

DFT Investigations on Organic Molecules Based on Thienothiophene for Electronic Devices Applications

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ABSTRACT

We report theoretical studies on the optoelectronic structural properties of four Thienothiophene (T) conjugated π conjugates. The geometries, the prediction of the optoelectronic structural properties of the four compounds are studied by calculations of Density Functional Theory (DFT). The absorption properties (λ_{max} , Etr, f) of molecules are gained by the (DFT) B3LYP/6-31G (d) ZINDO method, so that the Highest Occupied Molecular Orbitals (HOMO), the Lowest Unoccupied Molecular Orbitals (LUMO), the energy deficit being calculated using the factor Gaussian 09 and its Gauss View 5.0.8 graphical interface.

Key words: DFT, Structural properties, Optoelectronic properties, Thienothiophene, HOMO, LUMO, Gap

INTRODUCTION

Organic photovoltaic tool have opened up the potential for producing light energy in a simple and economical way. The bilayer technology typically uses organic semiconductor cables intercalated between the anode and cathode electrodes, the first is an electron acceptor and the second is an electron donor. In this work, we have based on unsubstituted thienothiophene Figure 1(a) as a π -conjugated organic semiconductor. We mainly used DFT to study the optoelectronic and structural properties of the four molecules.

Thienothiophene often refers to all the structurally related thiophene derivatives with the given formula C₆H₄S₂. As for importance, they are: thiophene thieno (3,2-b), thieno (2,3-b) thiophene and thieno (3,4-b) thiophene. The other isomers are characterized by S (IV) and are less stable [1]. Thieno (2,3-b) thiophene was the series' first member of the series to be isolated. The thienothiophene conjugate compounds have extensive delocalization of n electrons along the molecular backbone, making them attractive for various optoelectronic applications [2,3].

Because of this applicative interest and to that these shirt systems can be used as model compounds for the parent polymer, they have been extensively studied [4,5]. Also, because of their controllable and precisely defined structure, physical properties can be correlated with the conjugation length and the side chains. Therefor implementing these molecular structures by functionalization at the terminal and side positions permit their application as molecular materials in organic field-effect transistors [6,7], light-emitting devices [8-11], photovoltaic cells [12,13], or even as molecular wires for information storage or transfer [14,15].

Polymers and oligomers with low band gap are expected to show not only good intrinsic conductivity but also nonlinear optical properties [16,17]. For their successful design, it is vital to have a complete understanding of

the relationship between electronic properties and the chemical structure of polymers [18,19]. Different routes are here followed for designing novel conducting polymers, one is provided by donor-acceptor polymers, based on the approach suggested for the first time by Havinga et al. [20].

The study of conjugated oligomers is very attractive for finitesize systems can be achieved with a well-defined chemical structure and high purity. This opens the way for the investigation of electronic properties as a function of chain length and extent of the parent π -electron system.

In this paper, we present a detailed study of DFT (B3LYP/6-31 (d)) of the four thienothiophene compounds. We focus on the geometric structure of the compounds and the electronic properties. The chemical structure and optimized structures of the compounds studied are illustrated in Figure 1.

