Comparison of charge transport and opto-electronic properties of pyrene and anthracene derivatives for OLED applications

K. Uzun · S. Sayın ·Ö. Tamer · U. Çevik

Received: 23 February 2021 / Accepted: 11 May 2021 / Published online: 21 May 2021
© The Author(s), under exclusive licence to Springer-Verlag GmbH Germany, part of Springer Nature 2021

Abstract
In this paper, three organic semiconductors such as 9-[(5-nitropyridin-2-aminoethyl)iminoimethyl]-anthracene (a), N′-((pyren-4-yl)methylene)isonicotinohydrazide (b), and novel organic semiconductor N-((2-((pyren-4-yl)methyleneamino)ethyl)-5-nitropyridin-2-amine (c) were prepared. Their structures were assessed using NMR and elemental analysis techniques. While compound (a) and compound (c) have the same wing unit ([5-(nitropyridin-2-aminoethyl)iminoimethyl]), compounds (b) and (c) have the same core unit (5-nitropyridin-2-amine). Based on TD-DFT and Marcus theories, we have explored the effects of molecular structure on the opto-electronic properties for OLED applications. Our results show that wing units of molecules impact more on the opto-electronics properties than on core units. The compounds (a) and (c) with the same wing unit have exhibited quite similar behaviors in terms of both structural and opto-electronic parameters. However, a similar situation has not been observed for compounds (b) and (c) with the same core unit. In conclusion, our results indicate that compounds (a) and (c) exhibit obvious advantages for OLEDs in terms of calculated opto-electronic and charge transport properties such as better absorption and emission parameters, lower energy gaps and reorganisation energies and higher charge mobility.

Keywords DFT · Reorganisation energy · Opto-electronic properties · Pyrene · Anthracene

Introduction
Shirakawathe, MacDiarmid and Heeger [1], awarded with the Nobel Chemistry Prize in 2000, discovered some organic molecules showing semiconductor properties. Since then, the discovery has attracted the interest of scientists in organic semiconductors and also revealed an area called “organic electronics” [2]. Organic electronic has an enormous potential for enlargement completing the range of classic semiconductor applications and for executing the applications that are difficult to do with traditional semiconductors. In the last few years, conjugate organic molecules have been broadly investigated and used in the organic electronic applications such as field effect transistor, solar cells and light-emitting diode [3–5]. Opto-electronic properties of these devices associate with various factors, such as electron density on the frontier molecular orbitals (FMOs), suitable charge carrier, the structural properties of molecules such us core unit or wing unit and the intermolecular interactions [6].

Over the recent years, however, many theoretical researches have been investigated to predict and understand the characteristics of organic materials. The consequence of energy gap of organic semiconductors can be predicted theoretically with the help of conjugation degree, and the optical and electronic properties of organic semiconductor materials can be adjustable as required, and thus, the design of new materials becomes easier and economical. Many studies have shown that the DFT and TD-DFT theories provide accurate results for \( \pi \)-conjugated systems. Due to the wide \( \pi \)-electron system anthracene, the derivatives reach numerous applications in organic electronic devices such as thin-film transistors, solar cells, organic light-emitting diodes (OLEDs) and Schottky diodes [7, 8]. When both intra-molecular \( \pi \)-conjugation and powerful intermolecular \( \pi \)-stacking of pyrene are considered, the pyrene derivatives could be appropriate for
the structural requirements of organic semiconductors [9]. In this paper, theoretical investigations are conducted about the effect of molecular structure on the vibrational, opto-electronic and charge transport properties of molecules based on anthracene and pyrene. Compound a (9-[(5-nitropyridin-2- aminoethyl) iminiomethyl]-anthracene) with anthracene as central core, compound b (N-[2-((Pyren-4-yl)methyleneamino)ethyl-5-nitropyridin-2-amine) and compound c (N′-[(Pyren-4-yl)methylene)isonicotinohydrazide]) with pyrene as central core are shown in Scheme 1. While compounds a and b have the same wing group, compounds b and c have the same core group. For this reason, the effects of core and wing group thus electron donating, withdrawing and neutral groups on the opto-electronic and charge transport properties of molecules have been investigated and compared to each other.

Materials and computational details

Synthesis

9-[(5-Nitropyridin-2- aminoethyl) iminiomethyl]-anthracene (a) and N′-((pyren-4-yl)methylene)isonicotinohydrazide (b) were synthesised according to the literature procedures [S.F. Varol, S. Sayin, S. Eymur, Z. Merdan, D. Ünal. Org. Electron. 31, 25–30 (2016) [10]; S. Sayin, S. F. Varol, Z. Merdan, S. Eymur. J Mater Sci: Mater Electron (2017) 28:13094–13100 [11]. The synthesis of N′-(2-((pyren-4-yl)methyleneamino)ethyl)-5-nitropyridin-2-amine (c) was reported for the first time.

