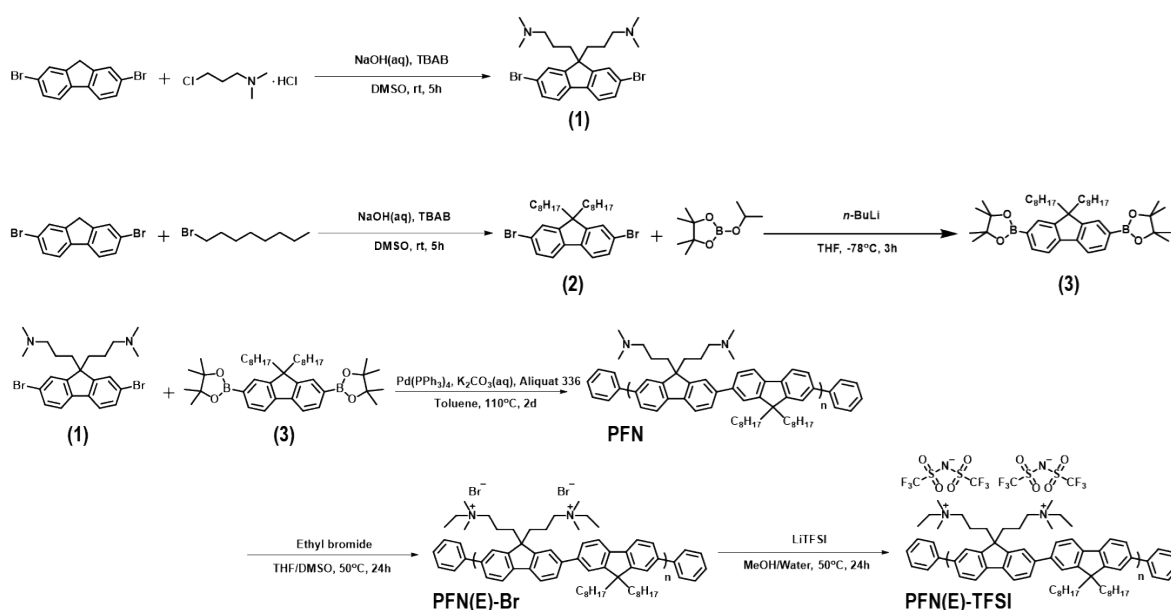## Supporting Information

## Counter-anion Size Engineering in Polyfluorene-based Cathode Interlayer to Enhance the Thickness Independence

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**Scheme S1**. Synthetic route of PFN(E)-Br and PFN(E)-TFSI.

**Synthesis of 3,3'-(2,7-Dibromo-9*H*-fluorene-9,9-diyl)bis(*N,N*-dimethylpropan-1-amine) (1) :** 2,7-Dibromofluorene (3.69 g, 15.4 mmol) was diluted in dimethyl sulfoxide (100 mL) with stirring under nitrogen atmosphere. 50wt% of NaOH in water (40 mL), tetrabutylammonium bromide (73 mg, 0.31 mmol), and 3-dimethylamino-1-propyl chloride hydrochloride (7.0 g, 60.1 mmol) were added to the solution, and stirred for 5 h at room temperature. The reaction was then quenched with cold water (200 mL). The organic materials were extracted with diethyl ether, and the combined organic layers were washed with aq. HCl and dried over anhydrous $MgSO_4$. Pure product was purified by recrystallization in methanol (2.31 g, 41%). $^1$H NMR (400 MHz, $CDCl_3$, $\delta$): 7.52-7.43 (m, 6H), 2.03-1.95 (m, 20H), 0.79-0.71 (m, 4H).

