

Supporting Information

Solvent free oxidative coupling polymerization of 3-hexylthiophene (3HT) in the presence of FeCl₃ particles

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1. Materials:

All solvents and chemicals for synthesis were used without further purification, except for chloroform (CHCl_3 , Wako Pure Chemical Industries, Ltd., 99%). Toluene, tetrahydrofuran (THF) and methanol (MeOH) were purchased from Wako Pure Chemical Industries, Ltd. Iron (III) chloride (FeCl_3 , 97%) and halloysite nanoclay (halloysite nanotube, HNT) were purchased from Sigma-Aldrich Co. LLC. Molecular sieve 13X (zeolite) and ethylenediaminetetraacetic acid (EDTA, 99%) were purchased from Nacalai Tesque Inc. Copper sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 99.5%) was purchased from Kanto Chemical Co., Inc. Terephthalic acid (99%), 3-hexylthiophene (3HT, 98%), triethylenediamine (98%), and formic acid (88%) were purchased from Tokyo Chemical Industry Co., Ltd. CHCl_3 was degassed by argon bubbling for 15 min.

2. Measurements:

^1H nuclear magnetic resonance (^1H NMR) spectra were recorded in CDCl_3 using Bruker Avance-400 spectrometer. Fourier-transform infrared spectroscopy (FT-IR) spectra were recorded using Spectrum One (PerkinElmer) and Hyperion 2000 (Bruker SPring-8 BL43IR). The number-average molecular weight (M_n) and polydispersity index (PDI) were determined using a HLC-8120GPC (TOSOH) equipped with three columns (TOSOH TSK gel super H2500, TSK gel super H 4000, and TSK gel super H 6000), a RI-2031 plus refractive index detector and a UV-8220 plus ultraviolet detector. Thermogravimetric analysis (TGA) was performed using a Seiko SII-EXSTAR TG/DTA6200 thermobalance. A 5 mg sample was loaded in an aluminum pan and heated at rate of 10 K/min with nitrogen as purge gas. Wide angle X-ray diffraction (WAXD) measurements were performed using a RINT-TTR III (Rigaku) employing $\text{CuK}\alpha$ radiation. X-ray absorption fine structure (XAFS) measurements were performed at the Kyusyu University Beamline (BL06) at the Kyushu Synchrotron Light Research Center (Saga, Japan).

2-1. Preparation of $[\text{Cu}_2(\text{bdc})_2(\text{ted})]_n$ (MOF):

The $[\text{Cu}_2(\text{bdc})_2(\text{ted})]_n$ MOF was synthesized following a previously reported method¹. Briefly, 20 mL of MeOH with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.310 g, 1.2 mmol) was added to a solution of 200 mL MeOH containing 0.210 g terephthalic acid (1.3 mmol) and 2.0 mL formic acid. The mixture was reacted at 313 K for 48 h. A solution containing 13 mL

toluene and 0.070 g triethylenediamine (0.062 mmol) was subsequently added to the mixture and stirred. The mixture was then replaced in an autoclave and kept at 433 K for 24 h. The obtained powder was washed by MeOH several times and dried at 373 K for 24 h under high vacuum (0.40 g, 67% yield).

2-2. Bulk Polymerization of 3HT:

3HT (0.18 g, 1.0 mmol) was slowly added to FeCl_3 (0.67 g, 4.1 mmol) under an inert gas environment. The components were mechanically mixed using a mortar and pestle until uniform, then stored at room temperature for 24 h to allow the reaction to process. An excess amount of MeOH was subsequently added to quench the reaction. The polymer was put into a EDTA aqueous solution for 24 h and the residue was filtered and dried under high vacuum. The primary structure of the portion soluble in common organic solvents (THF, CHCl_3) was evaluated using ^1H NMR spectrum and SEC measurements. Figure ESI 1. shows the ^1H NMR spectrum of P3HT obtained in bulk condition.

