Biaryl crosslinkers. I. Crosslinking of a bisazidobiaryl with poly(3-hexylthiophene)

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Abstract: A new biaryl-based bisazide has been used to crosslink poly(3-hexylthiophene), a conducting polymer useful for organic electronics. Crosslinking was monitored using infrared spectroscopy and film morphology was studied using scanning electron microscopy. Hole mobility studies of the devices prepared from pristine and crosslinked polymer show an increase in hole mobility of one order of magnitude for the latter devices.

Key words: crosslinkers, 2D NMR, bisazide, poly(3-hexylthiophene), hole mobility.

Résumé : On a utilisé un nouveau biazide à base de biaryle pour effectuer une réticulation du poly(3-hexylthiophène), un polymère conducteur utile en électronique organique. On a suivi la réticulation par spectroscopie infrarouge et on a étudié la morphologie du film par microscopie électronique à balayage. Des études de mobilité du trou sur des dispositifs préparés à partir de polymère vierge et réticulé ont permis de démontrer que la mobilité du trou est d'un ordre de grandeur plus grande pour les dispositifs à base de polymère réticulé.

Mots-clés : coupleur de réticulation, RMN-2D, bisazide, poly(3-hexylthiophène), mobilité du trou.

[Traduit par la Rédaction]

Introduction

Polythiophenes and their derivatives, especially poly(3-alkylthiophenes), have been investigated extensively owing to their relatively good environmental stability[1,2] and interesting electrical and electronic properties.[3] Among this class of polythiophenes, poly(3-hexylthiophene) (P3HT) is the most widely studied material because of its good film-forming properties, strong absorption, and high hole mobilities, making it one of the foremost candidates for large-area device applications. P3HT has been used for fabrication of photovoltaic devices,[4–8] memory devices,[9] and thin-film transistors,[10,11] for lithographic purposes,[12–14] and for biosensors.[15,16] Polymer-based diodes are typically fabricated using a "vertical stack architecture" in which the active polymer material is sandwiched between two electrodes having a desired difference in work function.[17] Hole mobility is an important parameter, especially for photovoltaic applications. Hole mobilities of regioregular polythiophene (Fig. 1) as calculated by the space charge limited current (SCLC) method are of the order of 10^{-5} cm^2 V^{-1} s^{-1}.[18–22] However, field-effect mobilities in the range of 0.1 to 1 cm^2 V^{-1} s^{-1} have been achieved using highly ordered films.[23]

To use conducting polymers in organic electronics, materials with good hole mobilities are required. Only a few methods are available to increase the hole mobility. Besides synthesizing new materials, some of the approaches employed in this respect involve increasing molecular weight and decreasing polydispersivity,[24,25] introducing conjugated bridges in the polymer backbone,[26] doping,[27] and using high-boiling solvents.[28]

Recently, we have shown the use of a biaryl natural product as a material for device fabrication.[29] In this paper, we report the synthesis and use of a new biaryl-based bisazide to crosslink P3HT. Hole mobility studies of devices fabricated using pristine and crosslinked polymer were carried out using the SCLC method, and film morphology was studied using scanning electron microscopy (SEM).

Materials and methods

Chemicals and solvents were purchased from Merck or S.D. Fine-Chem Ltd. Regioregular P3HT was purchased from Spectrochem Pvt. Ltd. and used without additional purification. Reactions were monitored by thin-layer chromatography on fluorescent indicator coated plates purchased from Merck. Purification of compounds was done by column chromatography over silica gel (60 to 120 mesh) with a gradient elution using hexane with increasing proportions of ethyl acetate. Melting points were measured on an electrothermal melting-point apparatus and are uncorrected. IR spectra were recorded on a Spectrum BX series spectrophotometer using KBr. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 300 MHz spectrometer and 2D NMR spectra were recorded on a Bruker 400 MHz instrument. TMS was used as the internal standard in all cases. Mass spectra were recorded on a Waters Microanalysis LCT mass spectrometer (model No. KC455). Film thickness was measured by a

