

Influence of Peripheral Modification of Electron Acceptors in Nonfullerene (O-IDTBR1)-Based Derivatives on Nonlinear Optical Response: DFT/TDDFT Study

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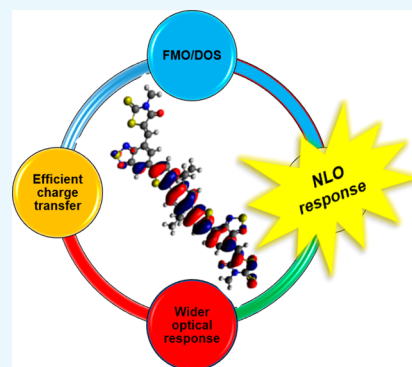


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ABSTRACT: Fullerene-based organic compounds have been reported as useful materials with some limitations; nonetheless, fullerene-free compounds are primarily considered to be the most substantial materials for the development of modern technology. Therefore, in this study, a series of compounds (NFBC2–NFBC7) having an A- π -D architecture were designed for the first time from a synthesized nonfullerene (O-IDTBR) compound by changing different acceptor groups. The synthesized nonfullerene (O-IDTBR1) compound and its designed derivatives were optimized with frequency analyses at the M06/6-311G(d,p) level. These optimized structures were further characterized by different quantum chemical approaches. The study required that the designed compounds possess a low energy gap in comparison to that of O-IDTBR1 (2.385 eV). Moreover, density of state (DOS) calculations supported the FMO analysis and displayed charge transfers from the HOMO to the LUMO in an effective manner. The λ_{max} values of the investigated chromophores were observed to be greater than that of the reference compound. Amazingly, the highest amplitude of linear polarizability $\langle\alpha\rangle$ and first (β_{tot}) and second hyperpolarizability values were achieved by NFBC6 at 1956.433, 2155888.013, and 7.868×10^8 au, respectively, among all other derivatives. Effective NLO findings revealed that nonfullerene-based derivatives may contribute significantly to NLO technology.



INTRODUCTION

In the past few years, extensive efforts in terms of nonlinearities have been made by using organic materials that have large and rapid nonlinear amplitudes. Organic compounds configured via electron acceptors and electron donors have attracted the interest of researchers at both the academic and industrial levels.^{1–3} Environmentally friendly organic compounds based on their availability, biodegradability, and involvement of a π -bond system electronic delocalization have shown promising nonlinear optical (NLO) behavior.^{4–6} Further, these compounds are utilized in different fields of research such as molecular switching, wireless communication, lasers, fiber optics, and materials sciences.^{7,8} The organic-based NLO-active compounds have been reported to be superior chromophores in comparison to inorganic systems due to their better electronic penetration and larger molecular polarizability and thus are regarded to be more competent candidates for optical technologies.⁹

Among the different classes of π -conjugated frameworks, fullerene-based compounds show a reasonably high nonlinear optical output^{3,10} and, as a result, are considered to be good candidates in the NLO field.¹¹ The NLO response of these fullerene derivatives could be enhanced by structural modifications using various electron-donor and -acceptor

moieties.¹² In addition to their NLO response, fullerene derivatives have also been used as essential part of organic solar cells over the last two decades.¹³ It is well-known that a fullerene is an electron-deficient molecule and has extremely strong π -aromaticity.¹⁴ Fullerenes have a 3D-conjugated cage like structure known to achieve a remarkable NLO response¹⁵ due to their extensive π -conjugated framework and a large charge delocalization.^{16,17} This delocalization of π -conjugated orbitals across a fullerene also helps the acceptors to have the ability to experience weak π – π interactions. Fullerenes have a number of valuable properties, and their early success in the field of organic photoelectronics has been reported. Despite their huge success, there exist many drawbacks that suggested the replacement of these fullerene-based acceptor moieties with nonfullerene organic acceptors, and this idea has strengthened the area of optoelectronics to some extent in

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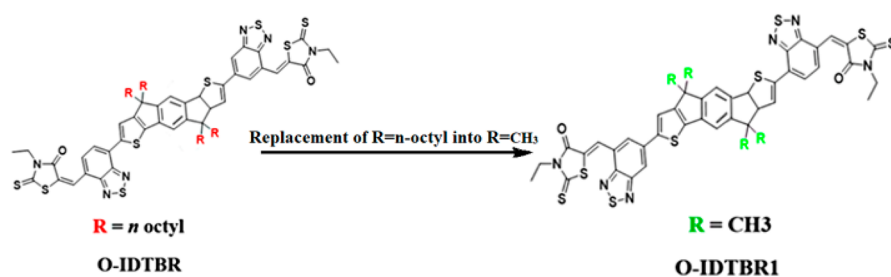


Figure 1. Modification of O-IDTBR into O-IDTBR1 via substitution of a small alkyl group.