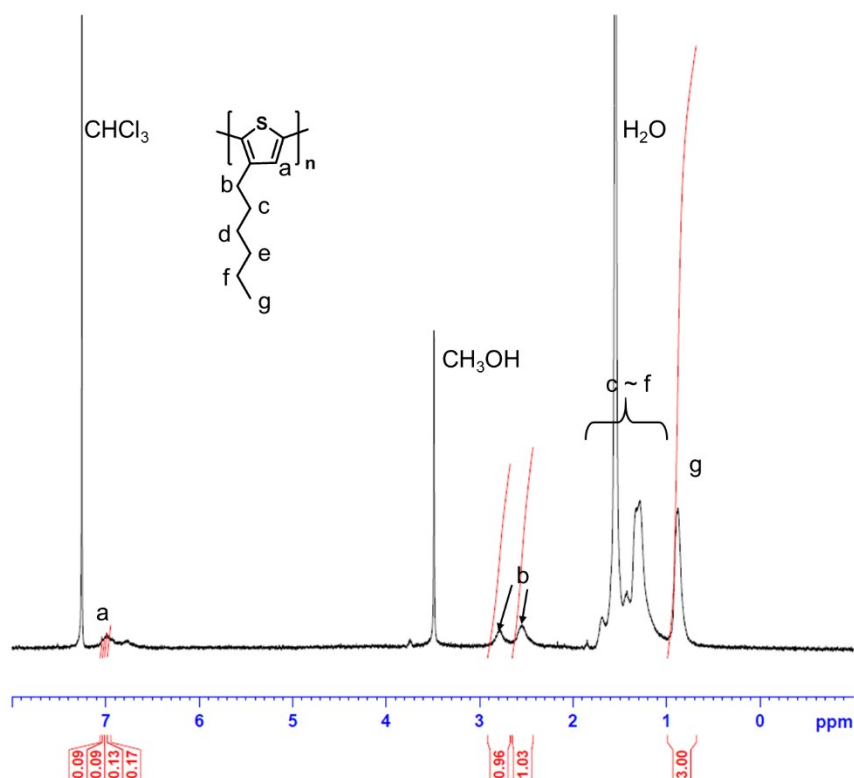


Figure ESI 1. ^1H NMR spectra for P3HT obtained in bulk condition.

2-3. 3HT Polymerization of 3HT in CHCl_3 :

FeCl_3 (0.666 g, 4.10 mmol) and 5 mL of CHCl_3 were mixed into a flask under inert gas

flow at room temperature and subsequently cooled to 273 K. A mixture of 1 mL of CHCl_3 and 3HT (0.180 g, 1.07 mmol) was then added to the flask. The reaction was allowed to proceed at room temperature for 24 h and was subsequently quenched by addition of MeOH. The precipitate was filtered and dried at room temperature for 24 h under high vacuum (0.135 g, 75% yield). The primary structure was identified using ^1H NMR spectrum and SEC measurements. Figure ESI 2. shows the ^1H NMR spectrum.

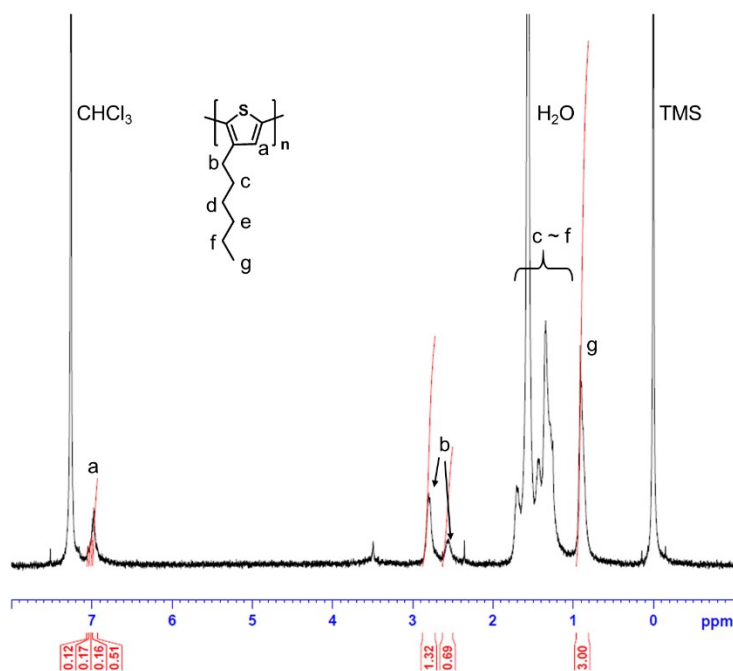


Figure ESI 2. ^1H NMR spectra for P3HT obtained from CHCl_3 .

