

Quantum Chemical Designing of Novel Organic Non-Linear Optical Compounds

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In the present study, ten metal free non-linear optical (NLO) compounds have been designed. These compounds have designed by structural modification of (2-cyano-5-(4-(phenyl(4-vinylphenyl)amino)phenyl) penta-2,4-dienoic acid (TC4). Density functional theory was used for structure optimization and determination of photo-physical properties. These compounds contain triphenylamine as electron-donor and cyanoacrylic acid as acceptor. Five π -spacers are used to connect the donor and acceptor. Two auxiliary donors are also used to assist the donor. Results of this study indicate that stronger electron-donating auxiliary groups and longer π -conjugation enhance NLO response. Major absorption peaks of all systems were in the visible region. These absorption peaks are associated with the π - π^* transitions of the entire molecule. From calculations it is clear that all system will be good NLO material. The present calculations will provide new ways for experimentalists to synthesize high-performance NLO material.

Key Words : Polarizability, Hyperpolarizability, TC4, Density functional theory

Introduction

During the past two decades, molecular materials have attracted considerable attention due to their potential applications in novel optoelectronic devices for telecommunications, information storage, optical switching and signal processing.¹⁻³

Nonlinear optical properties of organic compounds have been the subject of intense research activity in the past two decades. The reason for the focus on organic compounds is the many advantages they possess compared to inorganic structures with respect to optoelectronics device applications. Among these are their ultrafast- and broadband-electronic responses, low dielectric constants, and negligible one-photon and two-photon absorptions at wavelengths used for optical-fiber telecommunications. In addition, the structure of organic compounds is relatively easy to modify *via* synthetic routes to meet specific needs of electro-optic device technologies.⁴

The advances made in the design and synthesis of suitable structures with large nonlinear optical coefficients have been, in large part, due to advances in the understanding of the microscopic origins of these phenomena by means of theoretical studies.⁵⁻¹⁰ These studies have established that the large nonlinearities observed in conjugated organic structures are due to virtual excitations of π -electron states whose properties are determined primarily by the correlated motions of the π electrons due to repulsive Coulomb interactions.

Most NLO compounds of this kind are absorbing in the visible spectrum. For a high-density optical storage, complete transparency in the visible is required. One approach to achieve this property is balancing the electro-active properties of the donor and acceptor substituents.¹¹ Another approach is the synthesis of molecules with a (σ - π)-conju-

gated frame.¹²

This study was carried out to design high response NLO compounds. We have designed ten new metal free organic NLO compounds by structural modification of TC4. We have studied the effect of modification on electronic and photo-physical properties with the help of DFT. Structural modification of TC4 is achieved by changing auxiliary donor and π -spacer. Two auxiliary donor ($-\text{OCH}_3$, $-\text{CH}=\text{C}(\text{CH}_3)_2$) and five π -spacers are used. This study will be helpful to design and fast screen other organic sensitizers.

Computational Detail. TD-DFT-B3LYP is unsuitable for the estimation of excitation energies.^{13,14} For all systems having a strong charge transfer (CT) nature, B3LYP, a global hybrid that does not incorporate long-range coulombic effects will fail.

Long-range-corrected CAM-B3LYP functional was used to optimize the geometries of systems. CAM-B3LYP provides reliable results and is widely used to describe the intramolecular charge-transfer states of organic systems.¹³ Calculations were performed using 6-311+G** basis set, which has already been proven to be an optimal compromise between accuracy and computational cost.^{15,16} Absorption spectra of systems simulate by using TDDFT calculations with CAM-B3LYP/6-311+G** level. The 10 lowest singlet-singlet excitation energies were computed.

