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LIGHT-EMITTING PROPERTIES OF PYRIMIDINE-5-CARBONITRILE DERIVATIVES: A THEORETICAL CALCULATION

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Abstract

Conference paper

In this study, 4,6-Di (9H-carbazol-9-yl) pyrimidine-5-carbonitrile (C1), 4,6-bis (3,6-di-tert-butyl-9H-carbazol-9-yl) pyrimidine-5-carbonitrile (C2), 4,6-bis (3,6-dimethoxy-9H-carbazol-9-yl) pyrimidine-5-carbonitrile (C3) compounds were optimized at the B3LYP/6-31G(d) level. Energy densities of frontier molecular orbitals were investigated with molecular properties. Vertical ionization potentials (IPv), adiabatic ionization potential (IPa) (in eV), vertical electron affinity (EAv), adiabatic electron affinity (EAa), the hole reorganization energy (λ_h)and electron reorganization energy (λ_e) were calculated (in eV) for C1, C2 and C3 compounds. λ_e values of the C1 and C3 compounds are 0.29 and 0.30 eV and the λ_h value is 0.18 and 0.20 eV, respectively. It can be said that the C1 and C3 compounds are not suitable as an electron bearing layers (ETL) material since its λ_e values are greater than 0.276 eV and that its λ_h value is less than 0.290 eV, so they are a suitable material for the Hole bearing layers (HTL). The C2 compound is suitable for both ETL and HTL materials.

Keywords: *Electron bearing layers, Electron injection layer, DFT, Hole bearing layers, Hole injection layer, OLED materials.*

1 Introduction

With the use of organic devices in many areas of use, the investigation of compounds with different functions that can be obtained as a result of organic synthesis has turned the attention of scientists in this direction. Especially in recent years, the value of organic molecules with different properties has been understood, and conductive polymers and their derivatives have come to the fore. The most prominent discovery with these features is OLEDs (Organic Light Emitting Diode). OLEDs as an alternative to LCD (Liquid Crystal Display) technology are a technology developed by Kodak company in 1987. Since the most prominent features of OLEDs are thin, light and provide low energy consumption, their use in television, telephone and computer technology has expanded. Although OLED screen technology can be a good competitor to existing technologies due to its performance point, it is disadvantageous in terms of strength, costs and therefore sales prices. Problems regarding strength are largely related to the nature of organic semiconductors and QD: organic hybrids may answer this problem. The main reason for the high cost is that coating techniques that are used in the screen production phase and require high vacuum are used. Nowadays, hundreds of scientific studies are carried out to bring OLED technology to much better levels and studies are ongoing to eliminate the disadvantages of OLED technology. OLED is an emerging and promising technology [1-3].

Pyrimidine-5-carbonitrile has electron withdrawal due to carbazole, tert-butylcarbazole and methoxy carbazole substituents. This feature led to high photoluminescence yields and synthesized by Uliana et al. [4]. The donor-acceptor-donor properties of these synthesis components are intended for achieving both blue OLED and optical sensors. [4].

Nowadays, Organic light-emitting diodes (OLEDs) technology is very popular both in the scientific world and in the industry. The production phase is extremely easy, the drive voltage and power consumption are very low. In addition, its high brightness has attracted great attention. [5-9].Although OLED devices consist of organic materials called anode and cathode, it is basically the layers above the anode and below the cathode that determine the property of the OLED material.

The electron injection layer (EIL) is located just below the cathode. Beneath the EIL layer is the electron transport (ETL) layer responsible for carrying electrons. The top layer of the anode has a hole injection layer (HIL). Above this layer there is a hole carrying layer (HTL), which has good conductivity for positive charges (holes) (Fig. 1.) [10]. Thanks to the applications of computational chemistry methods, the suitability of the studied compounds for the said layers can be discussed with numerical results.

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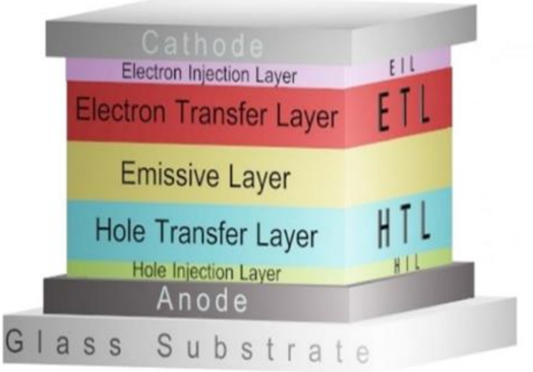

Figure 1. OLEDs layers [10].