Synthesis of 9-[(5-nitropyridin-2-aminoethyl) iminiomethyl]-anthracene (a): Yield 85%, m.p.; 169–170 °C. 1H NMR (400 MHz, DMSO-d6): δ 3.93 (brs, 2H, -CH2-NH), 4.14 (t, 2H, J = 5.2 Hz, -CH2-N), 6.66 (d, 1H, J = 8.8 Hz, ArH), 7.53 (p, 4H, J = 8.0 Hz, ArH), 8.12–8.15 (m, 3H, NH and ArH), 8.39 (brs, 1H, ArH), 8.51 (d, 2H, J = 8.4 Hz, ArH), 8.70 (s, 1H, ArH), 8.98 (brs, 1H, ArH), 9.46 (s, 1H, -CH=N) (see Figure 1). 13C NMR (100 MHz, DMSO): δ 42.17 (-CH2-NH), 61.26(-CH2-N), 125.45, 125.93, 127.15, 128.47, 129.20, 129.59, 129.77 and 131.24 (ArC), 134.81 (ArC-NO2), 147.38 (ArC), 162.06 (-CH=N), 162.26 (ArC-NH). Anal. calcd. for C23H15N3O (%): C; 79.07, H; 4.29, N; 11.97. Synthesis of N′-((pyren-4-yl)methyleneamino)ethyl)-5-nitropyridin-2-amine (c): A flask was charged with 2-(2-aminoethylamino)-5-nitropyridine (151.9 mg, 0.834 mmol), 1-pyrenecarboxaldehyde (230.3 mg, 1.0 mmol) and 20 mL a mixture of THF/MeOH (1/1, v/v). The reaction mixture was refluxed for 48 h. Then it was cooled to room temperature and filtered. The crude was re-crystallised from EtOH, filtered and dried in an oven. Yield (200 mg, 50.8%); mp 167–168 °C. 1H NMR (400 MHz DMSO-d6): δ 3.87 (brs, 2H, -CH2-NH), 4.03 (t, 2H, J = 5.6 Hz, -CH2-N), 6.66 (d, 1H, J = 8.8 Hz, ArH), 8.13 (t, 2H, J = 7.6 Hz, ArH), 8.21–8.38 (m, 7H, ArH), 8.55 (d, 1H, J = 8.0 Hz, ArH), 8.97 (brs, 1H, -NH), 9.07 (d, 1H, J = 9.6 Hz, ArH), 9.39 (s, 1H, -CH=N) (see Figure 1). 13C NMR (100 MHz, DMSO-d6): δ 161.94, 147.32, 134.78, 132.74, 131.23, 130.55, 129.70, 129.03, 128.87, 127.83, 126.99, 127.10, 127.84, 129.05, 129.36, 130.55, 131.27, 132.62, 140.93, 148.33, 150.10, 150.90, 162.11 (C=O). Anal. calcd. for C23H15N3O (%): C; 79.07, H; 4.33, N; 12.03. Found (%): C; 79.14, H; 4.29, N; 11.97. The reaction mixture was refluxed for 48 h. Then it was cooled to room temperature and filtered. The crude was re-crystallised from EtOH, filtered and dried in an oven. Yield (200 mg, 50.8%); mp 167–168 °C. 1H NMR (400 MHz DMSO-d6): δ 3.87 (brs, 2H, -CH2-NH), 4.03 (t, 2H, J = 5.6 Hz, -CH2-N), 6.66 (d, 1H, J = 8.8 Hz, ArH), 8.13 (t, 2H, J = 7.6 Hz, ArH), 8.21–8.38 (m, 7H, ArH), 8.55 (d, 1H, J = 8.0 Hz, ArH), 8.97 (brs, 1H, -NH), 9.07 (d, 1H, J = 9.6 Hz, ArH), 9.39 (s, 1H, -CH=N) (see Figure 1). 13C NMR (100 MHz, DMSO-d6): δ 161.94, 147.32, 134.78, 132.74, 131.23, 130.55, 129.70, 129.03, 128.87, 127.83,
126.99, 126.94, 126.52, 126.22, 125.38, 124.44, 124.18, 123.49, 123.05, 60.70, 42.33. Anal. calcd. for C24H18N4O2 (%): C; 73.08, H; 4.60, N; 14.20. Found (%): C; 73.13, H; 4.51, N; 14.09.

