# GEOMETRIC and ELECTRONIC PROPERTIES of OLIGOMERS BASED ON LUORINATED THIOPHENES and 1H-PHOSPHOLES: N- VERSUS P-TYPE MATERIALS

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***ABSTRACT:*** *A series of oligothiophenes and novel oligophospholes, consisting of fluorinated and perfluoroarene-substituted structures, were investigated by using density functional theory (DFT) method. The study focused on the geometrical structures and electronic properties. The degree of* $\pi$*-conjugation in the neutral oligomers was studied by different approaches including analysis of predicted Raman spectra. The character of the charge carrier of the new substituted oligomers, either electron (n-type doping) or hole (p-type doping) transport, was predicted by comparing their properties, including the HOMO and LUMO energies, excitation energies, and reorganization energies, with those of their non-substituted parent oligomers. The DFT results are consistent with the available experimental data on the oligothiophenes for both geometries and conductivity properties. The results strongly suggest that an effective way of designing new materials with n-type conductivity is to introduce electron-withdrawing groups into the oligomer backbone. Interesting results were also obtained for oligomers based on 1H-phospholes, which are predicted to have interesting properties as new semiconductor materials..*

***Keywords :****DFT, HOMO, LUMO, oligothiophenes, oligophospholes*

## 1. INTRODUCTION

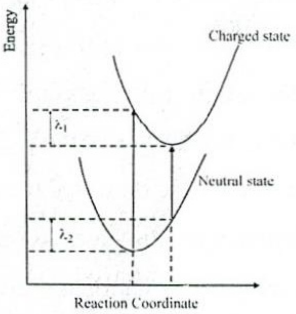
Organic heterocyclic oligomers and polymers based on thiophene and pyrrole derivatives have attracted significant attention during the last decade due to their useful electrical and/or optical properties.1-6 In particular, as well-defined thiophene oligomers and polymers with specific properties have become available, a wide range of semi-conductor devices have been fabricated, including thin-film field effect transistors,7 light-emitting diodes,8 and photovoltaic components9 for technological applications such as flat television screens and solar cells. Organic-based semiconductor devices offer advantages over conventional silicon-based semiconductors in that they can be made small as well as having the necessary flexibility in larger systems. The resulting organic electronic materials are generally fabricated by alternating layers of p-type and n-type materials. Thus, both p- and n-type compounds are needed. While organic compounds form a rich source for providing various p-type materials, they offer only rare and unstable materials for n-type counterparts. The deficiency and poor stability of n-type materials constitute a challenging issue for researchers in this field. Recently, some remarkable experimental results of group Suzuki[10] and Marks[11] show that it is possible to convert a p-type to an n-type material by introducing electron-withdrawing groups into the p-type molecular core. For example, tetradecafluorosexithiophene (denoted hereafter as pF-6T, pF stands for perfluoro and T for thiophene) or perfluoroarene-modified thiophene oligomers (denoted as TFTTFT, FTTTTF, where T stands for thiophene and F for perfluoroarene). Theoretical studies have also recently been reported on thiophene-based polymers.[13,14] In this paper, we have used computational chemistry methods: (1) to investigate the geometrical and electronic properties of oligomers based on thiophene monomers and (2) to search for potentially novel compounds with interesting properties. For the first goal, we considered the four known oligomers, namely α-sexithiophene (6T), perfluoro-α-sexithiophene (pF-6T), and two perfluoroarene modified thiophene oligomers (FTTTTF and TFTTFT). For the second goal, we studied the molecular structures and electronic properties of the yet unknown 1H-phosphole analogues of the thiophene oligomers mentioned above. Earlier theoretical studies[15,16] showed that phospholes exhibit promising properties as building blocks for π-conjugated polymers. The geometric and electronic properties of these phosphole oligomers have been calculated for comparison with their thiophene counterparts. We have studied the hexamers because of the availability of experimental results for the corresponding thiophenes.

## 2. COMPUTATIONAL DETAILS

Structure studied in this work is presented in Figures 1, 2. The geometries of the eleven oligomers were first fully optimized with trans-oriented monomer units using density functional theory (DFT) method with the hybrid Becke, Yang and Parr functional (B3LYP)[17] and the split-valence plus d-polarization functions on S and P atom 3-21G(d) basis set and the 3-21G basis set on H. Harmonic vibrational frequencies were calculated at this level in order to establish the nature of the stationary points, as well as to determine Raman intensities to aid in the characterization of π-conjugated oligomers. Experimentally this characterization is based on the spectral region of the stretching modes of the C=C and C–C bonds along the backbone, following the effective conjugation coordinate (ECC) suggested by Zerbi's group,[18] and widely used to study the electronic structure of molecular materials.[19-24]

The energy gap ($E_g$) can be calculated as the difference in energies of both the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO),[25] or determined, as in the present work, by computing the electronic excitation energy using a time-dependent TD-DFT method.[26,27] For the π-conjugated systems such as the heterocyclic oligomers considered here, the lowest allowed excitations correspond to singlet π*(LUMO) ← π(HOMO) transitions. This approach is an efficient and reliable method for predicting energy gaps.[28]

