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Effect of substituents on charge carrier dynamics in thiophene oligomers

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Abstract

Anion and cation radicals of substituted thiophene oligomers were generated and isolated from respective solutions at low temperature by gamma irradiation at a total dose of 4 kGy. The absorption spectra of these radicals were investigated using low temperature matrix isolation technique. Absorption bands in two typical regions: visible and infrared (IR) were observed experimentally for both anion (HOMO → SOMO and SOMO → LUMO) and cation (SOMO → LUMO and HOMO → SOMO) radicals of all molecules. The values of oscillator strength (*f*) decreases with the increase in the number of phosphate bridges in thiophene molecule for both the anion and cation radicals, suggesting the breaking conjugation by the dihedral angle of thiophene rings at centre of the molecule. The optical transitions in substituted thiophene oligomers were also investigated on the basis of a theoretical approach using ZINDO CI at B3LYP/6-31G(d) DFT geometry. The most stable backbone geometries of the anion and cation radicals are the planner ones in spite of twisted helical structures calculated for the steady-state molecules as the plausible structures. Transformation from twisted (helical) to planner structure plays a crucial role in the determination of energy levels of the molecules bearing negative and positive charge carriers. Incomplete transformation due to the low temperature matrix effects causes considerable decrease in the value of *f*.

Keywords: Thiophene oligomers; Low temperature matrix; Infrared; Anion radical; Cation radical

1. Introduction

The electronic properties of conjugated molecular aggregates, oligomers, and/or polymers have been studied extensively in recent years [1]. Conjugated molecules are important because of their possible use as active component materials in future molecular electronics applications. Fine control of optical and electronic properties of organic molecular semiconductors has been achieved by the modification of chemical structures of molecules and oligomers [2]. Tuning the electronic properties of organic semiconductors has been widely exploited to modify the redox potentials or the bandgap in polymers like polyphenylenes, polythiophenes, polyphenylene vinylenes, and polysilanes [1–5]. These polymer derivatives bearing main chain conjugated system are expected to represent their intrinsic semiconducting characters with the adequate atomic/molecular doping. However, a few polymeric materials have been successfully reported on their effective transport of negative charge carriers with high mobility in the bulk or the thin films because of the efficient trapping of electrons by potential defects and/or impurities. Oligomers of thiophenes are an important and promising class of organic materials due to their excellent chemical stability, electronic (in the doped state) and optical properties [6–9]. It is known that the electronic structures of oligothiophenes largely depend on their number of polymer repeating units [10,11]. The HOMO–LUMO gap of the oligothiophenes becomes small as increase in the thiophene unit without showing convergent limit in the range of 1–100 thiophene repeating units [12], which also changes oxidation potentials, singlet and triplet energies [13]. At the same time,

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the solubility of polymer decreases with the increase of repeat units.

Many theoretical and experimental investigations showed that conformational change influences the optical properties of the materials [14,15]. The electron delocalization is less for a twisted conformation than for a more planar conformation [16]. The optical properties of oligothiophenes and polythiophenes can be controlled by the number of thiophene units involved in the backbone and by the insertion of side chains at specific locations. The understanding of these effects on the spectroscopic and photo physical parameters of thiophene derivatives is still incomplete.

The objective of the present work is to understand the underlying electronic structures that give these polymers their unusual properties. It is well known that the non-planar conformations in the oligothiophene markedly influence the degree of its π-conjugation. The spectroscopic studies of anion and cation radicals of substituted oligothiophenes in low temperature matrices have been investigated. The effects of substituents on transition energies of thiophene oligomers and degree of delocalization of charge carriers along the main chain have also been discussed. Some semiempirical calculations have been carried out to support our experimental data.

2. Experimental

4-Phenyl-4H-phospholo[3,2-b:4,5-b′]dithiophene 4-oxide (T2P1), dimer of T2P1 (T4P2), 2,6-bis(2-thienyl)-4-phenyl-4H-phospholo[3,2-b:4,5-b′]dithiophene 4-oxide (T4P1), 2,6-bis(2-thienyl)-4-phenyl-4H-phospholo[3,2-b:4,5-b′]dithiophene 4-oxide (T4P1-O), 2,6-bis[2,2′-bithiophene-5-yl]-4-phenyl4H-phosphorous[3,2-b:4,5-b′] dithiophene 4-oxide(T6P1), and 3-*n*-hexyl-tetrathiophene (T4H4) were prepared by Suzuki cross coupling or reductive coupling reactions with corresponding bromide or borate monomers. The detailed synthetic and purification methods of oligomers can be seen elsewhere [17]. Sample solutions were prepared using methyl tetrahydrofuran (MTHF) and 2-chlorobutane (BuCl) as solvents. The solutions for irradiation were taken in a Suprasil quartz cells having 1 mm optical path. Sample solutions saturated with Argon gas were irradiated about a total dose of 4 kGy from a ^{60}Co source while freezing the solutions by liquid N_2 to 77 K. Substituted thiophenes are known to form anion and cation radicals after irradiation in methyl tetrahydrofuran and 2-chlorobutane, respectively [18,19]. Spectral analysis was made by using Shimadzu UV-3100PC spectrometer and oxford optistat DN cryostat system at low temperatures in the range of 80–150 K. The details of the set up of apparatus are given elsewhere [13,20]. The spectral resolution of the monochromator was set at 2 nm for continuous trace in vis–NIR region and at 0.5 nm for the determination of the extinction coefficients. Theoretical calculations were carried out for all anion and cation radicals in planar form to study the geometry and electronic structures using ZINDO CI at B3LYP/6-31G(d) geometry.