**Synthesis of 9,9-Dioctyl-2,7-dibromofluorene (2) :** The solution of 2,7-dibromofluorene (3.69 g, 15.4 mmol), 50wt% of NaOH in water (40 mL), tetrabutylammonium bromide (73 mg, 0.31 mmol), and 1-bromooctane (5.54 g, 60.1 mmol) was stirred for overnight at room temperature condition. The reaction was then quenched with cold water (200 mL). The organic materials were extracted with diethyl ether, and the combined organic layers were washed with aq. HCl and dried over anhydrous $MgSO_4$. Product was purified by silica column chromatography with hexane (4.11 g, 65%). $^1$H NMR (400 MHz, CDC1$_3$, $\delta$): 7.53-7.42 (m, 6H), 1.94-1.87 (m, 4H), 1.27-1.00 (br, 20H), 0.86-0.80 (t, 6H), 0.63-0.54 (br, 4H).

**Synthesis of 9,9-Dioctyl-9*H*-fluorene-2,7-diboronic acid bis(pinacol) ester (3) :** The compound **2** (1.5 g, 2.74 mmol) was diluted in THF (30 mL) and cooled to −78°C. The 2.5 M *n*-BuLi in hexane (2.85 mL) was slowly added to solution. After stirring at −78°C for 1 h, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.5 mL, 2.46 mmol) was added dropwise, and the mixture was gradually warmed to room temperature. The reaction mixture was stirred for 5 h, and then quenched with cold water (200 mL). Product was purified by silica column chromatography with DCM/hexane (5.5:4.5) as eluent following to recrystallization in methanol (980 mg, 56%). $^1$H NMR (400 MHz, CDC1$_3$, $\delta$): 7.82-7.69 (m, 6H), 2.03-1.95 (m, 4H), 1.41-1.36 (s, 24H), 1.26-0.95 (br, 20H), 0.84-0.77 (t, 6H), 0.59-0.48 (br, 4H).

**Synthesis of Poly [(9,9-bis(3'-(*N,N*-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9–dioctylfluorene)] (PFN) :** The neutral polymer was prepared by the Suzuki coupling polymerization method. Compound **1** (157 mg, 0.318 mmol), compound **3** (200 mg, 0.318 mmol), 2 M $K_2CO_3$ in water (1.07 mL), several drops of Aliquat 336, tetrakis(triphenylphosphine)palladium(0) (5 mg) and anhydrous toluene (5 mL) were mixed in a 50 mL Schlenk flask under argon condition. The mixture was heated to 110°C for 48 h. Then, 0.05 mL each of 2-bromobenzene and phenylboronic acid pinacol ester were injected sequentially and further heated for 6 h. The crude solution was precipitated in methanol (500 mL). The precipitate was collected into a Soxhlet thimble and the product was obtained from Soxhlet extraction with acetone, hexane, dichloromethane and chloroform. The chloroform portion was concentrated and precipitated in methanol. The precipitate was filtered and dried overnight to afford the yellow solid product (180 mg, 45%). GPC (chlorobenzene, 40°C): $M_n$ = 40kDa, $M_w$ = 84kDa, PDI = 2.1. $^1$H NMR (600 MHz, CDCl$_3$, $\delta$): 7.88-7.57 (m, 12H), 2.35-1.90 (br, 20H), 1.85-1.65 (br, 4H), 1.33-1.04 (br, 22H), 1.03-0.92 (br, 4H), 0.91-0.65 (m, 8H).

**Synthesis of Poly(9,9-bis(3'-(*N,N*-dimethyl)-N-ethylammoinium-propyl-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene))dibromide (PFN(E)-Br) :** To solution of **PFN** (100 mg) in tetrahydrofuran (20 mL) and dimethyl sulfoxide (10 mL), bromoethane (0.08 mL) was added and heated to 50°C. Then, the reaction

mixture was stirred for 24 h at dark condition. The resulting solution was precipitated in ethyl acetate (200 mL). The final product was filtered and dried in a vacuum to obtain yellow solid (90 mg, 57%). ^{1}H NMR (400 MHz, CD$_3$OD, $\delta$): 8.14-7.75 (m, 12H), 3.22-3.10 (m, 8H), 2.91-2.75 (s, 12H), 2.56-2.11 (br, 8H), 1.39-0.95 (br, 30H), 0.84-0.66 (br, 10H).

