Supporting Information for

C_{70}-based Aqueous-Soluble Fullerene for Water Composition-Tolerant Performance of Eco-friendly Polymer Solar Cells

Changkyun Kim,[a,†] *Hyunbum Kang,*[a,†] *Nayoun Choi,*[a] *Seungjin Lee,*[a] *Youngkwon Kim,*[a] *Jinwoo Kim,*[a] *Ziang Wu,*[b] *Han Young Woo,*[b] *and Bumjoon J. Kim* [a,*]

[a] Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 34141, Republic of Korea

[b] Department of Chemistry, Korea University, Seoul 02841, Republic of Korea

[*] Electronic e-mail: bumjoonkim@kaist.ac.kr

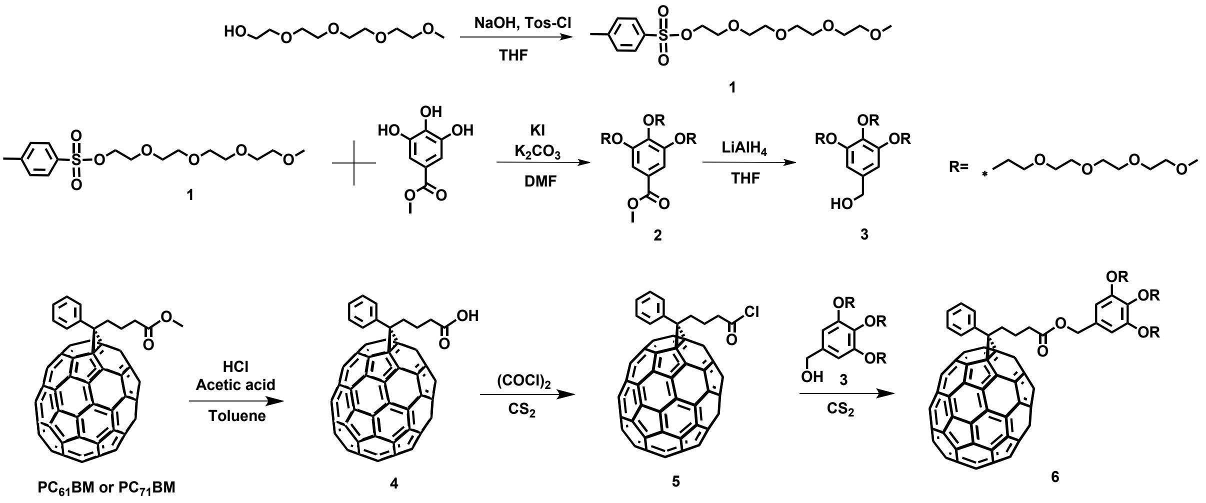
Keywords: aqueous process, eco-friendly polymer solar cells (eco-PSCs), water/alcohol-soluble C_{70}-fullerene derivatives, solvent-composition tolerance

Table of Contents

Supplementary Scheme

Supplementary Fig. S1-7

Supplementary Table S1-2



Scheme S1. Synthesis of PCBOs from PCBM: Acidification and chlorination of PCBM to yield PCBC **5** and esterification of **5** with tetraethyleneglycol-substituted benzyl alcohols **3** to afford the OEG-substituted fullerene mono-adducts **6** ($PC_{71}BO_{15}$ or $PC_{61}BO_{15}$).

Synthesis of tosylated tetraethyleneglycol monomethyl ether (1)

Tetraethyleneglycol monomethyl ether (**1**) were tosylated by following previously reported procedures. Tetraethyleneglycol monomethyl ether (30.00 g, 0.145 mol) was stirred in THF & H_2O mixture (ratio(v/v) : 4/1)) under argon gas in each of 500 mL round-bottom two-neck flasks. The reactor were cooled to 0°C followed by pouring *p*-toluenesulfonyl chloride (38.37 g, 0.201 mol) to the reaction flask. Then, the reactor was heated to room temperature. Excess sodium hydroxide (NaOH) were poured into the reaction flask. After 3 h, the organic compounds were extracted in DCM and the remaining solution was dried over $MgSO_4$, and the solvent was removed in vacuum to yield **1** as colorless and transparent oils (**1**: 57.4 g, 96%).

