

Research Article

Effects of Molecular Structure on Intramolecular Charge Carrier Transport in Dithieno [3,2-*b*: 2', 3'-*d*] Pyrrole-Based Conjugated Copolymers

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Intramolecular mobility of positive charge carriers in conjugated polymer films based on dithieno [2,3-*b*: 2', 3'-*d*] pyrrole (DTP) is studied by time-resolved microwave conductivity (TRMC). A series of DTP homopolymer and copolymers combined with phenyl, 2,2'-biphenyl, thiophene, 2,2'-bithiophene, and 9,9'-dioctylfluorene were synthesized by Suzuki-Miyaura and Yamamoto coupling reactions. Polymers containing DTP unit are reported to show high value of hole mobility measured by FET method, and this type of polymers is expected to have stable HOMO orbitals which are important for hole transportation. Among these copolymers, DTP coupled with 9,9'-dioctylfluorene copolymer showed the highest charge carrier mobility as high as 1.7 cm²/Vs, demonstrating an excellent electrical property on rigid copolymer backbones.

1. Introduction

Since the first observation of electrical conductivity in doped polyacetylene [1, 2], conjugated polymers have attracted much attention to intend a wide variety of optical and electrical applications such as batteries, sensors, photovoltaic cells, organic light-emitting diodes (OLEDs), and organic field effect transistors (OFETs) [3–12]. Maximization of charge carrier mobility plays a key role in the enhancement of the performance of these electronic devices. The charge carrier mobility has been usually measured by conventional direct current (DC) methods, for instance, time of flight (TOF), space-charge-limited current (SCLC), and field effect transistor (FET) techniques. In these DC measurements under strong and one-directional external electric field, charge carriers are forced to travel over a long distance between electrodes, and to repeat trapping and detrapping processes at impurities, defect sites, or interfacial barriers between semiconductors and electrodes. Accordingly, the mobility measured by DC methods is affected by extrinsic

factors mentioned above leading to rate-determining processes which are not reflecting effective transport along the extended conjugation of molecules.

In contrast to DC methods, time-resolved microwave conductivity (TRMC) technique is categorized into an AC method [13–19] and allows measurement of intrinsic mobility, because of proving nm-scale oscillating motion of charge carriers free from the above-mentioned extrinsic factors. In this AC measurement, the oscillating motion of charge carriers is induced by alternating electric field of microwave on conjugated molecules, and probed without electrodes (noncontact measurement).

Dithieno [3,2-*b*: 2',3'-*d*] pyrrole (DTP) has been expected as a new class of π -conjugated unit in organic electronics [20–26]. DTP unit possesses a large planarity of the rigid and fused ring structure, leading to a small perturbation of effective conjugation length, where the low reorganization energy of molecules can facilitate intermolecular hopping process of charge carriers. The polymers containing DTP units have attracted much

attention for one of candidate materials toward OFETs [20–22], organic solar cells [22–25], and so on.

In this paper, *N*-octyldithieno [3,2-*b*: 2',3'-*d*] pyrrole was polymerized in combination with phenyl, biphenyl, fluorine, thiophene, and bithiophene units by Suzuki-Miyaura coupling reaction. The copolymers were characterized by an optical spectroscopy and gel permeation chromatography. We focused on the correlation between polymer structure and charge carrier mobility studied by TRMC.

2. Experimental

To obtain the value of intramolecular mobility along the polymer backbone, mainly two techniques were used: flash photolysis-TRMC measurement and the photocurrent integration (PCI). The former gives transient conductivity, and the latter gives the number of charge carriers, or charge carrier generation quantum yield (ϕ).

For TRMC measurement, the resonance cavity was used to obtain a high degree of sensitivity in the conductivity ($\Delta\sigma$) measurement. Transient conductivity ($\Delta\sigma$) of the charge carrier is related to the reflected microwave power ($\Delta P_r/P_r$) as follows:

$$\langle\Delta\sigma\rangle = \frac{1}{A} \frac{\Delta P_r}{P_r}, \quad (1)$$

where A , ΔP_r , and P_r are the sensitivity factor, observed power of the reflected microwave and its transient changes, respectively.

