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Nonlinear optical response of D-π-A chromophores based on benzoxazin: quantum modification of π-spacer

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In this research article, four chromophores based on benzoxazine as the electron donor and tricyanovinyl dihydrofuran (TCF) as the electron acceptor have been designed to investigate the nonlinear optical (NLO) response. The geometric and electronic structures, absorption spectra, NBO analysis, and nonlinear optical response have been calculated by employing density functional theory (DFT) at PBEPBE/6-31G (*d,p*). The new design of chromophores has been proposed by the structural modification of π-spacers/conjugated systems. The DFT and TD−DFT computations at CAM−B3LYP/6−31G (*d,p*) have been performed to shed light on the influences of structural modification on the NLO properties. The absorption wavelength in different organic solvents, polarizability (α), and hyperpolarizability (β) are all determined. A strong NLO response indicates that this family of organic compounds with a D-π-A structure exhibits large first hyperpolarizability βtot values, these values are much greater than ones of urea. This theoretical model may be used to design other chromophores for usage in electro-optics.

1. Introduction

Over the past decade, organic compounds have attracted considerable attention due to ease of synthesis and fabrication, low cost, and their potential applications in novel optoelectronic devices for telecommunications, optical bistability, information storage, high-speed all-optical switches, and signal processing.[1-3] Indeed, the ease of modifying organic molecules structurally enables researchers to control the chemical structures and characteristics of desired nonlinear optical (NLO) responses.[4]These molecules with delocalized electrons are getting more attention due to their strong nonlinear optical characteristics. It has been determined that the characteristics of second-order nonlinear optical/first hyperpolarizability are related to intramolecular charge transfer (CT).[5] The charge transfer occurs between the donor and the acceptor via the p-spacer.[6,7] The NLO characteristics of basic molecules ascertain the NLO properties of the organic material. This criterion helps in the modeling of organic molecules with high NLO values.[8] To simulate and construct high-response NLO materials, it is necessary to modify the conjugation and therefore, the NLO activity of the materials.[9] The literature shows that donor and acceptor groups are responsible for supplying the essential ground-state charge asymmetry and the π-conjugated system offers a channel for the transfer and distribution of electric charges under the application of an electric field.[10] Generally, the D-π-A structure is developed to promote CT transitions. This structure enables us to investigate the influence of donor and acceptor group strengths, as well as the nature and the degree of π-conjugation on the functions of the nonlinear optical response. According to the structure-property relationship, the b value increases when the length of the π-conjugating chain is lengthened.[11-13]

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Recently, a new chromophore Z1 with the structure D-π-A was successfully prepared by Haoran Wang et al.[14] This chromophore contains benzoxazine as the electron donor, thiophene as the π-conjugated bridge, and tricyanovinyl dihydrofuran (TCF) as the electron acceptor Fig. 1. This chromophore was proposed for nonlinear optical (NLO) applications.

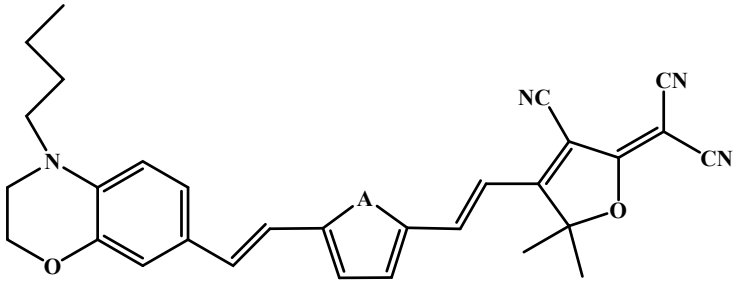


Fig. 1. Structure of chromophore Z1

The purpose of this work is to determine the influence of the length of conjugation on the NLO characteristics and UV-visible spectra of the organic chromophores. Indeed, large second-order NLO responses were simulated using the strategy of modifying organic molecules by lengthening the conjugated bridge. Four organic chromophores (Z1-Z4) with varying π-spacers were investigated. The structure of these four compounds is shown in fig. 2. Quantum chemical calculations were performed to compute the geometric and electronic structures, NBO analysis, nonlinear optical response, and absorption spectra of all compounds studied. We believe that our research will aid in the design and development of effective NLO organic chromophores in future experiments. Additionally, this work will aid experimentalists in developing more efficient NLO materials.