^1H NMR (300 MHz in $CDCl_3$): δ (ppm) 7.80 (d, 2H), 7.34 (d, 2H) 4.16 (t, 2H) 3.70 (t, 2H) 3.62 – 3.54 (m, 10H) 3.54 – 3.52 (m, 2H) 3.38 (s, 3H) 2.44 (s, 3H).

Synthesis of **3,4,5-OEG-benzoic acid methyl ester** *(2)*

3,4,5-OEG-benzoic acid methyl ester (**2**) were synthesized following reported literatures. Tosylated tetraethyleneglycol monomethyl ether (**1)** (20.00 g, 0.055 mol) were added to 500 mL 2-neck round-bottom flasks and dried under vacuum to eliminate existing water & oxygen. 300 mL of anhydrous DMF was added to each of the reaction flasks, followed by K_2CO_3 (4.84 g, 0.035 mol), KI (1.83 g, 0.011 mmol), and methyl 3,4,5-trihydroxybenzoate (2.02 g, 0.011 mol) were put into the reactor. The reaction mixtures were heated and stirred overnight under argon. The solution color changes into orange color. The solutions were poured into dichloromethane and washed with DI water. Remaining potassium salt was washed several times and was dried over $MgSO_4$. After filtration to remove $MgSO_4$, the solvents were evaporated in vacuum. The remaining crude product was purified by silica column chromatography by the elution of pure DCM to remove remaining DMF. After that, main product was eluted by ethyl acetate : methanol = 7:1 (v/v) blend eluent. The final transparent oil product can be yielded. (5.46 g, final yield : 80 %).

^1H NMR (300 MHz in $CDCl_3$): δ (ppm) 6.60 (2H), 4.55 (2H), 4.16 (2H), 4.12 (6H), 3.90 (1H), 3.83 – 3.47 (42H) 3.35 – 3.30 (9H). MALDI-TOF : $[M+Na^+]$ = 777.21 g/mol

Synthesis of 3,4,5-OEG-benzyl alcohol (3)

3,4,5-OEG-benzyl alcohol (**3**) was synthesized by the reduction of **2**. Briefly, 5.46 g of **3** (8.78 mmol) were put into 1-neck 500 mL round bottom flask followed by drying under vacuum to remove moisture and oxygen. 100 mL of THF was added under argon. After nitrogen bubbling, lithium aluminum hydride solution (2.0 M in anhydrous THF, 4.5 mL) was added dropwisely to the solutions at room temperature carefully. The mixtures were stirred overnight, and $LiAlH_4$ which didn't react was removed by slow addition of DI water at 0 ºC. The solution was diluted in DCM and washed with DI water. The organic layer was dried over $MgSO_4$ followed by being filtered, and concentrated under vacuum to yield **3** as colorless & transparent oils. (4.52 g, final yield : 86 %) MALDI-TOF : $[M+Na^+]$ = 749.21 g/mol

Synthesis of [6,6]-phenyl-C_{71} or C_{61}-butyric acid ($PC_{71}BA$ or $PC_{61}BA$) (4)

1 g of $PC_{71}BM$ or $PC_{61}BM$ was stirred in toluene (200 mL) in 2-neck 500mL flask. While being stirred under nitrogen, the mixture of HCl (35 wt.% in water, 45 mL) and acetic acid (90 mL) were added. The mixture was heated and stirred over the boiling point of toluene for 48 h, then heating was stopped. HCl & acetic acid were removed with DI water, and dried over $MgSO_4$. The $MgSO_4$ was filtered to be removed, and then washed with carbon disulfide to remove $MgSO_4$ partially adsorbed to the fullerenes. After that, purified product was obtained by silica gel chromatography by the elution of toluene to eliminate unreacted $PC_{71}BM$ or $PC_{61}BM$ followed by eluting by toluene/methanol/carbon disulfide mixture. MALDI-TOF MS: calculated for $PC_{71}BA$ 1016.3 g/mol (M^+), $PC_{61}BA$ 896.1 g/mol (M^+). (Yield : 71 %)

Synthesis of [6,6]-phenyl-C_{71} or C_{61}-butyric chloride ($PC_{71}BC$ or $PC_{61}BC$) (5)

600 mg of $PC_{71}BA$ and $PC_{61}BA$ (0.680 mmol) (**4**) was put into 500 mL 1-neck round bottom flask and dried under vacuum. Under Argon, 150 mL of CS_2 was added into the flasks. 5 mL of oxalyl chloride solution (2M in THF, anhydrous) was added dropwisely into the flask at room temperature. The solution was refluxed overnight followed by evaporating the carbon sulfide without additional purification. The solubility of the product in organic solvents is much

higher than $PC_{71}BA$ or $PC_{61}BA$ (**4**). (Yield : 99 %) Unpurified product was prepared to be reacted with *3,4,5-OEG-benzyl alcohol(3).*

