFD1 is designed by changing thiophene (π -spacer) with thieno[3,2-*b*] thiophene from the reference molecule (DTCFR) to enhance the resonance. After that DTCFD2 is designed from DTCFD1 by replacing the one acceptor unit with a donor (D₁) moiety (9*H*-carbazole) to create push-pull architecture. After that the other derivatives (DTCFD3-DTCFD7) are designed from DTCFD1 by just replacing the other terminal acceptor unit with more effective acceptor moieties as displayed in Figure S1. These designed D₁- π -D₂- π -A type systems comprise of three fragments: i) donors (D₁ and D₂), ii) π -linkers and iii) acceptors which extended the conjugation as well as electron withdrawing effect of the substituents result in enhanced NLO properties than reference molecule (DTCFR). The Cartesian coordinates are mentioned in table S1-S8. While, the IUPAC names of acceptors along with their abbreviations are demonstrated in Table S30. Moreover, the optimized conformations of DTCFR and DTCFD1-DTCFD7 are shown in Fig. 2. Further, the Gibbs free energy (ΔG) is also calculated for designed chromophores in order to verify the feasibility of synthesis and their stability. Literature data explained that the reaction with negative value of ΔG elucidates that the reaction is spontaneous with greater formation of products. The negative value ΔG is obtained for studied compounds (Table S31) which indicated the product formation (DTCFD3-DTCFD7 compounds) and supported that these new compounds could be synthesized in the laboratory. The detailed DFT analysis has been performed to reveal that how various acceptors effect the HOMO/LUMO energy gap, electronic properties, absorption spectra, intermolecular charge transference (ICT), linear polarizability (α), first hyperpolarizability (β_{tot}) and second hyperpolarizability (γ_{tot}). It is anticipated that the current investigation will trigger researchers to manufacture these compounds for achieving efficient NLO materials.

4. Electronic structure

The FMOs investigation is a significant way to understand the chemical reactivity, absorption and opto-electronic responses of chromophores (Khalid et al., 2022; Shafiq et al., 2023; Mahmood et al., 2018;

Srncac and Solomon, 2017; Asogwa et al., 2022; Mohammadi et al., 2024). The HOMO exhibited the electron donating capability, whereas the LUMO has the aptitude to capture the electron (Hadi et al., 2023; Ahmad et al., 2018). The HOMO-LUMO energy gap (ΔE) also provides key evidence related to ICT and NLO behavior (Khalid et al., 2023; Shafiq et al., 2023; Mahmood, 2019) The ΔE and ICT of a compound are inversely proportional to each other, the chromophores with high capability of CT among orbitals exposed substantial NLO response with reduced ΔE value and vice versa (Colladet et al., 2004) To study the effect of acceptor units on energy bandgap and ICT, the HOMO/LUMO energies and energy gap of DTCFR and DTCFD1-DTCFD7 were calculated and results are displayed in Table 1.

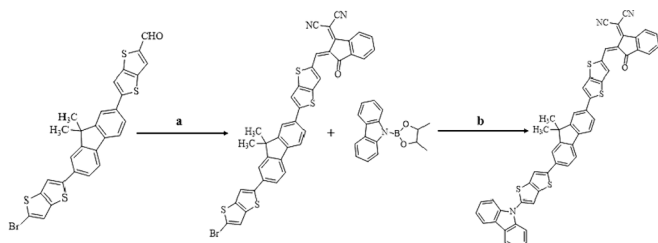
The computed HOMO/LUMO energies of DTCFR are -7.013 and -2.766 eV, respectively, with the energy gap of 4.247 eV as shown in Table 1. The E_{HOMO} is found to be -6.910, -6.838, -6.789, -6.869, -6.856, -6.843 and -6.867 eV while, the E_{LUMO} is examined to be -2.813, -2.743, -2.682-2.795, -2.721, -2.863 and -3.133 eV for DTCFD1-DTCFD7, respectively. The bandgap of said compounds is observed to be 4.097, 4.095, 4.107, 4.074, 4.135, 3.980 and 3.734 eV, respectively. The derivatives demonstrated a reduced bandgap compared to the reference compound (DTCFR) (4.247 eV).

Reduced energy bandgap in DTCFD1-DTCFD7 may be due to the enhancement in resonance and presence of electron withdrawing nature of nitro, cyano, chloro and fluoro, substituents at the acceptor moieties. The electron migration towards the acceptor region escalates with rising electronegativity, attributed to the inductive effects of -F, -CN, -NO₂, and -Cl groups (Nazeer et al., 2020; Sheppard, 1967). The lowest energy gap amidst all derivatives is exhibited by DTCFD7 with value of 3.734 eV due to the presence of -CN substituents at the terminal 3-(cyano-isocyano-methylene)-6-isocyano-2-methylene-1-oxo-indan-5-carbonitrile (CMC) acceptor group. These cyano groups exert strong electron withdrawing effect mesomerically and thus efficiently withdraws electronic charge towards itself (Huheey, 1966). Overall, the bandgap reduces in the following order: DTCFR > DTCFD5 > DTCFD3 > DTCFD1 > DTCFD2 > DTCFD4 > DTCFD6 > DTCFD7. This order verifies that incorporation of electron-withdrawing groups is useful in the reduction of E_{gap} and results in enhanced NLO response. The energy gap is pivotal in the charge transfer process; a smaller energy gap corresponds to a greater extent of ICT. (Doust Mohammadi et al., 2023; Undiandeye et al., 2022; Rafiq et al., 2022; Brédas et al., 2004). A similar trend for HOMO-1, HOMO-2, LUMO+1 and LUMO+2 is observed as shown in Table S9 and Figures S2-S9.

