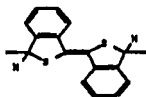


# Processable low band gap $\pi$ -conjugated polymer, poly(isothianaphthene): its synthesis and reaction mechanism

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**Abstract** Stable solution of the low band gap conducting polymer, polyisothianaphthene(PITN), is prepared by dehydrogenation of its precursor polymer, poly(1,3-dihydroisothianaphthene), with sulfuryl chloride under precisely controlled reaction condition and addition of the stabilizing agent, pyridine. This stable PITN solution can be cast into film. Structure characterization of the intermediate and final products indicates that the PITN structure is accomplished by propagation of the dimer structure (structure 2),



, accompanying with the generation of the structure defects, benzylchloride bonds and chlorine doped species. Through this intermediate analysis, a dehydrogenation mechanism is proposed.

## Introduction

Low band gap polymer is one of the important conjugated conducting polymers and has drawn great attention for its much higher conductivity at neutral state ( $10^{-2}$  S/cm) than those of the other conjugated polymers at neutral state ( $10^{-9} \sim 10^{-14}$  S/cm), colorless transparency after doping (1), and non-linear optical properties (2). The low band gap polymers that have been found so far include, poly(isothianaphthene)s (PITNs) 1 ( $E_g = 1.0$  eV) (3,4), poly(2,3-dihexylthieno[3,4-b]pyrazine) (0.95 eV) (5), poly(arene methine)s (0.69–1.47 eV) (6,7), poly(cyclopentadithiophene)s (0.8–1.2 eV) (8,9,10), ladder-type oligomers (1.2–1.6 eV) (11,12), tetrathiafulvalene oligomers (13), Zwitterionic-planar conjugated pyrrole derived oligomers (1.1 eV) (14), which have band gaps lower than 1.5 eV. Among these polymers, PITN is the most studied and its film prepared electrochemically (1,4,15) exhibits a high contrast and reversible color change from blue at the neutral state to nearly transparent light greenish-yellow at the doped state. All of the low band gap polymers mentioned above are insoluble except the oligomers and poly(2,3-dihexylthieno[3,4-b]pyrazine).



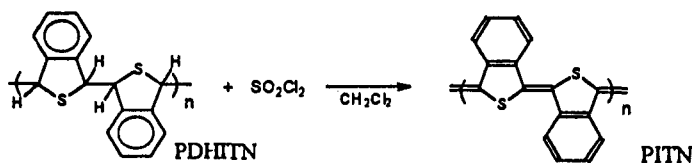
PITN is usually prepared via electrochemical polymerization (1,4 15) to obtain a deposited film on the electrode surface and via chemical method with  $\text{FeCl}_3$  as an oxidant (16). It can also be prepared via precursor route using  $\text{SO}_2\text{Cl}_2$  as dehydrogenation agent to remove the hydrogen from the main chains of its precursor polymer, Poly(1,3-dihydroisothianaphthene) (PDHITN)-(17). However using the chemical method, powdery products are resulted; while using the former method, to prepare a large area pinhole-free thin film with uniform thickness is difficult.

This work reports a method for preparation of stable PITN solution, which can be cast into film with a conductivity of  $10^{-1}$  S/cm and electrochromic property. Our approach of preparing PITN solution involves dehydrogenation of PDHITN in dichloromethane solution with precisely controlled amount of dehydrogenation agent and reaction time following with an addition of the organic base, pyridine, which behaves as a dehydrogenation, terminating and stabilizing agent. A dehydrogenation mechanism of PDHITN toward PITN is also proposed.

### Experimental

The syntheses of isothianaphthene (ITN) monomer and precursor polymer PDHITN are carried out essentially according to the procedures reported by Cava et al. (18) and by Wudl et al. (3). The PITN is prepared following the method used by Rose et al. (17) with a modification of the undoping steps by use of the organic base, pyridine.