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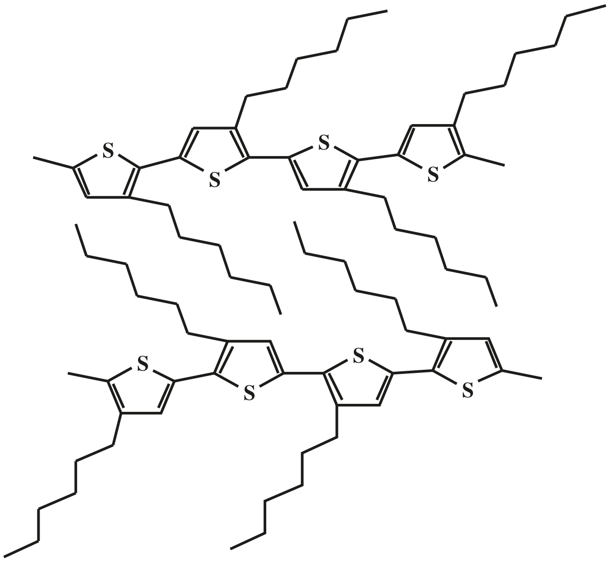


Fig. 1. Structure of head-to-tail regioregular P3HT.

SENTECH SE 500 ellipsometer. SEM investigations were carried out on a LEO 1430 instrument using films coated over indium tin oxide (ITO) coated glass.

Device fabrication

Devices were prepared on glass substrates coated with a thin layer of ITO, which were patterned by an etching process using a mixture of HNO_3–HCl–H_2O in a 1:12:12 ratio. The coated and etched substrates were cleaned by a standard wet process with detergent, followed by boiling acetone, isopropanol, and deionized water, with sonication at each step. Solutions of regioregular P3HT in chlorobenzene (2 wt %) were spin-coated at 2000 rpm, resulting in films with a thickness of about 175 nm. The solutions were prepared with different concentrations of the crosslinker and were filtered through a 0.2 μm pore size PTFE membrane syringe filter before spin coating. The solvent was removed in vacuo and metallic electrode contacts were formed by thermal evaporation of the metal, aluminum (~200 nm), in a vacuum coating unit using a base pressure of 2×10^{-6} mbar (1 bar = 100 kPa) in the evaporation chamber and a deposition rate of >1 Å s^{-1} over the film through a shadow mask. To avoid any doping by oxygen, the devices were kept in vacuum till measurements were done. Current–voltage (I–V) characteristics were recorded under normal class 10 000 clean room environmental conditions (temperature 25 °C and relative humidity ~45% to 50%) using a Keithley 2410 SourceMeter.

Results and discussion

Figure 2 shows the reaction sequence used to synthesize the crosslinker. 1,2,4-Trimethoxybenzene **(I)** was synthesized by Thiele's acetylation of *p*-benzoquinone followed by methylation with dimethyl sulfate in aqueous alkali. Lithiation of 1,2,4-trimethoxybenzene using *n*-butyllithium in diethyl ether gave the lithium salt, which on subsequent iodination gave compound **II**. The iodo-derivative, on Ullmann coupling in the presence of activated copper, yielded **III**, which on further nitration gave the corresponding dinitro compound (**IV**). The dinitro derivative, on reduction with stannous chloride in HCl, gave the corresponding diamino derivative (**V**), which on diazotization followed by displacement by sodium azide yielded the crosslinker (**VI**).

2D NMR studies of 2,2′,3,3′,6,6′-hexamethoxy-5,5′-dinitrobiphenyl (IV)

Previously we reported an aromatic nitro ipso substitution leading to a molecule belonging to a rare space group, *P*4$_2$.[30] Synthesis of compound **IV** was taken up to determine whether it too would belong to the rare space group *P*4$_2$. 2D NMR studies were then undertaken to establish its structure. The nuclear Overhauser effect (NOE) spectrum (see Fig. S1 in the Supplementary data) of the compound shows that the assignment from ^{1}H-3 at δ 7.59 corresponds to a peak at δ 3.94 (CH_3-10), indicating this methyl is ortho to C-3. In this NOE spectrum, cross peaks are observed between CH_3-8 at δ 3.77 and both of the other methyl groups, i.e., CH_3-10 at δ 3.94 and CH_3-14 at δ 3.62. ^{13}C NMR assignments from heteronuclear multiple bond coherence (HMBC) spectra (Fig. 3) were based on the magnitude of the observed coupling constants for C-4 (5.93 Hz) and C-6 (none resolved). However, it cannot be ruled out that these assignments could be reversed. The signal for C-4 appears at 137.7 ppm. From this, C-6 can be calculated and placed as being extremely shielded at 88.9 ppm. The observance of a four-bond coupling ($^4J_{HC}$) only for CH_3-8 may be the result of this being the only methyl group with the OCH_3 aligned in the plane with the aromatic ring. The other two methoxy groups exhibit an angle of ~125° from the plane of the ring. Complete NMR assignments for the compound are given in Table 1.

