Research Article

Mohammed A. Assiri*

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

https://doi.org/10.1515/chem-2019-0119
received September 10, 2018; accepted February 8, 2019.

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 ($\lambda_a$) and fluorescence emission spectra ($\lambda_f$) 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 $\lambda_a$ and $\lambda_f$ in various solvents. Furthermore, no significant effect was observed on the $\lambda_a$ and $\lambda_f$ 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 photo refractive 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 $\pi$- conjugated moiety [8]. Further, it has been proved that nitrogen-containing heterocyclic compounds are useful either as $\pi$- 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
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.

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. 1H-NMR (CDCl₃) 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); 13C-NMR (150 MHz, d₆-CDCl₃) 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, 168.4.74; 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 (S₀) 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 (λa and λe) were calculated by TDDFT at the TD-B3LYP/6-31G** level of theory. Various photovoltaic parameters, i.e. electron injection (ΔGinject.), electronic coupling constant (½V₉₀), and light harvesting efficiency (LHE), were computed as described [24].

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.
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).

\[ \text{EIE} = (\text{ELUMO} - (\text{W})) \]

where \( W \) is the work function of metal and \( \text{ELUMO} \) 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 \( (W = -4.08 \text{ eV}) \) 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 \( \text{EA of PBA} \) 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 \( \mu \text{M} \)) 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-polar and polar protic solvents, suggesting charge transfer character in the excited state \([5]\). Moreover, calculated absorption spectra \( (\lambda_a) \) and fluorescence emission spectra \( (\lambda_f) \) 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 \( \lambda_a \) and \( \lambda_f \) 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 ($\lambda_a$), fluorescence spectra ($\lambda_f$) and oscillator strengths ($f$) at TD-B3LYP/6-31G** and TD-PBE/6-31G** level of PBA in different solvents.

| Solvent   | $f$ (TD-B3LYP) | $\lambda_a$ | $f$ (TD-PBE) | $\lambda_a$ | $f$ (TD-B3LYP) | $\lambda_f$ | $f$ (TD-PBE) | $\lambda_f$ |
|-----------|----------------|-------------|--------------|-------------|--------------|-------------|--------------|-------------|
| 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         | 0.4672       | 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 (Voc) is an important photovoltaic parameter that significantly affects solar cell performance. Generally, Voc 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 Voc and the donor (D) HOMO and acceptor (A) LUMO energy gap was studied [27]. Scharber et. al. calculated the Voc 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].

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

By considering the acceptor CB and HOMO of PBA, the Voc value was determined to be 2.3 eV from donor to TiO$_2$, respectively. When considering Si as acceptor, the Voc value is 2.58 eV from HOMO of PBA to Si.

3.5 Electron coupling constants

The electron injection ($\Delta G^{inject}$), electron coupling constants ($|V_{spf}|$) 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 $\Delta G^{inject}$ 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 $|V_{spf}|$ of Dyenitro was estimated to be 0.195 and 0.295, respectively. From Table 3, it can be found that the $\Delta G^{inject}$ and $|V_{spf}|$ 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 $\Delta G^{inject}$ and LHE.

The $\Delta G^{inject}$ and $|V_{spf}|$ 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 $\Delta G^{inject}$ and $|V_{spf}|$ -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 $\Delta G^{inject}$ and $|V_{spf}|$ -1.19 and 0.53 eV at the TD-B3LYP/6-31G*//B3LYP/6-31G* level, respectively. The hydrazone dye (system5) displayed $\Delta G^{inject}$ and $|V_{spf}|$ -0.61 and 0.305 eV at TD-B3LYP/6-31G*//B3LYP/6-31G* level, respectively. The TPA (2TPA-R) exposed $\Delta G^{inject}$ -2.46 and 1.23 eV for first and second excited states, respectively.

Also, $\Delta G^{inject}$ and $|V_{spf}|$ were assessed by considering CB of TiO$_2$, -4.2 eV. The TPA TC4_system3 showed $\Delta G^{inject}$ and $|V_{spf}|$ -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 $\Delta G^{inject}$ and $|V_{spf}|$ 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.
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^\text{inject} and |V_{RP}| of PBA showed that it would be good electron transfer material to be used in photovoltaic and optoelectronic devices.

Acknowledgement: Author would like to acknowledge the support of Deanship of Scientific Research King Khalid University under the Research Group Project R.G.P.2/60/40.

Author Contributions: M. Assiri conceived and designed the experiments and computations; wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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

References

[1] Mukherjee B., Mukherjee M., Choi Y., Pyo S., Organic Phototransistor with N-Type Semiconductor Channel and Polymeric Gate Dielectric. J. Phys. Chem. C, 2009, 113(43), 18870-18873.

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

| System     | Phase | ΔG^\text{inject} (eV) | E^\text{dye}_\text{OX} (eV) | E^\text{dye}_\text{red} (eV) | λ_{\text{max}} IT (eV) | f | LHE | ΔGr^\text{inject} (eV) | |VRP| (eV) |
|------------|-------|----------------------|-----------------------------|-----------------------------|------------------------|---|-----|----------------------|--------|------|
| *Dyenitro  |       | -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  |

ΔG^\text{inject} = relative electron injection ΔG^\text{inject}(dye)/ ΔG^\text{inject}(Dyenitro)
[11] Rotili D., Tarantino D., Carafa V., Lara E., Meade S., Botta G., Nebbioso A., Schemes J., Jung M., Kazantses A.G., Esteller M., Fraga M.F., Altucci L., Mai A., Identification of Tri- and Tetracyclic Pyrimidinediones as Sirtuin Inhibitors. ChemMedChem, 2010, 5(5), 674-677.