**Synthesis of Poly(9,9-bis(3'-(*N*,*N*-dimethyl)-N-ethylammoinium-propyl-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene))bis(trifluoromethane)sulfonimide (PFN(E)-TFSI) :** To solution of **PFN(E)-Br** (30 mg) in methanol (1 mL) and water (3 mL), Bis(trifluoromethane)sulfonimide lithium salt (LiTFSI) (94 mg) was added and heated to 50°C. Then, the reaction mixture was stirred for 24 h at dark condition. The resulting solution was precipitated in ethyl acetate (200 mL). The final product was filtered and dried in a vacuum to obtain yellow solid (24 mg, 80%). ^{1}H NMR (400 MHz, CD$_3$OD, $\delta$): 8.12-7.72 (m, 12H), 3.19-3.00 (m, 8H), 2.88-2.70 (s, 12H), 2.57-2.08 (br, 8H), 1.40-0.95 (br, 30H), 0.86-0.59 (br, 10H).
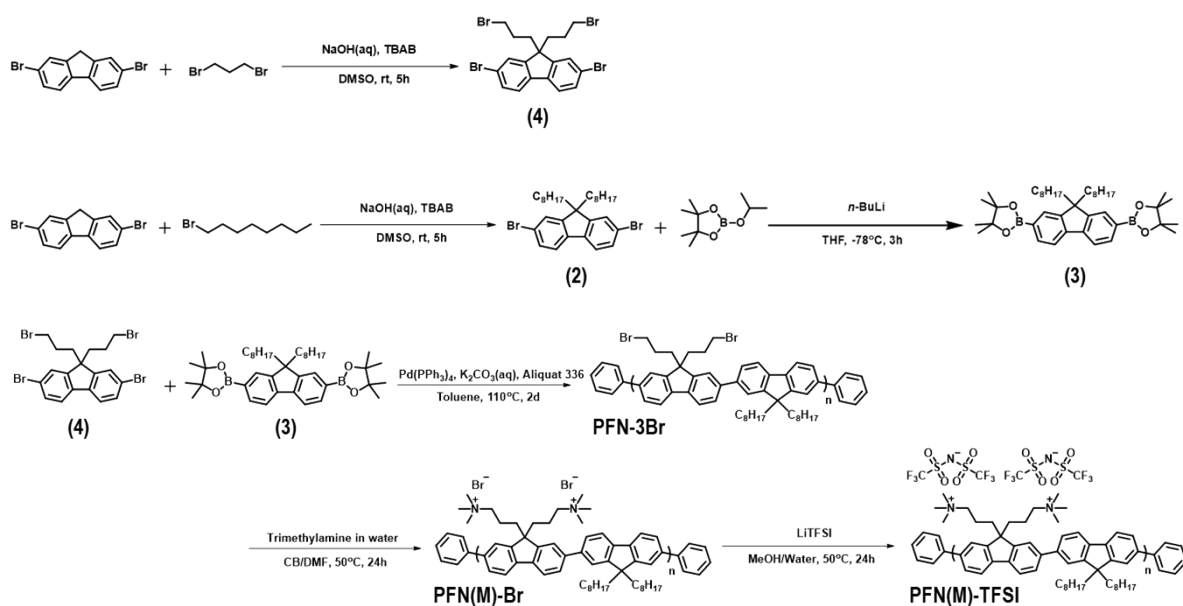
**Scheme S2**. Synthetic route of PFN(M)-Br and PFN(M)-TFSI.