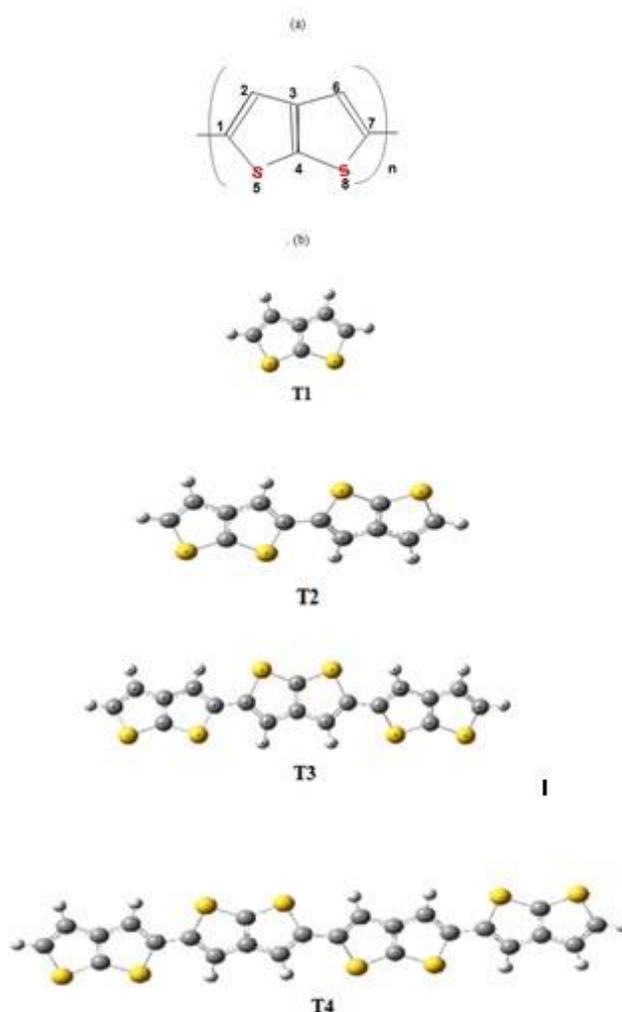


Figure 1. (a): Compounds chemical structures under investigation; (b): The compounds theoretical geometric structures of optimized by B3LYP/6-31G (d)

The general abbreviation of our studied compounds is T1 (Monothienothiophene), T2 (Dithienothiophene), T3 (Trithienothiophene) and T4 (Tetrathienothiophene), thienothiophene, varies between 1 and 4.

CALCULATION METHODOLOGY

The calculations done on the geometries of the four molecules were carried out under functional density theoretical theory (DFT) B3LYP and the set of bases 6-31G (d) [21]. The notation B3 indicates a parameter with three parameters of Becke [22] and LYP indicates the function Lee-Yang-Parr [23]. Calculations were given using the Gaussian 09

program [24]. All structures are fully optimized by B3LYP/6-31G (d) without any constraint.

RESULTS AND DISCUSSION

Geometric structure results

The optimized geometries of the four compounds (T1, T2, T3, and T4) obtained at B3LYP/6-31G (d) are shown in Figure 1.

The calculated lengths d_i ($i=1$ to 23) and the dihedral angles Θ_i ($i=1$ to 3) of the interatomic bonds are presented in Figure 2 and their optimized values are summed up in Tables 1 and 2 respectively.

