Electronic Supplementary Information

# Effects of bromination of poly(3-hexylthiophene) on the performance of bulk heterojunction solar cells

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## Crystal domain size in the Br-P3HT films and film thickness

The mean size of the P3HT and Br-P3HTs crystallites were calculated from the XRD pattern. (Fig. 3 in the main text.) From the line width of the diffraction at 5.4°, the crystal domain size of P3HT was estimated using the Scherrer equation,[1]

$$L \sim \frac{0.9\,\lambda}{\beta\cos\theta} \qquad (1)$$

where $L$ is the mean size of the polymer crystallites, $\lambda$ is the wavelength of the X-ray, $\beta$ is the full width at half maximum of the diffraction peak in radian, and $\theta$ is the Bragg angle of the diffraction peak. The crystallinity of the film is defined as a product of the peak height and the peak width.[2] The film thickness of each sample was estimated by using a laser scanning confocal microscope (KEYENCE VK-X100). The error in the thickness measurement was approximately ±10nm. The determined values are shown in Table S1.

**Table S1** Crystal domain size, crystallinity, and thickness of each sample.

| | **Domain size / nm** | **Crystallinity / a. u.** | **Thickness (single layer) / nm** | **Thickness (BHJ layer) / nm** |
|---|---|---|---|---|
| **pristine P3HT** | 11.2 | 80 | 62 | 186 |
| **2% Br-P3HT** | 12.6 | 67 | 67 | 164 |
| **11% Br-P3HT** | 14.1 | 46 | 83 | 165 |
| **22% Br-P3HT** | 13.8 | 37 | 96 | 162 |
| **37% Br-P3HT** | 9.6 | 18 | 76 | 165 |
| **66% Br-P3HT** | — | — | 46 | 113* |
| **84% Br-P3HT** | — | — | 35 | 171* |
| **100% Br-P3HT** | — | — | —* | 116* |

* ununiformed film structure

## Br-P3HT:PCBM bulk heterojunction solar cells with a conventional top electrode

We fabricated a solar cell with a conventional architecture, where Au was used as the top electrode instead of the CNT-sheet electrode. The device structure was glass/ ITO/ ZnO/ P3HT:PCBM/ PEDOT:PSS/ Au (from bottom to top). The device fabrication condition of the ITO/ZnO/P3HT:PCBM part was same as the main text. (See the device fabrication method in the main text.) After the spin coating, the samples were moved into a glove box and allowed to dry over 2 h and then were annealed at 120°C for 5 min. On top of the P3HT:PCBM bulk heterojunction layer, a solution of PEDOT:PSS (1.3 wt% dispersed in $H_2O$, conductive grade, Aldrich), mixed with 2-propanol in a 1:5 volume ratio, was spin coated (1500 rpm, 60 s) in an ambient atmosphere. Finally, the samples were transferred to a vacuum chamber for the deposition of Au top electrode (80 nm thick).

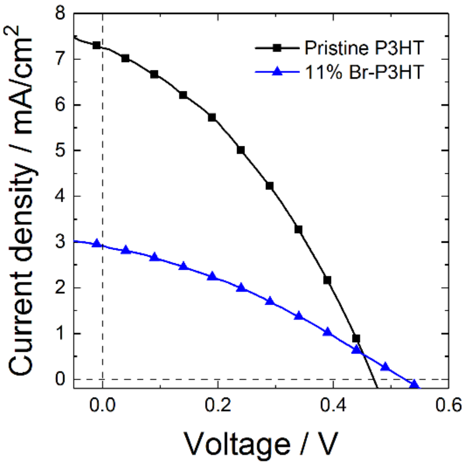


**Fig. S1** Typical photo *J–V* characteristics of ITO/ZnO/P3HT:PCBM/PEDOT:PSS/Au cell. ■ : pristine P3HT:PCBM BHJ cell ($J_{SC}$ = 7.25 mA/cm$^2$, $V_{OC}$ = 0.47 V, *FF* = 0.36, $\eta$ = 1.23 %) ▲: 11% BR-P3HT:PCBM BHJ cell($J_{SC}$ = 2.93 mA/cm$^2$, $V_{OC}$ = 0.52 V, *FF* = 0.32, $\eta$ = 0.49 %)

Figure S1 shows a typical photo *J–V* characteristics of the bulk heterojunction (BHJ) solar cells using the pristine P3HT (■) and the 11% Br-P3HT (▲) as the donor polymer. The $J_{SC}$ of 11% Br-P3HT cell was approximately 40 % of that of pristine P3HT. The relative difference of $J_{SC}$ between the two samples was comparable level of the difference in the CNT-sheet electrode cell (50%). The relatively thick BHJ layers (160 ~ 180 nm) were probably a reason of the poor performance.

## Bromination effects in the low regioregularity polymers

A representative P3HT was synthesized according to a literature procedure, in which $C_6H_{13}MgBr$ was used instead of $C_{12}H_{25}MgBr$.[3] The regioregular head-to-tail ratio was determined to be approximately 83% as estimated from $^1$H NMR analysis, in which the number-average molecular weight and polydispersity of synthesized P3HT derived from the GPC diagrams was $M_n = 22500$, $M_W/M_n = 1.5$. Thus, P3HT was synthesized repeatedly. Fully or partially brominated P3HT was synthesized according to a literature procedure,[4] in which partially brominated P3HT was prepared by changing the ratio of *N*-Bromosuccinimide toward P3HT. The Br concentrations of 4%, 12%, 27%, 51%, 65%, 90%, and 100% were synthesized.

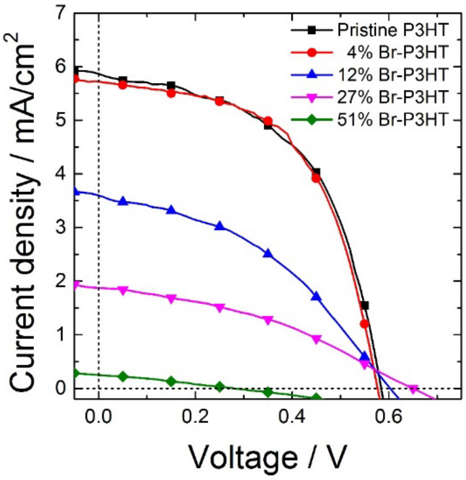


**Fig. S2** Typical photo *J*–*V* characteristics of ITO/ ZnO/ BHJ/ CNT-sheet: Ag NW :PEDOT:PSS cells. Each symbol corresponds to the structure of BHJ layer: –■– : pristine P3HT:PCBM, –●– : 4% Br-P3HT:PCBM, –▲–: 12% Br-P3HT:PCBM, –▼–: 27% Br-P3HT:PCBM, –◆–: 51% Br-P3HT:PCBM.

**Table S2** A summary of the photovoltaic characteristics; $J_{SC}$, $V_{OC}$, *FF* and $\eta$ as functions of bromination degree of P3HT.

| | $J_{SC}$ / mA/cm$^2$ | $V_{OC}$ / V | *FF* | $\eta$ / % |
|---|---|---|---|---|
| **pristine P3HT** | 5.86 | 0.58 | 0.52 | 1.77 |
| **4% Br-P3HT** | 5.63 | 0.57 | 0.52 | 1.67 |
| **12% Br-P3HT** | 3.6 | 0.6 | 0.41 | 0.89 |
| **27% Br-P3HT** | 1.84 | 0.65 | 0.37 | 0.44 |
| **51% Br-P3HT** | 0.25 | 0.28 | 0.28 | 0.02 |

Figure S2 shows the photo *J*–*V* characteristics of BHJ solar cells with 4%, 12%, 27%, and 51% Br-

P3HT as the donor polymer. The results from pristine P3HT devices are also shown for comparison. Each curve shows the best performance data from our fabricated solar cells. The solar cells made with a bromination degree greater than 65% showed no photovoltaic effect. The photovoltaic characteristics were summarized in Table S2. The $J_{\mathrm{SC}}$ was decreased with the increase of the bromination degree, which was also seen in the high regioregularity polymer case in the main text. The $J_{\mathrm{SC}}$ of the 4% Br-P3HT cell showed only a slight decrease compared with that of the pristine P3HT cell, although the 2% Br-P3HT cell in the main text showed a relatively large decrease. The low regioregularity may play a role for this difference since both the regioregularity and the bromination of P3HT would have an impact on the charge transport in P3HT:PCBM BHJ films. Note that the relative decrease of $J_{\mathrm{SC}}$ at around 10% of bromination degree showed similar value both in high and low regioregularity P3HT.

