

Bromination of Isothianaphthene Derivatives towards the Application in Organic Electronics

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Different approaches to brominate dialkyl isothianaphthene-5,6-dicarboxylate were tried and single crystals of target molecule and side product were obtained. A planar copolymer with the *trans*-ethene has been prepared, which shows good solubility in common organic solvents and broad absorption with edge to 967 nm in film.

Keywords bromination, isothianaphthene, planar copolymer

Introduction

In recent years, Yu *et al.*^[1-4] have developed a series of new semiconducting polymers with thieno[3,4-*b*]thiophene (TT) and benzodithiophene (BDT) alternating units, with power conversion efficiency (PCE) over 9.2%.^[5] These TT based polymers can support the quinoidal structure and lead to a narrow polymer bandgap, which is crucial to efficiently harvest solar energy.^[6]

Another important quinoidal unit is isothianaphthene (ITN, or benzo[c]thiophene), which was proved to have higher quinoidal resonance energy than TT.^[7] However, ITN is proved to be very unstable. Though much effort has been made to use this block into low band gap polymers, only a few examples seem to be successful.^[8,9] ITN was introduced as a construction unit into low band gap conjugated polymer-poly(isothianaphthene) (PITN) by Wudl *et al.*^[10] in 1984 through either electrochemical polymerization or chemical oxidation method. Substitutions with electron withdrawing groups or electron donating groups did not show any significant effect on the band gap of ITN derivatives.^[11] Wudl *et al.*^[12,13] also introduced a more stable isothianaphthene-imide derivative (EHI-ITN), as shown in Figure 1. With the strong electron withdrawing group, the ITN derivatives became stable and the copolymer with 3,4-ethylenedioxythiophene (EDOT) showed an absorption tail extended to 1240 nm. Hillmyer *et al.*^[14,15] reported the synthesis of 1,3-distannylated and dipinacolboryl isothianaphthene, which showed much enhanced stability toward air and moisture, and these intermediates can be used directly as building block in Stille or Suzuki couplings. Lin

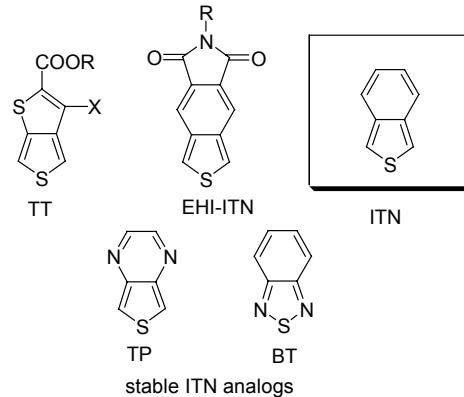


Figure 1 Representative quinoidal structures: TT (thieno[3,4-*b*]thiophene), EHI-ITN (isothianaphthene *N*-ethylhexylidicarboxylic imide), ITN (isothianaphthene), TP (thieno[3,4-*b*]pyrazine) and BT (benzothiadiazole).

et al.^[16] reported an improved and easy method to synthesize stable ITN derivatives. With the introduction of ester groups, the stability of ITN derivatives was enhanced, which could be isolated through flash chromatography. Naphtho[c]thiophene derivatives were also synthesized following the same strategy. Similar methods were also reported by other groups.^[17]

1,3-Dibromoisothalianaphthene derivatives would be an alternative and promising building block for synthesizing high performance organic electronic materials through Pd[0]-catalyzed coupling reactions. However the bromination of ITN was proved to be very difficult, and there was only one example of this compound described in a patent as a reaction intermediate.^[18]

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Hillmyer *et al.*^[14] attempted to obtain this compound through bromination using *N*-bromosuccinimide (NBS), and this process led to only intractable black solid presumably due to oxidative polymerization. In this contribution, different approaches to brominate dialkyl benzo[*c*]thiophene-5,6-dicarboxylate have been tried and two target bromination derivatives have been achieved successfully. A planar copolymer based on the successful bromination product has been prepared and characterized.

