A DFT study on the electronic and photophysical properties of biphenylyl/thiophene derivatives for organic light emitting transistors

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ABSTRACT

A theoretical study was carried out to understand the geometrical, electronic and optical properties of bipheylyl/thiophene based molecular system. For that, density functional theory along with classical Marcus charge transfer theory and time-dependent potentials were used. The results indicate that the structure-property relationship between the molecular parameters and ionization energy, electron affinity, reorganization energy, charge transfer integrals, mobility, energy gap, optical absorption and transition dipole moments. Low lying HOMO values and lower bandgaps of the molecules offer a higher charge transport in the systems and 5,5″-bis(4-biphenylyl)-2,2′:5′,2″-terthiophene (BP3T) molecule shows the maximum hole and electron mobility, $0.81 \, cm^2 \, V^{-1} \, S^{-1}$ and $0.17 \, cm^2 \, V^{-1} \, S^{-1}$, respectively. The results have shown that all the title compounds can be fabricated as ambipolar organic semiconductor materials and can be considered for the fabrication of efficient organic light emitting transistors.

1. Introduction

In the recent past, especially after the successful commercialization of organic light emitting diodes (OLED), there is a great surge of interest in organic semiconductor based laser active materials [1–3]. These materials are expected to give high optical gain in broad optical spectra. Since, it is easy to tailor the properties of individual organic molecules and the ease in processeability of organic devices, it is possible to fabricate robust and low-cost devices [4–7]. In order to achieve a good laser active material, much research is required in the area of organic gain medium in different configurations such as microcavities, wave guides, optically pumped thin films, etc. Due to their versatile device structure, organic light emitting field effect transistors (OLET) are generally considered for this purpose. It is easy to construct an organic field effect transistor (OFET) based OLET and it is possible to easily tune the electroluminescence of the device. Many materials have been studied for OLET application and have shown high ambipolar carrier mobility along with light emission in the system [1,2]. But one crucial point to achieve a potential OLET candidate is that the material should have both high carrier mobility as well as with high photoluminescence quantum yield (PLQY). Many benchmarking OFET systems based on ruberene, pentacene, athracene, and their derivatives as single crystals and thin films have been studied for OLET devices. Even though these materials exhibit good electron/hole mobility, they often show very less

PLQY. In some cases, a reverse, high PLQY and low mobility have also been observed [8]. So, it is a matter of great technological interest to find a potential candidate with both high mobility and good PLQY. Recent studies indicate thiophene/phenylene based co-oligomers have shown good mobility and PLQY values and are considered as the suitable candidates for the development of active medium for OLET [9,10]. As one of the pioneers in these systems, the ground breaking report by Hotta et al have shown that these systems have excellent charge transport property with high PLQY [11]. In addition, they have shown that the thiophene/phenylene co-oligomers are suitable candidates for the development of optical pumping organic laser. Also, recently one of the authors, Kanagasekaran et al reported the single crystals of 2,5-bis(4-biphenylyl) bithiophene (BP2T) in OLET structure have shown a carrier mobility of $1.28 \, cm^2 \, V^{-1} \, S^{-1}$ and the threshold for stimulated emission as low as $10.3 \, kA/cm^2$ [12,1]. Still it is challenging to achieve the complete organic laser by electrical pumping. Since, a variety of configurations are possible with these system, it is essential to understand the structure-property relation of the co-oligomers. Especially, it can be seen from the previous reports that 5,5″-bis(4-biphenylyl)-2,2′:5′,2″-terthiophene (BP3T) shows better results than that of 2,5-Bis(4-biphenylyl)thiophene (BP1T) and BP2T [12,1]. So, a systematic investigation is required to identify the role of number of thiophene rings in the system. Also, it is a curious question that what would be the possible output of 2,5-bis(4-biphenylyl) tetrathiophene

(BP4T). The questions "Does the presence of one more thiophene ring in the biphenylyl system improve the overall electric and optical property?", or "What is the exact role of thiophene rings in the biphenylyl system?" form the core objective of the present work. We have attempted a theoretical analysis of four different thiophene/phenelyne, bipheylyl,n-thiophene (BPT) [n = 1–4] systems and studied their electronic and optical properties. It is observed that the mobility and optical emission of the system improved with the addition of thiophene rings. Among the title compounds, BP3T system shows excellent charge transfer characteristics along with the high transition dipole moment. Further, its been observed that the molecular planarity changes with respect to the number of thiophene rings and with the addition of fourth ring to the system (BP4T) affects the molecular planarity to the level that performs lesser than that of BP3T.