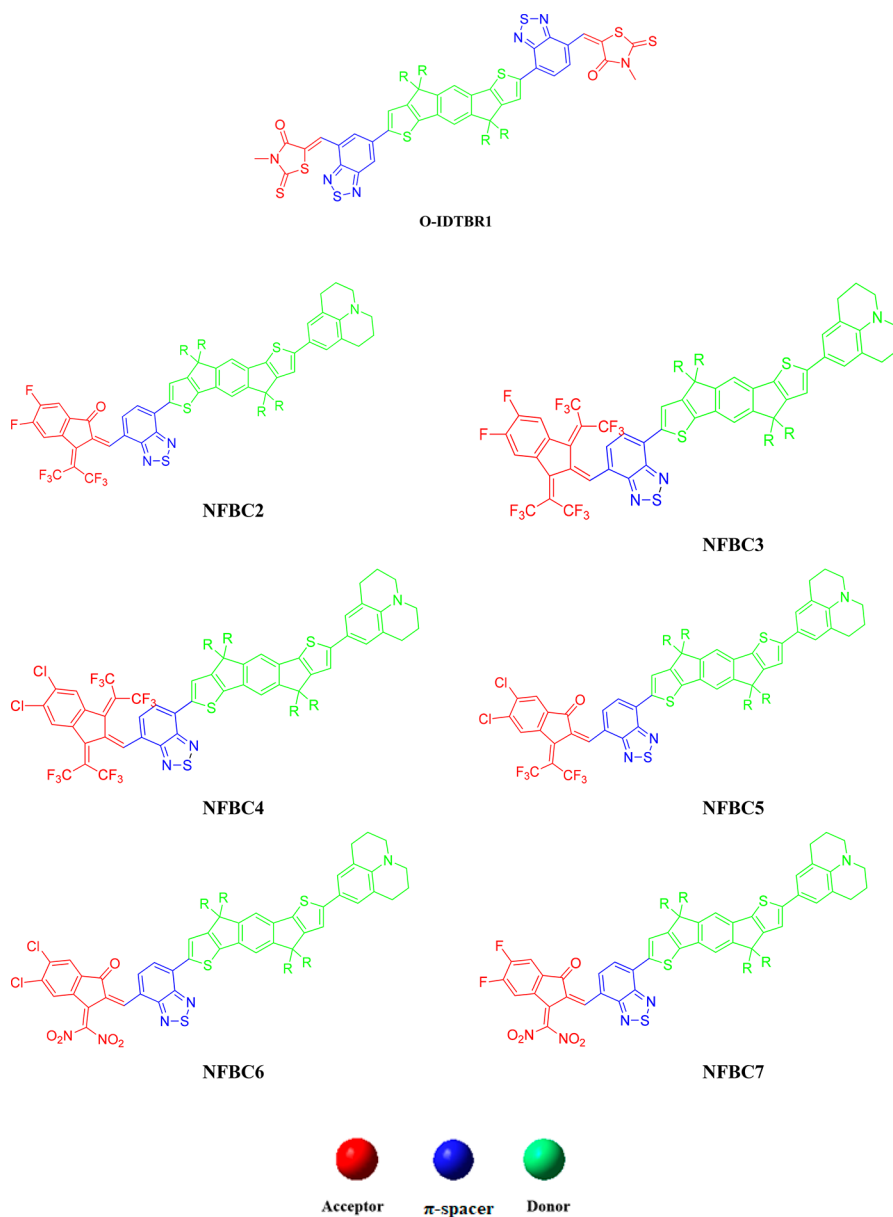


Figure 2. Displays of the acceptor, π -spacer, and donor structures in red, blue, and green, respectively, in the compounds O-IDTBR1 and NFBC2–NFBC7.

the past few years.¹⁸ In today's state of the art society, the requirement for more effective optoelectronic materials is growing with every passing day.^{19–21} Nonfullerene acceptors (NFAs) have substantial advantages such as tunable band gaps and structural planarity in comparison to fullerene acceptors. Moreover, NFAs have shown remarkable stability in

comparison with fullerene acceptor molecules.²² However, few reports about NFAs with NLO responses have been reported. According to a literature survey, the development of NFA-based nonlinear optical compounds has appeared as a new generation in materials sciences.^{23–26} On the basis of our continuing interest in the area of nonlinear optics (NLO), new

configurations of NFAs have been planned that reflect and elucidate their NLO properties.

Herein, we have considered a π -conjugated parent NFA molecule and a series of its derivatives have been designed by altering the fixed architecture with several donor and acceptor species to enhance the NLO properties.²⁷ The design is usually based on accommodating molecular entities that are comprised of twisted π -electron systems,^{28,29} extended conjugation, shift perturbations, donor- π -acceptor structures^{30,31} and so on. There are well-known conventional organic materials that possess good intramolecular charge transfer (ICT) abilities due to their in-built push–pull mechanisms.³² The ICT properties account for the polarization of molecular systems and could be enhanced by changing the basic D- π -bridge-A framework inside the molecule. Many desirable applications in optics and NLO³³ can be achieved by these structural modifications. Heteroatoms play a major role in effectively enhancing the NLO responses³⁴ in organic compounds. The first hyperpolarizability (β_{tot}) emerging from an NLO study is also associated with ICT that occurs from the donor (D) to the π -conjugated linker and the acceptor (A).³³

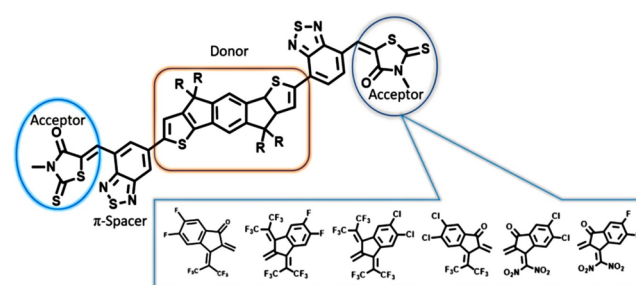
One of the emerging tools for molecular structural investigations is density functional theory (DFT), due to its consistency with experimental results. New NFA-based compounds would be a welcome addition to the development of NLO materials.

RESULTS AND DISCUSSION

The present work was focused on comprehensive NLO computational analyses of nonfullerene-based designed compounds. The designed A- π -D type compounds contain three fragments, donors, π -linkers and acceptor, exhibiting a strong push–pull architecture with greater polarity, resulting in an enhancement of their NLO properties. The configuration of **O-IDTBR** was reported to be A- π -D- π -D,²⁷ where an *n*-octyl ($-\text{C}_8\text{H}_{17}$) group was used as the hydrocarbon chain. However, in our study, the *n*-octyl hydrocarbon chain was altered to be methyl ($-\text{CH}_3$) groups at the donor moieties in **O-IDTBR** to overcome the computational cost. Hence, the code of the reference compound has been changed from **O-IDTBR** to **O-IDTBRI**, as shown in Figure 1. A series of compounds, namely **NFBC2**–**NFBC7**, have been developed via modifying the acceptors in the nonfullerene-based reference compound **O-IDTBRI**, as shown in Figure 2. In **NFBC2**, the acceptor and π -spacer 3-methyl-5-methylene-2-thioxothiazolidin-4-one and 4,7-dimethylbenzo[*c*][1,2,5]thiadiazole, respectively, were used. The acceptor present at one side of **NFBC2** has been replaced by the addition of the new donor 9-methyl-2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinoline. Further, a new nonfullerene acceptor entity, 5,6-difluoro-2-methylene-3-(perfluoropropan-2-ylidene)-2,3-dihydro-1*H*-inden-1-one, has an extraordinary electron-withdrawing ability was used instead of the previously used 3-methyl-5-methylene-2-thioxothiazolidin-4-one to achieve a simple (A- π -D) and more efficient push–pull mechanism. The quantum chemical based designed compounds have an A- π -D architecture, where benzothiadiazole is used as a π -linker with nonfullerene acceptor moieties in the computed molecules **NFBC2**–**NFBC7** as shown in Figure 2. The effect of various acceptor groups on HOMO/LUMO energy gaps, ICT, absorption spectra, linear polarizability ($\langle\alpha\rangle$), and the first (β_{tot}) and second hyperpolarizabilities ($\langle Y\rangle$) were investigated. In the current paper, we used the parent compound (Z)-3-methyl-5-((6-(4,4,9,9-tetramethyl-7-

(7-((*E*)-(3-methyl-4-oxo-2-thioxothiazolidin-5-ylidene)-methyl)benzo[*c*][1,2,5]thiadiazol-4-yl)-4,5,9,10-tetrahydro-s-indaceno[1,2-*b*:5,6-*b'*]dithiophen-2-yl)benzo[*c*][1,2,5]thiadiazol-4-yl)methylene)-2-thioxothiazolidin-4-one with an A- π -D- π -A structure (**O-IDTBRI**).²⁷ The parent was modified via modification of the acceptor part, and the designed compounds (**O-IDTBRI** and **NFBC2**–**NFBC7**) obtained are shown in Scheme 1 and Figure 2. This work might be a

Scheme 1. Sketches of the Designed Compounds **NFBC2**–**NFBC7** via the Reference Compound **O-IDTBRI**



marvelous addition in the area of nonlinear optics and also trigger further research in this field. The optimized designed compounds are shown in Figure 3.

