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Synthesis, characterization and DFT study of methoxybenzylidene containing chromophores for DSSC materials

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1. Introduction

The conversion of solar energy to electricity appears as one of the substitutes that can replace fossil fuels [1]. Dye-sensitized solar cells (DSSCs) have attracted considerable attentions due to the most promising low cost [2–4]. Although the efficiencies of DSSCs have not yet approached the theoretical limit and are not competitive with the silicon-based solar cells, organic dyes have their own advantages [5], such as high absorption coefficient and easy control of redox potentials of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels. Nonlinear optical have great potential [6,7] especially for use in optical communication, information processing, frequency doubling and integrated optics [8]. Organic NLO materials have many advantages over inorganic materials, such as large nonlinear optical coefficients, greater ease for synthetic design, easy preparation and lower cost [9,10].

The most common design of molecules with large π values comprises strong electron-donors and acceptors connected by a π -conjugated system (donor- π -acceptor or "push-pull" chromophores). The majority of push-pull chromophores are neutral organic molecules, with all three key components (donor, acceptor and connecting π -system) varied very widely.

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ABSTRACT

Novel tricyanovinyl derived from hydrazones have been prepared by the reaction of tetracyanoethylene and phenylethylidene hydrazone, and these dyes showed absorption in the region of 539–650 nm. The dyes showed pronounced solvatochromic effects as the polarity of the solvents changed. The torsion in E isomer is smaller than Z and azo isomers of MBD1 and MBD2. The HOMOs are delocalized on whole of the molecule while LUMOs are distributed on the tricarbonitrile. The LUMO energies are above the conduction band of TiO_2 and HOMOs of the dyes are below the redox couple of MBD1 and MBD2. The HOMO energies, LUMO energies and HOMO-LUMO energy gap of MBD1 and MBD2 are almost same. The absorption spectra of both the dyes in different solvents are approximately same except in cyclohexane. © 2012 Elsevier B.V. All rights reserved.

Many donor-acceptor conjugated organic molecules reported in the literature fall into the following categories: substituted benzene, biphenyls, stilbenes, azobenzenes ferrocenyl and schiff bases [11,12]. We have reported the synthesis of new tricyanovinyl based on hydrazones such as dyes [13–15]. In this paper, we report herein the synthesis of novel push-pull systems based on hydrazones and methoxy groups as donor groups to study the effect on the activity of these chromophores. The effect on geometries, electronic, spectroscopic especially absorption and IR spectra and conformational analysis has been investigated. We have also discussed the structure-property relationship. In addition, the synthesized compounds were subjected to computational study to make a comparison between the experimental and theoretical data.

2. Experimental methods

Melting points were recorded on a Thomas–Hoover capillary melting apparatus without correction. IR spectra were taken as KBr disk on a Nicolet Magna 520 FTIR Spectrometer, ¹H NMR were recorded in DMSO-d₆ on a Bruker DPX 400 Spectrometer using TMS as internal standard. UV–vis spectra were recorded on a Shimadzu 260 Spectrometer for solutions.

2.1. General procedure for the reaction of TCNE with hydrazones

A solution of aromatic amine (10 mmol) and TCNE in DMF (25 ml) was stirred at 60-90 °C for 8 h. The solvent was removed and the residual solid was collected and recrystallized from toluene–chloroform mixture.

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Table 1

Optimized geometrical parameters of investigated systems at B3LYP/6-31G* level of theory.



Systems	Bond lengths (A)							
	C5–C7	C7-N1	N1-N2	N2-C8	C8-C9	C11-C14		
MBD1-E	1.455	1.289	1.355	1.371	1.411	1.455		
MBD1-Z	1.457	1.290	1.380	1.377	1.416	1.455		
MBD1-azo	1.506	1.482	1.248	1.432	1.403	1.471		
MBD2-E	1.456	1.289	1.355	1.371	1.410	1.455		
MBD2-Z	1.475	1.291	1.360	1.375	1.410	1.457		
MBD2-azo	1.508	1.481	1.248	1.432	1.403	1.471		
	Dihedral angles (degrees)							
	C5-C7	C5-C7-N1-N2		C7-N1-N2-C8				
MBD1-E	MBD1-E –180.0		179.9		0.162			
MBD1-Z	180.0		45.90		178.2			
MBD1-azo	179.7		-179.5		8.172			
MBD2-E	179.9		-179.9		-0.079			
MBD2-Z	2-Z –2.342		-177.38		-8.963			
MBD2-azo	0.591		-179.6		5.928			