3. Results and discussion

Molecular structures of the substituted thiophene oligomers investigated in this paper are displayed in Fig. 1. The absorption spectra of anion radicals were recorded in the temperature range of 80–150 K. Anion radicals showed absorption bands in two typical regions: infrared (IR) and visible regions. Absorption spectra for anion radicals at 100 K are given in Fig. 2. On warming of the matrix to 150 K, the spectra disappeared due to recombination of oppositely charged ions confirming the formation of anion radicals. The absorption maxima and photon energy for anion radicals are shown in Table 1. For example, in T4P1$^{\bullet-}$, three absorption maxima are ascribed to HOMO → SOMO (690 nm), SOMO → LUMO + 1 (824 nm) and SOMO → LUMO (1016 nm), which is discussed in the following section. Unsubstituted tetrathiophene (T4) [21] in steady-state have shown an absorption maximum around 392 nm of photon energy equal to 3.15 eV, indicating good correspondence with the total transition energy from HOMO to LUMO of our phosphorous-bridged tetrathiophene oligomer (T4P1). Unsubstituted oligothiophenes show a strong red shift in the electronic spectra by increasing the repeat units in the molecules [22]. In the case of T6P1$^{\bullet-}$, one in visible and two bands in IR regions are observed, showing considerable red shift for each band (HOMO → SOMO, 802 nm; SOMO → LUMO, 1292 nm). There is a little disagreement between the total transition energy of anions and the HOMO–LUMO transition energy (2.6 eV) from the steady-state spectrum [11,17], suggesting that the SOMO of anions actually originates from LUMO of neutral molecules, and spreads over the thiophene chain. The spectra of T4P1$^{\bullet-}$ and T4P1-O$^{\bullet-}$ are identical to each other, and no differences are observed in the transition energies. This is suggestive that the effect of oxygen atom in the phosphate substituent has no influence on the energy level of SOMO state of anions. However, the doubly phosphate-bridged tetrathiophene: T4P2$^{\bullet-}$ indicates considerable increase in the transition energies. It should be noted that the optimized structure of T4P2$^{\bullet-}$ is the trans planner structure of dimer units bridged by phosphate groups. The relative localization of SOMO states over two thiophene rings might cause the increase in the transition energy.

Fig. 3 shows the absorption spectra for cation radicals measured at 100 K. However, the cation radical spectra are generally sharper with high extinction coefficients. Photon energy and absorption maxima for cation radicals are displayed in Table 1. On warming of the matrix, the spectra due to monomer cation radical (T4P1$^{\bullet+}$), dimer cation radical (T4P2$^{\bullet+}$) and cation radical of sexithiophene (T6P1$^{\bullet+}$) slowly decay without changing in their band positions. For phosphorous substituted tetrathiophene cation radical