Electronic Structure. The electronic structure comprises the HOMOs and LUMOs; the LUMO is inclined to receive incoming electrons from the HOMO.³⁵ The M06/6-311G-(d,p) functional was utilized to attain the dispersal pattern of electronic density in the HOMO/LUMO. The electronic and optical responses of chromophores are characterized from the distribution pattern of the electronic cloud obtained from frontier molecular orbital (FMO) studies. The HOMO–LUMO energies play crucial roles as electron donors and electron acceptors, respectively, consequently explaining the capability of a chromophore to absorb light and its reactivity. Further, they can also be utilized to predict the most reactive site in π -electron systems and elucidate the kinds of reactions in resonating systems. The energy band gap (ΔE) between the HOMO and LUMO indicates the charge-transfer abilities of a molecule. A low band gap implies an efficient transfer enhancing the NLO activity of the chromophore.³⁶ The computed HOMO–LUMO energies for the investigated chromophores in solvent media are presented in Table 1.

The molecular sketches of **O-IDTBRI** and **NFBC2**–**NFBC7** are displayed in Figure 2. The acceptors and donors of the newly designed chromophores **NFBC2**–**NFBC7** are organized in a 3-D pattern.³⁷

The HOMO and LUMO energies of the **O-IDTBRI** are -5.615 and -3.230 eV, respectively, while the energy gap is 2.385 eV (Figure 4). The HOMO energies of **NFBC2**–**NFBC7** are -5.110 , -5.092 , -5.064 , -5.121 , -5.162 , and -5.165 eV, respectively, while the energy levels of the LUMO are -3.307 , -3.173 , -3.001 , -3.367 , -3.658 , and -3.610 eV, respectively. The band gaps of **NFBC2**–**NFBC7** are 1.803 , 1.919 , 2.063 , 1.754 , 1.504 , and 1.555 eV, respectively. **O-IDTBRI** has a higher energy gap value, i.e., 2.385 eV, in comparison to the derivatives. This ΔE gap is lowered to 1.803 eV in **NFBC2** due to the insertion of the D moiety 2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinoline and A moiety 5,6-difluoro-2-methylene-3-(perfluoropropan-2-ylidene)-2,3-dihydro-1*H*-inden-1-one, as a result of which a strong push–pull

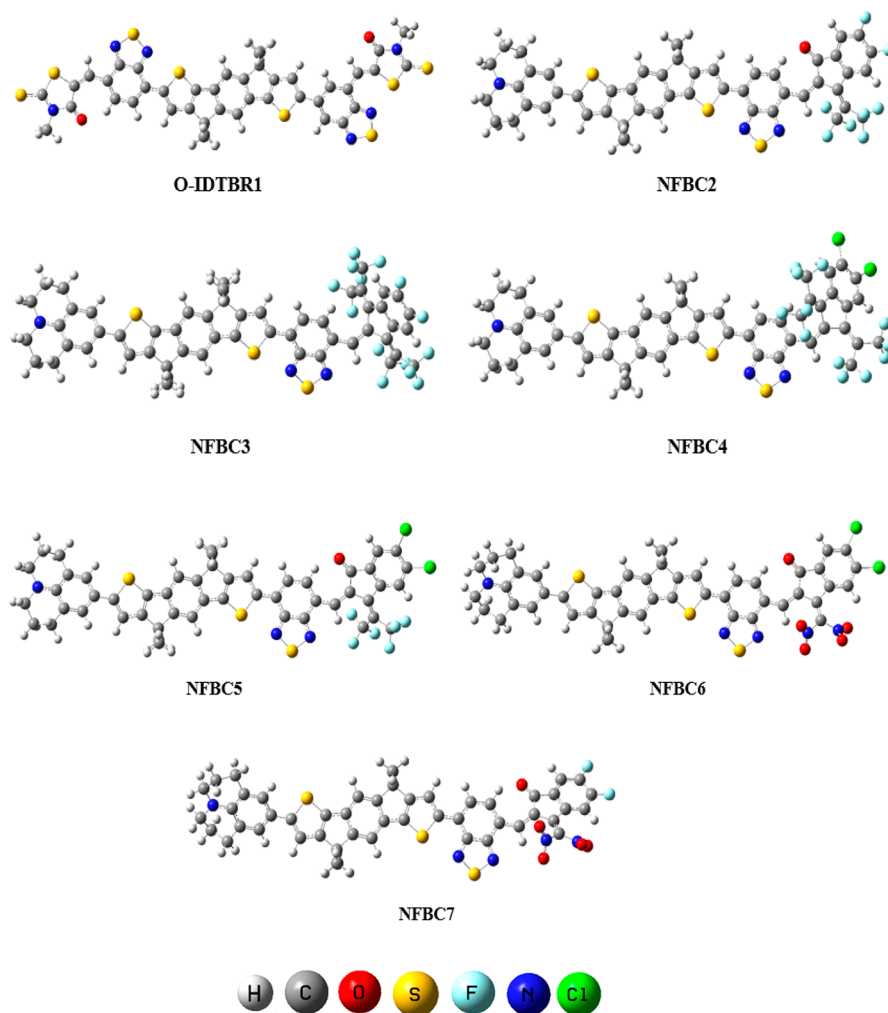


Figure 3. Optimized chemical structures of O-IDTBR1 and NFBC2–NFBC7 with different colored atoms indicated.

Table 1. E_{HOMO} , E_{LUMO} , and the Energy Gap ($E_{\text{LUMO}} - E_{\text{HOMO}}$) of the Investigated Compounds (in Units of eV)

compound	E_{HOMO}	E_{LUMO}	band gap
O-IDTBR1	−5.615	−3.230	2.385
NFBC2	−5.110	−3.307	1.803
NFBC3	−5.092	−3.173	1.919
NFBC4	−5.064	−3.001	2.063
NFBC5	−5.121	−3.367	1.754
NFBC6	−5.162	−3.658	1.504
NFBC7	−5.165	−3.610	1.555

architecture (D- π -A) is developed that reduces the band gap. This band gap is slightly expanded in NFBC3 due to the acceptor 1,1,1-trifluoro-2-(trifluoromethyl)but-2-ene-methane (1/1) being used instead of the acceptor used in NFBC2, thus increasing the band gap value to 1.919 eV, as a result of which the push–pull procedure is affected. Moreover, the band gap becomes larger (2.063 eV) in NFBC4 due to the incorporation of two chloro moieties at the acceptor site in 5,6-dichloro-1,3-bis(perfluoropropan-2-ylidene)-2,3-dihydro-1*H*-indene-methane (1/1); cyclopentanone is introduced in the proximity of the previously present fluoro moieties at the acceptor region in NFBC3. Subsequently, the electrons drift toward the acceptor side in the compounds due to the powerful withdrawing capability of the fluoro groups, which might be responsible for