2-4. 3HT Polymerization in Zeolite and HNT:

To investigate the role of nanocavity size on polymerization behavior, 3HT was mixed with either zeolite or HNT by 30 min ultra-sonication. After sonication, the non-encapsulated 3HT was removed by vacuum drying at 313 K for 48 h. The weight of 3HT encapsulated in the nanocavity was estimated using TGA measurements. Figure ESI 3 shows the TGA profiles of 3HT in HNT. The encapsulated content of 3HT in the nanocavity, estimated on the basis of TGA measurements, was used to determine the amount of FeCl_3 oxidizer to add to the system. The stoichiometric ratio of 3HT to FeCl_3 was set to 1:4. For the zeolite system, 0.38 g FeCl_3 (2.4 mmol) was added to the estimated 0.10 g encapsulated 3HT (0.59 mmol). For the HNT system, 1.00 g FeCl_3 (6.2 mmol) was added (3HT content estimated to be 0.26 g, 1.54 mmol). The mixtures were kept at room temperature for 24 h under inert gas condition. MeOH was added to

the system to quench the reaction. The obtained P3HT was washed extensively with THF for 24 h to remove from the zeolite or HNT. The recovered solution was subsequently filtered and evaporated. For both zeolite and HNT, the estimated yield of P3HT was 81%. These primary structure of the obtained polymer was evaluated using ^1H NMR spectrum and SEC measurements. Figure ESI 4 shows the ^1H NMR spectra for P3HT obtained in the a) zeolite and b) HNT systems.

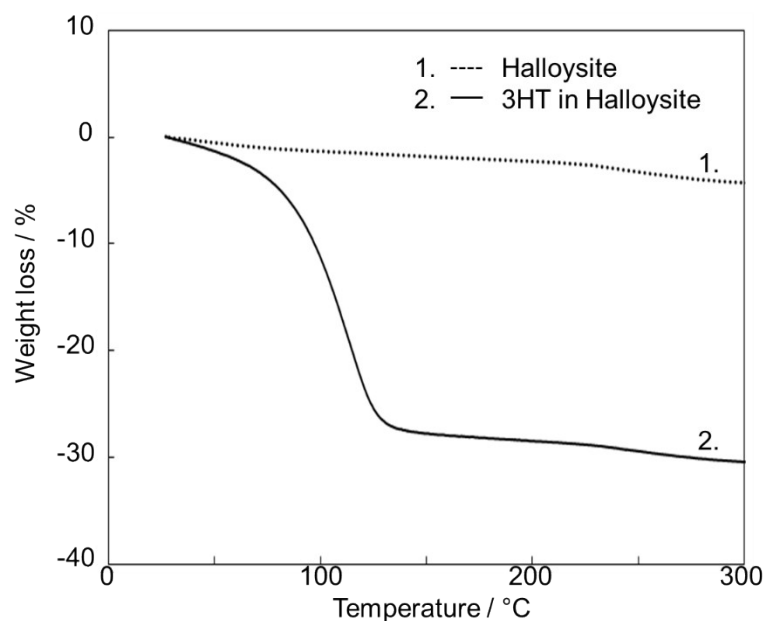


Figure ESI 3. TGA profiles of HNT (1, dashed line) and 3HT encapsulated in HNT (2, solid line).

