Synthesis and Characterization of New Monomer and New polymer of Naphthalene diimide: Electrochemical and Optical Studies

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Synthesis of a new monomer of 2,6-Difuran-2-yl-naphthalene-1,4,5,8-tetracarboxylic-N,N'-dodecyl diimide (F-NDI-F) by using Stille coupling reaction. The effect of furan as a donor unit on the optical and redox properties of NDIs has been studied, and compare it with 2,6-Di(2-thienyl)naphthalene-1,4,5,8-tetracarboxylic-N,N'-dodecyldiimide(Th-NDI-Th) monomer through cyclic voltammetry, UV-vis absorption and fluorescence measurements to determine the optical and electrochemical characteristics.

1. INTRODUCTION

Organic semiconductors have been of great research interest for use in low cost, ultrathin, and flexible products such as flexible transistors, light-emitting diodes, and photovoltaics [1-3]. While many p-channel organic semiconductors have been thoroughly characterized and have achieved acceptable device performance and stability, n-channel organic semiconductors are less numerous. There are several examples that are being explored for the latter, naphthalene diimides (NDIs) one of the earliest applied small molecule organic semiconductors, have been studied extensively as an n-type materials [4,5]. Their high electron affinities, high electron mobilities, excellent thermal, oxidative stability, low lying tunable LOMU, photochemical stability, air-stability and finally good light absorption characteristics [6-11] render these organic molecules as active parts of a variety of nonvolatile memory devices, organic diodes, organic field-effect transistors (OFETs), and organic photovoltaic cells (OPVs) [12-21].

The chemical modification of the NDIs can be achieved by two different methods. One is to introduce substituents at the N atoms of imide groups, and the other is functionalization of NDIs by core substitution [22].

The N,N'-substituents of NDIs generally have only minimal influence on the optical and electronic properties of isolated molecules, although they can be used to control solubility, aggregation, and intermolecular packing in the solid state. Core substituted NDIs typically have a much more significant effect on the redox potentials and optical spectra [9]. Moreover, these compounds do not absorb visible light, limiting their use in optoelectronic applications. To increase absorption into the visible range can be achieved by extend the conjugation of NDI through the core, or use electron-donating core substituents by attachment of electron-donating core substituents with an electron poor NDI core creates a push-pull system with tunable color[23]. The core substituents also greatly impact the fluorescent properties of these molecules; alkoxy or alkylamino groups have resulted in highly fluorescent molecules whereas arylamino groups have given non-fluorescent molecules [24, 25]. Numerous donor monomers have been copolymerized with NDI in a conjugated fashion to alter polymer electronic and photovoltaic properties. These groups have included thiophene-based [13,14], thiazole-based [26], and fluorene-based[15,27] donors. Although polyfuran has been reported [28-31], to the best of our knowledge there has been no single report on NDI–containing donor (D)–acceptor(A) comonomers based on directly connecting furan ring with moderate electron-donating properties as well as thiophene analogue with enhanced electron-donating characteristics relative to thiophene, which raises some interesting questions: Does the empirical electron-donating ability of furan (F) ring affect the optical and redox properties of NDI as well as thiophene (Th) does? Is it possible to synthesize PNDI-F and PNDI-Th copolymers by using electropolymerization? Together with a reference thiophene–based comomnomer Th-NDI-Th and PNDI-Th copolymer for accurate and meaningful comparison; herein we report the synthesis and detailed characterization of a new comonomer of 2,6-Difuran-2-yl- naphthalene-1,4,5,8-tetracarboxylic-N,N'-dodecyl diimide (F-NDI-F) by using Stille coupling procedure. The effect of furan as a donor unit on the optical and redox properties of NDIs has been studied to elicit a structure-property relationship, and compare it with 2,6-Di(2-thienyl) naphthalene-1,4,5,8-tetracarboxylic-N,N'-dodecyldiimide(Th-NDI-Th) comonomer through cyclic voltammetry, UV/vis absorption and fluorescence measurements to determine the optical and electrochemical characteristics of these comonomers.

2. EXPERIMENTAL

2.1. Instrument

All the synthesized compounds (1-6), except compound 2 (2, 6- di bromonaphthalene -1, 4, 5, 8-tetracarboxylic dianhydride were characterized by ^{1}H NMR, ^{13}C NMR.

NMR spectra were recorded on a Bruker Spectrospin Avance DPX-400 Spectrometer with TMS as the internal standard and CDCl$_3$ as the solvent. Chemical shifts were recorded in parts per

million (ppm), and splitting pattern are designated as s (singlet), d (doublet), t (triplet), m (multiplet) and br (broad).

The UV/vis spectra were recorded Hewlett–Packard 8453A diode array spectrometer.

Fluorescence measurements were carried out on Varian Carry Eclipse spectrophotometer.