2. Methodology

The charge transport property of an organic semiconductor material can be satisfactorily explained using hopping model [13]. In the present work, we have calculated the bulk charge carrier mobility of the material using hopping model. The molecules, biphenylyl with different number of thiophene rings, are shown in Fig. 1 and used for the computational simulations.

From Einstein's relation, the organic semiconductor's mobility at a particular temperature can be given as

$$\mu = \frac{e}{k_B T} D \tag{1}$$

where μ is the mobility, e is the electronic charge, k_B is the Boltzmann constant, T is the temperature. By assuming there is no correlation between the charge motion and hopping events, the diffusion coefficient D with n spatial dimensionality and i specific hopping pathway can be written as

$$D = \frac{1}{2n} \sum_i r_i^2 W_i P_i \tag{2}$$

here r_i is the hopping distance and P_i is the hopping probability, given as

$$P_i = \frac{W_i}{\sum_i W_i} \tag{3}$$

where W_i is the non-adiabatic electronic hopping rate via i^{th} hopping pathway. This non-adiabatic electronic hopping rate (W) at a particular temperature T can be written using Marcus-Hush equation as,

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

here V is the electronic coupling between neighboring molecules and λ is the reorganization energy of the organic semiconducting material.

Thus it can be evident from the above equations that the electronic coupling V and the reorganization energy λ are the two crucial parameters to estimate the mobility of an organic semiconductor. These two parameters can be obtained from first principle studies or density functional analysis using suitable program. In the present work, Gaussian 09 package was used for the charge transfer integral and transition dipole moment calculations, and all other calculations are carried out using ORCA suite with B3LYP/G functional in conjugation with 6-311G** basis set. Since, in organic crystals intermolecular reorganization energies are very low, we have considered only the intramolecular reorganization energy. For that, monomer geometries of neutral, cationic and anionic species are optimized separately then the corresponding energies are used to calculate the hole and electron transport reorganization energies as,

$$\lambda_{\text{hole}} = \lambda_0 + \lambda_+ = (E_0^*(Q_+) - E_0(Q_0)) + (E_+^*(Q_0) - E_+(Q_+)) \tag{5}$$

$$\lambda_{\text{electron}} = \lambda_0 + \lambda_- = (E_0^*(Q_-) - E_0(Q_0)) + (E_-^*(Q_0) - E_+(Q_-)) \tag{6}$$

here E_0 and E_+^*/E_-^* are the energies of the neutral and cationic/anionic monomer in the optimized neutral geometry Q_0 and E_0^* and E_+/E_- are the energies of neutral and cationic/anionic monomers in the optimized cationic/anionic geometry Q_+/Q_-. The intermolecular electronic coupling between donor and acceptor states can be given as,

$$V_{ij} = \left| \frac{(J_{ij} - 0.5(e_i + e_j). S_{ij})}{(1 - S_{ij}^2)} \right| \tag{7}$$

where S_{ij}, J_{ij} and e_i and e_j are the spatial overlap, charge transfer integrals and the site energies, respectively. These quantities can be estimated using the following relations:

$$e_{i(j)} = \langle \Psi_{i(j)} | H | \text{Psi}_{i(j)} \rangle \tag{8}$$

$$S_{ij} = \langle \Psi_i | \text{Psi}_j \rangle \tag{9}$$

$$J_{ij} = \langle \Psi_i | H | \text{Psi}_j \rangle \tag{10}$$

here, H is the Kohn-Sham Hamiltonian of the dimer system, and $\Psi_{i(j)}$ is the hole (in case of HOMO) or electron (in case of LUMO) transport in the monomer. The calculations are carried out using the CATNIP program can be found elsewhere [14,15]. The vibrational transition dipole moments are estimated using Gaussian 09 program and to estimate the optical properties such as vibrationally resolved absorption spectra and emission spectra, time dependent density functional theory (TD-DFT) as implemented in `orca_asa` have been used [16].