In this study, C1, C2 and C3 for compounds, the vertical ionization potentials, the adiabatic ionization potential, the vertical electron affinity, the adiabatic electron affinity, the hole reorganization energy and the electron reorganization energy were examined.

2 Calculation Methods

The structures and input files of organic compounds were prepared using Gauss-View 5.0.8 program [11]. Numerical calculations were carried out by using Gaussian 09 AML64L-Revision C.01 [12]. DFT calculations were performed using Becke’s three-parameter hybrid functional with the Lee-Yang-Parr correlation functional a combination that gives rise to the well-known B3LYP method [13]. The C1, C2 and C3 compounds were optimized in the gas phase at the B3LYP/6-31G(d) level. The 6-31G(d) are the basis sets used in calculations. This basis set is a basis set with polarized functions and this basic set was used to model the orbits of atoms [14]. Lowest empty molecular orbital energy (E_{LUMO}), the highest occupied molecular orbital energy (E_{HOMO}) values are taken directly from the calculation files of the optimized structures. The energy gap (ΔE) for the charge carrying capacity of the investigated organic compounds was calculated from the following Equ. 1.

$$\Delta E = E_{LUMO} - E_{HOMU} \tag{1}$$

OLED features are explained using Marcus theory. The parameters required to study the OLED properties of the respective compounds were calculated at B3LYP/6–31G(d). The compounds used in the OLED structure are classified as: the electron carrying layers (ETL), the hole carrying layers (HTL), the electron injection layer (EIL) and the hole injection layer (HIL) [15-16]. New designs can be made based on the afore mentioned references, where N, N'-diphenyl-N, N'-bis (3-methylphenyl) -1,1′-diphenyl-4,4′-diamine (TPD) and tris (8-hydroxyquinolinato) aluminum (III) (Alq3), respectively, are accepted as reference materials for a typical an ETL and a HTL material. In addition, since the reorganization energy, the adiabatic and vertical ionization potentials (IPa/IPv), and the electron affinities (EAa/EAv) (in eV) parameters determine the ease of load transfer in EIL and HIL materials, these parameters were examined.

3 Result and Discussion

3.1 Optimized Structure

In the gas phase, the molecular structure of C1, C2 and C3 was optimized using the B3LYP method with 6-31G (d) basis sets. The obtained optimized structures of C1, C2 and C3 are given Fig. 2.

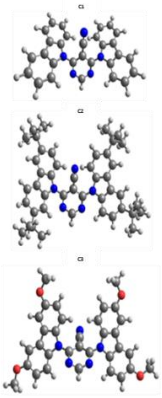

Figure 2. Optimized structures of C1, C2 and C3.

3.2 Frontier Molecular Orbital Analysis

The difference (ΔE) between the HOMO-LUMO and the LUMO-HOMO is an indicator of the type of electronic transition and energy in the molecule. The HOMO, LUMO and the LUMO-HOMO difference (ΔE) orbital energies values and figures of the investigated compounds are given in Fig. 3.

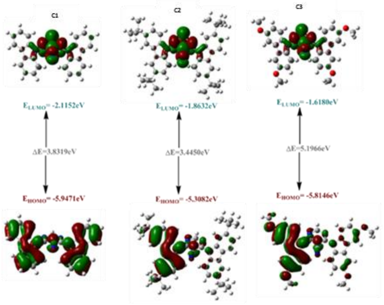

Figure 3. Contour diagrams of C1, C2 and C3.

