**Supporting Information**

**Novel NIR Absorbing Benzotrithiophene-Based Copolymers for Organic Photovoltaics**

Hyokwon Kima, 1, Mi-Jeong Choib, 1, Seok-In Nab, \*\*, Kyukwan Zonga, \*

a Department of Chemical Education, Institute of Fusion Science, Chonbuk National University, 567 Baekje-daero, Jeonju 54896, Republic of Korea

b Professional Graduate School of Flexible and Printable Electronics, Polymer Materials Fusion Research Center, Chonbuk National University, 567 Baekje-daero, Jeonju 54896, Republic of Korea

**Contents**

Molecular structures of seven benzotrithiophene isomers S2

1H NMR and 13C NMR of **6a** S3

1H NMR and 13C NMR of **6b** S4

Procedure of the device preparation S5

Device optimization:

1. Concentration S5

2. Additive (DIO) S6

3. Film thickness (RPM) S7

4. Solar cell parameters of the devices fabricated from **P1**~**P3** at optimized condition S8

5. Solar cell parameters of the devices fabricated from **P1** at DIO optimized condition S9



**Figure S1.** Molecular structures of seven benzotrithiophene isomers.

(a) benzo[1,2-c:3,4-c’:5,6-c”]trithiophene (ccc-BTT) (b) benzo[1,2-b:3,4-b’:5,6-b”]trithiophene (bbb-BTT-1) (c) benzo[2,1-b:3,4-b’:5,6-b”]trithiophene (bbb-BTT-2) (d) benzo[1,2-b:3,4-c’:5,6-c”]trithiophene (bcc-BTT) (e) benzo[1,2-b:4,3-b’:5,6-c”]trithiophene (bbc-BTT-1) (f) benzo[1,2-b:4,3-b’:5,6-c”]trithiophene (bbc-BTT-2) (g) benzo[2,1-b:3,4-b’:5,6-c”]trithiophene (bbc-BTT-3)