Average polarizability (α) is determined by considering only the diagonal elements.¹⁷

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

Ten components (β_{xxx} , β_{xxy} , β_{xyy} , β_{yyy} , β_{xxz} , β_{xyz} , β_{yyz} , β_{xzz} , β_{yzz} and β_{zzz}) present in Gaussian 09W output file. First hyperpolarizability (β_{tot}) is calculated using following formula:¹⁷

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

Results and Discussion

Reference System. Metal free organic compounds show the following advantages as compared to metal complexes:

(1) They have better light-harvesting properties than metal base complexes (2) They provide opportunity to control the light absorption ranges from visible to near-IR due to their structural versatility (3) Have low manufacturing cost.¹⁸

Triphenylamine is widely used as an electron donor for metal-free sensitizers due to its excellent electron-donating capability.¹⁹ TC4 has TPA as donor and cyanoacrylic acid as acceptor. The fame of triphenylamine (electron-donor) and the cyanoacrylic acid (acceptor) as valuable functional groups, inspired to select TC4 as reference system.^{20,21}

Theoretical Designing of Systems. Criterion of large hyperpolarizability is being applied in the search of NLO metal complexes. From the sum-overstates (SOS) approach, a two-state model linked between β and a low-lying charge-transfer transition has been recognized.²² In the static case, the following model expression is employed to estimate β_{CT} :

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

where $\Delta\mu_{gm}$ is the change of dipole moment between the ground and m^{th} excited state, f_{gm} is the oscillator strength of the transition from the ground state (g) to the m^{th} excited state (m), and E_{gm} is transition energy. In the framework of two-state model expression, the second-order polarizability caused by charge transfer (β_{CT}) is proportional to the product

of the transition dipole moments and oscillating strength and is inversely proportional to the cube of the transition energy.

These factors (μ_{ge} , f_{gm} , and E_{gm}) are closely related with each other and are governed by choice/strength of the donor/acceptor along with the conjugated bridge. The most favourable combination of these factors can provide a larger β value.

The fundamental issue in this investigation is to increase the electronic communication between donor and acceptor and hence decrease the HOMO–LUMO gap. To fulfill this ambition structural modification is used.

New systems have been designed by structural modification of TC4. We can change the auxiliary donor, donor and π -spacer groups. The π -conjugated spacer between the electron-donor and acceptor group, plays an important role in tuning the non-linear optical properties. It also controls the intra-molecular electron-transfer.²³ Auxiliary donor also has significant impact NLO properties.

Structures of designed systems are given in Figure 1. We have not changed donor because the presence of TPA in system imparts excellent photophysical properties. We have added auxiliary donors with Triphenylamine unit, because the presence of secondary donor increases the electron-donating ability of the donor moiety.^{24,25} Two auxiliary donor dimethyl vinyl $-\text{CH}=\text{C}(\text{CH}_3)_2$ (system 1, 3, 5, 7 and 9) and methoxy (system 2, 4, 6, 8 and 10) are used. Modification of π -spacer is one of the approaches to improve the harvest of solar energy.²⁶ Electronic and NLO properties can be tuned using different π -spacers.²⁷ According to this clue, five π -spacers are used in designing. These π -spacers are selected to understand the effect of π -conjugation and electron-withdrawing atom (fluorine) at the π -spacer.

