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# Theoretical study of fluorinated phenylthiophenes as candidate materials for charge-storage applications

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#### ARTICLE INFO

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ABSTRACT

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Keywords: Conducting polymer Fluorine-substituted phenylthiophene Density functional theory Charge storage A series of fluorine-substituted phenylthiophenes (FPTs) were studied by means of the density functional theory (DFT). The structural, electronic, and energetic properties of the titled molecules were discussed and rationalized in term of the number and position of the fluorine atoms. The calculations were performed on the *mono-*, *di-*, and *tri*-FPTs in their neutral and ionic species by employing the B3LYP/6-311G(d,p) level of theory. The results obtained revealed that the fluorine-substituted phenyl groups played a fine-tune effect on the properties of the FPT monomers. It was found that the electronic chemical potential and electrophilicity index could be successfully correlated with the electronic character of the substitution via a linear dependence behavior on the Hammet function ( $\sigma$ ). Moreover, the calculated first excitation energies for FPTs at the TD-DFT level indicated that both the *p*- and *n*-doped states had lower excitation spectra. The frontier molecular study revealed that the *p*- and *n*-doped states had more suitable properties with respect to the unsubstituted PT, reflecting the hole and electron transport characteristics of the FPT derivatives. We hope that the results obtained can be helpful in designing a series of modified materials with the facilities of hole and electron injections and efficient charge transport.

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#### 1. Introduction

Over the past decade, the  $\pi$ -conjugated organic materials have been extensively used in the electronic devices, electrochromic displays, batteries, and a number of other systems of industrial interest [1-8]. These applications have received a great deal of attention due to their effective conjugated length and the degree of electronic delocalization present in such materials. Conjugated polymers have recently received a growing attention as an interesting class of materials for use in the electrochemical capacitors, which are high-power energy storage devices [9,10]. Compared with batteries, the nature of charge storage in the electrode-active materials is capacitive, and the charge and discharge processes involve only the translation of ionic and electronic charges through the electronically and ionically conducting domains, respectively [11,12]. One of the most interesting anticipated applications of electrochemical capacitors is their use as a power storage device in an electric vehicle, which can be recharged within a long period of time [11,12]. The organic materials used as electron and hole transfers in these devices lag behind due to obstacles such as the low solubility, difficult processing, and instability in air. In this way, the design of stable  $\pi$ -conjugated materials with high efficiently of charge injection and fast charge transport is one of the key challenges in developing the charge-storage devices.

Conducting polymers based on thiophene and thiophene derivatives are attractive for use in the energy-storage devices [13,14] and organic light-emitting diodes (OLEDs) [15–17] since they can exist in both the oxidized and reduced states. From the neutral state or semi-conductor form, polythiophenes can be oxidized into the *p*-doped state or reduced into the *n*-doped state (conductor forms). The combination of an *n*-doped and *p*-doped polythiophenes in an appropriate electrolyte solution can be utilized in a charge-storage device. It has been found that the charge capacity and reversibility associated with n-doping of polythiophene are not as good as for *p*-doping [18]. Therefore, it is necessary to develop strategies to improve the charge capacity and stability for their applications involving the *n*-doped state. The electrical and optical properties of polythiophenes can be finetuned by derivatization of thiophene with suitable substituents on the monomer rings [19–23]. It has been known that the electronic and structural properties of a substituent contribute to the

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delocalization of a polymer  $\pi$ -conjugate system. Roncali and coworkers [24–26] have shown that the *n*-doping densities of polythiophenes can be increased by derivatization with a phenyl or a fluorine-substituted phenyl group at the  $\beta$ -position of the thiophene attached via different linkages. The specific features of fluorinated conjugated compounds such as the easy electron injection and great thermal and oxidative stabilities are related to the high electronegativity of the fluorine atom. Moreover, Searson et al. [27,28] have reported the synthesis and characterization of a number of monomers based on the substituted phenylthiophenes (PTs) with various fluorine atoms at the *ortho*-, *meta*-, and *para*positions of the phenyl ring. Searson and coworkers have shown that the charge capacity and reversibility for *n*-doping can be highly improved for PTs functionalized with fluorine atoms.

Theoretical calculations have recently been employed to investigate different aspects related to the molecular and electronic structures of thiophene derivatives using density functional theory [29,30]. DFT calculations for conjugated systems have been extensively used at the B3LYP level of theory [31–33]. Besides, DFT is now the preferred method for electronic structure theory for organometallic compounds [34]. In this paper, we report a theoretical investigation carried out on a series of fluorophenylthiophenes (FPTs), which can be used for a desirable design of novel functional materials for conducting polymers. In these molecules, the hydrogen atoms at different positions of the phenyl ring are substituted for the fluorine atoms, and this leads to the seven structures displayed in Scheme 1. We showed that the fluorine-substitute phenyl groups can modify some of the physical and electronic characteristics of the FPT monomers. This effect can be related to the steric and electronic influences of the substituents through consideration of the number and position of the fluorine atoms on the phenyl ring.

#### 2. Results and discussion

#### 2.1. Molecular structure

The sketch map of the structures with atom numbers for all FPTs is depicted in Scheme 1. It is noticeable that the carbon atoms adjacent to the heteroatom in the thiophene ring, the  $\alpha(C_{11})$  and  $\alpha'(C_9)$  positions, are the branching centers in the electropolymerization process, and thus control the stereochemistry of the polymer chains. Also both the  $\beta(C_7)$  and  $\beta'(C_8)$  positions are suitable for substitution [35,36]. In this work, the phenyl substitution was fixed at the  $\beta$ -position in all the molecules. The optimized geometrical characteristics of the studied molecules in the neutral form and in both the radical anion and radical cation forms are given in Tables S1–S3 of the supporting information.

