Electronic Supporting Information

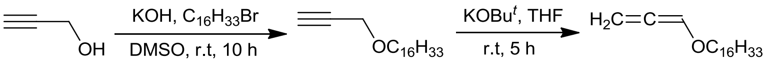
One pot synthesis of poly(3-hexylythiophene)-*block*-poly(hexadecyloxylallene) by sequential monomer addition

Zong-Quan Wu, Yu Chen, Ying Wang, Xiao-Yue He, Yun-Sheng Ding and Na Liu*
E-mail: zqwu@hfut.edu.cn

General Considerations. All reactions were carried out under a dry nitrogen atmosphere. All solvents were purified by the standard procedures before use. THF was further dried over sodium benzophenone ketyl, distilled onto $LiAlH_4$ under nitrogen, and distilled under high vacuum just before use. All starting materials were obtained commercially and used without further purification otherwise indicated. 2,5-Dibromo-3-hexylthiophene, poly(3-hexylthiophene) homopolymer,[1] hexadecyl-propargylether,[2] and hexadecyloxyallene[3] were prepared according to reported methods. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker 600 MHz or 300 MHz spectrometer. Chemical shifts are reported in delta (δ) units and expressed in parts per million (ppm) downfield with tetramethylsilane or chloroform as an internal standard. Size exclusion chromatography (SEC) was performed on Waters 1515 pump and Waters 2414 differential refractive index (RI) detector (set at 40 ^{o}C) using a series of linear Styragel HR1, HR2 and HR4 columns. THF was used as eluent at a flow rate of 0.3 mL/min. Molecular weight and polydispersity data are reported relative to the polystyrene standards. FT-IR spectra were recorded on Perkin-Elmer Spectrum BX FT-IR system using KBr pellets. Samples for atomic force microscopic (AFM) measurements were prepared by drop-casting THF solutions (0.5 mg/mL) of the resultant block copolymers onto freshly cleaved silicon wafers and the silicon wafers were further exposed to the same solvent vapor for 12 h according to the reported procedure.[4] AFM images were acquired in tapping mode with a Digital Instruments Dimension 3100 Scanning Probe Microscope performed at room temperature in air using standard silicon cantilevers with a nominal spring constant of 50 N m^{-1} and resonance frequency of ~300 kHz. The images were acquired at a scan frequency of 1 Hz in 1 × 1 μm^2 scan areas. Differential scanning calorimetry (DSC) was performed using a Mettler-Toledo DSC823e instrument under an atmosphere of nitrogen at a heating/cooling rate of 10 ºC/min. Thermogravimetric analyses (TGA) were performed under an atmosphere of nitrogen at a scan rate of 10 ºC/min using a Mettler Toledo TGA/SDTA851e instrument equipped with a TSO801RO sample automated loader.

Syntheitc Procedures

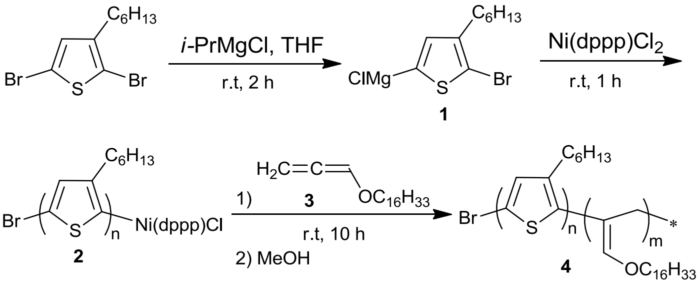
Scheme S1 Synthesis of hexadecyloxylallene **3**.



1-(Prop-2-yn-1-yloxy)hexadecane: To a suspension of KOH (16.8 g, 0.30 mol) in 100 mL DMSO was added 5.4 mL propargyl alcohol (5.60 g, 0.10 mol) at 0 ºC. After stirring for 30 min, cetyl bromide (31.5 mL, 0.10 mol) was added at 0 ^{o}C. Stirring was continued for 10 h at room temperature. The resulting brown suspension was diluted with 200 mL water and extracted with diethyl ether (3 × 50 mL). The combined organic layer was washed with water (2 × 20 mL) and brine (2 × 20 mL), dried over Na_2SO_4, filtered and concentrated in *vacuo*. The yellowish, oily liquid was purified by flash chromatography (petroleum ether) gave 1-(prop-2-yn-1-yloxy)hexadecane as a colorless liquid (22.4 g, 80%). ^{1}H NMR (600 MHz, $CDCl_3$, 25 ºC): δ 4.12 (s, 2H), 3.50 (t, 2H), 2.40 (s, 1H), 1.59 (t, 2H), 1.33 (m, 2H), 1.25 (m, 24H), 0.88 (t, 3H).