The inner-sphere reorganization energies of a hole, denoted by $\lambda^+$, and an electron, $\lambda^-$, corresponding to the cationic and anionic electronic states, were calculated for each oligomer. According to Marcus electron-transfer theory, the reorganization energy (λ) is an important parameter for predicting the self-exchange electron-transfer rate. The electron transfer rate correlates with λ such that a small value for λ corresponds to a fast rate.[29-31] Thus λ is a measure of the efficiency of charge carriers in materials. The value of λ can be obtained from both experiment and theory.[14,32-43] Following the original definition, λ for an electron-transfer process is associated with two geometry relaxation energies, $\lambda_1$ and $\lambda_2$, going from the neutral state to the charged-state and the reverse. A schematic definition of these parameters is given in Figure 3. The $\lambda^+$ and $\lambda^-$ terms can be estimated from the ionization energy (IE) and electron affinity (EA) of a neutral species as follows:



$$\lambda^{\pm} = \lambda_1^{\pm} + \lambda_2^{\pm} \qquad (1)$$

$$\lambda_1^{\pm} = \mathrm{IE}_v^{\pm} - \mathrm{IE}_a^{\pm} \qquad (2)$$

$$\lambda_2^{\pm} = \mathrm{EA}_v^{\pm} - \mathrm{EA}_a^{\pm} \qquad (3)$$

**Figure 3**. Potential energy surface of neutral and charged states that define $\lambda_1$ and $\lambda_2$.

where the superscripts + and − and the subscripts v and a used to denote the cationic, anionic electronic states, vertical and adiabatic quantities, respectively. The DFT method with the B3LYP functional has been shown to give reasonable values for $\lambda^+$ and $\lambda^-$,[32-34] so we used the B3LYP/SV(P) level with the unrestricted DFT formalism.

The vertical and adiabatic ionization energies ($\mathrm{IE}_v$, $\mathrm{IE}_a$), and adiabatic electron affinities ($\mathrm{EA}_a$) were calculated because they are needed for the reorganization energies. We used two different methods to evaluate the vertical ionization energies ($\mathrm{IE}_v$). The first is the difference in total energies of both neutral and cation ground states obtained from the neutral geometry at the B3LYP/SV(P) level. The other simply corresponds to the negative value of the HOMO energy derived from HF/SV(P) wavefunction, within the framework of Koopmans' theorem.

The geometries of the neutral, cation and anion species of each oligomer were optimized at the (U)B3LYP/SV(P), using the Turbomole 5.7 program.[44] For the structures with terminal perfluoroarenes (FTTTTF, 1H-FPPPPF and 1F-FPPPPF), we employed the Gaussian 03 program.[45] The Turbomole program was further used for .calculating frontier orbital properties such as ionization energies and energy gaps. Electronic density contours of 0.03 e/bohr$^3$ were used for plotting the frontier orbitals of the neutral compounds with Gaussview 3.0[46]. The vibrational spectra were calculated by using the Gaussian 03 program. The IR and Raman spectrum were produced by using the GaussSum 0.8 package.[47] The eigenvectors of Raman bands were displayed by the ChemCraft program,[48] and the Mercury 1.3 software[49] was used for crystal structure visualization.

## 3. RESULTS AND DISCUSSIONS

We first analyze the geometrical parameters of the oligomers 6T, pF-6T, FTTTTF and TFTTFT shown in Figure 1, in order to understand the reason(s) why they are candidates for n-type and p-type semiconductors, and what could be changed in their structure by substituting fluorine atoms or perfluoroarene groups. The fully optimized geometrical parameters of these oligomers are summarized in Table 1, together with available crystal results for the purpose of comparison. The data focus on the maximum torsion angles between the adjacent outer rings ($\gamma$) and the distances (d) of the C–C inter-ring bonds, C–S, C–C and C=C bonds in the thiophene rings. The $\gamma$ bond angle values of 5.6°, 0.0°, 17.9° and 4.4° in 6T, pF-6T, FTTTTF and in TFTTFT, respectively, show that pF-6T is planar, whereas the other compounds are quasi-planar. In comparison with the experimental $\gamma$ values, the calculations on pF-6T and TFTTFT predict an even more planar shape. The larger observed torsion is likely due to crystal packing effects. In contrast, 6T is predicted to be slightly less planar than observed experimentally. The $\gamma$ value for FTTTTF agrees well with the experimental result.[11a]

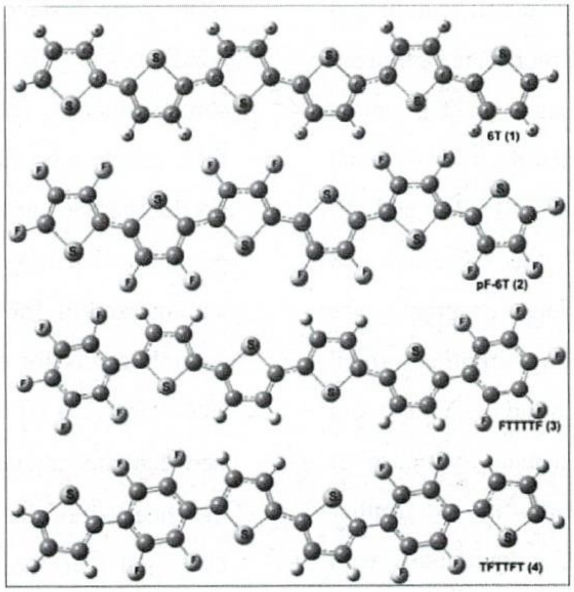


**Figure 1.** α-sexithiophene (**6T**), perfluoro-α-sexithiophene (**pF-6T**), perfluoroarene- modified thiophene oligomers (**FTTTTF**) and (**TFTTFT**).