Synthesis of [6,6]-phenyl-C_{71} or C_{61}-butyric-O_{15} ($PC_{71}BO_{15}$ or $PC_{61}BO_{15}$) (6)

600 mg of $PC_{71}BC$ or $PC_{61}BC$ (**5**) was put into 500 mL 1-neck round bottom flask and dried under vacuum. Under N_2, 100 mL of carbon disulfide was poured into the reactor. In another 500 mL 1-neck round bottom flask, 3,4,5-OEG-benzyl alcohol(**3**) (436 mg, 0.734 mmol) and 1 mL of triethylamine was stirred in 50 mL of carbon disulfide under N_2 gas. **3** & triethylamine solution were transferred into the flask which contains **5** solution, followed by being stirred overnight at room temperature. Remaining carbon disulfide was removed under vacuum. The remaining crude product was poured into DCM : IPA (3:1 (v/v)) co-solvent. Then, the product was centrifuged at 6000 RPM for 10 min, which was repeated three times. The unreacted $PC_{71}BA$ or $PC_{61}BA$ (**4**) was precipitated and removed. DCM & IPA were eliminated under vacuum. The purification of remaining product was done by silica column chromatography. The fullerene-like impurities were removed by pure DCM, EA elution. After DCM, EA elution, the remaining compounds were eluted by EA : MeOH (10:1 (v/v)) blend eluent. In this stage, the product includes only $PC_{71}BO_{15}$ or $PC_{61}BO_{15}$ (**6**) & remaining oligoethyleneglycol-like impurities. Oligoethyleneglycol-like impurities are liquid in room temperature and soluble in water or methanol. The remaining product was transferred into centrifugal tube and 40 mL of water was poured into the tube. The $PC_{71}BO_{15}$ or $PC_{61}BO_{15}$ (**6**) were precipitated and supernatant solution which contains oligoethyleneglycol-like impurities was removed. The purified product was dried under vacuum and 250 mg of $PC_{71}BO_{15}$ or $PC_{61}BO_{15}$ was yielded. (Yield = 39%)

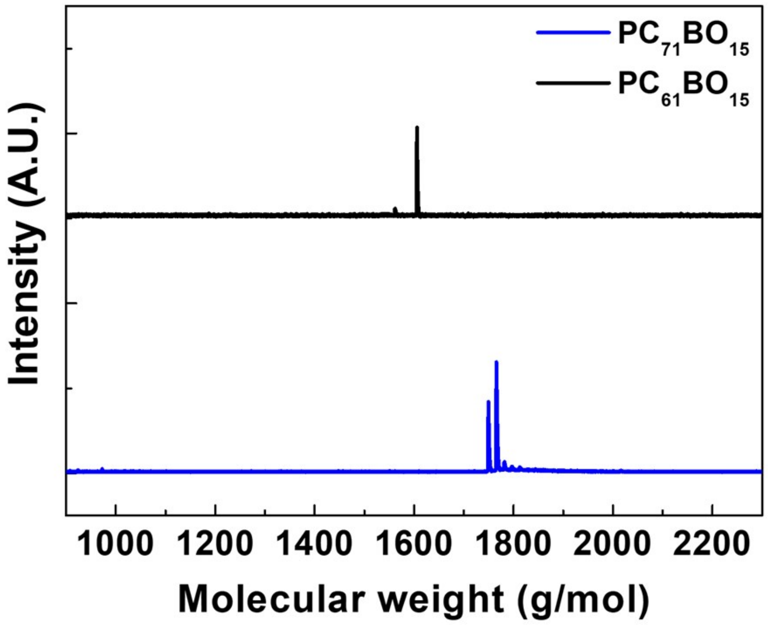


Fig. S1. MALDI-TOF results of synthesized $PC_{71}BO_{15}$ and $PC_{61}BO_{15}$.