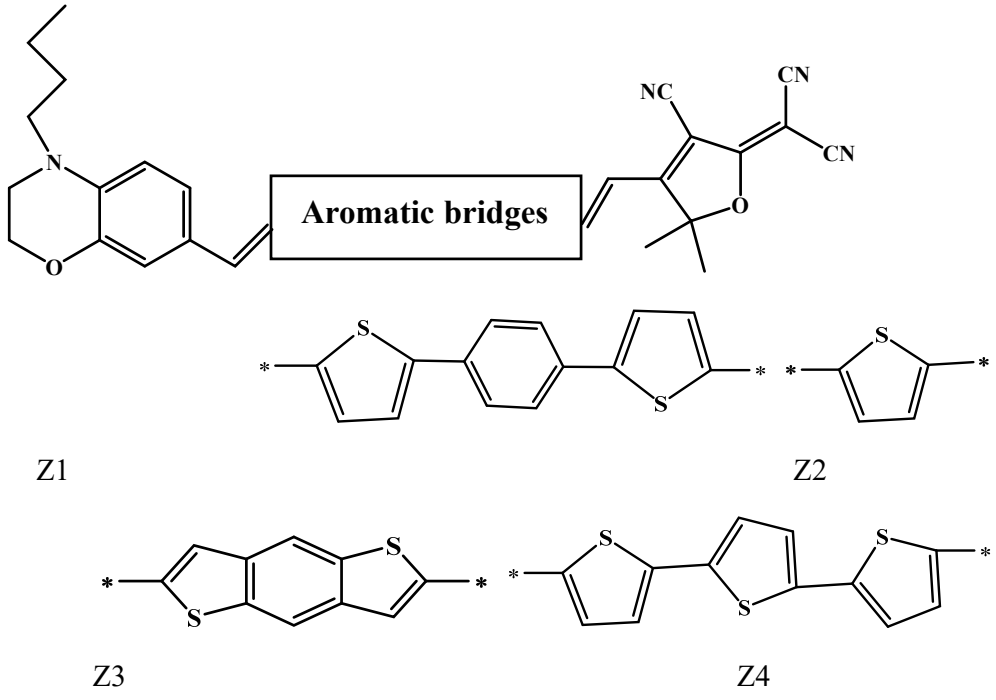


Fig. 2. Structures of chromophores Z1-Z4

2. Materials and methods

The hybrid functionals B3LYP,[15,16] PBEPBE,[17] B3PW91, [18] and mPW1PW9 [19] were employed in this study. All computations are performed using the 6-31G (*d,p*) basis set.[20,21] The density functional theory (DFT) and time-dependent DFT computations were carried out using the Gaussian 09 software.[22] Organic chromophores structures were optimized in the gas phase, and the HOMO, LUMO, and Egap energies were determined.[23-25] The computed orbital populations were used to forecast the natural bond orbital (NBO) [26] analysis using the NBO 6.0 software incorporated into the Gaussian 09 package program. For designed molecules, the spectrum of absorption, vertical absorption energies, and oscillator strengths was calculated in different organic solvents using the Time-Dependent Density Functional Theory (TD-DFT) [27] with coulomb-attenuated hybrid exchange-correlation functional (CAM-B3LYP).[28] Furthermore, we used DFT with the PBEPBE functional and the basis set 6-31G (*d,p*) to analyze NLO properties for molecules Z1, Z2, Z3 and Z4, such as the

first hyperpolarizability (β_{tot}) and their related parameters (μ,α). Indeed, the total dipole moment (μ), the mean polarizability (α), and the first hyperpolarizability (β_{tot}) are all characteristics that suggest their usefulness as nonlinear optical materials.[29-31]

They are calculated using the x, y, and z units in equations (1) – (3):

Here, combines the different quantities:

$$\mu_{tot} = \sqrt{\mu_x^2 + \mu_y^2 + \mu_z^2} \quad (1)$$

$$< \alpha > = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (2)$$

$$\beta_{tot} = \sqrt{\beta_x^2 + \beta_y^2 + \beta_z^2} \quad (3)$$

Here, $\beta_i = (i = x, y, z)$ combines the different quantities: $\beta_i = (\frac{1}{3})\sum_{j=x,y,z}(\beta_{ijj} + \beta_{jij} + \beta_{jji})$.