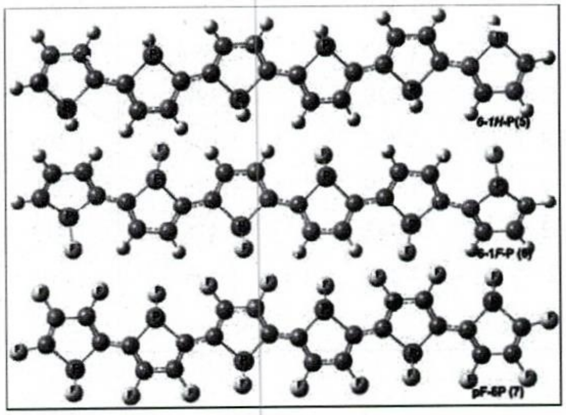
**Table 1:** Experimental[a] and Theoretical maximum torsional angles (degrees) and selected bond distances (Å) of **6T**, **pF-6T**, **FTTTTF** and **TFTTFT**

| Oligomer | γ | $d_{C\text{-}C}$[a] | $d_{C\text{-}C}$[b] | $d_{C=C}$ | $d_{C\text{-}S}$ |
|---|---|---|---|---|---|
| **6T** | 5.6 | 1.445-1.450 | 1.415-1.424 | 1.373-1.387 | 1.730-1.754 |
| | (4.1) | (1.439-1.444) | (1.400-1.416) | (1.342-1.388) | (1.709-1.738) |
| **pF-6T** | 0.0 | 1.439-1.442 | 1.413-1.425 | 1.368-1.383 | 1.741-1.757 |
| | (3.6) | (1.431-1.439) | (1.375-1.393) | (1.324-1.360) | (1.700-1.735) |
| **FTTTTF** | 17.6 | 1.445-1.466 | 1.413-1.414 | 1.386-1.388 | 1.744-1.757 |
| | (17.6) | (1.445-1.471) | (1.402-1.416) | (1.371-1.374) | (1.727-1.741) |
| **TFTTFT** | 4.4 | 1.448-1.465 | 1.412-1.420 | 1.374-1.392 | 1.721-1.761 |
| | (7.9) | (1.399-1.462) | (1.399-1.420) | (1.338-1.409) | (1.700-1.752) |

[a] In parentheses are the experimental values, taken from Ref. 12 for 6T, Ref. 10 for pE-6T and Ref. 11a for FTTTTF and TFTTFT. [b] C–C inter-ring bond. [c] C–C intra-ring bond.

The C–C inter-ring bond distances are consistently longer than the C–C intra-ring lengths. In 6T and pF-6T, on the one hand, the bonds belonging to the outermost rings are actually shorter as compared with the corresponding bonds in the inner rings. In contrast, the bonds connecting with the perfluoroarene rings in both FTTTTF and TFTTFT are found to be longer. The C–C inter-ring bond distances are dependent on the degree of conjugation of the π-system, the shorter the C–C inter-ring bond distance, the more pronounced the linear π-conjugation between these building blocks. This shows that perfluorination of the non-substituted oligothiophene 6T giving pF-6T slightly reinforces the linear π-conjugation, as manifested by a decrease of C–C inter-ring bond distances in going from 1.445 Å in 6T to 1.439Å inpF-6T. In contrast, replacement of two thiophene rings in 6T by two perfluoroarene rings tends to increase the C–C inter-ring bond distances to 1.455Å in FTTTTF and 1.448Å in TFTTFT. Thus, fluorination induces a linear π-conjugation in these oligomers, although the effect is not large.

The structures of the oligomers based on phosphole monomers are displayed in Figures 2. Important geometrical parameters are summarized in Table 2.