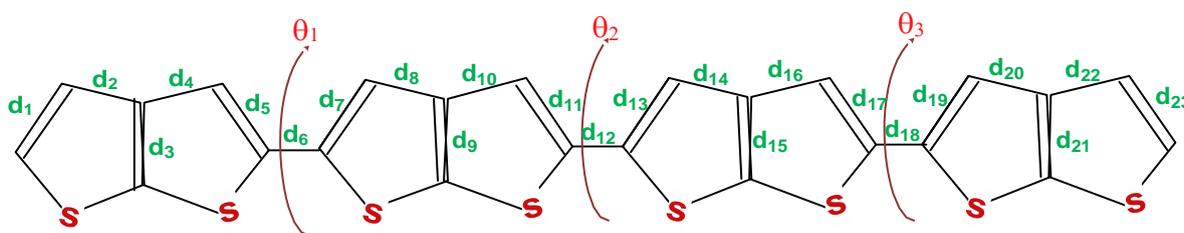


Figure 2. Marked bond lengths and dihedral angles

Table 1: The bond length values (Å) of the examined molecules

Molecules Inter-atoms distance	T1	T2	T3	T4
d_1 (C ₁ -C ₂)	1.36226	1.36206	1.36193	1.36191
d_2 (C ₂ -C ₁₀)	1.43565	1.43592	1.43590	1.43591
d_3 (C ₁₀ -C ₁₁)	1.39205	1.39138	1.39239	1.39240
d_4 (C ₁₀ -C ₇)	1.43565	1.42955	1.42993	1.42990
d_5 (C ₇ -C ₈)	1.36226	1.37364	1.37316	1.37316
d_6 (C ₈ -C ₁₂)		1.44892	1.44973	1.44975
d_7 (C ₁₂ -C ₁₃)		1.37364	1.37282	1.37275
d_8 (C ₁₃ -C ₁₆)		1.42955	1.43038	1.43041
d_9 (C ₁₆ -C ₁₇)		1.39138	1.39235	1.39250
d_{10} (C ₁₆ -C ₁₈)		1.43592	1.43038	1.43017
d_{11} (C ₁₈ -C ₂₀)		1.36206	1.37282	1.37304
d_{12} (C ₂₀ -C ₂₂)			1.44973	1.44932
d_{13} (C ₂₂ -C ₂₃)			1.37316	1.37304
d_{14} (C ₂₃ -C ₂₆)			1.42992	1.43016
d_{15} (C ₂₆ -C ₂₇)			1.39239	1.39254
d_{16} (C ₂₆ -C ₂₈)			1.43590	1.43043
d_{17} (C ₂₈ -C ₃₀)			1.36193	1.37272
d_{18} (C ₃₀ -C ₃₂)				1.44971
d_{19} (C ₃₂ -C ₃₃)				1.37315
d_{20} (C ₃₃ -C ₃₆)				1.42984
d_{21} (C ₃₆ -C ₃₇)				1.39249
d_{22} (C ₃₆ -C ₃₈)				1.43590
d_{23} (C ₃₈ -C ₄₀)				1.36192

The interatomic distances (d_i) take small values for d_i ($i = 1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23$) and high values for d_i ($i=2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22$). The inter-ring distances d_i ($i=6, 12, 18$) take the highest value which is close to 1.45 Å. This implies that these links are sometimes simple and sometimes double, thus favoring a good delocalization and combination of π electrons.

Table 2: The dihedral angles (°) of the compounds examined

Molecules	Θ_1 (C ₇ -C ₈ -C ₁₂ -C ₁₃)	Θ_2 (C ₁₈ -C ₂₀ -C ₂₂ -C ₂₃)	Θ_3 (C ₂₈ -C ₃₀ -C ₃₂ -C ₃₃)
T1			
T2	180.00000		
T3	153.63793	153.62605	
T4	153.55185	154.26296	153.76548

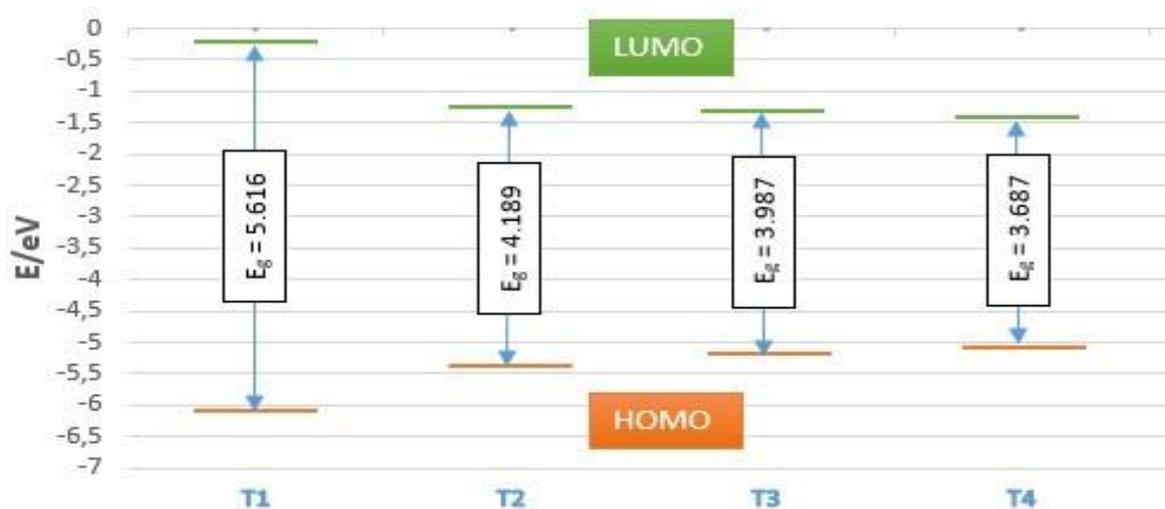
For the three systems, we observe a great difference in the optimized binding angles when we add thienothiophene (T) compound.

Electronic properties of the compounds examined

The electronic properties depend essentially on the fundamental and excited states. The Lowest Unoccupied Molecular Orbital (LUMO) and the Highest Occupied Molecular Orbital (HOMO). The gap energy is calculated by the difference between the LUMO and HOMO levels, their values for all the molecules examined are shown in Table 3. Calculations have been achieved by the method B3LYP/6-31 (d).