Increase of π -conjugation broadens the absorption spec-

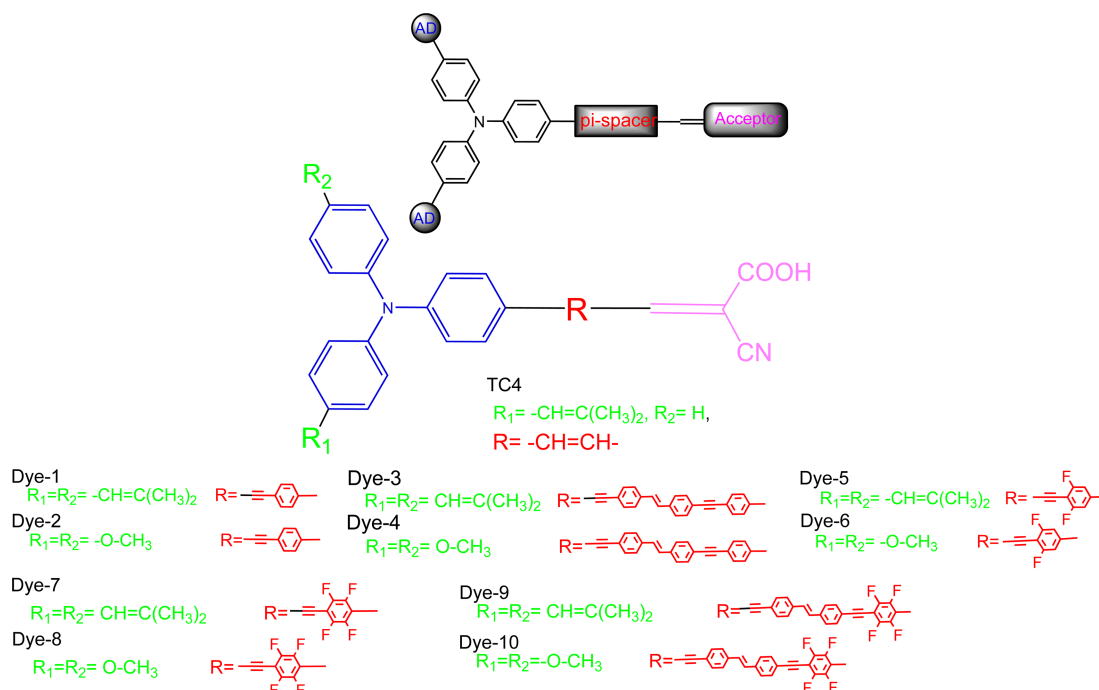


Figure 1. Structures of studied compounds.

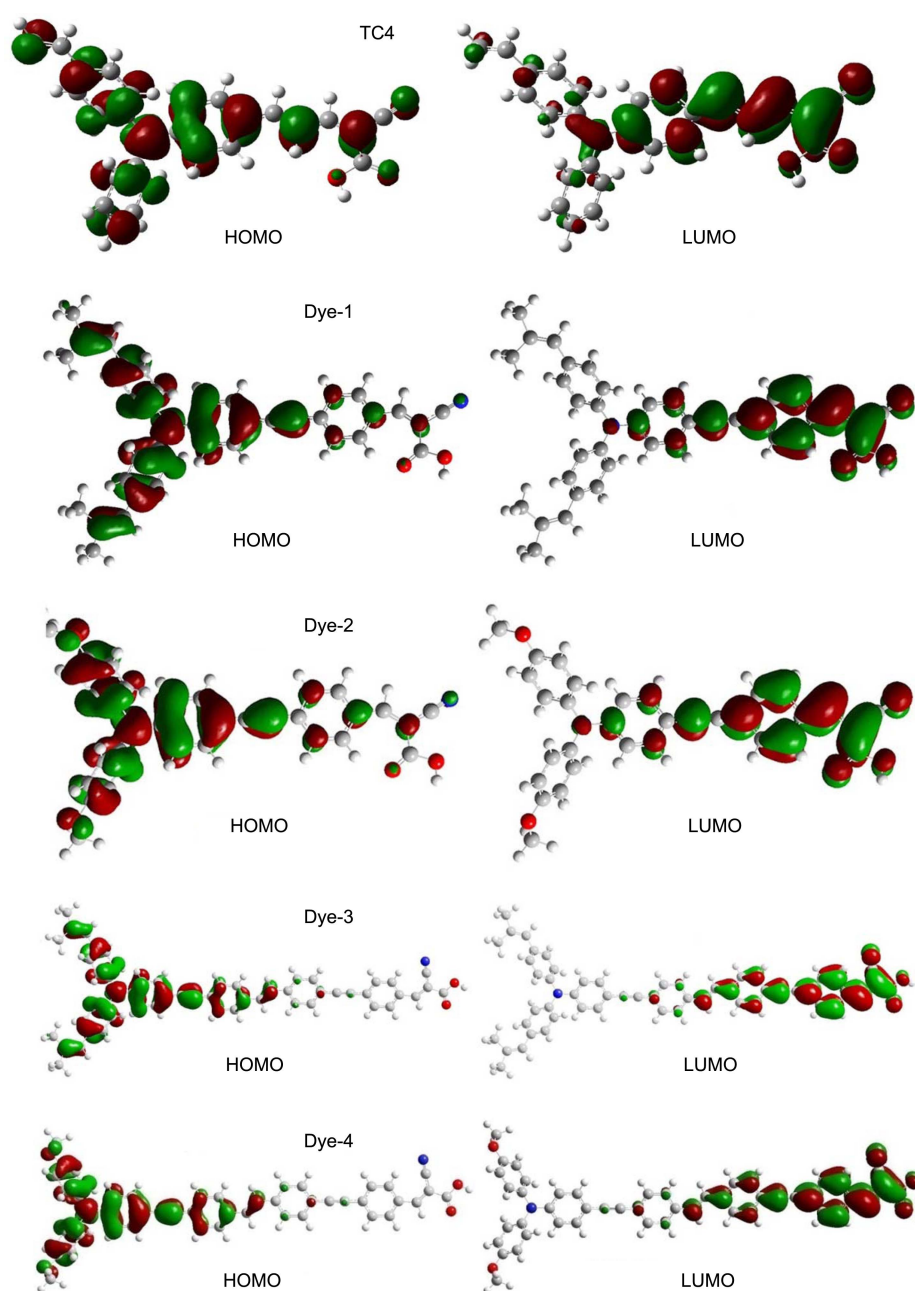
Table 1. E_{HOMO} , E_{LUMO} and energy gap (E_{g}) of studied systems (eV)