## Incident photon to current conversion efficiency

Incident photon to current conversion efficiency (IPCE) was performed using a homemade experimental system. Figure S3 shows IPCE spectra of ITO/ ZnO/ pristine P3HT:PCBM/ CNT-sheet:Ag NW:PEDOT:PSS cell and ITO/ ZnO/ 11% Br-P3HT:PCBM/ CNT-sheet:Ag NW:PEDOT:PSS cell. Note that the IPCE was normalized with the peak intensity of pristine P3HT cell.

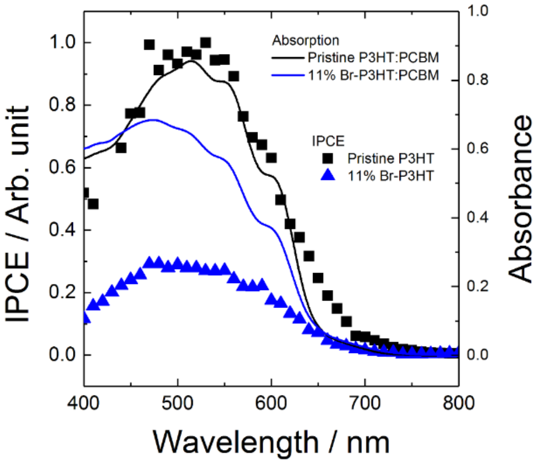


**Fig. S3** IPCE of pristine P3HT:PCBM (■) and 11% Br-P3HT:PCBM (▲) cells. The absorption spectra of each cell (balck line: pristine P3HT:PCBM, blue line: 11% Br-P3HT:PCBM) are also shown.

## Gel permeation chromatography (GPC) analysis

GPC curves are shown below. It was indicated that the peak around 20 min – 25 min in each curve is derived from the stabilizer in THF, which was used as the solvent in GPC analysis. All brominated P3HT samples were synthesized in the same procedure by changing ratio of *N*-Bromosuccinimide (NBS). However, the peak top in only two GPC curves of 22% Br-P3HT and 100%-Br P3HT was slightly separated. Although P3HT as starting material was monodisperse and synthetic procedure was based on the literature[4], in which 100%-Br-P3HT of monodisperse was prepared, the reason is not clear.

Pristine P3HT

Peak start: 12.000 min
Peak top: 13.757 min
Peak end: 18.000 min
Mn = 49231, Mw= 84496, Mw/Mn = 1.72