the reduction in their energy gaps: i.e., 1.754 eV for NFBC5. Furthermore, a decreasing pattern in the ΔE value is also observed as 1.504 and 1.555 eV for NFBC6 and NFBC7, respectively. In effect, the geometry of NFBC6 is derivatized through the substitution of six fluoro groups with two nitro groups at the primarily used A moiety in the NFBC5. Similarly, the structure of NFBC7 is modulated by altering two chloro groups with two fluoro groups in the acceptor part of NFBC5. As was anticipated, greater values of electronegativity of the substituents will drive more delocalization of the electronic cloud in the direction of the acceptor site due to the inductive electron withdrawal ($-\text{Cl} < -\text{F} < -\text{NO}_2$),³⁸ as observed in NFBC5–NFBC7. On the other hand, the inductive effect might compete with the deactivation of the ring. The $-\text{F}$ and $-\text{Cl}$ groups have less of an $-I$ effect in comparison to the $-\text{NO}_2$ group. The chloro and fluoro groups at the acceptor are present in NFBC6 and NFBC7, which exhibited little inductive electron withdrawal in comparison to the nitro moieties.³⁹ However, a drop in the ΔE value was detected in both chromophores, which may be due to the inductive effect and the particular configuration of the acceptor molecule. A much lower ΔE value was found at 1.504 eV in NFBC6 due to the two attached nitro ($-\text{NO}_2$) groups with two chloro atoms on the A part having a greater $-I$ effect in comparison to $-\text{Cl}$ and $-\text{F}$. These nitro moieties can withdraw electrons more strongly in the direction of the A unit. Subsequently, this

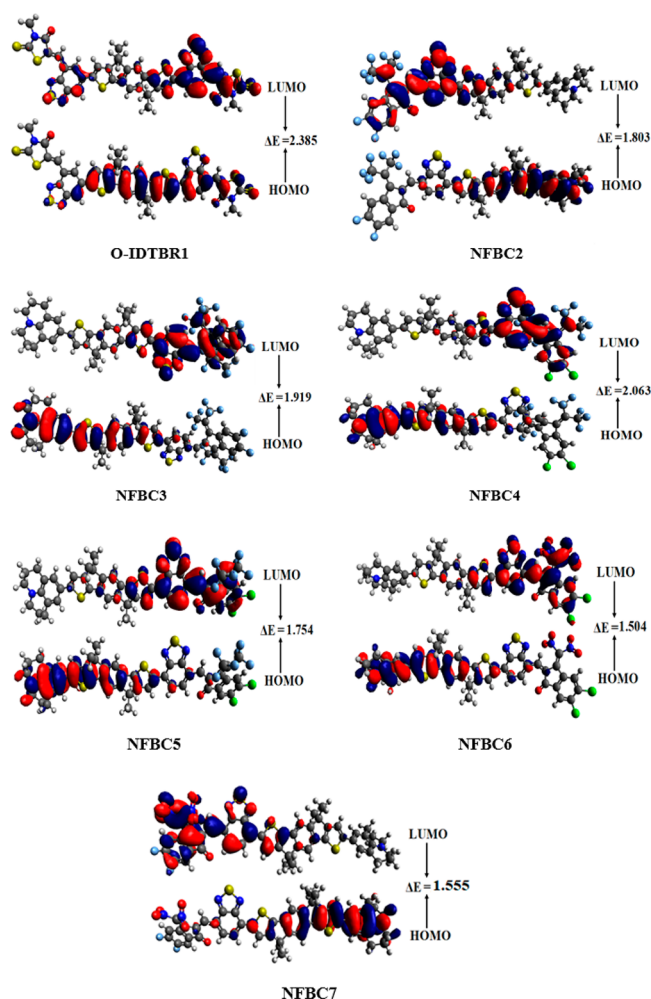


Figure 4. HOMOs and LUMOs of the studied compounds **O-IDTBR1** and **NFBC2–NFBC7** (units are in eV).

parameter accelerates the charge transfer and narrows the energy gap significantly. The E_{gap} value is found to be minimal in all of the aforementioned chromophores. However, compound **NFBC7** has been found to have a comparable E_{gap} value because it has also just two substituted $-\text{NO}_2$ moieties with two fluoro units at the acceptor part. Therefore, by modification of the structure of the acceptor moiety of **O-IDTBR1**, the HOMO–LUMO energy difference is reduced in the derivatives.

In a nutshell, the energy difference decreases in the following order: **O-IDTBR1** > **NFBC4** > **NFBC3** > **NFBC2** > **NFBC5** > **NFBC7** > **NFBC6**. This order confirms that the investigated compounds integrating *via* electron-withdrawing units would be an outstanding approach to lessen the E_{gap} ; hence, the NLO response would be more promising.⁴⁰

The extent of the energy gap entails the involvement of CT from the D toward the A part facilitated through a π -linker.⁴¹ In **O-IDTBR1**, the charge density for the HOMO is located over (E)-3-methyl-2-thioxo-5-((7-(4,4,6-trimethyl-4H-cyclopenta[b]thiophen-2-yl)benzo[c][1,2,5]thiadiazol-4-yl)methylene)thiazolidin-4-one, while the major part of A involved in the electronic distribution pattern is (Z)-5-((6-(4,5-dihydrothiophen-2-yl)benzo[c][1,2,5]thiadiazol-4-yl)methylene)-3-methyl-2-thioxothiazolidin-4-one. In **NFBC2–NFBC7**, the charge concentration for the HOMO is

predominantly located over 9-(4,4,9,9-tetramethyl-4,5,9,10-tetrahydro-s-indaceno[1,2-b:5,6-b']dithiophen-2-yl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline and little charge is located over benzothiadiazole (π -linker). The LUMO is concentrated partially on the π -spacer moiety and mostly on the acceptor moiety. Thus, a CT in the designed molecules is observed from the D to the A part *via* a π -bridge. This charge transfer shows that all of the designed chromophores would be promising NLO materials. It is inferred that the designed compounds have greater wavelengths and are more polarizable in comparison to the quinoline carbazole compounds.⁴²

UV–Visible Analysis. A UV–visible analysis entails various parameters such as absorption wavelength (λ_{max}), transition energy (E_{ge}), oscillator strength (f_{os}), and the nature of transitions of the compounds in this study. These considerations are studied by employing TD-DFT calculations at the M06/6-311G(d,p) level of theory in chloroform solvent. A shift in the wavelength of a molecule toward longer wavelength can be associated with the polarity of the solvent. As the excited state is more polar than the ground state, chloroform causes a greater stabilization of the excited state rather than the ground state.⁴⁰ The calculated results of transition energies, maximum absorption wavelengths (λ_{max}), oscillator strengths (f_{os}), and transition natures are presented in Table 2.