Figure S2. 1H NMR and 13C NMR of **6a**

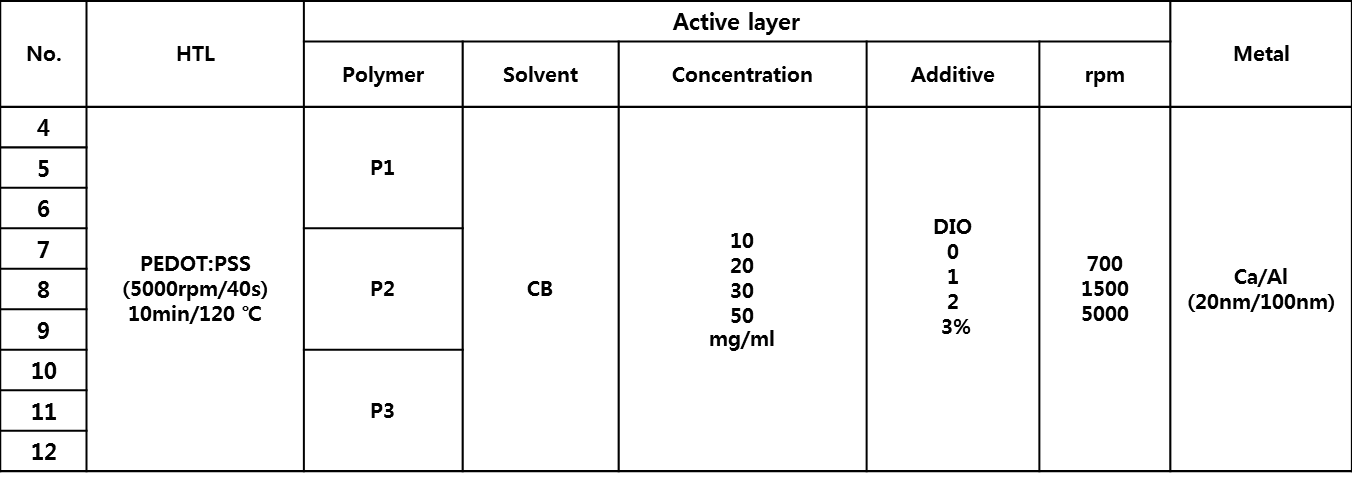




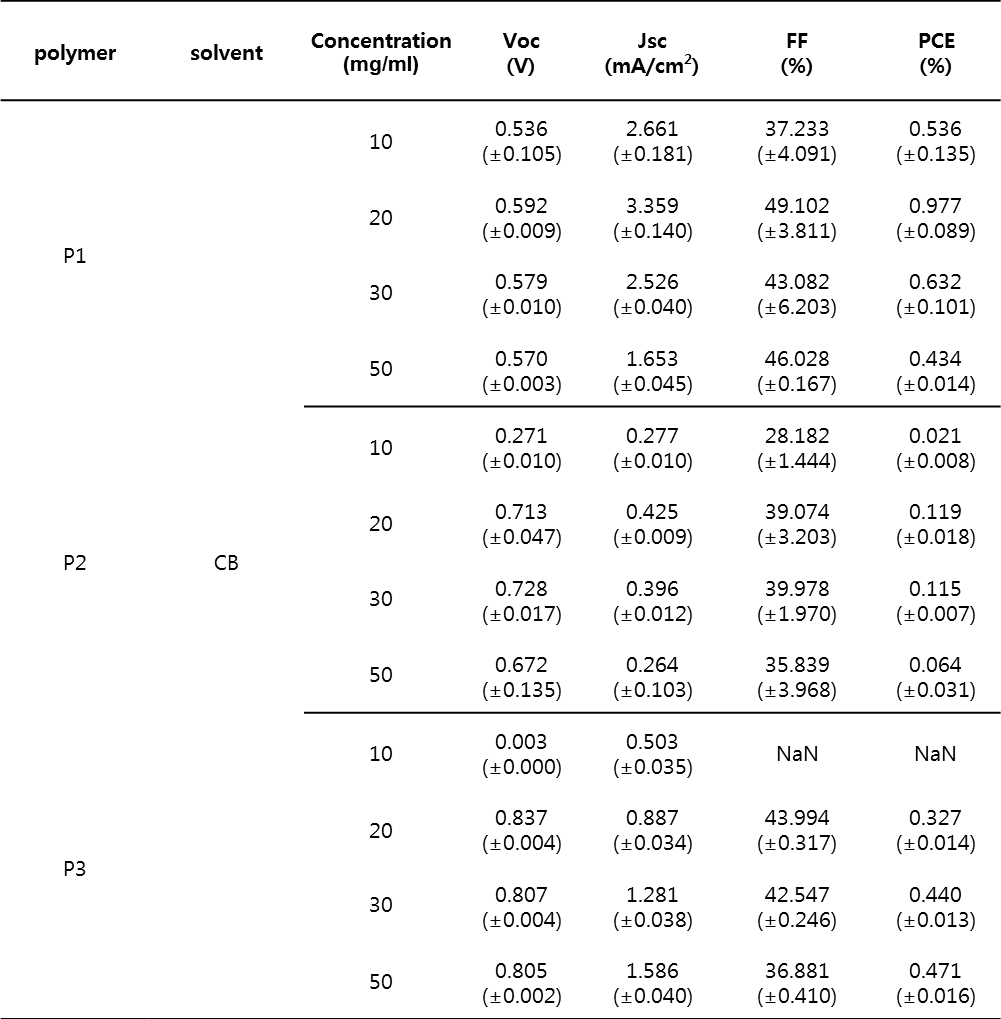
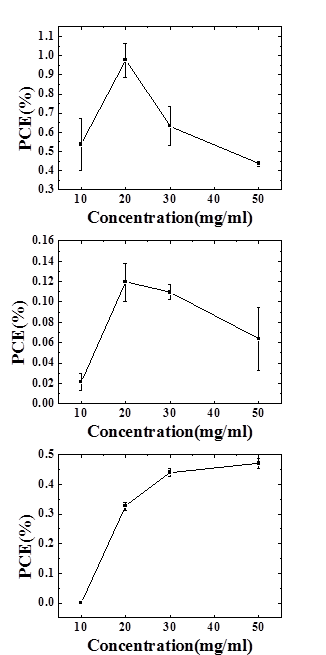
Figure S3. 1H NMR and 13C NMR of **6b**