Hexadecyloxyallene (3): At room temperature, $KOBu^{t}$ (2.40 g, 21.4 mmol) was added batch-wise into a solution of 1-(prop-2-yn-1-yloxy)hexadecane (5.00 g 17.9 mmol) in 100 mL THF within 30 min. The suspension was stirred at room temperature for 5 h, then filtered through a celite pad and washed with Et_2O (50 mL). Combined solution was concentrated under reduced pressure and purified by flash chromatography (0.5~0.8% diethyl ether in petroleum ether) to afford **3** as a colorless oil (4.10 g, 82%). ^{1}H NMR (600 MHz, $CDCl_3$, 25 ºC): δ 6.72 (t, J = 6.0 Hz, CH, 1H), 5.41 (d, J = 5.4 Hz, CH_2, 2H), 3.54 (t, J = 6.6 Hz, OCH_2, 2H), 1.63 (m, OCH_2CH_2, 2H), 1.26 (m, 26H), 0.88 (t, J = 7.2 Hz, CH_3, 3H). ^{13}C: δ 201.46, 121.63, 90.24, 68.91, 31.95, 29.72, 29.69, 29.62, 29.59, 29.43, 29.39, 29.19, 26.04, 22.71, 14.12. FT-IR: 2924, 2851, 1961, 1455, 1350 cm^{-1}. MS m/z calcd for $C_{19}H_{37}O$ $[M+H]^+$: 281.3; Found: 281.4. Anal. Calcd (%) for $C_{19}H_{36}O$ (280.3): C, 81.36; H, 12.94; Found (%): C, 81.39; H, 12.96.

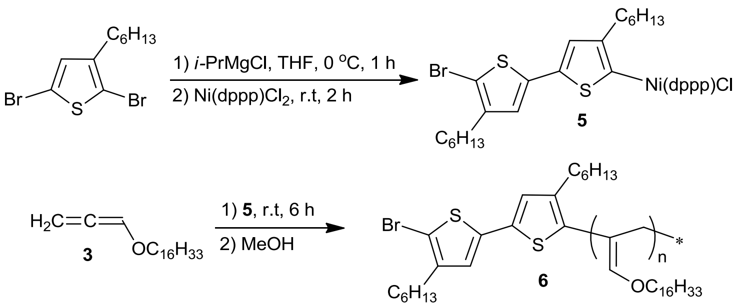
Scheme S2 Synthesis of poly(3-hexylythiophene)-*b*-poly(hexadecyloxylallene) block copolymers by sequential monomer addition.



Representative Copolymerization Procedure (4a). A 10 mL oven-dried flask was charged with 2,5-dibromo-3-hexylthiophene (0.26 g, 0.81 mmol), dry THF (8.0 mL), and a stiring bar. After a solution of isopropylmagnesium chloride (0.41 mL, 2.0 M solution in THF) was added via a syringe, the resulting mixture was stirred at ambient temperature for 2 h. $Ni(dppp)Cl_2$ (9.40 mg, 13.5 μmol, [**1**]/[$Ni(dppp)Cl_2$ = 60/1, dppp = 1,3-bis(diphenylphosphino)propane) was then added to the reaction mixture, and the polymerization progress was monitored by SEC until the molecular weight ceased to increase. SEC analysis of an aliquot removed from the reaction mixture showed that the polymer (**2a**) prepared in situ exhibited the following characteristics: M_n = 9.9 kDa, M_w/M_n = 1.30. Under an atmosphere of nitrogen, monomer **3** (0.22 g, 0.80 mmol, $[\mathbf{3}]_0/[\mathrm{Ni}]_0$ = 60/1) was added to the reaction solution. After the reaction mixture was stirred at room temperature for 10 h, 30 mL of methanol was poured into the reaction flask, which caused a dark-purple solid to precipitate. The solid was then isolated *via* filtration, and washed with excess cold methanol and *n*-hexanes to remove residual metal salts, unreacted monomer and oligomers. The resulting purple solid was then dried under vacuum to afford 0.30 g of the desired block copolymer **4a** (85% yield, two steps). SEC: M_n = 16.5 kDa, M_w/M_n = 1.42. ^{1}H NMR (600 MHz, $CDCl_3$, 25 ºC): δ 6.98 (s, P3HT, ArH), 6.07–5.77 (br, PHA, CH), 3.88–3.39 (br, PHA, OCH_2), 2.81–2.80 (t, P3HT, thiophene-CH_2), 2.87–2.13 (br, PHA main chain), 1.98–1.07 (br, P3HT and PHA, alkyl chains), 1.00–0.75 (br, P3HT and PHA, CH_3). FT-IR: 2922, 2850, 1668, 1469, 1263, 1136 cm^{-1}.