As shown in Fig. 3, in the C1 molecule, the HOMO is mostly on the molecule. In the C2 and C3 compound, the LUMO molecular orbitals are in a similar location. The LUMO molecular orbital is localized on nitrogen and carbon atoms in the middle part of the molecule in all organic compounds. Normally, the lowest energy excitation goes through the HOMO→LUMO transition. The contour diagram indicates that the HOMO→LUMO transition is the $\pi \rightarrow \pi^*$ transition. Lower values of the LUMO-HOMO difference indicate a higher load-bearing mobility. The energy gap of the C1 is 3.8319 eV. In the C2 compound to which the molecular alkyl groups are attached, the LUMO-HOMO difference has decreased even more. In the C3 compound to which the $-OCH_3$ groups are attached, the LUMO-HOMO difference has increased even more. Therefore, among the compounds studied, the ground energy range (3.4450 eV) of C2 makes it the most promising carrier mobility material.

3.3 OLED Properties

The hole bearing layers (HTL), the Electron bearing layers (ETL), the hole injection layer (HIL) and the electron injection layer (EIL) form the basis of the OLED structure [15-16]. New designs can be made based on the afore mentioned references, where N, N'-diphenyl-N, N'-bis (3-methylphenyl) -1,1′-diphenyl-4,4′-diamine (TPD) and tris (8-hydroxyquinolinato) aluminum (III) (Alq3), respectively, are accepted as reference materials for a typical an ETL and a HTL material.

A parameter, which is an application of the Marcus theory, is given in Equ. 2. This equation is used to estimate an ETL and a HTL materials.

$$K = t^2 \frac{2\pi}{\hbar} \frac{1}{\sqrt{4\pi\lambda k_B T}} exp\left[-\frac{(\lambda+\Delta G^0)^2}{4\lambda k_B T}\right] \qquad (2)$$

where k_B is the Boltzmann constant and T is the temperature value. ΔG° is expressed as the free energy of the hole transfer reaction. λ is reorganization energies and t is transfer integral parameter. The sum of hole (λ_h) and electron (λ_e) reorganization energy expresses the total reorganization energy of the molecule.

$$\lambda = \lambda_e + \lambda_h \qquad (3)$$

values of reorganization energies, λ_h and λ_e can be found in the equations given below[17].

$$\lambda e = (E_0^- - E_-^-) + (E_-^0 - E_0^0) \qquad (4)$$

$$\lambda h = (E_0^+ - E_+^+) + (E_+^0 - E_0^0) \qquad (5)$$

In equ. 4, E_0^- is the term expressing the anion energy calculated from the optimized neutral molecular structure. E_-^- is the energy of the anion. (E_-^0) is the energy value of the neutral molecule calculated in the anionic structure. In the equ. 5, E_0^+ is the term expressing the energy of the cation calculated with the optimized neutral molecule structure. E_+^+ is the energy of the cation. E_+^0 is the energy value of the neutral molecule calculated in the cationic structure. E_0^0 is the ground state energy value in neutral state [18].

In the literature, typical ETL and HTL materials reorganization data are evaluated with reference to Alq3 and TPD compounds. In this case, it is stated that λ_e of Alq3 is at 0.276 eV and λ_h of TPD is at 0.290 eV. [19].

In addition, since IPa, IPv, EAa, EAv parameters determine the ease of load transfer in EIL and HIL materials, these parameters were examined. Lower ionization potentials and higher electron affinities values mean better hole and electron transport as they show easier hole injection of holes (electrons) from the transport layer to the emitter layers [20]. In equ. 6, the IP_a value is calculated as the ionization potential. In equ. 7, the IP_v value is calculated as the vertical ionization potential. In equ. 8, EA_a is calculated as adiabatic electron affinity. In equ. 9, EA_v is calculated as vertical electron affinity.

$$IP_a = E_+ - E_0^0 \qquad (6)$$

$$IP_v = E_0^+ - E_0^0 \qquad (7)$$

$$EA_a = E_0^0 - E_- \qquad (8)$$

$$EA_v = E_0^0 - E_0^- \qquad (9)$$

Here, E_0^+ (E_0^-)is the term expressing the energy of the cation(anion) calculated with the optimized neutral molecule structure. $E_+(E_-)$ is expressed as the cation (anion) energy calculated with the optimized cation (anion) structure. [21]. The adiabatic ionization potential (IPa), the vertical ionization potentials (IPv) (in eV) the adiabatic electron affinity (EAa) and the vertical electron affinity (EAv) (in eV) of C1, C2 and C3 compounds calculated are listed in Table 1.