In a PDHITN solution in anhydrous  $\text{CH}_2\text{Cl}_2$  solvent (1 mg solute per 1 mL solvent),  $\text{SO}_2\text{Cl}_2$  at 1 ~ 0.25 equivalent (eq.) was added and the reaction was allowed to take place for 3 min. The resulting solution was then neutralized and terminated for the reaction by adding pyridine. The reaction is shown as Scheme 1.

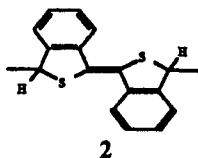


Scheme 1

### Result and Discussion

#### A. Intermediate Species Analysis

In the PDHITN system, the active hydrogen is a sterically hindered benzyl hydrogen, so the elimination reaction is more preferable than the substitution reaction, leading to a formation of tetrasubstituted alkenes in between two neighboring units (structure 2). The content of the intermediate (structure 2) is minor in the final product. In order to obtain the products containing more amount of the intermediate for an identification of its structure, partial dehydrogenation of PDHITN with less amount of  $\text{SO}_2\text{Cl}_2$  and with the less efficient dehydrogenation agent, sulfur, were carried out.



Structure identification of the intermediate by use of the products from the three reaction system is predicted below.

(1) Partial Dehydrogenation. Fig. 1, curves a and b show the IR spectra of PDHITN and PITN from dehydrogenation of PDHITN with 1.0 equivalent  $\text{SO}_2\text{Cl}_2$  and then neutralization with pyridine. From these spectra, we observe that the aromatic rings in PDHITN (having peaks at  $3062$  and  $3024$   $\text{cm}^{-1}$  (stretching vibration of aromatic C—H bond),  $1594$  and  $1490$   $\text{cm}^{-1}$  (asymmetrical and symmetrical stretching vibration of aromatic C=C bond) and  $757$   $\text{cm}^{-1}$  (out-of-plane deformation vibration of aromatic C—H bond)) are converted by  $\text{SO}_2\text{Cl}_2$  to fused thiophene ring of PITN (having peaks at  $1380$ ,  $1260$ ,  $840$ ,  $730$  and  $433$   $\text{cm}^{-1}$ , assigned as the deformation modes of thiophene ring as  $\nu_6$ ,  $\nu_{14}$ ,  $\nu_3$ ,  $\nu_{22}$ ,  $\nu_{33}$  respectively (19)). For the partial dehydrogenated product obtained by use of less amounts of  $\text{SO}_2\text{Cl}_2$  (0.25 and 0.5 equivalents), their UV-Vis-NIR spectra (Fig. 2, curves a and b) show the presence of the absorption peak at  $489$  nm ( $\pi - \pi^*$ ) of structure 2, for which the assignment is made based on the wavelengths of the absorption peaks of dialkylsulfide stilbene and the use of the empirical rule of enone and dienone absorptions (20). The IR absorption spectrum of the resulting polymer with 0.25 equivalent  $\text{SO}_2\text{Cl}_2$  is shown in Fig. 1 curve c, from which it can be found that the characteristic absorption peaks of PDHITN still remain but partially decrease and the characteristic absorption peaks of PITN appear but with intensities weaker than those of PITN (curve b). In addition, the new peaks at  $1680$ ,  $1580$  and  $1450$   $\text{cm}^{-1}$  are generated, which can be assigned as the absorption peaks of tetrasubstituted alkenes, asymmetry and symmetry stretching of aromatic C=C bonds respectively, which reflect the presence of the structure 2. However, these peaks are close to the absorption peaks of PDHITN at  $1694$   $\text{cm}^{-1}$  (overtone absorption of aromatic C—H bending),  $1594$  and  $1490$   $\text{cm}^{-1}$ . So we proceed another reaction system for a confirmation of the presence of structure 2 as depicted in the next paragraph.

