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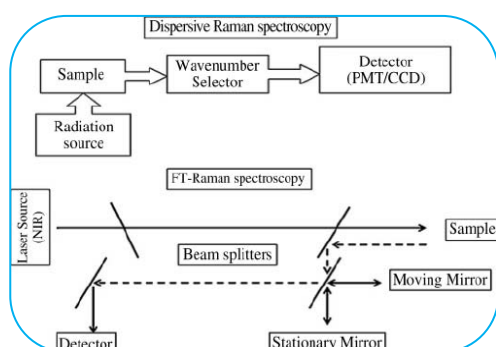
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DENSITY FUNCTIONAL THEORY CALCULATIONS, VIBRATIONAL SPECTRAL ANALYSIS AND LIGHT HARVESTING EFFICIENCY OF 2,4-DICHLOROMETHOXYBENZENE AS PI-CONJUGATE SPACER WITH DONOR-ACCEPTOR VARIATIONS EFFECT FOR DSSCs PERFORMANCE

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ABSTRACT:

The FT-IR and FT-Raman spectra of 2,4 dichloromethoxybenzene (2,4-DCMB) are recorded and analyzed. The spectra were taken with the assistance of normal coordinate analysis following full structure

optimization based on Density Functional Theory (DFT) using standard B3LYP/6-31G+(d) and 6-311G++(d,p) basis set. The IR and Raman spectra were predicted theoretically and compared with experimental spectra. The electronic and optical properties of the titled compound are studied theoretically. The quantum chemical parameters of the molecule are also calculated. Many approaches have been recently proposed to extend the efficiency of solar cells above the theoretical limit. The application of methoxybenzene in solar cell technology for improvement of harvesting the solar power efficiency (LHE) using organic sensitizers including donor, acceptor and binary linker conjugated bridges (D- π -A). The LHE, electron injection, exciton binding energy and open circuit voltage (V_{oc}) of 2,4-DCMB and their new designed dyes are investigated using TD-DFT.

KEYWORDS: FT-IR; FT-Raman; HOMO; LUMO; LHE; 2,4 dichloromethoxybenzene.

1. INTRODUCTION

Methoxybenzene could be recognized as monosubstituted aromatic hydrocarbon, which has an asymmetric substituent hooked up to the phenyl ring. It is of considerable interest attributable to the environmental concern and conjointly as a model compound for lot of chemically and biologically fascinating system [1]. Methoxybenzene and lot of its

derivatives are found in fragrances, as additive flavouring agent in food and also in the manufacture of different chemicals [2, 3]. Chloromethoxybenzene have immense interest because of their high environmental impact. They have been extensively found in air, in marine and seafood, in sediments and even in drinking water treated by the chlorination method [4, 5]. Depending on their physical and chemical properties of chloromethoxybenzene the environmental effects may vary. The functional groups present in

methoxybenzene leads to the variation of charge distribution within the molecule and consequently have an effect on the structural, vibrational and electronic parameters. In recent days, due to an economical concern as well as the shortage of electricity production needed for domestic and industrial usage, dye sensitized solar cells (DSSCs) have more attraction for the

conversion of solar power into electricity because of their high efficiency and low price [6]. The design and synthesis of functional dyes became attention of current analysis perspective of their potential application as sensitizers in dye-sensitized solar cells (DSSCs) technologies [7]. The designing of organic dyes sometimes adopt the donor- π -spacer-acceptor (D- π -A) structural motif so as to enhance the efficiency. The photovoltaic properties of such dyes are often clearly tuned by selecting appropriate groups within the D- π -A structure. The density functional theory (DFT) has emerged as a reliable customary tool for the theoretical treatment of structures further as electronic and absorption spectra. The computational cost of TD-DFT calculation has maintains uniform accuracy, so it is extensively used to study the structures and absorption spectra of sensitizing dyes for DSSCs.

In this paper, we studied the detailed spectral investigation of 2,4-DCMB using DFT (B3LYP) with 6-31G+(d) and 6-311G++(d,p). This study is also extended to focus on electronic and optical properties of the titled compound 2,4-DCMB. The Light Harvesting Efficiency of the titled compound and the new designed dyes are also obtained theoretically.

2. EXPERIMENTAL DETAILS

The titled compound 2,4-DCMB was acquired from Sigma Aldrich Company with a purity of 97% after that the compound is processed to record FT-IR and FT-Raman spectrum with no further purification. The FT-IR spectrum of the title compound is recorded in the region between 4000 – 400 cm^{-1} by using Bruker IFS 66V spectrometer with a MCT detector, KBr beam splitter and global source at a resolution of $\pm 2 \text{ cm}^{-1}$. For the title compound 2,4-DCMB, FT-Raman spectrum is recorded by using Bruker RFS 100/S (4000 – 100 cm^{-1}) with Neodymium doped Yttrium Aluminium Garnet (Nd:YAG) laser typically emit light with a wavelength of 1064 nm as the source of excitation at 200 mW power.

3. COMPUTATIONAL DETAILS

The vibrational frequency calculations and molecular geometry optimization of 2,4-DCMB were carried out with Gaussian 09W software packages developed by Frisch and co-workers [8]. The harmonic vibrational wave numbers combined with standard 6-31+G (d) and 6-311++G (d,p) basis sets was calculated using B3LYP, Becke's three hybrid functional parameter with Lee-Yang-Parr correlation methodology [9, 10]. Each parameter were permissible to relax and all the calculations are combined to optimized geometry that relates true minimum, as revealed by the absence of imaginary values within the wave number calculations [11,12]. The results obtained from GAUSSVIEW program is combined with symmetry considerations, vibrational frequency assignments were created with a high degree of confidence. The standardized analogy of DFT results with an experimental results showed that the method using functional B3LYP is the most promising to provide correct vibrational wave numbers [13].

4. RESULT AND DISCUSSIONS

4.1. MOLECULAR GEOMETRY

The geometrical parameters of the titled compound 2,4-DCMB were optimized with Becke3-Lee-Yang-Parr (B3LYP) at 6-31G+(d) and 6-311G++(d,p) basis sets using GAUSSIAN 09. The non-linear molecule having N atoms is adequate (3N-6) vibrational modes, except three translational and three rotational degrees of freedom [14]. The molecule is taken into an account under C1 point group symmetry. The optimized molecular structure of the titled molecule in accordance with the atom numbering scheme is shown in Fig. 1. The optimized structural parameters such as bond length, bond angle and dihedral angle are calculated for the molecule 2,4-DCMB and it is appeared in Table 1. The computed bond lengths and bond angles are compared with the experimental values. Both the values (calculated and experimental) are more or less same. The theoretical calculations are executed upon an isolated molecule in the gaseous phase however the experimental results are executed to the molecules in solid state [15].