Crosslinking with poly(3-hexylthiophene)

In regioregular P3HT, inter-chain interactions are enhanced by π-stacking of the polymer chains, and the formation of a lamellar stacking of the polymer chains with good π-orbital overlap between neighboring chains is promoted by the regular arrangement of the alkyl side chain in P3HT.[18] With better control of the structural order, the efficiency of charge transport is expected to improve with stronger π–π interactions. This π-overlap can be further improved by crosslinking the polymer chains, which in turn will improve the electronic communication between them. For this purpose a biaryl-based bisazide was synthesized and crosslinked with the polymer. Crosslinking was achieved in a Rayonet photoreactor fitted with eight UV tubes (λ = 254 nm) of 12 W each. To avoid the effect of heat, the fan of the instrument was kept on during the experiment. Photolysis of the azide generates highly reactive nitrenes that can insert into a single bond (C–H) or double bond (thiophene ring) of the polymer. IR spectroscopy was used as a tool to determine the progress of crosslinking in the polymer film. The disappearance of the characteristic peak (20 min) for the azide group at ~2100 cm^{-1} in the IR spectrum indicated the completion of crosslinking (Fig. 4).

To determine the effect of crosslinking on the hole mobility of P3HT, devices with a glass/ITO/polymer/Al structure were prepared. Pristine P3HT films were prepared from a 2 wt % solution of polymer in chlorobenzene after stirring for 24 h in the dark. For the crosslinking experiments, the crosslinker was mixed in an appropriate ratio, namely 10 or

Fig. 2. Synthesis of a new biaryl-based crosslinker.

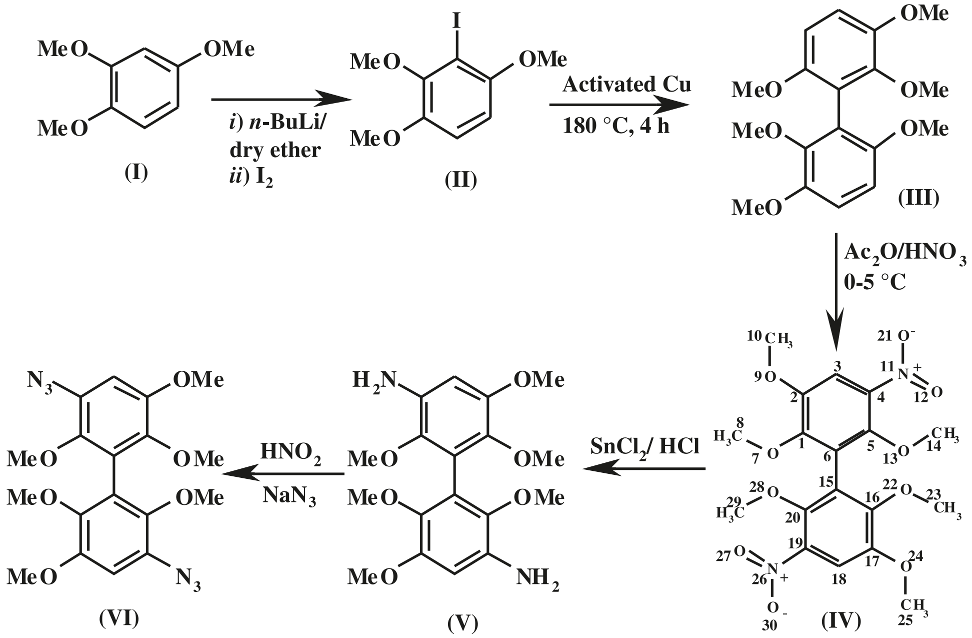
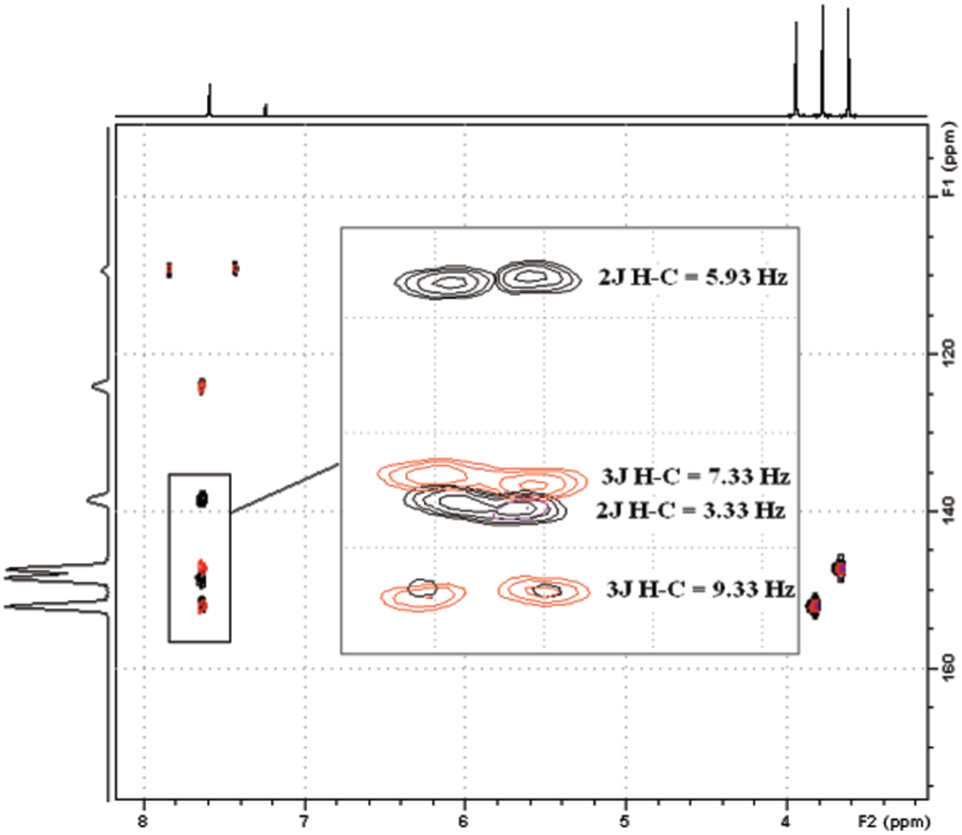