3. Results and discussion

3.1. Structural analysis

The geometrical parameters of the molecular system are extracted from the optimized structures and given in Supplementary. Major
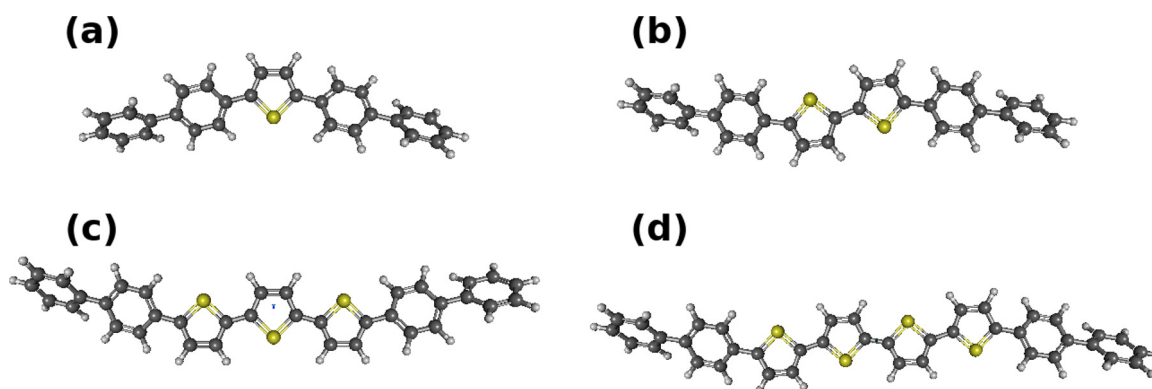

Fig. 1. Molecular structure of thiophene/phenylene co-oligomers (a) BP1T (b) BP2T (c) BP3T and (d) BP4T.

Table 1
Bond angle between the BPT molecules in degree (°).

System	BP1T	BP2T	BP3T	BP4T
$Ph_1 - Th_1$	120.54	120.50	120.50	120.51
$Ph_1 - Th_2$	121.60	121.46	121.44	121.42
$Ph_2 - Th_1$	121.96	121.94	121.96	121.94
$Ph_2 - Th_2$	128.61	128.62	128.64	128.64
$Ph_3 - Th_3$	120.54	120.50	120.50	120.51
$Ph_3 - Th_4$	121.60	121.46	121.44	121.42
$Ph_4 - Th_3$	121.96	121.94	121.96	121.94
$Ph_4 - Th_4$	128.61	128.62	128.64	128.64

Table 2
Bond length between the BPT molecules in Å.

BP1T	BP2T	BP3T	BP4T
P-T (1.4649)	P-T (1.4638)	P-T (1.4634)	P-T (1.4621)
T-P (1.4649)	T-T (1.4452)	T-T (1.4432)	T-T (1.4430)
	T-P (1.4638)	T-T (1.4432)	T-T (1.4420)
		T-P (1.4634)	T-T (1.4430)
			T-T (1.4621)

changes in structural parameters, such as bond length and bond angle, are observed in the junctions between the pheneylyl and thiophene rings and are given in Tables 1 and 2 . There is only a slight variation in bond angles in the phenylyl-thiophene junction have been observed and they are all gradually decreasing from BP1T to BP4T. Similarly, a significant reduction in bond length between the pheneylyl-thiophene rings from BP1T to BP4T has been observed. Also, the distance between thiophene-thiophene rings also reduced with the increase in the number of thiophene rings in the system, i.e., the system tends to be more closely packed when the molecular rings are increased.

Ionization potential and electron affinity of the molecular systems were estimated using [17]

$$IP = E_{(cation)} - E_{(neutral)} \qquad (11)$$

$$EA = E_{(neutral)} - E_{(anion)} \qquad (12)$$

where $E_{neutral}$, E_{cation} and E_{anion} are the energy of neutral, cationic and anionic molecular structures, respectively. The calculated adiabatic IP and EA values are given Table 3 and they represent the reduction and oxidation ability of the molecules respectively. Larger the electron affinity more stable would be the molecule in air and whereas ionization potential can be related to the hole injection [18,19]. In the case of p-type materials lower IP values are desired. It can be seen that the EA values increases with increase in the number of thiophene rings. But these values are less than the threshold value ~ 2.8 eV to become an air-stable medium. Further, increase in EA values with respect to the number of thiophene rings suggests that the electron withdrawing nature of these system. Also, based on Kuo et al. report if the IP values are in the range of 5.9–7.0 eV [20], the materials can be used for the construction of OFETs with ambipolar properties. The obtained results show the potentiality of the title compounds towards ambipolar properties and our previous experimental results have also shown that it is possible to construct an ambipolar OFET from BP2T and BP3T systems [21,12]. Natural bond analysis (NBO) is a second order interaction