Table 3: The energies of the compounds examined in (ev): E_{HOMO} , E_{LUMO} and E_{gap}

Compound	E_{LUMO} (ev)	E_{HOMO} (ev)	E_{gap} (ev) = $E_{\text{LUMO}} - E_{\text{HOMO}}$
T1	-0.420	-6.036	5.616
T2	-1.247	-5.436	4.189
T3	-1.314	-5.301	3.987
T4	-1.451	-5.138	3.687

**Figure 3.** Band structure diagram illustrating the LUMO and HOMO energies of oligomers (T1 to T4)

In this result, we first observed that the synthesized molecules generally have a high gap energy, especially the molecule (T1) of 5.616 eV, but when we add a base (T) the band gap decreased slightly for all molecules, then the gap energy gap decrease of the molecule (T1) to (T4) from 5.616 eV to 3.687 eV. Due to increasing conjugation of system.

Electronic structures of the compounds examined

In this section, we study the Lowest Unoccupied Molecular Orbitals LUMO and Highest Occupied Molecular Orbital HOMO for these compounds, because the relative order of occupied and virtual orbitals give a reasonable qualitative indication of the excitation properties [25] and the capacity of electron transitions or whole transport. We plotted the contour curves of the LUMO and HOMO orbitals of four molecules (T1, T2, T3 and T4) in their fully optimized conformation B3LYP/6-31G (d) in Figure 4.

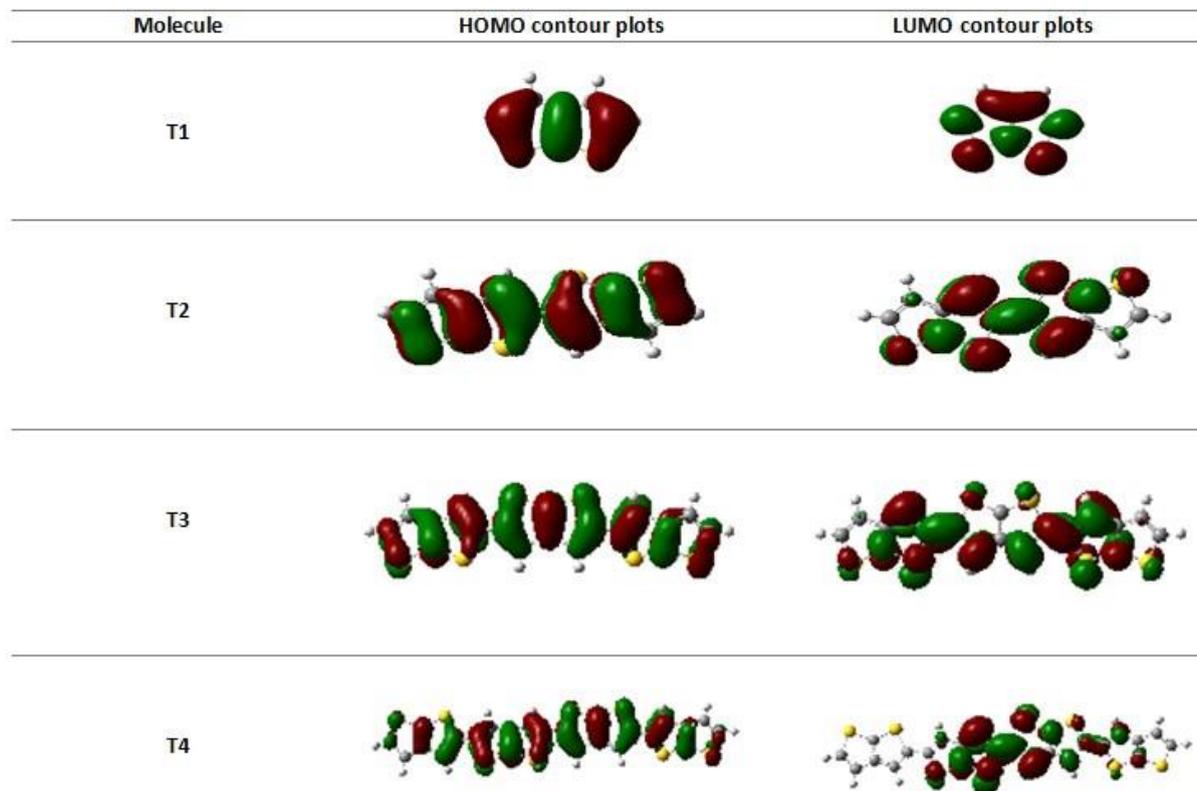


Figure 4. The LUMO and HOMO orbitals of the four compounds (T1, T2, T3 and T4) obtained by B3LYP/6-31G (d)