Procedure for Synthesis Poly(3-hexylythiophene)-*b*-Poly(hexadecyloxylallene) with Various Molecular Weights from a Common Macroinitiator 2. Under an atmosphere of nitrogen, to various quantities (2.0, 4.0, 6.3, 8.8 mL) of degassed THF solutions of **3** ($[\mathbf{3}]_0$ = 0.05 mM) were added to 4.3 mL of freshly prepared Ni(II)-P3HT **2** (M_n = 7.0 kDa, M_w/M_n = 1.22) in THF ($[\mathbf{2}]_0$ = 2.3 μM). Each of the reaction mixtures were then stirred for 10 h at room temperature and quenched by addition of large amount of methanol. The resulting block copolymers were then collected *via* filtration, washed with methanol, hexane, and dried under vacuum to afford block copolymer **4** (> 85% yield over two steps for all samples). The polymers were characterized by ^{1}H NMR and SEC.

Scheme S3 Synthesis of poly(hexadecyloxylallene) (PHA) homopolymer (**6**).



Preparation of initiator 5. This complex was prepared according to the reported literatures.[5] A round-bottomed flask equipped with a three-way stopcock was heated under reduced pressure and then cooled to room temperature under a nitrogen atmosphere. 2,5-dibromo-3-hexylthiophene (326 mg, 1.00 mmol) was placed in the flask, and the atmosphere was replaced with nitrogen. Into the flask was added dry THF (5.0 mL) via a syringe, and stirring was continued at 0 ºC. To the mixture was added isopropylmagnesium chloride (2.0 M solution in THF, 0.50 mL, 1.0 mmol) via a syringe, and the mixture was stirred at 0 ºC for 1 h. To a suspension of Ni(dppp)Cl_2 (271 mg, 0.500 mmol, 50 mol %) in dry THF (5.0 mL) was added the mixture via a syringe at 0 ºC, and the whole was stirred at room temperature for 2 h, afforded the initiator solution. A small aliquot of the solution was withdrawn *via* a syringe, quenched with 5 M HCl, and isolated for ^1H NMR analysis to confirm the structure. ^1H NMR (300 MHz, $CDCl_3$, 25 ºC): δ 7.18 (d, J = 6.0 Hz, ArH, 1H), 6.80–6.78 (m, ArH, 2H), 2.56–2.50 (m, $ArCH_2$, 4H), 1.57–1.52 (m, $ArCH_2CH_2$, 12H), 0.89 (t, J = 6.0 Hz, CH_3, 6H).

Preparation of homopolymer of hexadecyloxyallene (PHA, 6). A 10 mL oven-dried flask was charged with hexadecyloxyallene **3** (56 mg, 0.20 mmol), dry THF (2 mL), and a stir bar. After stirred at room temperature for 10 min, a solution of initiator **5** (0.05 M, 0.133 mL, 0.0067 mmol) was added to this solution *via* a microsyringe ([monomer]/[initiator] = 30). After the mixture solution was stirred for further 6 h, the solution was pour into large amount of methanol (10 mL). The precipitate solid was collected via filtration and dry under vacuum to afford the homopolymer PHA (**6a**) as a white solid (48 mg, 85 % yield). SEC: M_n = 7.1 kDa, M_w/M_n = 1.21. ^1H NMR (600 MHz, $CDCl_3$, 25 ºC): δ 6.10–5.67 (br, CH), 3.81–3.47 (br, OCH_2), 2.88–2.15 (br, CH_2 on main chain), 1.81–1.45 (br, OCH_2CH_2), 1.38–1.09 (br, PHA, CH_2), 0.92–0.82 (br, CH_3). FT-IR: 2923, 2851, 1668, 1469, 1144 cm^{-1}.