Table 3
Molecular energy of neutral, cationic and anionic systems (in a.u.), ionization potential and electron affinity values in eV.

Molecule	$E_{neutral}$	E_{cation}	E_{anion}	IP	EA
BP1T	−1477.2685	−1477.0310	−1477.2834	6.462	0.405
BP2T	−2029.0872	−2028.8597	−2029.1130	6.190	0.702
BP3T	−2580.9057	−2580.6863	−2580.9408	5.970	1.151
BP4T	−3132.7236	−3132.9449	−3132.7649	6.021	1.123

Table 4
Reorganization energy (λ) values in eV, Marcus charge transfer parameters (J_{eff}) in eV, charge integral mobility in $cm^2 V^{-1} S^{-1}$ (μ_h: hole mobility, $\mu_{h(exp)}$: experimental hole mobility, μ_e: electron mobility) and $\mu_{e(exp)}$: experimental electron mobility).

Molecule	λ_{hole}	λ_{elec}	J_{eff}	μ_h	μ_e	$\mu_{h(exp)}$	$\mu_{e(exp)}$
BP1T	0.116	0.029	− 0.5334	0.0081	0.003	~ 10^{-3}	NA
BP2T	0.114	0.043	− 0.0001	0.2955	0.054	0.08	0.011
BP3T	0.102	0.961	− 0.0163	0.8122	0.170	1.0	0.5
BP4T	0.248	0.039	− 0.0007	0.2768	0.049	NA	NA

between the filled and vacant orbitals and it can be used to estimate the intermolecular delocalization of the molecular systems. The ground state donor and acceptor NBO values have been simulated and the major perturbation interactions are given in the Supplementary. From the results, it can be seen that the major contributions are arise due to $\pi \rightarrow \pi *$ interactions of C-C. But with the increment in the number of thiophene rings, $n \rightarrow \pi *$ transition in the thiophene rings have been increased. It is due to the lone pair participation of sulfur ions in the molecule. Overall, with the introduction of more thiophene rings, the system tends to be stabilized in the ground state.