System	E_{HOMO}	E_{LUMO}	E_{g}
TC4	-5.17	-2.62	2.55
1	-4.98	-2.78	2.20
2	-4.95	-2.76	2.19
3	-4.88	-2.85	2.02
4	-4.82	-2.85	1.96
5	-5.02	-2.97	2.05
6	-4.98	-2.95	2.03
7	-5.13	-3.02	2.11
8	-5.04	-3.19	1.84
9	-4.88	-3.11	1.77
10	-4.82	-3.11	1.71

trum and results in red shift. It also decreases the HOMO and LUMO energy gap and thereby increases the solar cell performance.

HOMO-LUMO energy gap of TC₄ and all new systems are given in Table 1. Systems with longer π -conjugated chain have shown a smaller energy gap.²³ HOMO-LUMO energy gap of all new systems was lower than that of TC₄. Substitution of fluorine on π -spacer decreased the HOMO-LUMO energy gap. The above results indicate that the longer conjugate bridge and electron withdrawing atoms at the π -spacer result in smaller HOMO-LUMO energy gap.²⁸

In the ground state, distribution of the HOMO is mainly located on the electron-donor to the π -spacer. When radiations strike the system, electrons move from the HOMOs to the

**Figure 2.** HOMO and LUMO of studied systems.

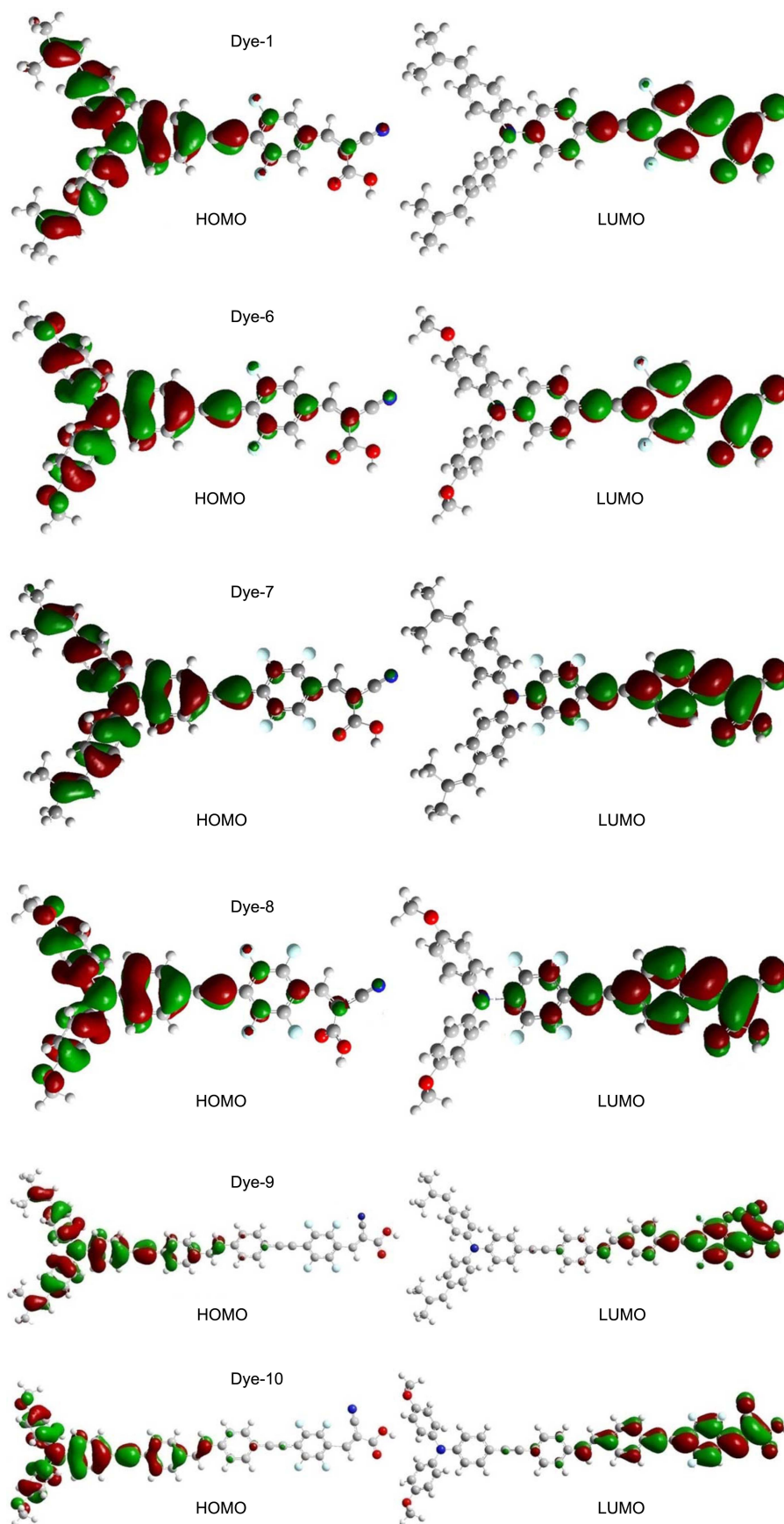
**Figure 2.** Continued.