With the same synthetic method, another PHA homopolymer (**6b**) was also prepared by change the initial feed ratio of monomer **3** to initiator **5** to 100 ($[\mathbf{3}]_0/[\mathbf{5}]_0$ = 100). SEC for **6b**: M_n = 24 kDa, M_w/M_n =1.30.

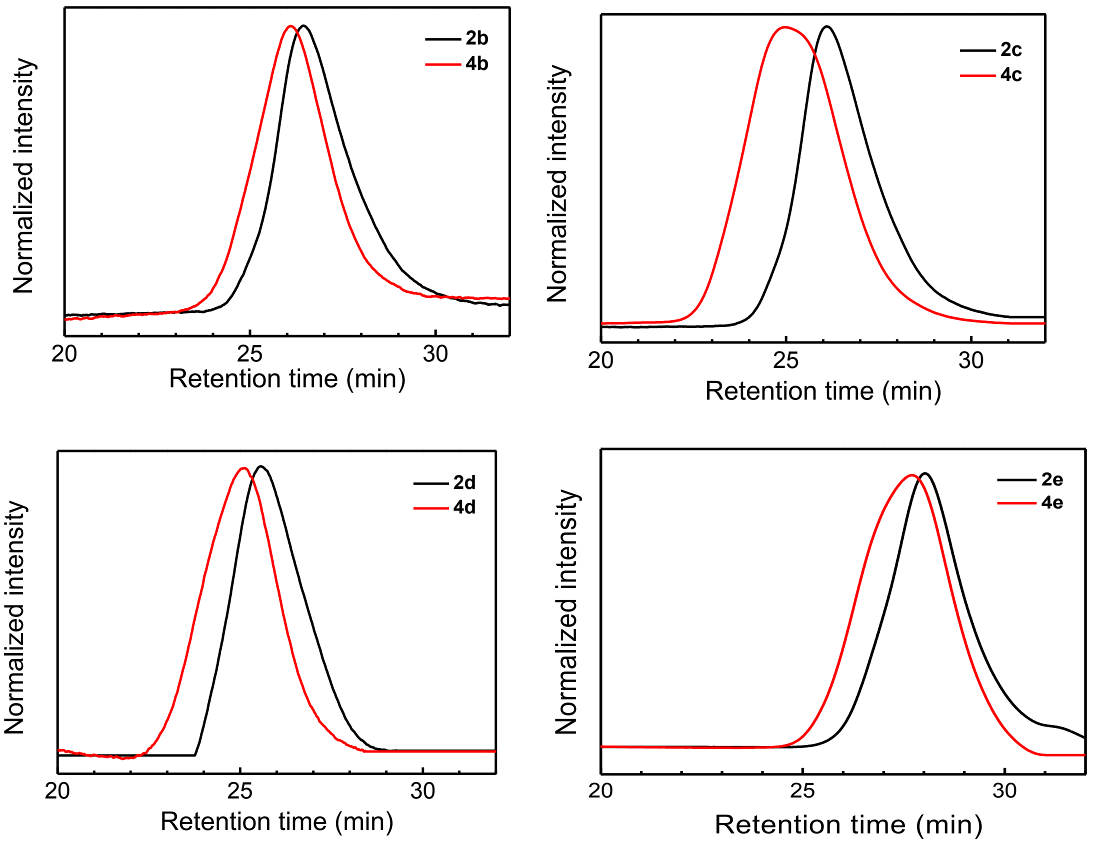


Fig. S1 Size exclusion chromatograms of macroinitiators **2b**, **2c**, **2d** and **2e** (black), and their respective block copolymers **4b**, **4c**, **4d** and 4**e** (red), respectively. (40^{o}C, THF as eluent)

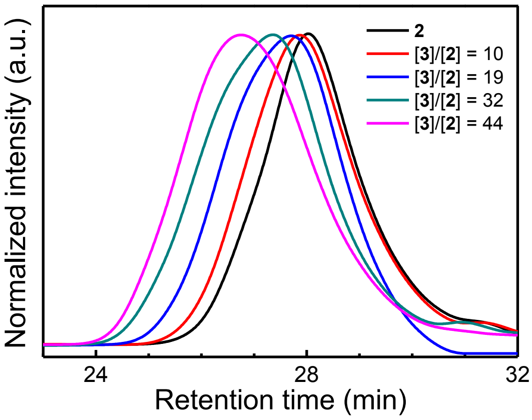


Fig. 2 Size exclusion chromatograms of **4** with various molecular weights synthesized using different feed ratios of **3** to macroinitiator **2** (indicated in legend).