**Computational methods**

All quantum chemical calculations involved in geometric parameters, opto-electronic and charge transport properties, and vibrational wave numbers of the compounds were carried out using the Gaussian 09w programme [12]. DFT/TD-DFT methods were used to correlate structure-charge transport properties to opto-electronic properties of these compounds. Hybrid functional of Becke three–Lee–Yang–Parr (B3LYP) and (6-31+G(d,p)) basis set were performed both to optimise structure in ground and excited states and to calculate HOMO, LUMO and energy gap [13, 14]. The absorption and emission spectrums were computed with TD-DFT-CAM-B3LYP [15]. The electronic transitions and oscillator strengths were also calculated using the same method.

The rate of charge transfer $K_{CT}$, which is extremely sensitive to structural parameters, can be calculated according to Marcus theory with the following equation [16]:

$$K_{CT} = \frac{2\pi t^2}{h} \sqrt{\frac{\pi}{\lambda k_B T}} \exp\left(-\frac{\lambda}{4k_B T}\right)$$  \hspace{1cm} (1)

where $T$ is the temperature, and $k_B$ is the Boltzmann constant. The intra-molecular reorganisation energy and intermolecular transfer integral are the major parameters for charge transfer properties of organic molecules [17]. $\lambda$ is the reorganisation energy relating to the strength of the electron-phonon (vibration) and used to analyse charge transfer performance in the organic molecules. The reorganisation energies are calculated using Eq. (2) for hole and electron ($\lambda_+$ and $\lambda_-$) respectively.

$$\lambda_{\pm} = [E_{\pm}(g_0) - E_{\pm}(g_\pm)] + [E_0(g_\pm) - E_0(g_0)]$$  \hspace{1cm} (2)

The reorganisation energy for hole ($\lambda_+$) represents the sum of the relaxation energy between the neutral back to cationic state and the relaxation energy between the cationic back to neutral state. The same for the reorganisation energy of electron transport ($\lambda_-$) is equal to the sum of the energies between neutral and anion state and the energy between anion back to neutral state [18, 19].

On the other hand, we calculated the transfer integral with Koopmans’s theorem. The transfer integral is strongly dependent on the charge and neutral molecules interactions and their geometries [20]. To evaluate the transfer integral, the method

---

**Fig. 1** $^1$H NMR (DMSO-d$_6$) spectra of N-(2-(pyren-4-yl)methyleneamino)ethyl)-5-nitropyridin-2-amine (c)
is used to the half of the splitting of the HOMO and HOMO-1 or LUMO and LUMO+1 levels, for holes \( t_h \) or electrons \( t_e \) are calculated according to Eqs. (3) and (4), respectively:

\[
t_h = \frac{E_{\text{HOMO}} - E_{\text{HOMO}-1}}{2} \tag{3}
\]

\[
t_e = \frac{E_{\text{LUMO}+1} - E_{\text{LUMO}}}{2} \tag{4}
\]

To evaluate the oxidation and reduction ability of molecules, we calculated the ionisation potential (IP) and electron affinity (EA) by the equations below.

\[
IP = E_s - E_0 \tag{5}
\]

\[
EA = E_0 - E_- \tag{6}
\]

### Results and discussion

#### Synthesis and characterisation of the organic semiconductors

9-[(5-Nitropyridin-2-aminoethyl) iminiomethyl]-anthracene (a) and \( N'-(\text{pyren-4-yl})\text{methylene} \text{isonicotinohydrazide} \) (b) were synthesised according to the literature procedures [S.F. Varol, S. Sayin, Z. Merdan, D. Ünal. Org. Electron. 31, 25–30 (2016) [10]; S. Sayin, S. F. Varol, Z. Merdan, S. Eymur. J Mater Sci: Mater Electron (2017) 28:13094–13100 [11].

\( N-(2-((\text{pyren-4-yl})\text{methyleneamino})\text{ethyl})-5\text{nitropyridin-2-amine} \) (c) illustrated in Scheme 2 was synthesised in 50.8% yield for the first time by the reaction of 2-(2-aminoethylamine)-5-nitropiridine and 1-pyrenecarboxaldehyde in the presence of THF/MeOH. The structure of \( N-(2-((\text{pyren-4-yl})\text{methyleneamino})\text{ethyl})-5\text{nitropyridin-2-amine} \) was assessed using \( ^1\text{H-NMR} \) and elemental analysis techniques.

NMR technique was used to confirm the structure of \( N-(2-((\text{pyren-4-yl})\text{methyleneamino})\text{ethyl})-5\text{nitropyridin-2-amine} \). Figure 1 shows that compound c was successfully synthesised by appearing the proton of imine group at 9.39 ppm (1H) in the \( ^1\text{H-NMR} \) spectra (see Figure 1).

#### Molecular design, energy and dipole moment

The optimised structures of the ground state of the studied compounds are shown in Figure 2. The related parameters calculated for each compound are listed in Table 1. Table 1 indicates that compound (a) has the shortest bond length meaning that compound (a) has the best charge transfer because the shorter length is an advantage for the intra-molecular charge transfer within the donor-acceptor type molecules [21].