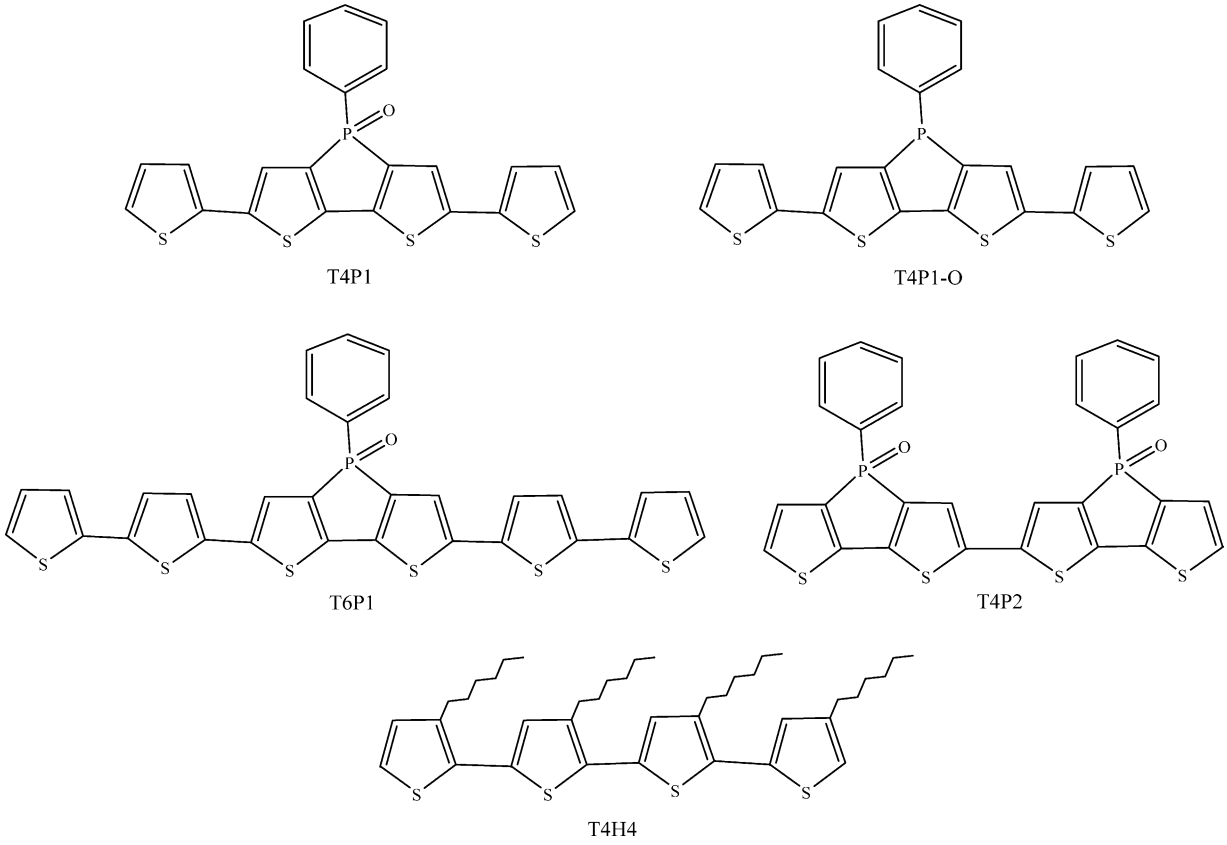

Fig. 1. Molecular structure of substituted thiophene oligomers.

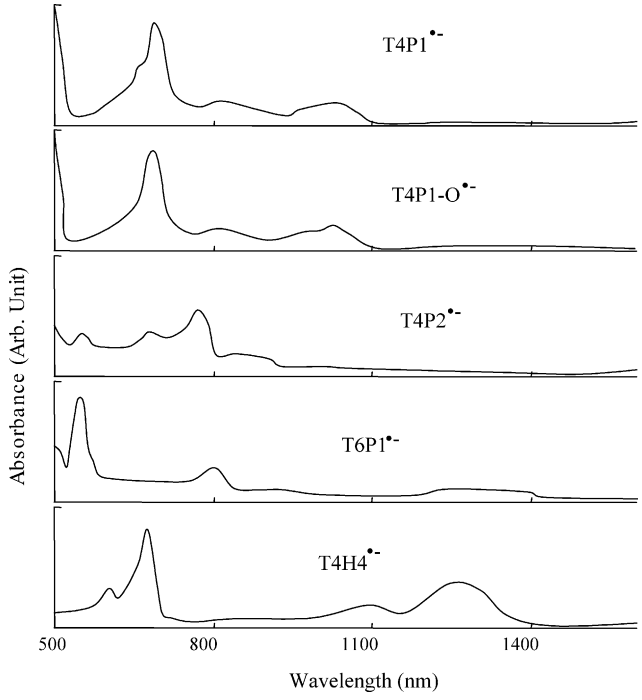

Fig. 2. Absorption spectrum at 500–1400 nm after gamma irradiation of 1 mM sample solutions in methyl tetrahydrofuran at 100 K.

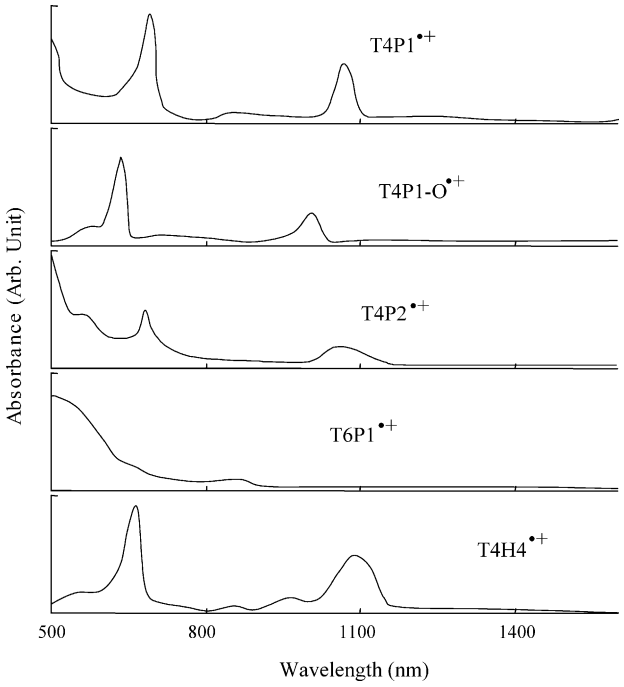

Fig. 3. Absorption spectrum at 500–1400 nm after gamma irradiation of 1 mM sample solutions in 2-chlorobutane at 100 K.