Table 2. Transition Energies (E), Maximum Wavelengths (λ_{max}), Oscillator Strengths (f_{os}), and MO Contributions of the Investigated Compounds

compound	λ (nm)	E (eV)	f	MO contributions
O-IDTBR1	670.946	1.847	2.087	H→L (96%)
NFBC2	839.546	1.476	1.287	H→L (96%), H-1→L (3%)
NFBC3	789.657	1.570	1.041	H→L (94%), H-1→L (5%)
NFBC4	729.318	1.700	0.841	H→L (93%), H-1→L (5%)
NFBC5	863.640	1.435	1.343	H→L (97%), H-1→L (3%)
NFBC6	1000.598	1.239	1.214	H→L (98%)
NFBC7	964.857	1.285	1.141	H→L (97%)

The absorption values of the designed compounds **NFBC2–NFBC7** lie in the range of 729.318–1000.598 nm. All of the geometrically designed compounds showed greater λ_{max} values in comparison to **O-IDTBR1**. It is clearly evident from the absorption values that the shift of absorbance toward a longer wavelength is also significantly influenced by the presence of the electron-accepting moieties.⁴³ The lowest value of the absorbance of 729.318 nm with a corresponding oscillation strength of 0.841 and 1.700 eV transition energy is observable in **NFBC4**. This absorbance value is enhanced in **NFBC3** by the inoculation of a powerful acceptor unit, to 789.657 nm with $f_{\text{os}} = 1.570$. This λ_{max} value increases to 839.546 nm in **NFBC2** with a corresponding transition energy of 1.476 eV. Furthermore, in **NFBC5** the absorbance value moved farther toward a red shift and the transition energy was also reduced to 1.435 eV. Similarly, the largest values of the absorbance are calculated in the case of **NFBC7** and **NFBC6** at 964.857 and 1000.598 nm, respectively, with transition energies of 1.285 and 1.239 eV showing 97% and 98% (HOMO → LUMO) electronic transitions, respectively. We observed that nitro ($-\text{NO}_2$) units installed in **NFBC6** and **NFBC7** permit more electronegative atoms to encourage an unexpected bathochromic shift in the optical rotational transitions of **NFBC6** and **NFBC7**. The nitro group is projected to shift the

Table 3. Global Reactivity Parameters of O-IDTBR1 and NFBC2–NFBC7 (in Units of eV)

compound	IP	EA	X	η	μ	ω	σ
O-IDTBR1	5.615	3.230	4.422	1.19	−4.423	8.201	0.419
NFBC2	5.110	3.307	4.208	0.901	−4.209	9.823	0.555
NFBC3	5.092	3.173	4.132	0.959	−4.133	8.899	0.521
NFBC4	5.064	3.001	4.033	1.031	−4.033	7.882	0.485
NFBC5	5.121	3.367	4.244	0.877	−4.244	10.268	0.570
NFBC6	5.162	3.658	4.410	0.752	−4.410	12.931	0.665
NFBC7	5.165	3.610	4.387	0.777	−4.388	12.379	0.643

transitions of NFBC6 even farther to the red. Electronegative substitution affects the electronic properties of NFBC6 to a much larger extent than anticipated. Consequently, NFBC6 might be regarded as an efficient NLO material on the basis of its highest $\lambda_{\max}$ value and smallest band gap. Overall, the increasing trend of the $\lambda_{\max}$ value is as follows: O-IDTBR1 < NFBC4 < NFBC3 < NFBC2 < NFBC5 < NFBC7 < NFBC6.

Global Reactivity Parameters. To successfully deduce the stability, chemical reactivity, and various other parameters, global reactivity parameters (GRPs) are employed.⁴⁴ The GRPs predict the chemical potential (μ), ionization potential (IP), electron affinity (EA), global softness (σ), hardness (η),⁴⁵ electronegativity (X)^{47,46} and electrophilicity index (ω)⁴⁷ of the studied compounds with the help of ΔE values calculated from FMO. All of these parameters were calculated by utilizing Koopmans's theorem⁴⁸ (eqs 1–7), and the results are collected and presented in Table 3.

$$IP = -E_{\text{HOMO}} \quad (1)$$

$$EA = -E_{\text{LUMO}} \quad (2)$$

$$X = -\frac{E_{\text{LUMO}} + E_{\text{HOMO}}}{2} \quad (3)$$

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

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

$$\sigma = \frac{1}{2\eta} \quad (6)$$

$$\omega = \frac{\mu^2}{2\eta} \quad (7)$$

The chemical hardness of a molecule is directly associated with the ΔE value, and an inverse relation is observed with the global softness and reactivity of the molecule under study. A greater ΔE value represents a harder, more stable, and less reactive system, whereas a smaller ΔE value signifies a softer, less stable, and greatly reactive molecule. The largest value of the hardness has been calculated in rgw case of O-IDTBR1 (1.1925 eV) which signifies a greater stability and lower reactivity, whereas the smallest value of hardness is observed at 0.752 eV for the NFBC6 system. The overall decreasing order of hardness in the entitled compounds is as follows: O-IDTBR1 > NFBC4 > NFBC3 > NFBC2 > NFBC5 > NFBC7 > NFBC6.

The highest global softness value is calculated to be 0.665 eV for NFBC6, which denotes its lower stability and greater reactivity factor, while the smallest value of 0.419 eV is observed in O-IDTBR1. The global softness values increase in

the following order: O-IDTBR1 < NFBC4 < NFBC3 < NFBC2 < NFBC5 < NFBC7 < NFBC6.

TDMs and Exciton Binding Energy (E_b). The TDM of three-dimensional nonfullerene acceptor-based chromophores have been calculated to elucidate the type and behavior of the transition in excited state.⁴⁹ A TDM analysis is achieved by utilizing data obtained by the transference of charges from the donor part to the acceptor part via the π -linker.⁵⁰ A TDM investigation of NF-based compounds demonstrates that the charge is effectively propagated from the donor to acceptor side lacking charge utilization by the π -bridge. For this objective, the compounds O-IDTBR1 and NFBC2–NFBC7 were evaluated with the aforementioned functional. The required atoms are separated into segments according to their contribution: i.e., donor (D), π -spacer (π), and acceptor (A). Hydrogen atoms have been omitted due to their low tendency in an effective charge transfer. All of the results for O-IDTBR1 and NFBC2–NFBC7 are shown in Figure 5.

Figure 5 illustrates that the electronic charge densities of the aforementioned chromophores are mostly on the diagonal of D as well as on π -linkers. A diagonal charge transfer is detected in all NF-based compounds investigated. The diagonal charge is effectively transferred via the π -bridge from the donor to the acceptor portion, which transfers the charge without or with less charge trapping.

The binding energy (E_b) is a useful tool to determine electronic properties of compounds. The E_b values of chromophores have been examined with the aforementioned functional. For the investigation of the hole interface (Coulombic force) with an electron, E_b values for all chromophores were calculated. Coulombic interactions and binding energies between holes and electrons are reciprocal of each other. If E_b is smaller, than larger charge mobilities would be observed.⁵¹ E_b has been investigated by using eq 8.

$$E_b = E_{\text{H-L}} - E_{\text{opt}} \quad (8)$$

In eq 8, $E_{\text{H-L}}$ is the band gap between LUMO/HOMO and (E_{opt}) is the first excitation energy.⁵² The investigated binding energies of O-IDTBR1 and designed chromophores are explained in Table 4. The binding energy of reference compound is noted as 0.538 eV. The binding energy values of compounds NFBC2–NFBC7 are 0.327, 0.349, 0.363, 0.319, 0.265, and 0.270 eV, respectively. All of the calculated values are given in Table 4.