Fig. 3 shows the counter surface diagrams of HOMOs and LUMOs, which disclosed that in studied compounds the electronic cloud for HOMOs is concentrated over the donors. (D₁ and D₂) and π -spacers. Whereas, in case of LUMOs charge density is positioned over the terminal acceptor group except DTCFR and DTCFD1, where a little amount of charge is located over the π -spacers. This reveals that electron donor group is linked to the electron acceptor moiety through π -linker, which accelerates the ICT between donor and acceptor groups. Therefore, the investigated compounds have shown efficient charge transfer from donor towards acceptor through π -spacers thus, proving them promising NLO materials.

4.1. UV-vis analysis

A useful electronic information is given by the UV-Vis analysis linked to the transitions contributing configurations, type of electronic transition and charge transference capability in the chromophores (Khan et al., 2019; Mahmood et al., 2019). Oscillator strength (*f*), absorption wavelength (λ_{max}), transition energy (*E*) and transition type of the investigated systems are investigated by the UV-Vis investigation. These aspects are calculated by using TD-DFT computations at M06-2X method and triple zeta basis set for DTCFR and DTCFD1-DTCFD7 molecules in dichloromethane (DCM) and gaseous phase for the exploration of the impact of different acceptor groups on absorption



Scheme 1. Systematic representation of DTCFR and DTCFD1-DTCFD7.

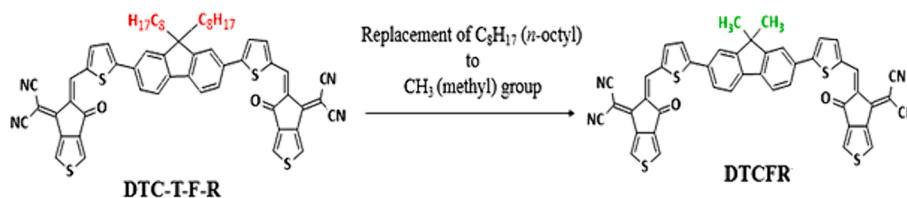


Fig. 1. Modification of DTC-T-F-R into DTCFR via substitution of small alkyl group.