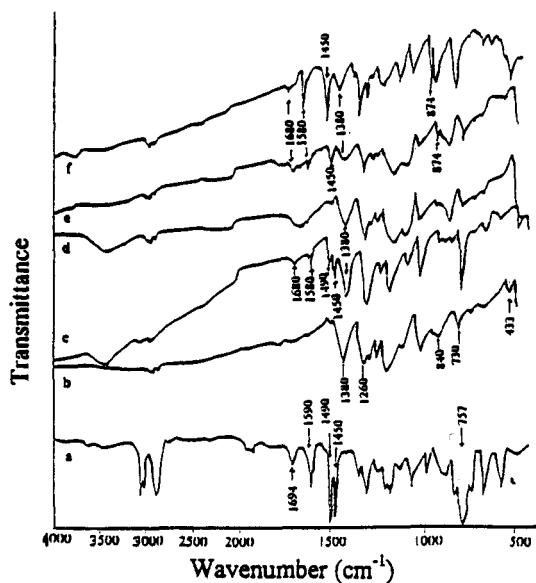
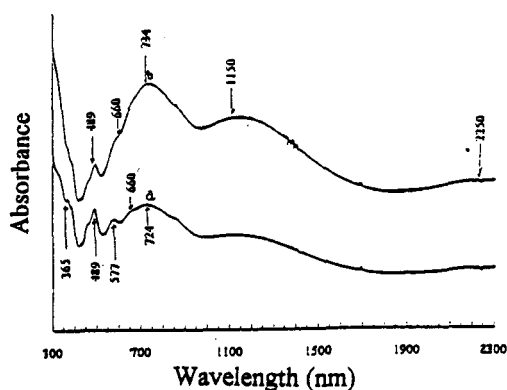


Fig. 1. IR spectra of PDHITN, PITN and their derivatives. (a) PDHITN, (b) PITN, neutral state, (c) partial dehydrogenation product from dehydrogenated PDHITN with 0.25 equivalent (eq.)  $\text{SO}_2\text{Cl}_2$ , (d) PITN with high chlorine content from dehydrogenation of PDHITN with 1.0 eq.  $\text{SO}_2\text{Cl}_2$  and without neutralization with base, (e) product from thermal treatment of PITN with high chlorine content at  $200^\circ\text{C}$  for 4 hours, (f) product from dehydrogenation of PDHITN (dissolved in NMP) with sulfur at  $190^\circ\text{C}$  for 48 hours.

Fig. 2. UV-Vis-NIR spectra of PDHITN after reactions with (a) 0.25 eq., (b) 0.25 eq.  $\text{SO}_2\text{Cl}_2$  and without neutralization with base.



(2) **Thermal Analysis.** PDHITN in solution was dehydrogenated with 1.0 equivalent  $\text{SO}_2\text{Cl}_2$  for 15 min. The product collected directly without neutralization with a base has the high chlorine content about 6.2 % by weight as determined from elemental analysis. This indicates that the product of this PITN contains chloride ions and benzyl chloride bonds in the backbone of the polymer as will be elucidated later. As this PITN is heated at  $200^\circ\text{C}$  for 4 hours under nitrogen atmosphere, its conductivity drops from  $10^{-1}$  to  $10^{-8}$  S/cm. IR spectra of this PITN before and after the heat treatment in Fig. 1 curves d and e respectively show that the heat-treatment causes a decrease in intensity of the peak at  $1380\text{ cm}^{-1}$  accompanying with a generation of the new peaks at 1680, 1580, 1450 and  $874\text{ cm}^{-1}$  (out-of-plane deformation vibration of aromatic C—H bond), indicating that the thermal treatment of this PITN leads to a generation of the conjugated bonds structure 2.

(3) **Dehydrogenation with Sulfur.** Sulfur at the high temperature above  $200 \sim 250^\circ\text{C}$  can decompose into radical species as Scheme 2