The microwave power and frequency were set at ~ 9.1 GHz and 3 mW, respectively. The strength of electric field applied in TRMC measurement is as low as 100 V/cm, the value of which is much lower than that in TOF and FET measurement ($\sim 10^5$ V/cm). Thus, the estimated value of mobility in TRMC measurement is regarded as a value at zero electric field. The TRMC signal from a diode was measured by a digital oscilloscope (Tektronix, TDS 3052 B, rise time 0.7 ns). All the measurements were carried out at room temperature.

The charge carriers were generated in the solid film by direct excitation of DTP-based copolymers by using a third harmonic generation (355 nm) from a Nd:YAG laser (spectra Physics, INDY-HG). The excitation density was tuned at around $10^{15} \sim 10^{16}$ cm $^{-2}$ photons per pulse.

Photocurrent integration (PCI) measurement was used to estimate the number of the charge carriers generated upon excitation. By combining the values of transient conductivity and the number of charge carriers derived from TRMC and PCI measurements, the intrinsic value of intramolecular mobility on the DTP-based polymer chains can be given based on the following equation:

$$\langle\Delta\sigma\rangle = e\phi N\Sigma\mu, \quad (2)$$

where e , ϕ , N , and $\Sigma\mu$ are elementary charge of an electron, photo-carrier generation yield (quantum efficiency), absorbed photon density, and the sum of mobilities of negative and positive carriers, respectively. *N*-octyldithieno [2,3-*b*: 2',3'-*d*] pyrrole was prepared according to the previous reports [20–23, 27–29]. The synthetic

route of DTP unit is shown in Figure 1. The synthetic routes for DTP polymers are shown in Scheme 1. DTP copolymers and DTP homopolymer were prepared by Suzuki-Miyaura coupling reaction and Yamamoto-type polymerization, respectively [28, 29]. The reaction scheme is displayed in Figure 1.

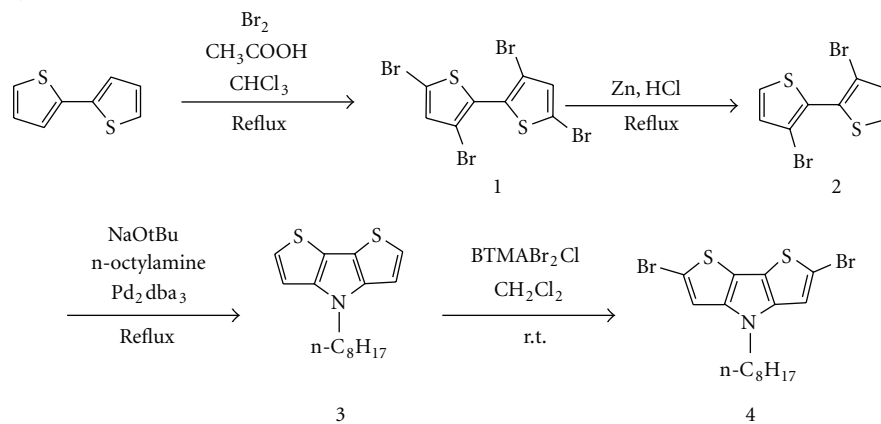
3,3',5,5'-Tetrabromo-2,2'-bithiophene (1). Bromine (21.7 g, 135.9 mmol) was added dropwise over 1.5 h to a solution of 2,2'-bithiophene (4.79 g, 28.8 mmol) in the mixed solvent glacial acetic acid (25 mL) and chloroform (50 mL) at 5–10°C. The mixture was subsequently stirred at room temperature for 4 h and then under reflux for 24 h. After cooling to room temperature, the reaction was quenched by the addition of 20 mL of 10% KOH aqueous solution. The mixture was extracted with CHCl $_3$ (2 \times 100 mL), the combined extracts were washed with water, dried over anhydrous MgSO $_4$, filtered, and the solvent removed by evaporation. Recrystallization from ethanol afforded off-white crystals in 85%.