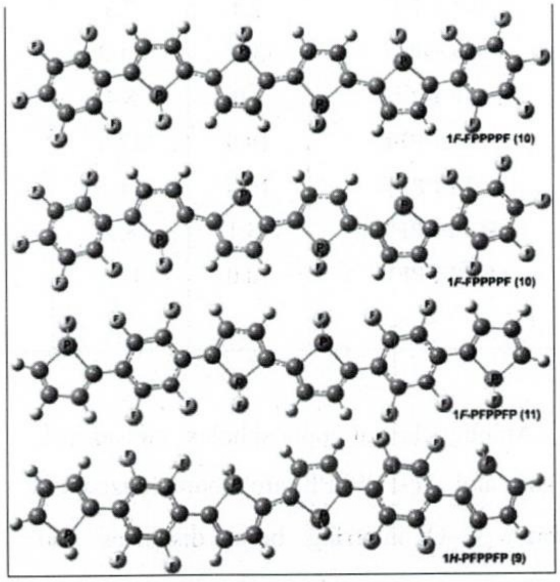


**Figure 2.** 1*H*-sexiphosphole (**6-1*H*-P**), 1*F*-sexiphosphole(**6-1*F*-P**) and perfluoro- sexiphosphole (**pF-6P**) oligomers.**igure 3.** Perfluoroarene-modified 1*H*-phosphole (**1*H*-FPPPPF**) and (**1*H*-PFPPFP**)**,** and perfluoroarene-modified 1*F*-phosphole oligomers (**1*F*-FPPPPF**), (**1*F*-PFPPFP**).

**Table 2:** Comparison calculation maximum torsional angle (degrees) and C–C inter-ring bond distances (Å) of neutral and charged states all compound

| | **Max torsional angles** | | | **C–C inter-ring** | | |
|---|---|---|---|---|---|---|
| **Oligomer** | **Neutral** | **Cation** | **Anion** | **Neutral** | **Cation** | **Anion** |
| **6T** | 5.6 | 1.9 | 2.0 | 1.445 | 1.418 | 1.418 |
| **pF-6T** | 0.0 | 0.0 | 0.0 | 1.439 | 1.414 | 1.414 |
| **FTTTTF** | 17.6 | 6.3 | 4.0 | 1.455 | 1.416 | 1.419 |
| **TFTTFT** | 4.4 | 2.0 | 2.1 | 1.448 | 1.420 | 1.421 |
| **6-1*H*-P** | 7.3 | 7.3 | 7.0 | 1.435 | 1.405 | 1.406 |
| **6-1*F*-P** | 10.7 | 11.8 | 9.2 | 1.427 | 1.3394 | 1.396 |
| **pF-6P** | 9.0 | 8.4 | 6.5 | 1.429 | 1.399 | 1.403 |
| **1*H*-FPPPPF** | 18.8 | 13.0 | 16.8 | 1.437 | 1.406 | 1.406 |
| **1*F*-FPPPPF** | 10.5 | 11.1 | 13.2 | 1.429 | 1.396 | 1.397 |
| **1*H*-PFPPFP** | 13.1 | 8.5 | 11.2 | 1.443 | 1.413 | 1.413 |
| **1*F*-PFPPFP** | 10.0 | 11.8 | 8.2 | 1.435 | 1.404 | 1.406 |

Among the oligophospholes considered, pF-6P and 1F-FPPPPF are characterized by shorter C–C interring bond distances and smaller $\gamma$ values. This implies a more pronounced linear $\pi$-conjugation between the building blocks. In this context, they could be considered as candidates for both n-type and p-type semiconductors, comparable to their oligothiophene counterparts. In order to get more insight into this important property, we studied their vibrational spectra and electronic properties.

### Predicted Raman Spectra of Neutral Compounds

The Raman profiles in the 1700–800 cm$^{-1}$ spectral region of all eleven oligomers are displayed in Figures 4 We do not in detail every peak appeared in these Raman spectra. In order to gain some qualitative but meaningful structural information, we used the effective conjugation coordinate (ECC) approach,[19] whose assumption is the existence of an effective $\pi$-electron delocalization (or conjugation) in the conjugated oligomer.