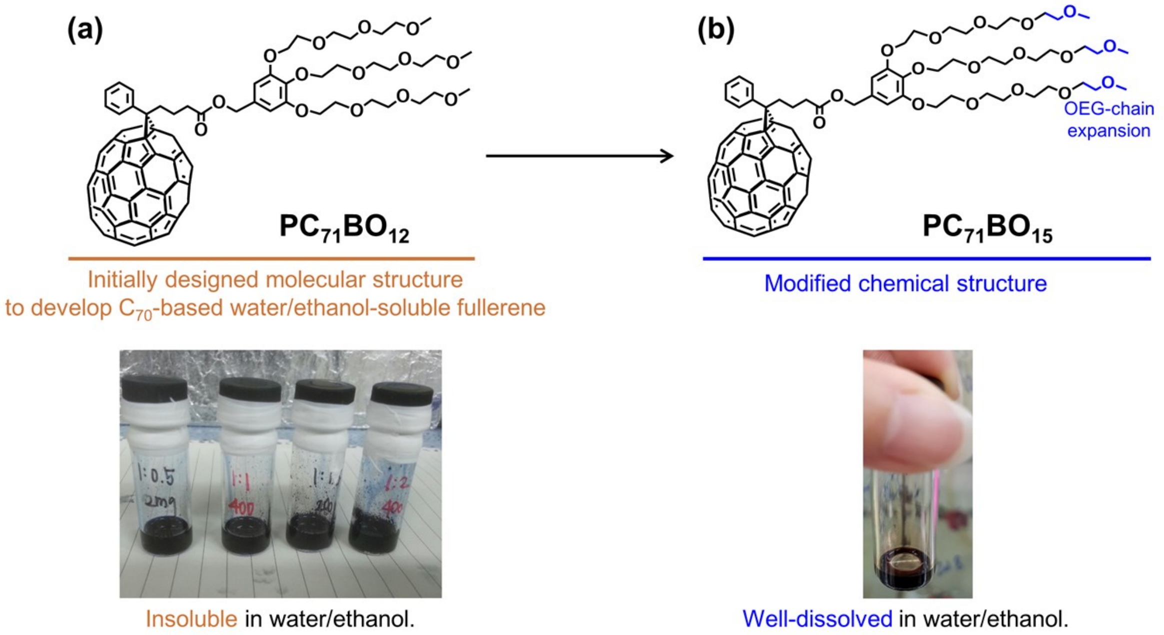


Fig. S2. Developed C_{70}-OEG fullerenes: (a) $PC_{71}BO_{12}$ which is insoluble in water/ethanol, and (b) $PC_{71}BO_{15}$ which is highly soluble in water/ethanol.

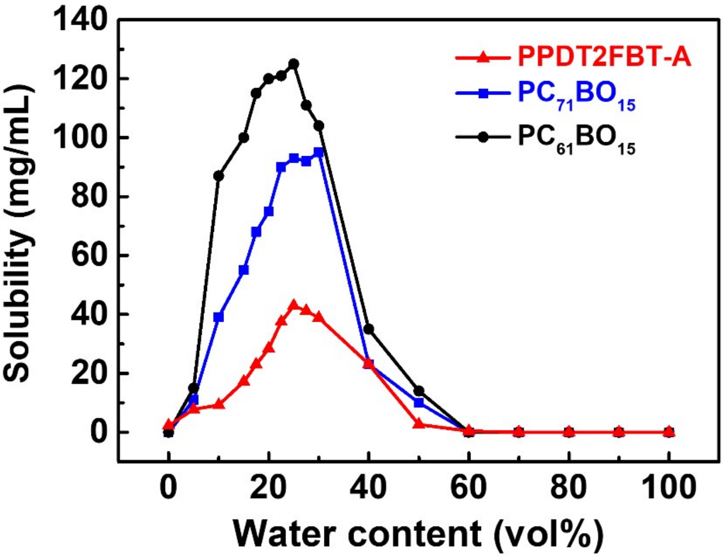


Fig. S3. The solubilities of PPDT2FBT-A donor polymer and PC_yBO_{15} (y= 71 or 61) by varying water content.