3.2. Electronic properties

The internal reorganization energies of all the four title compounds have been simulated and given in Table 4. The reorganization values can be used to interpret the electronic hopping rate in the system. It can be seen that with increase in the number of thiophene rings, the reorganization energy value gradually decrease, except the case of BP4T, in which it shows an increment. The decrement can be interpreted to the improvement in charge delocalization with increase in the length of the molecule. This means that with the increment in number of thiophene units the positive charge in the overall system is more delocalized and distributed uniformly throughout the system. Since the reorganization energy is related to the charge distributed on the carbon atoms, a decrement has been observed. Whereas in the case of BP4T, planarity of the molecule have been modified significantly and that limits the charge delocalization in the system, indicates the system exhibit steric hinderance effect and undergo smaller system relaxation during the hole transfer process [22,23]. Table 4 shows the calculated charge transfer integral of the systems, obtained by using cofacial dimers of the corresponding molecules. Depending upon the intermolecular separation, the transfer integrals of the system vary and BP2T system shows the largest transfer integral value, followed by BP4T. This is due to the variation in electronic coupling driven by orbital overlap of the systems and increases with the variation in molecular planarity [24]. Since we are expecting a vertical charge transition over a planar structure, no tilt angle measurements were carried out in the present work. In the case of face-to-face orientation, often net polarization is zero due to the equivalent contribution from the monomers. But in our case, the stacking is not exactly perpendicular. Due to the slight twisting in the stacking, the charge integral values are varying. The calculated reorganization energy and charge transfer integrals are used to calculate the charge transfer mobility in the systems and the calculated values are given in Table 4. BP3T system shows highest hole and electron mobility followed by BP2T and BP4T. BP1T shows the lowest mobility values. Very limited work is reported on DFT analysis of biphenylyl/thiophene systems for various applications. Upto our knowledge, theoretical hole and electron mobilities are available only for the BP2T system and the present results are in agreement with it [25]. The experimental FET parameters are available for BP2T and BP3T systems and the present data is comparable to them [11,21,26,27]. The variation in theoretical data with respect to the reported experimental data is due to the fact that the neglection of experimental conditions and surface properties during the DFT simulation. But the observation of
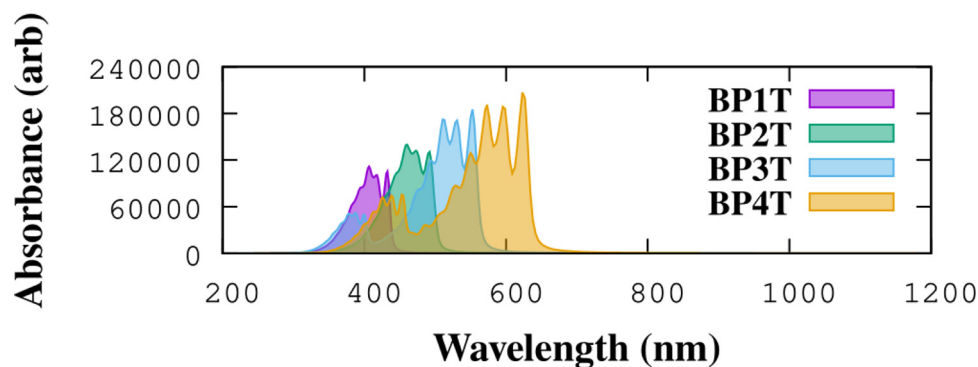
Fig. 2. Linear absorption spectrum of the BPT molecules.

similar trend in the BP2T and BP3T systems, indicate that the results of other two systems BP1T and BP4T are reliable. BPT systems are known for their ambipolar properties. The significant variation between the electron and hole mobilities, in the present work, are arise due to the fact, that we consider co-planar dimers for the charge transfer calculations. Such an assumption is important in the case OLET materials, in order to harvest the maximum transition dipole moment in the system. A seminal report by Bredas et al. have shown that molecular parameters like composition, planarity, intermolecular $\pi - \pi$ conjugation are selectively affecting hole and electorn hopping transport in the system [28]. In the present work, significant variation in electronic properties with respect to molecular planarity has been observed for different BPT systems. In addition to that, the variation in electron and hole mobilities can be attributed to the planarity dependent selective molecular response for different charge carriers. A similar phenomenon is observed in the case of conjugated polyemers reported elsewhere [29].

3.3. Optical properties

The optical absorption spectra obtained using TD-DFT method is shown in Fig. 2. Few reports available on the absorption spectrum of title compounds. Notably, Shang et al. reported the absorption spectrum of BP2T single crystals with a strong absorption band in the 400–550 nm region [30]. Similarly Bisri et al. reported a absorption spectrum of BP3T thin films, with a shoulder peak in the UV region and a strong absorption band in the 300–600 nm region [31]. Considering the fact that the broadening of the experimental peaks is due to their solid state feature, it can be seen that the present theoretical data is in well agreement with the reported data [32]. In the present work, the absorption maxima of the systems are found to be red shifted with the addition of more thiophene rings in the system. The exact nature of exciton dynamics in the BPT system with respect to the number of thiophene rings can be understood from the frontier orbital analysis. It is also can be used to estimate the hole/electron injections in the molecular systems. The optimized geometry in the neutral state was utilized to plot the frontier orbitals and energy gap of all the molecules, and the corresponding HOMO, LUMO values and the energy gap E_g of the systems are shown in Fig. 3. A phenomenal work by Kawaguchi et al. on BP1T shows that the HOMO, LUMO and E_g values as -5.27, -1.56 and $3.71\,eV$ respectively [33]. Their theoretical data is in agreement with the experimental data. We have also obtained a similar values for BP1T, indicates the scientific suitability of the obtained data. Most often, in OFETs, metals like Au, Ca, Mg and Al are used as electrodes for source and drain contacts. Commonly used Au's work function is around 5.1 eV and the lower HOMO levels than contacts would facilitate hole injection in the medium effectively [34]. Further, lower the energy gap value, easier the charge transfer between HOMO and LUMO levels. It can be seen that, with increase in the number of thiophene rings, the LUMO values are decreasing, whereas HOMO values are increasing. Further, in all the molecules HOMO and LUMO values
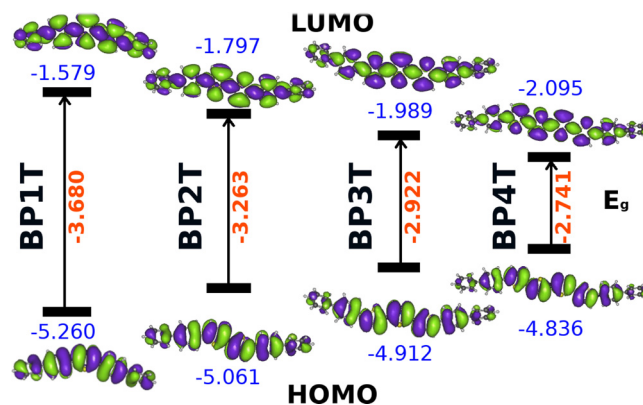

