Potential TADF Structures with Benzophenone Moieties

Selcuk GUMUS
Van Yuzuncu Yil University

Aysegul GUMUS
Van Yuzuncu Yil University

Abstract: The architectures of organic solar cells are based on two kinds of materials: electron donors (D) and electron acceptors (A), respectively. Organic compounds which possess donor-acceptor units exhibit important optical and photophysical characteristics. Donor-acceptor compounds are widely used in molecular electronics applications, and it is of interest to investigate how their properties can be manipulated and probed. The πelectronic characteristics of molecular donor (D) – acceptor (A) compounds have been attracting attention in solid state science as well as for their potential technological development in organic electronics. The DA solar cells apply the photoinduced electron transfer to separate the electron from the hole. The photo-induced electron transfer takes place from the excited state of the donor to the LUMO of the acceptor. One of the most important design considerations of TADF molecules is obtaining a small energy gap between the S1 and T1 states ($\Delta\mathcal{E}_{ST}$). A molecule meets this requirement only when its lowest-energy transition has low singlet–triplet exchange energy. Current trends in the research into novel TADF emitters are mainly focused on intramolecular donoracceptor (D-A)-type molecules, as in the present case In this work, we have constructed benzophenone based butterfly compounds and investigated the structural and electronic properties theoretically at the level of Density Functional Theory (DFT). These D-π-A type compounds may be potential candidates for organic solar cell applications, organic lightemitting diodes or fluorescent organic materials.

Keywords: TADF, Solar cells, OLED, DFT

Introduction

The amount of energy that the sun produces is enormous such that Earth receives enough energy to fulfill the yearly world demand of it in less than an hour although not all of that energy reaches the Earth's surface due to absorption and scattering [1]. The continous supply of energy from sun introduces the photovoltaic conversion of solar energy as an important challenge. Solar cells of inorganic materials have a record energy conversion efficiency of around 39%, [2] whereas commercially available solar panel systems, have a significantly lower efficiency range between 15 and 20%.

Solar energy industry is seeking for both high power conversion efficiency and low cost materials. Yet, the prices of silicon based solar cell power plants or solar energy panels are still not competitive with other traditional combustion rivals. Use organic materials can serve an alternative approach for lowering the manufacturing costs of solar cells which can be processed under less demanding conditions. The research for novel organic photovoltaic's has been continued for more than 30 years, however, within the last decade the developments in the field gained considerable momentum [3,4]. Organic solar cells bring the advantages of mechanical flexibility, ease of processing, and low cost of production. Moreover, chemical modification is easy for customization of desired properties. However, the energy conversion efficiency for these organics still needs to be improved, since a maximum efficiency of 4-5% could have only been reached, up to date [5].

The architectures of organic solar cells are based on two kinds of materials: electron donors (D) and electron acceptors (A), respectively. Organic compounds which possess donor-acceptor units exhibit important optical and photophysical characteristics [6]. Donor-acceptor compounds are widely used in molecular electronics

applications, and it is of interest to investigate how their properties can be manipulated and probed. The π-electronic characteristics of molecular donor (D)–acceptor (A) compounds have been attracting subjects for the solid state science as well as for the potential technological development in organic electronics. The DA solar cells apply the photo induced electron transfer [7] to separate the electron from the hole. The photo induced electron transfer takes place from the excited state of the donor to the LUMO of the acceptor.

In order to gain higher efficiencies for organic solar cells, the primary strategy can be adjusting the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels by chemical tailoring. This strategy is rather usefull since the difference between HOMO and LUMO determines the light absorption regions [8], the open-circuit voltage (V_{oc}) heavily depends on the gap of $LUMO_{acceptor}$-$HOMO_{donor}$ [9] and sufficient $\Delta\varepsilon$ (the difference between HOMOs or LUMOs of donor and acceptor), which usually needs to be at least 0.3 eV, is necessary for excitons dissociation at the interface of donor and acceptor [10]. Recently, two main methods have been used to modify the energy levels of potential molecules: (1) to establish a donor-acceptor (D-A) conjugated backbone by choosing appropriate donors and acceptors [11,12], (2) to introduce electron-donating or electron-withdrawing atoms and groups, such as F-atom, alcoxyl, cyano, rhodanine, etc. [13–17].

