

## Chemical Reactivities and Organic Light-emitting Diode Properties of some Polyaromatic Molecules

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### Research Article

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### ABSTRACT

High-performance organic-light emitting diode (OLED) display panels have been very popular lately due to their many advantages compared to liquid-crystal display (LCD) and light-emitting diode (LED) panels. It is also well known that the materials used in OLED panels are important in determining OLED performance. Starting with the selection of materials which have rich  $\pi$ -electrons will be a good start for the design of high-performance OLED materials. For this aim, the OLED properties of some cyclic aromatic structures with rich  $\pi$ -electrons such as 2,2'-bi-1,6-naphthyridine (BNP), 1,6-bis(4'-pyridine)-2,5-diazahexane (BPDH), 3,3'-bis[3-(2-pyridyl)pyrazol-1-yl]biphenyl (BPPB), 5,5'-dicyano-2,2'-bipyridine (DCBP), 2,2'-dimethyl-4,4'-bipyrimidine (DMBP), and 4'-phenyl-2,2':6'2''terpyridine (Ph-TERPY) were theoretically analyzed using computational chemistry tools. The calculations of monomeric and dimeric structures of mentioned molecules were carried out at B3LYP/6-31G(d) and B3LYP/TZP levels, respectively. The OLED properties of the investigated compound were explained by means of OLED parameters such as the reorganization energies, adiabatic-vertical ionization potentials and adiabatic-vertical electron affinities, the effective transfer integrals, and the charge transfer ratios. In the light of computational chemistry, it is indicated that these studied molecules will be utilized in which layers of OLED device. In addition to OLED analysis, in the light of the calculated reactivity descriptors, the chemical reactivities of the studied molecules were discussed.

**Keywords:** Compounds with rich  $\pi$ -electrons, Reorganization energies, Marcus theory, Charge transfer rate.

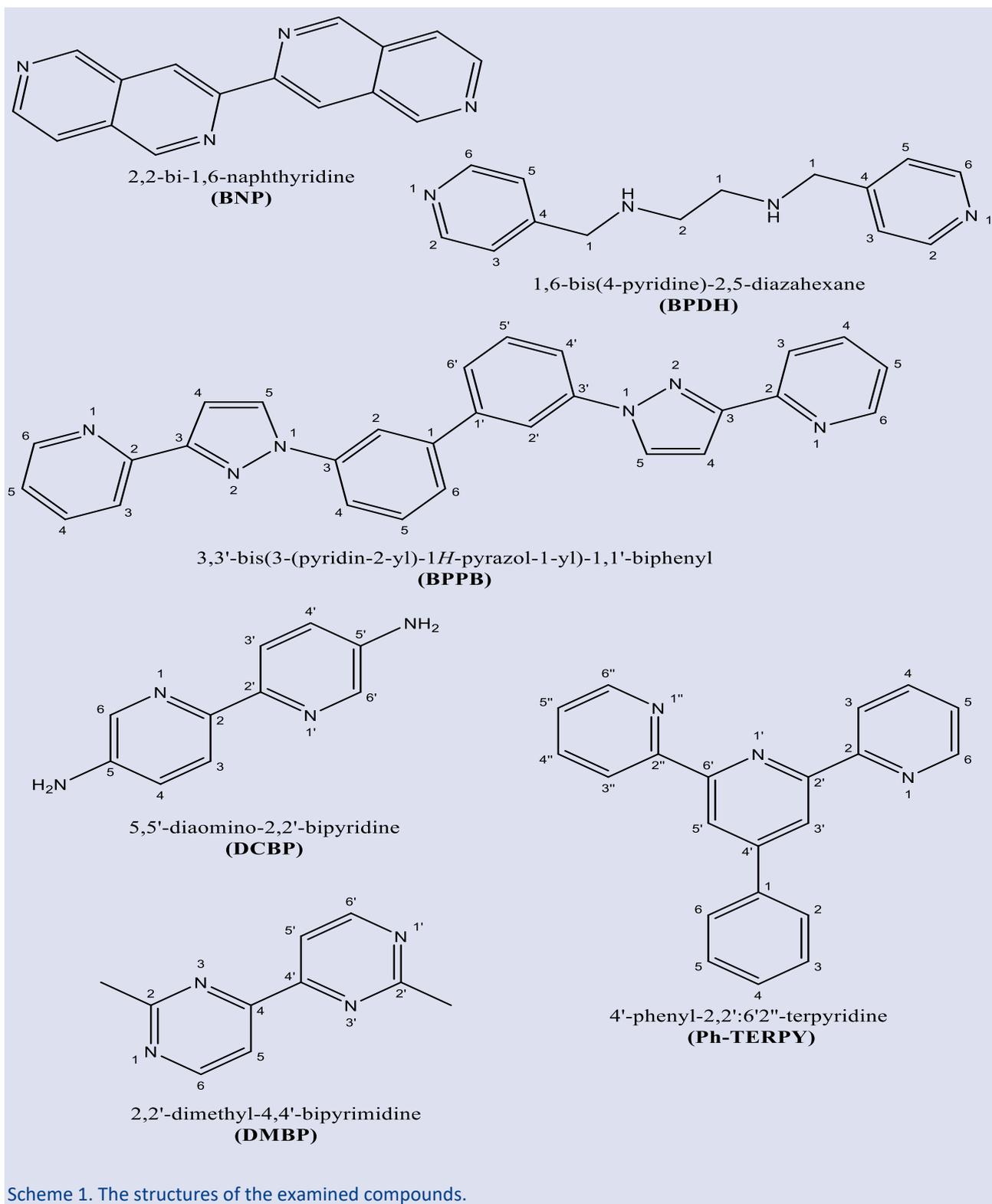
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## Introduction