(MBD2) 2-{4-[2-(3,4-Dimethoxybenzylidene)hydrazino] phenyl}ethylene-1,1,2-tricarobo- nitrile: $[C_{20}H_{15}N_5O_2(357.37)]$, M. P. 280–282 °C, yield 70%; UV–vis (ethanol): λ_{max} (nm): 550, 347; IR (cm⁻¹): 3226(sec. NH), 2212 (CN), 1609 (C=N), 1341(C–N); ¹HNMR (DMSO-d₆): 3.82, 3.86 (2 s, 6H, 2× OCH₃), 7.02–8.01 (m, 7H,Ar–H), 8.07(s, 1H, CH=N), 11.80(s, 1H, NH). ¹³C NMR (DMSOd₆): 55.49, 55.56 (2OCH₃), 78.11, 145.07(C=C), 114.86 (CN), 111.48, 114.16, 114.36, 119.16, 121.78, 126.90, 132.78, 136.75, 149.10, 150.75, 2 × 151.23(12C–Ar), 162.27 (CH=N), see Scheme 1.

3. Computational methods

The geometries of MBD1 and MBD2 have been optimized by using density functional theory with B3LYP/6-31G(d) level of theory [16–20]. The absorption spectra has been computed by using time dependant density functional theory (TD-DFT) at the B3LYP /6-31G(d) level of theory which has been proved to be accurate and reliable method [21,22]. Thermodynamic parameters; relative energies (ΔE_0), enthalpies (ΔH) and free energies (ΔG) (kcal/mol) for E, Z and azo isomers of MBD1 and MBD2 have been computed at B3LYP/6-31G(d) level. The calculations have been performed by using Gaussian03 program package [23]. Three possible classes of isomeric molecules for dyes are E, Z and azo are shown in Fig. S1. These isomers arise by rotating around torsion angles N1–N2–C3–C4 for investigated dyes. Then by fully optimization stable conformers have been achieved.

4. Results and discussion

4.1. Geometries

The computed geometrical parameters of MBD1 and MBD2 have been tabulated in Table 1. The fully optimized structures of studied isomers are shown in Fig. S1. The C–C, C–N and N–N bond lengths of E and Z isomer of MBD1 and MBD2 are almost similar except the C5–C7 in Z isomer of MBD2 which is 0.019Å longer compared to E isomer and N1–N2 of E isomer of MBD1 is 0.025Å shorter than Z isomer. We have observed that there is no significant change in bond lengths of azo isomers in MBD1 and MBD2. By comparing the bond lengths of the E, Z and azo



Scheme 1. The new synthesized sensitizers 2a (MBD1) and 2b (MBD2).

Table 2	2
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HOMO energy (E _{HOMO}), LUMO energy	ergy (ELUMO), HOMO-LUM	O energy gap (Egap) and al	bsorption spectra (λ _{max}) in solvents in eV.
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Dyes	Еномо	ELUMO	umo E _{gap}	$\lambda_{ m max}$					
				a	b	С	d	е	f
MBD1	-5.76	-3.21	2.55	541 328	550 332	539 331	650 343	573 339	579 400 320
MBD2	-5.74	-3.20	2.54	544 346	550 347	543 344	580 360	575 357	581 375 325

a, CH₃CN (37.5); b, CH₃CH₂OH (24.8); c, CHCl3 (4.7); d, cyclohexane (2.02); e, DMSO (46.8); f, TD-B3LYP/6-31G* level of theory in acetonitrile.

Table 3

Thermodynamic parameters (kcal/mol) for E, Z and azo isomers of studied sensitizers at B3LYP/6-31G(d) level.