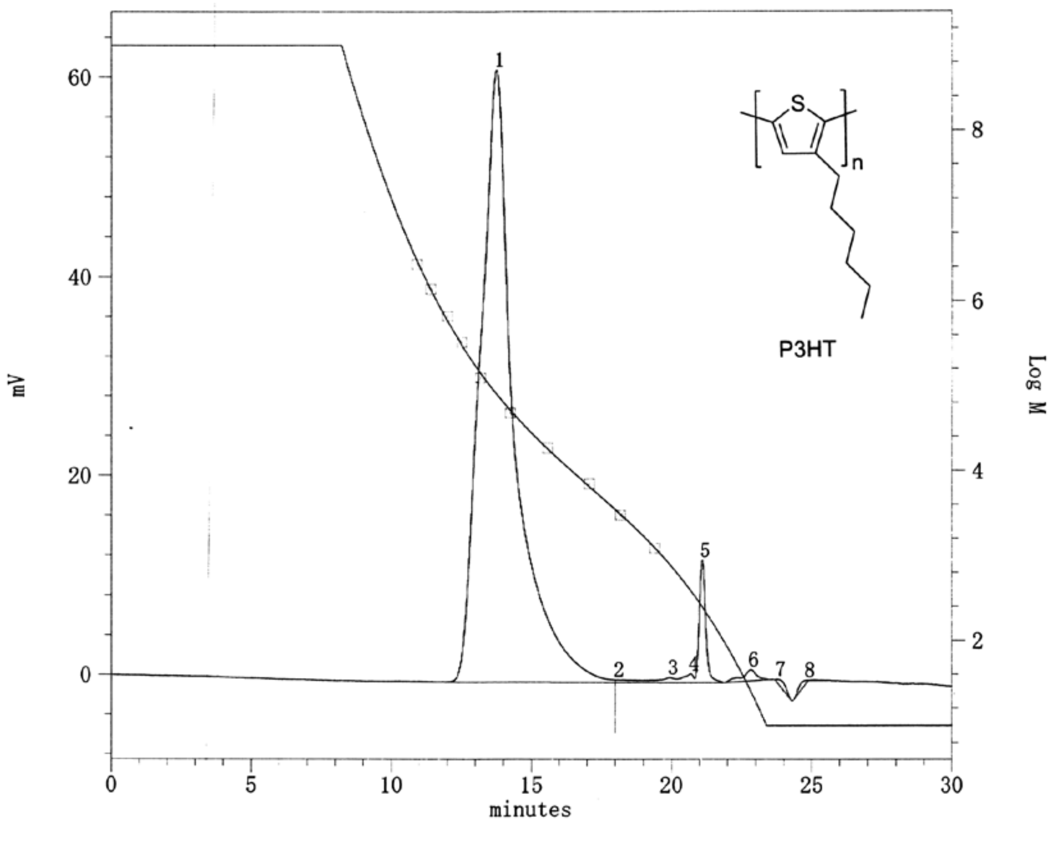


**Fig. S4** GCP curve of pristine P3HT

2% Br-P3HT

Peak start: 12.400 min

Peak top: 13.970 min

Peak end: 18.367 min

Mn = 28503, Mw= 49469, Mw/Mn = 1.74

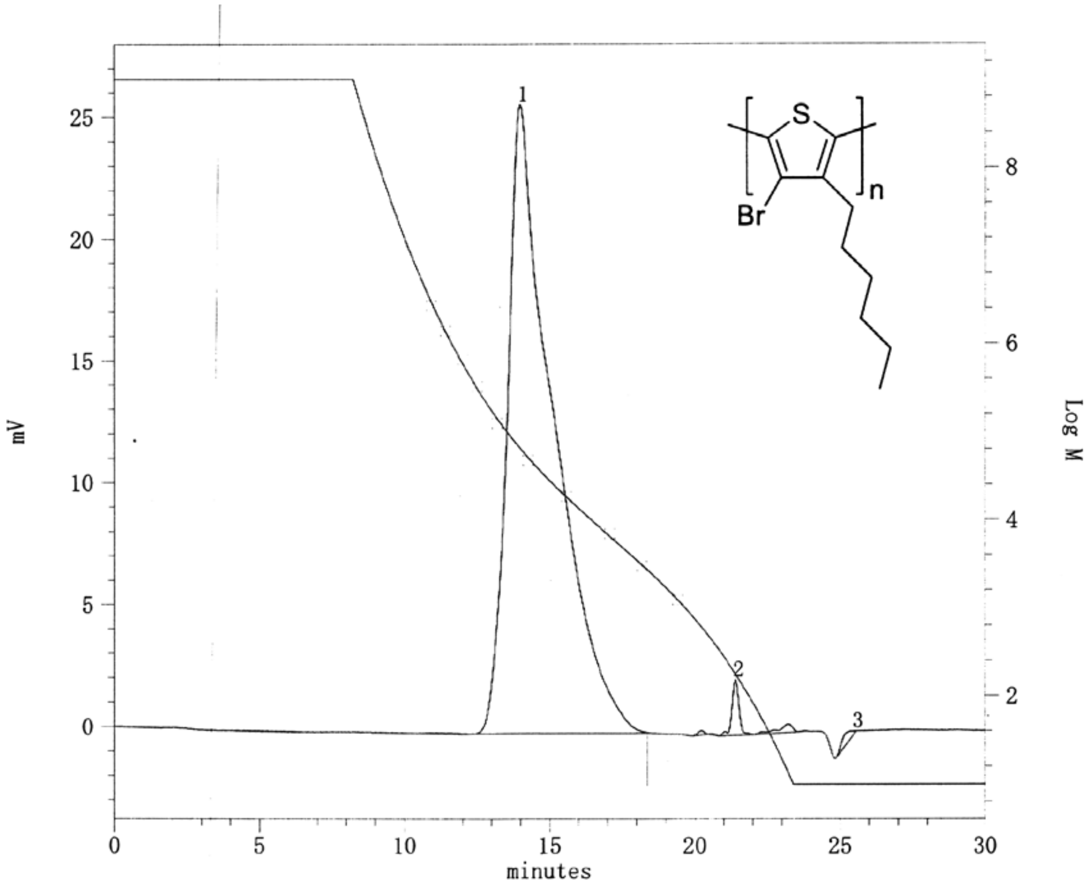


**Fig. S5** GCP curve of 2% Br-P3HT

11% Br-P3HT

Peak start: 11.400 min

Peak top: 13.702 min

Peak end: 18.367 min

Mn = 48849, Mw= 89328, Mw/Mn = 1.83

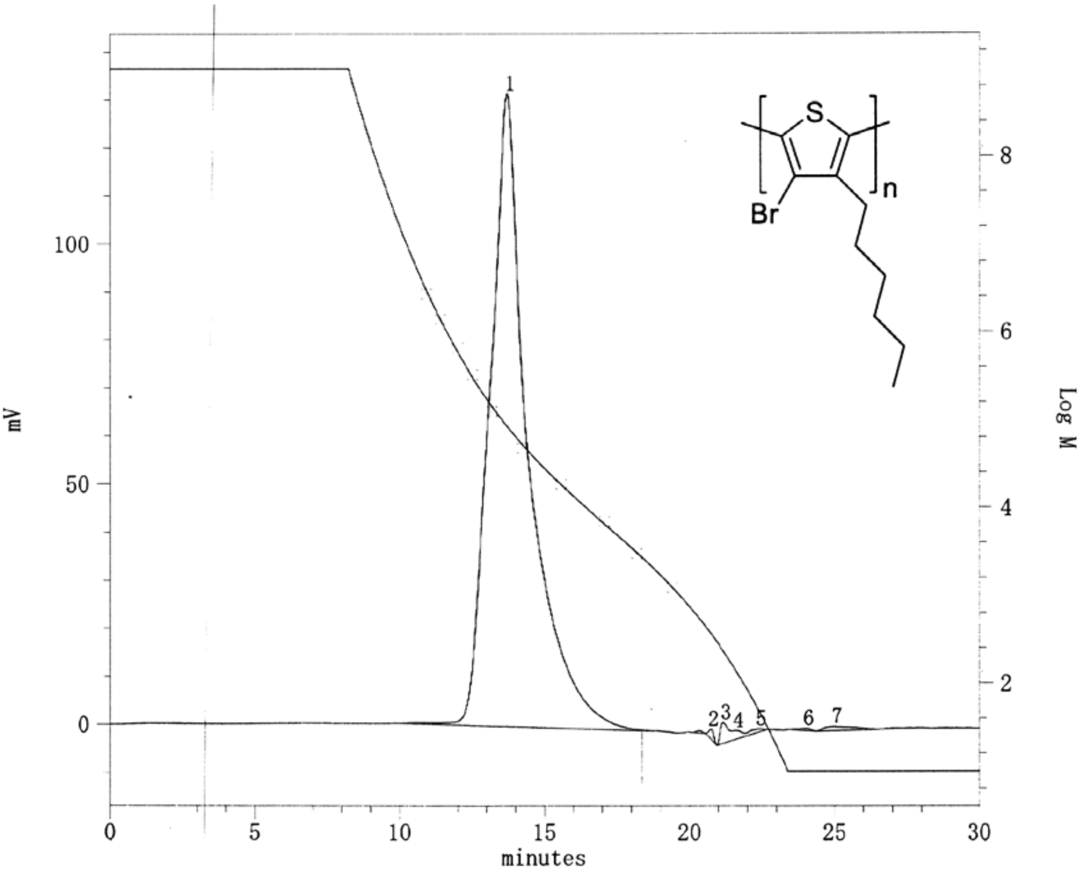


**Fig. S6** GCP curve of 11% Br-P3HT

22% Br-P3HT

Peak start: 11.767 min

Peak top: 14.198 min

Peak end: 18.067 min

Mn = 51158, Mw= 88799, Mw/Mn = 1.74