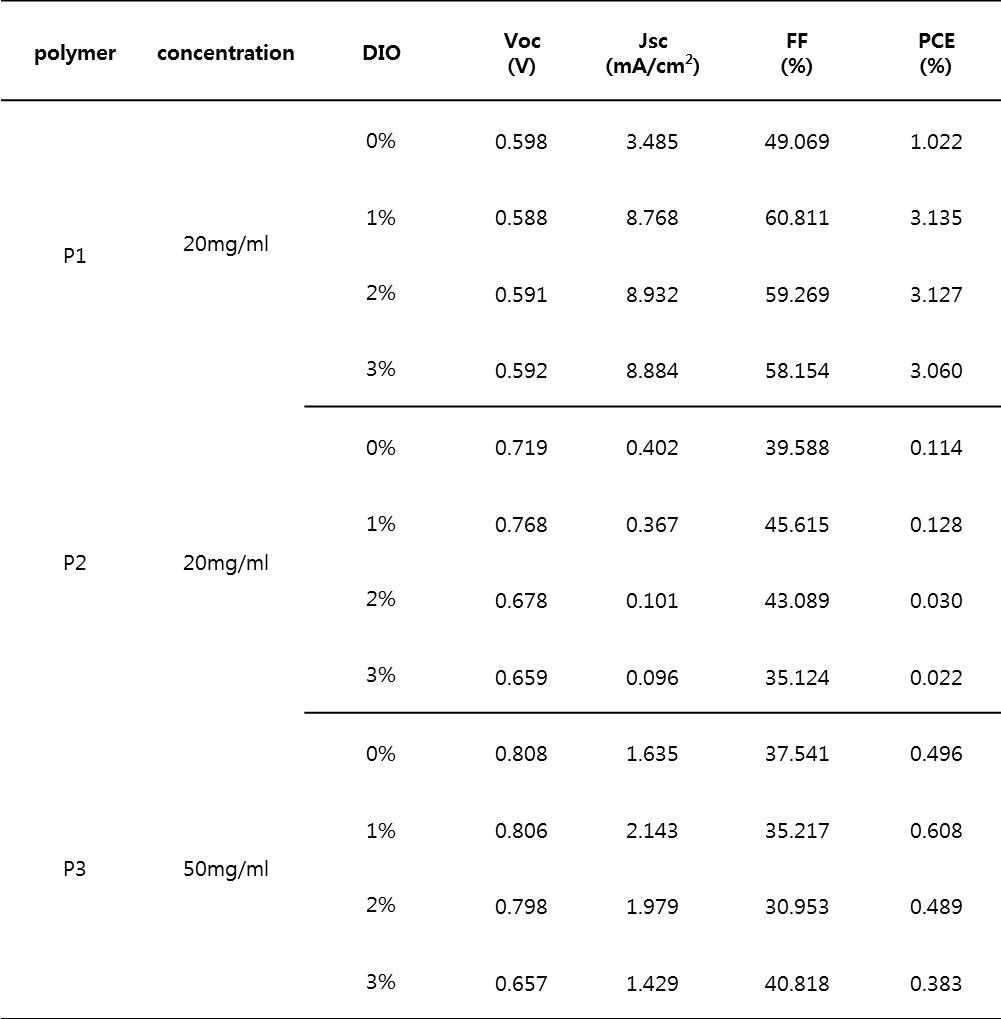
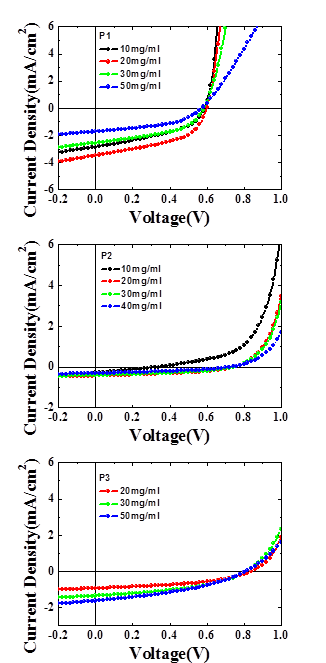