Table 1
Spectroscopic parameters of substituted thiophene oligomers at 100 K from experimental results

Sample name	Solvent	λ_{max} (nm)	f[a]
Anions			
T4P1	MTHF	690	0.44 ± 0.11
		824	
		1016	
T4P1-O	MTHF	689	0.46 ± 0.12
		832	
		1021	
T4P2	MTHF	551	0.34 ± 0.10
		687	
		774	
T6P1	MTHF	546	0.54 ± 0.08
		802	
		1292	
T4H4	MTHF	603	1.0[a]
		679	
		1064	
		1262	
Cations			
T4P1	BuCl	689	0.11 ± 0.030
		1064	
T4P1-O	BuCl	635	0.62 ± 0.21
		1009	
T4P2	BuCl	684	0.074 ± 0.025
		1057	
T6P1	BuCl	475	
		850	0.26 ± 0.050
T4H4	BuCl	659	1.0[a]
		943	
		1078	

MTHF—methyl tetrahydrofuran; BuCl—2-chlorobutane.
[a] The oscillator strength calculated by the numerical integration of the spectra based on the Eq. (2), relative to the value of T4H4.

($T4P1^{\bullet+}$), the spectra are ascribed to SOMO → LUMO (689 nm) and HOMO → SOMO (1064 nm). Cation radicals or polarons of oligothiophenes can be generated in solution from both the singlet and triplet excited states. It is interesting to note that the main transition between SOMO and LUMO for cation radicals of tetrathiophene oligomers (for T4P1 → 1.79 eV, T4P2 → 1.80 eV and T4H4 → 1.87 eV) are lower than the data given in the literature (T4 → 1.91 eV) [23] in dichloromethane except for T4P1-O (1.94 eV).

Comparison of the longer wavelength absorption bands for anion and cation radicals of substituted thiophene oligomers shows that the phosphate group has small effect/influence to the energy levels of SOMO states of both anion and cation radicals. To improve the solubility of thiophene based conjugated organic compounds, alkyl substituted oligothiophenes have been synthesized. Comparison of the results for $T4H4^{\bullet-}$ and $T4H4^{\bullet+}$ showed that the spectra are identical for both. For $T4H4^{\bullet+}$, the spectra are very specific and sharp. In the case of $T4H4^{\bullet+}$, a clear red shift is observed to the high energy (visible) band on softening of the matrix with increasing the temperature. For low energy absorption band (longer wavelength), a slightly blue shift is observed with the temperature. Since the shifted wavelength in the red shift is higher than in the blue shift, it cannot be assigned to the formation of charge resonance band. These results are given in Fig. 4. The remarkable spectral shifts were observed only for $T4H4^{\bullet+}$ at the temperature region of 100–150 K.

In the quantitative elucidation of the degree of charge delocalization on thiophene chain, simultaneous observation of transient absorption and bleaching was performed as shown in Fig. 5 for $T4P1\text{-}O^{\bullet+}$. Based on the molar extinction coefficient of the neutral molecule (ε_n), the apparent extinction coefficient of the ion radicals per charge ($\varepsilon^{\bullet\pm}$) is given by [18–20]:

$$\varepsilon^{\bullet\pm} = \frac{\Delta_{OD}^{\bullet\pm}}{\Delta_{OD}^{Bl}}\varepsilon_n \quad (1)$$

where $\Delta_{OD}^{\bullet\pm}$ and Δ_{OD}^{Bl} are the observed optical density of transient absorption and bleaching, respectively. Because of the spectral overlap of the observed bleaching on the strong steady-state absorption, the analysis based on the Eq. (1) was carried using the value of ε_n at the edge of steady-state absorption. The spectra are normalized by the values of $\varepsilon^{\bullet\pm}$, and the oscillator strength ($f^{\bullet\pm}$) of the main transition band (HOMO → SOMO for anions and SOMO → LUMO for cations) is calculated relative to the value of T4H4. The numerical integration of the spectra is carried out based on the following equation:

$$f^{\bullet\pm} = 4.32 \times 10^{-9} \int \varepsilon^{\bullet\pm} d\nu. \quad (2)$$

The calculated values are summarized in Table 1. The oscillator strength (f) of the cation radicals show dramatic decrease with an increase in the number of phosphate bridges, in spite of the small effect observed for $T4P1\text{-}O^{\bullet+}$ relative to $T4P1^{\bullet+}$. The dependence of f on the number of phosphate bridges is relatively small in anion radicals. The values of f in $T4P1\text{-}O^{\bullet-}$ is almost consistent with that of $T4P1^{\bullet-}$. The present results suggest that the density of state at HOMO level is reduced by the phosphate bridge including the P=O structure. This is also supported by the bipolar nature of phosphate-bridged compounds giving remarkable increase in the quantum efficiency of fluorescence [10,16].