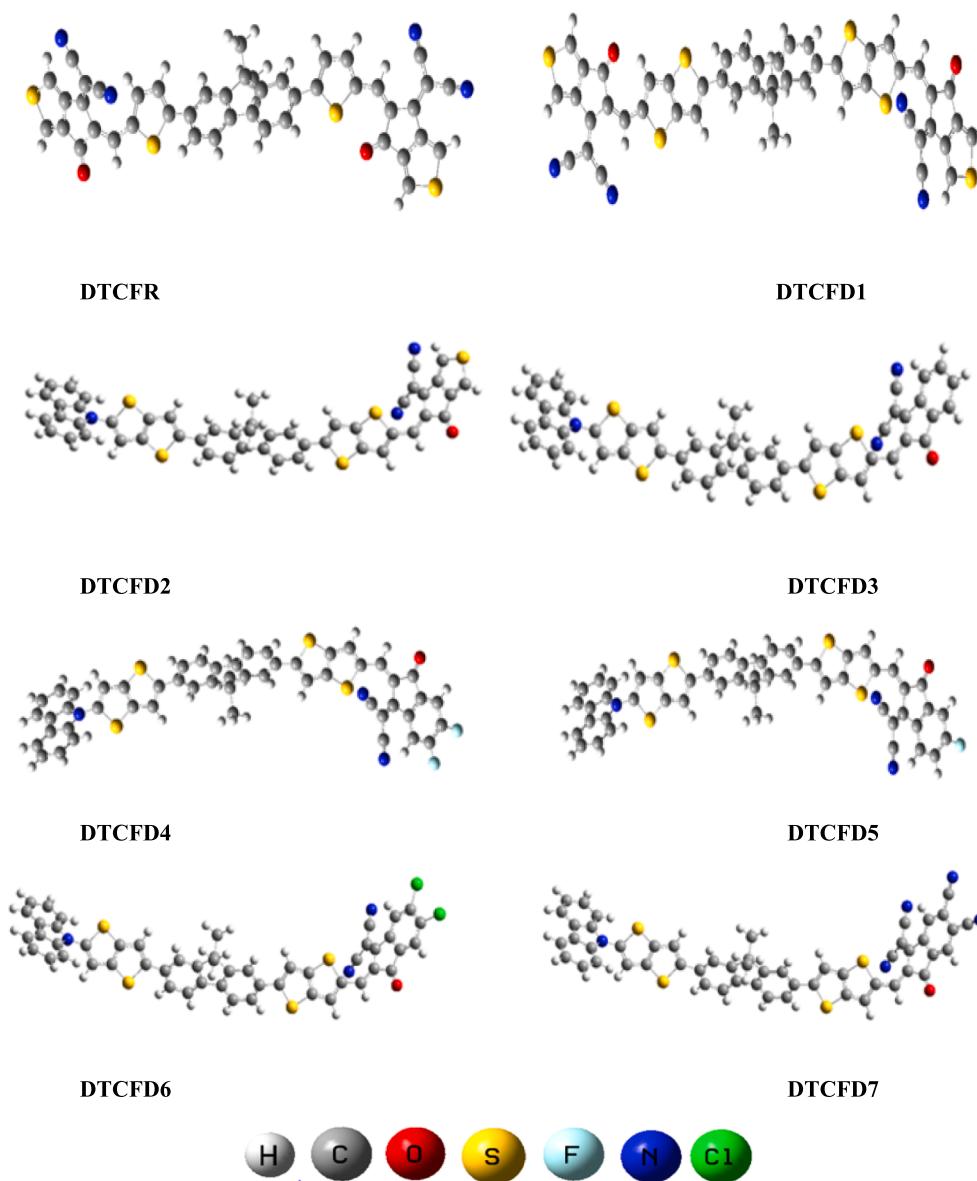


Fig. 2. Optimized structures of DTCFR and DTCFD1-DTCFD7.

properties and their absorption spectra are shown in Fig. 4. The calculated transition energy (E) in eV, λ_{max} (nm), oscillator strength (f) and molecular orbital contributions are shown in the Table 2. Other prominent molecular orbital contributions along with details are provided in Tables S22-S37.

Solvent's polarity greatly influences the wavelength and shifts it towards the longer range. DCM results in superior excited state stabilization due to high polarity relative to ground state (Kamlet et al., 1977). The absorption values of DTCFD1-DTCFD7 are in the range of 474.635–516.515 nm; with 2.400–2.618 eV transition energies and

oscillation strength of 1.111–2.473 in DCM solvent. All derivatives revealed a greater λ_{max} value than the DTCFR (473 nm). It can clearly be seen from the λ_{max} values that the presence of electron-withdrawing moieties in the acceptor region shifted the absorbance toward the longer wavelength (Khalid et al., 2020). Among all the derivatives; the absorption maxima was noticed in DTCFD7 at 516.515 nm, with transition energy of 2.400 eV and oscillation strength of 1.130. The cyano units in DTCFD7 allow more electronegative (EN) atoms to boost up red shifted phenomena in the optical rotational transitions. EN atoms influence the electronic characteristics of DTCFD7 to a longer extent than

Table 1

E_{HOMO} , E_{LUMO} and energy gap ($\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$) of DTCFR and DTCFD1–DTCFD7.

Compounds	E_{HOMO}	E_{LUMO}	ΔE
DTCFR	−7.013	−2.766	4.247
DTCFD1	−6.910	−2.813	4.097
DTCFD2	−6.838	−2.743	4.095
DTCFD3	−6.789	−2.682	4.107
DTCFD4	−6.869	−2.795	4.074
DTCFD5	−6.856	−2.721	4.135
DTCFD6	−6.843	−2.863	3.980
DTCFD7	−6.867	−3.133	3.734

Units in eV.

estimated. The overall ascending order of λ_{max} in DCM is as: **DTCFR** < **DTCFD3** < **DTCFD5** < **DTCFD2** < **DTCFD4** < **DTCFD1** < **DTCFD6** < **DTCFD7**.

Furthermore, this analysis is conducted in gas phase, the values lie in the range of 456.479–494.927 nm. The increasing order of the studied compounds based on λ_{max} examined in gaseous phase is as: **DTCFD3** < **DTCFR** < **DTCFD2** < **DTCFD4** < **DTCFD1** < **DTCFD6** < **DTCFD5** < **DTCFD7**. Among all the designed molecules prominent wavelength ($\lambda_{\text{max}} = 494.924 \text{ nm}$) in gaseous phase is observed in **DTCFD7** with transition energy of 2.505 eV and oscillation strength of 1.095. Interestingly all the studied compounds exhibited the maximum absorbance

spectra in DCM solvent than that of gaseous phase which might be due to the polarity difference. Due to structural modification of **DTCFR** with various acceptor units, various contribution of different orbitals in electronic transitions is observed. In the said compounds, shifting of electrons from HOMO to LUMO is responsible for the development of vital excited states. According to the findings of the literature, it has been observed that the polarity and characteristics of the solvent significantly impact absorption. This is supported by the bathochromic shift, which is most pronounced in dichloromethane (DCM) solvent across all investigated compounds, attributed to its higher polarity compared to the gaseous phase (Kamlet et al., 1977; Sissa et al., 2010). It is summarized that among all the derivatives, **DTCFD7** has the highest affinity for lowering the transition energy, least energy difference and shows bathochromic shift. All these characteristics make it a suitable optically active material to be used in nonlinear optics.