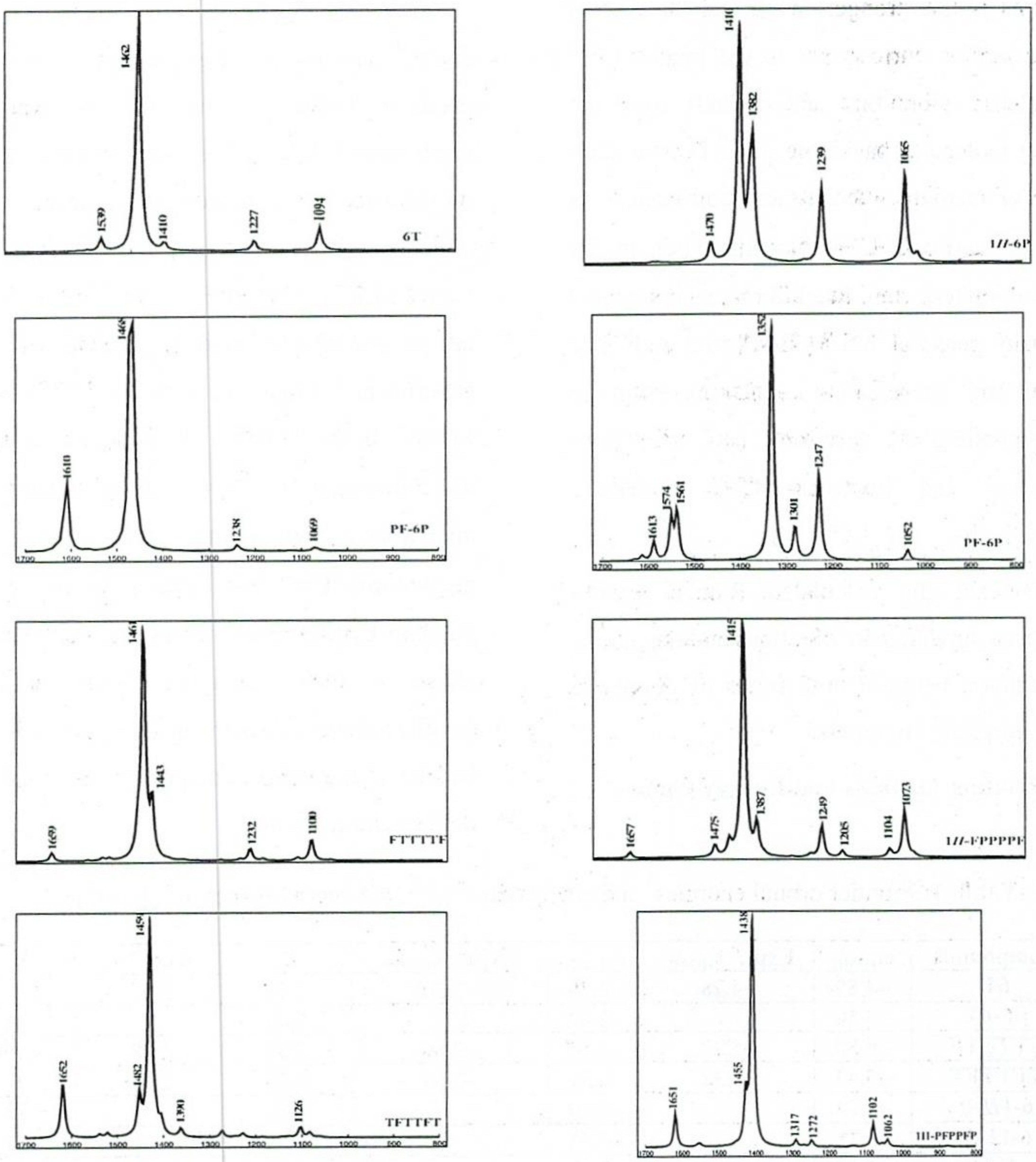


**Figure 4.** DFT//B3LYP/3-21G(d) Raman profiles (un-scaled, in cm$^{-1}$) for 6T, pF-6T, FTTTTF, TFTTFT, 6-1*H*-P, 6-1*F*-P, pF-6P, 1F-FPPPPF and-PFPPFP.

According to the ECC analysis, the Raman fingerprints for a class of oligomers and polymers can be recognized through four typical absorption bands and denoted as lines A, B, C and D. In the case of 6T, the lines A, B and D have been identified and the relevant frequencies are calculated (observed value[50] in parentheses) at 1539 (1505) cm$^{-1}$, 1462 (1459) cm$^{-1}$ and 1094 (1051) cm$^{-1}$, respectively. Line A is a band with weak intensity, and its normal mode is a collection of C=C anti-symmetric vibrations. These modes, lying on the outer-most rings, are mixed to a large extent with stretching modes of the inner C=C bonds. Line

B turns is the strongest band and the normal mode motion corresponds to the regular C=C symmetric vibrations and spreads over the whole molecular backbone. Line D is a sharp band of medium intensity and corresponds to the symmetric C–C–H bending mode in the inner thiophene ring. In addition, we notice low intensity peaks at 1410 (1368) $cm^{-1}$ and 1227 (1220) $cm^{-1}$; these bands are also present in the corresponding IR spectrum, and arise from intra-ring and inter-ring C–C stretching, respectively.

Overall, the calculated Raman spectra suggest a similarity in vibrations and degrees of conjugation between both series of thiophene and phosphole oligomers.

### Frontier Orbitals and Energy Gaps

Calculated frontier orbital energies and energy gaps for all oligomers considered are given in Table 3, along with the available experimental values. The experimental frontier orbital energies were determined from cyclic voltammetry of as thin films on Au/glass versus SCE[11a]. These DFT orbital eigenvaluess are in remarkably good agreement with the experimental values for both the HOMO and LUMO. In the HOMO, which can be regarded as π-bonding, the C=C units exhibit an alternating phase with respect to their neighboring C=C counterparts. In the π-anti bonding LUMO, the C=C units have the same phase as their neighbors. Although each frontier orbital is expanded over the entire π-backbone, the largest components are centered on the central atoms.