Experimental

Instruments

All reactions and manipulations were carried out under argon atmosphere with the use of standard Schlenk techniques, and the starting materials were purchased from commercial suppliers and used without further purification. Thiophene-3,4-dicarbaldehyde (**2**)^[16,19] and diethyl benzo[*c*]thiophene-5,6-dicarboxylate (**4**)^[16] were prepared according to the reported methods. The ¹H NMR and ¹³C NMR spectra were recorded on a Bruker AV300 and 400 Spectrometer. High resolution mass spectrometry (HRMS) was performed on an Agilent 6520 Q-TOF LC/MS instrument. Gel permeation chromatography (GPC) analysis was conducted on a Waters 510 system using polystyrene as the standard and tetrahydrofuran (THF) as the eluent at a flow rate of 1.0 mL/min at 40 °C. The thermogravimetric analyses (TGA) studies were carried out on a NETZSCH STA 409PC instrument under purified nitrogen gas flow with a 10 °C/min heating rate. Differential scanning calorimetry (DSC) analysis studies were carried out on a DSC Q100 V9.0 Build 275 instrument under purified nitrogen gas flow (50.0 mL/min) with a 20 °C/min heating rate. UV-Vis spectra were obtained with a JASCO V-570 spectrophotometer. Cyclic voltammetry (CV) experiments were performed with a LK98B II Microcomputer-based Electrochemical Analyzer. All measurements were carried out at room temperature with a conventional three-electrode configuration employing a glassy carbon electrode as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a Pt wire as the counter electrode. Acetonitrile was distilled from calcium hydride under dry argon immediately prior to use. Tetrabutylammonium phosphorus hexafluoride (Bu₄NPF₆, 0.1 mol/L) in acetonitrile was used as the supporting electrolyte, and the scan rate was 100 mV/s. The Fc/Fc⁺ vs. vacuum was measured to be -4.8 eV in this system. The X-ray crystal structures analyses were made on a Rigaku Saturn CCD area detector for **5** and Rigaku Saturn724 CCD for **6** with graphite-monochromated Mo K α radiation ($\lambda=0.71073$ Å). The data were collected at 113(2) K for **5** and 293(2) K for **6**, and the structures were refined by full-matrix least-square on F^2 . The calculations were performed with SHELXL-97 program. All-hydrogen atoms were refined anisotropically.

Materials

Thiophene-3,4-dicarbaldehyde (2)^[16,19] ¹H NMR (CDCl₃, 400 MHz) δ : 10.31 (s, 2 H), 8.22 (s, 2 H); ¹³C NMR (CDCl₃, 100 MHz) δ : 137.7, 140.3, 185.9

Diethyl 1,3-dibromobenzo[*c*]thiophene-5,6-dicarboxylate (5) Bromine (2.57 g, 16.08 mmol) in 25 mL of chloroform was added dropwise to a solution of **4** (2.24 g, 8.04 mmol) in 50 mL of chloroform. The mixture was stirred at room temperature for 10 min and then was washed with aqueous NaHSO₃, NaHCO₃, and water. The organic layer was dried over Na₂SO₄, and the solvent was removed under vacuum. The crude product was purified with flash chromatography (ethyl acetate/petroleum ether = 1/9) to give the product, which could be recrystallized from hexane to get the final product (406.6 mg, yield 11.6%). m.p. (DSC): 119.22 °C. ¹H NMR (CDCl₃, 300 MHz) δ : 7.87 (s, 2H), 4.39 (q, $J=7.1$ Hz, 4H), 1.39 (t, $J=7.1$ Hz, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ : 14.2, 61.8, 107.3, 123.6, 128.6, 136.0, 167.2; HRMS (ESI-TOF) calcd for C₁₄H₁₂Br₂O₄S (M+H⁺) 434.8896, found 434.8901 (M+H⁺).