In this work, we have constructed a triazophenone centred butterfly compound and investigated the structural and electronic properties theoretically at the level of Density Functional Theory. These D-π-A type compounds may be potential candidates for organic solar cell applications or organic light emitting diodes or fluorescent organic materials.

Method

The three-dimensional ground state (S_0) geometry of the compound was geometry optimized using Density Functional Theory (DFT) [18] by using the Gaussian 09W [19] package program and the hybrid functional B3LYP. The B3LYP is composed of Becke's three parameter exchange functional (B3) [20] and the nonlocal correlation functional by Lee, Yang, and Parr (LYP) [21]. The basis set used for all atoms was 6-31++G(d,p) in both DFT and time-dependent density functional theory (TD-DFT) method. We have applied default G09 grid for computations.

For the nonel compound, vibrational analyses were carried out using the same basis set employed in the corresponding geometry optimizations. The frequency analysis of none of the compounds yielded any imaginary frequencies, indicating that the structure of each molecule corresponds to at least a local minimum on the potential energy surface. The normal mode analysis was performed for 3N-6 vibrational degrees of freedom, N being the number of atoms in the molecule.

The low-lying triplet (T) and singlet excited states (S) of the compounds were relaxed to obtain their minimum energy geometries using the TD-DFT as implemented in G09 package program [22]. The vertical excitation energies and oscillator strengths were obtained for the lowest triplet and singlet transitions at the optimized ground state equilibrium geometries by using TD-DFT at the same hybrid functional and basis set [22]. Optimized ground state structures were utilized to obtain the electronic absorption spectra, including maximum absorption wavelengths, oscillator strengths, and main configuration assignment by using TD-DFT.

Results and Discussion

The demand for economically viable for large-scale power generation based on environmentally green materials with limitless availability and variaty force people to search for novel ideas and applications. Organic semiconductor materials are a cheaper alternative to inorganic counterparts like Si. Organic photovoltaics can have extremely high optical absorption coefficients which provide the potential for the production of very thin solar cells, therefore, they can be fabricated as thin flexible devices.

Semiconductor Properties

The electronic structure of all organic semiconductors is based on conjugation of π-electrons. A conjugated organic system consists of an alternation between single and double carbon-carbon bonds. Single bonds are named as σ-bonds and are associated with localized electrons, and double bonds are composed of a σ-bond and

a π-bond. The π-electrons are mobile and can jump between carbon atoms due to the mutual overlap of pi orbitals along the conjugation path, which causes the wave functions to delocalize over the conjugated skeleton. The empty π-bands are called the Lowest Unoccupied Molecular Orbital (LUMO) and π-bands filled with electrons are called the Highest Occupied Molecular Orbital (HOMO). The band gap ($\Delta\varepsilon$) of semiconductor materials ranges from 1 to 4 eV.

Rigid polyaromatic planar carbon or heterocyclic compounds with donor-π-acceptor architecture have attracted much attention in recent years due to their special electro-optical properties originating from their low band gap [23,24]. Benzophenone was used in literature a building block for butterfly compounds. It has strong ability as an acceptor. Triazophenone, a derivative of benzophenone electronically, is a thought to be a very well acceptor unit to be used in organic photovoltaics which can connect either side with donors to provide semiconductor system (Figure 1).
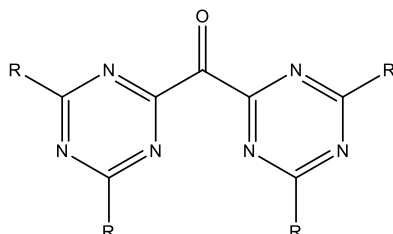
Figure 1. Chemical structure of triazophenone

