Research Article

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Exploring the optoelectronic properties of a chromene-appended pyrimidone derivative for photovoltaic applications

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Abstract: In the present study, a chromene-appended pyrimidone derivative (PBA) has been synthesized in order to account for the relationship between chemical structure and charge transport properties. The optical properties of PBA were studied in different solvents; it displays a weak emission profile in polar protic solvents but is highly emissive in polar aprotic solvents. Quantum chemical approaches on this molecule were performed in detail to highlight the importance of and to better understand the structural and electronic effects of introducing substituted pyrimidone rings in a polyaromatic molecule to support the development of new optoelectronic and photovoltaic devices. We shed light on the frontier molecular orbital, electron injection, electronic coupling constant, light harvesting efficiency, and photophysical properties of PBA by using density functional theory and time domain density functional theory. The absorption spectra (λ_a) and fluorescence emission spectra (λ_f) were computed in different solvents (Methanol, Ethanol, Butanol, Hexane, Chloroform and DMF) at the TD-B3LYP/6-31G** and TD-PBE/6-31G** levels of theory, and it was determined that the TD-B3LYP/6-31G** level is more accurate in the reproduction of experimental λ_a and λ_f in various solvents. Furthermore, no significant effect was observed on the λ_a and λ_f by changing the solvent polarity.

Keywords: Chromene; Electronic Properties; Absorption; Emission; Solvent effect; Density functional theory.

1 Introduction

Great effort has been made in the design and development of luminescent dyes, owing to their potential exploitation in materials sciences and biological applications [1, 2]. Among them, the development of dyes with tunable emissions and large Stokes shifts has received significant attention in recent years [3, 4]. Of the several fluorescent organic compounds that are known to date, molecules with a heterocyclic moiety with Sulphur or Nitrogen atoms appended to the main chromophore system have gained popularity as versatile fluorophores owing to easy chemical modifications and tunable optical properties, such as excellent fluorescence quantum yields and high absorption coefficients [5]. Hence, such compounds are extensively used to construct optoelectronic materials such as organic light emitting diodes (OLEDs) and dye sensitized solar cells (DSSCs) [6,7].

Molecular materials appended with pyrimidine or pyrimidine-like structures, including pyrimidines, have received great attention in the fabrication of photovoltaic and photorefractive materials. Their utility in this application owes to specific photophysical properties that may arise due to the decrease in the HOMO–LUMO energy band gap on incorporation of pyrimidine-like structures in the backbone of the π -conjugated moiety [8]. Further, it has been proved that nitrogen-containing heterocyclic compounds are useful either as π -conjugated linkers between donor and acceptor groups or as electron-accepting TiO_2 anchoring groups into the scaffold of dyes for solar cells [9, 10].

In the present study, a chromene-appended pyrimidone derivative (PBA) has been synthesized in order to account for the relationship between chemical structure and charge transport properties. The optical properties of PBA have been studied in different solvents, and the molecule showed a weak emission profile in polar protic solvents but was highly emissive in polar aprotic solvents. The computational investigations on

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this molecule have been studied in detail to highlight the importance and to better understand the structural and electronic effects of introducing substituted pyrimidone rings in small molecules and polymers in the development of new optoelectronic devices.

Scheme 1: Schematic diagram of PBA.

2 Methodology

2.1 Experimental Methodology

PBA was synthesized according to a published method [11]. Briefly, an equimolar mixture of 2-Hydroxy-1-naphthaldehyde and Barbituric acid was heated at reflux temperature for 1 h in 50 mL ethanol. After the completion of the reaction, the precipitate obtained was filtered off, and the resulting solid was recrystallized from hot ethanol to yield a bright yellow solid (Scheme 1). IR and NMR confirmed the structure of the compound. $^1\text{H-NMR}$ (CDCl_3) δ : 6.94 (1H, d), 7.24 (1H, dd), 7.31 (1H, dd), 7.48 (1H, d), 7.53 (1H, d), 7.63 (1H, dd), 7.80 (1H, s), 10.28 (1H, NH); $^{13}\text{C-NMR}$ (150 MHz, d_6 - CDCl_3) δ : 116.20, 117.2, 122.4, 123.2, 128.30, 128.7, 129.33, 132.6, 142.4, 150.8, 160.2, 164.8, 168.4, 174.74; FT-IR (KBr) (cm^{-1}); 2900-3200, 1730.2, 1239.9, 1197.1.