Electrochemical cyclic voltammetry measurements were carried out with Gamry PCI 1300 potensiostat-galvanostat in CH_2Cl_2 solution containing o.1M of tetrabutyl ammonium hexafluoro phosphate (Bu_4NPF_6) at a scan rate of 50mV/s using a three – electrode cell with a platinum working electrode, a platinum wire counter electrode, and a Ag/AgCl reference electrode. The reference electrode was calibrated using a ferrocene/ferrocenium redox couple as an internal standard, whose oxidation potential is set at -4.8 eV with respect to zero vacuum level.

2.2. Materials

All chemicals and reagents were obtained from commercial sources and used without further purification. Tetrahydrofuran (THF) and Toluene were dried over sodium and benzophenone and freshly distilled prior to use. All reactions were carried under an argon atmosphere. N,N'-dodecyl-1,4,5,8-naphthalenetetracarboxylicdiimide, 2,6-dibromonaphthalene-1,4,5,8-tetracarboxylicdianhydrid, and 2-tributylstannyl thiophene were synthesized in close analogy to the methods already described [26,32]

2.3. Synthesis of the monomers

The synthesis routes of the monomers are shown in Scheme 1. The detailed synthetic processes are as follows.

2.3.1. N, N'-dodecyl-1, 4, 5, 8-naphthalene tetracarboxylic diimide (1)

1-dodecylamine (0.5g, 2.7mmol) and 1, 4, 5, 8-naphthalene tetracarboxylic dianhydride (0.35g, 1.2mmol) in dry DMF (15ml) were stirred at 140 ºC for 6 h. The reaction mixture was allowed to cool to RT, and the solution was placed in the refrigerator for 30 min to get a cream-coloured solid product. The solution was filtered and washed with pure MeOH, and the obtained solid was further purified by column chromatography by using silica gel and $CHCl_3$ as an eluent to obtain the pure product as a slight pink solid (0.53g, 73%) . ^1H NMR ($CDCl_3$): δ (ppm) = 8.76 (s, 4H), 4.13 (t, 4 H), 1.7–1.62 (m, 4H), 1.35–1.28 (m, 4H), 1.17–1.03 (m, 36H), 0.81 (t, 6H).

^{13}C NMR ($CDCl_3$): δ (ppm) =162.79, 130.90, 126.65, 125.61, 40.99,31.92,29.63,29.59, 29.53, 29.34,28.08,27.09,22.69,14.12. HRMS-ESI$^+$ (m/z) : [M$^+$] Calcd for $C_{38}H_{54}N_2O_4$ 602.7636, found 602.7630.

2.3.2. 2,6-Dibromonaphthalene -1,4,5,8-tetracarboxylic dianhydride (2)

1,4,5,8-naphthalenetetracarboxylic dianhydride (1g, 3.73mmol) was suspended in oleum ($65\%SO_3$, 15ml) at RT and a catalytic amount of iodine was added to the mixture. Bromine (0.35ml, 6.82 mmol) was injected in small portions to the reaction mixture. After completion of the bromine injection the temperature was increased to 50 ºC and the mixture stirred for 48h. After cooling, the excess bromine was removed under a gentle stream of air and passed through a saturated solution of $Na_2S_2O_3$. The residue was then carefully poured into ice water to result in a yellow precipitate. The precipitate solid was filtered off, and washed with copious amount of water and dried under vacuum to give a bright yellow solid (1.97g), which was used as such without further purification.

2.3.3.N,N'-dodecyl-2,6-dibromonaphthalene-1,4,5,8-tetracarboxylic diimide(3)

A mixture of 2,6-dibromonaphthalene-1,4,5,8-tetracarboxylicdianhydride (2g, 4.7mmol) and 1-dodecylamine (4ml, 24.5 mmol) were refluxed at 130 ºC overnight under argon in (60 ml) of acetic acid. Upon cooling to RT, the mixture was poured into 100 ml cold water, filtrated, and washed with water. After drying under vacuum, the resulting reddish solid was purified by column chromatography on silica gel using a mixture of ethylacetate- hexane (1:15) as an eluent. And the resulting orange solid was further purified by recrystallization from isopropanole to obtain product [3] as slight orange solid (500 mg). ^{1}HNMR ($CDCl_3$): δ(ppm) = 8.88 (s, 2H); 4.14 (t, 4H); 2.05 (m,4H); 1.26-1.97(m,36H), 0.95 (t,6H).^{13}C NMR ($CDCl_3$):   δ (ppm) = 162.79, 130.88, 126.61, , 40.99, 31.91, 29.62, 29.33, 28.08, 27.09, 22.67, 14.10. HRMS-ESI$^+$ (m/z) : [M$^+$] Calcd for $C_{38}H_{54}N_2O_4Br_2$ 762.5716, found 762.5712.