Computational chemistry has become very popular in molecular design in recent years[1-3]. With computational chemistry tools, theoretical chemists develop new and helpful rules and theories for explaining the properties of molecules[4, 5]. Nano-structures such as organic light-emitting diodes (OLEDs), organic field-effect transistors (OFET), organic-based photovoltaic (OPV) cells can be designed with these developed theories and theories[6, 7]. Among these nanostructures, scientists have concentrated on OLEDs, as they are superior in many respects to their successors, liquid-crystal display (LCD) and light-emitting diode (LED)[8-11]. In addition, in studies on OLED design, OLED design with high performance comes to the fore[12, 13]. In order to produce high performance OLED, the materials in the OLED layer, which consists of many layers, such as the electron injection layer (EIL), the electron transfer layer (ETL), the hole blocking layer (HBL), the emission layer (EL), the electron blocking layer (EBL), the hole transfer layer (HTL), the hole injection layer (HIL) sandwiched between anode and cathode

electrodes, should be carefully selected[14-16]. Previous studies have shown that aromatic or  $\pi$ -electron-rich compounds are suitable for high-performance OLED devices[17-19]. For that reason, the organic compounds with aromatic rings or rich  $\pi$ -electrons in given their structures in Scheme 1 is preferred. The OLED performance of the studied molecules is predicted by means of OLED descriptors such as the reorganization energies, adiabatic-vertical ionization energies and adiabatic-vertical electron affinities, the effective transfer integrals, and the charge transfer rates using different computational chemistry tools[20-23].

The propose of this paper is to examine the OLED properties of the multiple aromatic compounds. In the light of the theoretically obtained results, the best OLED material among the structures examined will be determined. Via the popular Conceptual Density Functional Theoretical parameters like hardness, polarizability and electrophilicity, the chemical reactivities of the molecules will be discussed.



Scheme 1. The structures of the examined compounds.

## Methods

In all calculations we used Gaussian 16 and GaussView 6 software[24, 25]. In the calculations regarding to the dimeric forms of the studied molecules, Amsterdam Density Functional (ADF) 2019 program was used[26]. It is seen from the published literature that hybrid B3LYP functional is widely considered to explain

the charge transfer properties of the materials[27, 28]. Here, we also used same functional to get reliable results. In the computations about the monomeric and dimeric forms of the systems studied, B3LYP/631G(d) and B3LYP/TZP levels were taken into consideration, respectively. For the calculation of electronic hopping rate ( $K$ ), the following formula derived by Marcus and Hush is used[29-31].

$$K = \frac{V^2}{\hbar} \left( \frac{\pi}{\lambda k_B T} \right)^{1/2} \exp \left( -\frac{\lambda}{4k_B T} \right) \quad (1)$$

In the given formula, V stands for the effective (generalized) transfer integral.  $\lambda$  means the reorganization energy,  $k_B$  is the Boltzmann constant.  $\hbar$  and T determine reduced Planck's constant and the absolute temperature taken as 298.15 K in such computations. Additionally, the reorganization energies ( $\lambda$ ) can be divided into two classes as external reorganization energy ( $\lambda_{\text{ext}}$ ) and internal reorganization energy ( $\lambda_{\text{int}}$ ). In this paper, in the analysis of OLED performances of studied compounds, it was focused on only  $\lambda_{\text{int}}$  because  $\lambda_{\text{ext}}$  values have been ignored in previous studies. The  $\lambda_{\text{int}}$  which are electron reorganization energy ( $\lambda_e$ ) and hole reorganization energy ( $\lambda_h$ ) were calculated by means of the following equations.