2.2 Computational methodology

Previous studies showed that Density Functional Theory (DFT) is a good and reliable method to reproduce and predict various properties of interest [12-22], and, here, DFT was implemented using the Gaussian 09 package [23]. The DFT was treated according to Becke's three parameter gradient-corrected exchange potential and the Lee-Yang-Parr gradient-corrected correlation potential (B3LYP), and all calculations were performed by using a 6-31G** basis set. The structure investigated in the present study was optimized in the ground state (S_0) at the B3LYP/6-31G** level of theory. The excited state geometry was optimized by using Time dependent DFT (TDDFT) at the TD-B3LYP/6-31G** level of theory. The absorption and emission wavelengths (λ_a and λ_e) were calculated by TDDFT at the TD-B3LYP/6-31G** level of theory. Various photovoltaic parameters, i.e. electron injection (ΔG^{inject}), electronic coupling constant ($1/2V_{\text{RP}}^{1/2}$), and light harvesting efficiency (LHE), were computed as described [24].

Figure 1: Charge density of HOMO and LUMO at ground (bottom) and excited (top) states.

3 Results and Discussion

3.1 Electronic properties

The energy levels of the frontier molecular orbitals (FMO), i.e. the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs), are noteworthy in the determination of various electrochemical, optical and photovoltaic properties. Ground and excited state energies of the FMOs (HOMO and LUMO) are displayed in Table 1. Figure 1 illustrates the charge density delocalization and localization pattern of these FMO. In the ground state, the HOMO is distributed on entire compound while LUMO is on the pyrimidone side. In the excited state, HOMO is distributed at the pyrimidone while LUMO is in the center of the compound. Clear intra-molecular charge transfer has been observed in the ground and excited states (see Figure 1). The dipole of the excited state is higher than that of the ground state, which demonstrates that **PBA** is more polar in the excited state than in the ground state.

Table 1: HOMO energies (E_{HOMO}), LUMO energies (E_{LUMO}), HOMO-LUMO energy gap (E_{gap}) in (eV) and dipole moment (in Debye) for **PBA** computed at the B3LYP/6-31G** level of theory.

State	E_{HOMO}	E_{LUMO}	E_{gap}	Dipole moment
Ground	-6.80	-3.36	3.44	9.24
Excited	-6.58	-3.91	2.67	12.64

3.2 Electron injection barrier

The hole and electron injection energies for **PBA** were calculated at the B3LYP/6-31G** level of theory. The electron injection energy (EIE) of was calculated by using the following equation (1).

$$\text{EIE} = (-E_{\text{LUMO}} - (-W)) \quad (1)$$

where W is the work function of metal and E_{LUMO} is the LUMO energy.

Aluminum (Al) is conductive, easy to manufacture, and inexpensive, and it is easily accessible in sheets of many sizes; therefore, Al ($W = -4.08$ eV) has been used as an electrode in the present work. The EIE from **PBA** to the Al electrode was observed at 0.72 eV ($= -3.36 - (-4.08)$). The hole injection energy (HIE) of **PBA** is 2.72 eV ($= -4.08 - (-6.80)$) from **PBA** to the Al electrode, when the HOMO of the Compound and work function of Al are considered. Moreover, in previous studies, the electron affinity correlated with LUMO energy as $\text{EA} = -\text{LUMO}$ energy. By considering this relation, it can be found that EA of **PBA** is 3.36, which is greater than 3, thus revealing that this compound would be more stable when it has electron transfer ability.

3.3 Optical properties

The electronic absorption and emission spectra of **PBA** (20 μM) have been recorded in solvents of varying different polarity and are displayed in Figures 2 and 3. **PBA** shows distinct broad absorption bands around 428 nm in all solvents studied except in chloroform, where the spectra are more structured. On excitation at the respective absorption maxima, **PBA** shows an emission band at 475 nm with emission intensity enhancement in polar aprotic solvents such as CHCl_3 and DMF. It was found that the change in absorption and emission maxima in solvents with different polarities was not significant, and only the intensity and spectral shape vary. Moreover, the observed fluorescence quantum yield was significantly lower in non-

Figure 2: Electronic absorption spectra of **PBA** (20 μM) in different solvents.