Table 2. Dipole polarizabilities and major contributing tensors (1×10^{-24} esu)

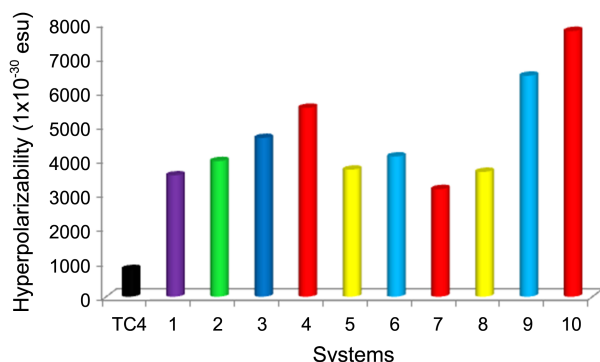
System	α_{xx}	α_{yy}	α_{zz}	α
TC4	108.41	38.59	116.64	87.88
1	196.58	166.05	73.24	145.29
2	265.88	176.00	79.76	173.88
3	298.13	171.71	101.55	190.46
4	293.67	170.34	106.35	190.12
5	260.22	177.54	84.39	174.05
6	184.92	137.91	80.79	134.54
7	193.67	157.64	68.78	140.03
8	190.41	128.99	79.93	133.11
9	276.69	206.36	81.99	188.35
10	274.98	209.62	86.11	190.23

LUMOs and reach the anchoring groups. From Figure 2 it is clear that for most of the systems HOMOs are present on the auxiliary donor, donor and some parts of the π -spacer near to donor, while LUMOs are present on acceptor and some parts of π -spacer near to acceptor. Such electron density distributions are beneficial for efficient charge separation and electron injection. This indicates the charge transfer from donor to acceptor through π -spacer.

Non-Linear Optical Properties. Polarizability of studied systems is given in Table 2. Polarizability of newly designed systems is very large as compared TC4. Longer conjugation is responsible for higher polarizability. Values α_{xx} tensor was very large as compared to other tensor.