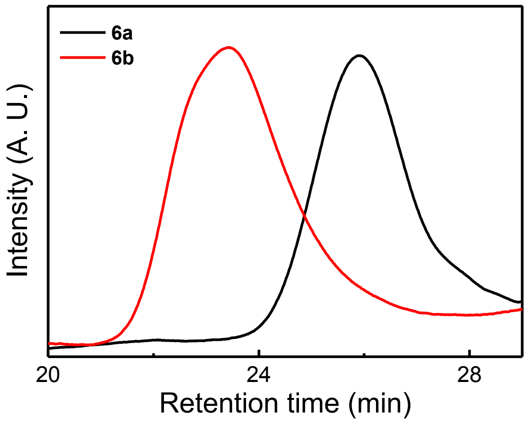


Fig. S3 Size exclusion chromatograms of PHA homopolymer **6a** and **6b** (SEC conditions: eluent = THF; temperature = 40 ºC).

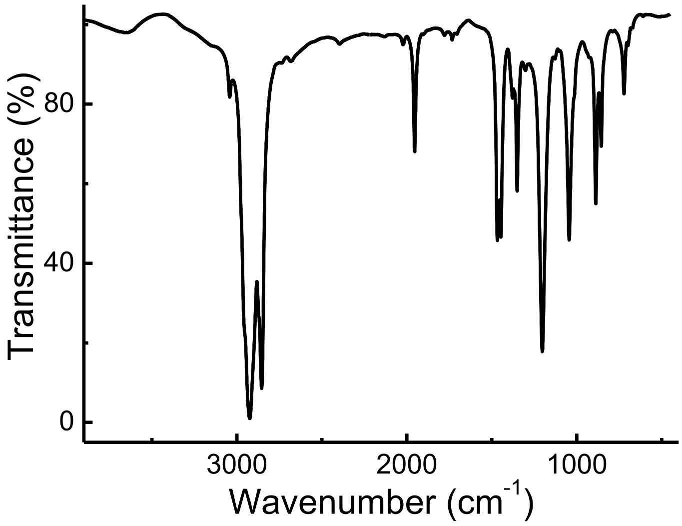


Fig. S4 FT-IR spectrum (KBr) of hexadecyloxylallene (**3**) measured at 25 ^{o}C.

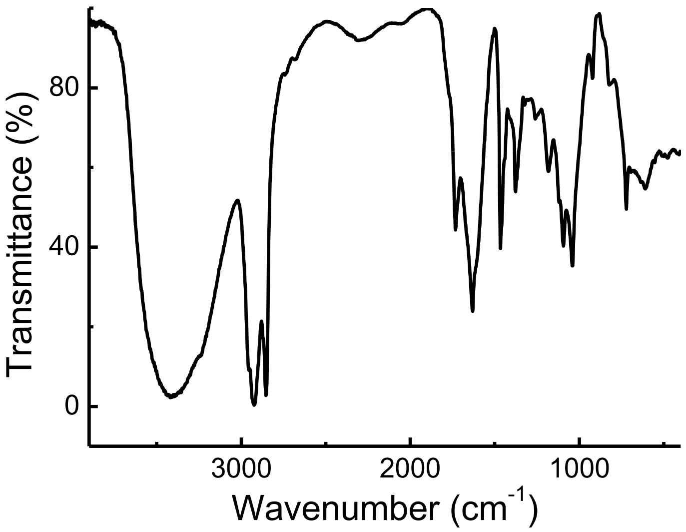


Fig. S5 FT-IR spectrum (KBr) of P3HT homopolymer (**2a**) measured at 25 °C.