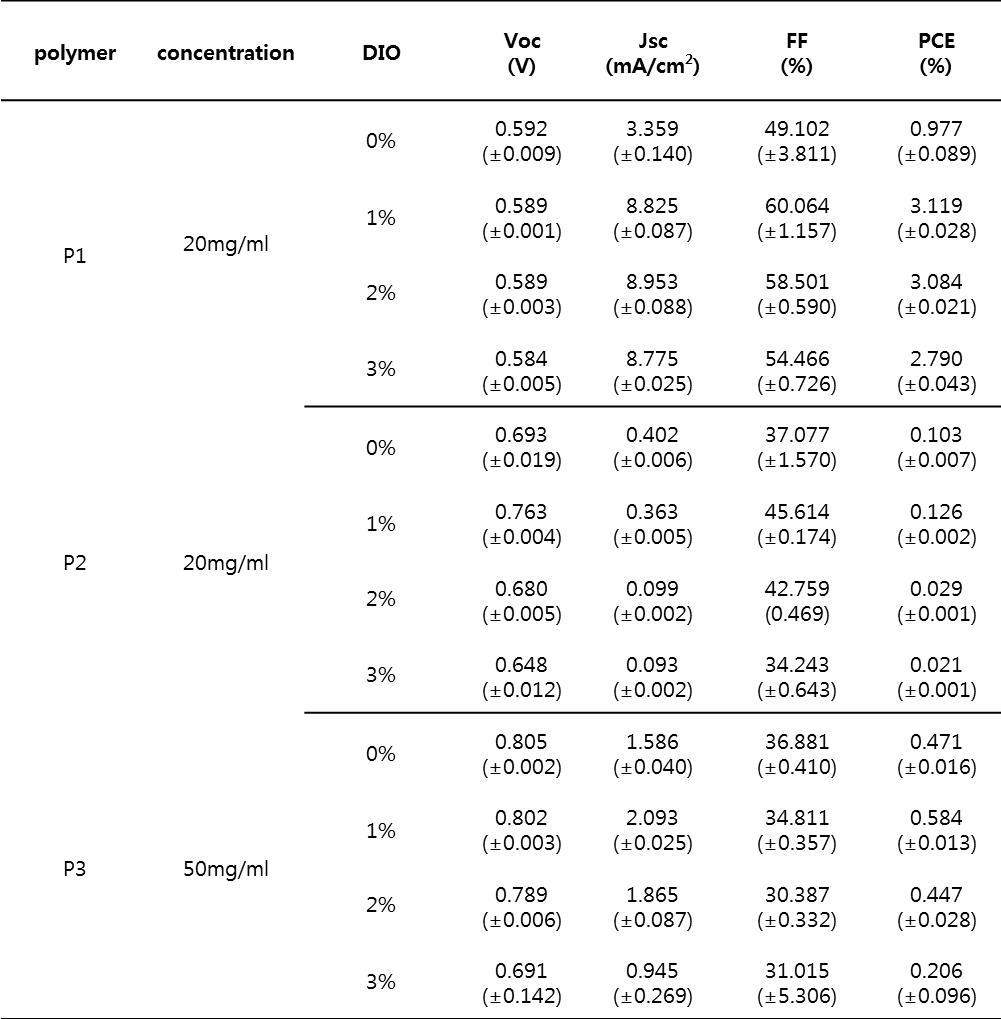
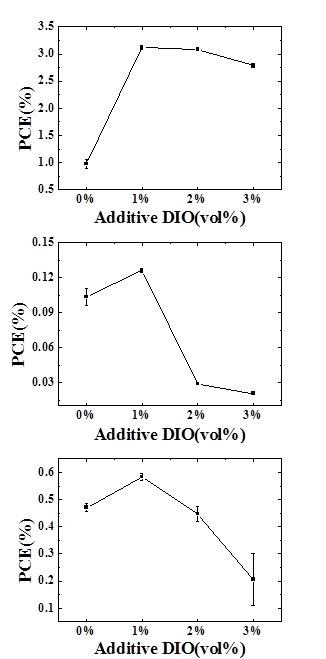
**Figure S4**. Procedure of device preparation