**Synthesis of 2,7-Dibromo-9,9-bis(3-bromopropyl)-9*H*-fluorene (4) :** To a solution of 2,7-dibromofluorene (3.69 g, 15.4 mmol), tetrabutylammonium bromide (73 mg, 0.31 mmol), and 1,3-dibromopropane (23 mL, 115 mmol), 50wt% of NaOH in water (40 mL) was added and stirred for overnight at room temperature condition. The reaction was then quenched with cold water (200 mL). The organic materials were extracted with diethyl ether, and the combined organic layers were washed with aq. HCl and dried over anhydrous MgSO$_4$. Product was purified by silica column chromatography with hexane/DCM (9.5:0.5) as eluent (3.92 g, 50%). $^1$H NMR (500 MHz, CDCl$_3$, $\delta$): 7.54-7.40 (m, 6H), 3.11-3.03 (t, 4H), 2.24-2.12(m, 4H), 1.14-1.04(m, 4H).

**Synthesis of Poly [(9,9-bis(3'-bromopropyl)-2,7-fluorene)-alt-2,7-(9,9–dioctylfluorene)] (PFN-3Br) :** The neutral polymer was prepared by the Suzuki coupling polymerization method. Compound **4** (176 mg, 0.318 mmol), compound **3** (200 mg, 0.318 mmol), 2 M K$_2$CO$_3$ in water (5 mL), several drops of Aliquat 336, tetrakis(triphenylphosphine)palladium(0) (5 mg) and anhydrous toluene (5 mL) were mixed in a 50 mL Schlenk flask under argon condition. The mixture was heated to 110°C for 48 h. Then, 0.05 mL each of 2-bromobenzene and phenylboronic acid pinacol ester were injected sequentially and further heated for 6 h. The crude solution was precipitated in methanol (500 mL). The precipitate was collected into a Soxhlet thimble and the product was obtained from Soxhlet extraction with acetone, hexane, dichloromethane and chloroform. The chloroform portion was concentrated and precipitated in methanol. The precipitate was filtered and dried overnight to afford the yellow solid product (220 mg, 68%). GPC (chlorobenzene, 40°C): $M_n$ = 31kDa, $M_w$ = 70kDa, PDI = 2.26. $^1$H NMR (600 MHz, CDCl$_3$, $\delta$): 7.91-7.79 (br, 4H), 7.76-7.65 (br,

8H), 3.26-3.15 (m, 4H), 2.58-2.24 (br, 4H), 2.21-1.95 (br, 4H), 1.45-1.28 (br, 4H), 1.25-1.06 (br, 24H), 0.84-0.78 (t, 6H).

**Synthesis of Poly(9,9-bis(3'-(*N,N*-dimethyl)-N-methylammoinium-propyl-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene))dibromide (PFN(M)-Br) :** To solution of **PFN-3Br** (700 mg) in chlorobenzene (30 mL) and *N,N*-dimethylformamide (21 mL), aqueous trimethylamine (4.1 mL, 4.3 M) was added and heated to 50°C. Then, the reaction mixture was stirred for 24 h at dark condition. The resulting solution was precipitated in ethyl acetate (200 mL). The final product was filtered and dried in a vacuum to obtain yellow solid (815 mg, 65%). ^{1}H NMR (600 MHz, CD$_3$OD, $\delta$): 8.08-7.75 (br, 12H), 3.30-3.16 (m, 4H), 2.95-2.87 (br, 18H), 2.68-2.07 (br, 8H), 1.34-1.03 (br, 24H), 0.86-0.65 (br, 10H).