Hyperpolarizability of studied systems is given in Table 3. From table it is clear that newly design systems have remarkable high β values as compared to TC4. This is due to the increase of π -conjugation. Longer conjugation results better charge transfer from donor to acceptor *via* π -spacer. From table it is also clear that systems with stronger electron-donating auxiliary group ($-\text{OCH}_3$) (systems 2, 4, 6, 8 and 10) have shown relatively high β values as compared to systems which contain $-\text{CH}=\text{C}(\text{CH}_3)_2$. Comparison of β values of TC4 and newly design systems is given Figure 3.

Higher NLO response of newly design compounds is due to a smaller energy gap between HOMO and LUMO as compared to TC4. These newly designed compounds would be ideal candidates to obtain materials with enhanced non

**Figure 3.** Comparison of β values of TC4 and newly design systems.**Table 3.** Second-order polarizabilities β_{tot} and major contributing tensors (β_{xxx} , β_{xxy} , β_{yyy} and β_{zzz}) (1×10^{-30} esu)

System	β_{xxx}	β_{xxy}	β_{yyy}	β_{zzz}	β_{tot}
TC4	-361.79	11.28	1.05	-317.16	804.89
1	-1829.70	1267.13	559.02	-584.68	3544.24
2	-1630.26	1400.10	1111.04	-286.01	3962.50
3	-2031.18	1704.41	1197.40	-331.59	4638.95
4	-2278.09	1950.44	1554.86	-376.28	5518.83
5	-1484.57	1333.04	1058.83	-288.82	3711.41
6	-1895.88	1494.68	895.74	-465.83	4096.06
7	-1480.20	1140.10	648.29	-395.43	3143.18
8	-1580.43	1313.05	867.96	-423.56	3646.83
9	-2799.15	2372.00	1699.40	-438.49	6456.69
10	-3045.74	2725.78	2346.64	-473.77	7765.79

Table 4. Excitation energy (E) Oscillator strength (f) and Transition character of studied systems (H = HOMO, L = LUMO, L+1 = LUMO+1, etc.)

System	E/eV	λ/nm	(f)	Major contribution	assignment
TC4	2.96	417	1.6630	H \rightarrow L (89%)	$\pi \rightarrow \pi^*$
	4.27	273	0.3554	H \rightarrow L+1 (71%)	$\pi \rightarrow \pi^*$
1	2.91	424	1.8461	H \rightarrow L (77%)	$\pi \rightarrow \pi^*$
	3.84	295	0.6918	H \rightarrow L+2 (86%)	$\pi \rightarrow \pi^*$
2	2.90	426	1.7670	H \rightarrow L (81%)	$\pi \rightarrow \pi^*$
	3.92	316	0.3617	H-1 \rightarrow L (72%)	$\pi \rightarrow \pi^*$
3	2.92	423	3.8470	H-1 \rightarrow L (84%)	$\pi \rightarrow \pi^*$
	3.60	344	0.7230	H \rightarrow L (71%)	$\pi \rightarrow \pi^*$
4	2.91	425	3.6550	H-1 \rightarrow L (78%)	$\pi \rightarrow \pi^*$
	3.59	345	0.5484	H \rightarrow L (58%)	$\pi \rightarrow \pi^*$
5	2.78	445	1.6404	H \rightarrow L (82%)	$\pi \rightarrow \pi^*$
	3.75	330	0.5495	H-1 \rightarrow L (66%)	$\pi \rightarrow \pi^*$
6	2.77	447	1.6121	H \rightarrow L (84%)	$\pi \rightarrow \pi^*$
	3.82	333	0.4737	H-1 \rightarrow L (74%)	$\pi \rightarrow \pi^*$
7	2.72	454	1.3863	H \rightarrow L (83%)	$\pi \rightarrow \pi^*$
	3.70	334	0.7538	H-2 \rightarrow L (58%)	$\pi \rightarrow \pi^*$
8	2.71	456	1.3568	H \rightarrow L (85%)	$\pi \rightarrow \pi^*$
	3.78	327	0.6374	H-1 \rightarrow L (62%)	$\pi \rightarrow \pi^*$
9	2.86	432	3.1400	H \rightarrow L (88%)	$\pi \rightarrow \pi^*$
	3.43	360	0.5070	H \rightarrow L+1 (61%)	$\pi \rightarrow \pi^*$
10	2.84	435	2.9229	H \rightarrow L (88%)	$\pi \rightarrow \pi^*$
	3.34	370	0.6590	H-1 \rightarrow L (73%)	$\pi \rightarrow \pi^*$

linear optical properties.