In an organic compound, λ_e values less than 0.276 eV means that it is suitable as an ETL material and that the organic compound's λ_h values are less than 0.290 eV means that it is a suitable material for the HTL layer. Finally, the charge transfer property of EIL and HIL materials can be evaluated with IPa, IPv and EAa, EAv results, respectively. In general, lower ionization potentials and higher electron affinity mean better electrons and holes charge transfer, respectively [22].

When the λ_e and λ_h values of the organic compounds in Table 1 are examined, it is seen that the λ_e values of the C1 and C3 compounds are 0.29 and 0.30 eV and the λ_h values are 0.18 and 0.20 eV, respectively. It can be said that the C1 and C2 compounds are not suitable as an ETL material since its λ_e values are greater than 0.276 eV and that its λ_h value is less than 0.290 eV, so it is a suitable material for the HTL layer.

It is seen that λ_e values of C2 compound is less than 0.276 eV and λ_h values are lower than 0.290 eV. Therefore, since π-electron delocalization is very important in OLED materials, C2 compound may be suitable for this situation.

C1 and C3 compounds are only suitable for use as a HTL material. The C2 compound is suitable for both ETL and HTL materials. C1 and C3 compounds are only suitable for use as a HTL material. The C2 compound is suitable for both ETL and HTL materials. This means that the same compounds can be used as OLED material in two layers.

Table 1. Vertical ionization potentials (IPv) (in eV), Adiabatic ionization potential (IPa) Vertical electron affinity and Adiabatic electron affinity(EAa)(EAv) (in eV) of C1, C2 and C3 compounds calculated.

Complex	IP_a	IP_v	EA_a	EA_v	λ_e	λ_h
C1	0.3600	0.2600	0.0244	0.0344	0.29	0.18
C2	0.2562	0.2462	0.0314	0.0325	0.27	0.24
C3	0.2017	0.2317	0.0390	0.0290	0.30	0.20

4 Conclusion

They were examined for OLED properties by computational chemistry methods for C1, C2 and C3 compounds. The organic compounds investigated were optimized at the B3LYP / 6-31G (d) level.

It was found that frontier molecular orbitals correspond to the transition $\pi\rightarrow\pi^*$ with the HOMO→LUMO transitions with contour diagrams. In the C2 compound to which the alkyl groups were attached, the LUMO-HOMO difference was further reduced. In the C3 compound to which the $-OCH_3$ groups are attached, the LUMO-HOMO difference increased even more. As a result, C2 was found to have the best load-bearing mobility among the compounds studied, thanks to the lowest energy range (3.4450 eV). The vertical ionization potentials (IPv), the adiabatic ionization potential (IPa) (in eV), the vertical electron affinity (EAv), the adiabatic electron affinity (EAa), the hole reorganization energy (λ_h) and electron reorganization energy (λ_e) were calculated (in eV) for C1, C2 and C3 compounds.

It was concluded that the C1 and C3 compounds are only suitable for use as HTL material. The C2 compound was found suitable for both ETL and HTL materials.

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References

[1] Kasapseçkin, M. A., & Altuncu, D. (2013). Innovative Materials in Interior Design: Organic Light Emitting Textiles (Oleds). In *Advanced Materials Research* (Vol. 689, pp. 254-259). Trans Tech Publications Ltd.

[2] Özkan, N., Erkan, S., Sayın, K., & Karakaş, D. (2020). Research on structural, spectral (IR, UV-Vis, 1H-and 13C-NMR) and light emitting properties of triisocyano-based trinuclear Au (I) complexes. *Chemical Papers,* 74(8), 2415-2425.

[3] Erkan, S., & Karakaş, D. (2020). A theoretical study on cyclometalated iridium (III) complexes by using a density functional theory. *Journal of Theoretical and Computational Chemistry,* 19(02), 2050006.

[4] Tsiko, U., Bezvikonnyi, O., Sych, G., Keruckiene, R., Volyniuk, D., Simokaitiene, J., ... & Grazulevicius, J. V. (2021). Multifunctional derivatives of pyrimidine-5-carbonitrile and differently substituted carbazoles for doping-free sky-blue OLEDs and luminescent sensors of oxygen. *Journal of advanced research,* 33, 41-51.

[5] Ko, C. W., & Tao, Y. T. (2001). Bright white organic light-emitting diode. *Applied Physics Letters,* 79(25), 4234-4236.