**Synthesis of Poly(9,9-bis(3'-(*N,N*-dimethyl)-N-methylammoinium-propyl-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene))bis(trifluoromethane)sulfonimide (PFN(M)-TFSI) :** To solution of **PFN(M)-Br** (445 mg) in methanol (10 mL) and water (3 mL), LiTFSI (1.4 g) was added and heated to 50°C. Then, the reaction mixture was stirred for 24 h at dark condition. The resulting solution was precipitated in ethyl acetate (200 mL). The final product was filtered and dried in a vacuum to obtain yellow solid (456 mg, 71%). ^{1}H NMR (600 MHz, CD$_3$OD, $\delta$): 8.08-7.70 (br, 12H), 3.29-3.12 (m, 4H), 2.95-2.82 (br, 18H), 2.56-2.17 (br, 8H), 1.36-1.02 (br, 24H), 0.87-0.60 (br, 10H).
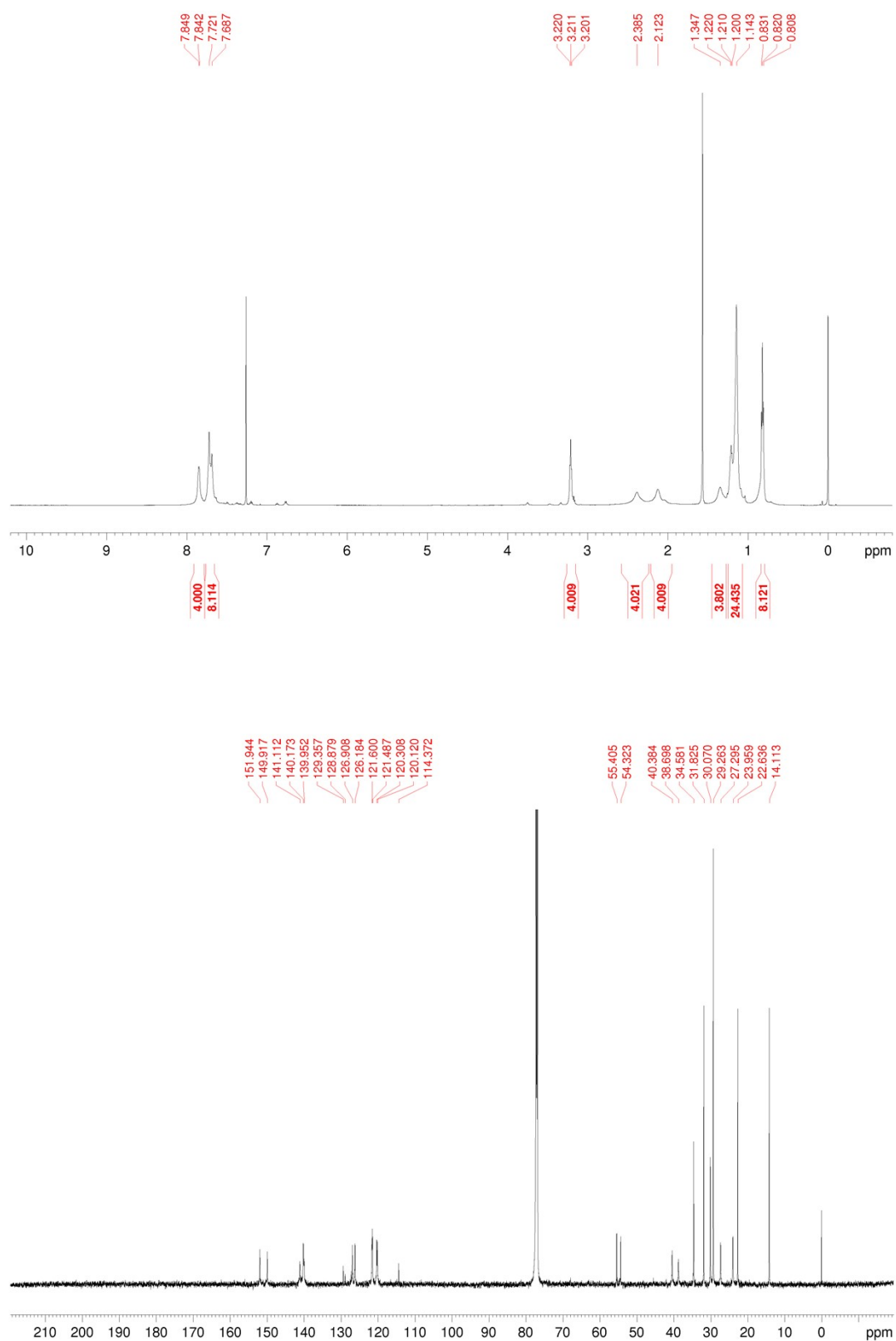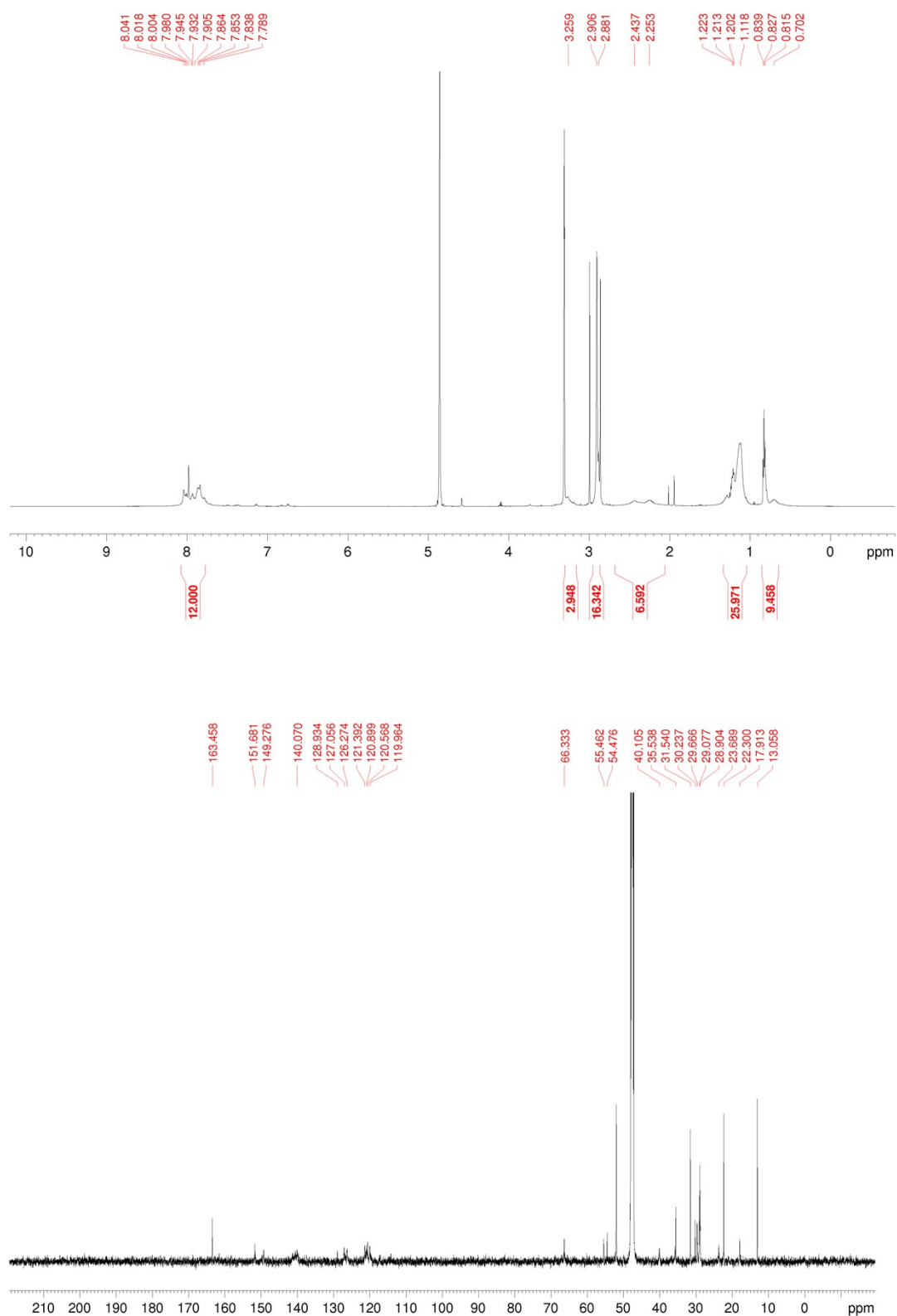
**Figure S1.** $^1$H NMR and $^{13}$C NMR of PFN-3Br.