The total molecular energy is used as a base criterion to validate a stable molecular geometry. It can be seen that from the total energy values of the molecules, compound (c) has the best stable structure and in the second place is compound (a) which has same wing unit with compound (c). Thus, it can be stated that wing unit plays an important role in the molecular energy values, and wing units of compounds (a) and (c) create more stable structure. In addition, while compounds (a) and (c) have similarity and big dihedral angle, compound (b) shows growth tendency. These indicate that compounds (a) and (c) have a good planarity and thus have better mobility of charges. In that, non-planar structures could reduce the inter-molecular interaction and affect the gap energy to be realised in the next sections.

We have calculated the vibrational frequencies to ensure the stability of the optimised geometries and confirm the lack of imaginary frequencies. The calculated IR spectra of the investigated compounds are shown in Figure 3. The strongest absorption bands from IR spectrums are observed at 1520.6 cm\(^{-1}\), 1367.8 cm\(^{-1}\) and 1261.8 cm\(^{-1}\) for compounds (a), (b) and (c), respectively. They correspond to C-N stretching vibrations. \( \text{C=C, C=N and N=O stretching, and N-H out of plane bending} \) are observed at double band range 1500–1800 cm\(^{-1}\). The vibrations at 3524.6 cm\(^{-1}\) and 3796 cm\(^{-1}\) for compound (a), 3197.6 cm\(^{-1}\) and 3213.8 cm\(^{-1}\) for compound (b), and 3549 cm\(^{-1}\) and 3557.2 cm\(^{-1}\) for compound (c) correspond to C-H and O-H stretchings.
UV-vis spectral analysis

In order to reveal the molecular structure and opto-electronic properties relationships, the absorption spectra of molecules calculated with TD-DFT/CAMB3LYP method, 6-31G(d,p) basis sets. The UV-vis spectra of molecules are shown in Figure 4. The positions of absorption peaks and their assignment, the optical gap, the oscillator strengths (f), the light absorption efficiency ($\eta_A$) and the electronic dipole moments of molecules are calculated as in Table 2 to analyse the optical properties further and discover the nature of electronic transitions.

The compounds (a), (b) and (c) show maximum absorption wave lengths peaks at 581.2, 556 and 691.2 nm, respectively. The dominant absorption bands are due to $\pi \rightarrow \pi^*$ electronic transitions and the maximum absorption wavelength corresponding to the excitation of an electron from HOMO to LUMO in all the compounds. In this respect, the studied compounds have broad absorption bands and red-shifts, causing the improved light harvesting ability. On the other hand, optical band gaps are computed from onset of compounds absorption via the equation below [17]. The optical band gaps are 1.66 eV, 1.58 eV and 1.18 eV for compounds (a), (b) and (c), respectively. This result is also reflected from the computed absorption maxima of the compounds. Thus, it can be said that compound (c) is the most stable compound with lowest optical band gap.

$$E_g = \frac{1240}{\lambda_{onset} \text{ (nm)}}$$

(7)

Furthermore, we have also computed the light absorption efficiency ($\eta_A = 0.34, 0.30$ and $0.40$ for compounds a, b and c respectively (see Table 2)) that is an essential parameter for the opto-electronic materials [22]:

$$\eta_A = 1 - 10^{-f}$$

(8)

### Table 1

| Molecule | Total energy (Hartree) | Dipole moment (Debye) | 1-2  | 2-3  | 3-4  | 4-5  | 1-2-3-4  | 2-3-4-5  |
|----------|-----------------------|-----------------------|------|------|------|------|----------|----------|
| a        | $-1217.967$           | 11.080                | 1.420| 1.108| 1.276| 1.342| 178.51   | 141.45   |
| b        | $-1108.318$           | 4.131                 | 1.428| 1.294| 1.369| 1.343| 170.66   | -1.386   |
| c        | $-1294.219$           | 12.172                | 1.467| 1.282| 1.456| 1.498| 175.33   | 132.90   |
It can be seen from the light absorption efficiency values that compound (c) has the best light absorption efficiency among the others. This result has caused the transition electronic dipole moments values of each compound. In this respect, the calculations indicate that the optical properties of organic semiconductors can be tuned with suitable wing units. These results show that compound (c) has best optical parameters in terms of OLED applications with (5-nitropyridin-2-aminoethyl) wing unit, and compound (a), which has same wing unit with compound (c), exhibits similar behaviors.