2.3.4. 2-(tributylstannyl) thiophene (4)

At -78 ºC a 1.6 M solution of n-BuLi in hexane (5.9ml, 14.72mmol) was added drop-wise to a solution of 2-bromothiophene (2g, 12.27mmol) in dry THF (40ml). The mixture was stirred for 1 h at -78 ºC under argon atmosphere. Then, tributylstannyl chloride (4.8g, 14.72mmol) was slowly added and stirred for another 1 h at -78 ºC. Afterwards, the solution was allowed to return to room temperature, and the solvent was removed by rotary evaporation before being poured into 100 ml of water. The mixture was extracted with $CHCl_3$ (2x80 ml). The combined organic layers were dried over anhydrous $MgSO_4$ and the solvent was removed by rotary evaporation. The residue was purified via column (alumina) using hexane/ triethyl amine (95/5) as eluent to give the product [4]. ^{1}H NMR ($CDCl_3$): δ(ppm) =7.63(d,1H), 7.25(dd,1H), 7.20(d,1H), 1.55-1.63(m,6H), 1.31-1.41(m, 6H), 1.14-1.10(t,6H), 0.9-0.89(t,9H). ^{13}C NMR ($CDCl_3$): δ (ppm) =136-135, 130-127, 29-28, 27-25, 13-12,10-8.

2.3.5. 2,6-Di(2-thienyl) naphthalene-1,4,5,8-tetracarboxylic-N,N'-dodecyl diimide(5)

2-tributylstannyl thiophene (570mg, 1.3mmol) and 2,6-dibromonaphthalene-1,4,5,8-tetracarboxylic-N,N'-didodecyl diimide (142 mg, 0.186 mmol) were dissolved in dry toluene (20 ml),

reaction mixture degassed and reflux at 110 ºC for 30 min under argon atmosphere. Then dichlorobis(triphenylphosphine)-palladium (II) (75mg, 0.11mmol) was added, the mixture was refluxed for 24h and then allowed to return to room temperature. After removing the solvent under vacuum, 2N HCl (100ml) was added and the mixture was extracted with dichloromethane. The organic phase was washed with water and brine and solvent evaporated. The product was purified by column chromatography using an ethyl acetate/hexane as eluent. The resulting product was further purified by re-crystallization from ethanol to give the pure product as a deep red solid (53mg). ^{1}H NMR (CDCl$_3$): δ(ppm) =8.73(s,2H); 7.56(d,2H); 7.27(d,2H); 7.19(t,2H); 4.09(t, 4H); 1.7(m, 4H); 1.35-1.28(m, 36H); 0.86(t,6H). HRMS-ESI$^+$ (m/z) : [M$^+$] Calcd for C$_{46}$H$_{62}$N$_2$O$_4$S$_2$ 771.0756, found 771.0749.

2.3.6. 2,6-Difuran-2-yl- naphthalene-1,4,5,8-tetracarboxylic-N,N'-dodecyl diimide (6)

Tributyl (furan-2-yl) stannane (284mg, 0.8mmol) and 2,6-dibromonaphthalene-1,4,5,8-tetracarboxylic-N,N'-didodecyl diimide (88 mg , 0.12mmol) were dissolved in dry toluene (20ml), the solution was flushed with argon and reflux at 110ºC for 30min. Then dichlorobis(triphenylphosphine)-palladium(II) (75mg, 0.11mmol) was added, the mixture was heated to refluxed for 30h. After cooling to room temperature, the reaction mixture was poured into saturated ammonium chloride solution. The product was extracted with dichloromethane (3 x100 ml). The extracts were combined and washed with water and brine then dried over anhydrous MgSO$_4$. After filtration, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel, using chloroform /hexane (2/1) as eluent to give a deep orange solid (75mg). ^{1}H NMR (CDCl$_3$): δ(ppm) = 8.67(s,2H); 7.52(d, 2H); 6.54(d,2H); 6.0(d,2H); 4.11(t,4H); 1.67(m,4H); 1.2-1.5(m,36H); 0.84(t,6H). HRMS-ESI$^+$ (m/z) : [M$^+$] Calcd for C$_{46}$H$_{62}$N$_2$O$_6$ 738.912, found 738.8992
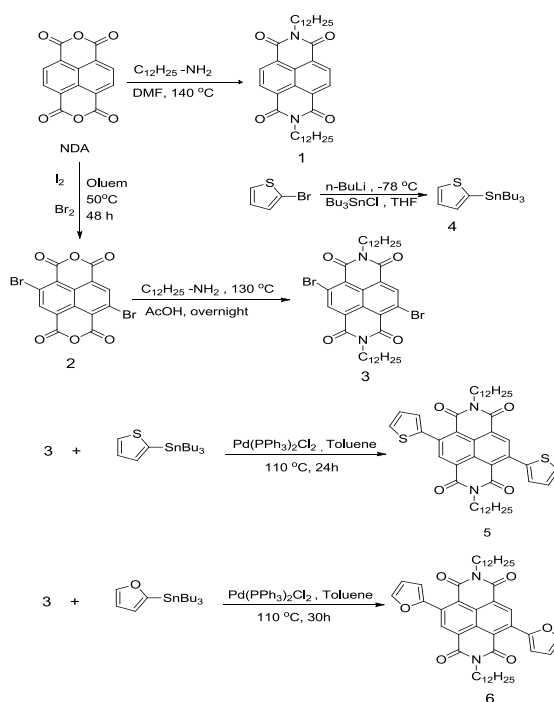
Scheme 1. Synthesis route of monomers