We observe that in the HOMO orbital the electron density is mainly distributed throughout the chain of compounds. However, it moves completely to the acceptor unit in the case of LUMO. In the case of T4 the electron cloud are delocalized to the innermost ring in orbit LUMO.

ABSORPTION SPECTRA

The Table 3 shows the vertical excitation energy E_{ex} (eV), the maximum absorption λ_{max} (nm), and the oscillator strength (f) in all studied molecules. These properties are counted by the DFT-B3LYP/6-31G (d) ZINDO method.

Table 4: Calculated wavelength λ , Transition Energies and Oscillator Strengths (f) of the four compounds (T1, T2, T3 and T4) obtained by (DFT) B3LYP/6-31G (d) ZINDO method

Compound	E_{ex} (eV)	λ^{max} (nm)	f	Transition
T1	3.9537	313.59	0.0473	HOMO \rightarrow LUMO (0.68444)
	4.6276	267.93	0.0155	HOMO \rightarrow LUMO+2 (0.70015)
	4.6451	266.91	0.1470	HOMO-1 \rightarrow LUMO (0.19816), HOMO \rightarrow LUMO+1 (0.66255)
T2	3.1521	393.34	0.5265	HOMO-1 \rightarrow LUMO+1 (0.10822), HOMO \rightarrow LUMO (0.67979)
	3.8673	320.60	0.0000	HOMO-1 \rightarrow LUMO (0.28357), HOMO-1 \rightarrow LUMO+2 (-0.20956) HOMO \rightarrow LUMO+1 (0.57056), HOMO \rightarrow LUMO+3 (0.11205)
	4.1664	297.58	0.4423	HOMO-1 \rightarrow LUMO+1 (-0.28134), HOMO-1 \rightarrow LUMO+3 (0.13432) HOMO \rightarrow LUMO+2 (0.60142)
T3	3.2164	385.48	0.0332	HOMO-1 \rightarrow LUMO+1 (0.25774), HOMO \rightarrow LUMO (0.62061)
	3.2221	384.79	1.1269	HOMO-1 \rightarrow LUMO (0.36278), HOMO \rightarrow LUMO+1 (0.56830)
	3.8428	322.64	0.0099	HOMO-4 \rightarrow LUMO (0.10447), HOMO-2 \rightarrow LUMO (0.25220) HOMO-2 \rightarrow LUMO+2 (0.12861), HOMO-1 \rightarrow LUMO+1 (0.35411) HOMO-1 \rightarrow LUMO+3 (0.21991), HOMO \rightarrow LUMO+2 (0.40247) HOMO \rightarrow LUMO+4 (-0.16176)

T4	3.1885	388.84	1.2046	HOMO-2 → LUMO (0.27286), HOMO-1 → LUMO+1 (0.15035) HOMO-1 → LUMO+5 (0.10521), HOMO → LUMO (-0.34301) HOMO → LUMO+2 (0.48199)
	3.2011	387.32	0.6869	HOMO-2 → LUMO+2 (0.13917), HOMO-1 → LUMO+1 (0.42911) HOMO → LUMO (0.46262), HOMO → LUMO+2 (0.18931)
	3.2363	383.11	0.0065	HOMO-2 → LUMO+1 (0.13319), HOMO-1 → LUMO (0.36783) HOMO-1 → LUMO+2 (0.24387), HOMO → LUMO+1 (0.48603)

The compounds T1, T2, T3 and T4, have absorption maxima (λ_{\max}) respectively at 313.59 nm 393.34 nm, 385.48 nm and 388.84 nm, reflecting the transition HOMO-LUMO. In addition, the absorption spectra simulated for all studied dyes have a peak; this can be attributed to the charge transfer intermolecular band caused by acceptor unit introduced in the molecular structures. This indicates that these organic oligomers could absorb the maximum amount of incident radiation light, especially T2 and T4 molecules. In the excitation state S1, it corresponds exclusively to the promotion of an electron from the HOMO to the LUMO. Moreover, the largest oscillation force ($f < 1$) that comes from the S0 to S1 electronic transition. The simulated absorption spectra of the four compounds (T1, T2, T3 and T4) are illustrated in Figure 5.