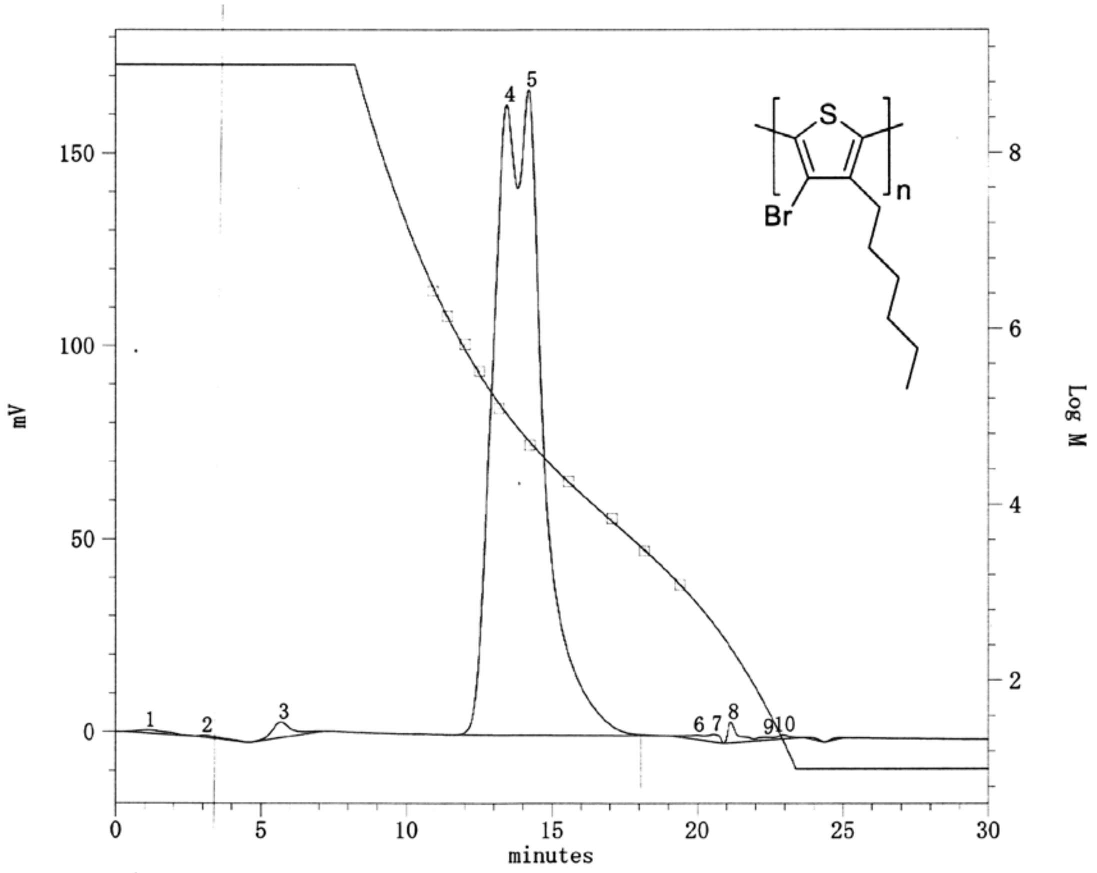


**Fig. S7** GCP curve of 22% Br-P3HT

37% Br-P3HT

Peak start: 11.000 min

Peak top: 13.720 min

Peak end: 17.900 min

Mn = 59021, Mw= 114799, Mw/Mn = 1.95

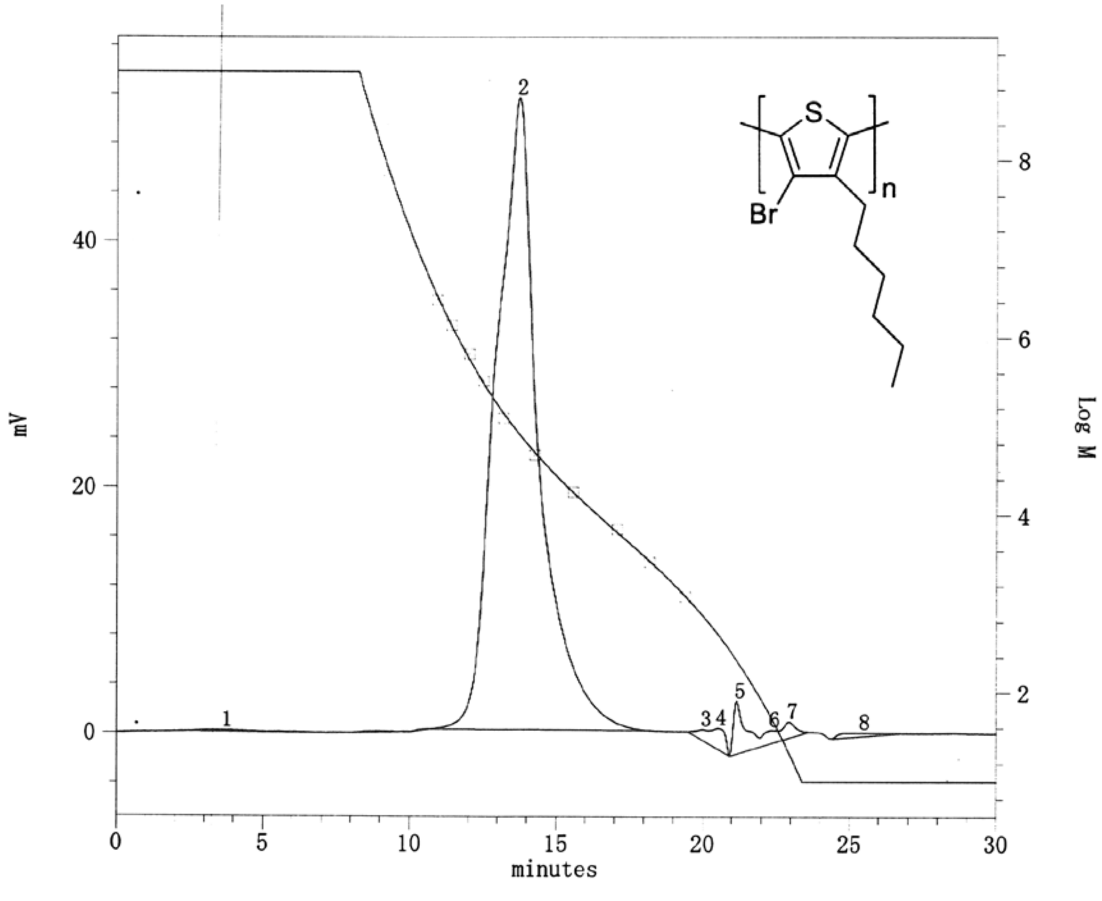


**Fig. S8** GCP curve of 37% Br-P3HT

66% Br-P3HT

Peak start: 11.300 min

Peak top: 13.732 min

Peak end: 18.167 min

Mn = 49040, Mw= 97031, Mw/Mn = 1.98

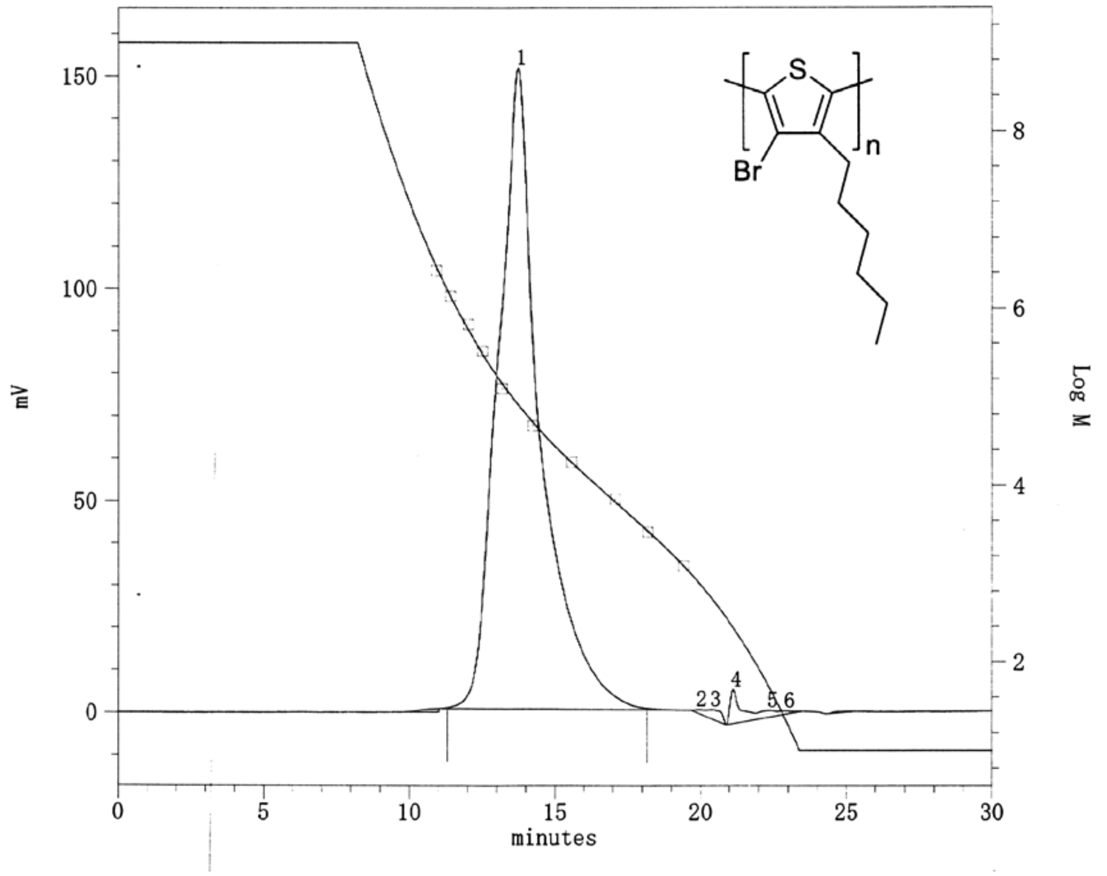


**Fig. S9** GCP curve of 66% Br-P3HT

84% Br-P3HT

Peak start: 11.233 min

Peak top: 13.783 min

Peak end: 18.100 min