3. RESULT AND DISCUSSION

3.1 Synthesis and Characterization.

The synthesis of the functionalized NDI (1) [32] molecules, Th-NDI-Th and F-NDI-F, is outlined in **Scheme 1**. The key NDI monomer, 2,6-Dibromonaphthalenediimide(3)[13] was prepared from dibrominated,1,4,5,8-naphthalenetetracarboxylic dianhydride(2)[5] and 1-dodecylamine using the previously reported method. The donor co-monomer 2-(tributylstannyl)thiophene(4)[26]**,** was prepared by the literature procedures. Stille coupling of compound **3** with **4** afforded Th-NDI-Th,**5,** as a red solid in 40% yield. Stille coupling of 3 and Tributyl (furan-2-yl) stannane gave compound **6** as a deep orange solid in 80% yield. All final compounds were purified by column flash chromatography and recrystallized from isopropanol and ethanol solvents. The molecular structure of the five monomers was confirmed by ^{1}H, ^{13}C NMR spectra and Mass spectra showed that the monomers were obtained in high purity. All functionalized NDIs are readily soluble in organic solvents including chloroform, toluene, and dichloromethane.

3.2 Electrochemical Properties

The electrochemical redox properties and associated electronic structures (HOMO/LUMO energy levels) of the NDI monomers were investigated by cyclic voltammetry (CV). Figure 1 shows the cyclic voltammograms of NDI monomers and the associated numerical results are summarized in Table1. Th-NDI-Th and F-NDI-F showed two reversible reduction waves corresponding to the sequential reduction of each NDI to the radical anion and dianion. The electrochemical reduction potential of the first and second half-wave reduction potentials ($E_{1/2}^1{}_{red}$ and $E_{1/2}^2{}_{red}$) were estimated by using the formula ($E_{Pa} - E_{Pc}$)/2. F-NDI-F exhibited $E_{1/2}^1{}_{red}$ and $E_{1/2}^2{}_{red}$ at -0.63 and -1.05 V and for Th-NDI-Th is about -0.60 V and -1.03 V, and irreversible oxidation wave was detected at 1.41V. The difference in the first reduction potential between NDI and F-NDI-F is 34 meV, and 64 meV between NDI and Th-NDI-Th or 30 meV between F-NDI-F and Th-NDI-Th. As expected, Th-NDI-Th exhibits electrochemical activity in both anodic and cathodic potential scans. When an anodic potential is applied, the thiophene moiety gets oxidized and shows the p-doping properties, whereas in the cathodic potential scan the NDI moiety gets reduced and show n-doping characteristics. In the p-doping process the onset irreversible oxidation wave is around 1.41V, which is typical for thiophene moiety. In the n-doping process, NDI shows two reversible reduction waves are around (-0.6 and -1.03) V, implying the formation of radical anion and dianion[37,43]. However, in contrast to Th-NDI-Th, F-NDI-F shows two reversible reduction waves are clearly observed during the cathodic potential, no oxidation wave is detected during the anodic potential, regardless of scan rate [43].

From $E_{1/2}^1{}_{red}$ values, LUMO energies for the present monomers can be estimated by taking Fc/Fc$^+$ energy level to be 4.8 eV below the vacuum level and using the formula $E_{LUMO} = -4.8 - E_{1/2}^1{}_{red}$ The LUMO energy levels of Th-NDI-Th and F-NDI-F monomers showed low-lying LUMO levels in the range from -4.20 eV to -4.17eV (Table 1), which is comparable to the LUMO level of the parent NDI small molecule (-4.02 eV). HOMO energy level for Th-NDI-Th monomer was (-6.21eV)

calculated from the onset of the oxidation peak by using the formula $E_{HOMO} = -4.8 - E_{OX}$, in sharp contrast to F-NDI-F which did not show oxidation peak at any positive potential.

Therefore, F-NDI-F and Th-NDI-Th monomers are typical n-channel organic semiconductors with the low-lying LUMO energies (<-4.0 eV) that can thermodynamically resist electron carrier trapping under ambient conditions, and in agreement with similar observations by other investigations [32,35-36]. The stable LUMO energy and good solubility make F-NDI-F and Th-NDI-Th promising candidates for solution-processed, ambient stable, n-channel organic thin film transistors.

Table 1. Electrochemical properties of NDIs monomers[*].