**Photoluminescence spectral analysis**

The excited state geometries of compounds are optimised using TD-B3LYP/6-311G(d,p) level of theory and the optimised geometries. The emission spectra are calculated using the TD-DFT method at CAM-B3LYP/6-311G(d,p). The emission energies and corresponding oscillator strength are summarised in Table 3. The calculated emission spectra for compounds are shown in Figure 5. Figure 5 indicates that the molecular structure has attention grabbing effect on photoluminescence process. The highest emission wavelengths of the studied compounds are 636 nm, 851 nm and 741 nm for compounds (a), (b) and (c), respectively. All maximum emission peaks are assigned to $\pi \rightarrow \pi^*$ electronic transition arisen from excited to the ground state ($S_1$ to $S_0$), and the emission spectra exhibit a red shift for studied compounds. Among the studied compounds, the highest emission wavelength is observed in compound (b) with 851 nm, meaning a strong electron withdrawing with wing unit. All the abovementioned emission bands correspond to the electronic transition between HOMO and LUMO.

On the other hand, the radiative lifetime $\tau$ (ns) meaning the average time that molecules stay in their excited state before emitting photon of studied compounds is calculated using Einstein transition probabilities [23]:

$$\tau = \frac{c^3}{2f(E_m)^2}$$  \hspace{1cm} (9)

where $c$ is the velocity of light, $E_m$ is the fluorescent energy and $f$ is the oscillator strength. The radiative life times are found to be 24.32 ns, 77 ns and 38 ns for compounds a, b and c, respectively. The short radiative lifetimes lead to a high light-emitting efficiency, while long radiative lifetime facilitates the electron and energy transfer [21]. Thus, it can be stated that compound a has the shortest time in the excited state and has the best efficiency in the emission, followed by compound c. So they are good-emitting materials for OLED applications, while compound (b) has more efficiency for photovoltaic cell applications with longer radiative life time. The radiative lifetime of compounds is shorter with increased oscillator strength, leading to an increase in the luminescent efficiency. It should be emphasised again that compounds (a) and (c) have the same wing unit. This fact indicates that introducing (5-nitropyridin-2-aminoethyl) wing unit decreases strongly the lifetime emission of the organic semiconductors. Consequently, they should be good-emitting materials for OLEDs applications with a high efficiency.

As for Stokes shift, compounds (a) and (c) have quite similar behavior again, and compounds (a) and (c) show considerable smaller Stokes shifts with 55 nm and 50 nm values, respectively. These results present small changes between
ground and excited states and less energy loss along the relaxation process. Thorough investigations of emission properties indicate that compounds (a) and (c) have similar parameters and can be more suitable for OLED applications with the same wing unit, and the optical properties of the organic semiconductors can be tuned with a more suitable wing unit.

Opto-electronic properties

Frontier molecular orbitals

Frontier orbital distributions are known to affect the charge transport properties and energy levels can be specified with electron giving away ability of a core [24]. The molecular transport is characterised as “electron-hole transport” if the conduction is mediated by tunnelling through the LUMO (HOMO). So, it is required to have a comprehensive theoretical understanding of the electronic structure of the organic semiconductors [25]. In order to understand the relation between the molecular structure and electronic properties, we have investigated the charge density patterns of the frontier molecular orbitals: the highest occupied molecular orbitals (HOMO and HOMO-1) and the lowest unoccupied molecular orbitals (LUMO and LUMO+1) with their spatial distributions. The computed HOMOs, LUMOs and energy gap (E_g) values of molecules at B3LYP/6-311G(d,p) are shown in Table 4. These values match well with most work function of indium tin oxide (ITO) electrode and suitable for exciton dissociation. The HOMO energy levels of compounds (a) and (c) are higher than that of compound (b), while the LUMO energy levels of compounds (a) and (c) are lower than that of compound (b). This means that the injected electrons would be more stable for compounds (a) and (c), because their lower LUMO energy levels will enable the electron tunnelling from metal electrode to the organic molecule via the LUMO orbital in organic photoelectric devices, such as OLED. Furthermore, the low HOMO energy level for compound (b) allows hole injection to efficiently reach the emitting layer. On the other hand, the energetic gap between HOMO and LUMO is higher in compound (b) with E_g = 3.0 eV, and the lower value is associated to molecule c with E_g = 1.86 eV. These results are in good agreement with the optical spectra, indicating a lower optical gap for compounds (a) and (c). These results indicate that the wing unit of compounds (a) and (c) could reduce E_g values. Thus, compounds (a) and (c) are more stable than compound (b). This result again means that compound (c) has the most efficient electron injection from donor to acceptor. A profound understanding of frontier molecular orbital (FMO) of organic molecules is a needed property to adjust the opto-electronic properties of the molecules. In the π-conjugated molecules, the holes migrate through HOMOs, and electrons migrate through the LUMOs of the nearby molecules (see FMO distribution in Figure 6). HOMO and LUMO lobes are spread over the molecule only for compound (b). HOMO and LUMO lobes are spread over the molecule only for compound (b). It shows that the spatial lap over between the HOMO and LUMO is strong. Thus, stronger optical absorption can be observed for the transfer from HOMO to