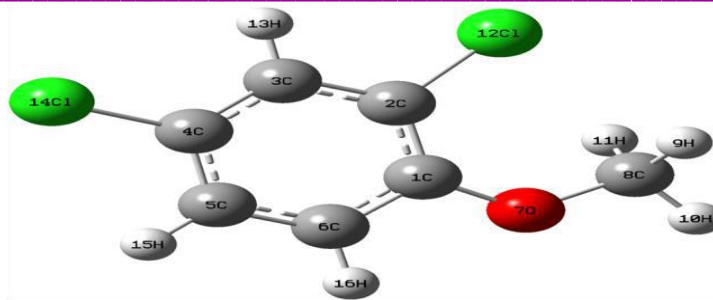


Fig. 1 Optimized molecular structure of 2,4-dichloromethoxybenzene

The optimized molecular geometry shows that methoxy group ($\text{O}-\text{CH}_3$) is substituted in the first position and the Cl group is substituted in the second and fourth positions of the ring. The bond length between C1-C6 has high value compared with remaining five C-C bonds in the ring. The experimental value of bond length between C1-O7 is 1.370 \AA [18] and the calculated bond length is 1.359 \AA . Due to the substitution of methoxy group in the first position of the ring the bond angle of C2-C1-C6 is 1.69 \AA which is compressed than the bond angle of C4-C5-C6 [16]. From this it is clear that the phenyl ring appears to be little distorted and the angles are slightly out of the perfect hexagonal structure.

4.2. VIBRATIONAL ASSIGNMENTS

The computed frequencies are calculated by using DFT/B3LYP/631G+d and 6311G++d,p basis set. The non-linear organic compound 2,4-DCMB consists of 16 atoms and its has 42 normal modes which are distributed as,

$$\sqrt{3N - 6} = 29 A' (\text{in plane}) + 13 A'' (\text{out of plane})$$

The vibrational assignments of 2,4-DCMB along with the calculated and experimental FT-IR and FT-Raman frequencies are displayed in Table 2 and the corresponding spectrums are shown in Fig. 2 and Fig. 3.

4.2.1 Methyl group Vibrations:

Each CH_3 group has basically nine fundamental vibrations namely: 1-symmetric stretching, 2-asymmetric stretching, 3-inplane bending and 3- out-of-plane bending. Generally in the aromatic ring, methyl group substituent is associated as giving an electron. For methoxy group compounds [17, 18], the asymmetric and symmetric stretching vibrations are usually appear in the range $2860 - 2935 \text{ cm}^{-1}$ and $2825 - 2870 \text{ cm}^{-1}$ respectively. The CH_3 stretching vibrations are identified at 3012 cm^{-1} in FTIR and the bands $3015, 2948$ and 2848 cm^{-1} in FT-Raman spectrum. The theoretically computed values $3134, 3123$ and 3044 cm^{-1} by DFT/B3LYP/6-311++G(d,p) are for asymmetric and symmetric stretching vibrations. The bending vibrations are usually observed at 1450 cm^{-1} for methyl substituted benzenes [19]. As expected, the peaks at $1489, 1448 \text{ cm}^{-1}$ in FT-IR and 1449 cm^{-1} in FT-Raman are observed due to CH_3 bending vibrations. The calculated values by DFT/B3LYP/6-311G++(d,p) for bending vibrations are obtained in $1511, 1501$ and 1476 cm^{-1} respectively. These theoretically calculated values are also well coincide with an experimental values.

4.2.2 C-H Vibrations:

The range $3000 - 3100 \text{ cm}^{-1}$ is the characteristic region for C-H stretching vibrations [20]. The expected stretching vibrations are assigned at $3102, 3075 \text{ cm}^{-1}$ in FT-IR and 3070 cm^{-1} for FT-Raman. The C-H in-plane and C-H out-of-plane bending vibrations are usually appears in the region of $1000 - 1300 \text{ cm}^{-1}$ and $1000 - 750 \text{ cm}^{-1}$ [21]. The in-plane bending vibrations are seen at the bands of $1280,$

1132, 1080 cm^{-1} in FT-IR spectrum and 1283 cm^{-1} in FT-Raman spectrum. The out-of-plane bending vibrations are identified at 883, 818 cm^{-1} in FT-IR and 823 cm^{-1} in FT-Raman for the titled compound (2,4-DCMB).

4.2.3 C-C Vibrations:

The (C=C) vibrations are all more fascinating if the double bonds are in conjugation with the ring [22]. In the ring C=C and C-C stretching vibrations are usually appears in the range 1625-1400 cm^{-1} and 1380-1280 cm^{-1} [23-25]. The C=C stretching vibration is observed at 1580 and 1400 cm^{-1} in IR spectrum and 1570 cm^{-1} in Raman spectrum. For the titled compound, C-C stretching vibrations are seen at 1300 cm^{-1} in IR spectrum and also the corresponding Raman spectrum are seen at 1241 cm^{-1} . And the in-plane bending and out-of-plane bending vibrations for the titled compound are observed at 732, 631 cm^{-1} and 415 cm^{-1} .

4.2.4 C-Cl Vibrations:

The C-Cl stretching vibrations are usually appears as a strong band in the region 760-505 cm^{-1} [20]. Most of the aromatic chloro compounds have a band of strong to medium magnitude within the region of 385-265 cm^{-1} for in-plane bending vibrations [26]. The C-Cl stretching vibration is observed at 648 cm^{-1} in FT-IR and 546 cm^{-1} in FT-Raman. The theoretically computed frequencies by DFT/B3LYP/6-311++G (d,p) method having 331 and 240 cm^{-1} for in-plane bending vibrations. The out of plane bending vibration for C-Cl is 164 and 106 cm^{-1} respectively.

4.2.5 O-CH₃ Vibrations:

The O-CH₃ stretching vibration is generally appeared in the region 1100-1000 cm^{-1} for methoxybenzene and its derivatives. In FT-Raman, O-CH₃ stretching vibration is observed at 1100 cm^{-1} . Raman Rao et al., has suggested an assignment for bending vibration of C-O-CH₃ within the range 670-300 cm^{-1} [27]. The C-O stretching vibration is observed at 1048 cm^{-1} in FT-IR spectrum and in-plane bending vibration is observed at 588 cm^{-1} in FT-Raman spectrum. The observed values are in good agreement with the literature data [28] and well coincides with the theoretically calculated values.

5. LOCAL REACTIVITY DESCRIPTOR

Fukui function (FF) is one of the broadly used local reactivity descriptor to display chemical reactivity as well as site selectivity [29]. The atom with highest Fukui function is highly reactive compared to the other atoms in the molecule. Fukui function is characterized as the subordinate of electron density $\rho(r)$ as for the complete number of electrons N in the system, at uniform external potential $v(r)$ following on an electron due to all the nuclei in the system, where μ is chemical potential of the system.

$$f(r) = \left[\frac{\partial \rho(r)}{\partial N} \right]_{v(r)} = \left[\frac{\delta \mu}{\delta v(r)} \right]_N$$

Electronic chemical potential is the derivative of total energy (E) with relevancy of an electron density. It is more convenient to represent the Fukui function values around every atomic site into a single value that characterizes the atoms in a molecule. In chemical reaction, a modification within the number of electrons involves the addition or subtraction of at least one electron within the frontier orbital. Throughout the reaction, behaviour of an electrophilic and nucleophilic attack depends on the local behaviour of molecule.