Diethyl 1,1-dibromo-1,3-dihydro-3-oxobenzo[*c*]thiophene-5,6-dicarboxylate (6) To a solution of compound **4** (0.8 g, 2.87 mmol) in 50 mL of dry DMF was added dropwise a solution of NBS (1.18 g, 6.61 mmol) in 30 mL of DMF under argon protection in the dark. The reaction mixture was stirred at 0 °C for 2 h, then at room temperature overnight. Then the mixture was poured into CH₂Cl₂, which was washed by brine so as to remove DMF. The organic phase was dried by Na₂SO₄. The solvent was removed and the crude product was purified with flash chromatography using ethyl acetate/petroleum ether (1/9) to yield the products **5** and **6** with ratio of 1 : 3.81. **6** was obtained through recrystallization from hexane as purple solid (176 mg, yield 13.5%). m.p. (DSC): 108.84 °C; ¹H NMR (CDCl₃, 400 MHz) δ : 8.35 (s, 1 H), 8.12 (s, 1 H), 4.48 (dd, $J=5.7$, 12.9 Hz, 2H), 4.43 (dd, $J=5.8$, 12.9 Hz, 2H), 1.44 (t, $J=7.08$ Hz, 3H), 1.41 (t, $J=7.08$ Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ : 14.0, 14.1, 44.3, 62.5, 62.8, 124.2, 127.7, 131.3, 134.4, 139.2, 155.6, 165.1, 165.9, 188.2; HRMS (ESI-TOF) calcd for C₁₄H₁₂Br₂O₅S (M+H⁺) 450.8845, found 450.8846.

Diocetyl benzo[*c*]thiophene-5,6-dicarboxylate Compound **2** (0.50 mg, 3.57 mmol) and diocyl maleate (1.34 g, 3.92 mmol) were dissolved in dry CH₂Cl₂, and the solution was immersed in an ice bath. To this cooled solution was then slowly added a CH₂Cl₂ solution of tri-*n*-octylphosphine (1.45 g, 3.92 mmol) and DBU (53.5 mg, 0.35 mmol) under argon. After being stirred for 30 min on the ice bath and 6 h at room temperature, the reaction mixture was directly concentrated in vacuum and the residue was purified with flash chromatography (ethyl acetate : petroleum ether = 1 : 25) to give the pure diester product (442 mg, 27.8%). ¹H NMR (CDCl₃, 300 MHz) δ : 8.04 (s, 2H), 7.88 (s, 2H), 4.17–4.27 (m, 4H), 1.64–1.77 (m, 4H), 1.49–1.26 (m, 16H), 0.99–0.83 (m, 10H); ¹³C NMR (CDCl₃, 100 MHz) δ :

11.0, 14.1, 23.0, 23.8, 29.0, 30.4, 38.8, 68.0, 120.5, 124.8, 127.2, 136.7, 168.0; HRMS (ESI-TOF) calcd for $C_{26}H_{38}O_4S$ ($M + H^+$) 447.2564, found 447.2570.