Mn = 49471, Mw= 94183, Mw/Mn = 1.90

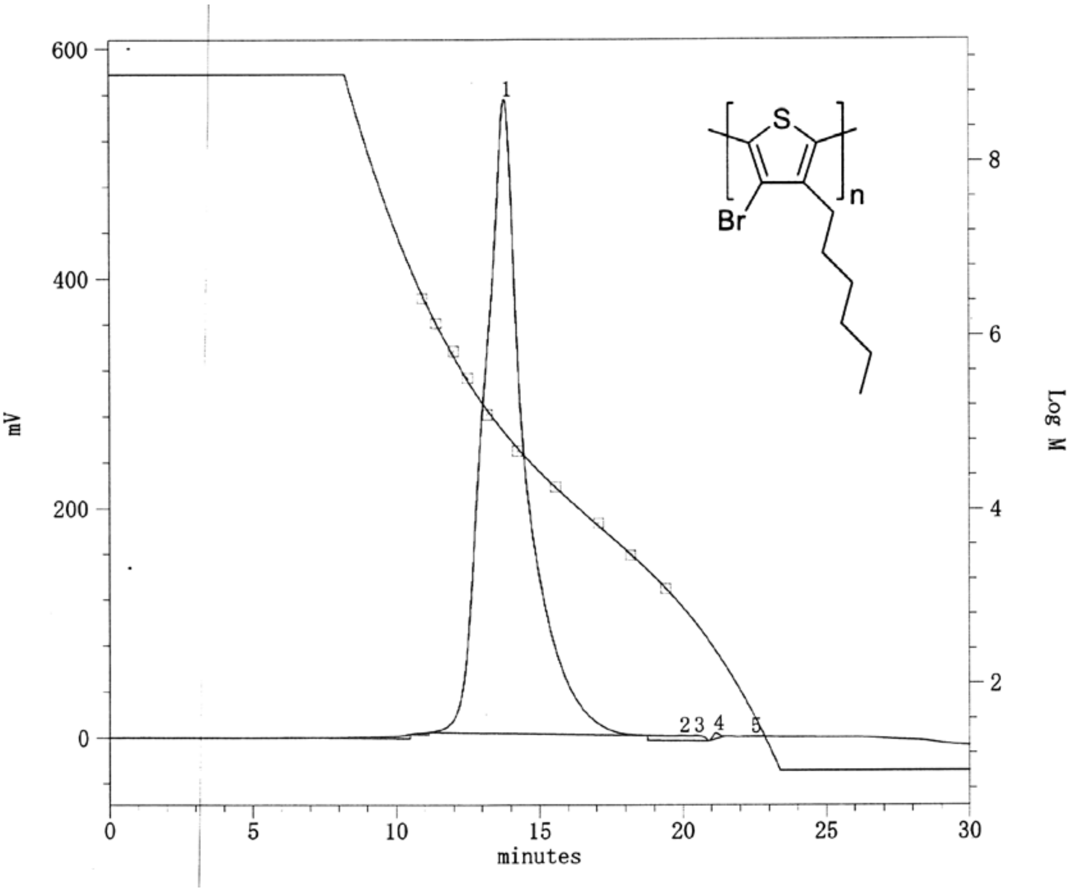


**Fig. S10** GCP curve of 84% Br-P3HT

100% Br-P3HT

Peak start: 11.367 min

Peak top: 14.263 min

Peak end: 18.322 min

Mn = 50617, Mw= 84329, Mw/Mn = 1.67

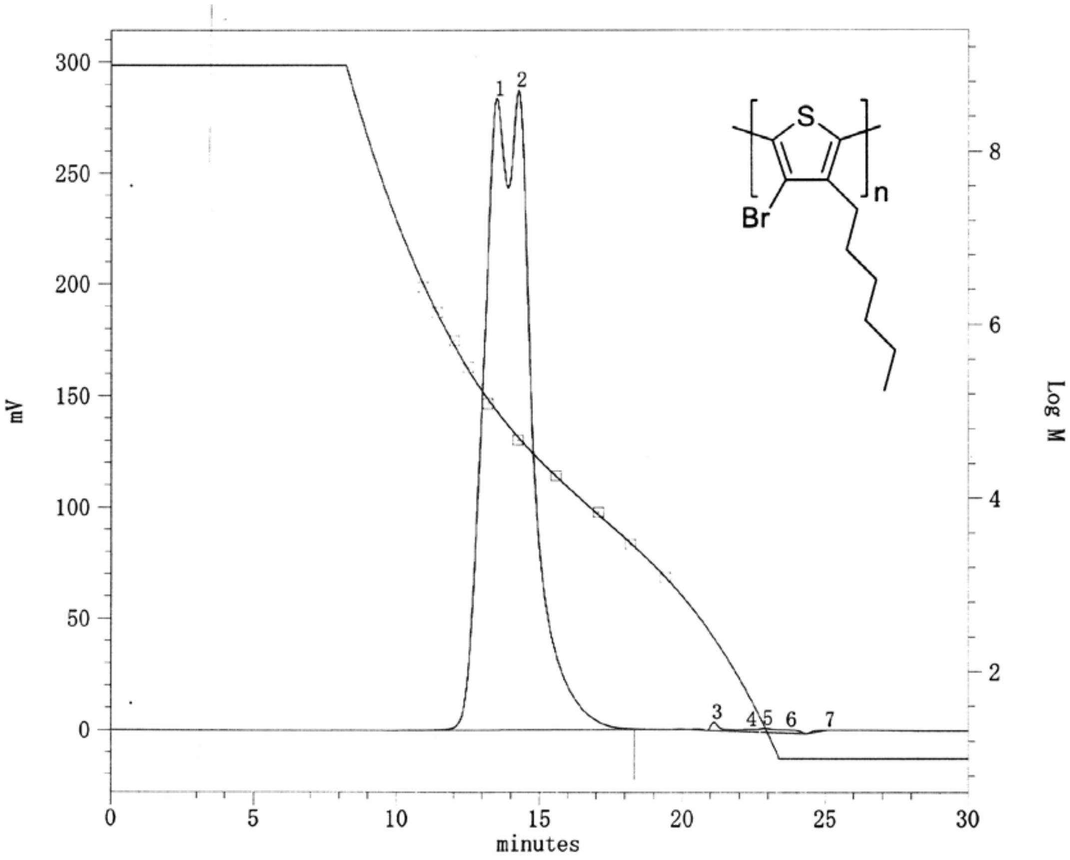
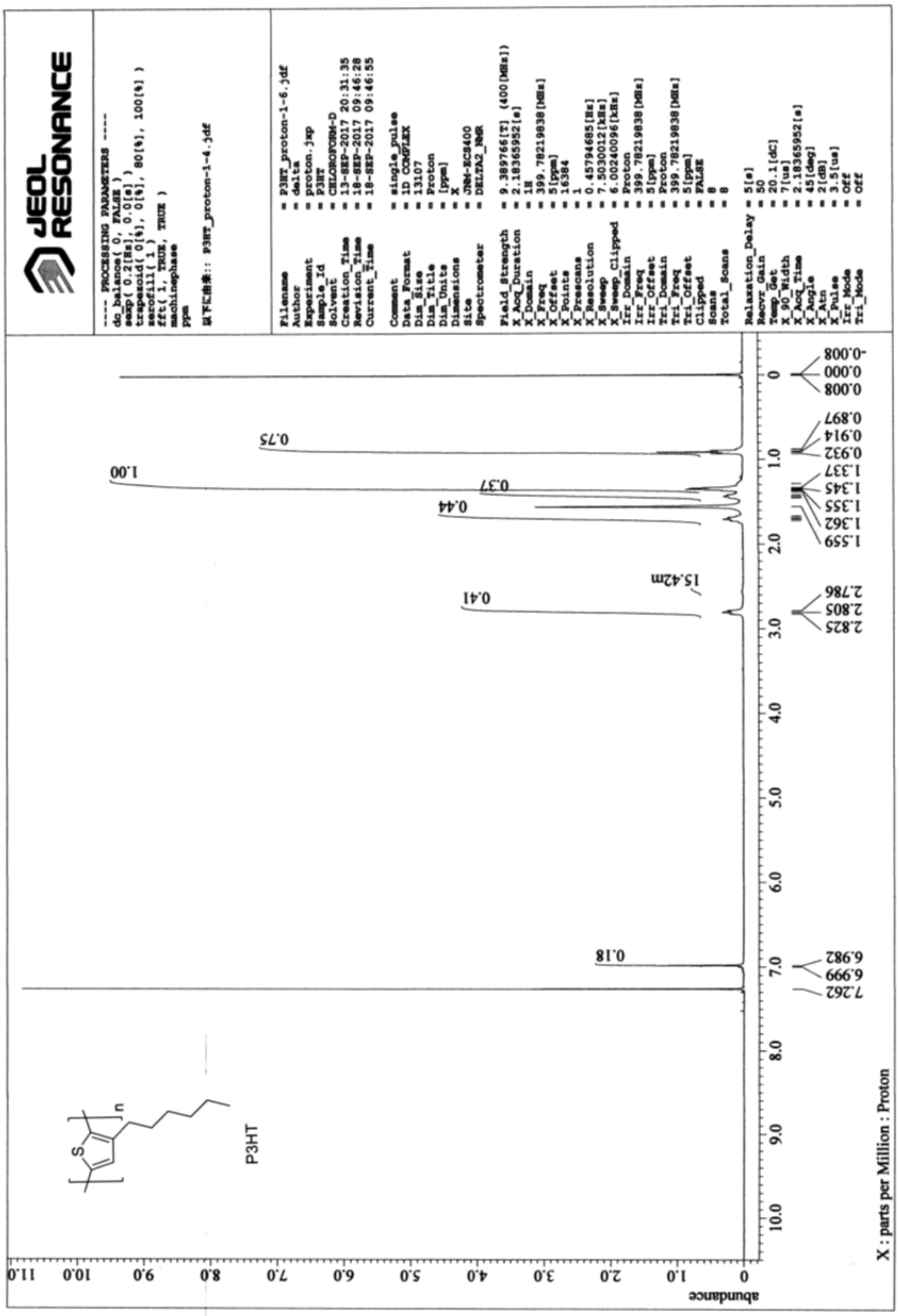


**Fig. S11** GCP curve of 100% Br-P3HT

$^1H$ NMR spectrum in $CDCl_3$



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ppm

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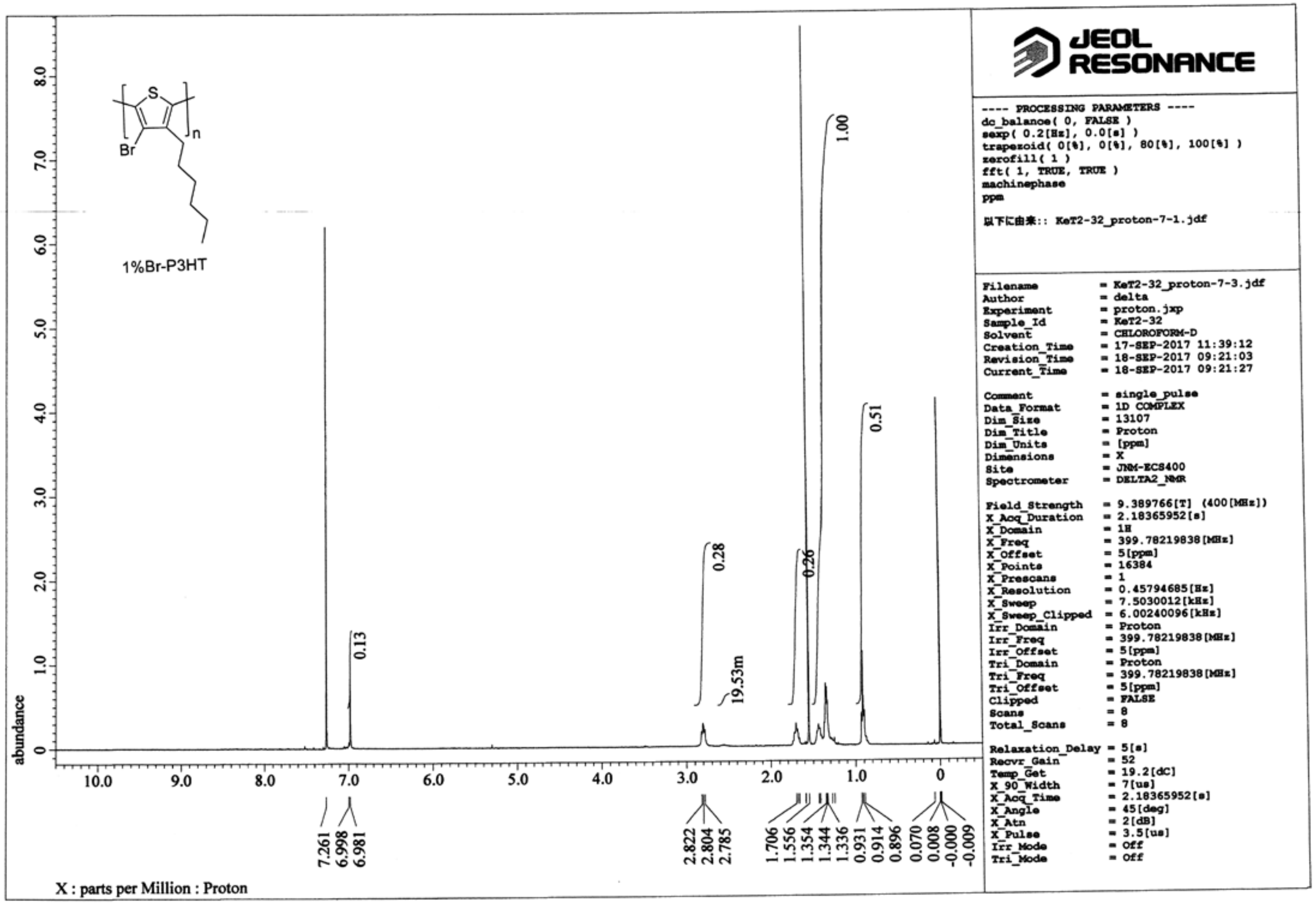
**Fig. S12** $^1H$ NMR spectrum of pristine P3HT