The condensed form of Fukui function is the more convenient way to study the local reactivity of the molecule at the atomic level which are expressed as follows: [30]

$$\begin{aligned} f_k^n &= [q_k(N+1) - q_k(N)], \text{ for nucleophilic attack,} \\ f_k^e &= [q_k(N) - q_k(N-1)], \text{ for electrophilic attack,} \\ f_k^r &= [q_k(N+1) - q_k(N-1)]/2, \text{ for radical attack} \end{aligned}$$

Table 1: The calculated geometric parameters of 2,4-dichloromethoxybenzene using DFT/B3LYP-631G+d and 6311G++d,p basis sets.

Parameters	Bond Length (Å)			Parameters	Bond Angle (Å)			Parameters	Dihedral angles(Å)	
	6-31G+(d)	6-311G++(d,p)	Exp.		6-31G+(d)	6-311G++(d,p)	Exp.		6-31G+(d)	6-311G++(d,p)
C1-C2	1.408	1.405	1.362	C2-C1-C6	117.189	117.081	120.7	C6-C1-C2-C3	0.002	0.002
C1-C6	1.410	1.407	1.384	C2-C1-O7	130.186	130.233		C6-C1-C2-C112	-179.996	-179.996
C1-O7	1.361	1.359	1.370	C6-C1-O7	112.626	112.686		O7-C1-C2-C3	-179.999	180.001
C2-C3	1.402	1.399	1.427	C1-C2-C3	120.593	120.680	120.8	O7-C1-C2-C112	0.003	0.003
C2-C112	1.765	1.766		C1-C2-C112	124.207	124.170		C2-C1-C6-C5	0.000	0.000
C3-C4	1.388	1.384	1.385	C3-C2-C112	115.200	115.150		C2-C1-C6-H16	180.000	180.000
C3-H13	1.084	1.081	1.08	C2-C3-C4	120.420	120.362	119.9	O7-C1-C6-C5	-179.999	-179.999
C4-C5	1.397	1.393	1.363	C2-C3-H13	119.045	119.072		O7-C1-C6-H16	0.001	0.001
C4-C114	1.757	1.757		C4-C3-H13	120.535	120.566		C2-C1-O7-C8	0.040	0.044
C5-C6	1.387	1.383	1.440	C3-C4-C5	120.287	120.336	119.3	C6-C1-O7-C8	-179.962	-179.957
C5-H15	1.085	1.082	1.08	C3-C4-C114	119.627	119.621		C1-C2-C3-C4	-0.002	-0.002
C6-H16	1.086	1.083	1.08	C5-C4-C114	120.086	120.043		C1-C2-C3-H13	179.999	179.999
O7-C8	1.430	1.431	1.422	C4-C5-C6	118.879	118.875	121.4	C112-C2-C3-C4	179.996	179.996
C8-H9	1.093	1.091	1.09	C4-C5-H15	120.607	120.576		C112-C2-C3-H13	-0.003	-0.003
C8-H10	1.092	1.089	1.09	C6-C5-H15	120.514	120.549		C1-C2-C112-C8	-0.018	-0.020
C8-H11	1.093	1.091	1.09	C1-C6-C5	122.633	122.666	118.5	C3-C2-C112-C8	179.984	179.983

* Ref. [15]

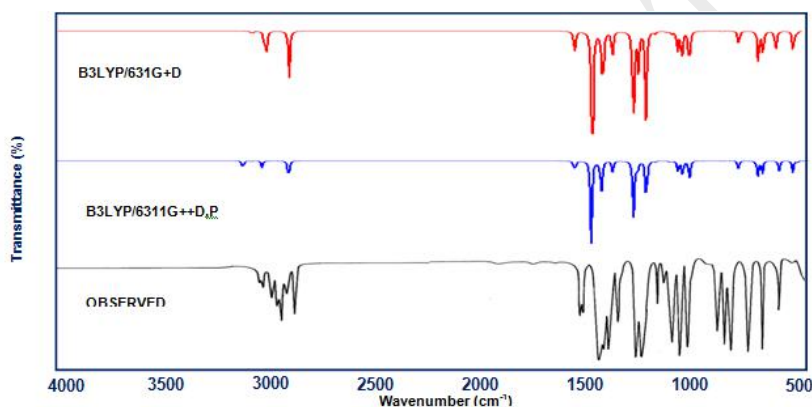


Fig. 2 Experimental and calculated FT-IR spectra of 2,4 dichloro methoxybenzene

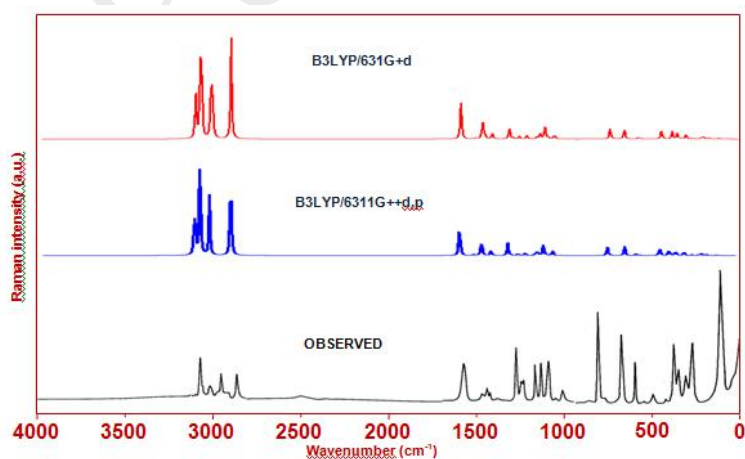


Fig. 3 Observed and simulated FT-Raman spectra of 2,4 dichloro methoxybenzene

Where $q_k(N)$, $q_k(N+1)$ and $q_k(N-1)$ are the charge for neutral, anionic and cationic species on the k^{th} atom of the molecule. The Fukui functions f_k^n and f_k^e will give the regions at which the molecule is most able to accommodate the addition and removal of an electron, respectively. The large values of f_k^n and f_k^e will point out the molecular regions susceptible to nucleophilic and electrophilic attacks.

A dual descriptor ($\Delta f(r)$) is proposed by Morel et al., [31] which is the difference between fukui functions such as nucleophilic and electrophilic attack. It is given by the equation,

$$\Delta f(r) = [f_k^n - f_k^e]$$

If the value of dual descriptor is positive then the site is favoured for a nucleophilic attack, whereas if it is negative then the site is favoured for an electrophilic attack. The values of local reactivity descriptors are calculated at B3LYP/6-311G++(d,p) method from Mulliken atomic charges in molecules which are listed in Table 3.