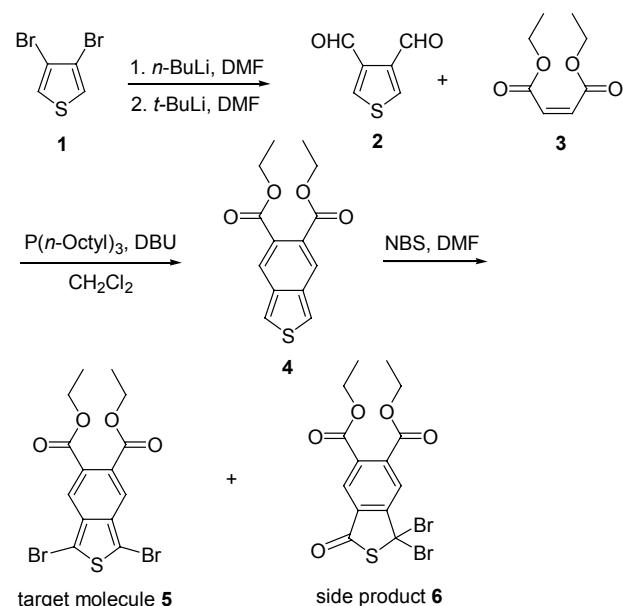
Diethyl 1,3-dibromobenzo[c]thiophene-5,6-dicarboxylate (7) Bromine (0.57 g, 3.54 mmol) in 15 mL of chloroform was added dropwise to a solution of diethyl benzo[c]thiophene-5,6-dicarboxylate (1.58 g, 3.54 mmol) in 30 mL of chloroform. The mixture was stirred at room temperature for 10 min and then was washed with aqueous $NaHSO_3$, $NaHCO_3$, and water. The organic layer was dried over Na_2SO_4 , and the solvent was removed under vacuum. The crude product was purified with flash chromatography (ethyl acetate/petroleum ether = 1/250) to give the product (1.04 g, yield 48.8%). 1H NMR ($CDCl_3$, 400 MHz) δ : 7.86 (s, 2H), 4.19–4.26 (m, 4H), 1.67–1.73 (m, 4H), 1.44–1.25 (m, 16H), 0.96–0.91 (m, 10H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ : 11.0, 14.0, 23.0, 23.9, 29.0, 30.5, 38.8, 68.4, 107.3, 123.5, 128.8, 136.0, 167.2; HRMS (ESI-TOF) calcd for $C_{26}H_{36}Br_2O_4S$ ($M + H^+$) 603.0774, found 603.0773.

Poly[diethyl-benzo[c]thiophene-5,6-dicarboxylate-alt-ethene]] (PVinylITN) Diethyl 1,3-dibromobenzo[c]thiophene-5,6-dicarboxylate (375.4 mg, 0.62 mmol), (*E*)-1,2-bis(tributylstannyl)ethene (376.5 mg, 0.62 mmol) and $P(o-Tol)_3$ (20.3 mg, 0.050 mmol) were dissolved in 15 mL dry chlorobenzene. The mixture was purged by argon, then bubbled with argon for 20 min, $Pd_2(dbu)_3$ (11.4 mg, 0.012 mmol) was added. After being purged with argon, the mixture was refluxed at 110 °C for 72 h. After cooling to room temperature, the organic solution was added dropwise to 100 mL methanol to obtain precipitate, which was collected by filtration and washed with methanol and dried. Then the precipitate was subjected to Soxhlet extraction with methanol, hexane, and chloroform, respectively. The fraction in chloroform was concentrated and 50 mL methanol was added. The precipitate was filtrated to afford the target polymer. Then the residue polymer was dried under vacuum, affording a black solid powder. (199.2 mg, yield 68.1%, $M_n = 7.96$ kDa, PDI = 2.42). T_d (TGA): 317.83 °C; 1H NMR (CD_2Cl_2 , 400 MHz) δ : 8.10 (br, 2H), 7.14 (br, 2H), 4.18 (br, 4H), 1.28 (br, 16H), 0.84 (br, 14H).

Results and Discussion

As shown in Scheme 1, ITN derivative **4** was synthesized in two steps following the literature method. Then, we tried to brominate **4** with NBS using $CHCl_3$ /acetic acid following Wudl's approach.^[13] However, only minor or no product was obtained. Then $CuBr/CH_2Cl_2$ was employed according to the patent,^[18] and the method also did not work for us. We also attempted NBS in DMF, which is also a widely used method for bromination.^[3] As shown in the Scheme 1, two main products with total yield about 18% were obtained, which were difficult to separate through flash chromatography. The ratio of these two compounds was

Scheme 1 Synthesis of the stable dibromoisothenaphthene derivative



varied by the amount of NBS in DMF. Increasing the amount of NBS, more **6** was obtained, which was in agreement with Hart's results.^[20] Typically, brominating **4** with 2.3 equiv. NBS, the ratio of **5** and **6** was 1 : 3.81 after flash chromatography to separate other side products. The mechanism for the formation of molecule **6** is uncertain to us. The 1H NMR of **5** and **6** were shown in Figures 2a, 2b. The structures of target compound **5** and side product **6** were also confirmed by the single crystal X-ray analysis (Figures 2c–2d). As shown in Figures 2e–2f, compound **5** shows cofacial π -stacking motif in the single crystal, and the distance between the aromatic backbones is 3.43 Å. The yield of **5** after separation is about 4%, which indicates the above bromination strategy is not a good choice.