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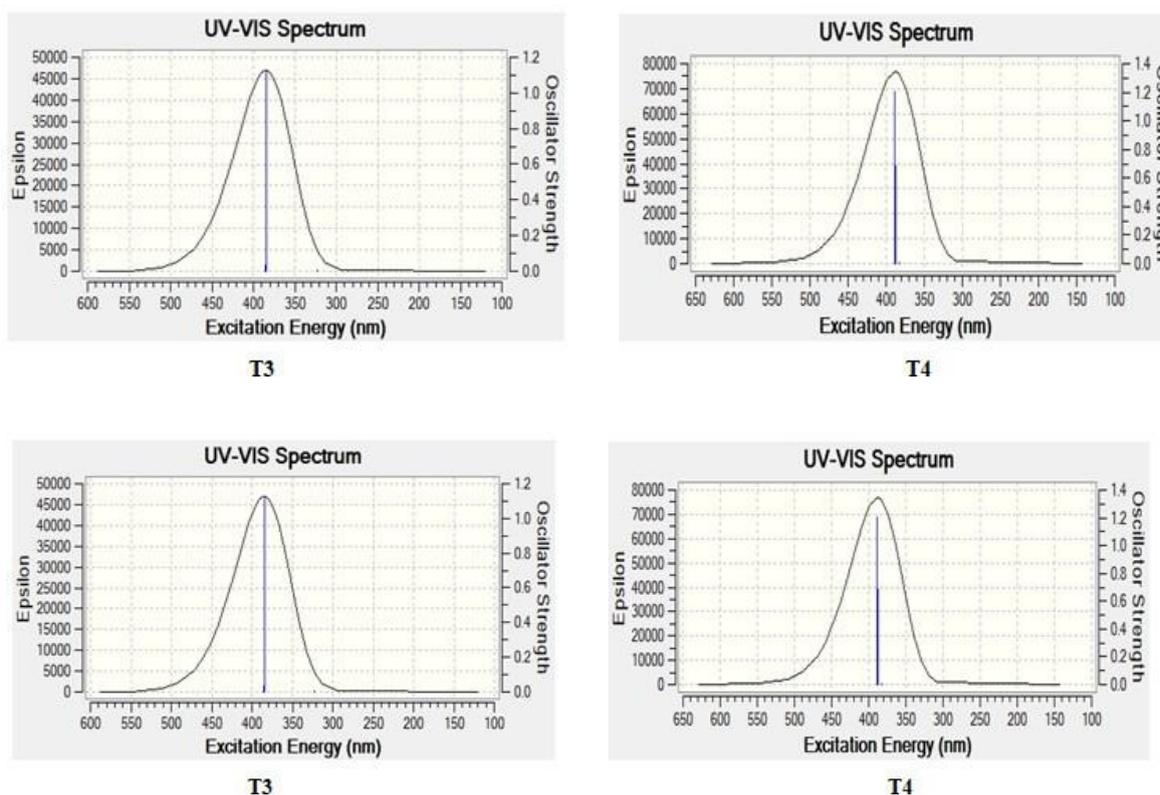


Figure 5. Computed UV-vis spectra of the examined molecules (T1, T2, T3 and T4) by DFT/B3LYP/6-31(G) ZINDO method

CONCLUSION

The geometric parameters of the four Thienothiophene-based π -conjugated organic compounds (T1, T2, T3 and T4) were obtained by B3LYP/6-31G (d) calculations. The gap energy calculated with the same method decreases when a base (thienothiophene) is added for all the molecules. Is basically due to the stabilization of the LUMO level and destabilization of the HOMO level of several compounds leads the reduction of energy gaps HOMO-LUMO. Regarding the T4 the reduction of the observed energy deficit is likely to guarantee the best electronic properties of the corresponding polymers. These results showed that the T4 are promising materials for optoelectronic application.

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