Table 2: Experimental FT-IR, FT-Raman and Calculated DFT-B3LYP/6-31G+(d), DFT-B3LYP/6-311G++(d,p) levels of vibrational frequencies (cm⁻¹), IR intensity (kmmol⁻¹) and Raman activity of 2,4-dichloromethoxybenzene

No	Observed frequencies (cm ⁻¹)		Calculated frequencies (cm ⁻¹)				IR Intensity (kmmol ⁻¹)		Raman Activity		Vibrational assignments/PED (≥ 10%)
	IR	Raman	B3LYP/6-31G+(d)		B3LYP/6-311G++(d,p)		B3LYP/6-31G+(d)	B3LYP/6-311G++(d,p)	B3LYP/6-31G+(d)	B3LYP/6-311G++(d,p)	
			Unscaled	Scaled	Unscaled	Scaled					
1	3102		3233	3108	3213	3105	0.271	0.750	74.327	72.627	v-CH(95)
2	3075		3227	3082	3208	3079	1.915	0.632	144.258	136.367	v-CH(93)
3		3070	3211	3073	3191	3076	2.025	1.169	71.611	68.661	v-CH(96)
4	3012	3015	3159	3020	3134	3023	20.135	18.999	122.377	117.239	v-CH ₂ as (95)
5		2948	3149	3009	3123	3112	22.721	21.419	43.912	42.007	v-CH ₂ as (97)
6		2848	3068	2905	3044	2901	58.619	54.238	161.747	176.085	v-CH ₂ s (96)
7	1580		1641	1589	1629	1586	7.183	6.736	40.699	40.705	Ring deformation(82), p-CH ₂ (13)
8		1570	1601	1581	1591	1578	22.511	24.422	3.834	3.776	Ring deformation(86), p-CH ₂ (12)
9	1489		1525	1501	1511	1504	219.112	219.928	1.472	1.248	δ-CH ₂ (68), β-CH(32)
10			1521	1467	1501	1464	1.594	21.384	6.339	5.012	δ-CH ₂ (88)
11			1520	1463	1496	1460	9.318	10.737	14.730	13.363	v-CC(76), p-CH ₂ (12)
12	1448	1449	1490	1452	1476	1455	83.489	68.526	6.725	5.354	p-CH ₂ (82), β-CH(13)
13	1400		1416	1409	1406	1405	36.176	31.147	7.423	6.600	v-CC(81), p-CH ₂ (15)
14	1300		1346	1311	1330	1309	138.807	147.877	14.971	16.700	Ring deformation(86), ω-CH ₂ (12)
15	1280	1283	1290	1288	1279	1291	48.029	34.197	1.341	1.023	β-CH(86)
16		1241	1271	1253	1254	1250	109.819	114.675	2.915	2.637	Ring deformation(73), v-CO(21)
17	1200		1215	1211	1204	1209	2.889	2.652	3.533	3.346	ω-CH ₂ (84), β-CH(14)
18		1149	1173	1154	1162	1151	1.197	0.694	2.028	2.583	ω-CH ₂ (91)
19	1132		1168	1135	1159	1137	3.934	4.402	6.445	6.275	β-CH(87)
20		1100	1125	1107	1117	1104	27.371	29.933	13.899	14.294	v-O-CH ₂ (72), β-CH(25)
21	1080		1084	1087	1067	1083	40.735	38.761	1.995	1.056	β-CH(64), v-CCl(32)
22	1048		1061	1053	1036	1051	50.905	51.603	5.272	6.440	v-CO(61), v-CC(34)
23	883		962	900	961	901	0.668	0.505	0.030	0.011	γ-CH(94)
24	818	823	880	823	879	825	19.564	20.337	0.012	0.023	γ-CH(92)
25	732		839	733	837	736	44.281	44.849	11.470	10.700	β-CC(65), β-CO(31)
26		700	829	711	829	714	34.354	33.257	0.315	0.261	γ-CH(87)
27	648		693	653	710	650	26.600	0.482	10.023	0.128	v-CCl(85)
28		631	680	640	692	637	1.349	26.811	0.242	10.161	β-CC(78), τ-CH ₂ (21)
29	564		653	571	653	574	28.986	31.062	1.664	1.624	β-O-CH ₂ (72), β-CH(14)
30		546	556	555	562	552	3.493	3.566	0.503	0.638	v-CCl(83)
31		438	548	439	546	436	1.198	1.184	8.472	8.308	β-CC(72), τ-CH ₂ (18)
32		415	461	416	462	419	3.630	3.269	0.025	0.008	γ-CC(86)
33		376	400	378	400	382	2.957	3.147	6.740	6.396	γ-O-CH ₂ (77)
34		346	377	349	377	346	0.118	0.098	4.833	5.082	β-CO(70)
35			332	330	331	333	0.494	0.441	0.863	0.590	β-CCl(66)
36			304	298	303	296	4.495	4.525	4.594	4.442	γ-CC(85)
37			264	255	255	252	0.431	0.362	0.727	0.859	τ-CH ₂ (93)
38		207	241	212	240	215	1.349	1.373	0.764	0.721	β-CCl(71)
39			192	200	192	197	0.185	0.197	2.389	2.428	γ-CC(78)
40			166	170	164	168	0.522	0.447	1.121	1.076	γ-CCl(59), γ-CC(36)
41			107	112	106	109	1.190	1.175	0.605	0.567	γ-CCl(64)
42			77	83	80	86	5.897	5.928	0.013	0.013	γ-CO(58)

Abbreviations: s-symmetrical, as-asymmetrical, v-stretching, β-in-plane bending, γ-out of plane bending, τ-torsion, δ-scissoring, ω-wagging, ρ-rocking and t-twisting

Table 3: Condensed Fukui functions for 2,4-dichloromethoxybenzene calculated at B3LYP/6-311G++(d,p) method