Theoretical methodology: To support our experimental data, the theoretical methodology has been adopted. We first optimized the geometry of the isolated (both anion and cation form) oligomers using B3LYP/6-31G(d) DFT method. Figs. 6 and 7 show the optimized geometry of anion and cation radicals of the molecules with electron density maps of their SOMO orbitals, respectively. The geometrical optimization was also performed for steady-state neutral molecules as shown in Fig. 8. Both phosphorous and phosphate bridging structure cause considerable effects on the planner structure of the neutral molecules. Thiophene rings at both ends of the molecules of T4P1 and T4P1-O are twisted at 159.8° and

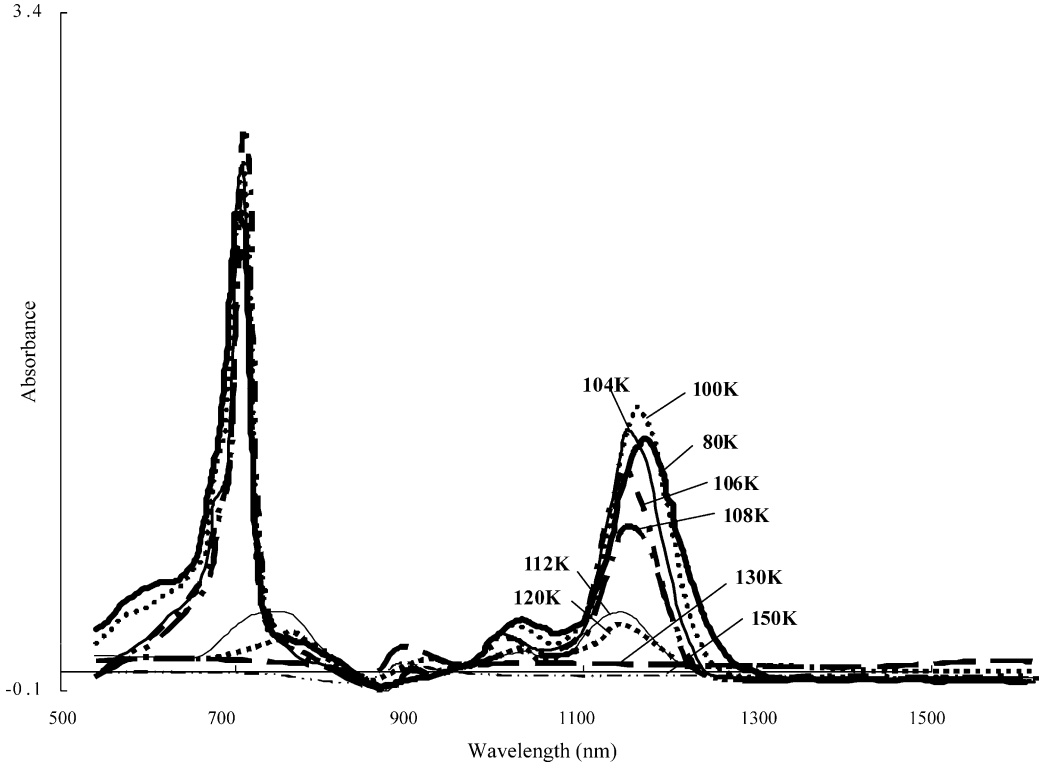

Fig. 4. Absorption spectrum at 500–1500 nm after gamma irradiation of 1 mM T4H4 sample solutions in 2-chlorobutane at 80–150 K.

162.0°, respectively. The two dithiophene units in T4P2 are also twisted each other with the dihedral angle of 160°. The deformation from the planner structure is relatively smaller in the case of T6P1, but the helical structure of the backbone is certainly induced along the thiophene chain. The twisted structures, which decrease the overlap of π orbitals in the adjacent thiophene rings, are well reflected as the blue shift in the steady-state absorption spectra of T4P1, T4P1-O, and T4P2 in comparison with that of T4H4 [17].