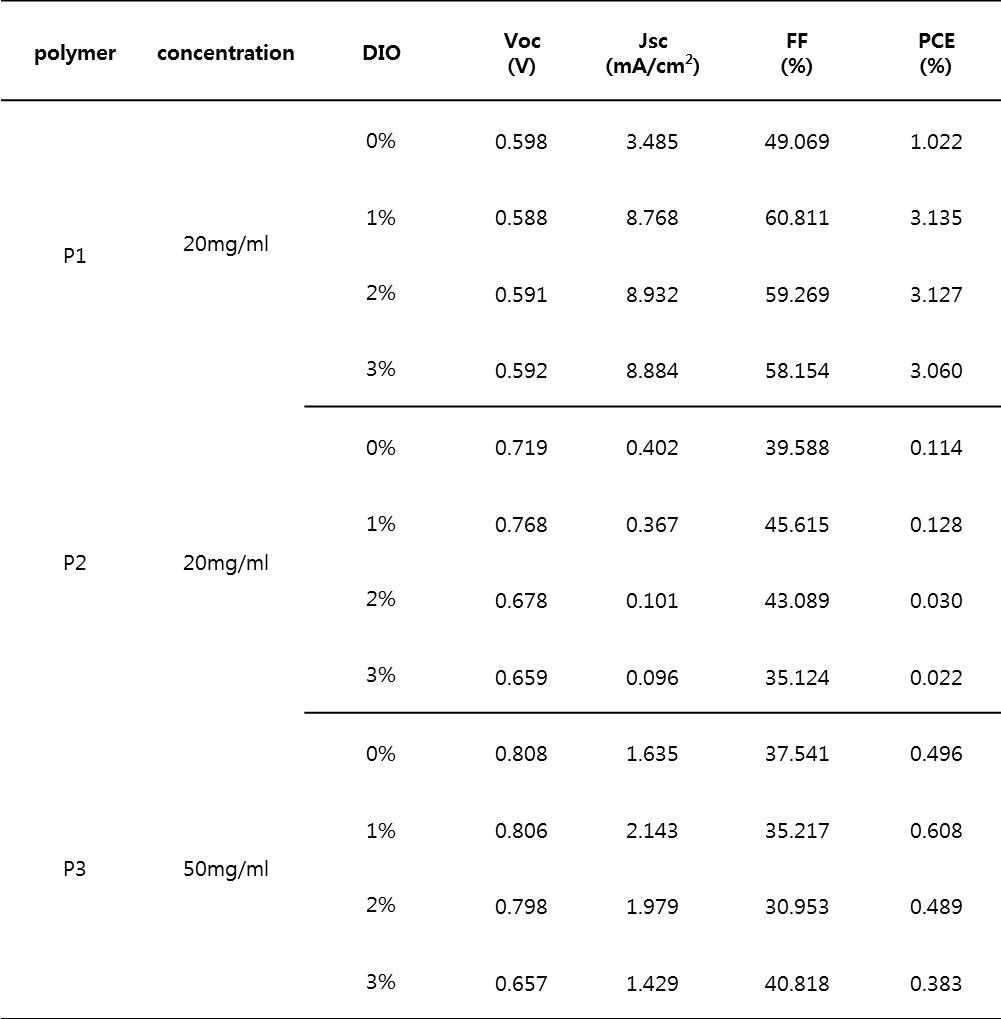
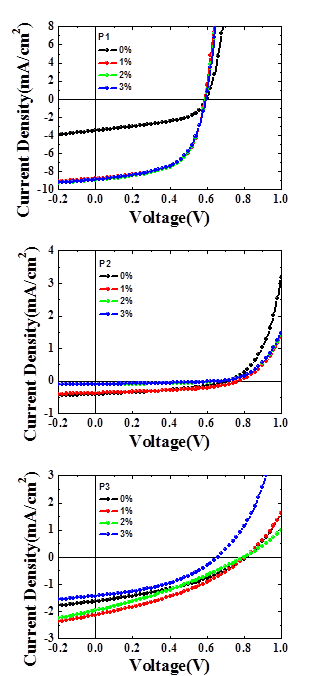
**Figure S5**. Variation of PCE based on concentration optimization