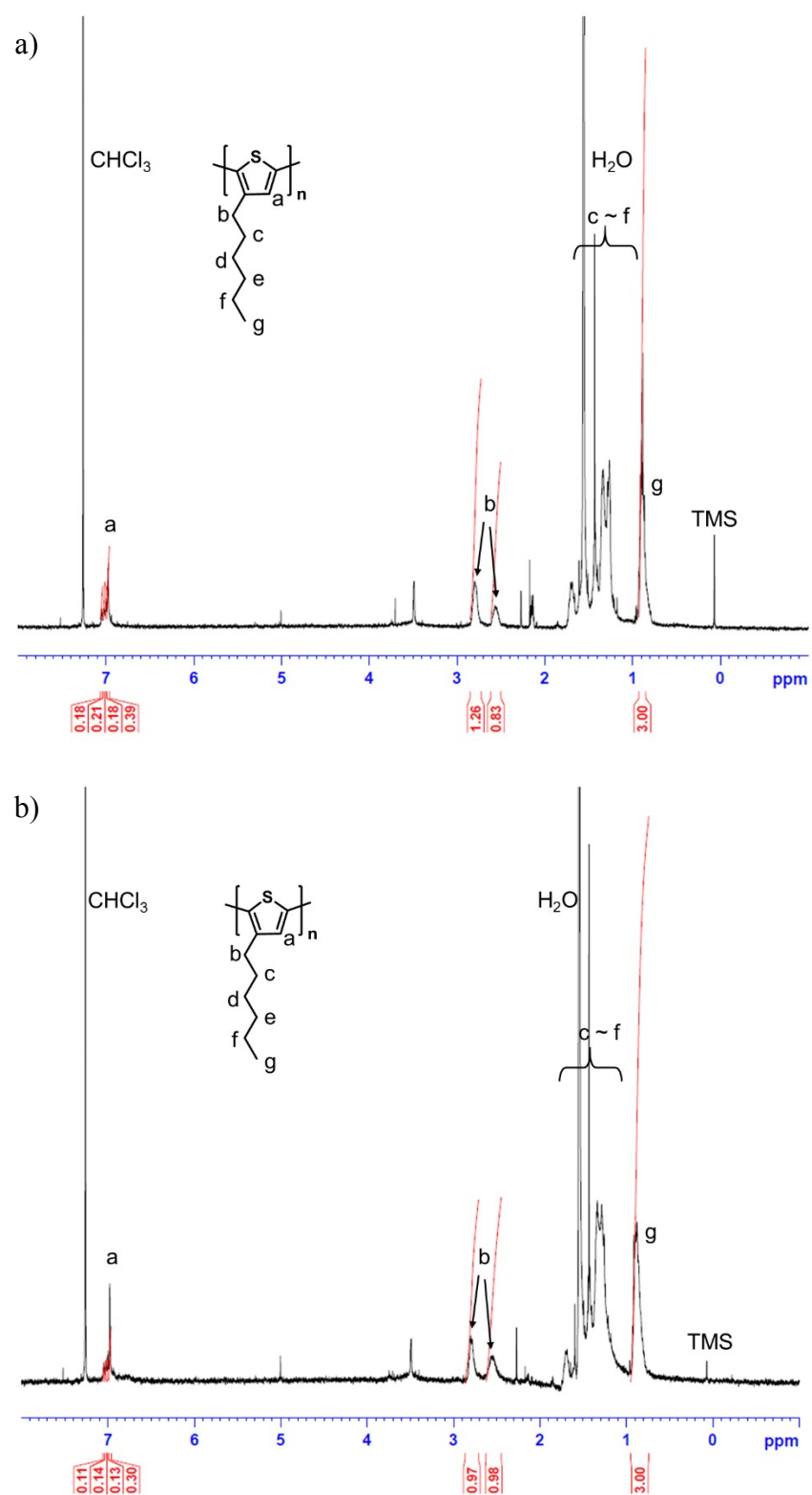


Figure ESI 4. ^1H NMR spectra for P3HT obtained from a) zeolite and b) HNT.

2-5. 3HT Polymerization in MOF:

The MOF was mixed with 3HT and subsequently ultra-sonicated for 30 min to introduce the 3HT in the nanocavity. After mixing, the non-encapsulated 3HT was removed by vacuum drying at 313 K for 48 h. The weight of 3HT in the nanocavity was estimated based on the TGA profile, which is shown in Figure ESI 5. The FeCl_3 oxidizer was added at stoichiometric ratios of 3HT: $\text{FeCl}_3 = 1:4$, $4:1$, and $10:1$. After mixing, the reaction was allowed to proceed at room temperature for 24 h. MeOH was subsequently added to the system to quench the reaction. The residue was placed in 40 mL of EDTA aqueous solution (0.05 M) for 24 h with vigorous stirring to remove the MOF. The mixture was filtered and dried under vacuum. The estimated yield was 69 %, 5 %, and 2 % for systems with stoichiometric ratio of 3HT: $\text{FeCl}_3 = 1:4$, $4:1$, and $10:1$, respectively. The primary structure was evaluated using ^1H NMR spectrum and SEC measurements. Figure ESI 6 shows the ^1H NMR spectra for P3HT obtained using ratios a) 3HT: $\text{FeCl}_3 = 1:4$, b) 3HT: $\text{FeCl}_3 = 4:1$ and c) 3HT: $\text{FeCl}_3 = 10:1$.