3,3'-Tetrabromo-2,2'-bithiophene (2). 3,3',5,5'-Tetrabromo-2,2'-bithiophene (1) (14.97 g, 31.06 mmol) was added in portions within 0.5 h to a refluxing dispersion of zinc powder (7.8 g, 0.12 mol) in 156 mL of ethanol containing 9.7 mL of water, 37.2 mL of glacial acetic acid, and 3.1 mL of 3 M HCl. After refluxing for an additional 3 h and then cooling to room temperature, the mixture was filtered and washed three times with ethanol, and the filtrate was collected. The solvent was then removed by evaporation, and 100 mL of H $_2$ O was added. The mixture was then extracted with diethyl ether, and the combined extracts were washed with water, dried over anhydrous MgSO $_4$, and filtered. The solvent was removed by evaporation, and the crude product was recrystallized from hexane to give colorless crystals (7.24 g, yield 71.9%).

N-octyl Dithieno [3,2-*b*: 2',3'-*d*] Pyrrole (3). A solution of 3,3'-dibromo-2,2'-bithiophene (3.22 g, 9.94 mmol), NaOt-Bu (2.37 g, 25 mmol), Pd $_2$ dba $_3$ (0.228 g, 0.249 mmol) and BINAP (0.601 g, 0.965 mmol) in dry toluene (32.2 mL) was purged with argon for 20 min. 1-Octylamine (1.28 g, 9.89 mmol) was added, and the mixture was stirred overnight at 110°C under an argon atmosphere. After cooling down, water (60 mL) was added, and the layers were separated. The water phase was extracted twice with diethyl ether. The combined organic layers were dried over MgSO $_4$, and the solvents were removed under reduced pressure. Finally, the crude product was purified by column chromatography (hexane as solvent) to give a yellow oil (2.29 g, 79.4%).

*2,6-Dibromo-N-octyl Dithieno [3,2-*b*: 2',3'-*d*] Pyrrole (4)*. PhCH $_2$ N(CH $_3$) $_3$ Br $_2$ Cl (0.927 g, 2.69 mmol) was added slowly to a mixture of compound 3 (307 mg, 0.762 mmol) and CH $_2$ Cl $_2$ (67 mL) and stirred for 3 h at room temperature. The reaction was quenched with an aqueous solution of sodium metabisulfite (Na $_2$ S $_2$ O $_5$) and the product extracted with CH $_2$ Cl $_2$. The organic fraction was dried with MgSO $_4$,

Monomer synthesis:



Polymerization:

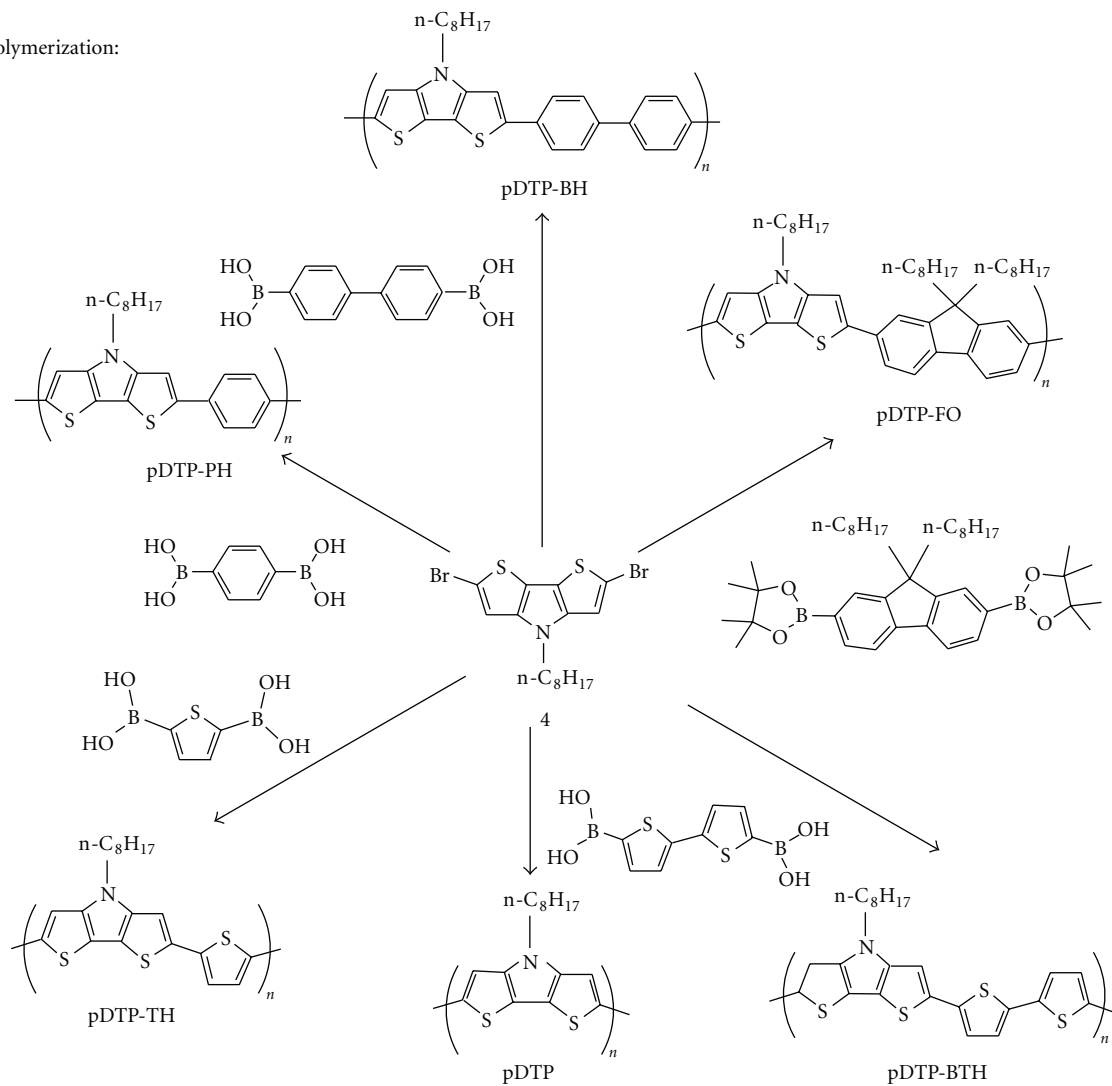


FIGURE 1: Synthetic schema of DTP-based copolymers.

and the solvent was removed under reduced pressure. The product was purified by column chromatography (eluent: hexane) to give a light yellow liquid.

Poly (9,9'-n-octylfluorenyl-N-octyl Dithieno [3,2-b: 2',3'-d] Pyrrole) (pDTP-FO). A mixture of 5,5'-dibromo-N-octyl dithieno [3,2-b: 2',3'-d] pyrrole (111.9 mg, 0.25 mmol), 9,9-dioctylfluorene-2,7-diboronic acid (119.7 mg, 0.25 mmol), and Pd(PPh₃)₄ (49 mg, 0.04 mmol) in 10 mL of THF, and 3 mL of a Bu₄NOH (10%) aqueous solution was stirred in a Schlenk tube at 100°C for 48 h. The mixture was then stirred at 100°C for additional 12 h after adding 4-Bromo-1-butyl-benzene (22 mg, 0.10 mmol), and stirred at 100°C for a further 12 h after adding phenylboronic acid (16 mg, 0.10 mmol). The resulting mixture was then poured into 200 mL methanol. The precipitate was collected by filtration, and the resulting polymers were washed with 1 N HCl aq and extracted with toluene. Evaporation of toluene afford crude polymer. The polymer was further purified by precipitation. The other DTP copolymers containing 1,4-dioctloxyphenyl (PH), 1,4-dioctloxy2,2'-biphenyl (BPH), 3-dodecylthiophene (TH), 3,3'-didodecyl-2,2'-bithiophene (BTH), and 9,9'-dioctylfluorene (FO) were synthesized following the same procedure.

Poly (N-octyl Dithieno [3,2-b: 2',3'-d] Pyrrole) (pDTP). Ni(COD)₂ (0.303 g, 1.10 mmol), COD (0.123 mL, 1.00 mmol), and 2,2'-bipyridine (0.172 g, 1.10 mmol) were dissolved in dry, argon-purged DMF (3 mL). The solution was heated at 80°C for 0.5 h, and an argon-purged solution of 5,5'-dibromo-N-octyl dithieno [3,2-b: 2',3'-d] pyrrole (0.500 mmol) in dry toluene (3 mL) was added via a syringe. The reaction was maintained at 80°C for 96 h in the dark. After cooling, an aqueous solution of HCl (1 mL, 4 M) was added to quench the polymerization. The mixture was diluted with chloroform, transferred into a separatory funnel, and washed successively with an aqueous HCl (2 M) solution, with a saturated EDTA solution, with a saturated NaHCO₃ solution, and with brine. The combined organic layers were dried over Na₂SO₄, subsequently concentrated, and finally precipitated into methanol. The polymer was further purified by precipitation.