Pyrene is a polycyclic aromatic hydrocarbon consisting of four fused benzene rings, resulting in a flat aromatic system. This yellow solid is the smallest peri-fused polycyclic aromatic hydrocarbon (one where the rings are fused through more than one face). Pyrene forms during incomplete combustion of organic compounds. Pyrene and its derivatives are used commercially to make dyes and dye precursors, for example pyranine and naphthalene-1,4,5,8-tetracarboxylic acid. It has strong absorbance in UV-Vis in three sharp bands at 330 nm in DCM. The emission is close to the absorption, but moving at 375 nm. The morphology of the signals change with the solvent. Its derivatives are also valuable molecular probes via fluorescence spectroscopy, having a high quantum yield and lifetime (0.65 and 410 nanoseconds, respectively, in ethanol at 293 K). Pyrene was the first molecule for which excimer behavior was discovered.

In the present research, a triazophenone based structure has been studied computationally at B3LYP/6-31++G(d,p) level of theory. These highly conjugated systems are important in terms of their structural and electronic properties. They may be strong candidates for organic semiconductors and their potential applications as organic solar cells. The structures are designed in the form of D-π-A type organic systems. The geometry optimized ground state structure of the pyrene triazophenone structure is shown in Figure 2.
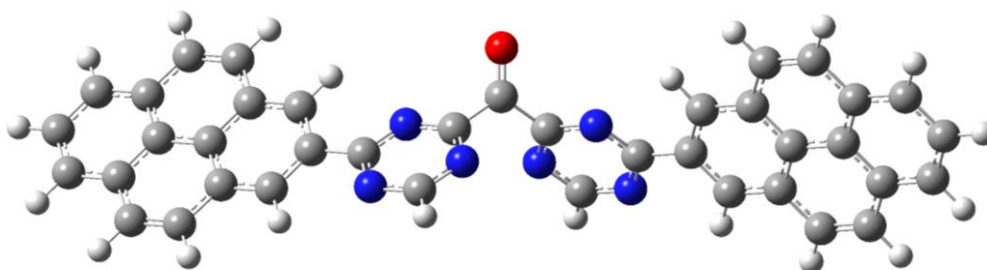
Figure 2. Geometry optimized structure of pyrene triazophenone

The interfrontier molecular orbital energy gap ($\Delta\varepsilon$) provides information about the conductivity of the system. According to the literature data, $\Delta\varepsilon \leq 0.1$ eV conductors, $\Delta\varepsilon = 0.5$-3.5 eV semiconductors and $\Delta\varepsilon \geq 4.0$ eV insulator. The interfrontier molecular orbital energy gap ($\Delta\varepsilon$) for the present structure is 3.22 eV. Therefore, the novel compound is a potential semicoductor for OLED.

TADF Properties

One of the most important design consideration of TADF molecules is to obtain a small energy gap between the S_1 and T_1 states ($\Delta\varepsilon_{ST}$). A molecule meets this requirement only when its lowest-energy transition has a small

singlet–triplet exchange energy. Current trends in research of novel TADF emitters are mainly focusing on intramolecular donor-acceptor (D-A)-type molecules as in the present case. Therefore, appropriate donor-acceptor units have to be selected carefully to obtain full-color TADF molecules, with their HOMO and LUMO being localized on different constituents. To obtain details about the geometric and electronic structures of the present compound time-dependent density functional theory (TD-DFT) calculations were performed at the B3LYP/6-31++G(d,p) level.