**Table 3:** Frontier orbital energies[a] and energy gaps[b] ($E_g$). All energy values are given in eV

| Compounds | $\varepsilon_{HOMO}$ | Expt.[c] $\varepsilon_{HOMO}$ | $\varepsilon_{LUMO}$ | Expt.[c] $\varepsilon_{LUMO}$ | $E_g$ | Expt.[d] $E_g$ | f[f] |
|---|---|---|---|---|---|---|---|
| 6T | –4.89 | –4.78 | –2.24 | –2.36 | 2.41 | 2.42[d] | 2.01 |
| pF-6T | –5.50 | | –2.82 | | 2.47 | | 1.98 |
| FTTTTF | –5.30 | –5.27 | –2.54 | –2.69 | 2.50 | 2.58[e] | 1.99 |
| TFTTFT | –5.43 | –5.32 | –2.51 | –2.67 | 2.66 | 2.65[e] | 2.10 |
| 6-1*H*-P | –4.74 | | –2.80 | | 1.82 | | 1.94 |
| 6-1*F*-P | –5.15 | | –3.55 | | 1.52 | | 1.67 |
| pF-6P | –5.69 | | –3.83 | | 1.72 | | 1.52 |
| 1*H*-FPPPPF | –5.16 | | –3.02 | | 1.98 | | 1.83 |
| 1*H*-PFPPFP | –5.34 | | –2.84 | | 2.26 | | 1.88 |
| 1*F*-FPPPPF | –5.44 | | –3.62 | | 1.67 | | 1.50 |
| 1*F*-PFPPFP | –5.60 | | –3.38 | | 1.96 | | 1.52 |

[a] The frontier orbital energies are calculated at B3LYP/SV(P)//B3LYP/SV(P) level.

[b] The energy gaps are determined by using TD-DFT at the B3LYP/SV(P)//B3LYP/SV(P) level.

[c] Experimental frontier orbital energies were determined from cyclic voltammetry of 1-3 as thin films on Au/glass versus SCE[11a]. [d] The UV-VIS absorption measurement was carried out on sexithiophene single crystals.[12] [e] Film optical[11a] $E_g$ , [f] Oscillator strength.

The results in Table 3 indicate that oligophospholes are characterized by lower energy gaps as compared to oligothiophenes. A perfluoro- or fluoroarene substitution on the parent oligothiophene 6T, or oligophosphole 6-1H-P leads to a reduction of the gap. In FTTTTF and TFTTFT, the $\varepsilon_{HOMO}$ ($\varepsilon_{LUMO}$) are reduced by 0.4 eV (0.3 eV) and 0.5 eV (0.3 eV), respectively, with respect to 6T. Since FTTTTF has a more stable LUMO, as compared to TFTTFT, it is expected that FTTTTF with two ending perfluoroarene moieties is more favored for electron injection into its LUMO, and thereby a better n-type material. A similar trend is found for oligophospholes. pF-6P has the largest frontier orbital stabilization of the entire series of oligomers considered, with a stabilization of both orbitals of ~1.0 eV.

When fluorine substitution occurs only at P-atoms, 6-1F-P, the energy gap becomes strongly reduced. This can be attributed to the stronger LUMO stabilization as compared to that of HOMO. In 1F-FPPPPF, the gap is decreased by ~0.15 eV, as the LUMO is stabilized by 0.8 eV as compared to a stabilization of 0.65 eV for the HOMO. The HOMO's for 1H-FPPPPF, 1H-PFPPFP and 1F-PFPPFP are stabilized with smaller changes in the LUMO so that the gaps are increased by 0.16, 0.44 and 0.14 eV, respectively. Thus, it should be easier to create a hole in the HOMO's of these compounds. Overall, the calculated gaps show that substitution in the backbone of non-substituted oligophospholes by fluorine atoms or perfluoroarene, can modify their optical properties. Among these, the 6-1F-P and 1F-FPPPPF can be regarded as potential candidates for n-type materials, whereas 1H-PFPPFP is better suited for a p-type material.

These results prompted us to further investigate the more doped derivatives for the sake of a comprehensive understanding of the factors influencing their charge carriers by evaluating the reorganization energies of both holes and electrons.