4.2. Transition density matrix (TDM) analysis

The TDM of entitled molecules for any transition between two eigen states (S_0 to S_1) were calculated by utilizing the aforesaid level of DFT and basis set. It is a proficient method for the determination and interpretation of electronic excitations in molecular systems (Chung, 1960; Marcus, 1971). It explained charge transference from D towards A through π -linker (Asogwa et al., 2022; Dennler et al., 2008). For TDM investigation, the studied compounds (**DTCFR** and **DTCFD1–DTCFD7**)

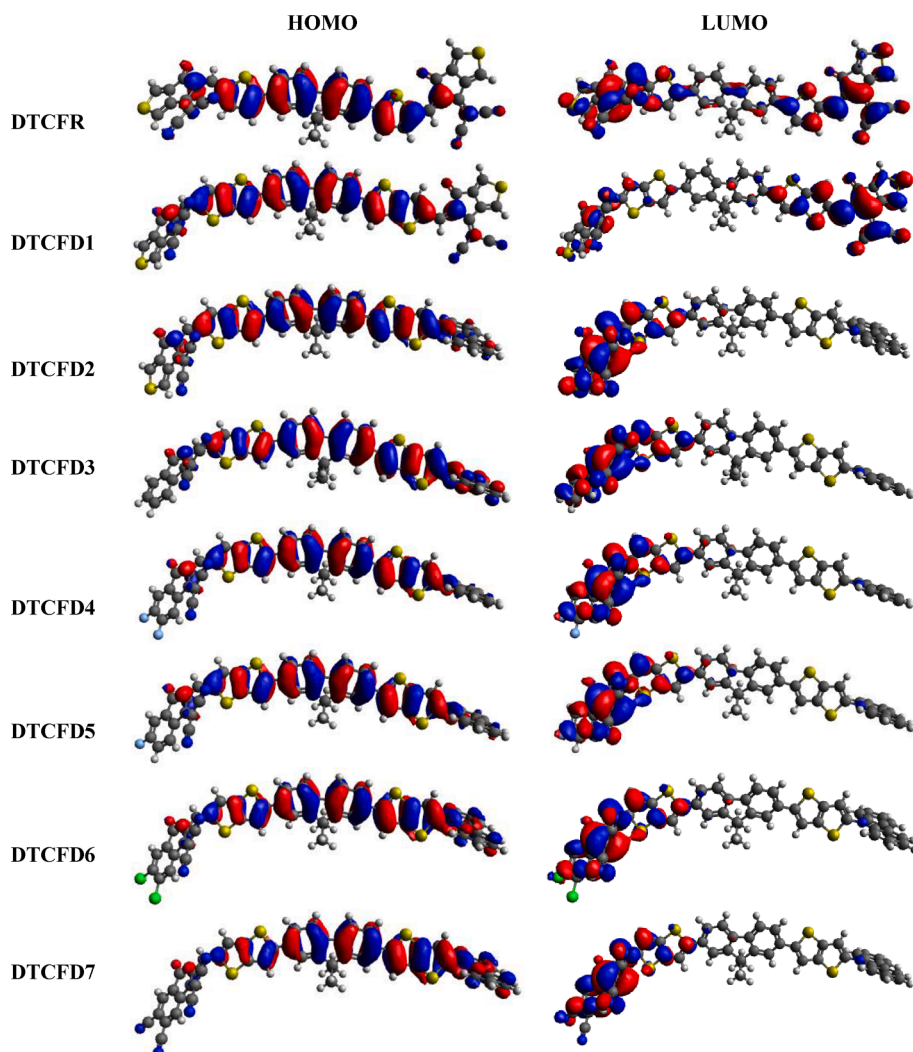


Fig. 3. HOMOs and LUMOs of the **DTCFR** and **DTCFD1–DTCFD7**.

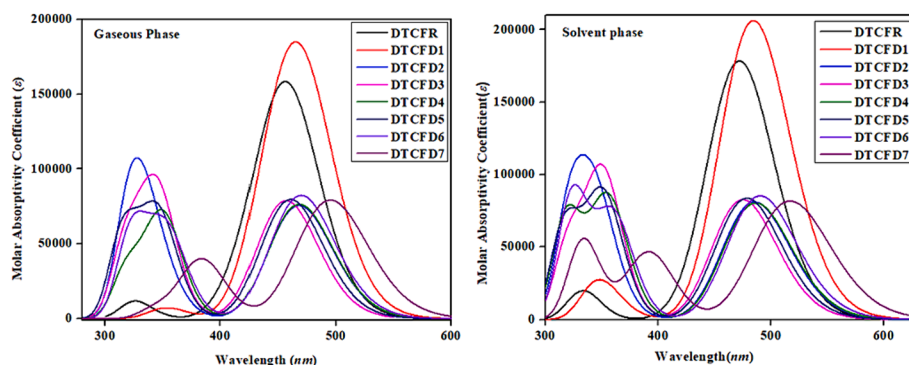


Fig. 4. Absorption spectra of DTCFR and its derivatives in dichloromethane (DCM) solvent and gaseous phase.

Table 2

Transition energy (E), λ_{max} , f and MO participation of entitled molecules.