The clear separation of the frontier molecular orbitals results in narrower $\Delta\varepsilon_{ST}$ values. $\Delta\varepsilon_{ST}$ data for the pyrene triazophenone unit is coputed top be 0.42 eV. Thus, ΔE_{ST} predicted by the TD-DFT calculation is small enough for thermal repopulation of the S_1 state via $T_1 \rightarrow S_1$ reverse intersystem crossing (RISC) for all the compound. It might suggest a very high potential as TADF emitters by possessing the narrow S_1-T_1 energy difference and well separated HOMO and LUMO schemes. All computed lowest-energy excited states may be described by the HOMO-LUMO transition corresponds to an intramolecular charge transfer (ICT) with small exchange energy (Figure 3).
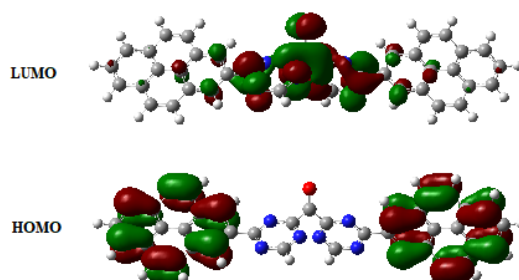

Figure 3. 3D frontier molecular orbital schemes of the present compound

Conclusion

In the present study, we performed a computational study by the application of Density Functional Theory at B3LYP/6-31++G(d,p) level on a triazophenone derivative.

The structure was constructed as D-A motif in order to increase the ability to achieve intramolecular charge transfer so that it may act as potential solar cell organic semiconductor. The interfrontier energy gap of the compound was obtained from DFT calculations and found to be 2.52 eV. Thermally activated delayed fluorescence (TADF) properties of the compound were discussed upon the results obtained by TDDFT calculations. Two critical points for potential TADF structures are; (i) separate distribution HOMO and LUMO orbitals throughout the molecule for small exchannge energy and (ii) nanrow energy gap between the S_1 and T_1 states ($\Delta\varepsilon_{ST}$). The $\Delta\varepsilon_{ST}$ data was computed to be 0.42 eV. Thus, it may be considered for future TADF applications.

Acknowledgements or Notes

References

A.S. Bagher, Introduction to Organic Solar Cells, *Sustainable Energy* **2**, 85-90 (2014).

H. Spanggaard, F.C. Krebs, A brief history of the development of organic and polymeric photovoltaic's, *Sol. Energy Mater. Sol. Cells* **83**, 125-146 (2004).

C. Brabec, V. Dyakanov, J. Parisi, N.S Sariciftci, *Organic photovoltaics: Concepts and Realization*, Springer, New York, 2003.

H. Hoppe, N.S. Sariciftci, Organic solar cells: an overview, *J. Mater. Res.* **19**, 1924-1945 (2004).

G. Li, V. Shrotriya, J. Huang, Y. Yao, T. Moriarty, K. Emery, Y. Yang, *Nature Mater.* **4**, 864-868 (2005).

H.N. Kim, Z.Q. Guo, W.H. Zhu, J.Y. Yoon, H. Tian, Recent progress on polymer-based fluorescent and colorimetric chemosensors, *Chem. Soc. Rev.* **40**, 79-93 (2011).

N.S. Sariciftci, L. Smilowitz, A.J. Heeger, F. Wudl, Photo induced electron transfer from a conducting polymer to buckminsterfullerene, *Science* **258**, 1474-1476 (1992).

Y. Lin, Q. He, F. Zhao, L. Huo, J. Mai, X. Lu, C.J. Su, T. Li, J. Wang, J. Zhu, Y. Sun, C. Wang, X. Zhan, A facile planar fused-ring electron acceptor for as-cast polymer solar cells with 8.71% efficiency, *J. Am. Chem. Soc.* **138**, 2973–2976 (2016).

S.H. Liao, H.J. Jhuo, Y.S. Cheng, S.A. Chen, Fullerene derivative-doped zinc oxide nanofilm as the cathode of inverted polymer solar cells with low-bandgap polymer (PTB7-Th) for high performance, *Adv. Mater.* **25**, 4766–4771 (2013).