3. Results and Discussion

Intramolecular mobilities reflecting backbone structures were measured using TRMC and PCI measurements. The observed conductivity transients by TRMC measurement in oxygen atmosphere are shown in Figure 2. All TRMC transients reach maximum values of conductivity within 2 μs, and kinetic traces of all TRMC signals show pseudo-first-order decay. These trends have been common for organic semiconductors with the presence of oxygen as a strong electron scavenger. Photo-ionization of the conjugated polymer molecules with small adiabatic ionization potentials gives radical cations of the polymer molecules and photo-electrons which are scavenged rapidly by oxygen molecules within the time constant of the present TRMC system (~50 ns), leading

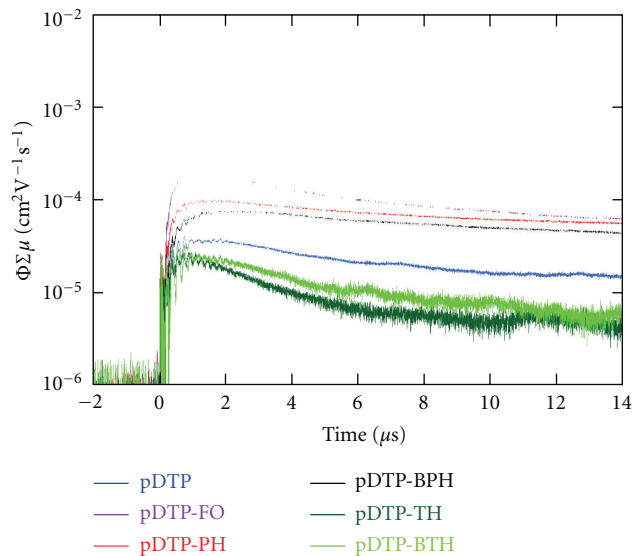


FIGURE 2: Conductivity transients observed for thin films of DTP-based copolymers. The transients were recorded under 355 nm laser pulse excitation at $1.1 \sim 1.3 \times 10^{16} \text{ cm}^{-2} \text{ photons pulse}^{-1}$.

to the formation of superoxide anion (O_2^-) [30, 31]. The superoxide anions are inactive for the TRMC measurement because of the far lower mobility of the ionic molecules in the solid state than those of charge carriers, resulting in their small contribution to the recombination processes of the radical cations. This is the case giving the pseudo-first-order decay kinetics in the present materials.

Poly(9,9'-n-octylfluorenyl-N-octyl)dithieno [3,2-b: 2',3'-d] pyrrole (pDTP-FO) exhibits the highest conductivity, the lower values are observed sequentially for poly(biphenyl-N-octyl dithieno [3,2-b: 2',3'-d] pyrrole) (pDTP-BPH) and poly(phenyl-N-octyl dithieno [3,2-b: 2',3'-d] pyrrole) (pDTP-PH). Phenyl groups in the backbones such as phenyl, biphenyl, and fluorenyl units tend to give the higher conductivity than thiophenyl groups in poly(thiophenyl-N-octyl dithieno [3,2-b: 2',3'-d] pyrrole) (pDTP-TH), poly(bithiophenyl-N-octyl)dithieno [3,2-b: 2',3'-d] pyrrole) (pDTP-BTH), and poly(N-octyl dithieno [3,2-b: 2',3'-d] pyrrole) (pDTP). UV-vis absorption, emission properties, and the values of molecular weight of DTP-based polymers were also measured and summarized in Table 1.

To discuss the factors affecting the hole transporting property [20, 21], several types of monomer units whose HOMO orbital energies varied in relation to that of DTP unit were adopted because charge-transfer rate between donor units and acceptor units is affected by the difference of the energy levels of HOMO orbitals especially in case of hole transfer rate based on Marcus theory [32]. In Figure 3, the energy levels of HOMO orbital were calculated by density functional theory (DFT) at B3LYP/6-31G level. As the homopolymer, pDTP, does not have an energy mismatch between neighboring units, pDTP has been expected to show the highest value of mobility. However, pDTP-FO showed the highest value of the intramolecular mobility of $1.7 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ along with their backbones. Thus, not

TABLE 1: Optical properties, molecular weights, and charge carrier mobilities of DTP-based copolymers.