3. Results and discussion

3.1 Choice of methods

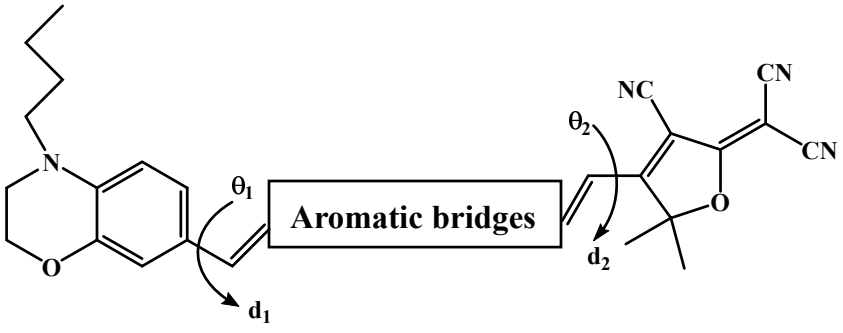
The selection of the functional using DFT approach is essential to properly explain the electronic properties (E_{HOMO}, E_{LUMO}, E_{gap}) of the chromophore studied.[14] Particularly, B3LYP, PBEPBE, B3PW91, and mPW1PW91 with the same basis set 6- 31G (*d,p*) has been used in this regard. The results of the four functional groups applied for the reference chromophore Z1 are listed in **Table 1**. We observe that the energy gap obtained by the PBEPBE functional with 6- 31G (*d,p*) level is similar to that obtained experimentally with a tolerable margin of error. Furthermore, the energy gap (E_{gap}) values obtained by the B3LYP, B3PW91, and mPW1PW91 functionals are larger than those determined experimentally. As a result, we conclude that PBEPBE is a great suited for describing the electronic characteristics and the ground-state geometries of all our organic chromophores.

Table. 1. Energies of HOMO, LUMO, and the gap energy for Z1 chromophore obtained by DFT/6-31G (*d,p*) with different functional levels, compared with those obtained experimentally.

	Chromophore Z1				
Functionals	E_{HOMO} (eV)	E_{LUMO} (eV)	$E_{g\ theoretical}$ (eV)	Eg_{exp} (eV)	$\Delta E_{(Error)}$ (eV)
B3LYP	-5.213	-3.125	2.08		0.77
B3PW91	-5.311	-3.225	2.08		0.77
mPW1PW91	-5.447	-3.100	2.34	1.31	1.03
PBEPBE	-4.656	-3.505	1.15		0.16

3.2 Optimized ground-state geometries

All optimized geometries of the (Z1-Z4) chromophores obtained by DFT/PBEPBE with 6-31G (*d,p*) levels are shown in **Fig. 3**. The primary optimization geometrical parameters such as bond lengths and dihedral angles are listed in Table 2.



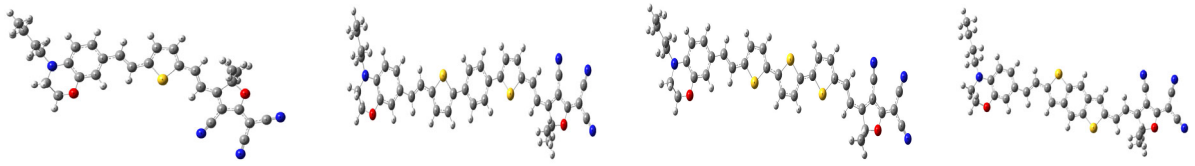
Scheme 1. Studied geometric parameters

According to **Scheme 1**, d_1 and d_2, represent the bond length obtained between benzoxazine as the electron donor (D) and the π-spacer and between the tricyanovinyl dihydrofuran (TCF) as the electron acceptor (A) and the same π-spacer, respectively. Based on data in **Table 2**, The shortest values estimated lengths d_1 and d_2 for all organic chromophores are in the range of 1.42 Å to 1.45 Å, indicating a C=C character that confirms and simplifies intramolecular charge transfer ICT,[32] this affects the redshift of the absorption spectrum.[33] For dihedral angles, the values of $\theta 1$ produced by the benzoxazine

moiety and the π-spacer for all designed molecules (Z1-Z4) are 179.85°, 177.86°, 178.80°, and -178.94°, respectively. Additionally, the dihedral angles θ2 created by the acceptor group and the π-spacer of all compounds (Z1-Z4) are -179.71, -179.72, 179.82, and -178.83, respectively. Indeed, the results obtained for θ1and θ2 indicate that all the chromophores proposed have a planar conformation.