Medium	Compounds	λ_{max} (nm)	E (eV)	f	MO contributions
Dichloromethane	DTCFR	473.653	2.618	2.315	HL (64 %), H-1 \rightarrow L + 1 (24 %)
	DTCFD1	487.206	2.545	2.473	HL (48 %), H-1 \rightarrow L + 1 (30 %)
	DTCFD2	484.976	2.557	1.119	H \rightarrow L (52 %), H-1 \rightarrow L (20 %)
	DTCFD3	474.635	2.612	1.141	H \rightarrow L (41 %), H-1 \rightarrow L (32 %)
	DTCFD4	486.098	2.551	1.111	H \rightarrow L (53 %), H-1 \rightarrow L (12 %)
	DTCFD5	478.334	2.592	1.156	H \rightarrow L (53 %), H-1 \rightarrow L (15 %)
	DTCFD6	490.037	2.530	1.178	H \rightarrow L (39 %), H-1 \rightarrow L (29 %)
	DTCFD7	516.515	2.400	1.130	H \rightarrow L (33 %), H-1 \rightarrow L (29 %)
	DTCFR	457.807	2.709	2.069	H \rightarrow L (66 %), H-1 \rightarrow L (4 %)
	DTCFD1	468.906	2.644	2.231	H \rightarrow L (49 %), H-1 \rightarrow L + 1 (30 %)
Gaseous phase	DTCFD2	467.670	2.651	1.046	H \rightarrow L (43 %), H-1 \rightarrow L (25 %)
	DTCFD3	456.479	2.716	1.089	H \rightarrow L (34 %), H-1 \rightarrow L (37 %)
	DTCFD4	467.847	2.650	1.056	H \rightarrow L (44 %), H-1 \rightarrow L (17 %)
	DTCFD5	475.728	2.606	1.012	H \rightarrow L (38 %), H-1 \rightarrow L (23 %)
	DTCFD6	469.495	2.641	1.138	H \rightarrow L (28 %), H-1 \rightarrow L (35 %)
	DTCFD7	494.927	2.505	1.095	H \rightarrow L (22 %), H-1 \rightarrow L (34 %)

f = oscillator strength, H = HOMO, L = LUMO, MO = molecular orbital.

are divided into three segments: (i) Donor (D), (ii) Acceptor (A) and (iii) π -spacer. Because of less efficient charge transference and less involvement, the impact of hydrogen atoms has been excluded. The TDM heat maps of DTCFR and DTCFD1-DTCFD7 are presented in Fig. 5.

The FMO study revealed that the charge density primarily resides on the acceptor over the LUMOs, resulting in same pattern is observed in TDM maps. Electron excitation can be defined as a transition from a hole to an electron. The diagonal pattern in the TDM heat map indicate the atoms consisting of the hole and electron simultaneously have a large distribution at colored region. In the TDM maps, most atoms along the diagonal exhibit green or red colors. This observation suggests that electrons from non-hydrogen atoms are transferred to adjacent atoms.

TDM findings imply efficient and enhanced charge separation from the ground state (S_0) to an excited state (S_1). Fig. 5 indicates that the excitation from S_0 to S_1 causes electrons to move cohesively from the carbazole (donor) to the terminal acceptor via the π -bridge, facilitating smooth intramolecular charge transfer (ICT) without hindrance.

4.3. Exciton binding energy (E_b)

One of the key parameters for assessing optoelectronic properties in compound is the exciton binding energy (E_b) (Nf Mott and Jones, 1936). A lower E_b value is generally associated with a higher charge migration capability, making it a valuable metric for evaluating the potential of molecules in opto-electronic applications. (Ans et al., 2019; Mahmood et al., 2021) In this study, the exciton binding energy (E_b) are calculated by using Eq. (5) (Runge, 2003).

$$E_b = E_{L-H} - E_{\text{opt}} \quad (5)$$

In Eq. (5), E_{L-H} is the energy gap and E_{opt} is first singlet excitation energy (Kim et al., 2012; Dkhissi, 2011). The computed E_b of DTCFR and its derivatives is described in Table 3. The binding energy (E_b) of DTCFR is noticed as 1.629 eV. The E_b values of DTCFD1–DTCFD7 are 1.552, 1.538, 1.495, 1.523, 1.543, 1.450 and 1.334 eV, respectively.

Table 3 presents the computed E_b values for all the studied molecules. Notably, DTCFD7 stood out as the most efficient among the derivatives, boasting the lowest binding energy of 1.334 eV. This remarkable reduction in E_b values is attributed to the specific acceptor group incorporated into DTCFD7. Importantly, lower E_b values are indicative of a higher exciton dissociation rate, which is a critical factor in achieving efficient charge separation.

The E_b values of studied molecules is from lowest to highest is as follows: DTCFD7 < DTCFD6 < DTCFD3 < DTCFD4 < DTCFD2 < DTCFD5 < DTCFD1 < DTCFR. This order indicated the unique efficiency of DTCFD7, making it a particularly promising candidate for opto-electronic applications. This reduction in E_b values is attributed to the incorporation of different acceptor groups in the derivatives. Notably, all molecules demonstrate E_b values less than 1.9 eV. There exists a direct relationship between E_b and NLO properties. Lower E_b values often correlate with enhanced NLO responses due to the increased likelihood of exciton dissociation, which can lead to improve nonlinear optical behavior. Therefore, the observed trend of decreasing E_b values across the studied molecules suggests the potential for favorable NLO properties.