Monomer	$^aE_{1/2}{}^1{}_{red}$ (V)	$^aE_{1/2}{}^2{}_{red}$ (V)	$^bE_{LUMO}$ (eV)	E_{ox} (V)	$^cE_{HOMO}$ (eV)
NDI	−0.77	−1.10	−4.02	N/A	N/A
F-NDI-F	−0.63	−1.05	−4.17	N/A	N/A
Th-NDI-Th	−0.60	−1.03	−4.20	1.41 irrev	−6.21

*Experimental conditions: 0.1 M (n-Bu)4N·PF6 in DCM as supporting electrolyte, Pt disk as working electrode, Pt wire as counter electrode, Ag/ AgCl as reference electrode, scanning rate: 50mV/s. [a]Values for (Epa+Epc)/2 in eV versus Fc/Fc[+]. [b]$E_{LUMO} = -4.8 - E_{1/2}{}^1{}_{red}$. [c]$E_{HOMO} = -4.8 - E_{ox}$

Table 2. Electronic Energy levels of PNDI-Th.

| Polymer	λ_{onset} (nm)	$E_{ox}{}^{onset}$ (V)	$^dE_g{}^{opt}$ (eV)	$^eE_{HOMO}$ (eV)	$^fE_{LUMO}$ (eV)
PNDI-Th	620	0.75	2.0	−5.55	−3.55

[d] Optical band gap calculated from the onset of thin film absorption ($E_g{}^{opt} = 1240/ \lambda_{onset}$). [e]Electrochemically determined vs Fc/Fc[+], [e]$E_{HOMO} = -(E_{ox}{}^{onset} + 4.8)$, [f]$E_{LUMO} = E_{HOMO} + E_g{}^{opt}$

It is well-recognized that organic semiconducting materials should have delocalized electron-density-state and appropriate levels of HOMO and LUMO to facilitate efficient transport of holes and electrons, respectively. Therefore, the electrochemistry and associated electronic structures of the PNDI-Th copolymer was investigated as thin films using cyclic voltammetry (CV) [18]. Figure 2 shows the multiple scan voltammetry of the monomer Th-NDI-Th solution on Indium Tin Oxide (ITO) in CH_2Cl_2 solution containing 0.1 M NBu_4PF_6 between the potential 0.0 and 1.8V at a scan rate of 200mV/s versus Ag wire reference electrode. It can be seen that there are reversible p-doping/dedoping (oxidation/re-reduction) processes at positive potential range. During the CV measurement we observed an increase in current density after the second oxidation cycle, indicating possible oxidative electrochemical polymerization due to the presence of terminal thiophenes. After several scans, the working electrode was covered with a film of PNDI-Th, confirming electrochemical polymerization[37].
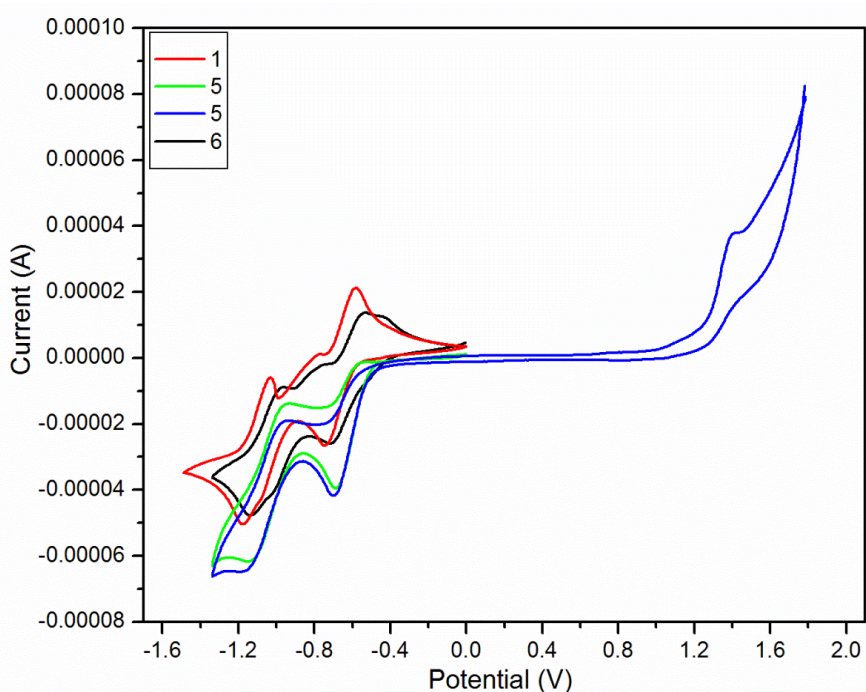
Figure 1. Cyclic voltammograms of NDI and compounds 5-6 in 0.1M NBu4PF6/ CH$_2$Cl$_2$ solution at scan rate of 50mV/s.
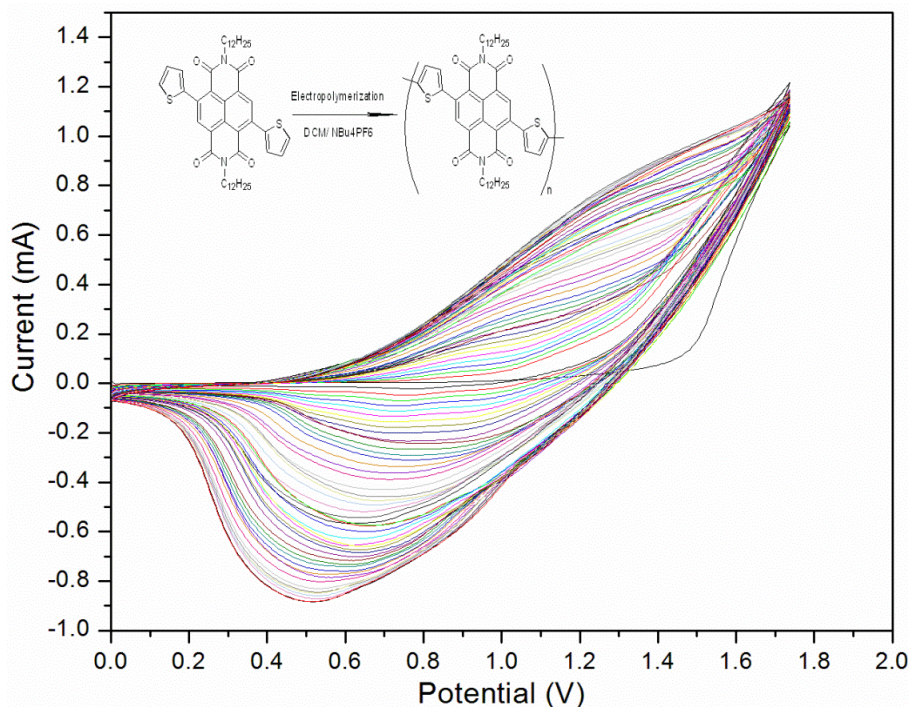
Figure 2. Electropolymerization of Th-NDI-Th monomer in 0.1 M NBu$_4$PF$_6$ / CH$_2$Cl$_2$ solution at scan rate of 200mV/s.