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X_Sweep_Clipped       = 6.00240096[kHz]
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Tri_Freq              = 399.78219838[MHz]
Tri_Offset            = 5[ppm]
Clipped               = FALSE
Scans                 = 8
Total_Scans           = 8

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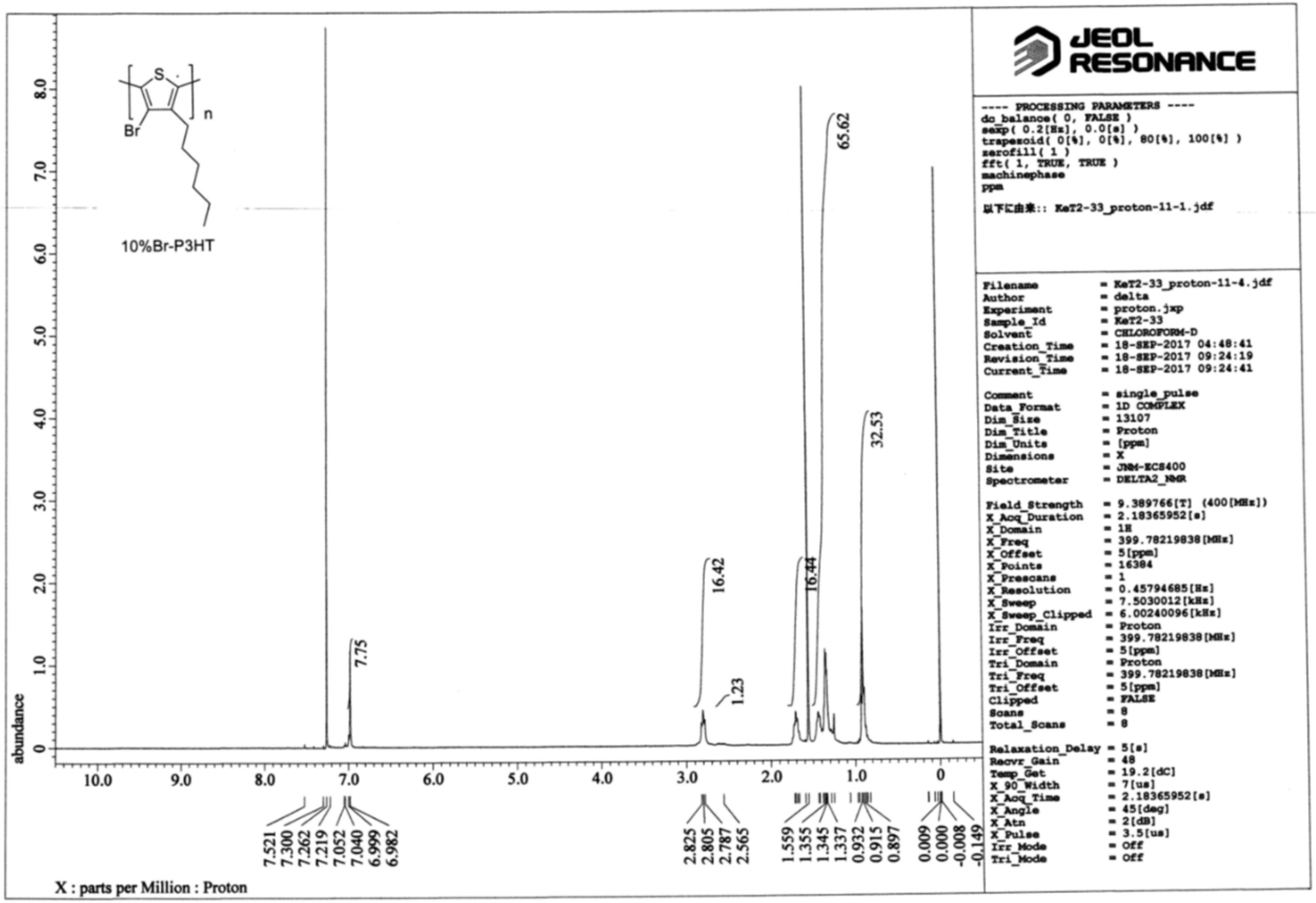
**Fig. S13** $^1$H NMR spectrum of 2% brominated P3HT (The ratio of used NBS to P3HT was 1%.)



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ppm

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Total_Scans        = 8

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**Fig. S14** $^1$H NMR spectrum of 11% brominated P3HT (The ratio of used NBS to P3HT was 10%.)