Figure 3: Emission spectra of **PBA** (20 μM) in different solvents.

polar and polar protic solvents, suggesting charge transfer character in the excited state [5]. Moreover, calculated absorption spectra (λ_a) and fluorescence emission spectra (λ_f) and oscillator strengths (f) in different solvents (Methanol, Ethanol, Butanol, Hexane, Chloroform and DMF) at the TD-B3LYP/6-31G** and TD-PBE/6-31G** levels of theory are tabulated in Table 2. It has been found that the TD-B3LYP/6-31G** level is more accurate to reproduce the experimental absorption and emission spectra in various solvents. Additionally, no significant effect has been observed at the λ_a and λ_f by changing the solvent. Thus, this level of theory has been adopted to shed light on electronic coupling constant, electron injection and light harvesting efficiency.

Table 2: The computed values for absorption spectra (λ_a), fluorescence spectra (λ_f) and oscillator strengths (f) at TD-B3LYP/6-31G** and TD-PBE/6-31G** level of **PBA** in different solvents.

Solvent	f	λ_a	f	λ_a	f	λ_f	f	λ_f
	TD-B3LYP		TD-PBE		TD-B3LYP		TD-PBE	
Methanol	0.4237	412	0.2953	468	0.4449	467	0.3205	532
Ethanol	0.4310	418	0.3014	468	0.4523	469	0.3253	534
Butanol	0.4394	418	0.3080	468	0.4606	470	0.3310	536
Hexane	0.4464	415	0.0001	488	0.4307	492	0.2752	571
Chloroform	0.4501	418	0.3233	466	0.4632	478	0.3184	549
DMF	0.4455	419	0.3127	469	0.4671	470	0.3388	534

3.4 Open-circuit voltage

The Open-circuit voltage (V_{oc}) is an important photovoltaic parameter that significantly affects solar cell performance. Generally, V_{oc} depends on the materials and some other factors, including light intensity, light-source, energy levels, device temperature, work functions of the electrodes, external fluorescence efficiency, and charge-carrier recombination [25, 26]. The relationship between the electronic structure and V_{oc} is still not clear. Previously, the relationship between V_{oc} and the donor (D) HOMO and acceptor (A) LUMO energy gap was studied [27]. Scharber et. al. calculated the V_{oc} by using the equation below (2). Previously, valance band (VB) and conduction band (CB) values for TiO_2 were found to be -7.40 and -4.20 eV, respectively [28]. According to Liu et al. VB and CB of Si are -5.43 and -3.92 eV [29].

$$V_{oc} = (|E_{HOMO}^D| - |E_{LUMO}^A|) - 0.3 \text{ eV} \quad (2)$$

By considering the acceptor CB and HOMO of **PBA**, the V_{oc} value was determined to be 2.3 eV from donor to TiO_2 , respectively. When for considering Si as acceptor, the V_{oc} value is 2.58 eV from HOMO of **PBA** to Si.

3.5 Electron coupling constants

The electron injection (ΔG^{inject}), electron coupling constants ($|V_{RP}|$) and light harvesting efficiency (LHE) of **PBA** were computed at the B3LYP/6-31G** and TD-B3LYP/6-31G** levels of theory and tabulated in Table 3. The ΔG^{inject} of Dyenitro was estimated to be -0.39 and -0.59 by considering the CB of TiO_2 -4.0 and -4.20, respectively. The $|V_{RP}|$ of Dyenitro was estimated to be 0.195 and 0.295, respectively. From Table 3, it can be found that the ΔG^{inject}

and $|V_{RP}|$ of **PBA** are greater than the reference compound. It is expected that in **PBA**, the short-circuit current density (J_{SC}) value would be higher due to high ΔG^{inject} and LHE.