Table 2. Distances (Å) and dihedral angles θi (°) of the studied chromophores calculated by PBEPBE/6- 31G (*d,p*)

Chromophore	d1(Å)	d2(Å)	θ1(°)	θ2(°)
Z1	1.42	1.45	179.85	-179.71
Z2	1.42	1.45	177.86	-179.72
Z3	1.42	1.45	178.80	179.82
Z4	1.42	1.45	-178.94	-178.83

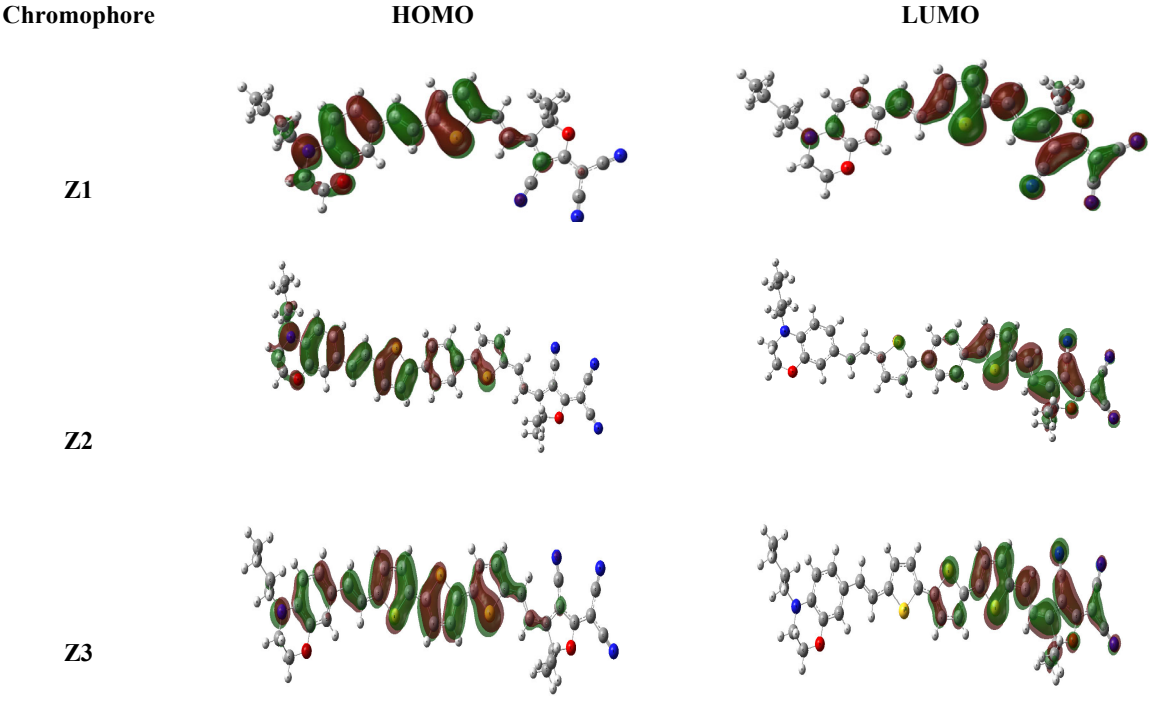


Z1 Z2 Z3 Z4

Fig. 3. Optimized structures of all studied chromophores (Z1-Z4) using PBEPBE/6-31G (*d,p*) level

3.3 Molecular orbitals

To understand more about intramolecular charge transfer (ICT), the electronic distributions of molecular orbital frontiers of four chromophores were computed using the PBEPBE functional with 6-31G (*d,p*) level, which is represented in **Fig. 4.** From the obtained results, the electronic distribution of the HOMO of Z1, Z2, and Z3 are mainly distributed on the donor and the π-bridge, while Z4 is predominantly delocalized on the π-bridge. On the other hand, the LUMO of all chromophores (Z1-Z4) shows a distribution on the π-bridge and acceptor groups. Accordingly, absorption occurs when an electron transitions from the HOMO to the LUMO level. In this context, chromophores with a smaller energy band gap are more conductive to electron excitations, which improves the absorption properties of the chromophores. Therefore, the energy gap (E_{gap}) of all studied chromophores was calculated according to the following relation: $E_{gap} = E_{HOMO} - E_{LUMO}$ [33] and is listed in Table 3. According to this table, the gap energy for Z1 is 1.15 eV, which is in excellent agreement with the experimental measurement (1.31 eV).[18] In comparison to Z1, the gap energy decreases in the following order: Z1 (2.09 eV) > Z4 (0.90 eV) > Z3 (0.85 eV) > Z2 (0.79 eV).



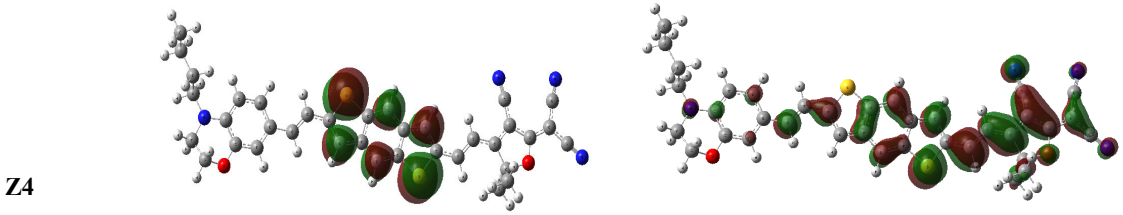


Fig. 4. Contour plots of the frontier orbitals of all chromophores

Table. 3. Energy values in eV of HOMO (E_{HOMO}), LUMO (E_{LUMO}) and gap (E_{gap}) of all studied chromophores.