Fig. 3. HMBC spectrum of compound **IV**. In the expanded inset view appearing as the inner box, the $^2J_{HC}$ and $^3J_{HC}$ values are optimized for digital resolution of 4 Hz (black) and 2.5 Hz (red), respectively.

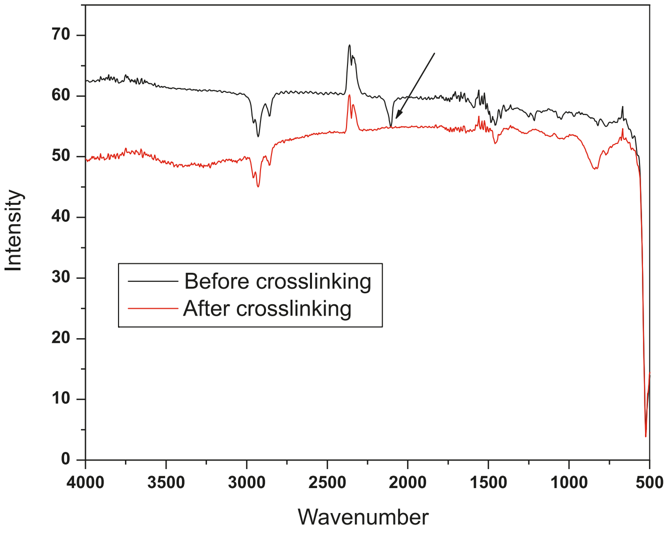


20 wt % of the polymer. The prepared films were protected from light until crosslinking was complete. As a control, pristine P3HT films were also studied after being subjected to similar conditions. The hole mobility can be described by the Mott and Gurney model of space charge limited current, considering the current flow in the trap-free limit.[31] Figure 5 shows a linear rise in current with voltage and a subsequent transition at high voltages to the region towards V^2 dependence. The field-independent mobility, μ, can be calculated by applying Child's Law,

Table 1. NMR assignments for compound **IV**.