Table 3  Emission parameters obtained by TD-DFT/CAM-B3LYP method for the compounds

| Molecule | λ^max_{em} (nm) | E^em (eV) | Oscillator strength (f) | τ(ns) | Transition | Stoke shifts |
|----------|-----------------|-----------|-------------------------|------|------------|--------------|
| a        | 636             | 1.83      | 0.28                    | 24.32| L→H (88%)  | 55           |
| b        | 851             | 1.38      | 0.16                    | 77   | L→H (80%)  | 295          |
| c        | 741             | 1.62      | 0.23                    | 38   | L→H (88%)  | 50           |
LUMO for compound (b). Figure 6 shows also that the wing unit of an organic semiconductors has strong interaction with FMO distribution, because compound (a) and compound (c) have the same wing unit and the same FMO behavior.

**Charge transport properties**

In this section, we have determined the key parameters of OLEDs such as ionisation potential (IP), the electron affinity (EA), reorganisation energies (λ), binding energy and the chemical potential (η). These parameters are essential to evaluate the energy barrier of holes and electron injection including charge mobility, as summarised in Table 4.

The IPs and EAs can be used to enable characterisation of reduction and oxidation. The above properties also provide some other useful information about organic semiconductor devices [16]. The IP values of compounds (a) and (c) are approximately the same and higher than compound (b). Small IP values of emissive layer provide active hole transfer from the origin electrode. Thus, we can say that molecule b is the best structure to create hole transfer from origin electrodes as an emission layer in OLED devices. It has been known that if molecules have high EA values, they display a good electron-accepting capacity [26]. Among the studied molecules, compound (b) has the biggest value of EA 2.85. Therefore, compound (b) could attain electrons from electrodes more easily than compounds (a) and (c).

Low reorganisation energy is required for a better charge transfer and mobility, because charge hopping rates (K\_ET, K\_HT) are inversely related to reorganisation values. In fact, the reorganisation energy consists of nuclear reorganisation and external polarised energy. Since the external polarised energy is quite smaller compared to the nuclear reorganisation energy [27], we only considered the nuclear part in this study. Table 4 indicates that compounds (a) and (c) may be better for electron transport since they have electron-transport reorganisation energy λ\_e lower than hole one λ\_h. Hence, compounds (a) and (c) can be used as promising electron transport materials in the OLEDs. In addition, it can be stated that while compound (b) is a p-type organic semiconductor, compounds (a) and (c) are n-type organic semiconductors. It is an understood thing that most of organic electronics are composed of p-type materials, because hole transporting materials have higher charge mobility and more stable [7]. Hence, we can say again that compounds (a) and (c), which have the same wing unit, are more suitable organic electronic applications such as OLEDs. The binding energy is the energy difference between the neutral exciton, and two free electron holes can be calculated with the energy difference among the electronic band gap and optical band gap (the first singlet excitation energy). It is a very important factor for the electroluminescence materials [28]. The exciton binding energies (E\_b) are 0.60 eV for compound (a), 1.42 eV for compound (b), and 0.68 eV for compound (c), as shown in Table 4. The results indicate that excitons of molecules can be separated easily to free electrons and holes for all molecules due to the quite low E\_b values. But compounds (a) and (c) have exhibited a similar behavior again and they have lower E\_b values than compound (b) implying that compound (b) allows more easily the formation of excitons even at room temperature after excitation and leading to higher fluorescence quantum efficiency after recombination in OLEDs. Table 4 shows that compounds (a) and (c) have better values for both electron and hole intermolecular charge hopping (K\_et = 6.1.10\^15, K\_ht =

**Table 4** DFT/B3LYP/(6-31G(d,p)) calculated electronic and charge transport parameters of studied molecules

| Electronic parameters | Molecule a | Molecule b | Molecule c |
|-----------------------|------------|------------|------------|
| \(E_{HOMO}\)       | -4.89      | -5.39      | -4.52      |
| \(E_{LUMO}\)       | -2.65      | -2.39      | -2.66      |
| \(E_H\)            | 2.24       | 3.00       | 1.86       |
| \(E_{HOMO-1}\)    | -5.76      | -5.66      | -6.08      |
| \(E_{LUMO+1}\)    | -2.15      | -2.38      | -2.25      |
| \(\lambda_e\)     | 0.15       | 0.23       | 0.22       |
| \(\lambda_h\)     | 0.21       | 0.18       | 0.26       |
| \(IP\)            | 1.47       | 2.85       | 1.63       |
| \(\eta\)          | 6.22       | 3.67       | 6.06       |
| \(\tau_h\)        | 2.37       | 0.42       | 2.21       |
| \(\tau_e\)        | 0.44       | 0.13       | 0.43       |
| \(t\_h\)          | 0.25       | 0.05       | 0.20       |
| \(t\_e\)          | 0.60       | 1.42       | 0.68       |
| \(K_{et}\)        | 6.1.10^{15}| 9.8.10^{12}| 2.2.10^{15}|
| \(K_{ht}\)        | 0.86.10^{15}| 4.1.10^{13}| 1.16.10^{15}|