The ΔG^{inject} and $|V_{RP}|$ of **PBA** are compared with values from several other studies by considering CB of TiO_2 -4.0 and -4.20 eV. The triphenylamine (TPA) TC4_system3 unveiled ΔG^{inject} and $|V_{RP}|$ -2.0 and 1.0 eV at the TD-BHandHLYP/6-311+G**//B3LYP/6-31G** level while values for 3b_TPA were -2.49 and 1.24 eV at the TD-CAM-B3LYP/6-31G**//B3LYP/6-31G** level, respectively. The azo dye (4b) exhibited ΔG^{inject} and $|V_{RP}|$ -1.19 and 0.53 eV at the TD-B3LYP/6-31G**//B3LYP/6-31G** level, respectively. The hydrazone dye (system5) displayed ΔG^{inject} and $|V_{RP}|$ -0.61 and 0.305 eV at TD-B3LYP/6-31G**//B3LYP/6-31G** level, respectively. The TPA (2TPA-R) exposed ΔG^{inject} -2.46 and 1.23 eV for first and second excited states, respectively. Also, ΔG^{inject} and $|V_{RP}|$ were assessed by considering CB of TiO_2 -4.2 eV. The TPA TC4_system3 showed ΔG^{inject} and $|V_{RP}|$ -2.2 and 1.1 eV, 3b_TPA -2.69 and 1.345 eV, azo dye (4b) -1.39 and 0.695 eV, hydrazone dye (system5) -0.81 and 0.405 eV and TPA (2TPA-R) -2.66 and 1.33 eV, respectively [31]. In this work, the ΔG^{inject} and $|V_{RP}|$ of **PBA** are smaller than the above mentioned reference compounds but reasonable values are enlightening that this compound might be good solar cell material.

4 Conclusions

In conclusion, a chromene-appended pyrimidone derivative (PBA) has been synthesized, and its optical properties have been studied in detail in different solvents. The observed shift in the absorption and emission spectra were found to be not significant, but the emission profile showed high emission intensity in polar aprotic solvents

Table 3: the ΔG^{inject} , ΔG^{inject} , oxidation potential, light harvesting efficiency (LHE), $|V_{\text{RP}}|$ of investigated dyes at B3LYP/6-31G** and TD-B3LYP/6-31G** levels of theory.

System	Phase	ΔG^{inject} (eV)	$E_{\text{OX}}^{\text{dye}}$ (eV)	$E_{\text{OX}}^{\text{dye*}}$ (eV)	$\lambda_{\text{max}}^{\text{ICT}}$ (eV)	f	LHE	ΔG^{inject} (eV)	$ V_{\text{RP}} $ (eV)
^a Dyemitro		-0.39	5.96	3.61	2.35	1.3189	0.9520	1.000	0.195
Compound1	Methanol	-0.21	6.80	3.79	3.01	0.4237	0.6230	0.538	0.105
	Ethanol	-0.17	6.80	3.83	2.97	0.4310	0.6293	0.436	0.085
	Butanol	-0.17	6.80	3.83	2.97	0.4394	0.6364	0.436	0.085
	hexane	-0.19	6.80	3.81	2.99	0.4464	0.6422	0.487	0.095
	Chloroform	-0.17	6.80	3.83	2.97	0.4501	0.6452	0.436	0.085
	DMF	-0.16	6.80	3.84	2.96	0.4455	0.6415	0.410	0.080

$\Delta G_r^{\text{inject}}$ = relative electron injection $\Delta G^{\text{inject}}(\text{dye}) / \Delta G^{\text{inject}}(\text{Dyemitro})$

and low fluorescence quantum yield in non polar and polar aprotic solvents. An intra-molecular charge transfer was observed from occupied to unoccupied molecular orbitals. No significant effect of solvent polarity on the absorption wavelengths was observed at the TD-B3LYP/6-31G** and TD-PBE/6-31G** levels of theory as well. The TD-B3LYP/6-31G** theory was found better to reproduce the experimental absorption and emission spectra. Moreover, LUMO energy, electron injection, LHE, ΔG^{inject} and $|V_{\text{RP}}|$ of **PBA** showed that it would be good electron transfer material to be used in photovoltaic and optoelectronic devices.

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Ethical approval: The conducted research is not related to either human or animal use.

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