Entry	$\lambda_{\max}^{\text{abs}}$ (nm)	ϵ_{abs}	$\lambda_{\max}^{\text{em}}$ (nm)	M_n^{b}	PDI ^c (M_w/M_n)	Stokes shift (eV)	$f_{\text{VB-ES}}$	μ_+ ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)
pDTP-FO	489	5.4×10^4	525	1.8×10^4	2.9	0.17	0.66	1.7
pDTP-BPH	443	2.7×10^{3a}	500	2.1×10^3	1.1	0.35	0.05	0.32
pDTP-PH	486	5.9×10^{3a}	537	2.0×10^3	1.2	0.24	0.12	0.59
pDTP	508	6.1×10^3	564	2.0×10^3	1.2	0.24	0.13	0.49
pDTP-BTH	493	3.8×10^3	569	1.0×10^3	1.1	0.33	0.67	0.16
pDTP-TH	478	1.7×10^4	559	9.3×10^2	1.1	0.37	0.31	0.13

^aLow solubility in THF. ^bNumber-average molecular weight determined by GPC with polystyrene calibration standards. ^cPolydispersity index (PDI).

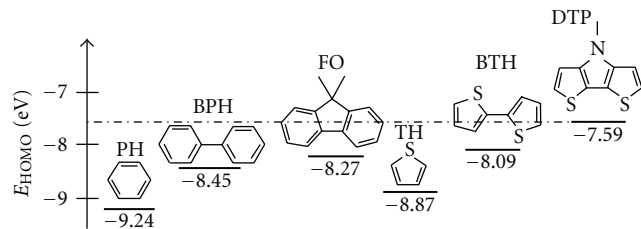


FIGURE 3: HOMO energy levels (eV) of phenyl (PH), biphenyl (BPH), fluorene (FO), thiophene (TH), bithiophene (BTH), and dithienopyrrole (DTP) monomers calculated by DFT at B3LYP/6-31G level.

only energy level matching between monomer units but also extended conjugation is considered to be an important factor for the high intra-molecular mobility. To examine the extended conjugation and planarity of polymer backbone, UV-vis absorption and photoluminescence spectra were measured. Figure 4 shows UV-vis absorption spectra of DTP polymers in THF. The absorption maxima have been attributed to π - π^* transition in the main chains of DTP-based copolymers. From the absorption and photoluminescence spectra, the values of Stokes shift and oscillator strength (f) have been estimated.

Stokes shift is the primary factor reflecting the conformational changes of conjugated backbones between ground state and excited state [33]. The rigidity of polymer backbone is presumed as an important factor to determine electric conductivity because the rigid backbone is responsible for the large effective conjugation length, leading to high hole mobility. The values of mobility increase symmetrically with decreasing Stokes shift in both phenyl-incorporated (pDTP-FO, pDTP-BPH, and pDTP-PH) and thiophene-incorporated (pDTP, pDTP-BTH, and pDTP-TH) incorporated into their backbones, suggesting that the rigidity of DTP-based copolymer is indicative primarily of the intra-molecular charge carrier mobility.

Oscillator strength (f) also reflects extended degree of conjugation along the backbones, as this parameter corresponds to π - π^* transition dipole moments [30, 31, 34]. Therefore, Stokes-shift and oscillator strength are of help to discuss the intra-molecular mobility of negative and positive charge carriers. In general, conjugated polymers possessing high intra-molecular charge carrier mobility have

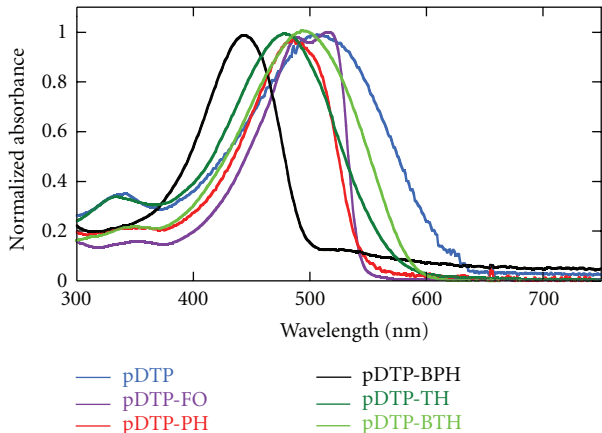


FIGURE 4: UV-vis absorption spectra of DTP-based copolymers in THF.