From Table 4, it is clear that a change in the donor moiety plays a key role in lowering the binding energies. The binding energy values are noted to be in increasing order as follows: NFBC6 < NFBC7 < NFBC5 < NFBC2 < NFBC3 < NFBC4 < O-IDTBR1. All of the calculated designed molecules NFBC2–NFBC7 give lower values of binding energy in comparison to the reference compound O-IDTBR1. The NF-based designed compounds show promising binding energy

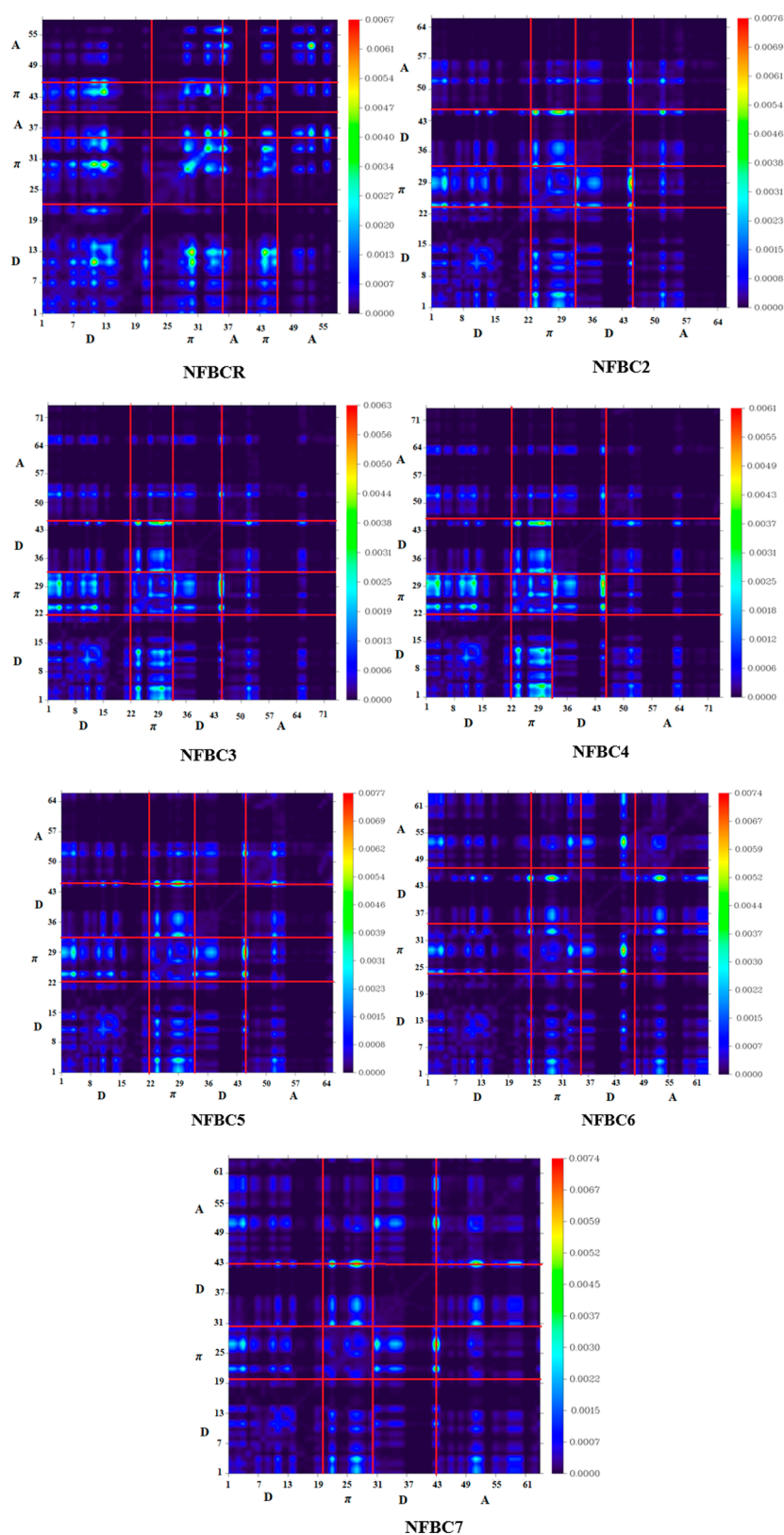


Figure 5. TDM graphs of compounds O-IDTBR1 and NFBC2–NFBC7.

values which may also suggest their use in a vast range of NLO applications.

Density of State. A DOS investigation was performed for an extension of results derived from the FMO charge distributions, as shown in Figure 6. The DOS reinforced the

particulars defined in the FMO analysis. Diverse acceptor entities change the distribution design of electrons on the molecular orbital, which was further affirmed by the DOS percentages on the HOMO–LUMO.⁵³ The energy gap also plays an essential role in determining the charge transference

Table 4. Calculated Energy Gaps ($E_{\text{H-L}}$), First Singlet Excitation Energies (E_{opt}), and Exciton Binding Energies (E_{b}) of the Investigated Compounds

compound	$E_{\text{H-L}}$ (eV)	E_{opt} (eV)	E_{b} (eV)
O-IDTBRI	2.385	1.847	0.538
NFBC2	1.803	1.476	0.327
NFBC3	1.919	1.57	0.349
NFBC4	2.063	1.70	0.363
NFBC5	1.754	1.435	0.319
NFBC6	1.504	1.239	0.265
NFBC7	1.555	1.285	0.270

of electrons due to the different nature of the A material utilized.⁵⁴ The HOMOs/LUMOs of **O-IDTBRI** are strongly located on acceptor and π -spacer moieties from both sides. In the case of **NFBC2**, the HOMOs are predominantly located over the donor part without the contribution of any acceptor chromophore. However, in the LUMOs, a lower electron charge density is found on the A group. This delocalization of electrons is also supported by DOS and percentage contributions of the HOMO and LUMO (Figure 4). Here, the donor contributes 17.0, 19.4, 15.1, 12.4, 19.6, 15.2, and 14.3% to the LUMO and 69.6, 94.9, 95.5, 96.3, 94.8, 94.3, and 94.6% to the HOMO in **O-IDTBRI** and **NFBC2**–**NFBC7**, respectively. The acceptor contributes 30.0, 35.4, 35.5, 38.5, 37.2, 59.5, and 60.4% to the LUMO and 9.6, 1.8, 1.2, 0.7, 1.9, 2.4 and 2.2% to HOMO for **O-IDTBRI**–**NFBC7**, respectively. Similarly, the π -linker contributes 52.9, 45.2, 49.4, 49.1, 43.2, 25.3 and 25.3% to LUMO whereas it contributes 20.8, 3.3, 3.2, 3.1, 3.3, 3.2, and 3.2% to the HOMO for **O-IDTBRI** and **NFBC2**–**NFBC7**, respectively. These significant contributions prove that variable acceptors can be facilitated *via* different means for electronic transitions. The density of states envisages that electrons with different withdrawing acceptors account for different electron density distribution patterns.