Chromophore	E_{HOMO} (eV)	E_{LUMO}(eV)	E_{gap}(eV)
Z1	-4.656	-3.505	1.15
Z2	-4.405	-3.613	0.79
Z3	-4.443	-3.593	0.85
Z4	-4.543	-3.643	0.90

3.4 NBO analysis

The NBO study is an excellent method for exploring charge transfer between the occupied and unoccupied orbitals, and it is an efficient technique to investigate the ICT. NBO analysis is also believed to be able to show the charge densities that transfer from a donor group to an acceptor group via a π-linker in the D-π-A architecture. Therefore, NBO analysis of optimized structures of Z1-Z4 chromophores has been performed using the DFT-PBEPBE/6-31G (*d,p*) method in the gas phase, and the calculated data are shown in **Table 4.**[34] It is important to note that all compounds have positive charges in the donor and π-spacer groups, whereas the acceptor group has negative charges. On the other hand, the positive charges in the inserted bridge reveal that this unit functions as a donor. The highest positive charge on the donor of the chromophores Z1 and Z4 and the π-spacer for all chromophores indicates the most effective electron donor, while the most negative (NBO) charge on the acceptor portion indicates the best acceptor group for all chromophores investigated. These findings indicate that electrons migrate effectively from the donor to the acceptor groups through π-conjugated linkers, this corresponds to the formation of a state of charge separation.

Table 4. The NBO analysis of all chromophores (Z1-Z4) obtained at DFT/ PBEPBE/6-31G (*d,p*) level

Compound	Donating Group	π- spacer	Acceptor Group
Z1	0.145	0.121	-0.266
Z2	0.096	0.169	-0.265
Z3	0.093	0.167	-2.260
Z4	0.131	0.112	-0.243

3.5 Molecular electrostatic potential (MEP)

The electron density is an essential factor for determining both the reactivity of electrophilic and nucleophilic sites, as well as the interactions of hydrogen bonding. It is also associated with the molecule electrostatic potential (MEP).[35] In order to assess the reactivity of nucleophilic and electrophilic site attacks of the investigated chromophores, we predicted the MEP of these compounds by applying DFT / PBEPBE / 6-31G (*d,p*) approaches on the optimized geometry. The map of the MEP surface is given in **Fig. 5** using a variety of colors. As seen in **Fig 5**, the MEP demonstrates that the maximum positive region (blue color) of all chromophores is around the sulfur atoms of the π-spacer fragment. Whereas the negative region (red color) is predominantly concentrated around the nitrogen atoms of the tricyanovinyl dihydrofuran (TCF) groups in all investigated chromophores.

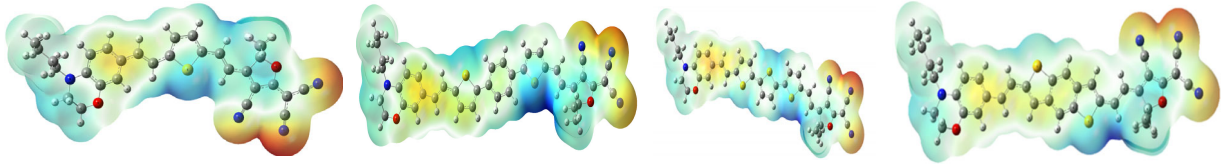


Fig. 5. MEP surfaces of the four studied compounds

3.6 Chemical concepts of reactivity

The DFT method is a very useful framework for the study of chemical reactivity. It offers information on the electronic structure of chemical species.[36] Using the HOMO and LUMO energies (E_{HOMO} and E_{LUMO}), the chemical potential (μ),[37] chemical hardness (η),[38,39] softness (S) and electronegativity (χ) [40] are all computed for the chromophores listed in **Table 5**. These Chemical reactivity indices may be determined using the following formulae:

$$\text{Chemical hardness: } \eta = \frac{E_{LUMO} - E_{HOMO}}{2} \quad (4)$$

$$\text{Chemical potential: } \mu = \frac{E_{LUMO} + E_{HOMO}}{2} \quad (5)$$

$$\text{Electronegativity: } \chi = -\mu = \frac{-(E_{LUMO} + E_{HOMO})}{2} \quad (6)$$

$$\text{Chemical softness: } S = \frac{1}{2\eta} = \frac{1}{E_{LUMO} - E_{HOMO}} \quad (7)$$