Next, another bromination reagent, liquid Br_2 was employed. We found that the reaction proceeded smoothly only in 10 min by blending of 2 equiv. liquid Br_2 with **4** in chloroform (Scheme 2). In addition, we found that longer reaction time was not beneficial for improving the product yield. On the contrary, more side reaction products were observed in the TLC. ITN derivatives are easy to be oxidized and liquid Br_2 is a strong oxidation reagent. It might be one of reasons why short reaction time was preferred. On the other hand, the side products for this reaction are complicated indeed. Except trace of compound **6**, other side products were hard to be characterized. After washed with $NaHSO_3$ and $NaHCO_3$, the target molecule was obtained through flash chromatography separation, which could be further purified through recrystallization from hexane. However, the yield was still relatively low with value of 11.6%. It is noted that the yield could increase significantly to 48.8% after replacing the ethyl with octyl groups in the ITN benzene ring. The enhanced solubility with long

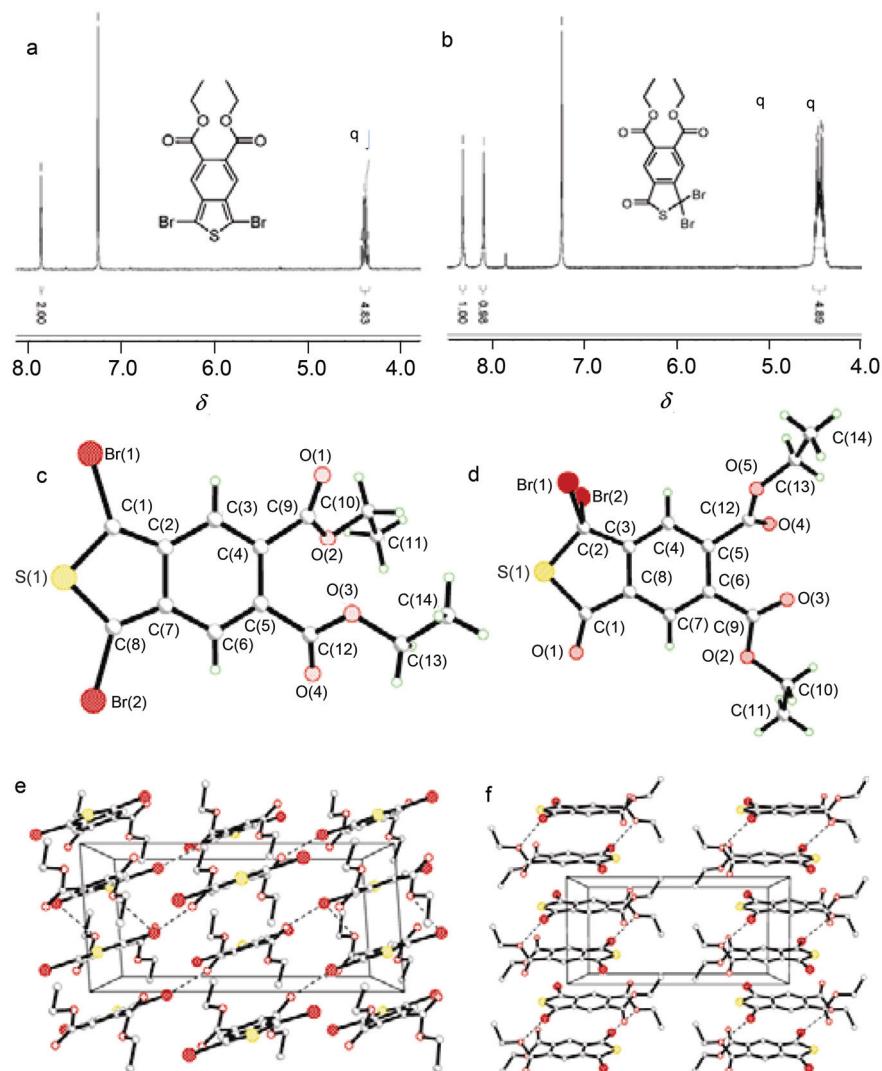
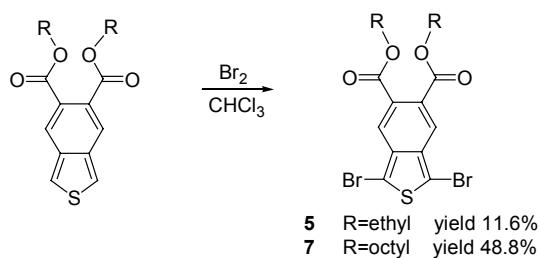