### Ionization Energies and Electron Affinities

The vertical and adiabatic ionization energies ($IE_v$, $IE_a$) and adiabatic electron affinities ($EA_a$) were calculated to determine the reorganization energies and the carrier polarity of oligomers. The IE can be interpreted as a measure of the possibility of a polymer (or oligomer) to be useful for p-type doping, whereas the EA indicates the possibility of n-type doping. Thus the changes in IE's and EA's provide us with information on the injection barriers of electrons and holes. The calculated results are tabulated in Tables 4 and we summarize some conclusions: i) the differences in the $IE_v$ and $IE_a$ are 0.11–0.20 eV indicating a rather small geometry relaxation upon ionization. ii) most of the compounds studied have quite low $IE_v$'s, ranging from 5.73 to 6.69 eV as noted above. A larger IE implies that the corresponding cation has a higher energy as compared to its neutral parent and is less stable toward reduction. Thus, the corresponding compound is more likely to form a p-doped state. iii) all of the adiabatic EA's are positive so electron attachment invariably results in stable anions. iv) The calculated EA's vary in the range of 1.29–3.04 eV, with 6T having the smallest EA and pF-6P having the largest EA. The large effect of fluorine on EA's has been emphasized in previous studies.[15,51] A larger EA implies a low-energy anion and the material is thus more likely to form a n-doped state. v) A comparison of the properties of both 6T to PF-6T allows us to examine the perfluorination effect. The calculated IE and EA of 6T are 5.82 eV and 1.29 eV, respectively. These values agree well with previous ab initio results.[14a] The IE and EA of pF-6T are predicted to be both 0.60 eV higher than those of 6T. Thus, pF-6T can form an n-doped species as observed experimentally.[52] vi) The IE of FTTTTF is 6.35 eV, a value similar to that of TFTTFT (6.38 eV). Its EA is 0.16 eV larger than that of TFTTFT, suggesting that FTTTTF would be more more stablilized in the n-doped form than TFTTFT. Experimentally, FTTTTF has an electron mobility μ− = 0.08 cm2/Vs, whereas TFTTFT has a hole mobility of μ+ = 0.01cm2/Vs. vii) For the unsubstituted oligophosphole 6-1H-P, the IE is predicted to be 0.24 eV smaller and its EA 0.67 eV larger than the corresponding values of 6T. Thus 6-1H-P could form either p- or n-doped materials. viii) the IE's and EA's of the fluorinated oligophospholes 6-1F-P and PF-6P are also predicted to be larger than those of the non-substituted oligophosphole 6-1H-P. As a result, fluorine substitution tends to increase the stability of the n-doped forms. ix) As expected, the IE and EA of 1F-FPPPPF and 1F-PFPPFP are larger than those of 1H-FPPPPF and 1H-PFPPFP, due to the effect of the fluorine atoms so 1F-FPPPPF is more suitable for an n-doped material as compared to 1H-FPPPPF. x) and, the IE and EA of 1F-PFPPFP are 0.24 and 0.57 eV larger than those of 1H-PFPPFP. However, the IE and EA of the substituted oligophospholes with terminal perfluoroarene rings 1H-FPPPPF and 1F-FPPPPF are larger than those of 1H-PFPPFP and 1F-PFPPFP. These results show that the terminal fluoroarenes, substituted in the oligophospholes backbone, consistently increase the preference for n-doped forms.

**Table 4:** DFT//B3LYP/SV(P) vertical, adiabatic ionization potential and adiabatic electron affinities (all in eV)

| **Oligomer** | **Ionization Potential** | | **Adiabatic Electron Affinities** |
|---|---|---|---|
| | **Vertical ($IE_v$)** | **Adiabatic ($IE_a$)** | **$EA_a$** |
| 6T | 5.95 | 5.82 | 1.29 |
| pF-6T | 6.56 | 6.42 | 1.89 |
| FTTTTF | 6.48 | 6.35 | 1. 74 |
| TFTTFT | 6.49 | 6.38 | 1.58 |
| 6-1*H*-P | 5.73 | 5.58 | 1.96 |
| 6-1*F*-P | 6.12 | 5.91 | 2.79 |
| pF-6P | 6.69 | 6.49 | 3.04 |
| 1*H*-FPPPPF | 6.28 | 6.14 | 2.25 |
| 1*H*-PFPPFP | 6.37 | 6.24 | 1.95 |
| 1*F*-FPPPPF | 6.55 | 6.37 | 2.90 |
| 1*F*-PFPPFP | 6.63 | 6.47 | 2.52 |

## Reorganization Energy

The reorganization energies (in eV) were calculated at the UB3LYP/SV(P) level. Table 5 lists the relaxation energies $\lambda_1^{\pm}$, $\lambda_2^{\pm}$, and reorganization energies $\lambda^{\pm}$ of hole and electron transport processes.

**Table 5**: Relaxation energies $\lambda_1^{\pm}$, $\lambda_2^{\pm}$ and reorganization energies $\lambda^{\pm}$ (in eV) of hole and electron transport processes at the B3LYP/SV(P)

| **Compounds** | **Hole-transport** | | | | **Electron-transport** | | |
|---|---|---|---|---|---|---|---|
| | $\lambda_1^+$ | $\lambda_2^+$ | $\lambda^+$ | | $\lambda_1^-$ | $\lambda_1^-$ | $\lambda^-$ |
| 6T | 0.12 | 0.12 | 0.24 | | 0.11 | 0.10 | 0.21 |
| pF-6T | 0.14 | 0.15 | 0.29 | | 0.13 | 0.12 | 0.25 |
| FTTTTF | 0.13 | 0.13 | 0.26 | | 0.14 | 0.14 | 0.28 |
| TFTTFT | 0.11 | 0.11 | 0.22 | | 0.11 | 0.11 | 0.22 |
| 6-1*H*-P | 0.15 | 0.16 | 0.31 | | 0.13 | 0.14 | 0.27 |
| 6-1*F*-P | 0.20 | 0.20 | 0.40 | | 0.19 | 0.19 | 0.38 |
| pF-6P | 0.20 | 0.23 | 0.43 | | 0.19 | 0.20 | 0.38 |
| 1*H*-FPPPPF | 0.15 | 0.15 | 0.30 | | 0.15 | 0.16 | 0.31 |
| 1*F*-FPPPPF | 0.18 | 0.18 | 0.36 | | 0.19 | 0.20 | 0.39 |
| 1*H*-PFPPFP | 0.13 | 0.14 | 0.27 | | 0.12 | 0.13 | 0.25 |
| 1*F*-PFPPFP | 0.16 | 0.16 | 0.32 | | 0.15 | 0.16 | 0.31 |