[12] Irfan A., Chaudhry A.R., Muhammad S., Al-Sehemi A.G., Exploring the Effect of Halogens on Semiconducting Nature of Boron Doped Molecular Precursor Graphene Nanoribbons at Molecular and Bulk Level. Optik, 2019, 179526-534.

[13] Wazzan N., Irfan A., Theoretical Study of Triphenylamine-Based Organic Dyes with Mono-, Di-, and Tri-Anchoring Groups for Dye-Sensitized Solar Cells. Org. Electron., 2018, 63328-342.

[14] Irfan A., Mahmood A., Designing of Efficient Acceptors for Organic Solar Cells: Molecular Modelling at Dft Level. J. Clust. Sci., 2018, 29(2), 359-365.

[15] Irfan A., Chaudhary A.R., Muhammad S., Al-Sehemi A.G., Bo H., Mumtaz M.W., Qayyum M.A., Tuning the Optoelectronic and Charge Transport Properties of 2,5-Di(Pyrimidin-5-Yl) Thieno[3,2-B]Thiophene by Oligocene End Cores Substitution. Results in Physics, 2018, 11599-604.

[16] Irfan A., Assiri M., Al-Sehemi A.G., Exploring the Optoelectronic and Charge Transfer Performance of Diaz[a]-Helicenes at Molecular and Bulk Level. Org. Electron., 2018, 57211-220.

[17] Irfan A., Al-Sehemi A.G., Chaudhry A.R., Muhammad S., The Structural, Electro-Optical, Charge Transport and Nonlinear Optical Properties of Oxazole (4z)-4-Benzylidene-2-(4-Methylphenyl)-1,3-Oxazol-5(4h)-One Derivative. Journal of King Saud University - Science, 2018, 30(1), 75-82.

[18] Irfan A., Al-Sehemi A.G., Chaudhry A.R., Muhammad S., How Methoxy Groups Change Nature of the Thiophene Based Heterocyclic Chalcones from P-Channel to Ambipolar Transport Semiconducting Materials. Journal of King Saud University - Science, 2018, 30(4), 458-465.

[19] Irfan A., Abbas G., Exploring the Photovoltaic Properties of Metal Bipyridine Complexes (Metal = Fe, Zn, Cr, and Ru) by Density Functional Theory. Z. Naturforsch. A, 2018, 73(4), 337-344.

[20] Abbas G., Irfan A., Hameed S., Al-Sehemi A.G., Jin R., Tang S., Synthesis, Characterization of Two New Bicyclic Oxazolidines and Investigation of Their Optoelectronic Properties Using Density Functional Theory. Journal of the National Science Foundation of Sri Lanka, 2018, 46(2), 197–204.

[21] Wazzan N., El-Shishtawy R.M., Irfan A., Dft and Td–Dft Calculations of the Electronic Structures and Photophysical Properties of Newly Designed Pyrene-Cored Arylate Derivatives as Hole-Transporting Materials for Perovskite Solar Cells. Theor. Chem. Acc., 2017, 137(1), 9.

[22] Jin R., Irfan A., Molecular Design of Organic Small Molecules Based on Diindole-Diimide with Fused Aromatic Heterocycles as Donors for Organic Solar Cells. RSC Advances, 2017, 7(63), 39899-39905.

[23] Frisch M.J., Trucks G.W., Schlegel H.B., Scuseria G.E., Robb M.A., Cheeseman J.R., et al., Gaussian 16 Rev. A.03. 2016.

[24] Irfan A., Absorption spectra and electron injection study of the donor bridge acceptor sensitizers by long range corrected functional. Iranian J. Chem Chem. Engineer., 2014, 33(2) 11-28.

[25] Brabec C.J., Gowrisanker S., Halls J.M., Laird D., Jia S., Williams S.P., Polymer–Fullerene Bulk Heterojunction Solar Cells. Adv. Mater., 2010, 22(24), 3839-3856.

[26] Brabec C.J., Cravino A., Meissner D., Sariciftci N.S., Fromherz T., Rispens M.T., Sanchez L., Hummelen J.C., Origin of the Open Circuit Voltage of Plastic Solar Cells. Adv. Funct. Mater., 2001, 11(5), 374-380.

[27] Deibel C., Dyakonov V., Polymer–Fullerene Bulk Heterojunction Solar Cells. Reports on Progress in Physics, 2010, 73(9), 096401.

[28] Scharber M.C., Mühlbacher D., Koppe M., Denk P., Waldauf C., Heeger A.J., Brabec C.J., Design Rules for Donors in Bulk-Heterojunction Solar Cells—Towards 10% Energy-Conversion Efficiency. Adv. Mater., 2006, 18(6), 789-794.

[29] Liu C.-Y., Holman Z.C., Korthagen U.R., Hybrid Solar Cells from P3ht and Silicon Nanocrystals. Nano Letters, 2008, 9(1), 449-452.

[30] Al-Sehemi A., Irfan A., Asiri A., The DFT Investigations of the Electron Injection in Hydrazene-Based Sensitizers. Theor. Chem. Acc., 2012, 131(3), 1199.

[31] Al-Sehemi A.G., Irfan A., Fouda A.M., Synthesis, Characterization and Density Functional Theory Investigations of the Electronic, Photophysical and Charge Transfer Properties of Donor–Bridge–Accept Triaminopyrazolo[1,5-a]Pyrimidine Dyes. Spectrochimica Acta Part A, 2013, 111(0), 223-229.