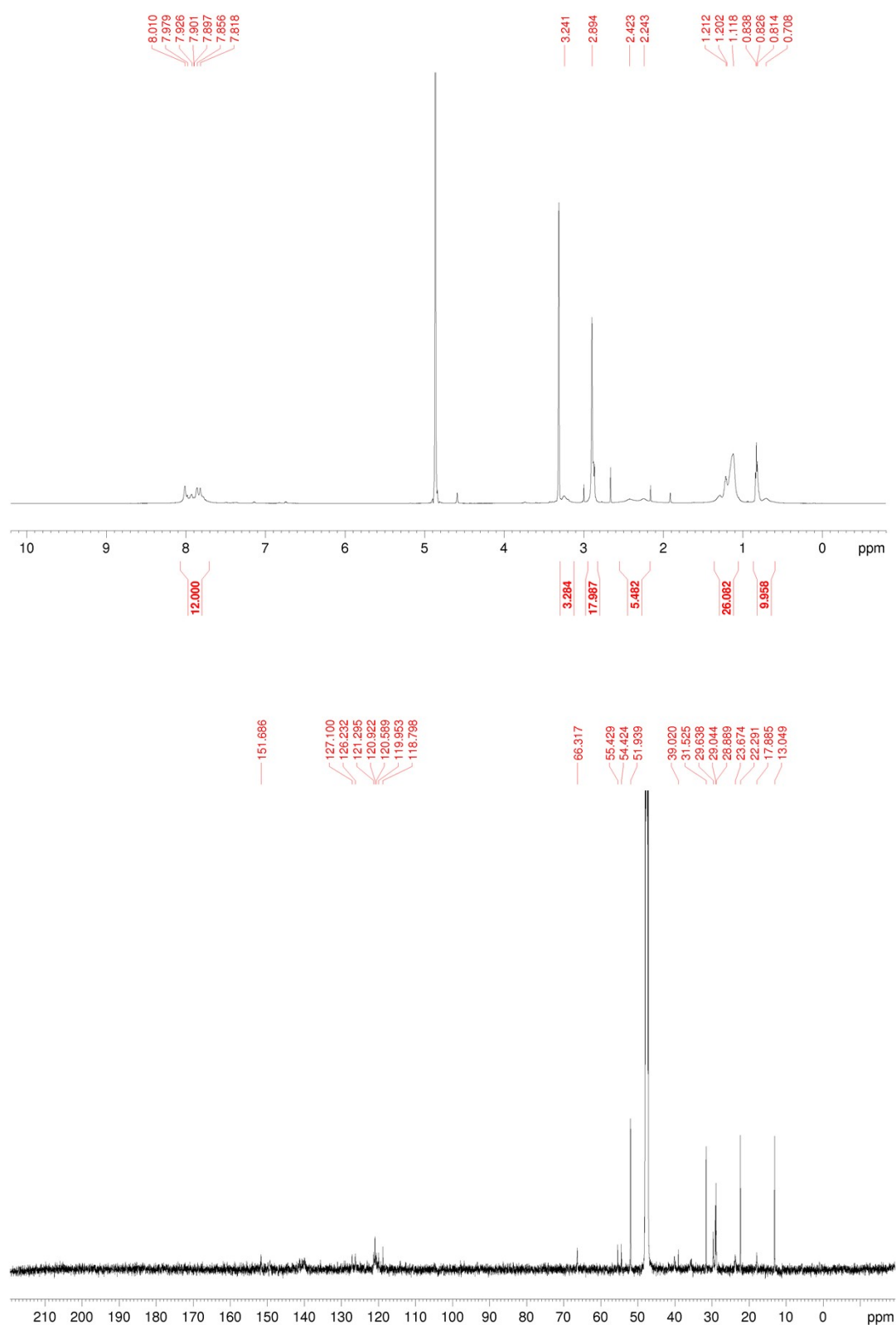**Figure S2.** $^1$H NMR and $^{13}$C NMR of PFN(M)-Br.