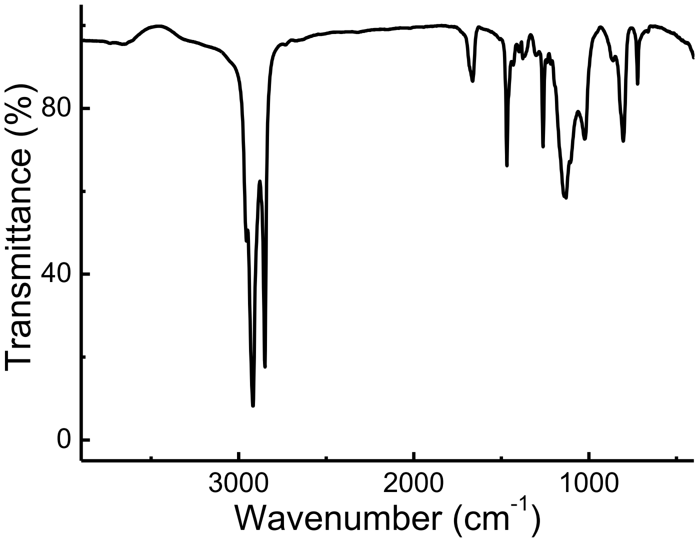


Fig. S6 FT-IR spectrum (KBr) of P3HT-*b*-PHA block copolymer measured at 25 °C.

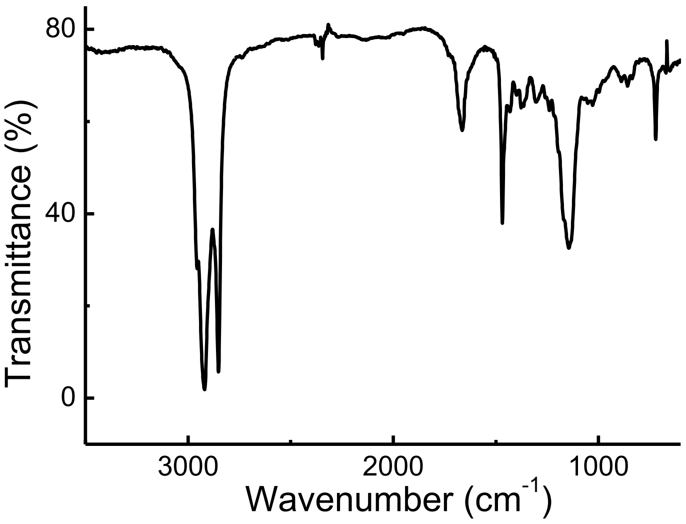


Fig. S7 FT-IR spectrum (KBr) of PHA homopolymer (**6a**) measured at 25 ^{o}C.

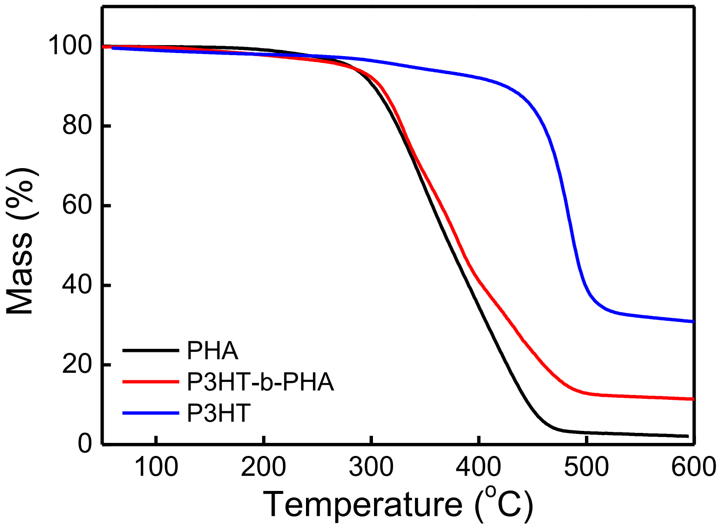


Fig. S8 Thermogravimetric analysis curves recorded for homopolymer PHA and P3HT and the block copolymer P3HT-*b*-PHA (conditions: N_2 atmosphere; scan rate = 10 ºC/min).