This film is very robust and showed good stability toward repeated redox cycling. The slight increase in the peak separation potential reflected the increase in the polymer film resistance as the thickness of the film increased with increasing cycles. Thus, the LUMO energy level was calculated

from using the optical band gap (E_g^{opt}) from the calculated HOMO (Table 2). The optical band gap (E_g^{opt}) from the absorption edge of the thin film PNDI-Th is 2.0 eV, which indicates the chromatic shift and band gap is predominantly a function of electron–donating ability of the donor counit in NDI–based D-A copolymer [18]. The LUMO level for PNDI-Th is -3.55eV, which is comparable to the LUMO level of the parent NDI small molecule –4.02 eV. However, the HOMO energy level is -5.55 eV as a function of elctrone donating ability of donor monomer and polymer backbone conformation. These CV results indicate that the band gap of NDI copolymer are determined largely by the donor counits, while the LUMO energy level remains a constant due to the NDI unit. For comparison, the LUMO energy level of a common electron acceptor, phenyl-C61- butyric acid methyl ester (PCBM) [39], had a LUMO level of -4.0 eV. The electronic properties of the NDI constituting the LUMO of the polymer and the thienyl unit affecting the HOMO and E_g^{opt} of the material were further confirmed by reports stating similar values for related materials. It is noted that specific tuning of the band gap and HOMO of NDI-based polymers can be achieved by altering the thienyl content of the bulk structure which is similarly achieved in polyfluorenes[7,13-14]. However, the low-lying LUMO level for PNDI-Th, which is close to that commonly used n-type conjugated polymers reported to date [18-19,27,37,39], suggest that electropolymerization of Th-NDI-Th monomer considered as a useful method for developing n-channel OFETs. Electrochemical polymerization of F-NDI-F on ITO was unsuccessful due to film delamination upon bias.

3.3 Optical properties:

The UV-visible electronic absorption and fluorescence properties of NDI, Th-NDI-Th, F-NDI-F, in the CH_2Cl_2 solution were measured, and the details are summarized in Table 3.

Table 3. Absorption maxima (λ_{abs}) and emission maxima (λ_{em}) of NDIs in CH_2Cl_2 solution.

| Monomer	λ_{abs} / nm	λ_{em} / nm
NDI	360, 380	-----
F-NDI-F	360, 380	554
Th-NDI-Th	360, 380	500

The absorption spectra of Th-NDI-Th and F-NDI-F show two prominent vibronically structured absorption bands consisting of relatively sharp ones at the high energy region 360-380 nm similar to that of the corresponding NDI, and shoulders at the low energy region (400-550 nm) Figure 3(left)). The former bands can be assigned to π-π^* transition of the NDI core whereas the low-energy shoulders, which are relatively less intense, are largely of intermolecular charge transfer (ICT) characteristics between the electron-donor and NDI electron–deficient moieties. As expected, when comparing Th-NDI-Th and F-NDI-F monomers versus NDI monomer, the intermolecular charge