$$\lambda_e = (E_0^- - E_-^-) + (E_-^0 - E_0^0) \quad (2)$$

$$\lambda_h = (E_0^+ - E_+^+) + (E_+^0 - E_0^0) \quad (3)$$

To calculate the adiabatic-vertical ionization energies and adiabatic-vertical electron affinities of studied aromatic structures, the following equations can be used.

$$IPa = E_+^+ - E_0^0 \quad (4)$$

$$IPv = E_0^+ - E_0^0 \quad (5)$$

$$EAa = E_0^0 - E_-^- \quad (6)$$

$$EAv = E_0^0 - E_0^- \quad (7)$$

In the equations given above, where  $E_0^-(E_0^+)$  stands for energy of the anion (cation) obtained from the neutral structures of the molecules examined. In the same way,  $E_-^-(E_+^+)$  determines the energy of the anionic (cationic) structures obtained with the optimized anionic (cationic) forms,  $E_-^0(E_+^0)$  refers to the energy of the neutral molecule computed at the anion (cationic) structures. Finally,  $E_0^0$  shows the energy of the neutral form of structures at the ground state.

Conceptual Density Functional Theory (CDFT)[32] presents the following mathematical relations for the calculation of the chemical potential ( $\mu$ ), electronegativity ( $\chi$ ) and hardness ( $\eta$ ). E and N appearing in the given relations are total electronic energy and total number of the electrons, respectively

$$\mu = -\chi = \left[ \frac{\partial E}{\partial N} \right]_{v(r)} \quad (8)$$

$$\eta = \frac{1}{2} \left[ \frac{\partial^2 E}{\partial N^2} \right]_{v(r)} \quad (9)$$

Based on the finite differences approach, Parr and Pearson derived the following formulae based on ground state ionization energy (I) and electron affinity (A) of chemical species.

$$\chi = \frac{I + A}{2} \quad (10)$$

$$\eta = \frac{I - A}{2} \quad (11)$$

Another important parameter of the chemical reactivity studies is electrophilicity index ( $\omega$ ) introduced by Parr, Szentpaly and Liu. This index is mathematically calculated as:

$$\omega = \chi^2 / 2\eta \quad (12)$$

For the calculation of electrodonating power ( $\omega^-$ ) and electroaccepting power ( $\omega^+$ ) of the molecular systems. Gazquez and coworkers derived the following equations.

$$\omega^+ = (I + 3A)^2 / (16(I - A)) \quad (13)$$

$$\omega^- = (3I + A)^2 / (16(I - A)) \quad (14)$$

## Results and Discussion

To predict the chemical reactivity of any chemical systems, theoretical and computational chemists use widely well-known quantum chemical descriptors like hardness, electrophilicity and polarizability[33]. Electronic structure rules regarding these descriptors present the relation with chemical stability of the corresponding descriptor. The most popular parameter of the chemical reactivity analysis is the chemical hardness of Prof Pearson[34]. Hard molecules exhibit high resistance against electron cloud polarization. For that reason, the absolute hardness is reported as the resistance against the polarization of atoms, ions and molecules as given many papers penned by Kaya[35, 36]. The electronic structure rule emphasizing the powerful link between chemical stability and absolute hardness is Maximum Hardness Principle. According to this principle, a chemical system tends to reach maximum hardness and the hardness is a measure of stability". Looking to the inverse relation highlighted by Ghanty and Ghosh[37] between hardness and polarizability, Chattaraj and Sengupta[38] noted that "in stable states, polarizability should be minimized unlike the chemical hardness.

Another electronic structure rule introduced by Chattaraj and coworkers is Minimum Electrophilicity Principle. This principle also implies the minimization in stable states or forms of the electrophilicity index. The validity and limitations of Minimum Electrophilicity Principle[38] have been thoroughly examined by Szentpaly and Kaya[39]. In Fig. 1, The optimized structures of the monomeric forms of the investigated compounds at B3LYP/6-31G(d) level are given. Fig. 2 visually presents the optimized structures of the dimeric forms of the studied molecules at B3LYP/TZP level. Table 1 includes the calculated quantum chemical parameters reflecting the chemical reactivity and stability of the studied molecules. According to the calculated chemical hardness values, the hardest chemical system is BPDH. One can say that BPDH is the most stable molecule among the studied chemical systems. It is clear that polarizability of this molecule is also relatively low. It can be said that our results are in good agreement with Minimum Electrophilicity Principle because the hardest molecule has the lowest electrophilicity index value as can be seen in the related table. Electron transfer ability of BPDH compound is lower than that of others because its hard character.