Absorption Spectra. TDDFT calculations have been performed to understand electronic transitions of all the studied systems. Energy, maximum wavelengths, oscillator strength, main configurations, and transition character are presented in Table 4. Simulated absorption spectra of systems are shown in Figures 4 and 5.

All the systems have shown absorbance in visible region. Spectra of all newly designed systems were red shifted as compared to TC4 due to the small energy gap resulting from better conjugation and an electron withdrawing atom on the π -spacer.^{29,30} Major absorption peaks of new systems exist between 423 and 456 nm. HOMO to LUMO transition is the most probable and lowest energy transition of all systems except system 3 and 4, for which HOMO-1 to LUMO is

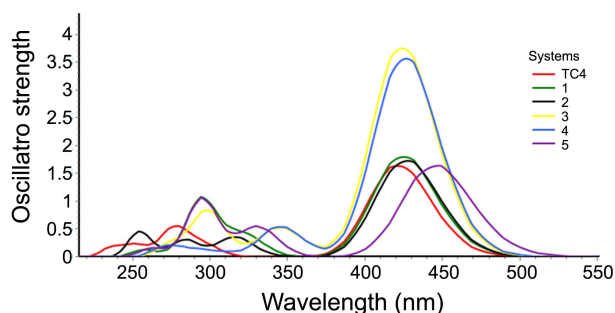


Figure 4. Absorption spectrum of studied systems (TC4, 1-5).

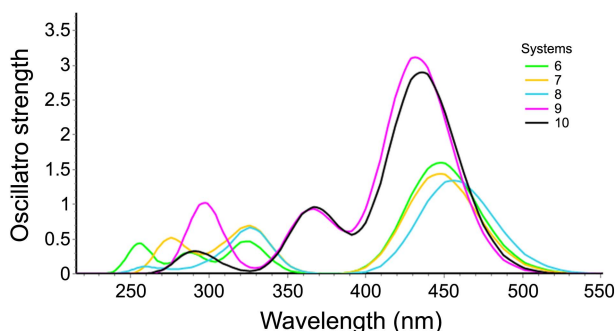


Figure 5. Absorption spectrum of studied systems (6-10).

transition is most probable transition.

Systems with a stronger electron-donating auxiliary group ($-\text{OCH}_3$) (systems 2, 4, 6, 8 and 10) showed slight red-shifted absorption relative to other systems which contain $-\text{CH}=\text{C}(\text{CH}_3)_2$. Auxiliary donors concentrate electron density on the electron-donor, which is the main chromophore responsible for the sensitization of photo-to-current conversion processes.

Systems 1, 3, 5, 7 and 9 have identical auxiliary electron-donor ($-\text{CH}=\text{C}(\text{CH}_3)_2$) but different π -spacer. System 5 and 9 with electron withdrawing fluorine has red-shifted absorption relative to system 1. Electron withdrawing fluorine decreases the energy of the LUMO and reduces HOMO-LUMO energy gap. Red-shift is due to a low HOMO-LUMO energy gap, which results in a low energy transition. Similarly system 6 and 10 have red-shifted absorption relative to systems 2 due to the presence of electron withdrawing fluorine. Systems 2, 6 and 10 also have identical auxiliary electron-donor ($-\text{OCH}_3$) but different π -conjugated spacer.

System 3 with longer π -conjugation has red-shifted absorption wavelength relative to system 1. Longer conjugation raises the HOMO energy level and reduces HOMO-LUMO energy gap. Red-shift is due to low HOMO-LUMO energy gap, which results low energy transition. Similarly system 4 has red-shifted absorption relative to systems 2 due to longer conjugation. Oscillating strength (f) is directly related to length of conjugation.²⁴

Conclusion

In this study we have reported theoretical designing of NLO compounds. All systems might be good NLO material.

All the design systems were better than TC4. Among designed systems, system 10 was highest non-linear optical properties. Effective π -conjugation between the donor and acceptor group of the system is more important than the electron donating ability of auxiliary donor to enhance the NLO properties. This study will pave way for experimentalists to design and synthesize efficient NLO materials.

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