Each designed molecule is fragmented into three parts: i.e., acceptor, spacer, and donor. In the case of **O-IDTBRI**, the highest density on the HOMO at around -6.5 eV is localized on D, indicating that electrons transfer from the donor to the acceptor. These electronic transitions are the basis of ICT. For **NFBC2**, on the HOMO the maximum electron density around -5 eV is due to the presence of the donor, while on the LUMO the maximum density at around -3.5 eV is confined by the donor and π -linker. For **NFBC3**, most of the density on the HOMO in a range of around -5 eV is contained by the donor, while on the LUMO most of the density is around -3.3 eV and is confined by the donor and π -linker, thus indicating the transfer of electrons from the donor to the spacer. For **NFBC4** onward, on the HOMO a maximum density of around -5 eV is contained by the donor, and on the LUMO maximum density of around 2 – 4 eV is restricted by the acceptor, which not only increases the electron-withdrawing nature but also extends the conjugation. These energy series are valuable and explain that the acceptor is mainly responsible to increase the HOMO for the designed molecules.

Nonlinear Optics (NLO). In the past few decades, many organic-based NLO materials, due to their fast electronic response and low dielectric constant, have become important in optoelectronics applications.⁵⁵ Moreover, ICT and extensive delocalization of electrons in such compounds extend their applications to the field of optical fiber telecommunications. The noncentrosymmetric characteristics^{56–58} further trigger

the NLO responses, leading to better optical signal processing, high data rates, electro-optical modulation for data storage, and key functions such as frequency and potential harmonic generation in optical communications technology.⁵⁹ The NLO technique elaborates the concepts of polarizability (α) and first (β) and second hyperpolarizabilities (γ_{tot}) and determines the structural properties after these concepts are understood. There is a direct relationship between the optical response intensity and the electronic properties of the entire material, which is consistent with α , β , and γ .⁶⁰ It is verified from a literature review that a large value of linear polarizability gives higher β values. The NLO parameters, i.e. dipole moment (μ), average polarizability ($\langle\alpha\rangle$), and first (β_{tot}) and second hyperpolarizability (γ_{tot}) values, of the aforementioned compounds are displayed in Table 5, while their major contributing tensors are discussed in detail in Tables S8–S10.

The urea molecule is used as a standard molecule for the relative investigation of dipole moment and first hyperpolarizability values, as shown by a literature survey. The values of dipole moments found for all of the molecules are larger than that of urea (1.373 D).⁴² The overall dipole moments observed are as follows: **NFBC6** > **NFBC7** > **NFBC5** > **NFBC2** > **NFBC3** > **NFBC4** > **O-IDTBRI**. Similarly, the decreasing order of average linear polarizability of the entitled compounds is as follows: **NFBC6** > **NFBC7** > **NFBC5** > **NFBC2** > **O-IDTBRI** > **NFBC3** > **NFBC4**.

The designed compound **NFBC6** shows the highest average polarizability value (1956.433 au). However, **NFBC4** had the lowest β_{tot} value, due to the poor charge transfer. The incorporation of 8 and 14 fluorine atoms (electron acceptors) in **NFBC2** and **NFBC3** change the acceptance tendency to the opposite side. **NFBC2** has an effectively high NLO value due to the strong accepting tendency of the eight fluorine atoms present in it. There is a pyrido quinoline ring as a donor entity and 14 atoms of the fluoro ($-F$) atoms present in contrast in the case of **NFBC3**. Thus, the β_{tot} value was found to be quite lower in the case of **NFBC3** (590625.190 au) as compared to **NFBC2** (979137.839 au). This is based on the fact that the presence of a fluorine atom with cyclopentanone moieties offers a remarkably greater amplitude of intramolecular interaction energy, and as a result the strain energy is greatly increased. Among all derivatives, the lowest value of β_{tot} found is 344818.636 au in **NFBC4**, as the presence of a chlorine electron acceptor on the phenyl ring boosts the accepting power in **NFBC4**. The strong electron-accepting tendency of chlorine enhances the β_{tot} value in **NFBC5**, i.e. 1150372.918 au, as well as the NLO response. Better NLO responses are observed in **NFBC6** and **NFBC7** in comparison to the other designed compounds due to the incorporation of a nitro ($-\text{NO}_2$) group, which enhanced the accepting tendency of molecules from the opposite ends. The $-\text{NO}_2$ group is more electron withdrawing than $-\text{Cl}$ and, hence, effectively leads to better NLO dimensions for **NFBC6** and **NFBC7**. Moreover, there is a pyrene ring as a donor part along with the two chlorine atoms on the acceptor that compete from opposite ends in the case of **NFBC6**. In these molecules, the highest and the lowest NLO responses can also be analyzed by π -linked interactions within each donor- π -acceptor scheme studied. A greater electron delocalization means less of a HOMO–LUMO energy difference and an upsurge in hyperpolarizability (β_{tot}) values in the designed compounds. The β_{tot} values for all designed compounds decreased in the following order:

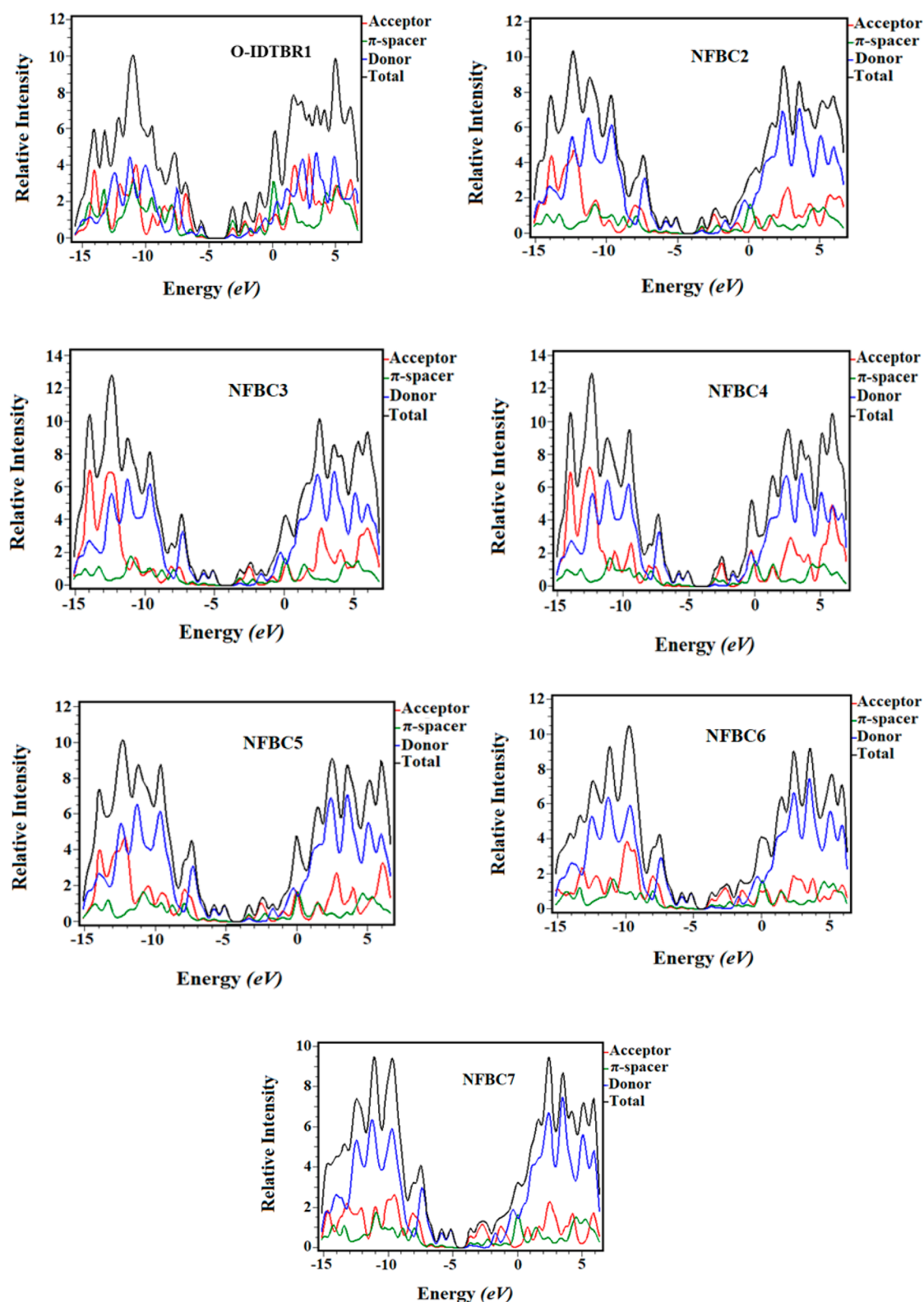


Figure 6. DOS plots of the reference O-IDTBRI and designed compounds NFBC2–NFBC7.

NFBC6 > NFBC7 > NFBC5 > NFBC2 > NFBC3 > NFBC4 > O-IDTBRI.

A related study has been performed with the standard urea molecule with a hyperpolarizability value of 43 au. The first hyperpolarizability values of NFBC2–NFBC7 are respectively 3825.363, 22770.65, 196875.1, 8019.038, 26752.86, 50136.93,

and 40847.81 times greater than the β_{tot} value of urea. The main reason behind this increase is the structural variations that result due to the incorporation of strong electron-withdrawing species in the designed compounds, resulting in large polarizability and larger NLO parameters. The first hyperpolarizability values are found in the reverse order of E_{gap}

Table 5. Dipole Moments, Average Polarizabilities, and First and Second Hyperpolarizabilities^a

compound	μ_{tot}	$\langle\alpha\rangle$	β_{tot}	$10^8\gamma_{\text{tot}}$
O-IDTBR1	1.6809	1489.200	164490.595	0.659
NFBC2	16.4066	1549.282	979137.839	2.721
NFBC3	13.4425	1399.576	590625.190	1.565
NFBC4	10.9079	1306.437	344818.636	0.854
NFBC5	17.3995	1661.909	1150372.918	3.330
NFBC6	21.7911	1956.433	2155888.013	7.868
NFBC7	20.4966	1789.312	1756455.686	6.155

^aDipole moments are given in units of debye (D); average polarizabilities and first and second hyperpolarizabilities are given in units of au.

values between the HOMO/LUMO orbitals. The highest value of γ_{tot} of 7.868×10^8 au is also found for NFBC6. Overall, the descending order of the aforementioned chromophores has been found to be as follows: NFBC6 > NFBC7 > NFBC5 > NFBC2 > NFBC3 > O-IDTBR1 > NFBC4. All of the derivatives expressed significant NLO responses with reduced band gaps, which elucidated that chromophores with an A- π -D architecture had more polarity in comparison to that of an A- π -D configuration.

CONCLUSION

Herein, seven new molecules with an A- π -D configuration have been explored, containing benzothiadiazole unit as a π -bridge and pyrido[3,2,1-ij]quinoline as a donor with different acceptor units via a reference molecule (O-IDTBR1). The energy band gap order is obtained as follows: NFBC6 < NFBC7 < NFBC5 < NFBC2 < NFBC3 < NFBC4 < O-IDTBR1. The UV-vis spectra of the investigated compounds are reported to have stronger absorption values and narrower transition energy values in comparison to O-IDTBR1 in chloroform. These designed derivatives with smaller E_b values in comparison to O-IDTBR1 offer less Coulombic force which affects the results. a TDM analysis indicated that the electronic transitions occur at the highest level via D and the spacer. The values of $\langle\alpha\rangle$, β_{tot} , and $\langle\gamma\rangle$ are found to be larger for the designed molecules in comparison to the reference (O-IDTBR1). Among the designed molecules, the values of $\langle\alpha\rangle$, β_{tot} and γ_{tot} are found to be 1956.433, 2155888.013, and 7.868×10^8 au, respectively, for NFBC6. To summarize all of the data, better results have been obtained for designed derivatives in comparison to O-IDTBR1. It can be concluded that the designed organic chromophores would be promising materials in the field of NLO.

COMPUTATIONAL PROCEDURES

A DFT-based exploration was performed to find optimized geometric and electronic parameters as well as NLO properties at the M06 level of theory with a 6-311G(d,p) basis set for the nonfullerene-based designed compounds NFBC2–NFBC7 with an A- π -D configuration with the help of the Gaussian 09 program.⁶¹ FMO and UV-vis analyses were carried out using the TDDFT approach with the same level and basis set as those for the aforementioned compounds. The computations and input files of nonfullerene compounds were developed using GaussView 9.0.⁶² A frequency analysis was also used to analyze the true minima of the compounds O-IDTBR1 and NFBC2–NFBC7 at the potential energy surface. The solvent effect was calculated by means of a conductor-like

polarizable continuum (CPCM) model.⁶³ An FMO examination was also used to compute the global reactivity parameters. For an interpretation of results from output files, Avogadro⁶⁴ and Chemcraft were employed.

The dipole moment was determined by using eq 9:⁶⁵

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \quad (9)$$

The linear polarizability $\langle\alpha\rangle$ was determined by using eq 10:⁶³

$$\langle\alpha\rangle = 1/3(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (10)$$

The magnitude of the total first hyperpolarizability (β_{tot}) was calculated by using eq 11:⁶³

$$\beta_{\text{tot}} = [(\beta_{xxx} + \beta_{xyy} + \beta_{zzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyz})^2]^{1/2} \quad (11)$$

An analysis of the Gaussian output file yielded 10 hyperpolarizability tensors oriented along the x , y , and z directions.

The second hyperpolarizability was determined by using eq 12:⁶³

$$\gamma_{\text{tot}} = \sqrt{\gamma_x^2 + \gamma_y^2 + \gamma_z^2} \quad (12)$$

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.1c06320>.

UV-vis data (wavelengths, excitation energies, and oscillator strengths), dipole moments, linear polarizabilities with major contributing tensors, and the first (β_{tot}) and second hyperpolarizabilities (γ_{tot}) with their contributing tensors of the reported compounds calculated using the M06/6-311G(d,p) basis set (PDF)

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Notes

The authors declare no competing financial interest.

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