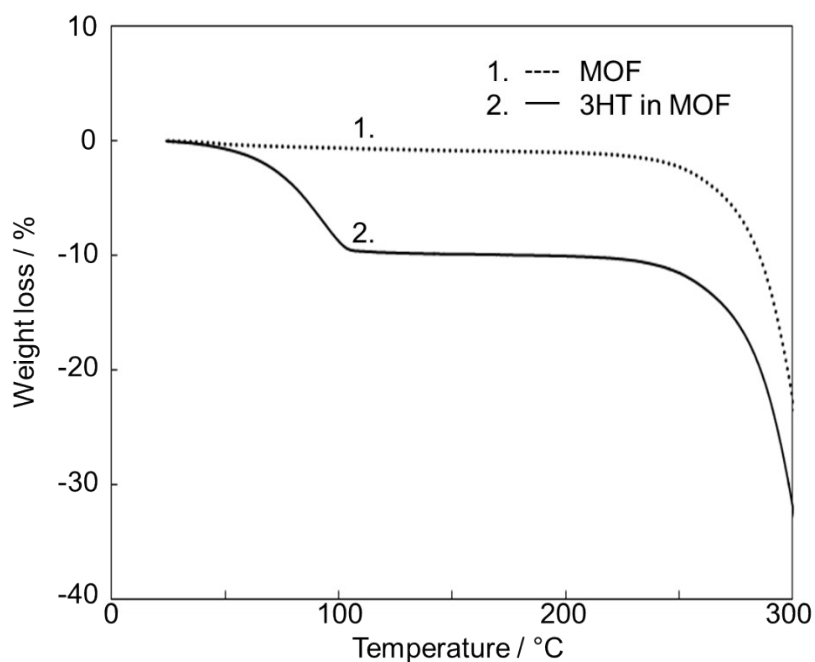
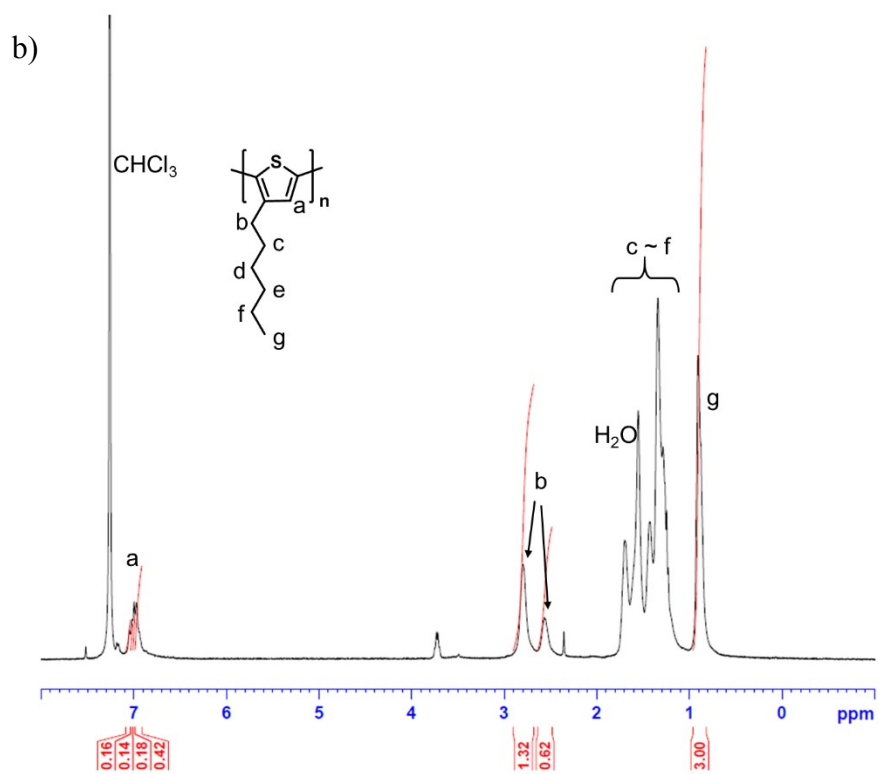
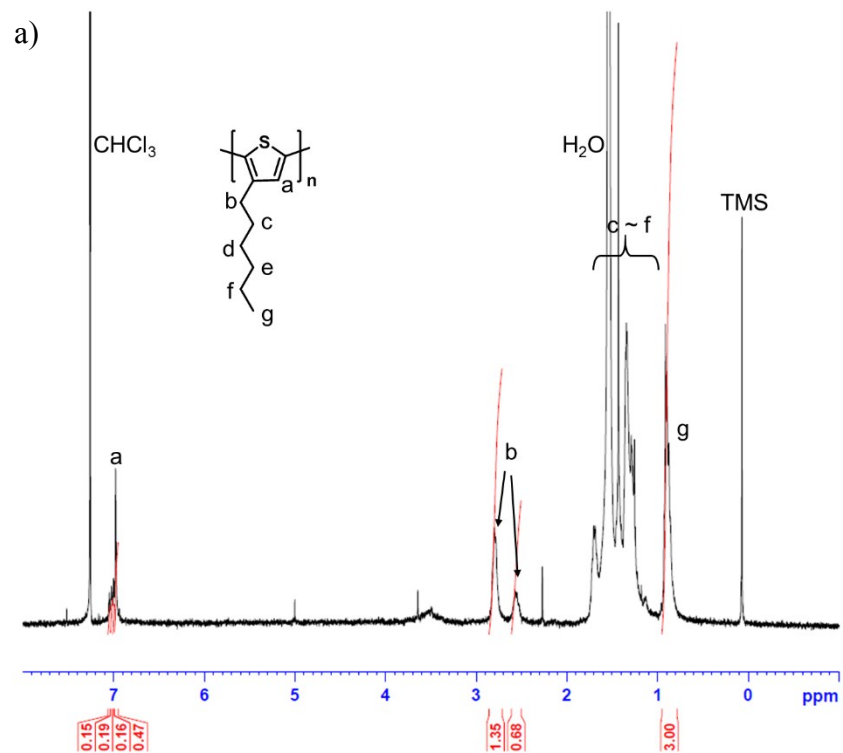