Figure 2 ¹H NMR and single crystal structure of compounds **5** (a, c) and **6** (b, d). Crystal packing (2e for viewing along *b* axis and 2f for *c* axis, thermal ellipsoids are set at the 50% probability level) of compound **5**. See Figure S1 for more details on the crystal pack of **6**.

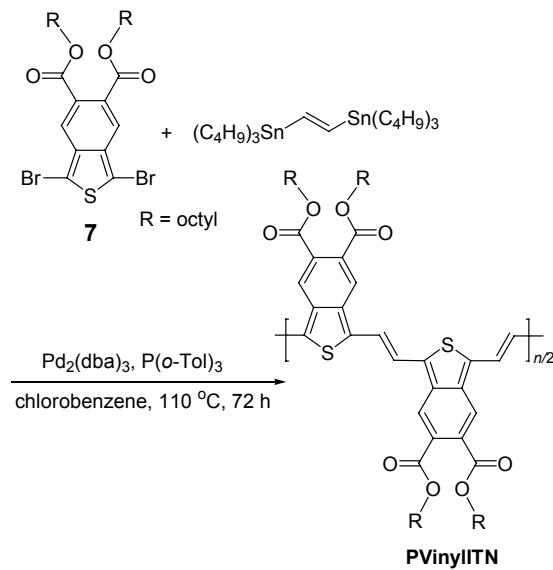
Scheme 2 Improved bromination procedure



alkyl chains should be one of determining reasons for the yield improvements.

PITN is not planar because of repulsion between sulfur atom and hydrogen atom on the phenyl ring. This was proved by extrapolation of the X-ray structure of the dimer (*syn* conformation with a dihedral angle of 50.1°).^[21,22] In order to obtain the planar backbone of ITN based polymers, a polymer based on ITN was designed and synthesized. As shown in Scheme 3, polymer

Scheme 3 Synthesis of soluble ITN copolymers



PVinylITN was synthesized by Stille coupling with (*E*)-1,2-bis(tributylstannyl) ethene and compound **7**. **PVinylITN** was achieved in 68.14% yield with $M_n = 7.96$ kDa (PDI = 2.42). The polymer was readily soluble in common organic solvents, such as THF, chloroform and dichlorobenzene.

As shown in Figure 3a, the optical spectrum of **PVinylITN** in chloroform presents an absorption peak at 703 nm. The **PVinylITN** film spin-coated from CHCl_3 exhibits a small blue-shifted $\lambda_{\max} = 682$ nm, while absorption onset shifted from 901 to 967 nm. The optical band gap of **PVinylITN** is estimated to be 1.28 eV by extrapolation of the absorption onset in film state. The HOMO and LUMO levels of **PVinylITN** were measured by electrochemical cyclic voltammetry (CV).^[23] As displayed in Figure 3b, the HOMO and LUMO levels were estimated to be at -5.19 and -3.60 eV, respectively. The electrochemical band gap (1.59 eV) is comparable to the optical bandgap. Thermogravimetric analysis (TGA) suggests that **PVinylITN** exhibits great stability with decomposition temperature (T_d) larger than 310 °C under a N_2 atmosphere (see Figure S4). X-ray diffraction (XRD) analysis was used to investigate the structural ordering of **PVinylITN** in the solid state. In Figure S6, the $d_{(100)}$ -spacing of 24.25 Å is the interchain distance separated by the octyl side chains.