M.C. Scharber, D. Mühlbacher, M. Koppe, P. Denk, C. Waldauf, A.J. Heeger, C.J. Brabec, Design rules for donors in bulk-heterojunction solar cells-towards 10% energy-conversion efficiency, *Adv. Mater.* **18**, 789–794 (2006).

J.A. Love, C.M. Proctor, J. Liu, C.J. Takacs, A. Sharenko, T.S. van der Poll, A.J. Heeger, G.C. Bazan, T.-Q. Nguyen, Film morphology of high efficiency solution-processed small-molecule solar cells, *Adv. Funct. Mater.* **23**, 5019–5026 (2013).

L. Liang, J.-T. Wang, X. Xiang, J. Ling, F.-G. Zhao, W.-S. Li, Influence of moiety sequence on the performance of small molecular photovoltaic materials, *J. Mater. Chem.* A **2**, 15396-15405 (2014).

B. Kan, Q. Zhang, M. Li, X. Wan, W. Ni, G. Long, Y. Wang, X. Yang, H. Feng, Y. Chen, Solution-processed organic solar cells based on dialkylthiol-substituted benzodithiophene unit with efficiency near 10%, *J. Am. Chem. Soc.* **136**, 15529-15532 (2014).

B. Kan, M. Li, Q. Zhang, F. Liu, X. Wan, Y. Wang, W. Ni, G. Long, X. Yang, H. Feng, Y. Zuo, M. Zhang, F. Huang, Y. Cao, T.P. Russell, Y. Chen, A series of simple oligomer-like small molecules based on oligothiophenes for solution-processed solar cells with high efficiency, *J. Am. Chem. Soc.* **137**, 3886-3893 (2015).

T.L. Nguyen, H. Choi, S.J. Ko, M.A. Uddin, B. Walker, S. Yum, J.E. Jeong, M.H. Yun, T.J. Shin, S. Hwang, J.Y. Kim, H.Y. Woo, Semi-crystalline photovoltaic polymers with efficiency exceeding 9% in a 300 nm thick conventional single-cell device, *Energy Environ. Sci.* **7**, 3040-3051 (2014).

J. Lu, J. Peng, Y. Wang, J. Yuan, C. Sheng, H.-Q. Wang, W. Ma, Benzo[1,2-b:4, 5-b0] dithiophene-fumaronitrile-based D-A type copolymers with different p-bridges: synthesis, characterization and photovoltaic properties, *Synth. Met.* **188**, 57-65 (2014).

Z. Du, W. Chen, M. Qiu, Y. Chen, N. Wang, T. Wang, M. Sun, D. Yu, R. Yang, Utilizing alkoxyphenyl substituents for side-chain engineering of efficient benzo[1,2-b:4,5-b']dithiophene-based small molecule organic solar cells, *Phys. Chem. Chem. Phys.* **17**, 17391-17398 (2015).

W. Kohn, L.J. Sham, Self-consistent equations including exchange and correlation effects. *Phys. Rev.* **140**, 1133-1138 (1965).

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian 09, Revision D.01*, Gaussian, Inc., Wallingford CT, 2013.

A.D. Becke, Density-functional exchange-energy approximationwith correct asymptotic behavior. *Phys. Rev. A* **38**, 3098–3100 (1988).

C. Lee, W. Yang, R.G. Parr, Development of the Colle–Salvetti correlation energy formula into a functional of the electron density. *Phys. Rev. B* **37**, 785–789 (1988).

M.E. Casida, C. Jamorski, K.C. Casida, D.R. Salahub, Molecular excitation energies to high-lying bound states from timedependent density-functional response theory: characterization and correction of the time-dependent local density approximation ionization threshold. *J. Chem. Phys.* **108**, 4439–4449 (1998).

Author Information

Selcuk Gumus
Van Yuzuncu Yil University
Department of Chemistry, Van/Turkey
Contact E-mail: *gumuss@gmail.com*

Aysegul Gumus
Van Yuzuncu Yil University
Department of Chemistry, Van/Turkey