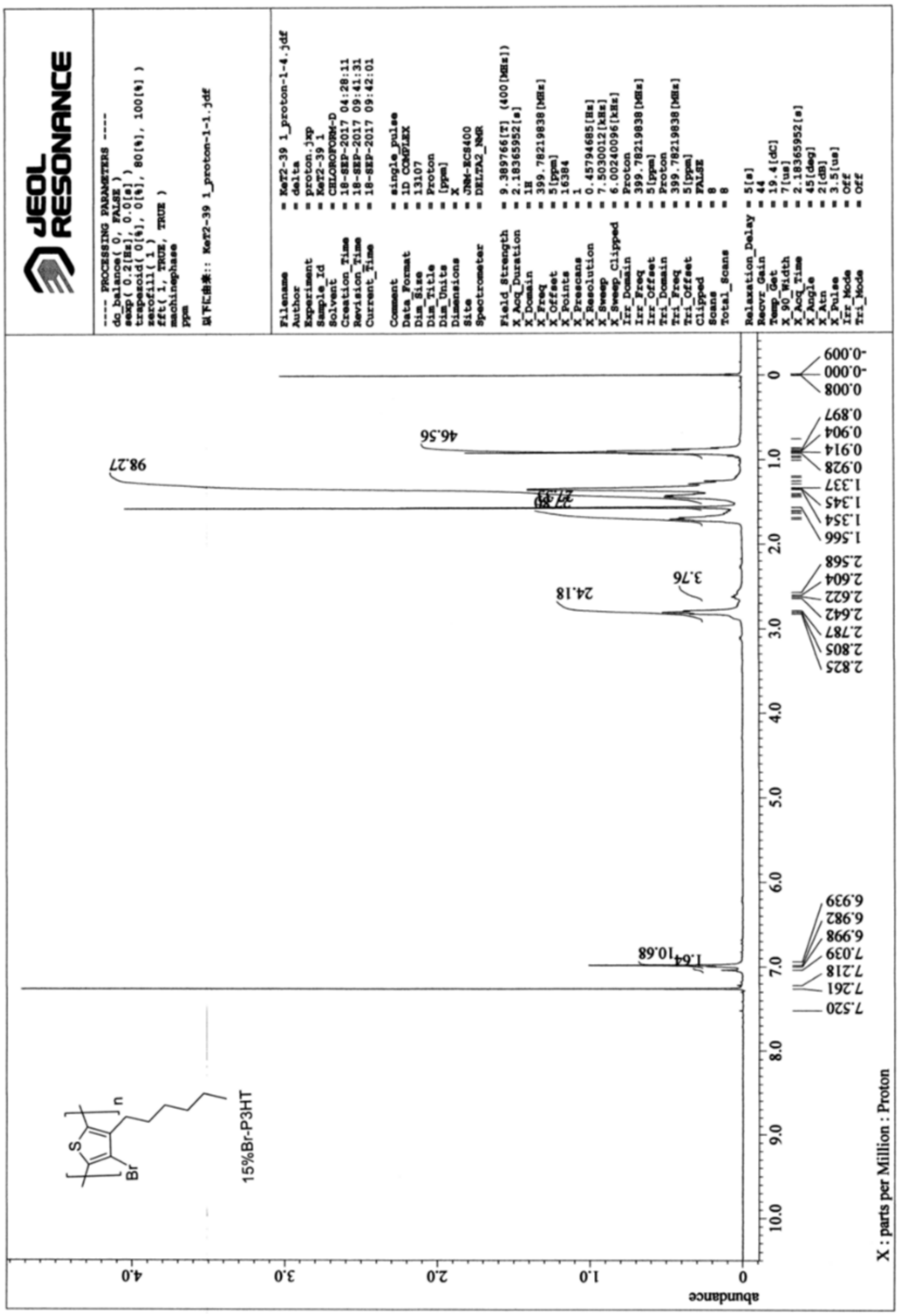


**Fig. S15** $^1$H NMR spectrum of 22% brominated P3HT (The ratio of used NBS to P3HT was 15%.)

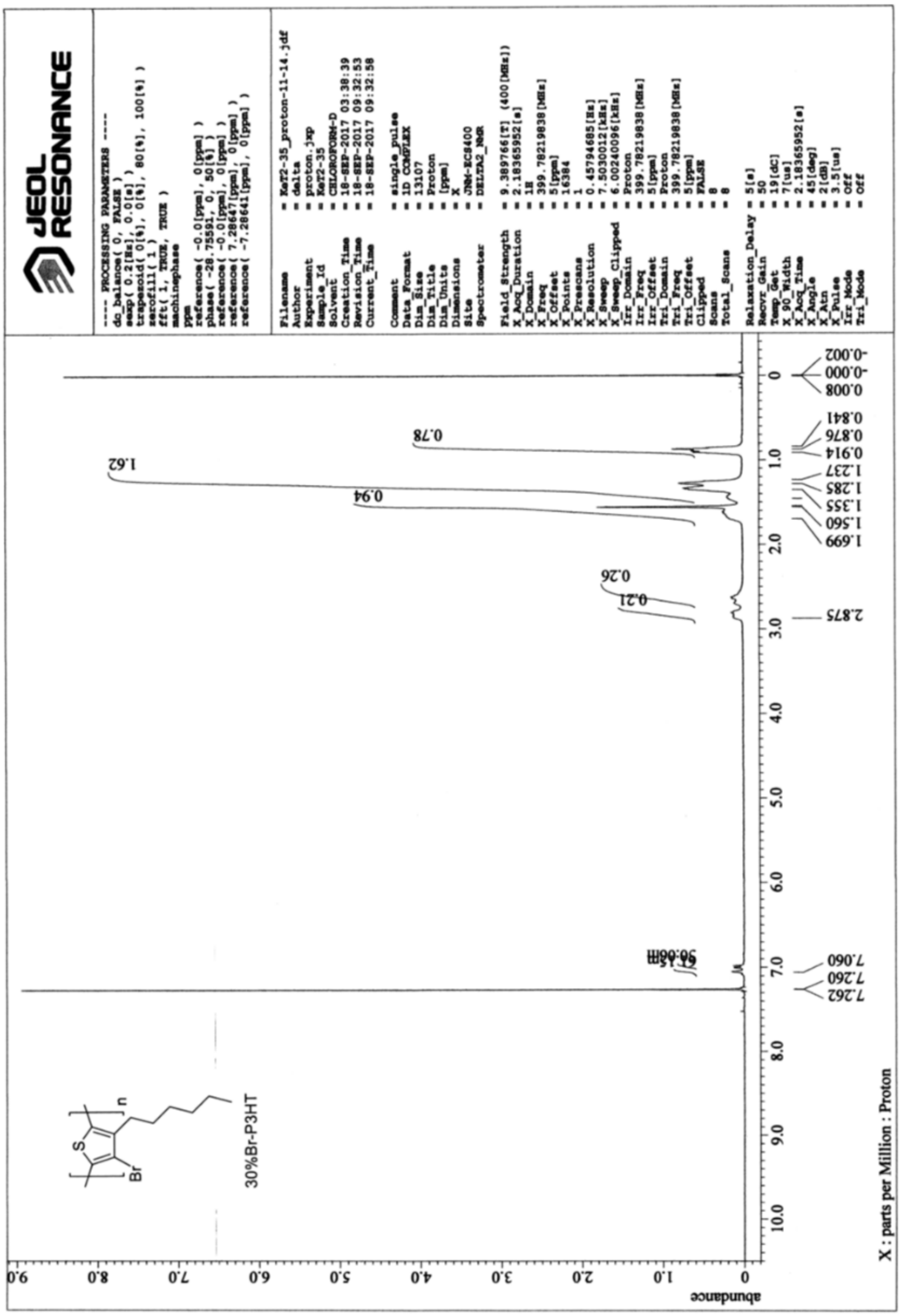


**Fig. S16** $^1$H NMR spectrum of 37% brominated P3HT (The ratio of used NBS to P3HT was 30%.)

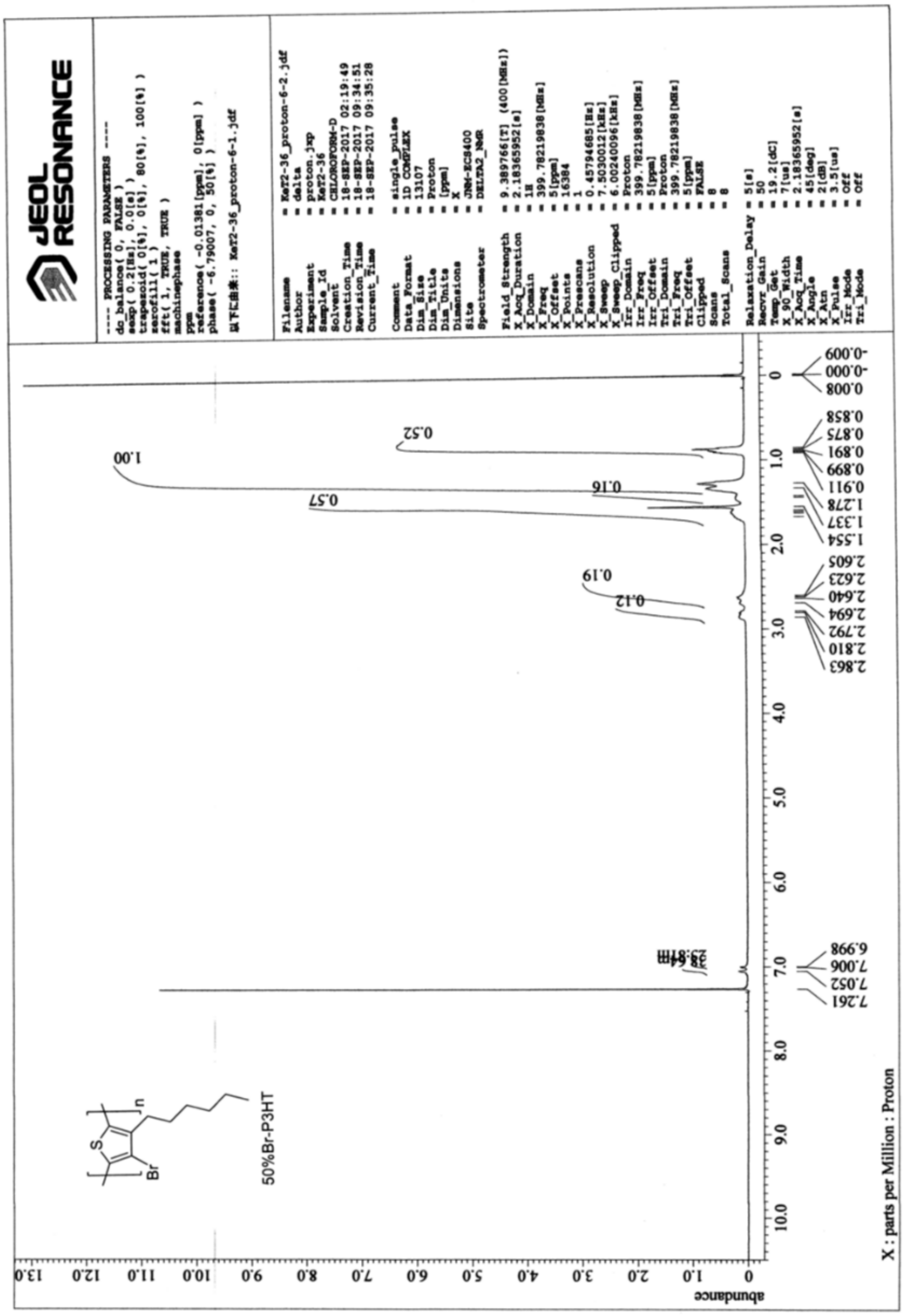
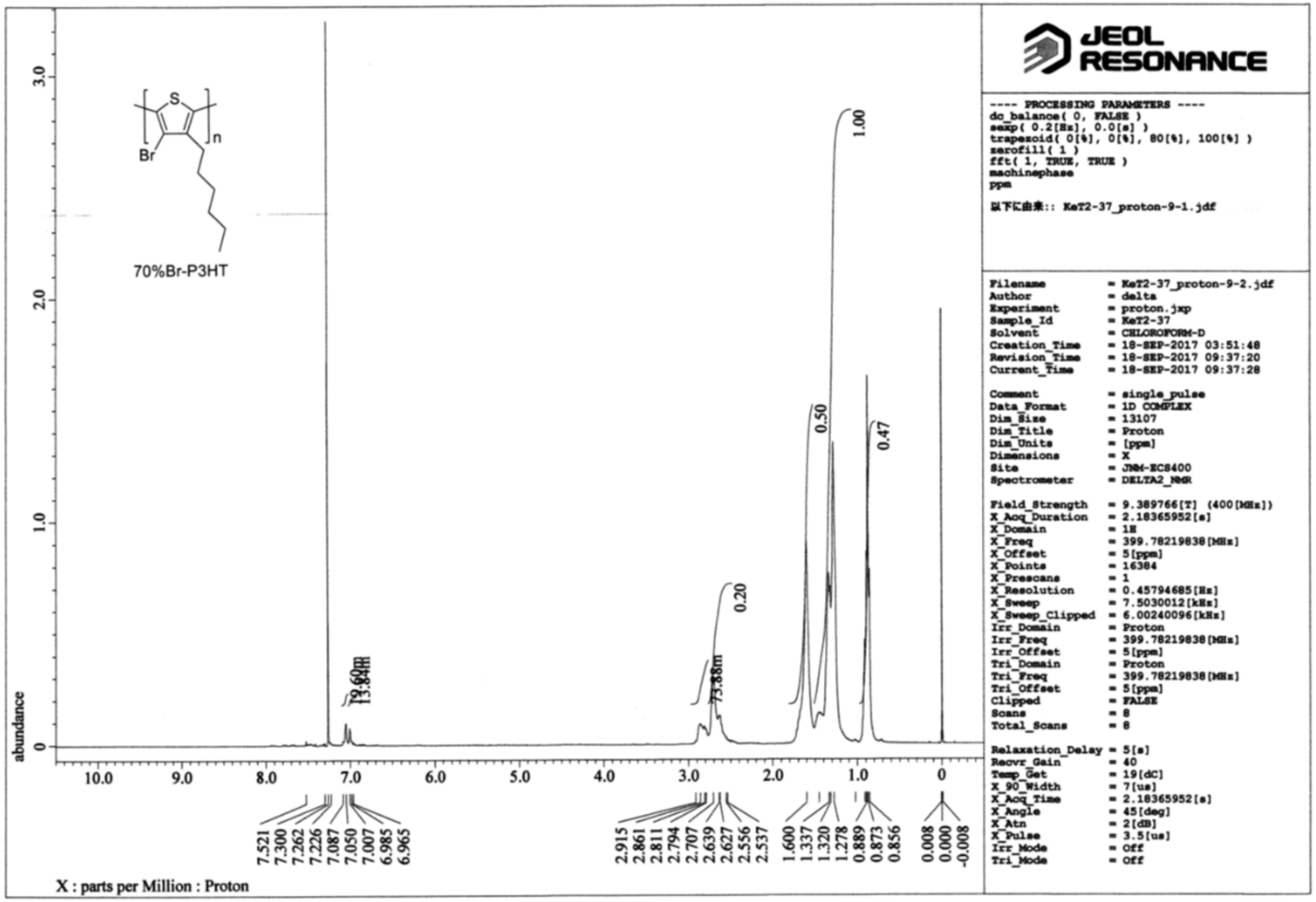


**Fig. S17** $^{1}$H NMR spectrum of 66% brominated P3HT (The ratio of used NBS to P3HT was 50%.)



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X_Sweep_Clipped    = 6.00240096[kHz]
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Clipped            = FALSE