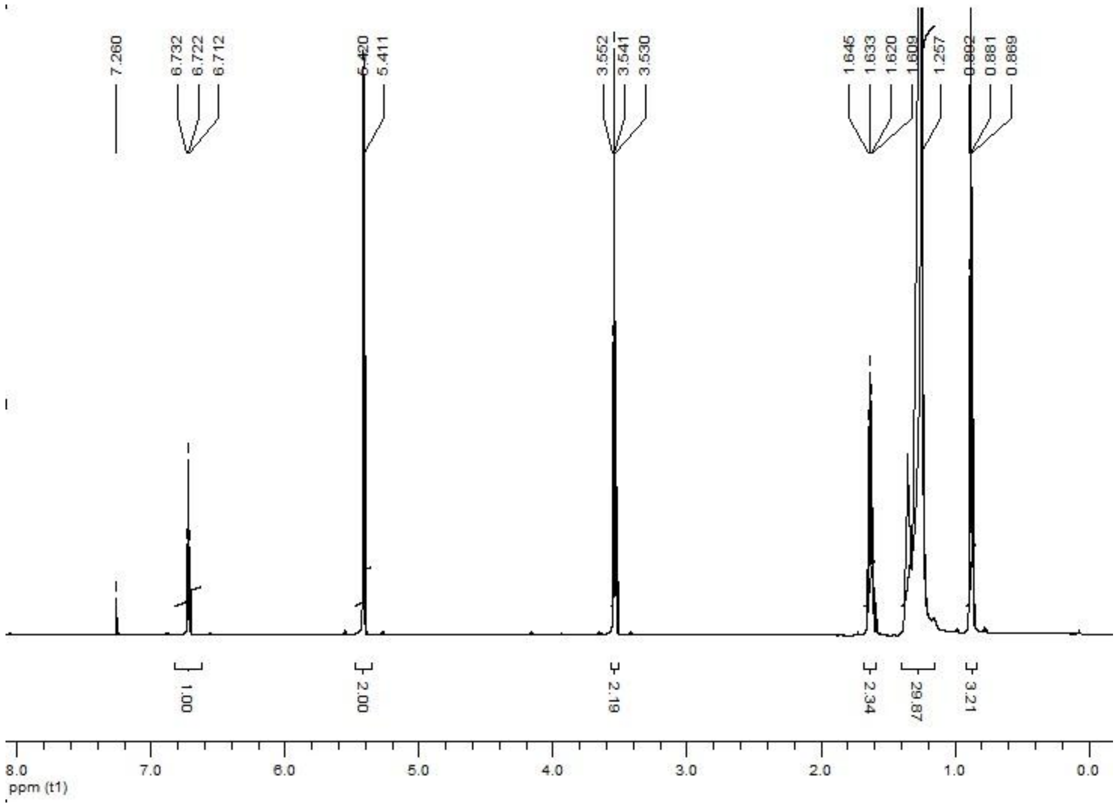


Fig. S9 ^{1}H NMR spectrum of monomer **3** measured in $CDCl_3$ at 25 °C (600 MHz).