Scheme 2

and these radicals can abstract hydrogen atoms at allylic or benzylic positions (21). For the purpose of producing high concentration of structure 2, reaction of PDHITN with 2 equivalent sulfur in 1-methyl-2-pyrrolidone (NMP) was carried out at the lower temperature  $190^\circ\text{C}$  for 48 hours. At this temperature level, only partially dehydrogenated product was produced as reflected in its IR spectrum (Fig. 1 curve (f)), in which the characteristic absorption peaks of PDHITN are at  $757\text{ cm}^{-1}$  and of PITN at  $1380\text{ cm}^{-1}$ . The later peak is much weaker than those obtained by dehydrogenation with  $\text{SO}_2\text{Cl}_2$  (curves b, c and d). In addition, the characteristic absorption peaks of the intermediate, structure 2, at 1680, 1580, and  $1450\text{ cm}^{-1}$  also appear in this spectrum. Further examination on the

final product by use of solid state  $^{13}\text{C}$  NMR was carried out, and the spectra are shown in Fig 3; curve a is the original spectrum, curve b is the spectrum obtained by use of insensitive nucleus enhancement by polarization transfer (INEPT) for nonprotonated carbon, and curve c is obtained by subtracting spectrum (b) from (a). The chemical shifts of protonated and nonprotonated aromatic carbons are at 126 and 139 ppm respectively. In curve b, additional nonprotonated carbon absorption peak at 125.7 ppm appears, which is upfield shift by 14.3 ppm than the normal nonprotonated aromatic carbon absorption at 140 ppm. This indicates that this product has intermediate structure with quaternary carbons linking with electron rich group or element, which is sulfur for the present system. With the IR and NMR data stated above, it is assured that, after the sulfur treatment for PDHITN, the final product has the structure unit, structure 2.

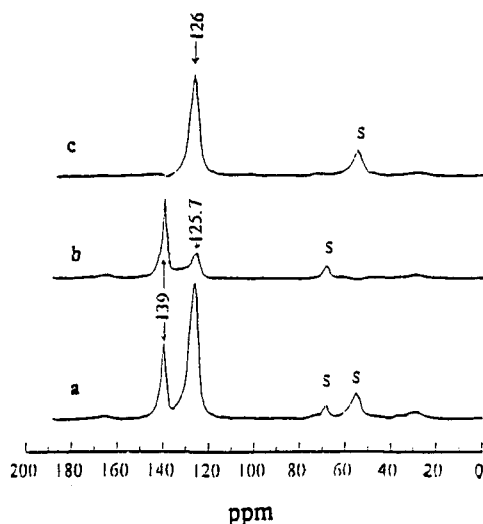
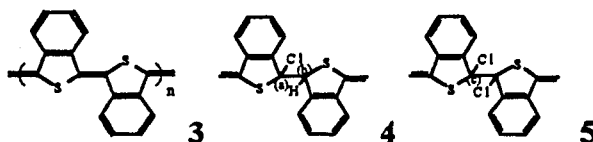


Fig. 3. Solid state  $^{13}\text{C}$  NMR spectra of (a) product from dehydrogenation of PDHITN (dissolved in NMP) with sulfur at  $190^\circ\text{C}$  for 48 hours, (b) nonprotonated carbon spectrum obtained from INEPT technique, (c) protonated carbon spectrum obtained from subtraction of curve (b) from curve (a). s : side band.

### B. Side Reaction Analysis

The PITN subchains so produced are of structure 3, since the quinoid structure has lower energy than the aromatic structure (22) and no rearrangement is required in the propagation of structure 2 during the dehydrogenation step. However during the dehydrogenation reaction, substitution of the hydrogen by chlorine can not be avoided and thus can result in a formation of benzyl chloride bonds, which are randomly dispersed in the backbone of PITN. The presence of benzyl chloride bonds can be observed from solid state  $^{13}\text{C}$  NMR spectrum (Fig. 4, curve a) of PITN with high chlorine content (which was obtained by dehydrogenation of PDHITN with 1.0 equivalent  $\text{SO}_2\text{Cl}_2$  and without neutralization with base). In comparison with that of the neutral PITN (which was obtained by dehydrogenation of PDHITN with 1.0 equivalent  $\text{SO}_2\text{Cl}_2$  followed with an undoping with triethylamine) in Fig. 4, curve b, there appears some additional minor peaks. For the precursor PDHITN, the chemical shift at 59.2 ppm (Fig. 4, curve c) can be assigned as benzylic carbon (23), which is to be used as a reference. In conjunction with the empirical rule of NMR shift (which is an empirical correlation of NMR shift by substituent effects upon replacement of hydrogen by various substituents in linear and branched alkanes (24)), the minor NMR peaks in Fig. 4, curve a can be assigned for various carbon atoms (a, b and c) indicated in structures 4 and 5 as : 104.6 ppm (carbon c), 89.5 ppm (carbon a) and 72 ppm (carbon b). These peaks are very weak in comparison with those of the tertiary and quaternary aromatic carbons. These aromatic form structures can be considered as structure defects in the backbone of PITN. The amounts of structures 4 and 5 are very minor, since X-ray photoelectron spectrum of the doped PITN (i.e. PITN without neutralization with organic base) exhibits a very small chlorine peak at 192.4 eV.