Figure ESI 5. TGA profiles of MOF and 3HT in MOF.



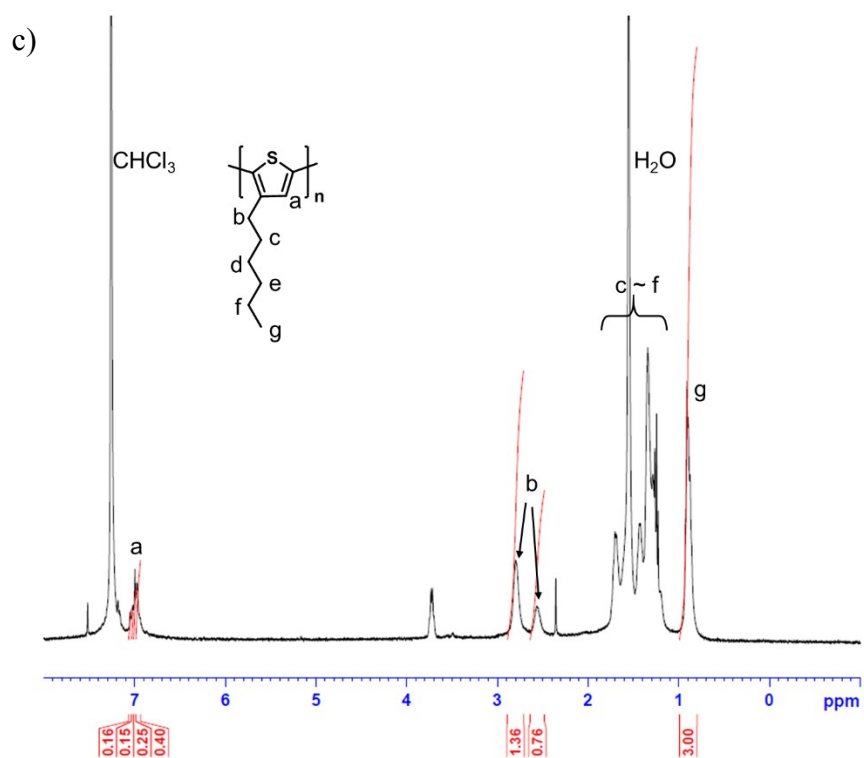


Figure ESI 6. ¹H NMR spectra for P3HT obtained from a) 3HT: FeCl₃ = 1:4, b) 3HT: FeCl₃ = 4:1 and c) 3HT: FeCl₃ = 10:1.

3. Reference

1. K. Seki and W. Mori, *J. Phys. Chem. B*, 2002, **106**, 1380-1385.