As shown in **Table 5**, the electronic chemical potential (μ) of four studied chromophore increases in the following order: Z4 (-4.09) < Z1 (-4.08) < Z3 (-4.02) (eV) < Z2 (-4.01) (eV). The values of hardness (η) show that the compounds Z1, Z2, Z3 and Z4 have the lowest hardness values, i.e., 0.57, 0.39, 0.42 and 0.45 (eV), respectively. Hence, they are soft molecules. In addition, the electronegativity (χ) values of the compounds Z1-Z4 were found to be 4.08, 4.01, 4.02 and 3.99 (eV), respectively. Finally, the values of softness (S) for all the investigated compounds increase in the following order: Z1 (0.87) < Z4 (1.11) < Z3 (1.19) (eV) < Z2 (1.28) (eV).

Table. 5. HOMO, LUMO, and gap energies, chemical potential (μ), chemical hardness (η), chemical softness (S), and electronegativity (χ)

Chromophore	E_{HOMO}(eV)	E_{LUMO}(eV)	Egap(eV)	μ	η	*S*	χ
Z1	-4.656	-3.505	1.15	-4.08	0.57	0.87	4.08
Z2	-4.405	-3.613	0.79	-4.01	0.39	1.28	4.01
Z3	-4.443	-3.593	0.85	-4.02	0.42	1.19	4.02
Z4	-4.543	-3.643	0.90	-4.09	0.45	1.11	4.09

3.7 Nonlinear optical (NLO) properties

The nonlinear optical (NLO) responses are intriguing in a variety of domains, including electro-optics and data storage.[41] Indeed, the molecular structure, which contains the appropriate donor and acceptor groups in the strategic positions is the primary characteristic of NLO, which may be further modified by extending π-conjugation.[42,43] To verify their utility as NLO materials, NLO parameters of the studied chromophores (Z1-Z4) have been estimated using the PBEPBE theory and the 6-31G (*d,p*) basis set. The total dipole moment (μ_{tot}) was calculated using the diagonal elements in equation (1). Similarly, equations (2) and (3) were also used to calculate average polarizability (α) and first hyperpolarizability (β_{tot}), respectively. The calculated values for total dipole moment, average polarizability, and first hyperpolarizability for the chromophores Z1, Z2, Z3, and Z4 are presented in **Tables** 6.

Table. 6. The dipole moments μ, average isotropic polarizability <α> and the first hyperpolarizability βtot of Z1-Z4

Parameters	Z1	Z2	Z3	Z4
μx	8.98	11.64	-10.95	-10.18
μy	-3.24	1.73	-1.32	-2.70
μz	-0.60	-0.02	0.21	0.23
$\mu_{tot\ (D)}$	9.56	11.77	11.03	10.54
αxx	1711.91	3392.92	3344.28	2718.41
αxy	-54.32	46.34	107.13	112.52
αyy	436.54	499.47	495.85	481.86
αxz	-47.72	-51.21	41.99	23.61
αyz	19.96	26.28	-50.58	-20.36
αzz	188.17	232.84	253.97	210.40
<α> (a.u)	**778.87**	**1375.07**	**1364.70**	**1136.89**
βxxx	89128.40	-782688.00	517710.00	-386020.0
βxxy	10191.80	-35215.60	15295.70000	-9856.18
βxyy	-1000.82	-1808.58	346.19700	1297.90
βyyy	460.77	-298.30600	214.55400	60.20
βxxz	-1116.45	-2436.17000	-5862.05	-4671.27
βxyz	-368.07	-141.85400	-2.62	-290.27
βyyz	95.13	27.77490	17.75	44.14
βxzz	-87.87	-179.37600	47.72	117.06
βyzz	-28.49	-18.92280	-35.39	8.98
βzzz	10.95	2.08982	-0.79	2.06
β_{tot}(a.u)	**88684.17**	**785483.75**	**518367.92**	**384757.33**

As shown in **Table 6**, the linear polarizability results indicate that the polarizability tensor is along the x-axis is more dominant in all examined chromophores. According to the literature reviews, the energy difference between HOMO and