The geometry of anion and cation radicals shows a dramatic change from those of neutral molecules. The dihedral angles are >178° for both anion and cation radicals of all molecules, suggesting that the planner structures of the charged molecules are favorable energetically rather than the twisted helical structure of the backbones in the case of steady-state neutral molecules. The helical structures of the neutral molecules may be induced by Coulomb repulsion between sulfur atoms in adjacent thiophene rings and/or between sulfur and phosphorous atoms; therefore, the structural stabilization by an excess electron of holes on the backbone is high enough to cancel the repulsive effects for all molecules in the present study. The SOMO orbitals of anion and cation radicals reflect the shape of the respective original MOs of neutral molecules: LUMO and HOMO of neutral molecules. The asymmetric nature of HOMO and LUMO of the oligomers with bridges induces the smaller extinction coefficients observed for the absorption band with the lowest transition energies: SOMO → LUMO (anion radicals) or HOMO → SOMO (cation radicals). The SOMO orbitals are widespread along the thiophene planes, and the delocalization is higher in the cation radicals relatively to the anions. The transition energies were also calculated using ZINDO CI at current geometry. For each sample, we have observed broad vis and IR absorption peaks, and the results are listed in Table 2. Based on the experimental results, the transition energies of the band are always observed as the lower for cation radicals than those of anion radicals, which suggests the relatively higher degree of delocalization of positive charges than the negative ones for all molecules. However, the optimized (calculated) structure of the molecules shows strong dependence of the transition energies on the substitution patterns.

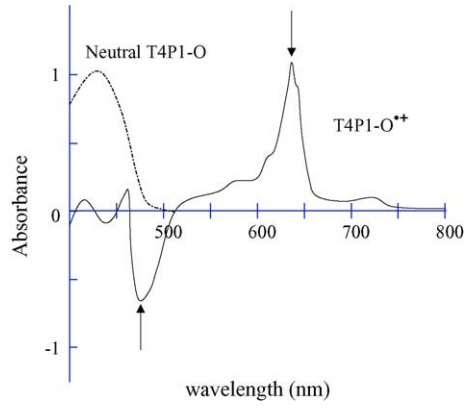

Fig. 5. Absorption spectra of after gamma irradiation of 1 mM T4P1-O solutions in 2-chlorobutane at 80 K. Dashed line displays the steady-state spectrum of the solutions at 0.1 mM conc.

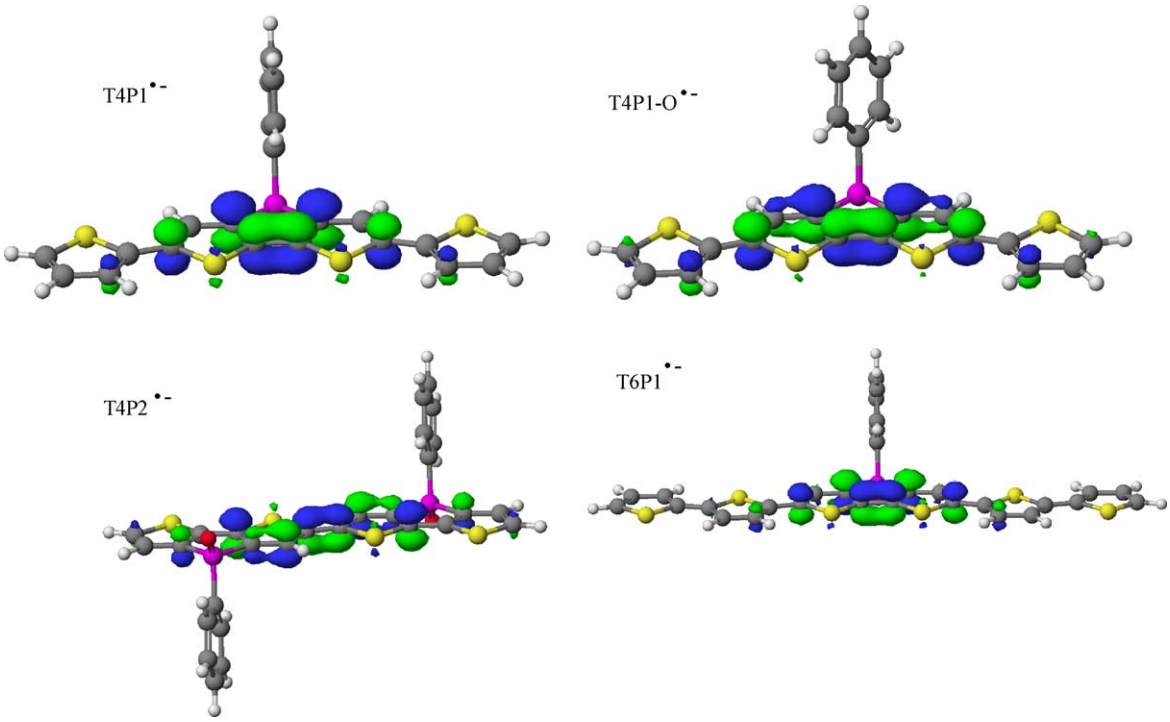

Fig. 6. Optimized geometry of anion radicals of the molecules by B3LYP/6-31G(d) DFT method. The map of electron density is attributed to the SOMO orbital.