4.4. Nonlinear optical (NLO) properties

The NLO investigation developed rapidly after the invention of lasers and is supposed to be the most promising technology towards the progress of photonics, optoelectronics, and biomedicine (Eaton, 1991; Hakim et al., 1991) In recent years, due to lower dielectric constant and ultra-fast electronic response, organic compounds have attracted much

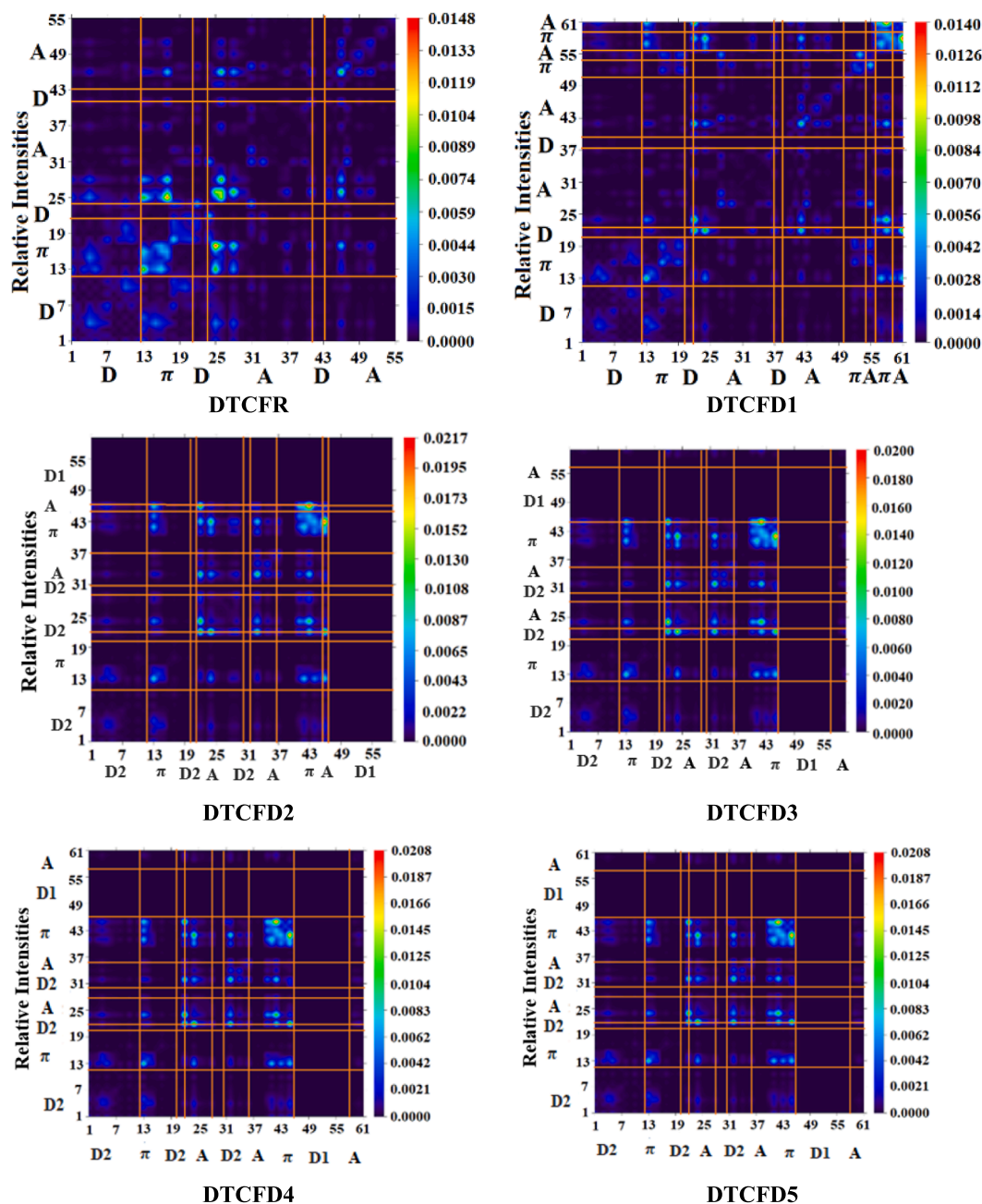


Fig. 5. TDM heat maps of compounds (DTCFR and DTCFD1 to DTCFD7).

concentration in various opto-electric applications (Mahmood et al., 2015; Lesar and Milošev, 2009). The NLO properties are boosted up by changing non-centrosymmetric properties of the compound (Mahmood et al., 2019; Hussain et al., 2020). Moreover, the non-NLO properties are associated with the interplay of structural features and α , along with β_{tot} and γ_{tot} , which govern optical behavior. The investigational and computational societies of materials science, chemistry and physics are providing multi-disciplinary opportunities for the improvement of NLO materials with greater optical signal processing, electro-optical variation of data storage, and potential frequency harmonic generation in optical communication equipment (Hussain et al., 2020; Kara Zaitri and Mekelleche, 2020; Breitung et al., 2000). Literature shows that β_{tot} is affected by E_{gap} value. It is assumed that systems having small E_{gap} and exhibited greater β_{tot} (Mohammadi et al., 2024; Pimenta et al., 2019). Further, the charge transference process is increased in the studied

molecules (DTCFR and DTCFD1-DTCFD7) by introducing different substituents like chloro (-Cl), fluoro (-F), nitro (-NO₂) and cyano (-CN) groups on terminal acceptor, which pull the electrons efficiently. Therefore, by linking the various acceptor groups via π -spacer is an effective method to lower the E_{gap} and to boost the polarizabilities (Khalid et al., 2022; Panneerselvam et al., 2017). To evaluate the impact of different acceptor groups on NLO response of DTCFR and DTCFD1-DTCFD7, the dipole moment (μ in Debye), $\langle\alpha\rangle$, β_{tot} and γ_{tot} values of above-mentioned compounds are estimated in *esu* and listed in Table S10-S12. The average linear polarizability, dipole moment, first hyperpolarizability and second hyperpolarizability of the said compounds are determined by applying the same functional/basis set in DCM and the results are mentioned in Table 4.