The results in Table 5 show that in a hole-transport process involving the cationic state, the two reorganization energy components $\lambda_1^+$ and $\lambda_2^+$ are approximately equal. Similarly, the two components $\lambda_1^-$ and $\lambda_2^-$ for an electron-transport process involving the anionic species, are also nearly equal. Our prediction the pF-6T is an n-type semiconductor is in good agreement with previous theorical[14a] and experimental[10,52] studies. The sequence of calculated reorganization energies, TFTTFF ($\lambda^+$ = 0.22 eV) < 6T ($\lambda^+$ = 0.25 eV) < FTTTTF ($\lambda^-$ = 0.27 eV), is consistent with the trend of experimental mobilities, TFTTFF ($\mu^+$ = 0.01 cm$^2$/Vs) < 6T ($\mu^+$ = 0.03 cm$^2$/Vs) < FTTTTF ($\mu^-$ = 0.08 cm$^2$/Vs). The type of transport predicted for these compounds based on $\lambda^+$ and $\lambda^-$ is not well correlated with the reported results that 6T is better able to transport electrons than to transport holes (cf. refs. 11, 12). In fact, 6T is well known to be a p-type semiconductor material. However, it should be stressed that the calculated $\lambda^+$ = 0.25 eV is marginally larger than $\lambda^-$ = 0.21 eV. Although our calculated reorganization energies for 6T agree quite well with those previously reported,[32] an oligomer having six units as used as our model may not be large enough to predict the properties of a much longer polymer. Similarly, FTTTTF is predicted to transport holes ($\lambda^+$ = 0.26 eV is smaller than $\lambda^-$ = 0.28 eV), whereas TFTTFF can transport both holes and electrons with equal probability ($\lambda^+$ = $\lambda^-$ = 0.22 eV). The hole mobilitys of FTTTTF and electron mobility of TFTTFF have been reported to be $\mu^-$ = 0.08 cm$^2$/Vs and $\mu^+$ = 0.01 cm$^2$/Vs, respectively. In spite of the limited size of the oligomers considered, these results lend strong support for the view that although reorganization energy terms are important factors, they are not the only properties that determine the polarity of the charge carriers.

## 4.CONCLUSIONS

We have investigated the molecular structures and electronic properties of a series of thiophene and phosphole oligomers, substituted by either fluorine atoms or perfluoarence moieties. For the experimentally known oligothiophene derivatives (6T, pF-6T, FTTTTF and TFTTFT), our calculations predict geometrical parameters in good agreement with the structures from X-ray diffraction studies[10, 12]. The electronic structure/thermochemical properties such as HOMO and LUMO energies, the energy gap ($E_g$), ionization energies (IE), and electron affinities (EA) are consistent with experimental results. Together, these show that pF-6T and FTTTTF are candidates for new n-type materials, whereas TFTTFT should be a p-type material. Fluorination of of the oligothiophene (pF-6T) not only increases the chain planarity, thus enhancing its $\pi$-conjugation, but also reduces the LUMO energy, thus stabilizing the anion. The oligomers with terminal perfluoroarene rings are predicted to be p-type materials. For the unknown oligophospholes,

the 6-1F-P and 1F-FPPPPF derivatives are found to exhibit interesting electronic properties such as small energy gaps, and a favorable LUMO stabilization, and can thus be regarded as potential candidates for n-type materials. In contrast, the 1H-PFPPFP oligomer has a larger HOMO stabilization and is predicted to be a p-type material. If these F-phosphole derivatives can be synthesized, they should have novel and interesting semiconductor properties.

# CẤU TRÚC HÌNH HỌC VÀ TÍNH CHẤT ĐIỆN TỬ CỦA MỘT SỐ OLIGOME DẪN XUẤT FLO HÓA CỦA THIOPHEN VÀ 1H-PHOSPHOL: VẬT LIỆU BÁN DẪN HỮU CƠ LOẠI N HAY P ?

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***TÓM TẮT:*** *Sử dụng hóa tính toán với phương pháp phiếm hàm mật độ (DFT) nghiên cứu cấu trúc và tính chất điện tử của một số dẫn xuất thế flo, perfloaren của oligome thiophen và phosphol. Độ liên hợp pi của mạch oligome được dự đoán bằng nhiều cách khác nhau, trong đó có cả phương pháp dựa trên sự phân tích của phổ Raman. Đặc tính hạt tải điện của một số oligome với nhóm thế mới ở dạng điện tử dẫn (dẫn loại –n) hay những lỗ trống điện tử (dẫn loại – p) được dự đoán dựa trên năng lượng biên HOMO và LUMO, năng lượng ở trạng thái kích thích và năng lượng tái cấu trúc. Kết quả tính toán phù hợp với một số kết quả thực nghiệm cả về cấu trúc và tính chất dẫn điện. Kết quả cũng cho thấy để thiết kế vật liệu dẫn mới loại n cần đưa nhóm rút điện tử vào mạch oligome. Một số tính chất thu vị dự đoán được từ oligome 1H-phosphol hứa hẹn cho một loại vật liệu bán dẫn hữu cơ mới.*

***Từ khóa:*** *DFT, HOMO, LUMO, oligothiophenes, oligophospholes*

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