The energies of cation radicals are predicted to be higher than those of the anions for T4P1-O and T4P2. Furthermore, most of all values of the calculated transition energies are slightly lower than those observed experimentally. These imply that the transformation from the twisted (neutral) to the planner (charged) structure is not achieved completely in the low temperature matrices. The considerable shifts of the absorption bands were observed only for T4H4$^{\bullet+}$ with increasing

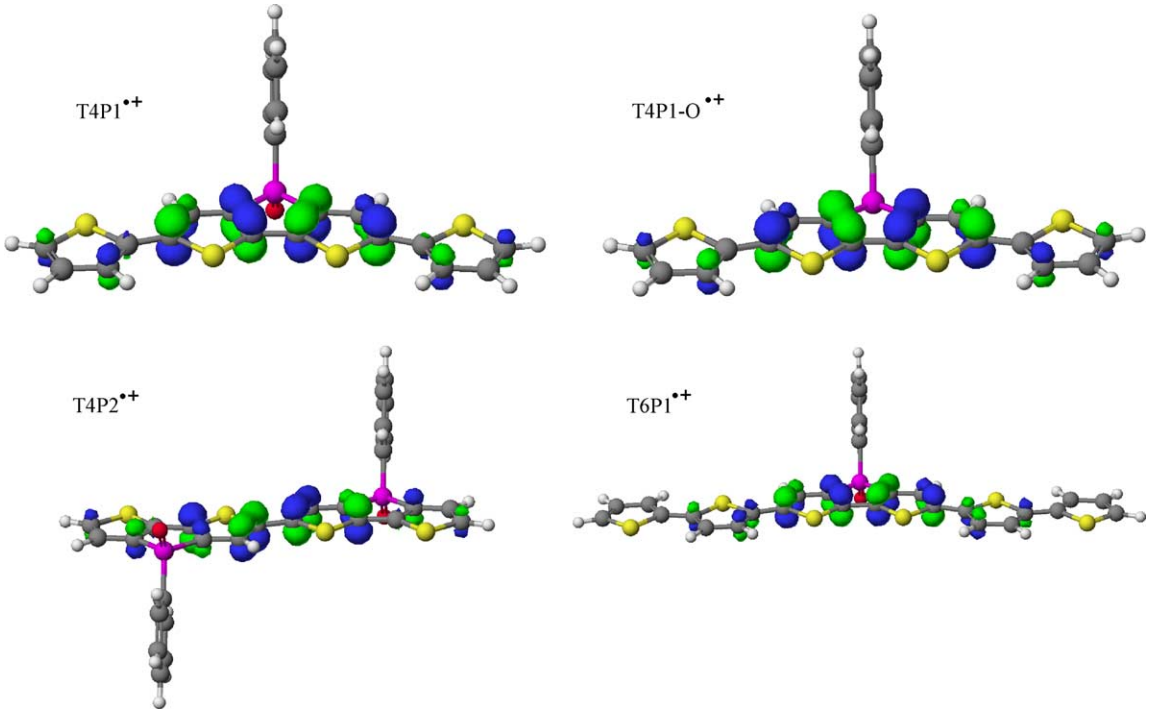

Fig. 7. Optimized geometry of cation radicals of the molecules by B3LYP/6-31G(d) DFT method. The map of electron density is attributed to the SOMO orbital.