Atom	$q_k^{(N+1)}$	$q_k^{(N)}$	$q_k^{(N-1)}$	f_k^+	f_k^-	f_k^r	Δf_r	s_k^+	s_k^-	s_k^r	ω_k^+	ω_k^-	ω_k^o
C1	0.052	0.389	0.179	-0.337	0.210	-0.063	-0.548	-0.130	0.081	-0.024	-1.103	0.688	-0.208
C2	0.792	-0.302	0.133	1.094	-0.434	0.330	1.528	0.421	-0.167	0.127	3.577	-1.421	1.078
C3	-0.082	0.069	-0.074	-0.152	0.144	-0.004	-0.295	-0.058	0.055	-0.002	-0.496	0.469	-0.013
C4	0.051	-0.314	0.301	0.365	-0.615	-0.125	0.980	0.140	-0.237	-0.048	1.192	-2.011	-0.409
C5	-0.041	-0.004	-0.052	-0.037	0.047	0.005	-0.084	-0.014	0.018	0.002	-0.119	0.155	0.018
C6	0.039	-0.210	0.094	0.249	-0.305	-0.028	0.554	0.096	-0.117	-0.011	0.815	-0.997	-0.091
O7	0.004	-0.536	0.245	0.539	-0.781	-0.121	1.320	0.208	-0.301	-0.046	1.764	-2.553	-0.395
C8	0.004	-0.284	-0.015	0.288	-0.269	0.009	0.557	0.111	-0.104	0.004	0.942	-0.880	0.031
H9	-0.001	0.203	0.014	-0.205	0.190	-0.007	-0.394	-0.079	0.073	-0.003	-0.669	0.620	-0.024
H10	-0.001	0.200	0.000	-0.201	0.200	0.000	-0.401	-0.077	0.077	0.000	-0.657	0.655	-0.001
H11	-0.001	0.203	0.014	-0.205	0.190	-0.007	-0.394	-0.079	0.073	-0.003	-0.669	0.620	-0.024
Cl12	0.233	-0.002	0.048	0.235	-0.050	0.092	0.285	0.090	-0.019	0.036	0.768	-0.163	0.302
H13	0.030	0.217	0.002	-0.186	0.215	0.014	-0.402	-0.072	0.083	0.006	-0.610	0.704	0.047
Cl14	0.012	-0.011	0.117	0.024	-0.128	-0.052	0.152	0.009	-0.049	-0.020	0.078	-0.419	-0.171
H15	0.001	0.192	0.001	-0.190	0.191	0.000	-0.381	-0.073	0.074	0.000	-0.622	0.624	0.001
H16	0.012	0.189	-0.006	-0.177	0.195	0.009	-0.372	-0.068	0.075	0.003	-0.580	0.638	0.029

Table 4: The DFT/ B3LYP/6-31G+(d) and B3LYP/631G++(d,p) calculated electric dipole moments (Debye), Dipole moments compound, polarizability (in a.u.), β components and β_{tot} (esu) value of 2,4-dichloromethoxybenzene and its derivatives (NON LINEAR OPTICAL PROPERTIES)

Parameters	B3LYP/6-31+G(d)	B3LYP/6-311++G(d,p)	631G+d (Ben:CN)	631G+d (Ben:COOH)	631G+d (Ben:NO ₂)	631G+d (Thio:CN)	631G+d (Thio:COOH)	631G+d (Thio:NO ₂)
μ_x	-0.8211	1.9779	5.0874	1.7172	5.1112	5.3166	-2.0449	5.3503
μ_y	0.4328	-0.7696	1.2948	2.4595	1.181	0.3165	-1.748	0.2368
μ_z	0.001	0.001	-0.0027	0.0018	-0.0013	-0.0027	0.0004	-0.0027
μ_{tot}	0.9281	2.1223	5.2496	2.9997	5.2459	5.326	2.6901	5.3555
α_{xx}	-71.7517	-68.8012	-137.7392	-118.2187	-136.3106	-137.2025	-118.5495	-135.7551
α_{yy}	-71.7991	-70.336	-104.928	-117.1588	-113.4308	-106.8923	-118.2776	-115.4204
α_{zz}	-74.3601	-74.7936	-119.4389	-124.9474	-123.4281	-119.9895	-125.499	-123.973
α_{xy}	4.7101	0.989	-5.7516	-13.4063	-5.2928	-5.2462	-15.0661	-5.8249
α_{yz}	-0.002	0.0036	0.0105	-0.0046	0.0141	0.0106	0.0102	0.0082
α_{zx}	-0.0062	-0.0008	0.0117	0.008	0.0035	0.009	-0.012	0.0066
$\Delta\alpha(esu)$	-72.63696	-71.31026	-120.702	-120.108	-124.389	-121.361	-120.775	-125.049
β_{xxx}	-35.0263	52.455	192.4729	-11.7467	115.5716	211.1007	-19.8533	136.0893
β_{yyy}	6.2119	-2.3394	35.8366	34.7191	34.6697	30.0878	-29.1898	28.8105
β_{zzz}	0.0043	0.0011	-0.0007	0.0199	0.0226	0.0066	0.0245	0.0274
β_{xyx}	14.2327	-8.0599	7.8109	15.208	11.283	7.0852	-9.2826	10.3658
β_{xyy}	-7.4649	-3.7415	4.5965	44.4856	-1.2828	-7.7659	-44.2619	-8.5856
β_{xyx}	0.0031	0.0092	-0.0773	0.0743	-0.0257	-0.0825	0.0406	-0.0557
β_{yyx}	-5.0015	-8.0599	-18.471	-30.9067	-34.2088	-13.7718	26.0002	-29.2645
β_{yxx}	-3.4626	-3.7415	6.6138	5.9018	5.8003	8.4047	-8.1365	8.1973
β_{yyz}	-0.0043	0.0092	-0.0067	0.0037	0.004	-0.0097	-0.0078	-0.0114
β_{zxx}	-0.0063	-0.0051	0.0215	-0.0169	0.0096	0.0215	-0.0009	0.0312
$\beta_{tot}(esu)$	1.958E-30	2.8104E-30	1.4023E-29	6.6769E-30	7.5109E-30	1.5434E-29	6.0964E-30	9.0039E-30

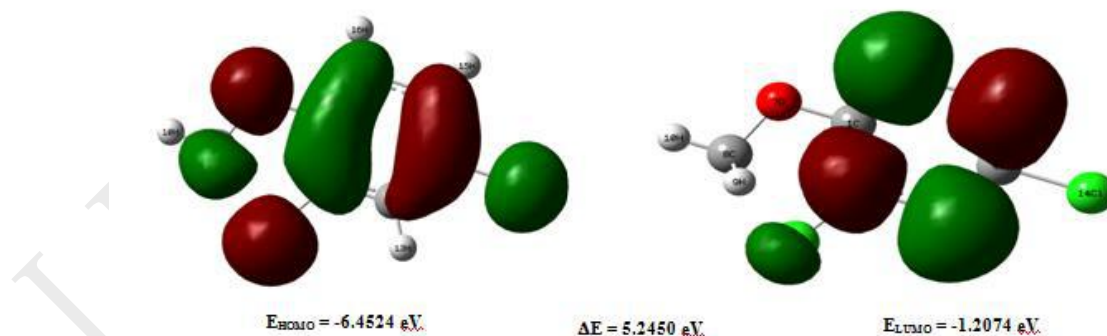


Fig. 4 HOMO - LUMO plot of 2,4-dichloromethoxybenzene

6. FIRST ORDER HYPERPOLARIZABILITY

Non linear optics is an interaction of applied electromagnetic fields in several materials to produce new electromagnetic fields [32]. Organic molecules are used in technologies like fibre optical communication and optical computing [33, 34]. Generally these materials have high molecular hyperpolarizabilities due to that the molecule has variety of NLO properties.