[6] Li, J., Hu, L., Wang, L., Zhou, Y., Grüner, G., & Marks, T. J. (2006). Organic light-emitting diodes having carbon nanotube anodes. *Nano letters,* 6(11), 2472-2477.

[7] Wen, W., Bo, W., Lu, L., Jun-Sheng, Y., & Ya-Dong, J. (2009). High performance white organic light-emitting devices based on a novel red fluorescent dye 3-(dicyanomethylene)-5, 5-dimethyl-1-(4-dimethylamino-styryl) cyclohexene. *Acta Physica Sinica,* 58(11), 8014-8020.

[8] Krames, M. R., Amano, H., Brown, J. J., & Heremans, P. L. (2002). Introduction to the issue on high-efficiency light-emitting diodes. *IEEE Journal of selected topics in quantum electronics,* 8(2), 185-188.

[9] Liu, N. L., Ai, N., Hu, D. G., Yu, S. F., Peng, J. B., Cao, Y., & Wang, J. (2011). Effect of spin-coating process on the performance of passive-matrix organic light-emitting display. *Acta Physica Sinica,* 60(8), 679-684.

[10] Üngördü, A. (2019). Charge transfer properties of Gaq3 and its derivatives: An OLED study. *Chemical Physics Letters,* 733, 136696.

[11] Dennington, R. D., Keith, T. A., & Millam, C. M. (2009). GaussView 5.0 Wallingford. In *CT.*

[12] Frisch, Æ., & Frisch, M. J. (1998). GAUSSIAN 98 User's reference, Gaussian. *Inc., Pittsburgh,* PA, 15106.

[13] Kaya, S., Erkan, S., & Karakaş, D. (2021). Computational investigation of molecular structures, spectroscopic properties and antitumor-antibacterial activities of some Schiff bases. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy,* 244, 118829.

[14] Karakaş, D., & Kariper, S. E. (2014). Theoretical investigation on the vibrational and electronic spectra of three isomeric forms of dicobalt octacarbonyl. *Journal of Molecular Structure,* 1062, 77-81.

[15] Kim, J. H., Triambulo, R. E., & Park, J. W. (2017). Effects of the interfacial charge injection properties of silver nanowire transparent conductive electrodes on the performance of organic light-emitting diodes. *Journal of Applied Physics,* 121(10), 105304.

[16] Zhao, J., Chen, X., Yang, Z., Liu, T., Yang, Z., Zhang, Y., ... & Chi, Z. (2018). Highly-efficient doped and nondoped organic light-emitting diodes with external quantum efficiencies over 20% from a multifunctional green thermally activated delayed fluorescence emitter. *The Journal of Physical Chemistry C,* 123(2), 1015-1020.

[17] Stark, M. S. (1997). Epoxidation of alkenes by peroxyl radicals in the gas phase: structure− activity relationships. *The Journal of Physical Chemistry A,* 101(44), 8296-8301.

[18] Erkan, S. (2019). Activity of the rocuronium molecule and its derivatives: A theoretical calculation. *Journal of Molecular Structure,* 1189, 257-264.

[19] Gruhn, N. E., da Silva Filho, D. A., Bill, T. G., Malagoli, M., Coropceanu, V., Kahn, A., & Brédas, J. L. (2002). The vibrational reorganization energy in pentacene: molecular influences on charge transport. *Journal of the American Chemical Society,* 124(27), 7918-7919.

[20] Gao, J., Li, J., Li, X., Han, D., Guo, P., Zhu, X., & Shang, X. (2019). Theoretical investigation on the effect of the modification of 2-phenylpyridine ligand on the photophysical properties for a series of iridium (III) complexes with carbazate ancillary ligands. *Journal of Luminescence,* 209, 365-371.

[21] Üngördü, A. (2020). Electronic, optical, and charge transfer properties of porphyrin and metallated porphyrins in different media. *International Journal of Quantum Chemistry,* 120(6), e26128.

[22] Chan, R. K., & Liao, S. C. (1970). Dipole moments, charge-transfer parameters, and ionization potentials of the methyl-substituted benzene–tetracyanoethylene complexes. *Canadian Journal of Chemistry,* 48(2), 299-305.