Fig. 3. Frontier orbitals of (a) BP1T (b) BP2T (c) BP3T (d) BP4T.

are delocalized over the entire molecule and the band gap values decreasing uniformly. Also, addition of thiophene rings does not affect charge distrubtion in the system. Instead, even with the addition of thiophene rings, the charges are equally distributed over the molecule. This explains the fact that the gradual increment in optical properties of BPT system, in contrast to their electrical properties. But the increment in the number of absorption peaks along with the presence of shoulder peaks (Fig. 2) in BP3T and BP4T systems indicates the effect of molecular planarity [35,36]. The emissive nature of the molecule can be understood from the superposition of the transition dipole moments. In crystalline systems, maximum efficiency can be obtained with the perfect horizontal alignment the molecules. In this work, since we concentrate only on molecular systems, we have simulated the transition dipole moments along with the vibrational excitation spectrum for each molecule. The obtained transition dipole moments data is given in the Supplementary and the obtained vibrational spectra is shown in Fig. 4. Eight distinct absorption peaks can be identified in Fig. 4, of which, two peaks, around $3250\,cm^{-1}$ and $1500\,cm^{-1}$ shows distinct characteristics with respect to the number of thiophene rings. The small peaks with intensity less than 0.2 can be attributed to the static charge distribution upon excitation. Whereas, strong absorption peaks are due to the charge transfer process in the system, with different charge transfer capabilities. For example, the peak around $1500\,cm^{-1}$ is stronger than other peaks, and it gradually increasing with the addition of thiophene rings in the system. Thus, this peak could play a dominant role in the size of exciton induced in the molecule [37,38]. The fluorescence spectrum is plotted using the calculated oscillator strengths (f_{osc}) and given in Fig. 5 and the obtained data is compared to the previous experimental data and given in Table 5 [25,39]. Even though the major peaks are in agreement with the experimental data, observation of shoulder peaks in BP2T and BP3T in the blue region, corresponding to characteristic molecular emission, is not present in the experimental data. These peaks could have quenched due to crystal
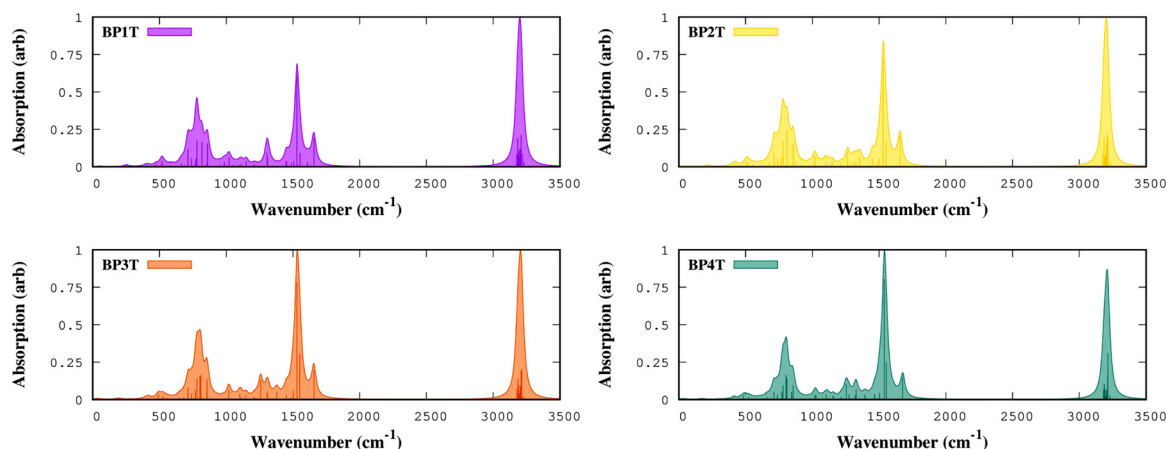
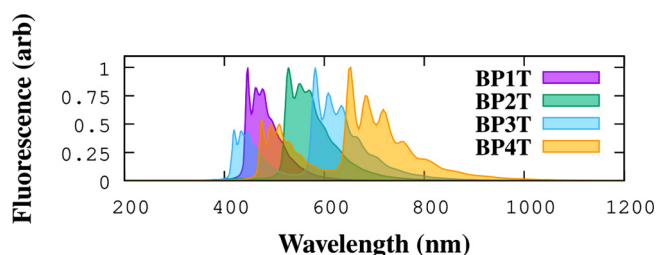**Fig. 4.** Vibrational spectrum of the BPT molecules.