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Total_Scans        = 8

Relaxation_Delay   = 5[s]
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X_Angle            = 45[deg]
X_Atn              = 2[dB]
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**Fig. S18** $^1$H NMR spectrum of 84% brominated P3HT (The ratio of used NBS to P3HT was 70%.)

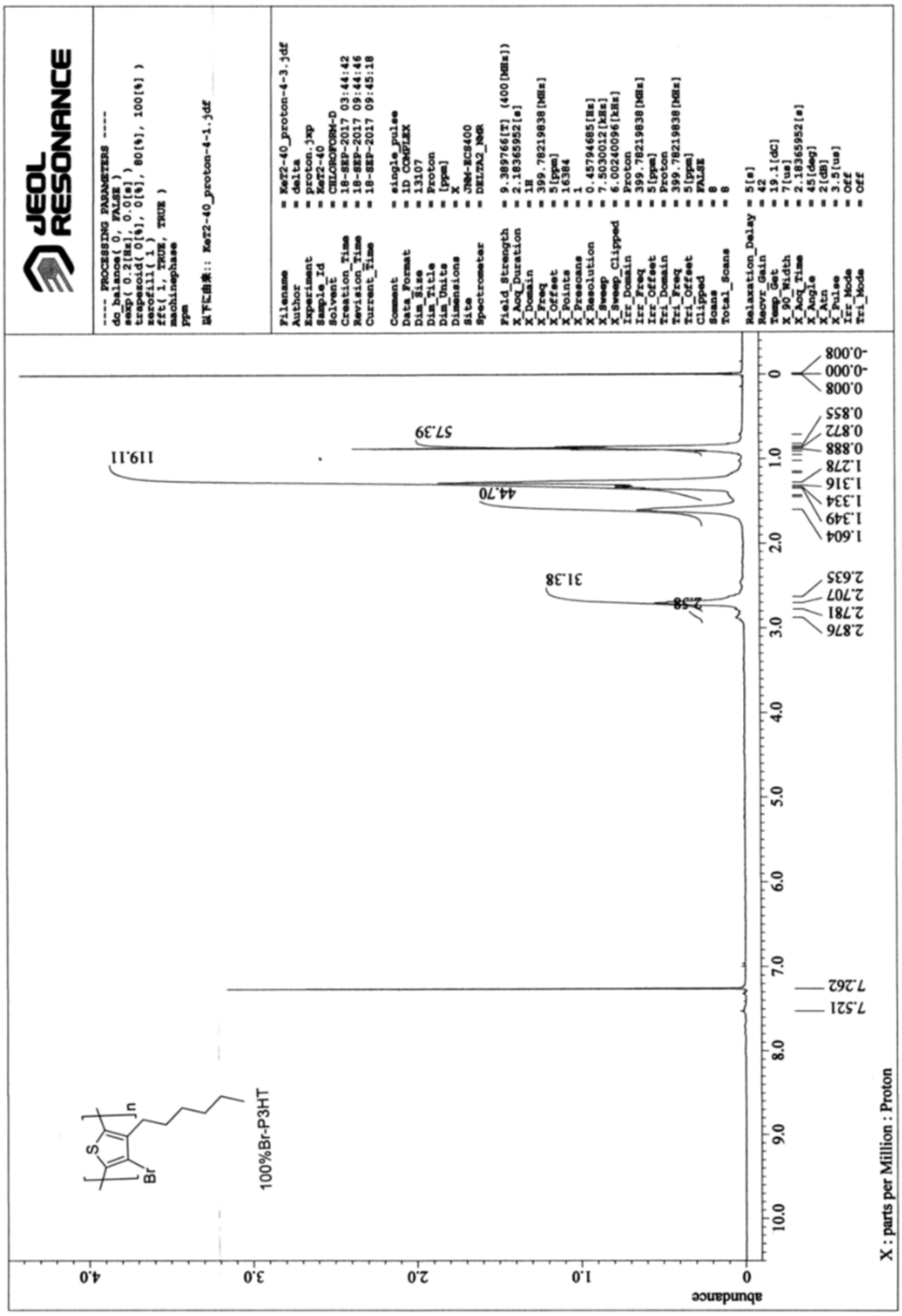

**Fig. S19** $^1$H NMR spectrum of 100% brominated P3HT (The ratio of used NBS to P3HT was 100%.)

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