	ΔE_0	ΔH	ΔG	ΔE	Dipole
MBD1 E	0.00	0.00	0.00	0.00	14.5762
MBD1 Z	7.48	7.48	7.57	7.28	11.1691
MBD1 azo	17.3	17.4	16.4	18.0	7.8082
MBD2 E	0.00	0.00	0.00	0.00	15.2058
MBD2 Z	4.77	4.71	5.17	4.45	12.3185
MBD2 azo	18.2	18.4	17.6	19.1	7.3037

isomer of MBD1, we have observed that C5–C7 of azo isomer stretched 0.051 Å compared to E isomer and 0.049 Å than Z isomer. The C7–N1 of azo isomer elongated almost 0.193 Å than E and Z isomers. The N1–N2 of azo isomer shortened 0.107 and 0.132 Å compared to E and Z isomers. The N2-C8 of azo isomer lengthened 0.061 and 0.055 Å than E and Z isomers. In MBD2, C5–C7 of azo isomer stretched 0.033 Å compared Z isomers. The C7–N1 of azo isomer elongated almost 0.192 and 0.190 Å than E and Z isomers, respectively. The N1–N2 of azo isomer shortened 0.107 and 0.112 Å compared to E and Z isomers, respectively. The N2–C8 of azo isomer lengthened 0.061 and 0.053 Å than E and Z isomers, respectively. The torsion in E isomer is smaller than Z and azo isomers of MBD1 and MBD2.

4.2. Electronic properties and absorption spectra

Fig. 1 illustrates the calculated spatial distributions of the HOMO and LUMO levels. As can be seen clearly, HOMO is delocalized on whole of the molecule; the oxygens of methoxy also take part in the formation of HOMO. The strong electron withdrawing groups CN attract the charge density while on other hand electron donating group methoxy is attached on left hand of the molecule which would strengthen the donor ability. Due to this, the LUMOs are distributed on the tricarbonitrile. The HOMO–LUMO energy gap of these dyes was calculated at the B3LYP/6-31G(d) level of theory, see Table 2. The orbital energy level analysis at the B3LYP/6-31G(d) level show HOMO energy (E_{HOMO}), LUMO energy (E_{LUMO}) and HOMO–LUMO energy gap (E_{gap}) has been used as an indicator of kinetic stability of the molecule. The E_{HOMO} , E_{LUMO} and E_{gap} of MBD1 and MBD2 are same which showed that di-substituted methoxy would have no additional improvement.

For good DSSC sensitizers following factors to be considered: a narrow band gap, with LUMO lying just above the conduction band of TiO₂ and HOMO below the redox couple. As a model for nanocrystallinity the HOMO and LUMO energies of bare cluster (TiO₂)₃₈ are -7.23 and -4.1 eV, respectively, resulting in a HOMO-LUMO gap of 3.13 eV [24]. Usually an energy gap more than 0.2 eV between the LUMO of the dye and the conduction band of the TiO₂ is necessary for effective electron injection [25]. The LUMO energies of MBD1 and MBD2 are above the conduction band of TiO₂. The HOMO of the redox couple (I^-/I_3^-) is -4.8 eV [26]. It can be found that HOMOs of the dyes are below the redox couple. The smaller HOMO-LUMO energy gaps of MBD1 and MBD2 revealed that these dyes would be efficient for DSSC.



Fig. 1. The HOMOs and LUMOs of the most stable isomers of MBD1 and MBD2.



Fig. 2. IR spectra of MBD1 (top) and MBD2 (bottom).

The electronic absorption spectra of the new chromospheres are characterized by an intense, low-energy band that is dependent on the nature of the substituted on the aromatic rings. MBD1 showed absorption band at 539 nm in chloroform and 541 nm in CH₃CN, no

significant effect has been observed in absorption spectra toward red shift by changing chloroform to CH_3CN . It showed 11 nm red shift in ethanol. Most significant effect toward bathochromic shift has been observed in DMSO (34 nm) and cyclohexane (111 nm). By substituting one more methoxy group as in MBD2 has approximately same absorption spectra in different solvents alike MBD1 except in cyclohexane which has absorption spectra 580 nm.