LUMO affects a molecule's polarizability. Chromophore with a small energy gap value has large linear polarizability.[44] This statement is applicable for our investigated systems, where Z2 exhibits the highest linear polarizability value of 1375.07 a.u and Z1 presents the lowest linear polarizability value of 778.87 a. u. Z3 and Z4 polarizability values were 1364.70 a. u and 1136.89 a. u, respectively. Indeed, the decreasing order of linear polarizability values Z2 > Z3 > Z4 > Z1 is found to be in reverse of energy gap order Z2< Z3 < Z4 < Z1. In the case of first hyperpolarizability (β_{tot}), the dominant contribution to βtot is made by x-axis direction transition with positive values (89128.40, 517710.00 a. u) in Z1 and Z3, while with negative value (-782688.00, -386020.0 a. u) in Z2 and Z4, respectively. Generally, larger hyperpolarizability values are shown by chromophores with a small energy gap. This statement also exists in our studied systems where Z1, Z2, Z3, and Z4 presented the highest 88684.17, 785483.75, 518367.92, and 384757.33 a.u, respectively. Indeed, the decreasing order of βtot values Z2 > Z3 > Z4 >Z1 is discovered to correspond to the decreasing order of linear polarizability values Z2 > Z3 > Z4 >Z1 and to the opposite order of energy gap values Z2 < Z3 < Z4 < Z1, respectively. In summary, the greatest β_{tot} values observed for the examined chromophores might be a consequence of the modification of various π-conjugated spacers. It can be noted that the NLO values of all compounds exceed those of the urea molecule, which is typically utilized as the organic molecule of reference (β_{tot} value of urea = 43 a. u).[45] Overall, the results imply that all compounds studied exhibit polarizable properties.

3.8 Absorption properties

To assess the effect of the solvent on the absorption spectra of chromophore Z1-Z4, various solvents with different polarities were employed. The TD−DFT computations at CAM−B3LYP/6−31G (*d,p*) [46,47] have been performed. The transition energy (Eex), oscillator strength (*f*), transition natures, maximum absorption wavelength (λ_{max}) of chromophore Z1-Z4 are summarized in Table 7, whereas absorption spectra of Z1–Z4 are displayed in fig. 6. According to Table 7 and fig. 6, the theoretical results suggest that the absorption wavelength values of Z1, Z2, and Z4 ranges from 567.84 to 593.30 nm, while the absorption wavelength values of Z3 range from 638.89 to 646.45 nm in the solvents studied. In addition, the S0 → S1 excitations of the chromophores Z1-Z4 having the oscillator strength between 2.23–2.80 are mainly contributed to HOMO → LUMO transitions (85%, 50%, 62%, and 68%, respectively). We note that TD-DFT results suggest that there was no influence of solvent polarity on the absorption of chromophores Z1-Z4.