Table 4 shows that the dipole moment of DTCFD7 is greater (10.88 $\times 10^{-18}$ *esu*) among all designed compounds, which is due to the

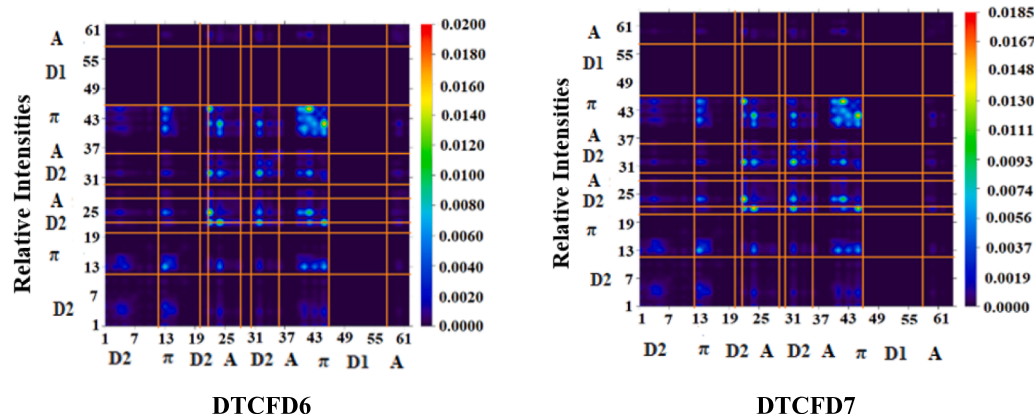


Fig. 5. (continued).

Table 3

 $E_{LH} = E_L - E_H$, E_{opt} and E_b of investigated compounds.

Compounds	E_{LH} (eV)	E_{opt} (eV)	E_b (eV)
DTCFR	4.247	2.618	1.629
DTCFD1	4.097	2.545	1.552
DTCFD2	4.095	2.557	1.538
DTCFD3	4.107	2.612	1.495
DTCFD4	4.074	2.551	1.523
DTCFD5	4.135	2.592	1.543
DTCFD6	3.980	2.530	1.450
DTCFD7	3.734	2.400	1.334

Units in eV.

Table 4

Dipole moment (μ_{tot}), average linear polarizability ($\langle\alpha\rangle$), first hyperpolarizability (β_{tot}) and second hyperpolarizability (γ_{tot}) of investigated compounds.

Compounds	$\mu_{tot} \times 10^{-18}$	$\langle\alpha\rangle \times 10^{-22}$	$\beta_{tot} \times 10^{-28}$	$\gamma_{tot} \times 10^{-33}$
DTCFR	6.839	1.533	1.835	5.037
DTCFD1	6.722	1.786	3.690	7.229
DTCFD2	4.421	1.548	4.226	3.467
DTCFD3	4.819	1.557	3.975	3.329
DTCFD4	4.812	1.561	4.231	3.499
DTCFD5	4.100	1.557	4.021	3.356
DTCFD6	5.155	1.633	4.659	3.852
DTCFD7	10.88	1.674	6.549	4.825

Unit for μ_{tot} (D) and $\langle\alpha\rangle$, β_{tot} and γ_{tot} are in *esu*.

presence of four strongly electron withdrawing cyano (-CN) groups. Thus, these groups pulled out the bonded electrons towards themselves and induced the polarity in **DTCFD7**. Among individual tensor components, the highest values (8.110 and $5.040 \times 10^{-18}D$) for **DTCFD7** and **DTCFR**, respectively, are displayed by μ_{xx} showing that said compounds are more polarizable along x-axis.

The average linear polarizability ($\langle\alpha\rangle$) with their respective tensors constituents has been computed and values in *esu* are shown in Table S11. Table S11 shows that α_{xx} tensor discloses greater values 2.737, 3.112, 2.376, 2.393, 2.412, 2.401, 2.506 and $2.586 \times 10^{-22} esu$ for **DTCFR-DTCFD7**, respectively, which shows that high polarization occurred along x-axis. The α_{yy} also contributed notably to average linear polarizability, which specifies that inter-molecular charge transfer followed along y-axis as well. The molecule **DTCFD1** showed highest ($\langle\alpha\rangle$) value of $1.786 \times 10^{-22} esu$ among all the derivatives, which may be because of the presence of strongly electron capturing nature of substituents on acceptor (MTM) region. The electron density is enhanced towards acceptor moiety due to the presence of -CN substituent which made it more electron-withdrawing and extended the conjugation. The

linear polarizability values for compounds **DTCFD1-DTCFD7** are 88.6, 103.2, 89.47, 90.1 and 96 *esu* times greater than standard *p*-NA molecule ($\langle\alpha\rangle = 1.173 \times 10^{-24} esu$). Similarly, the comparative study with reported similar analogues (**Q4**, and **Q4D1**) (Ali et al., 2021), demonstrating higher linear polarizability response (1.965–2.29 *esu* times) in **DTCFR-DTCFD7**.