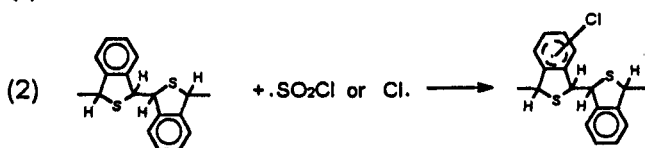


### C. The Proposed Dehydrogenation Mechanism

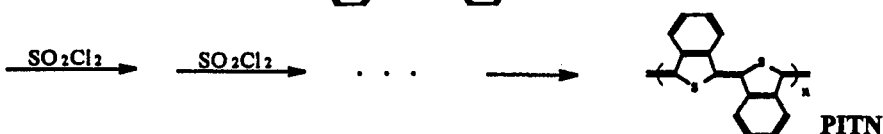
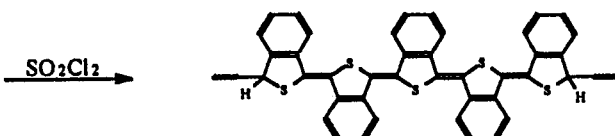
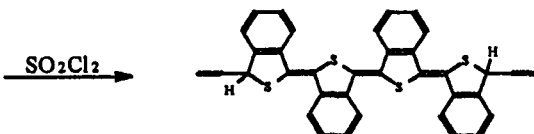
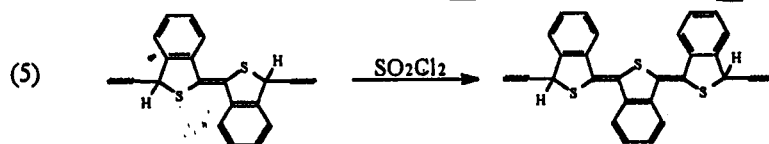
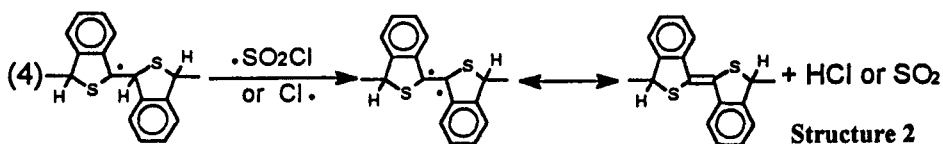
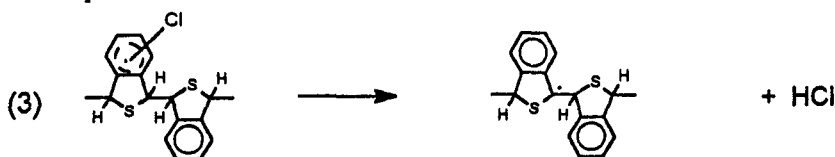
Sulfuryl chloride  $\text{SO}_2\text{Cl}_2$  is a highly efficient chlorination reagent. It can split into  $\cdot\text{SO}_2\text{Cl}$  and  $\cdot\text{Cl}$  radicals by thermal activation or visible light irradiation at room temperature (step 1 below), which can attack the active hydrogen of the reactant and result in a generation of radical intermediate species (25). These generated radicals then couple with  $\text{Cl}\cdot$  to form alkyl chloride bonds (26). In the presence of aromatic hydrocarbons, the  $\text{Cl}\cdot$  or  $\cdot\text{SO}_2\text{Cl}$  radicals can form complexes with aromatic rings (27,28) first (step 2) and then react to yield new species. The complex formation can retard the reaction rate but increase the reaction selectivity. In the case of PDHITN, each repeat unit consists of two benzyl hydrogens and an aromatic ring. As PDHITN is attacked by chlorine radicals, the aromatic ring-chlorine complexes form first and the chlorine atoms then eliminate with the active hydrogens to yield benzylic radicals (step 3). Because of the resonance and sterical hindrance effects, the benzylic radicals have long life time and are not easy to react with  $\text{SO}_2\text{Cl}_2$  to form benzyl chloride bonds such that the amount of this bond is small. Moreover, two neighboring benzylic radicals of the same chain can couple to form a tetrasubstituted alkenes, thus yield structure 2 (step 4). As dehydrogenation reaction proceeds further, the conjugation in the back bone is mainly of quinoid type (step 5).