The electronic and vibrational supplement to first order hyperpolarizabilities are thought about hypothetically for organic and inorganic systems. The values of first order hyperpolarizability were ascertained to be very extensive for pi-conjugated molecules with an electron giving and therefore an electron accepting substituent connected to the aromatic ring, as compared with the monosubstituted molecule [35]. The thought of boosting NLO properties for an organic material is still followed by the conventional method. For the designing of second-order NLO materials, a theoretical calculation on molecular hyperpolarizability is one of the key factors [36, 37]. The hyperpolarizability is useful in understanding the relationship between the structure and nonlinear optical properties of the molecule. This theoretical information gives a supportive guidance to experimentalists to design as well as synthesis of new NLO materials [38].

The first order hyperpolarizability of titled compound is calculated using B3LYP/6-31G+(d) and 6311G++(d,p) basis set, established on finite field approach. The components of first order hyperpolarizability (β) are characterized as the coefficient in Taylor's series expansion of energy in an external electric field [39]. The energy of an uncharged molecule under electric field can be expressed by Buckingham type expansion [40].

$$E = E_0 - \mu_\alpha F_\alpha - \frac{1}{2} \alpha_{\alpha\beta} F_\alpha F_\beta - \frac{1}{6} \beta_{\alpha\beta\gamma} F_\alpha F_\beta F_\gamma + \dots$$

where, E is the energy of a molecule under the electric field F, E_0 is the energy of an unperturbed free molecule, F_α is the field at the origin, μ_α , $\alpha_{\alpha\beta}$ and $\beta_{\alpha\beta\gamma}$ are the components of dipole moment, polarizability and first order hyperpolarizabilities respectively.

The total dipole moment (μ) and first order hyperpolarizability (β) are calculated for monosubstituted aromatic hydrocarbon and the new designed dyes which are listed in Table 4. The better results were obtained by using different donors and acceptors and the titled compound is as π -linker (D- π -A). The large value of hyperpolarizability is a measure of non-linear optical activity of the sub-atomic system is expounded with the intermolecular charge transfer, ensuing from the electron cloud movement through pi-conjugated system from electron benefactor to electron acceptor gatherings. From the results the new designed dye 2,4-DCMB4 (ie. Thiophene and Cynate are substituted as donor and acceptor) is most efficient for intermolecular charge transfer upon photo excitation.

7. ELECTRONIC AND UV-VIS SPECTRAL PROPERTIES

7.1 ELECTRONIC PROPERTIES

Among electronic applications of these materials as associate organic photovoltaic cell, the theoretical information concerning the energy levels (HOMO and LUMO) of the components is mandatory. The HOMO and LUMO energies of the molecules are combined to create frontier molecular orbital (FMO). The FMOs strongly participate in investigating the electronic and chemical properties of the molecule [41]. HOMO and LUMO acts as an electron donor and electron acceptor and the corresponding energy segments are an essential element for photovoltaic devices to decide if effective charge transfer will occur within the molecule [42, 43].

The HOMO-LUMO energies and band gaps for the titled compound and additionally for six new designed dyes are calculated by using B3LYP/6-311++G (d,p) basis set which are listed in Table 5 and the corresponding HOMO-LUMO image is shown in Fig. 4. The dye 2,4-DCMB6 has lowest energy gap (E_g). Due to this reason this dye has the most outstanding photo physical property which shows a powerful impact of intramolecular charge transfer than others (ie. band gap value is smaller than that of other Dyes and the titled compound). From that the dye 2,4-DCMB6 which might make the absorption spectra red shifted.

7.2 GLOBAL REACTIVITY DESCRIPTOR

Nature of the molecule is understood with the help of global reactivity descriptors. Based on density functional theory, global reactivity descriptors of compounds such as hardness, chemical potential, softness, electronegativity and electrophilicity index as well as local reactivity have been defined.

From Koopman's theorem, the ionization potential (I) and electron affinity (A) are the energies of HOMO and LUMO with change of sign [44]

$$\text{Ionization potential (I)} = -E_{\text{HOMO}}; \text{ Electron affinity (A)} = -E_{\text{LUMO}}$$

Electron affinity is the negative energy of LUMO which measures the capability of electron acceptance from an electron donor. The quantity of energy required to extract an electron from an atom is characterized as ionization potential (I). If the ionization energy is high, atoms in the molecule have high stability and chemical immobility and if it is low, then the molecule has high reactivity [45]. The molecular stability and reactivity are measured from absolute hardness and softness [46]. The electrochemical potential (μ) measures an escaping tendency of an electrons and it is very well may be related with the molecular electronegativity in a compound [47].

Using Koopman's theorem for closed shell compounds, hardness (η), softness (S) and chemical potential (μ) can be defined as,

$$\eta = \frac{I-A}{2} \text{ -----(1); } S = \frac{1}{2\eta} \text{ -----(2) and } \mu = \frac{-(I+A)}{2} \text{ -----(3)}$$

The electrophilicity index (ω) as a measure energy lowering due to maximal electron flow among donor and acceptor which was proposed by Parr et al. [48]. It is a combined descriptor which contains electronic chemical potential (μ) and absolute hardness(η). They characterized electrophilicity index (ω) as follows:

$$\omega = \frac{\mu^2}{2\eta} \text{ -----(4)}$$

Maximum amount of electronic charge that an electrophile system may accept is given by the following equation.

$$\Delta N_{max} = -\frac{\mu}{\eta} = \frac{\omega}{\eta} \text{ -----(5)}$$

The two new reactivity indices nucleofugality (ΔE_n) and electrofugality(ΔE_e) are proposed by Ayers and co-workers. It is used to quantify the nucleophilic and electrophilic capabilities of leaving group. They can be defined as follows,

$$\Delta E_n = A + \omega = \frac{(\mu+\eta)^2}{2\eta} \text{ -----(6)} \quad \Delta E_e = I + \omega = \frac{(\mu-\eta)^2}{2\eta} \text{ -----(7)}$$

Gomez et al. proposed an uncomplicated charge transfer exemplary for donation and back-donation of charges [49]. An electronic back-donation mechanism is an interaction between the inhibitor molecule and the metal surface. This idea builds up that if both progresses occur, namely charge transfer to the molecule and back-donation from the molecule. Thus the energy change is preciously proportional to the hardness of the molecule. It can be denoted by the subsequent equation,

$$\Delta E_{back-donation} = -\frac{\eta}{4} \text{ -----(8)}$$

The values of hardness, softness, electrochemical potential, electrophilicity index, maximum charge transfer ΔN_{\max} are summarized in Table 5. It is shown that the value of 2,4-DCMB has the largest chemical hardness and progressively negative chemical potential which is less stable and more reactive compared with the others. The hardness value is decreased by substituting the donor and acceptor to the titled molecule. The reactivity data displays if a molecule is equipped for giving charge. A nucleophile is described by a lower value of electrophilicity index, while higher values indicate the existence of a decent electrophile. By comparing with all those dyes, the Dye 6 (Thiophene as donor and NO_2 as acceptor) have the lowest hardness value, high value of electrophilicity index, maximum charge transfer, high (ΔE_n) and (ΔE_e) values. From the results, the dye 2,4-DCMB6 is the best inhibitor (ie. it has the highest value) than the others.