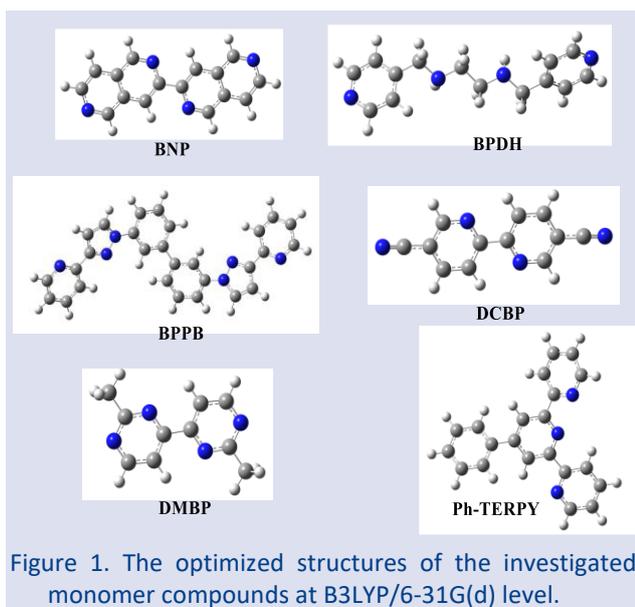


Figure 1. The optimized structures of the investigated monomer compounds at B3LYP/6-31G(d) level.

Marcus theory[40] is widely preferred to explain the charge transfer properties of molecules. As can be seen from the equation related to the mentioned theory that charge transfer ratio is closely related to the reorganization energy and the effective transfer integral. One can report that charge transfer ratio increases with increasing effective transfer integral while low reorganization energy values correspond to higher charge transfer ratios. The molecule having larger values of  $\lambda_e$  and  $\lambda_h$  act as electron blocking material and hole blocking material, respectively. It should be noted that DMBP is an electron blocking material while BPDH acts as a hole blocking material. In Table 2, the calculated reorganization energies, adiabatic-vertical ionization potentials, and adiabatic-vertical electron affinities are presented.

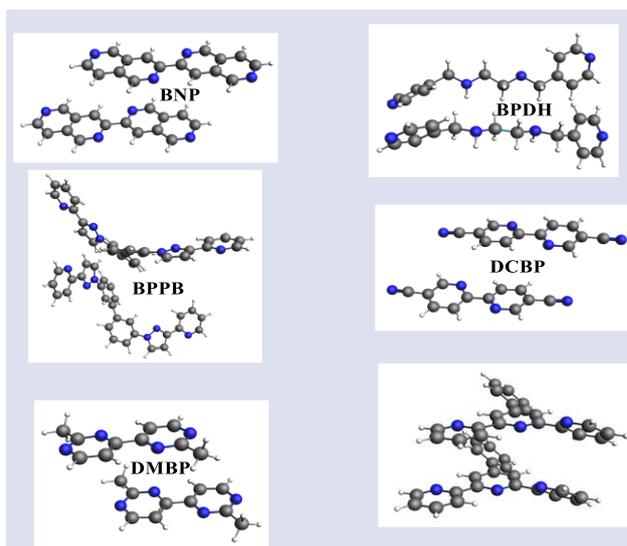


Figure 2. The optimized structures of the studied dimeric molecules at B3LYP/TZP level.

Table 1. The calculated quantum chemical descriptors (in eV) for studied molecules at B3LYP/6-31G(d) level

Compound	$\eta$	$\chi$	$\omega$	$\omega^+$	$\omega^-$	$\alpha$ (a.u.)
BNP	2.06	4.04	3.95	2.19	6.22	214.74
BPDH	2.87	3.49	2.12	0.73	4.22	166.37
BPPB	2.33	3.52	2.66	1.19	4.71	364.69
DCBP	2.20	5.07	5.85	3.59	8.66	162.07
DMBP	2.38	4.48	4.22	2.28	6.76	128.04
Ph_TERPY	2.40	3.77	2.96	1.38	5.15	250.04

Table 2. The obtained reorganization energy, adiabatic-vertical ionization energy, and electron affinity values (all in eV) of molecules investigated at B3LYP/6-31G(d) level in vacuum.