The first hyperpolarizability (β_{tot}) along with its contributing tensors has been investigated at same method of DFT and respective values are arranged in the Table S13. Among the designed compounds **DTCFD7** showed highest β_{tot} amplitude of $6.549 \times 10^{-28} esu$ owing to the presence of 3-(cyano-isocyano-methylene)-6-isocyano-2-methylene-1-oxoindan-5-carbonitrile (CMC) acceptor group. Accompanying with this, first hyperpolarizability values were compared with urea ($\beta_{tot} = 0.372 \times 10^{-30} esu$) and *p*-NA ($\beta_{tot} = 9.6 \times 10^{-30} esu$) (Muhammad et al., 2019), a standard compound to investigate the NLO behavior (Kanis et al., 1994; Khalid et al., 2021). The β_{tot} value of **DTCFR-DTCFD7** is found to be 210–1760 *esu* times greater than urea molecule, and 19–68 *esu* times greater than *p*-NA molecule, respectively. Additionally, the comparative study with **Q4** and **Q4D1** showed that **DTCFD1-DTCFD7** showed approximately 0.718–2.588 *esu* times greater β_{tot} response as compared to **Q4** and 0.404–1.439 *esu* times greater than that of **Q4D1** chromophore. Among the individual tensor components, the highest values (1.998, 2.777, 3.837, 3.691, -3.737, -4.516 and $6.095 \times 10^{-28} esu$) for **DTCFR-DTCFD7**, respectively, are demonstrated by β_{xxx} which cause improved intermolecular charge (ICT) transfer along the x-axis. Shortly, for **DTCFR-DTCFD7**, the NLO behavior is exposed higher due to the existence of stronger electron-withdrawing substituents (-F, -Cl, -NO₂, -CN) on acceptor part which reduces the energy gap of HOMO/LUMO and increase the ICT among orbitals and make the system polarized. The β_{tot} values of all the designed systems were revealed with the reverse order of the E_{gap} among the HOMO–LUMO orbitals. The γ_{tot} of all the studied molecules with their contributing tensors is tabulated in Table S12. The highest value of γ_{tot} ($7.229 \times 10^{-33} esu$) is also observed in **DTCFD1** as compared to other investigated compounds. Among the individual tensor components, γ_x shows remarkably higher values (4.937, 6.863, 3.224, 3.114, 3.283, 3.140, 3.610 and $4.543 \times 10^{-33} esu$) than other tensors as reflected by Table S12. It can clearly be seen that **DTCFD1** reveals the highest value ($6.863 \times 10^{-33} esu$) among all the designed molecules, which describes the more ICT along x-axis and denotes the projecting diagonal tensor. Overall, the decreasing order of all of the titled molecules is: **DTCFD1** > **DTCFR** > **DTCFD7** > **DTCFD6** > **DTCFD4** > **DTCFD2** > **DTCFD5** > **DTCFD3**. Likewise, the second hyperpolarizability values of all the designated chromophores were compared to *p*-NA, and all investigated chromophores demonstrated higher efficiency compared to standard *p*-NA ($2.75 \times 10^{-36} esu$). From the above-mentioned results, it can be concluded that electron accepting ability of the molecules plays crucial role in the development of

significant NLO properties.

5. Conclusion

The primary objective of current study is to elucidate the effect of various acceptors units for the photophysical and NLO properties of carbazole-based designed **DTCFD1–DTCFD7** chromophores. A significant improvement in NLO response was observed due to the change in configuration from A- π -D- π -A in **DTCFR** to D1- π -D2- π -A in derivatives (**DTCFD2–DTCFD7**). Notably, **DTCFD7** exhibited the lowest energy gap (3.734 eV) attributed to electron-withdrawing -CN substituents, enabling effective charge transfer. Additionally, **DTCFD7** displayed distinctive optical characteristics, with a λ_{max} of 494.927 nm in the gas phase and a significantly higher λ_{max} of 516.515 nm in the DCM solvent phase, then that of other derivatives in both phases. NLO analysis revealed significant values, in **DTCFD7** ($\beta_{tot} = 6.549 \times 10^{-28}$ esu) and **DTCFD1** ($\gamma_{tot} = 7.229 \times 10^{-33}$ esu). Comparative study with standard chromophores: urea and *p* = NA showed that the current studied chromophores exhibited 210–1760 esu times greater first order hyperpolarizability response than urea molecule, and 19–68 esu times greater than *p*-NA. Additionally, comparison with reported similar analogues (**Q4** and **Q4D1**) also elucidate the **DTCFD1–DTCFD7** chromophores may be as effective NLO materials.

CRedit authorship contribution statement

Muhammad Khalid: Data curation, Funding acquisition, Validation, Visualization, Writing – review & editing. **Sidra Yasmeen:** Data curation, Formal analysis, Methodology, Writing – original draft, Writing – review & editing. **Sarfraz Ahmed:** Conceptualization, Formal analysis, Funding acquisition, Methodology, Resources, Supervision, Writing – original draft, Writing – review & editing. **Muhammad Adnan Asghar:** Data curation, Funding acquisition, Validation, Visualization, Writing – review & editing. **Muhammad Imran:** Data curation, Funding acquisition, Validation, Visualization, Writing – review & editing. **Ataulpa A. C. Braga:** Conceptualization, Formal analysis, Investigation, Methodology, Software, Writing – review & editing. **Suvash Chandra Ojha:** Conceptualization, Data curation, Funding acquisition, Validation, Visualization, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.arabjc.2024.105753>.

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