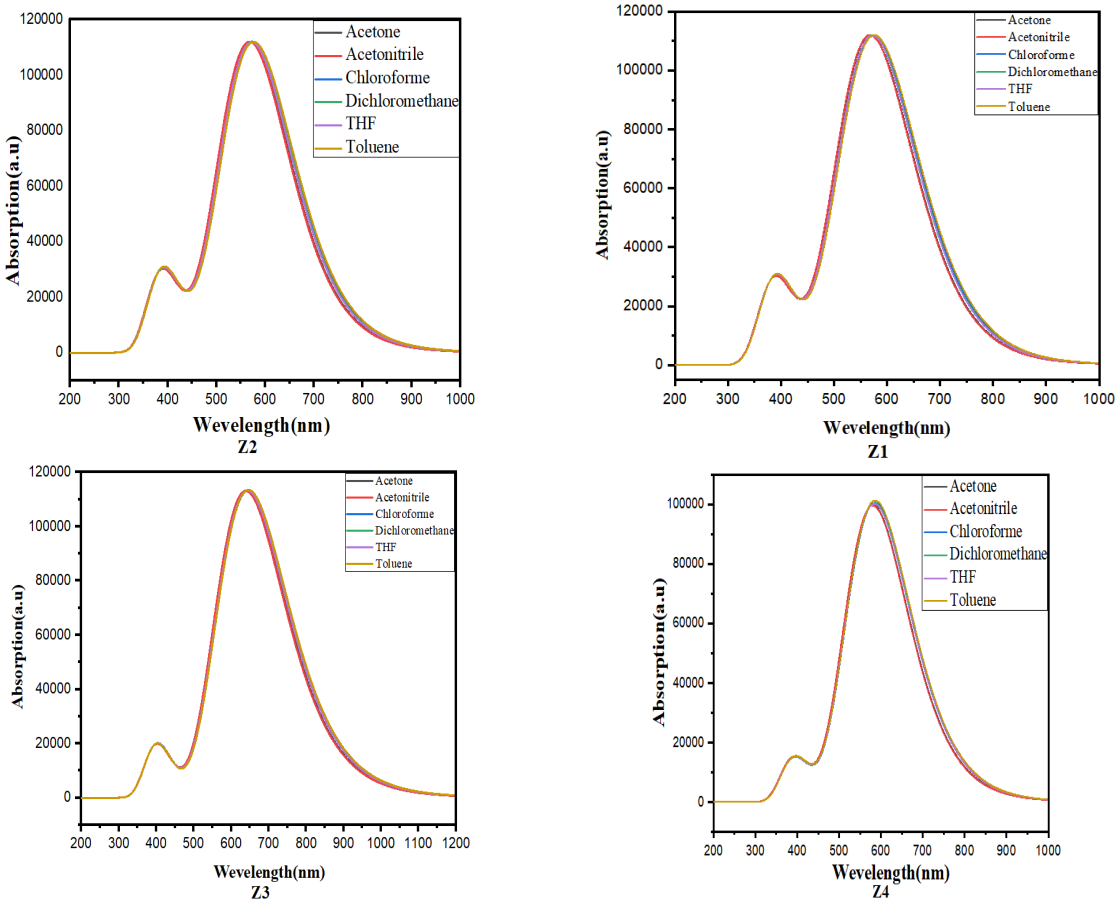


Fig. 6. UV-vis spectrum of four chromophores Z1-Z4 in various solvents

Table. 7. Absorption spectra data obtained at TD-DFT/ CAM-B3LYP/6-31G (*d,p*) level.

Chromophore	Solvent	λmax(nm)	Eex (eV)	*f*	MO/character	(%)
Z1	Acetone	590.11	2.10	2.23	HOMO->LUMO	(85%)
	Acetonitrile	589.41	2.10	2.23	HOMO->LUMO	(85%)
	Chloroform	574.58	2.15	2.75	HOMO->LUMO	(85%)
	Dichloromethane	593.30	2.08	2.24	HOMO->LUMO	(85%)
	THF	591.38	2.09	2.23	HOMO->LUMO	(85%)
	Toluene	588.71	2.10	2.24	HOMO->LUMO	(85%)
Z2	Acetone	568.93	2.17	2.76	HOMO->LUMO	(50%)
	Acetonitrile	567.84	2.18	2.76	HOMO->LUMO	(50%)
	Chloroform	574.58	2.15	2.75	HOMO->LUMO	(50%)
	Dichloromethane	572.80	2.16	2.76	HOMO->LUMO	(50%)
	THF	572.30	2.16	2.76	HOMO->LUMO	(50%)
	Toluene	576.26	2.15	2.76	HOMO->LUMO	(50%)
Z3	Acetone	640.17	1.91	2.79	HOMO->LUMO	(62%)
	Acetonitrile	638.89	1.94	2.79	HOMO->LUMO	(62%)
	Chloroform	645.98	1.91	2.79	HOMO->LUMO	(62%)
	Dichloromethane	644.80	1.92	2.79	HOMO->LUMO	(62%)
	THF	643.70	1.92	2.79	HOMO->LUMO	(62%)
	Toluene	646.45	1.91	2.80	HOMO->LUMO	(62%)
Z4	Acetone	581.26	2.13	2.46	HOMO->LUMO	(68%)
	Acetonitrile	580.09	2.13	2.45	HOMO->LUMO	(68%)
	Chloroform	586.43	2.11	2.48	HOMO->LUMO	(68%)
	Dichloromethane	586.26	2.11	2.50	HOMO->LUMO	(68%)
	THF	584.49	2.12	2.47	HOMO->LUMO	(68%)
	Toluene	586.26	2.11	2.50	HOMO->LUMO	(68%)

4. Conclusion

This study designed a series of organic chromophores (Z1-Z4) based on benzoxazine as the electron donor (D) and tricyanovinyl dihydrofuran (TCF) as the electron acceptor (A) having D-π-A architecture and explored the potential effect of π-spacers (bridges) on their NLO properties. All designed organic compounds showed maximum wavelengths λmax in the visible region with small transition energy values. FMO analysis of Z1 to Z4 indicated that energy band gaps of the entitled chromophores were reduced from 1.15 eV to 0.79 eV. Their NBO charge analysis indicates that electrons could effectively migrate from donor to acceptor through π-spacers, resulting in a high charge separation state. Generally, all dyes (Z1-Z4) present a large NLO response ranging from 88684.17 to 785483.75 (a.u), Z2 especially presents the highest <a> [(1375.07 (a.u)) and βtot (785483.75(a.u)] values. The studied chromophores exhibited good NLO properties because of their β values and were much greater than that of urea. The polarizability and hyperpolarizabilities parameters of the chromophores studied indicate that they are accomplished candidates for NLO material.

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