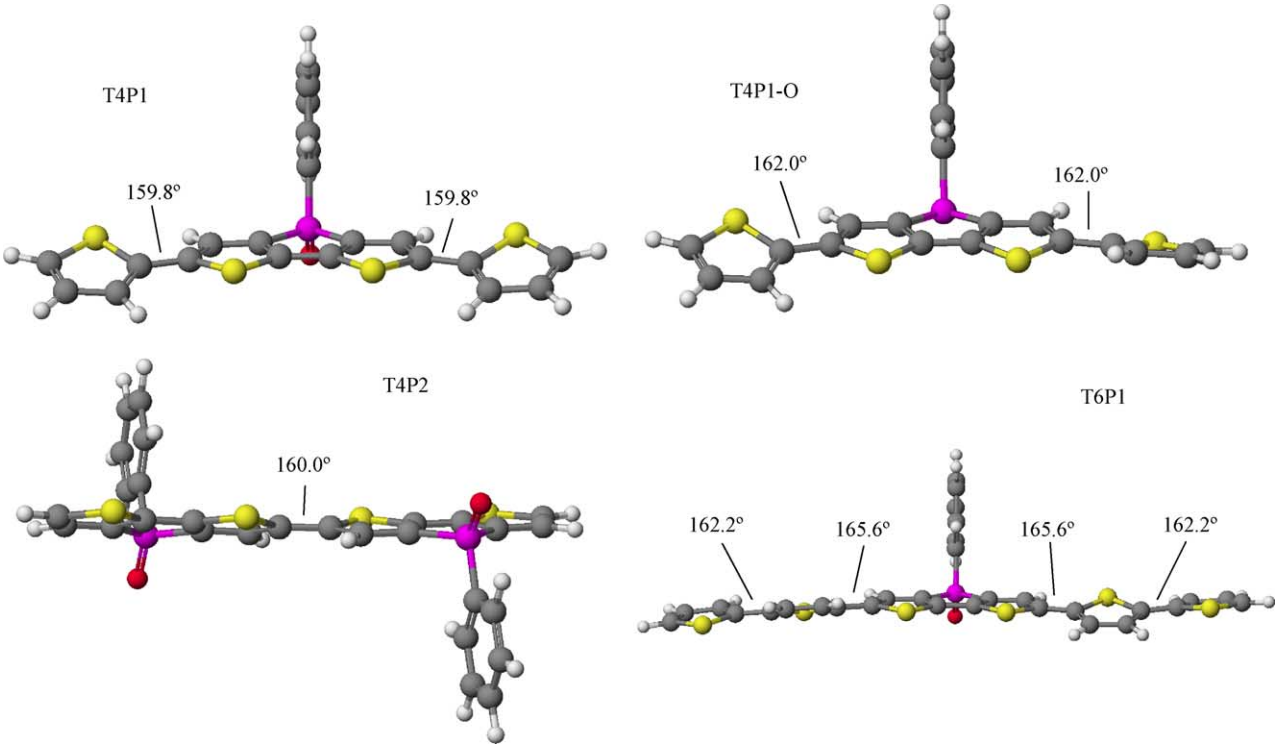

Fig. 8. Optimized geometry of the steady-state neutral molecules by B3LYP/6-31G(d) DFT method. The values denote the calculated dihedral angles of bonds indicated in the molecule.

temperature above 100 K. This suggests that the low temperature matrices of BuCl at 100 K is not soft enough to allow the rotation thiophene rings in the backbone to achieve the most stable conformers even in the case of T4H4 with unsubstituted thiophene rings. The barriers of the rotation are predicted to be the maximum for T4P2 because the rotation of the dithiophene unit with bulky phosphate substituents is necessary to give the planner structure of cation or anion radicals. With the optimized geometry, the SOMO orbitals of both $T4P2^{\bullet -}$ and $T4P2^{\bullet +}$ show a considerable contribution

Table 2
Spectroscopic parameters of substituted thiophene oligomers obtained from theoretical calculations

Sample name	λ_{max} (nm) (calculated)	Photon energy (eV) (calculated)	Photon energy (eV) (experimental)
Anions			
T4P1	734	1.69	1.79
	1140	1.09	1.21
T4P1-O	756	1.64	1.79
	1250	0.99	1.21
T4P2	786	1.58	1.59
	1420	0.87	–
T6P1	888	1.40	1.54
	1310	0.95	0.95
Cations			
T4P1	716	1.73	1.79
	1190	1.04	1.16
T4P1-O	680	1.82	1.94
	1120	1.11	1.2
T4P2	681	1.82	1.80
	1190	1.04	1.17
T6P1	648	1.91	2.60
	958	1.29	1.45
	1490	0.83	–

from π orbitals of two adjacent thiophene units at the center of the molecule. The delocalized SOMO states are affected by the dihedral angle between thiophene units at the centre of the molecule. The imperfect transformation to the planner structure of the ion radicals divides the SOMO into two dithiophene moieties (localized). This is the case, giving the large decrease in the value of *f* of both $T4P2^{\bullet -}$ and $T4P2^{\bullet +}$.

4. Conclusion

The two thiophene rings in the centre part of the molecules mainly contribute towards the delocalization of SOMO orbitals. The planner structure of charged molecules having dihedral angles >178° are the most energetically favorable structure than the twisted structure of respective neutral molecules. As oscillator strength of the transient absorption decreases from $T4P1^{\bullet -}$ to $T4P2^{\bullet -}$ or from $T4P1^{\bullet +}$ to $T4P2^{\bullet +}$, the delocalization degree of excess charges becomes rather smaller with increase in the number of phosphate bridges though the perfect planner structure can be provided between two thiophene rings by the bridge. Transition energies obtained from theoretical calculations are slightly lower than those observed experimentally for all molecules, this implies that the transformation from the twisted (neutral) to planner (charged) structure is not completely achieved in low temperature matrices. The large barrier of the rotation of dithiophene units in T4P2 causes the imperfect transformation to the planner structure of ion radicals, leading subsequently to the relative localization of the charges on the dithiophene units. Thus, finally we conclude that it is important in the design of the electronic conductive thiophene oligomers to introduce the bridging substituents, which can minimize the differences in the backbone structures of neutral and ionic state of the molecules.

Acknowledgments

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