Thus the dehydrogenation mechanism can be proposed as Scheme 3 below.

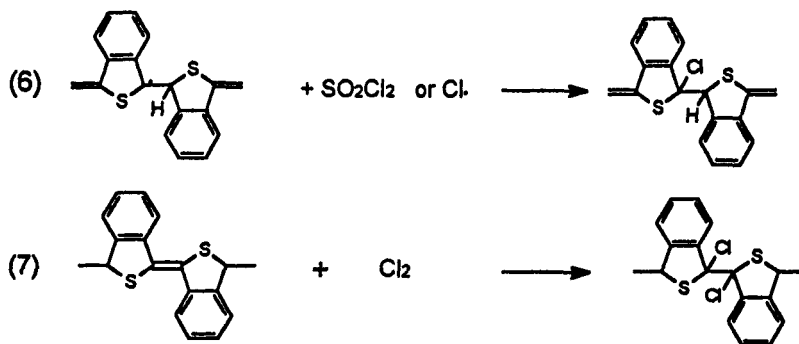
#### 1. Initiation step



#### 2 Propagation step



## 3. Side reaction



Scheme 3

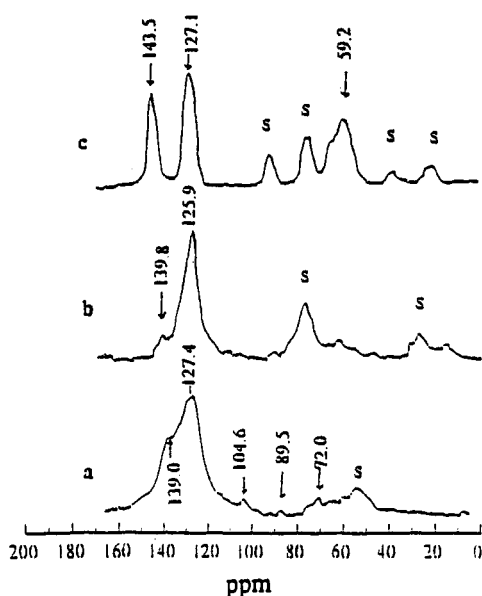


Fig. 4. Solid state  $^{13}\text{C}$  NMR spectra of (a) PITN with high chlorine content, (b) PITN after neutralization with triethylamine, and (c) PDHITN. s : side band.