Fig. 5. Fluorescence spectrum of the BPT molecules.

Table 5
Calculated and experimental data (in *nm*) of major emission peaks in BPT system.

Molecule	Calculated	Experiment
BP1T	462	471
BP2T	529	516
BP3T	607	613
BP4T	652	NA

packing or suppressed due to the experimental limitations. A detailed and in-depth experimental analysis is required to understand the same.

In the present work, similar to the absorption spectrum the emission bands are gradually red shifted with the increase in number of thiophene rings in the system. The dominant emission peak in all the systems corresponding to $\pi \to \pi*$ character arising due to the LUMO $\to$ HOMO transitions. The highest f_{osc} corresponds to $S_1 \to S_0$ transition and the most of the emission is obtained due to this transition. Hence, tailoring the PLQY can be done by tweaking this transition. Using E_g of the system and the fluorescence oscillator strengths, exciton binding energy can be calculated and it can be used as an estimation for the emission strength of different systems. The obtained values are in the order of BP4T > BP3T > BP2T > BP1T. This means that, higher the exciton binding energy, it would be harder to destroy the hole-electron pair in the system and to obtain the emission. Overall, the addition of electron withdrawing thiophene molecules to the BPT system improves its emission properties.

4. Conclusions

In summary, we have theoretically studied the structural, electronic and optical properties of four biphenylyl/thiophene oligomers. From the results, it is found that the addition of thiophene rings to the BPT system, significantly modified the geometrical, electronic and optical parameters. The low lying HOMO orbitals with increase in thiophene ring has been greatly contributed to the reduction of energy gap as well as advantageous for charge transport in the system. For a better carrier mobility, the system should have small reorganization energy and large transfer integrals and the same was observed in the BPT systems up to BP3T. But significant contribution of planarity affects the electrical transport in BP4T. Due to the donor-acceptor interactions and the electron withdrawing nature of the thiophene rings, larger electron affinity values has been obtained, which in turn affected the reorganization energy, transfer integrals and charge carrier mobility of the BPT systems. In all the four molecules, BP3T shows better electronic property than the other three systems. But based on their ionizarion potential and electron affinity studies, all the four systems can be utilized as ambipolar materials. Particularly, BP3T shows ionization potential values around 1.5, which is the half mark to obtain an air stable system. So, in future, with proper substituent, the system can be tweaked to obtain an air-stable ambipolar material. In optical absorption spectrum the peaks are red shifted with respect to the addition of thiophene rings. From the transition dipole moment analysis, it has been found that the major dipole moment contribution is observed around $1500 \, cm^{-1}$ and it increases from BP1T to BP4T. More and in depth studies are required to analyse the alignment of these dipole moments, so that their emissive property can be completely understood.

Declaration of Competing Interest

The authors report no declarations of interest.

Acknowledgement

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.mtcomm.2020.101509.

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