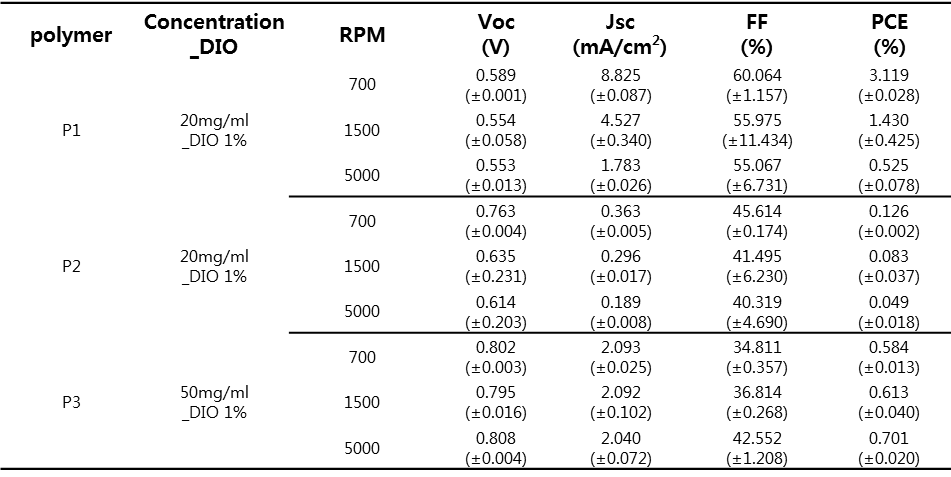
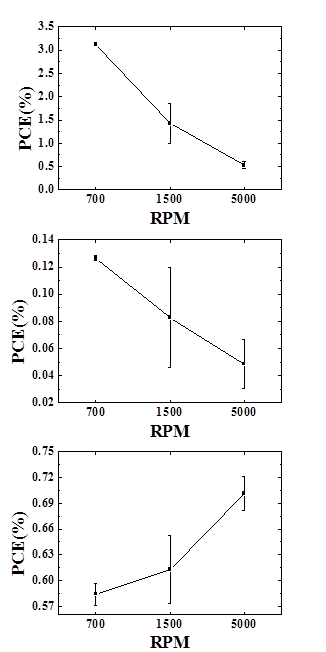
**Figure S6.** Variation of *J-V* curves based on concentration optimization.