Position	^{1}H NMR	^{13}C NMR	NOESY	HMBC
1/16		151.9		3, 8
2/17		148.3		3, 10
3/18	7.59	109	10, 14	10
4/19		138.3		3
5/20		147		3, 14
6/15		124		3
8/23	3.77	61.1	10, 14	
10/25	3.94	56.2	8	
14/29	3.62	62.2	8	

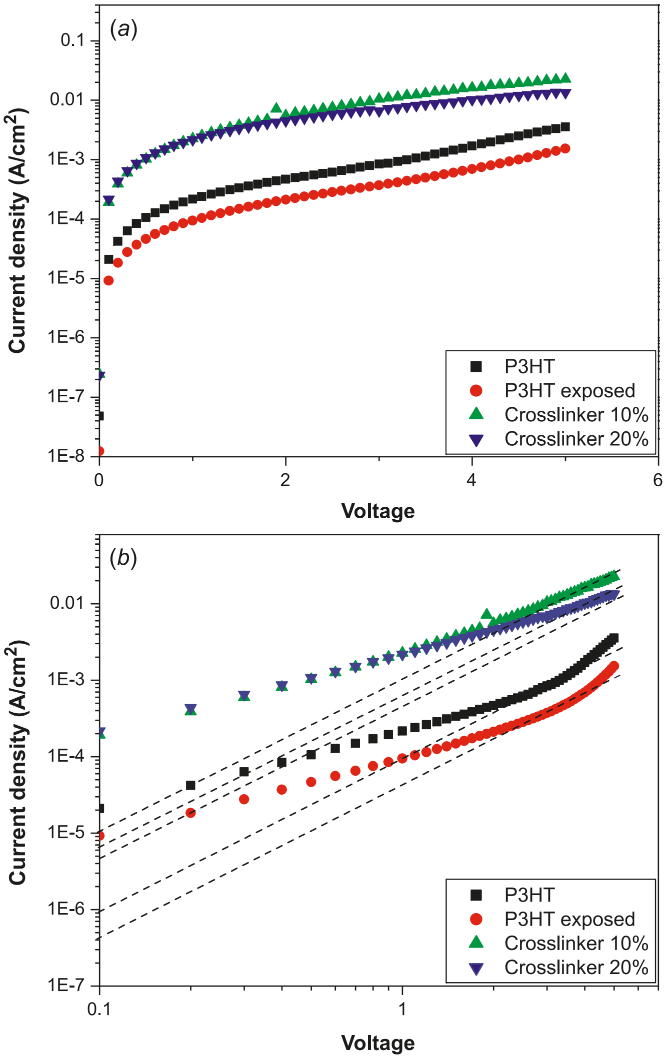
Fig. 4. IR spectrum of the P3HT film before (upper trace) and after (lower trace) crosslinking with 20 wt % crosslinker (disappearance of the azide is shown by the arrow).



$$J = \frac{9}{8}\mu\varepsilon\varepsilon_0\frac{V^2}{d^3} \qquad [1]$$

where J is the current density, μ is the free carrier hole mobility, ε is the dielectric constant (taken to be 3), ε_0 is the permittivity in a vacuum, V is the applied voltage, and d is the film thickness. The hole mobility was calculated from the intercept of the corresponding lines on the axis of current density. Using the above J–V relationship, the SCLC mobility (Fig. 5) of P3HT and the blank was calculated to be of the order of ~10^{-5} cm^2 V^{-1} s^{-1}, which is in accordance with values reported earlier.[18–22] Hole mobility values for the crosslinked polymer, as compared with pristine P3HT (4.5×10^{-5} cm^2 V^{-1} s^{-1}), increased by an order of magnitude of one, reaching 5×10^{-4} cm^2 V^{-1} s^{-1} and 3×10^{-4} cm^2 V^{-1} s^{-1} for devices fabricated after crosslinking with 10 wt % and 20 wt % crosslinker, respectively. A slight decrease in hole mobility was observed in devices fabricated using pristine P3HT exposed to UV as a control. The increase in hole mobility after crosslinking may be a result of better molecular ordering due to better π-overlap of the polymer chains. When a higher concentration of crosslinker is used, there is formation of an amorphous region due to twisting and bending of the polymer chains, resulting in a decrease in hole mobility.

Fig. 5. Comparison of current–voltage characteristics of the glass/ITO/polymer/Al devices. (*a*) Semi-log plot and (*b*) logarithmic plot. The hole mobilities were found to be 4.5×10^{-5} cm^2 V^{-1} s^{-1} for P3HT, 2×10^{-5} cm^2 V^{-1} s^{-1} for UV-exposed P3HT, 5×10^{-4} cm^2 V^{-1} s^{-1} for 10 wt % crosslinker, and 3×10^{-4} cm^2 V^{-1} s^{-1} for 20 wt % crosslinker.