Molecule	$\lambda_e$	$\lambda_h$	IPa	IPv	EAA	EAV
BNP	0.209	0.186	7.45	7.54	0.65	0.55
BPDH	0.357	1.386	7.24	7.92	-0.54	-0.73
BPPB	0.161	0.136	6.87	6.94	0.19	0.11
DCBP	0.355	0.204	8.74	8.84	1.47	1.29
DMBP	0.496	0.495	8.46	8.65	0.60	0.35
Ph_TERPY	0.351	0.245	7.45	7.58	0.20	0.02

It is seen previously published papers that for Alq3 complex used as reference electron transfer material  $\lambda_e$  is 0.276 eV. The compounds with lower  $\lambda_e$  value than that of Alq3 complex can be used as effective electron transfer material. If so, it can be seen from the Table 2 that BNP and BPPB molecules can act effective electron transfer material compared to others. The best one is BPPB molecule. TPD is one of the hole transfer materials used as reference in the literature. For this compound, determined  $\lambda_h$  is 0.290 eV. The molecule with lower  $\lambda_h$  values than 0.290 eV is effective hole transfer materials. Calculated hole reorganization energy values imply that BNP, BPPB, DCBP and Ph\_TERPY molecules can act effective hole transfer material candidates for future

experimental studies. The best hole transfer material among them is BPPB. If so BPPB is both electron transfer material and hole transfer material. Such materials are called as ambipolar material. Ionization energy and electron affinity parameters provide important hints about electron-donating and electron-accepting capabilities of molecules. It is well-known that the materials with small ionization energy and high electron affinity values act as hole and electron transport materials, respectively. From this explanation, it is easy to predict that the best hole injection material and the best electron injection material are BPPB and DCBP compounds, respectively.

Table 3. The computed electron and hole transfer integrals<sup>a</sup> (in eV) and the charge transfer ratios ( $s^{-1}$ ) of compounds studied in the gas phase.

Molecule	$V_e$	$V_h$	$K_e$	$K_h$
BNP	-0.03195	0.02448	$4.91 \times 10^{12}$	$3.82 \times 10^{12}$
BPDH	-0.00131	-0.00316	$1.50 \times 10^5$	$1.98 \times 10^5$
BPPB	0.00168	0.00015	$2.47 \times 10^{10}$	$2.73 \times 10^8$
DCBP	-0.01784	-0.02351	$2.84 \times 10^{11}$	$2.82 \times 10^{12}$
DMBP	0.00502	0.00007	$4.82 \times 10^9$	$9.47 \times 10^5$
Ph_TERPY	-0.04182	0.01404	$1.63 \times 10^{12}$	$1.17 \times 10^{11}$

<sup>a</sup>Transfer integrals were calculated at 298.15 K. For calculation of charge transfer rates, Boltzmann constant is  $8.6173 \times 10^{-5} \text{ eV K}^{-1}$ .

Table 3 shows the computed electron-hole transfer integrals and the charge transfer ratios of studied molecular systems. As the absolute value, the highest electron transfer integral value was obtained for Ph\_TERPY although the highest hole transfer integral belongs to BNP molecule. Additionally, the optimized structures of the studied dimeric molecules are obtained at B3LYP/TZP level and they are presented in Fig. 2. Using optimized dimeric geometries, the electron and hole charge transfer integrals of the studied molecules are achieved at B3LYP/TZP level. Moreover, the charge transfer rates are calculated using the Marcus equation. From the obtained results, it can be said that the highest  $K_e$  and  $K_h$  values are obtained for BNP as presented in Table 2.

## Conclusion

In this paper, firstly, we investigated the chemical reactivities of (BNP), (BPDH), (BPPB), (DCBP), (DMBP), and (Ph-TERPY) compounds using popular electronic structure rules. With the help of Maximum Hardness and Minimum Electrophilicity Principles, it was noted that the most stable compound between studied chemical systems is BPDH. From the calculations regarding to monomeric and dimeric forms, OLED performances of the studied molecules were predicted. The best candidates as electron transfer, electron injection, electron blocking, hole transfer, hole injection and hole

blocking materials were determined. Based on the comparisons made with reference materials in the literature, this computational work will shed light on future experimental studies including the design of new OLED structures.

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## Conflicts of interest

The authors declare that they have no conflict of interest.

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