The dyes were measured in various solvents having different polarity, see Table 2. The trend of absorption spectra toward red shift of MBD1 and MBD2 in different solvents is $CHCI3 < CH_3CN < CH_3CH_2OH < DMSO < cyclohexane.$ The absorption spectra of MBD1 and MBD2 in all the investigated sensitizers are almost same except in cyclehexane in which MBD2 is 7 nm is blue shifted. The maximum absorption spectra computed at TD-B3LYP/6-31G* level of theory is 579 and 581 nm for MBD1 and MBD2, respectively which are in reasonable agreement with the experimental evidence.

4.3. IR spectra

The IR spectra of these new dyes exhibited three important absorption bands; the first band centered at 3279 cm^{-1} and 3226 cm^{-1} for the υ NH absorption in MBD1 and MBD2, respectively. The second band is a sharp absorption band in the region of 2217 cm^{-1} and 2212 cm^{-1} , which was attributed to the cyano group absorption in MBD1 and MBD2, respectively. The third is an absorption band in the region of 1614 cm^{-1} and 1609 cm^{-1} ascribed for the C=N absorption in MBD1 and MBD2, respectively, see Fig. 2. The tricyanovinylation undoubtedly takes place at a position para to the hydrazine group as evidenced from the ¹H NMR signals for the doublet two hydrogen. The azomethine hydrogen of the synthesized dyes was located in the region of 8.1-9.13 ppm (see Supporting information for detail).

4.4. Thermodynamic stabilities

Thermodynamic parameters and energy barrier for investigated dyes have been tabulated in Table 3. The isomers (E, Z and azo) relative energy, ΔE_0 , is defined as a difference between its zeropoint corrected total energy and that of the most stable one *E*, in each case. Relative enthalpies and free energies at 298 K are also defined as the difference between the enthalpy or free energy of a given *E/Z* or *azo* isomers and that of E form. As shown in Table 3, the order of relative stability of those isomers is the same when



Fig. 3. Molecular energy profile using DFT against the selected torsional degree of freedom of MBD1 and MBD2.

considering relative energy or relative free energy. DFT calculation shows that E isomers are the most stable. We have observed that dipole moment of E isomer is highest while azo isomer is lowest. The trend in different isomers is E > Z > azo. The dipole moments of all isomers of MBD2 are larger than MBD1.

4.5. Conformation analysis

For modeling and scanning calculation the initial guess for the stable isomers E was first obtained from the optimization using B3LYP/6-31G(d) and transformed into the Z-matrix format with Babel program; the model starting geometry of E-isomers was obtained by driving procedure in HyperChem [27]. To aid the future design of isomerism, we set about to determining how well quantum chemical methods calculation could predict the rotation barriers around the, e.g. N1-N2-C8-C9 selected torsional angle on these compounds. To identify low energy conformations, the potential energy surface shape has been examined at the B3LYP/6-31G(d) level. The potential energy surfaces of dihedral angle (N1–N2–C8–C9) from +180° to -180° in 5° or 10° steps (Fig. 3). The conformational energy profile shows two maxima near $(-90^{\circ} \text{ and } 90^{\circ})$. The aromatic rings are nearly perpendicular at these values of selected torsion angle. The energy barriers may be due to the steric interactions between the π electrons of the two aromatic rings. It is clear from Fig. 3, there are three local minima observed at (-180, 0 and 180) for N1-N1-N2-C8-C9 torsional angle and these are most stable conformers for this torsion angle. The DFT optimized geometry of these dyes is coplanar at these values of selected torsion angle.

5. Conclusions

The DFT calculation of thermodynamic parameters revealed that the most stable isomers are E. Three local minima have been viewed at (-180, 0 and 180) for N1–N2–C8–C9 torsional angle which revealed that these would be the most stable conformers for this torsion angle. The HOMO is localized on intact molecule while LUMO is distributed on the tricarbonitrile which showed best intra charge transfer. The dyes were measured in various solvents having different polarity. Generally increasing the solvent polarity gave a bathochromic shift of the maximum absorption bands of dyes. The IR spectra of the investigated dyes showed three significant absorption bands. The LUMO energies of MBD1 and MBD2 are above the conduction band of TiO₂. The HOMOs of the dyes are below the redox couple and smaller HOMO–LUMO energy gaps revealed that these dyes would be efficient for DSSC.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.saa.2012.01.016.

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