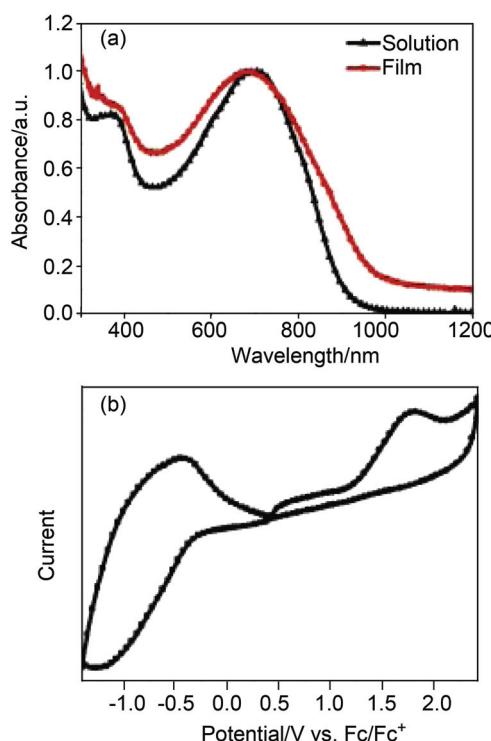


Figure 3 (a) Normalized solution and solid state absorption spectra of **PVinylITN**. (b) Cyclic voltammograms of **PVinylITN** films on a platinum electrode in 0.1 mol/L Bu_4NPF_6 , CH_3CN solution.

DFT calculations^[24] were performed to the oligomers (dimer, tetramer, hexamer and octamer) of **PVinylITN**

with the B3LYP function and a 6-31g(d) basis set,^[25,26] and the frequency analysis was followed to assure that the optimized structures were stable states. Alkyl groups were replaced by ethyl groups so as to simplify the calculation. **PVinylITN** takes an almost planar backbone based on the calculated results. As shown in Figure S7, the electron densities of both HOMO and LUMO were all delocalized along the backbones of the octamer, which is particular different from most of the donor-acceptor molecules, the same phenomenon is observed in these all donor counterparts (e.g., P3HT).^[27]

Initial photovoltaic properties of **PVinylITN** were investigated with device structure of ITO/PEDOT:PSS/**PVinylITN** : PC₆₁BM (3 : 4, $w:w$)/LiF(0.8 nm)/Al (100 nm). Figure S8 shows $J-V$ curves of the devices. Power conversion efficiency of 0.075% was achieved with open-circuit voltage (V_{oc}) of 0.52 V, short-circuit current density (J_{sc}) of 0.41 mA•cm⁻² and fill factor (FF) of 0.35. The poor device performance was mainly attributed to the inefficient packing in solid film of the polymers and thus low charge mobility. From the XRD result, no clear diffraction peak was observed, meaning a poor stacking of **PVinylITN** in the solid film. The hole mobility of **PVinylITN** was measured by space-charge limited current (SCLC) method and gave the value of only 1.9×10^{-5} cm²•V⁻¹•s⁻¹ (Figure S9), which is much lower than those of polymers with high photovoltaic performances.^[4] High hole mobility is one of necessary factors for charge transport and thus high photovoltaic device performance.^[28] So, for the next work, designing new ITN based low band gap polymers with high hole mobility is expected to achieve high PCEs.

Conclusions

In conclusion, stable ITN derivatives with different alkyl groups were synthesized, which could be the potential building block for high performance organic electronic materials. We tried several approaches to brominate these quinoidal units and found that bromination with liquid Br_2 could give acceptable yield of 48.8%. *trans*-Vinylene group was introduced to construct a planar ITN polymer, which exhibited broad absorption in the visible region and absorption edge extended to 967 nm in film. We are currently working on synthesizing low band gap polymers with alternative monomers based on ITN, so as to get high hole mobility and broad absorption based on these quinoidal polymers.

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