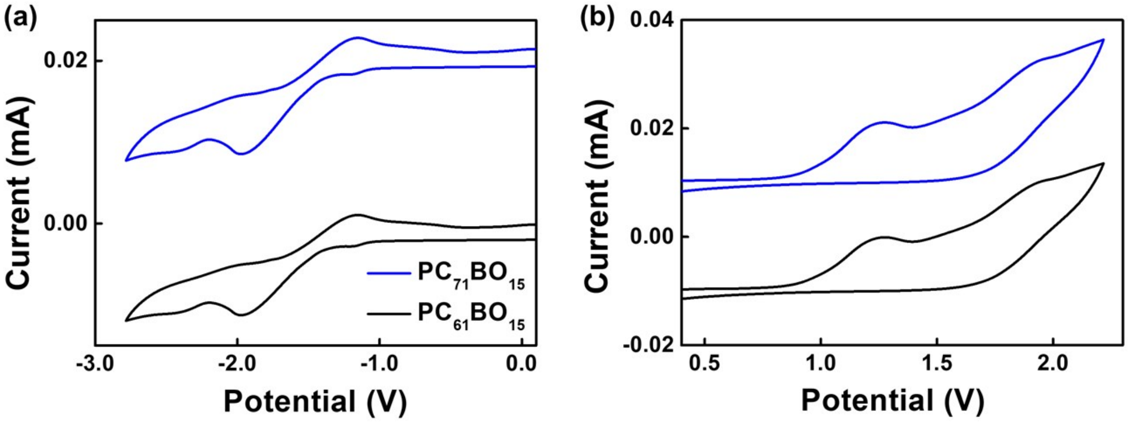


Fig. S4. (a) Reduction and (b) oxidation potentials of $PC_{71}BO_{15}$ and $PC_{61}BO_{15}$ measured by cyclic voltammetry.

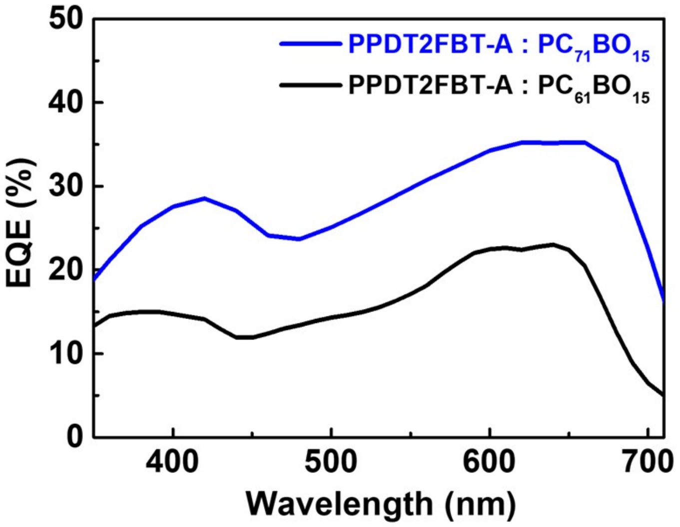


Fig. S5 EQE characteristics of optimized blend film of PPDT2FBT-A:$PC_{71}BO_{15}$ and PPDT2FBT-A:$PC_{61}BO_{15}$.

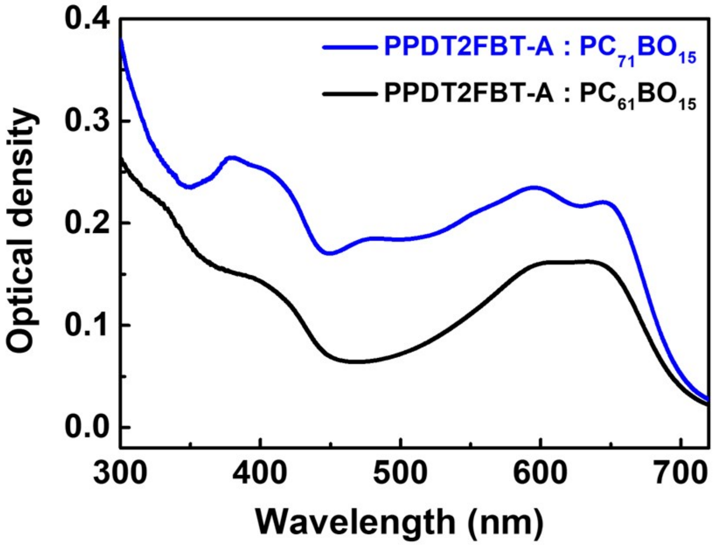


Fig. S6. Optical densities of optimized blend film of PPDT2FBT-A:$PC_{71}BO_{15}$ and PPDT2FBT-A:$PC_{61}BO_{15}$.