Table 5: Quantum Chemical Parameters: HOMO-LUMO energies, Energy gap, Global reactivity descriptors and Back donation of 2,4-dichloromethoxybenzene calculated at B3LYP/6-311++G(d,p) basis set.

Parameters	Values (eV)						
	2,4DCMB	2,4DCMB1	2,4DCMB2	2,4DCMB3	2,4DCMB4	2,4DCMB5	2,4DCMB6
HOMO energy	-6.4524	-6.6428	-6.0611	-6.3016	-6.4216	-6.0548	-6.2951
LUMO energy	-1.2074	-2.0375	-2.0145	-2.6925	-2.0825	-2.049	-2.7116
Energy gap	5.2450	4.6053	4.0466	3.6091	4.3391	4.0058	3.5835
Hardness(η)	2.6225	2.3027	2.0233	1.8046	2.1696	2.0029	1.7918
Softness(S)	0.1907	0.2171	0.2471	0.2771	0.2305	0.2496	0.2791
Chemical potential(μ)	-3.8299	-4.3402	-4.0378	-4.4971	-4.2521	-4.0519	-4.5034
Electrophilicity index(ω)	2.7966	4.0903	4.0290	5.6035	4.1667	4.0985	5.6593
Charge Transfer (ΔN_{\max})	1.4604	1.8849	1.9957	2.4921	1.9599	2.0230	2.5134
Nucleofugality (ΔE_n)	0.2779	0.9014	1.0029	2.0087	0.9995	1.0481	2.0518
Electrofugality (ΔE_e)	7.9377	9.5817	9.0785	11.0028	9.5036	9.1519	11.0585
Back donation ($\Delta E_{\text{back-donation}}$)	-0.6556	-0.5757	-0.5058	-0.4511	-0.5424	-0.5007	-0.4479

Table 6: Calculated light harvesting efficiency (LHE) of 2,4-dichloromethoxybenzene and its derivatives calculated using TD-DFT/B3LYP/6-31+G(d) basis set.

System	Wavelength (λ) nm	Excitation energy (E) eV	Oscillator Strength (f)	LHE
2,4DCMB	273.78	4.5286	0.0497	0.1081
2,4DCMB1 (Ben+CN)	301.53	4.1119	0.2097	0.3829
2,4DCMB2 (Ben+COOH)	321.34	3.8583	0.1568	0.3031
2,4DCMB3 (Ben+NO ₂)	353.69	3.5055	0.1294	0.2576
2,4DCMB4 (Thio+CN)	314.29	3.9449	0.3049	0.5044
2,4DCMB5 (Thio+COOH)	302.71	4.0958	0.2665	0.4586
2,4DCMB6 (Thio+NO ₂)	366.48	3.3831	0.1938	0.3599

7.4 LIGHT HARVESTING EFFICIENCY FOR DSSCs

The Light Harvesting Efficiency (LHE) is extremely vital factor for the organic dyes within the DSSC, i.e. absorbs photonic energy and injecting photoexcited electrons to the conduction band of the semiconductor [50]. It can be expressed as,

$$\text{LHE} = 1 - 10^{-A} = 1 - 10^{-f}$$

Where, f is the oscillator strength of the dye associate to the wavelength λ_{\max} . We have a tendency to ascertain that the larger value of f, obtained the higher LHE value. For an efficient photocurrent response, the LHE of the dye molecule ought to be high. The values of LHE are calculated

for all the dyes and it is shown in Table 6. The D- π -A structure scheme is shown in Fig. 6a and chemical structure of 2,4-dichloro methoxybenzene for newly designed dyes is shown in Fig. 6b. The LHE values are calculated in gaseous phase. Out of seven, together with 2,4-DCMB dyes, 2,4-DCMB4 is producing most efficient LHE than other dyes.

7.5 ELECTRON INJECTION

The efficiency of solar cell is extremely depends on the electron injection from an excited state of the molecule to the conduction band of the semiconductor and it was theoretically proposed by Preat et al. [51-53].

The free energy change (in eV) for the electron injection can be expressed as,

$$\Delta G^{inject} = E_{OX}^{dye*} - E_{CB}^{TiO_2} \text{ -----(1)}$$

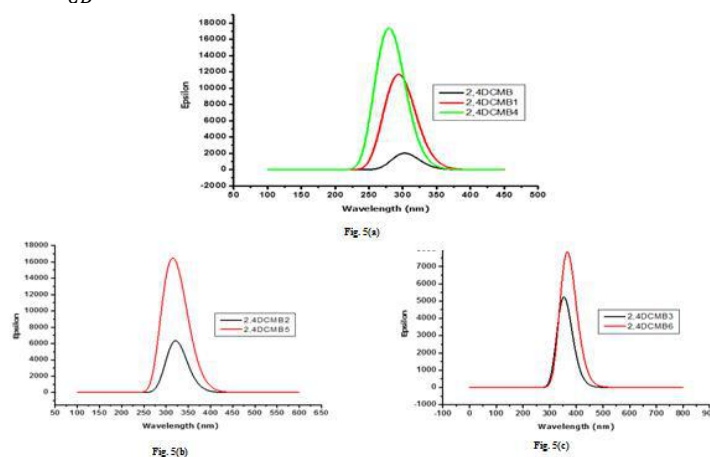


Fig. 5 (a), (b) (c) Theoretical UV-Vis spectrum of 2,4-dichloro methoxybenzene and its derivatives

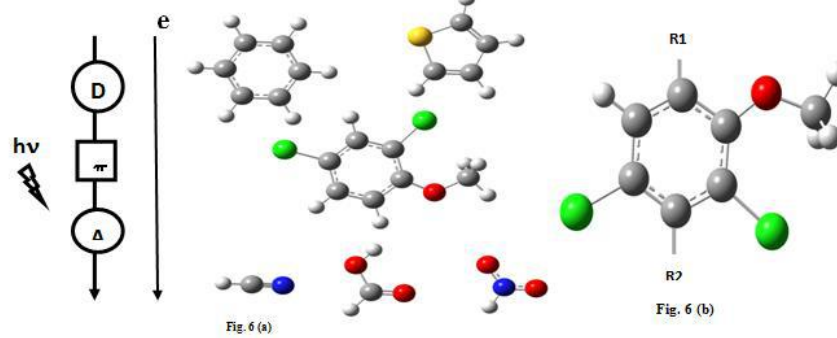


Fig. 6(a): Different parts of Donor- π spacer-Acceptor system
 6(b): Chemical structure of 2,4-dichloromethoxybenzene
 R1-Benzene, Thiophene; R2 - CN, COOH, NO₂