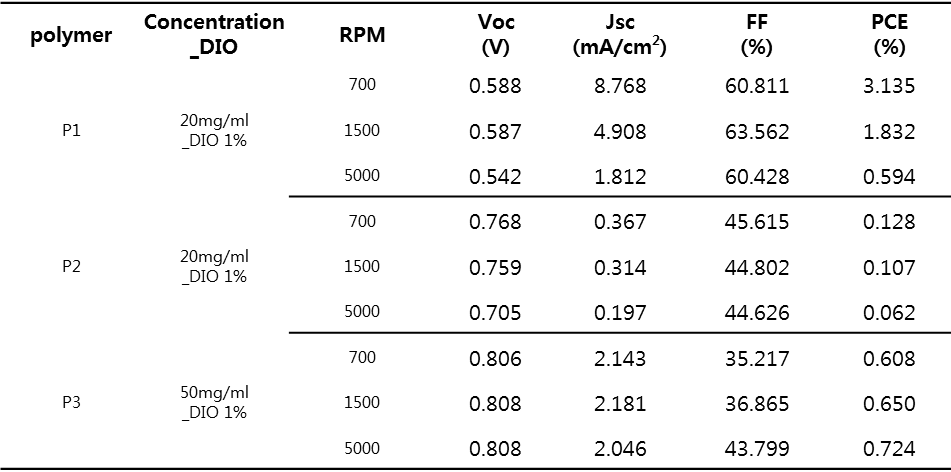
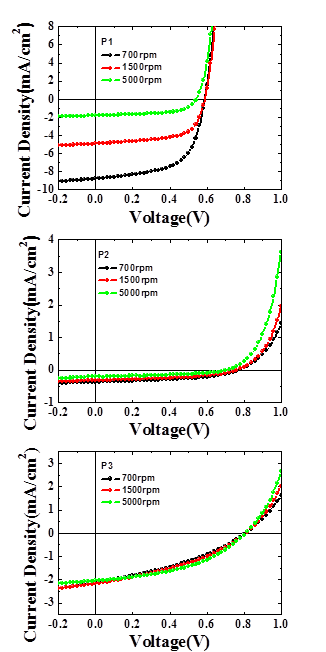
**Figure S7.** Variation of PCEs based on DIO optimization



**Figure S8.** Variation of *P-V* curves based on DIO optimization



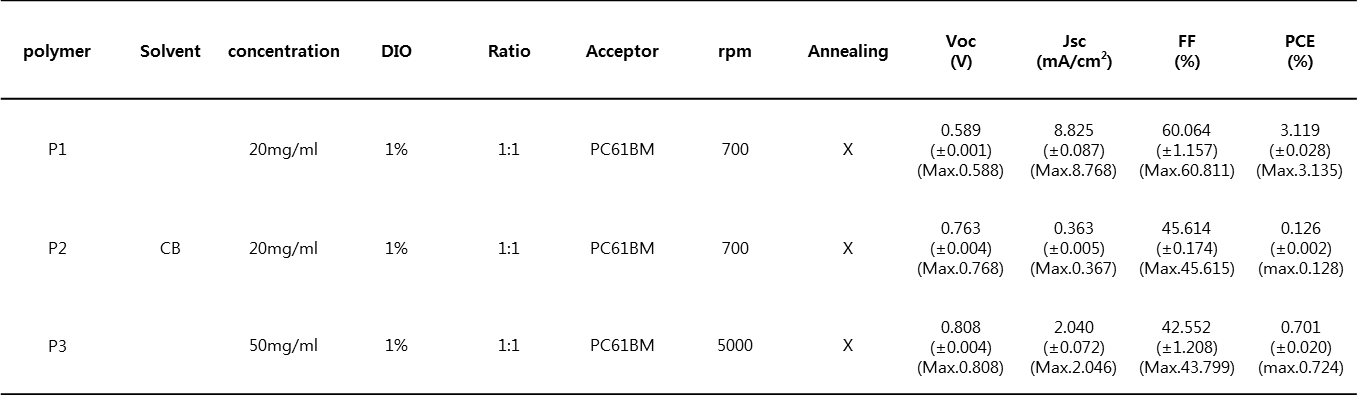
**Figure S9.** Variation of PCE based on film thickness optimization





**Figure S10.** Variation of *P-V* curves based on film thickness optimization

**Table S1.** Solar cell parameters of the devices fabricated from P1~P3 at optimized condition





**Table S2.** Solar cell parameters of the devices fabricated from P1 at DIO optimized condition