Fig. 5 Calculated emission spectra for compounds at the TD-DFT/CAMB3LYP method, 6-31G(d,p)
Thus, we highlight again that compounds (a) and (c) exhibit the same behavior in this respect. Furthermore, Table 4 shows that the $K_{ct}$ values are bigger than $K_{ht}$ values for compounds (a) and (c). Hence, compounds (a) and (c) can be used as promising electron transport materials in the OLED devices from the standpoint of the charge transport properties.

Conclusions

Theoretical calculations enabled us to assess the role of the wing unit and core unit of the organic molecules on their opto-electronic properties. The fundamental parameters involved in structural, vibrational, charge transport and opto-electronic properties of pyrene and anthracene derivatives were analysed using quantum chemical methods. The calculated optical properties indicated that both compounds (a) and (c) with the same wing units have better absorption and emission properties for organic electronic devices especially OLEDs compared to compound (b). Depending on the molecular structure, the analysis of frontier molecular orbitals showed that compounds (a) and (c) have the same FMO distribution, yet have lower energy gap values than compound (b). These results indicate that the wing unit of compounds (a) and (c) could reduce $E_g$ values. Thus, it can be inferred from this research that the wing unit of an organic semiconductor has strong interaction with FMO distribution of molecules and it affects electronic parameters dramatically. We can see from calculated charge transport properties that while compound (b) is a p-type semiconductor, compounds (a) and (c) are n-type semiconductors. But all three compounds have efficient electron and hole transport with quite high intermolecular charge hopping rates. The calculated binding energies ($E_b$) of compounds show that compounds (a) and (c) have exhibited similar behavior again, and they have lower $E_b$ values than compound (b). This implies that compound (b) allows more easily the formation of excitons even at room temperature after excitation and leads to higher fluorescence quantum efficiency than compounds (a) and (c) after recombination in OLEDs. The interesting opto-electronic and charge transport properties provide opportunities for all three studied compounds to be a potential candidate for opto-electronic devices especially in OLED application. However, compounds (a) and (c) exhibit obvious advantages over compound (b) for organic electronic devices in terms of the properties such as better absorption and emission parameters, lower energy gaps and reorganisation energies, and higher charge mobility. We emphasise that wing units of molecules affect the opto-electronic and charge transport properties more than that of the core units. Compounds (a) and (c) with the same wing units have exhibited quite similar behaviors in terms of both structural and opto-electronic and charge transport properties. However, a similar
situation has not been observed for compounds (b) and (c) with the same core unit. Thus, we can conclude that wing units play a key role in the charge transport and opto-electronic properties. We hope that our study could provide some evidences for the experimentalists to design and synthesise new organic semiconductors to gain better understanding of the effects of molecular structures on the opto-electronic and charge transport properties.

**Code availability** The codes generated during the current study are available from the corresponding author on reasonable request.

**Author contribution** All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Kübra Uzun, Serkan Sayın. The first draft of the manuscript was written by Kübra Uzun and all of the authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

**Data availability** All data generated or analysed during this study are included in this published article (and its Supplementary information files).

**Declarations**

**Competing interests** The authors declare no competing interests.

**References**

1. Shirakawa H, Louis EJ, MacDiarmid AG, Chiang CK, Heeger AJ (1977) Synthesis of electrically conducting organic polymers: halogen derivatives of polyacetylene, (CH)x. J Chem Soc Chem Commun:578–579

2. Rasmussen SC (2011) Electrically conducting plastics: revising the history of conjugated organic polymers. Am Chem Soc 10:147–163

3. Ahmad A (2014) Organic semiconductors for device applications: current trends and future prospects. J Polym Eng 34:279–338

4. Senthilkumar RNK (2014) Charge transport and optical properties of cross-conjugated organic molecules: a theoretical study. Org Electron 15:1607–1623

5. Guo X, Zhou N, Lou SJ, Smith J, Tice DB, Hennek JW, Ortiz RP, Navarrete JTL, Li S, Strzalka J, Chen LX, Chang RPH, Facchetti A, Marks TJ (2013) Polymer solar cells with enhanced fill factors. Nat Photonics 7:825–833

6. Ahmed S, Kalita DJ (2018) Charge transport in isoidigo-dithiophenepyrrole based D-A type oligomers: a DFT/TD-DFT study for the fabrication of fullerene-free organic solar cells. J Chem Phys 149:234906–234917