### a) PT: $X_{i}$ =H b) 2-FPT: $X_{12}$ =F c) 3-FPT: $X_{13}$ =F d) 4-FPT: $X_{14}$ =F e) 2,4-FPT: $X_{12}$ =X<sub>14</sub>=F f) 3,4-FPT: $X_{13}$ =X<sub>14</sub>=F g) 3,5-FPT: $X_{13}$ =X<sub>15</sub>=F

h) 3,4,5-FPT: X<sub>13</sub>=X<sub>14</sub>=X<sub>15</sub>=F

**Scheme 1.** Molecular structure and numbering schemes used for: a) phenylthiophene (PT), b) 3-(2-fluorophenyl)thiophene (2-FPT), c) 3-(3-fluorophenyl)thiophene (3-FPT), d) 3-(4-fluorophenyl)thiophene (4-FPT), e) 3-(2,4-fluorophenyl)thiophene (2,4-FPT), f) 3-(3,4-fluorophenyl)thiophene (3,4-FPT), g) 3-(3,5-fluorophenyl)thiophene (3,4,5-FPT).

#### Table 1

Some geometry parameters including the torsion angle (in degree) and the bond length (in angstrom) for FPT species in neutral state at B3LYP/6-311G(d,p) level of theory.

Species	$\varphi_{7123}$	C <sub>7</sub> -C <sub>1</sub>	C <sub>2</sub> -F <sub>12</sub>	C <sub>3</sub> -F <sub>13</sub>	C <sub>4</sub> -F <sub>14</sub>	C <sub>5</sub> -F <sub>15</sub>
PT	180	1.480	_	_	-	_
2-FPT	180	1.478	1.357	-	-	-
3-FPT	180	1.479	-	1.353	-	-
4-FPT	180	1.480	-	-	1.351	-
2,4-FPT	180	1.478	1.354	-	1.348	-
3,4-FPT	180	1.479	-	1.346	1.344	-
3,5-FPT	180	1.478	-	1.350	-	1.350
3,4,5-FPT	180	1.477	-	1.343	1.338	1.3434

In Table 1, some selected bond lengths and the dihedral angles defining the torsion between the phenyl group and thiophene ring  $(\varphi_{7123})$  of the FPT derivatives are shown. According to this table (column 2), our calculations indicated that all monomers had planar structures ( $\varphi_{7123}$  = 180°), in which the fluoro-substituted phenyl groups were slightly away from the thiophene ring due to their steric hindrances ( $C_7$ — $C_1$  bond length in column 3). It is interesting that the introduction of fluorine atoms on the phenyl ring did not affect the planarity of the parent molecule (PT). Planarity of the thiophene derivatives is an important parameter in their electrical conductivity. In general, crystalline oligothiophenes have been found to be nearly planar as a result of more favorable crystal packing [37]. Using the optimized geometries for the monofluorosubstituted derivatives (2-FPT, 3-FPT, and 4-FPT species), it was found that the C-F bond length in the phenyl substitution increased in the order of *ortho* > *meta* > *para* position. In general, in all the molecules under study, the C-F distance for the orthoposition (in the 2-FPT and 2,4-FPT molecules) was larger than the ones at the other positions. This may be attributed to the steric effect resulting from the proximity of the ortho-substituted fluorine atom to the thiophene ring.

#### 2.2. Electronic properties

One of the important parameters involved in the polymerization mechanism of a heterocycle monomer is the charge density of the  $\alpha$ - $\alpha'$  carbon atoms, as the nucleation centers in the growth polymer chains. We investigated qualitatively the "push-pull" effect of the fluorophenyl substituents on the FPT monomers by the Mulliken population analysis using the net atomic electric charge distribution. The results obtained for the radical anions and radical cations of FPTs (corresponding to the *n*- and *p*-doped states, respectively) were summarized in Table 2. According to this table, in all the radical anions, the main influence of the injection of one negative charge is manifested in the increased negative charge on the  $\alpha$ -carbon atoms with respect to the  $\alpha'$ -carbon atoms. Consequently, a  $\alpha$ -carbon atom that is close to the substitution position is a more reactive zone to the nucleation processes than a  $\alpha'$ -carbon atom that is far from it (see Scheme 1). The same trend

Table 2

Atomic charge distribution on the branching centers of FPTs,  $C_{11}(\alpha)$  and  $C_{9}(\alpha')$  carbons, in radical cation (*p*-type doped) and radical anion (*n*-type doped) states.

Species	Radical anio	n	Radical catio	on
	C <sub>11</sub> (α)	C <sub>9</sub> (α')	$\overline{C_{11}(\alpha)}$	C <sub>9</sub> (α')
PT	-0.365	-0.317	-0.195	-0.244
2-FPT	-0.358	-0.307	-0.197	-0.241
3-FPT	-0.357	-0.313	-0.191	-0.244
4-FPT	-0.367	-0.320	-0.201	-0.245
2,4-FPT	-0.362	-0.307	-0.201	-0.242
3,4-FPT	-0.359	-0.315	-0.197	-0.246
3,5-FPT	-0.355	-0.309	-0.188	-0.239
3,4,5-FPT	-0.358	-0.310	-0.194	-0.242

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