Where E_{OX}^{dye*} is the oxidation potential of the dye in the excited state and $E_{CB}^{TiO_2}$ is the reduction potential of conduction band of semiconductor TiO₂. Two models can be used for the evaluation of E_{OX}^{dye*} [54]. The oxidation potential is calculated from the redox potential of the ground state (E_{OX}^{dye}) and the absorption energy associated with the photo-induced intramolecular charge transfer (λ_{max}^{ICT})

$$E_{OX}^{dye*} = E_{OX}^{dye} - \lambda_{max}^{ICT} \text{ -----(2)}$$

$$E_{OX}^{dye} = -E_{HOMO}^{dye} \text{ -----(3)}$$

The ΔG^{inject} and E_{OX}^{dye*} values are calculated using eqn. (1) and (2). For the effective functioning of photovoltaic cell, the amount of electron injection from the dye molecule to the conduction band of the semiconductor ought to be high. The calculated values of 2,4-DCMB and designed dyes are listed in Table 7. The calculated ΔG^{inject} value is negative implying that they are exergonic injection reaction which is favourable for an electron transfer [55]. This implies that an excited state of dyes lie above the conduction band of TiO_2 . This shows a decent electron injection from these dyes to the acceptor TiO_2 , indicating that these dyes is also sensible candidates for application of photovoltaic devices.

Table 7: The calculated redox potential of the ground state (E_{OX}^{dye}), oxidation potential of the dye (E_{OX}^{dye*}), absorption energy (λ_{max}^{ICT}), free energy change for electron injection (ΔG^{inject}) of 2,4 dichloromethoxybenzene and the studied dyes using B3LYP/631G+d basis set.

System	E_{OX}^{dye}	E_{OX}^{dye*}	λ_{max}	λ_{max}^{ICT}	ΔG^{inject}
2,4DCMB	6.4524	1.9238	273.78	4.5286	-2.0762
2,4DCMB1 (Ben+CN)	6.6428	2.5309	301.53	4.1119	-1.4691
2,4DCMB2 (Ben+COOH)	6.0611	2.8916	391.18	3.1695	-1.1084
2,4DCMB3 (Ben+NO2)	6.3016	3.7784	490.40	2.5282	-0.2216
2,4DCMB4 (Thio+CN)	6.4216	2.4767	314.29	3.9449	-1.5233
2,4DCMB5 (Thio+COOH)	6.0548	2.9208	395.61	3.1340	-1.0792
2,4DCMB6 (Thio+NO2)	6.2951	3.7848	493.90	2.5103	-0.2152

7.6 EXCITON BINDING ENERGY AND OPEN CIRCUIT VOLTAGE

To attain high energy conversion efficiency, the excited electron and hole pairs ought to dissociate into separate positive and negative charges to escape from recombination due to the coulombic attraction. To attain this process, the binding energy has got to be overcome. That is, the dye molecule should possess less exciton binding energy for high energy conversion. Here, the exciton binding energy was calculated using the formula [56, 57].

$$E_b = E_g - E_x = E_{H-L} - \lambda_{max}$$

Table 8: Exciton binding energy (E_b) and open circuit voltage (V_{oc}) of 2,4DCMB and their derivatives

System	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g (eV)	E_x (eV)	E_b (eV)	V_{oc} (eV)
2,4DCMB	-6.4524	-1.2074	5.2450	4.5286	0.7164	2.4524
2,4DCMB1 (Ben+CN)	-6.6428	-2.0375	4.6053	4.1119	0.4934	2.6428
2,4DCMB2 (Ben+COOH)	-6.0611	-2.0145	4.0466	3.1695	0.8771	2.0611
2,4DCMB3 (Ben+NO2)	-6.3016	-2.6925	3.6091	2.5282	1.0809	2.3016
2,4DCMB4 (Thio+CN)	-6.4216	-2.0825	4.3391	3.9449	0.3942	2.4216
2,4DCMB5 (Thio+COOH)	-6.0548	-2.049	4.0058	3.1340	0.8718	2.0548
2,4DCMB6 (Thio+NO2)	-6.2951	-2.7116	3.5835	2.5103	1.0732	2.2951

where E_g is the band gap which is approximated as the HOMO-LUMO energy difference and E_x is the optical gap defined as the first singlet excitation energy λ_{max} . The calculated exciton binding energy of 2,4-DCMB and designed molecules are listed in Table 8. The result shows that the dye 2,4-DCMB4 is most suitable for DSSC application by the substitution of Thiophene as donor and Cynate as acceptor. The maximum open circuit voltage (V_{oc}) is an important photovoltaic parameter that can be determined theoretically by the difference between HOMO energy of the dye and LUMO energy of an

electron acceptor (i.e. conduction band of semiconductor TiO₂). The theoretically calculated data of V_{oc} is determined from the following equation [58]:

$$V_{OC} = |E_{HOMO}^{Donor}| - |E_{LUMO}^{Acceptor}| - 0.3 \quad \text{----- (5)}$$

While in DSSCs, V_{oc} can be approximately estimated as the difference between LUMO energy of the dye and energy of the conduction band (CB) of semiconductor TiO₂ (E_{CB} = - 4.0 eV):

$$V_{OC} = E_{LUMO}^{dye} - E_{CB} \quad \text{-----(6)}$$

The values of open circuit voltage (V_{oc}) of 2,4-DCMB and new designed dyes are calculated using equation (6). These values of open circuit voltage are positive, which suggests that an electron transfer will be easy from the dyes to semiconductor TiO₂. Further, these values are sufficient to obtain the high efficient electron injection. Besides, these compounds can be utilized as sensitizers by virtue of an electron injection process from an excited molecule to the conduction band of TiO₂.

8. CONCLUSION

In this work, FT-IR and FT-Raman spectrum were recorded for 2,4-dichloromethoxybenzene. On the basis of potential energy distribution, the vibrational assignments of frequencies for titled compound were analyzed. The results are correlated with the frequencies attained from an experimentally observed FT-IR and FT-Raman spectra. The theoretical values are in good agreement with the experimental frequencies. The active sites for the electrophilic and nucleophilic reactions are also observed by the local reactivity descriptors (Fukui function) of 2,4-DCMB. The Non-linear optical property of the titled compound is calculated theoretically by the determination first order hyperpolarizability. From the results, it have been seen that 2,4-DCMB4 has the greater value than those of Urea, and then the titled compound is good candidature for NLO study. All the theoretically designed dyes are in bathochromic shift as compared with the titled compound. Light Harvesting Efficiency (LHE), free energy change for electron injection (ΔG^{inject}), exciton energy (E_b) and open circuit voltage (V_{oc}) for the titled compound and new designed dyes are calculated. From the above results, it is clear that the 2,4-DCMB based dyes having the best photovoltaic properties for the dye sensitized solar cells (DSSCs).

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