transfer (ICT) shoulders and absorption onsets of Th-NDI-Th and F-NDI-F are significantly red-shifted relative to the NDI monomer, as a reflection of a strong donating ability of thiophene and furan units. The presence of thiophene unit does influence the absorption behavior of NDI chromophore, more than furan unit does [18].
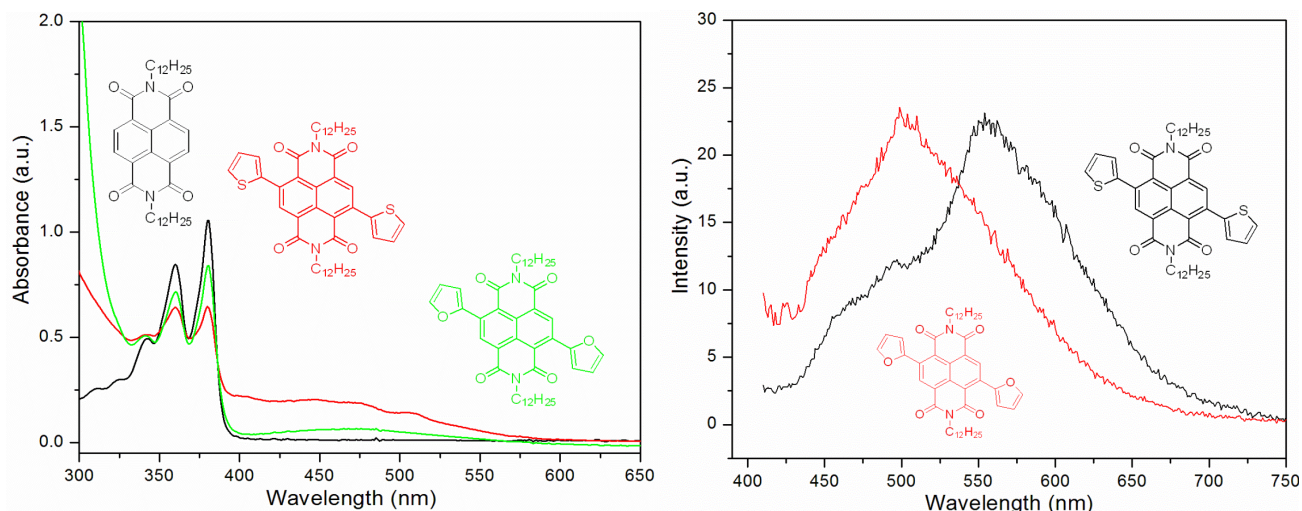
Figure 3. Absorption maxima (left) and emission maxima (right) in CH_2Cl_2 of NDI and the monomers Th-NDI-Th & F-NDI-F.

The Fluorescence spectra of the monomers Th-NDI-Th and F-NDI-F show high emission maxima in dichloromethane solution at 500 and 554 nm, respectively (Figure 3(right). The strong fluorescence for F-NDI-F and Th-NDI-Th is increased relative to the NDI monomer, and in some cases is comparable to that of core-substituted NDIs bearing an amine[43,44], This underscores the benefit of the carbon-carbon bond on the fluorescence of these compounds and the potential they may have in optoelectronic devices[24,37, 43,46].
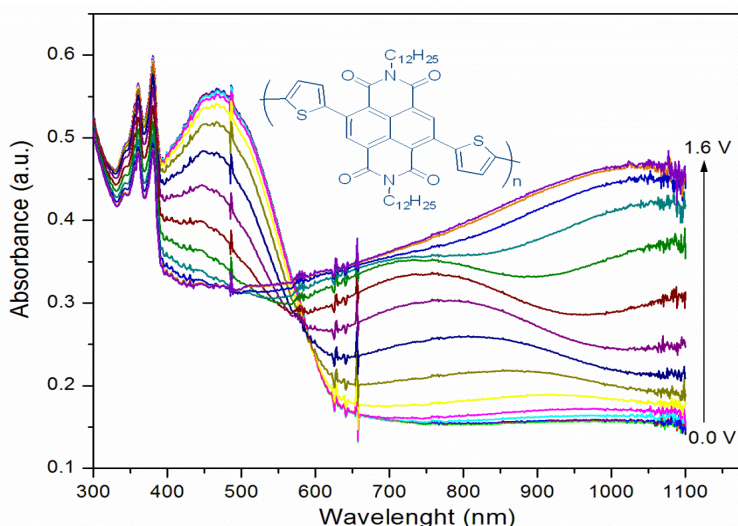
Figure 4. UV-vis spectra of PNDI-Th between 0.0V and 1.6V within 0.05V potential intervals.