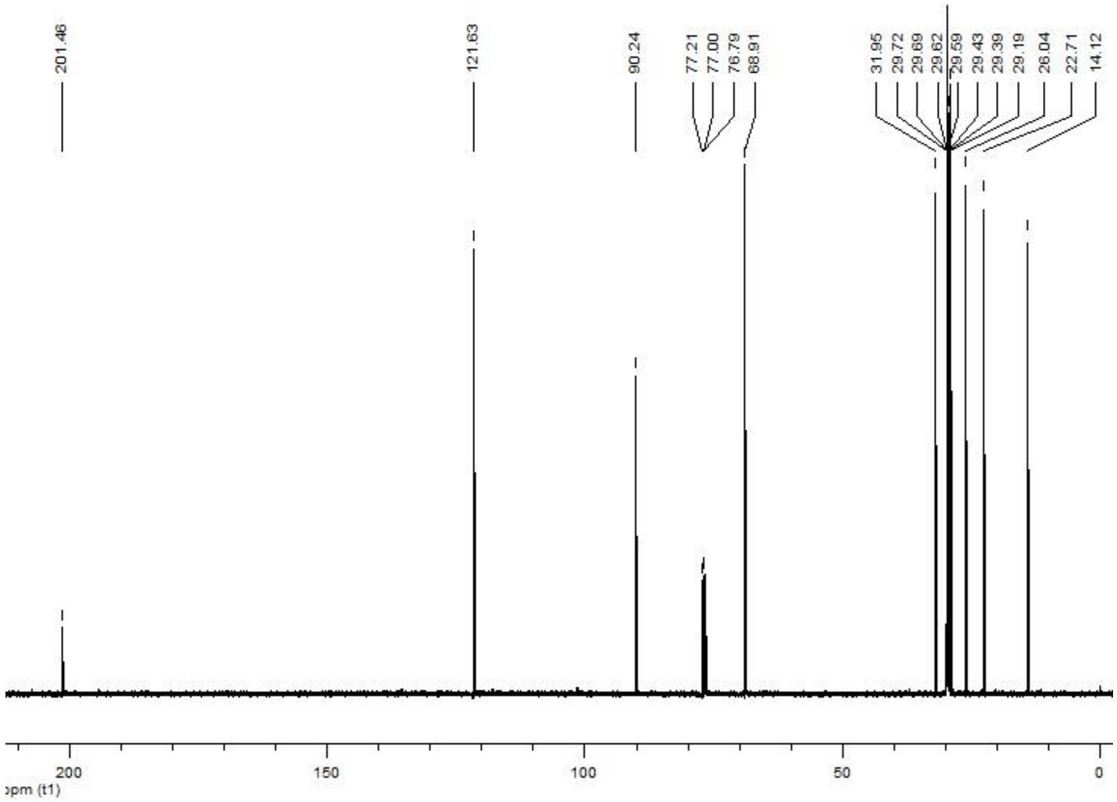


Fig. S10 ^{13}C NMR spectrum of monomer **3** measured in $CDCl_3$ at 25 °C (600 MHz).

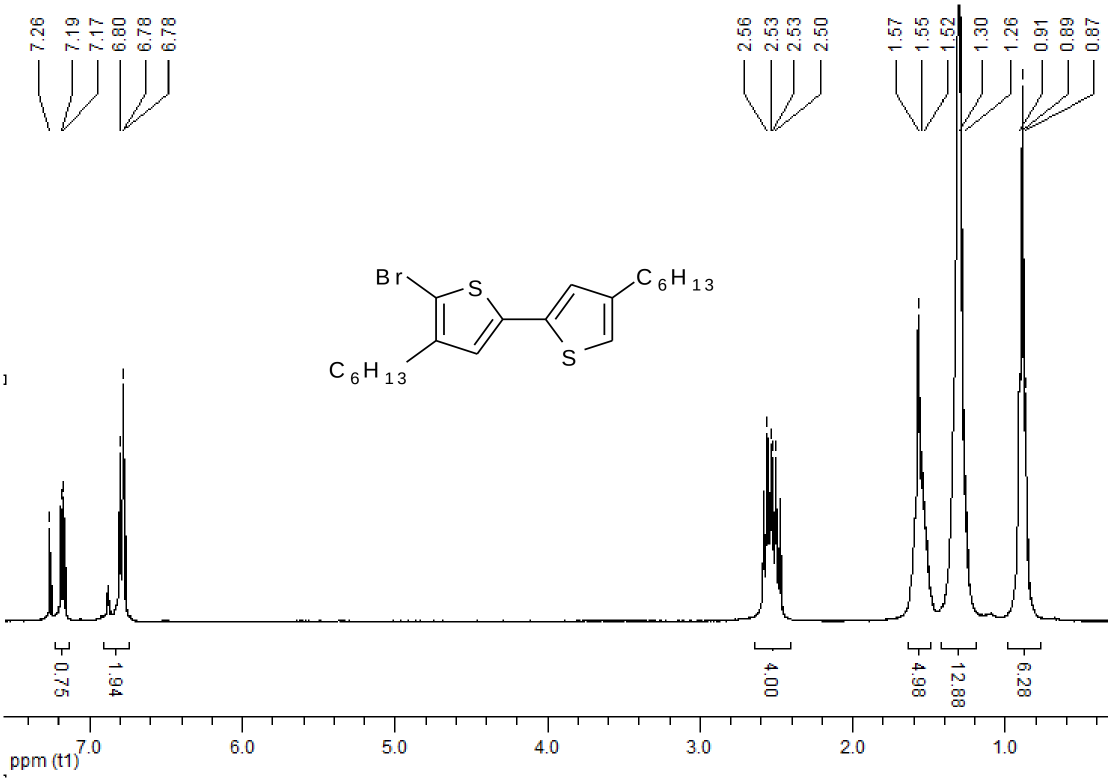


Fig. S11 ^{1}H NMR spectrum of initiator **5** (quenched by 5M HCl) measured in $CDCl_3$ at 25 °C (300 MHz).

References

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