7. Pramanik A, Sarkar P (2015) Theoretical studies on the carrier tenability of oxidized oligothiophenes. Phys Chem Chem Phys 17:26703–29709

8. Perdew JP, Chevary JA, Vosko SH, Jackson KA, Pederson MR, Singh DJ, Fiolhais C (1992) Atoms, molecules, solids, and surfaces: applications of the generalized gradient approximation for exchange and correlation. Phys Rev B 46:6671–6687

9. Baryshnikov GV, Minaev BF, Pietkow ML, Nielsen CB, Saledo R (2013) Nucleus-independent chemical shift criterion for aromaticity in π-extended tetraoxa [8] circulenes. J Mol Model 19:847–850

10. Varol SF, Sayın S, Eymur S, Merdan Z, Unal D (2016) Synthesis of isoniazid substituted pyrene (PINHy), and investigation of its optical and electrochemical features as tunable/flexible OLEDs. Org Electron 31:25–30

11. Sayın S, Varol SF, Merdan Z, Eymur S (2017) Synthesis of isoniazid substituted pyrene (PINHy), and investigation of its optical and electrochemical features as tunable/flexible OLEDs. J Mater Sci Mater Electron 17:13094–13100

12. Yanai T, Tew DP, Handy NC (2004) A new hybrid exchange-correlation functional using the Coulomb-attenuating method (CAM-B3LYP). Chem Phys Lett 393:51–57

13. Marcus RA, Sutin N (1985) Electron transfers in chemistry and biology. Biochim Biophys Acta Rev Bioenergy 811:265–322

14. Mikkelsen KV, Ratner MA (1987) Electron tunneling in solid-state electron-transfer reactions. Chem Rev 87:113–153

15. Tavernier HL, Fayer MD (2000) Distance dependence of electron transfer in DNA: the role of the reorganization energy and free energy. J Phys Chem B 104:11541–11550

16. Nithya R, Sowmiya M, Kolandaivel P, Senthilkumar K (2014) Structural, optical, and charge transport properties of cyclopentadithiophene derivatives: a theoretical study. Struct Chem 25:715–731

17. Chouk R, Bergaoui M, Jahallah N, Majdoub M, Khalfaoui M (2019) Shedding light on structural, optoelectronic and charge transport properties of PPV stereoisomers for multilayer OLED application: a first principle computational studies. J Mol Liq 284:193–202

18. Lin BC, Cheng CP, Lao ZPM (2003) Reorganization energies in the transports of holes and electrons in organic amines in organic electroluminescence studied by density functional theory. J Phys Chem A107:5241

19. Ma H, Liu N, Huang J-D (2017) A DFT study on the electronic structures and conducting properties of rubrene and its derivatives in organic field-effect transistors. Sci Rep 7

20. García JCS, Jiménez AJP (2014) Theoretical study of stability and charge-transport properties of coronene molecule and some of its halogenated derivatives: a path to ambipolar organic-based materials. J Chem Phys 141:134708–134716

21. Helil A, Mabrouk A, Chemek M, Ben Khalifa I, Alimi K (2015) A DFT study of charge transfer and opto-electronic properties of some new materials involving carbazole units. Comp Cond Matter 3:30–40

22. Norton JE, Brédas JL (2008) Polarization energies in oligoacene semiconductor crystals. J Am Chem Soc 130:12377–12384

23. Nalwa HS (2001) Handbook of advanced electronic and photonic materials and devices: semiconductors, vol 1. Academic Press, pp 313–316

24. Wazzan N, Reda, El-Shishawy M, Irfan A (2018) DFT and TD–DFT calculations of the electronic structures and photophysical properties of newly designed pyrene-core arylamine derivatives as hole-transporting materials for perovskite solar cells. Theor Chem Acc 137:1–15

25. Ürında S, Pramanik A, Sarkar P (2017) Quantum chemical investigation on the Ir (III) complexes with isomeric triazine-based
imidazolium carbene ligand for efficient blue OLED. Phys Chem Chem Phys 19:29629–29640

26. Ottonelli M, Piccardo M, Duce D, Thea S, Dellepiane G (2012) Koopmans’ transfer integral calculation: a comparison between the Hartree-Fock and the density functional results. Energy Procedia 31:31–37

27. Zhang L, Shen W, He R, Liu X, Tang X, Yang Y, Li M (2016) Fine structural tuning of diketopyrrolopyrrole-cored donor materials for small molecule-fullerene organic solar cells: a theoretical study. Org Electron 32:134

28. Suna ZZ, Xua YL, Zhub R, Liuc HY (2018) How to stabilize the HOMO levels and to improve the charge transport properties of hole-transporting materials? Probing the effects of molecular symmetry. Org.Electron. 63:86–92

Publisher’s note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.