3.4. Spectroelectrochemistry

Spectroelectrochemical properties of the PNDI-Th was investigated between 0.0 and 1.6V in 0.1 M NBu_4PF_6 / CH_2Cl_2 electrolyte – solvent couple and UV-vis spectra was recorded upon external bias. Electrochemically produced polymer film on ITO was reduced to its neutral state at a constant potential to remove any trapped charge and dopant ion during electro-chemical polymerization before spectroelectrochemical analysis. The Changes in the absorption spectral features of PNDI-Th as a function of the applied potential are presented in Figure 4. The evolution of the absorption spectra of PNDI-Th with applied potential is similar to that of thin films of polypyrrole and 3,8-diethyl-1,10-dihydro-benzoas[e]pyrrolo-[3,2-g]indole observed in acetonitrile media[38]. However, there are important differences in the spectral features of PNDI-Th relative to both of polypyrrole and 3,8-diethyl-1,10-dihydro-benzoas[e] pyrrolo-[3,2-g] indole. Fully oxidized PNDI-Th is blue in color. It exhibits a broad absorption band that extends into the near-IR region at 750 nm, as well as a band at 360-380 nm in the visible region. Fully oxidized polypyrrole highly doped with perchlorate ions is characterized by two bipolaron bands at 1240 nm and 450-475 nm , as well as a π-π^* band[38,40-41, 47], and is gray–black or brownish black in color. Notably, the blue color observed for oxidized PNDI-Th differs from the deep blue color reported for oxidized 3,8-diethyl-1,10-dihydro-benzoas[e]pyrrolo-[3,2-g] indole. We ascribe this difference to the presence of core-substituted NDI as compared to the system of Nadeau and Swager[40]. When the applied potential is decreased, the peak in the spectrum of PNDI-Th at 380 nm shifts to 450 nm and the absorbance in the near-IR region decrease. At a potential that corresponds to partially oxidized PNDI-Th, the absorption spectrum show two peaks at 380 nm and 450 nm in the visible region, while the film shows brown color. At 0.0 applied voltages, the film appears orange color [38]. PNDI-Th undergoes two oxidations in the range of 0.0 to 1.6V (Figure4), which are accompanied by a reversible color change from orange (neutral form), to brown (partially oxidized) and then blue (fully oxidized). Upon stepwise oxidation of PNDI-Th, the absorption in the visible region started to decrease as the new bands were intensified at 700, 850 and 1060 nm.

Table 4. Coloration Efficiency of the PNDI-Th film at different cycles in the visible region.

Wavelength (nm)	[a] Coloration Efficiency(CE)			
	Cycle			
	200	300	400	500
465	564	624	919	1255
760	580	881	1236	2217

[a] Calculated from the charge density(Q_D) and Optical density (ΔO_D) of the polymer film, CE= $\Delta O_D/Q_D$

The increased absorbance in the electronic absorption spectra of the polymer film in lower energy regions indicates the formation of charge carriers such as polarons and bipolarons[34]. These chromatic changes are easily described in terms of the formation of dominating forms (states) of the

polymer, namely the neutral form, as well as polaronic, bipolaronic, and so-called transverse bipolaronic states, with the latter state being caused by efficient interchain coupling of polarons on adjacent polymer chain[38,47]. The terms "polaron" and bipolaron" were introduced to identify the charge carriers in polypyrrole, which are not unpaired electrons, and were used to explain its conductivity and optical features [34,47].. Coloration efficiency, defined as the ratio between the change in optical density units and the injected/ ejected charge as a function of electrode area, was estimated from the data shown in Figure 4 and table 4 and was found to be 123 cm^2/C at 760 nm and 94 cm^2/C at 465nm. These values are lower than what can be attained in the case of the widely used electrochromic material, poly(3,4- ethylenedioxythiophene) (183 cm^2/C). Moreover, the first maximal coloration efficiency approaches the 100 cm^2/C, a value considered acceptable for a working electrochromic device[38,42].

4. CONCLUSION

In conclusion, 2,6-Difuran-2-yl-naphthalene-1,4,5,8-tetracarboxylic-N,N'-dodecyldiimide has been synthesized for the first time from the reaction of 2,6-Dibromonaphthalenediimide and tributyl (furan-2-yl) stannane by a simple one step stille coupling procedure and compare it with 2,6-Di(2-thienyl) naphthalene-1,4,5,8-tetracarboxylic-N,N'-dodecyldiimide(Th-NDI-Th) comonomer through cyclic voltammetry, UV-vis absorption and fluorescence measurements. The absorption spectra of Th-NDI-Th and F-NDI-F show two prominent vibronically structured absorption bands consisting of relatively sharp ones at the high energy region 360-380 nm similar to that of the corresponding NDI, and shoulders at the low energy region (400-550 nm). The Fluorescence spectra of the monomers Th-NDI-Th and F-NDI-F show high emission maxima in dichloromethane solution at 500 and 554 nm. The cyclic voltammetry measurements of F-NDI-F shows two reversible reduction waves at -0.63 and -1.05 V are clearly observed during the cathodic potential, no oxidation wave is detected during the anodic potential, Th-NDI-Th shows two reversible reduction waves at -0.60 V and -1.03 V, and irreversible oxidation wave was detected at 1.41V. Both monomers are n-type organic semiconductors with the low-lying LUMO energies (<-4.0 eV). Electrochemical polymerization of F-NDI-F on ITO was unsuccessful due to film delamination upon bias. In contrast with Th-NDI-Th provided polymer film which has been investigated by spectroelectrochemical method. With HOMO/ LUMO (-5.55/-3.55) eV energy levels, the film obtained is highly active in p- and n-doping processes. However, more work is required for a complete understanding for the electropolymerization of F-NDI-F process involved.

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