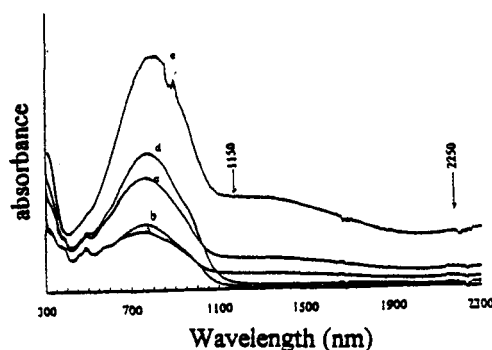


Fig. 5. UV-Vis-NIR spectra of PITN solutions after dehydrogenation of PDHITN with various content of  $\text{SO}_2\text{Cl}_2$ . (a) 0.25 equivalent (eq.), neutralized with pyridine,  $\lambda_{\text{max}} = 747$  nm, (b) 0.25 eq., neutralized with triethylamine,  $\lambda_{\text{max}} = 760$  nm, (c) 0.50 eq., neutralized with pyridine,  $\lambda_{\text{max}} = 757$  nm, (d) 0.50 eq., neutralized with triethylamine,  $\lambda_{\text{max}} = 768$  nm, (e) 1.0 eq., neutralized with pyridine,  $\lambda_{\text{max}} = 794$  nm.

## D. Properties of PITN Solution and Film.

As the content of  $\text{SO}_2\text{Cl}_2$  increases to 1.0 equivalent, the UV-Vis-NIR spectrum of the resulting solution (Fig. 5, curve e) exhibits a  $\lambda_{\text{max}}$  at 794 nm contributed from structure 3, which is higher than those with 0.25 and 0.5 equivalents  $\text{SO}_2\text{Cl}_2$  by 70 nm and 60 nm respectively. This indicates an increase in conjugation length after the increase in extent of dehydrogenation.

As the resulting solutions with 0.25 and 0.5 equivalents  $\text{SO}_2\text{Cl}_2$  are added with the strong base, triethylamine, the  $\lambda_{\text{max}}$  of UV-Vis-NIR absorption due to  $\pi - \pi^*$  transition (Fig. 5 curves b and d) exhibit a red-shift toward 760 and 768 nm respectively and a disappearance of the absorptions at 1150 and 2250 nm (due to polaron/bipolaron resulting from the chlorine doping). This indicates that the strong base can eliminate the benzyl chloride bond, resulting in an increase of conjugation length, and can completely neutralize (undope) the sample. The undoped PITN in the solutions can only be

stable for about 1 hr and can not be cast into film. For the case with 1 equivalent  $\text{SO}_2\text{Cl}_2$ , precipitation of PITN occurs immediately. This is due to that triethylamine can attack the benzyl chloride bond through substitution nucleophilic bimolecular reaction (SN2) for its strong basicity. During the dehydrogenation process, the side reaction of chlorination substitution always takes place simultaneously, which induces an aggregation. However, as a weak base is added, in our case pyridine, partial undoping and solvation by pyridine occur simultaneously. Since the weak base, pyridine, does not attack the benzyl chloride bond, a precipitation of PITN can be prevented. For the cases with 0.25 and 0.5 equivalents  $\text{SO}_2\text{Cl}_2$ , their UV-Vis-NIR spectra (Fig. 5 curves a and c) show an absorption due to  $\pi$ - $\pi^*$  transition with  $\lambda_{\text{max}}$  at 747 and 757 nm, which are higher than those without addition of pyridine by 23 nm. However, very weak absorption bands at 1150 and 2250 nm still appear, indicating that the undoping by pyridine is not complete. By the addition of pyridine, these PITN solutions can be stable for about 2 to 4 weeks at room temperature and that with 1.0 equivalent  $\text{SO}_2\text{Cl}_2$  can be stable for about 2 days. All of these PITN solutions can be cast into films.

The film from the case with 1 equivalent  $\text{SO}_2\text{Cl}_2$  and termination by pyridine has a conductivity of 0.1 S/cm (measured using the four probe method) and also exhibits electrochromic property with high contrast from blue (at the undoped state) to pale yellow green (at the doped state).

### Conclusion

The dehydrogenation of PDHITN by  $\text{SO}_2\text{Cl}_2$  can yield PITN with quinoid structure with structure 2 as intermediate, accompanying with a substitution of the active hydrogen in the back bone by chlorine. Partial undoping by addition of pyridine in the dilute reaction solution with precisely controlled reaction condition can provide a stable solution, which can be cast into film.

### Acknowledgment

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