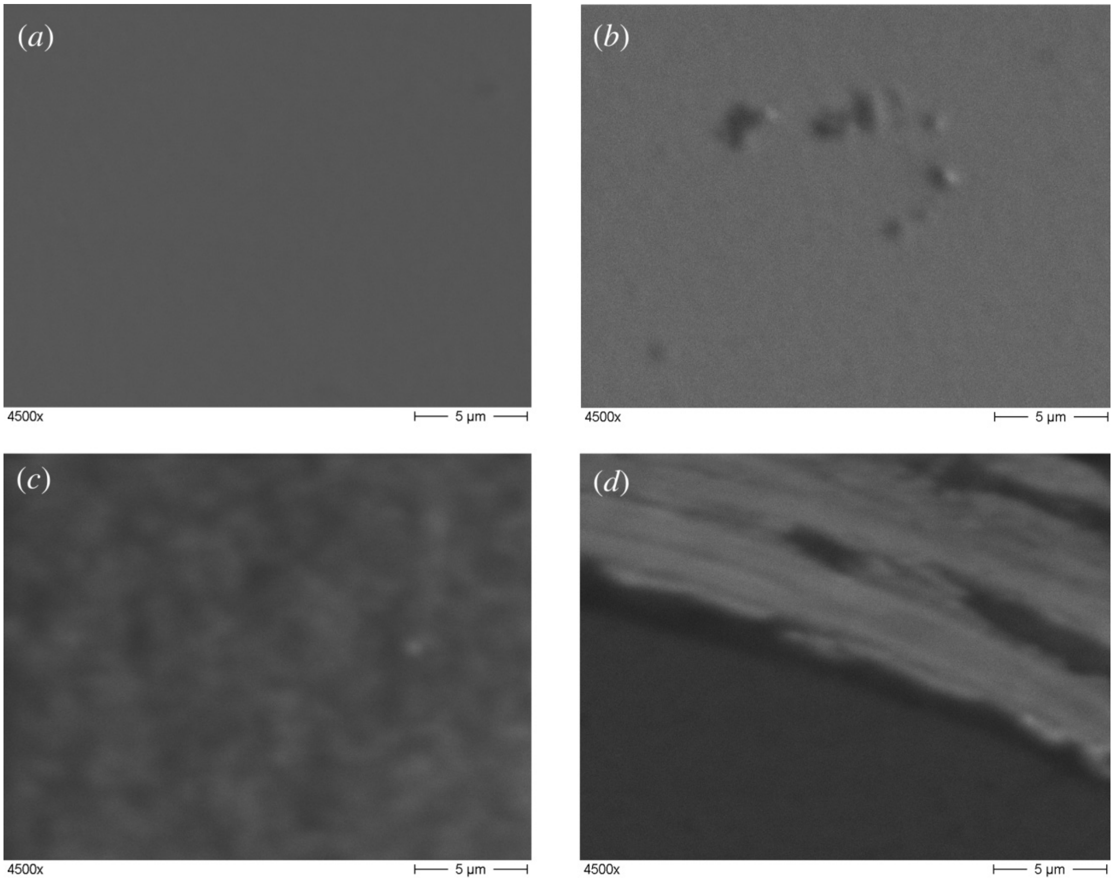
The film morphology was studied using SEM. Film morphology for P3HT, both pristine and exposed, is smooth (Figs. 6*a* and 6*b*). After crosslinking a change in film morphology is seen. Films with a crosslinker concentration of 10 wt % show granular morphology (Fig. 6*c*) and those with a higher crosslinker concentration show fibrous structure (Fig. 6*d*), possibly due to excessive crosslinking.

To conclude, a new biaryl-based bisazide has been synthesized and evaluated as a crosslinker. Devices fabricated using crosslinked P3HT show an increase in hole mobility, as determined by the SCLC method, by a factor of one order of magnitude. This study could be useful for fabrication of devices, especially thin-film transistors and solar cells.

Supplementary data

Supplementary data (the NOE spectrum along with synthe-

Fig. 6. SEM images of the films before crosslinking (*a*, pristine P3HT; *b*, pristine P3HT exposed to UV radiation) and after crosslinking (*c*, 10 wt % crosslinker; *d*, 20 wt % crosslinker).



sis and characterization data) are available with the article through the journal Web site (www.nrcresearchpress.com/cjc).

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