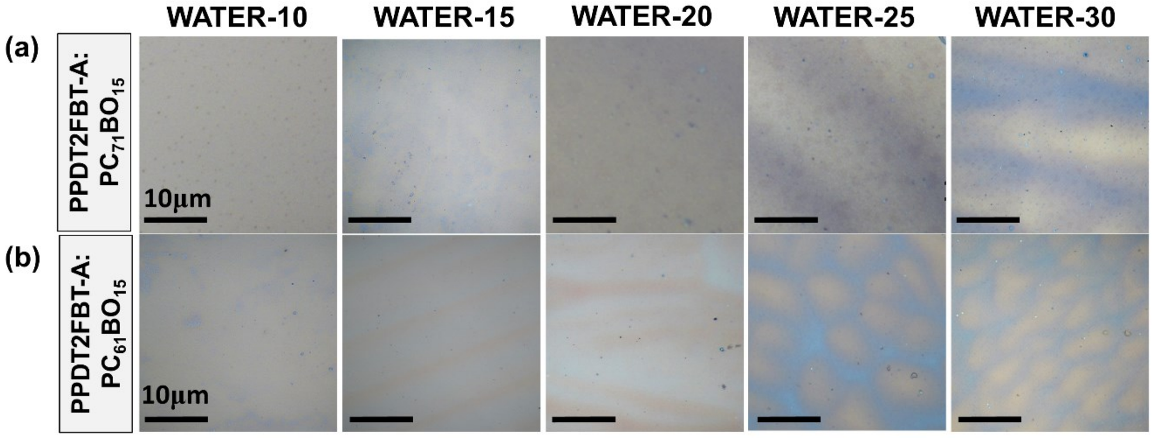


Fig. S7. Optical microscopy images of (a) PPDT2FBT-A:$PC_{71}BO_{15}$, and (b) PPDT2FBT-A:$PC_{61}BO_{15}$ with various ratios of processing co-solvents.

Table S1. Molecular properties of donor polymer PPDT2FBT-A used in this study.

Polymer	$\boldsymbol{M_n/M_w}$[a] **[kg mol^{-1}]**	**Đ**[a]	λ_{max}^{Film} **[nm]**	E_g^{opt} **[eV]**	$\boldsymbol{E_{HOMO}}$[b] **[eV]**	$\boldsymbol{E_{LUMO}}$[c] **[eV]**
PPDT2FBT-A	24.7 / 75.3	3.1	345, 626	1.73	−5.19	−3.46

[a] Determined by SEC with *o*-dichlorobenzene eluent relative to polystyrene standards

[b] Measured from CV curves.

[c] Calculated from $E_{HOMO} = E_{LUMO} - E_g^{opt}$ (optical band gap).

Table S2. Photovoltaic properties of PPDT2FBT-A:$PC_{71}BO_{15}$ and PPDT2FBT-A:$PC_{61}BO_{15}$ devices depending on water content from WATER-10 to WATER-30.*

Active layer	Water content (vol %)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE$_{max}$ (PCE$_{avg}$) (%)
PPDT2FBT-A :$PC_{71}BO_{15}$	10.0	0.75	4.05	0.51	1.56 (1.48)
	12.5	0.75	5.19	0.56	2.16 (2.05)
	15.0	0.75	5.70	0.52	2.20 (2.11)
	17.5	0.74	5.32	0.54	2.12 (2.05)
	20.0	0.76	5.37	0.54	2.16 (2.00)
	22.5	0.76	5.30	0.54	2.15 (1.99)
	25.0	0.75	5.45	0.51	2.09 (1.88)
	27.5	0.73	5.65	0.49	2.02 (1.80)
	30.0	0.73	5.63	0.48	1.96 (1.75)
PPDT2FBT-A :$PC_{61}BO_{15}$	10.0	0.71	2.50	0.42	0.74 (0.69)
	12.5	0.72	3.78	0.44	1.19 (1.11)
	15.0	0.76	4.81	0.45	1.65 (1.51)
	17.5	0.72	4.06	0.49	1.43 (1.35)
	20.0	0.72	4.01	0.46	1.33 (1.25)
	22.5	0.72	3.90	0.45	1.26 (1.14)
	25.0	0.73	3.82	0.43	1.20 (1.12)
	27.5	0.72	3.46	0.47	1.17 (1.09)
	30.0	0.72	2.48	0.42	0.75 (0.68)

[*] Device architecture of ITO/c-PEDOT:PSS/Active layer/PNDIT-F3N-Br/Ag was used.