a planar and rigid backbone, which is rationalized by small Stokes shift [33] or large oscillator strength [34]. However, a poor correlation among intra-molecular mobility, Stokes shift, and oscillator strength were found in the thiophene-incorporated (pDTP, pDTP-TH, and pDTP-BTH). Considering this result, conformational changes in the conjugated backbones with a positive charge (radical cation) are expected to be different from those in the exciton states. The values of oscillator strength for radical cations were reported to be much larger than that for excitons [34]; therefore, extended conjugations for radical cations are responsible for the effective intra-molecular transport of holes on the conjugated backbones. This is the case giving the poor correlation between the parameters observed for the exciton state and the intrinsic intra-molecular mobilities determined in the present study.

On the contrary, the mobilities of pDTP-FO, pDTP-BPH, and pDTP-PH increase with an increase in their oscillator strength. In term of molecular weight of the polymers, the values of intra-molecular mobility are expected to depend also on the molecular weight. However the range of molecular weights of the polymers varying from 2×10^3 to 1.8×10^3 is long enough in comparison with the size of the oscillating motion (<1 nm) of the charge carriers on the backbone [35]. Recently, ultra-high value of FET mobility as high as $3.3 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ has been reported by Tsao et al. [36]. The polymer bearing intra-molecular charge

transfer interactions between cyclopentadithiophene and benzothiadiazole moieties exhibited strong dependence of positive charge carrier mobility ($0.28 \sim 3.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) on its molecular weight ranging from 1.3×10^3 to 3.5×10^4 . This is indicative that inter-molecular stacking and hence inter-molecular hopping processes of charge carriers are predominant in the long-range translational motion of positive charge carriers in FET device structures. This is the case giving the high values of intra-molecular mobility in dithieno [3,2-*b*: 2',3'-*d*] pyrrole-based conjugated polymers derived from the TRMC measurement, and we can expect the intra-molecular mobility values as a benchmark value of positive charge mobility in defect-free device structures of the polymers with enough high chain length.

The better correlation between the values of f and μ in pDTP-FO, pDTP-BPH, and pDTP-PH than that in pDTP, pDTP-TH, and pDTP-BTH also suggests the smaller conformational change in neutral to charged states of phenyl-incorporated copolymer systems, while the larger change occurs in the thiophene ones. This also suggests that oscillator strength of radical cations is important principally than that of exciton states (electron-hole pair) to predict the degree of extended conjugation directly relating to the conductive properties such as charge carrier mobility.

4. Conclusions

DTP-based copolymer and homopolymer have been prepared by Suzuki-Miyaura coupling reaction and Yamamoto coupling reaction, respectively. TRMC and PCI experiments showed that all DTP-based copolymers have good intra-molecular hole-transport properties. There is good correlation between oscillator strength and charge carrier mobility in phenyl group in contrast to thiophenyl group. The highest value of charge carrier mobility was found to be as high as $1.7 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for pDTP-FO. This excellent electrical property demonstrates the feasibility of DTP-based copolymer to a potential material replacing amorphous silicon.

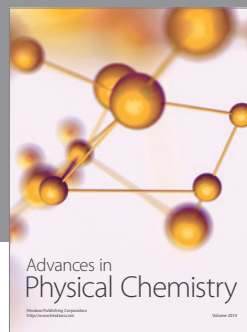
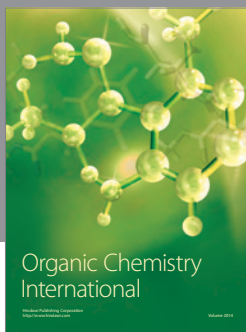
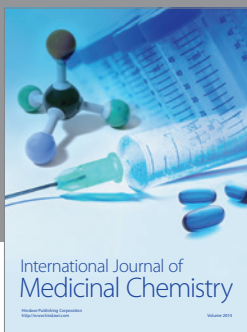
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