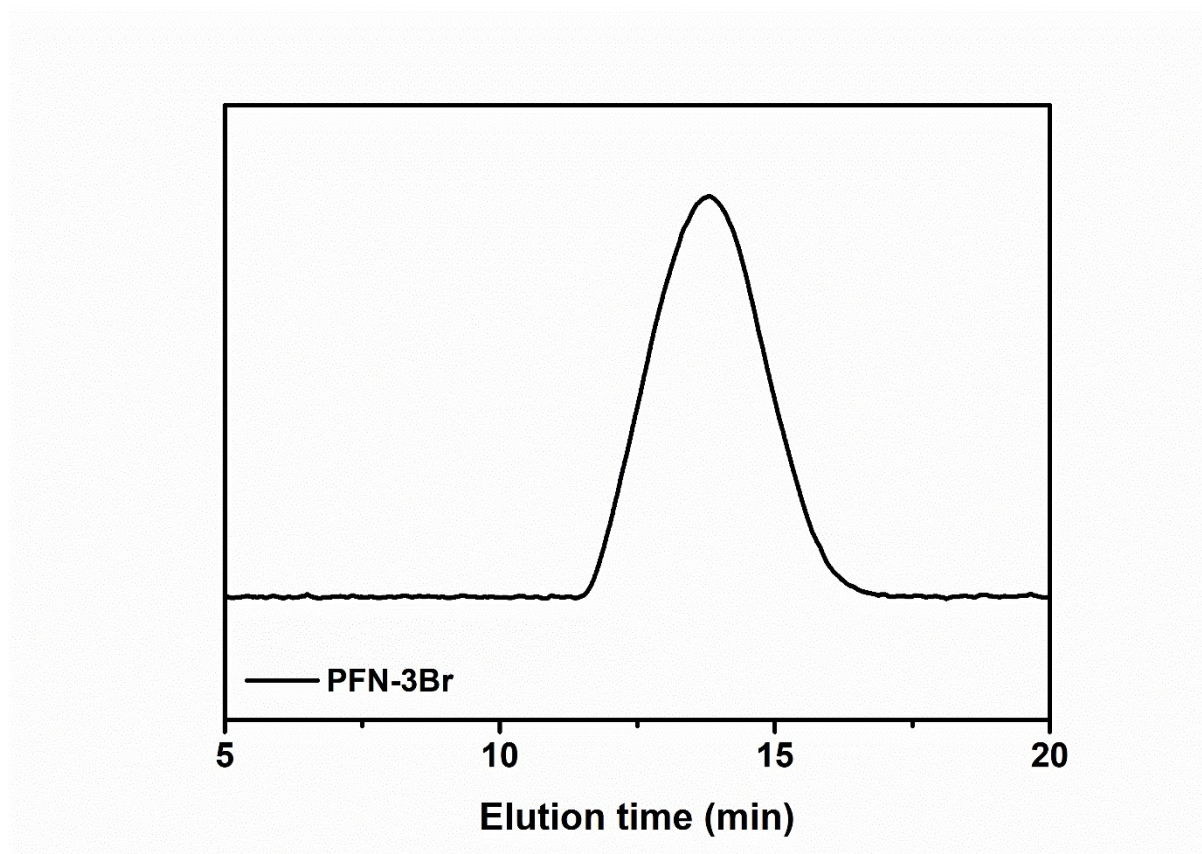**Figure S3.** $^1$H NMR and $^{13}$C NMR of PFN(M)-TFSI.

**Figure S4.** Gel permeation chromatography (GPC) profile of neutral polymer PFN-3Br
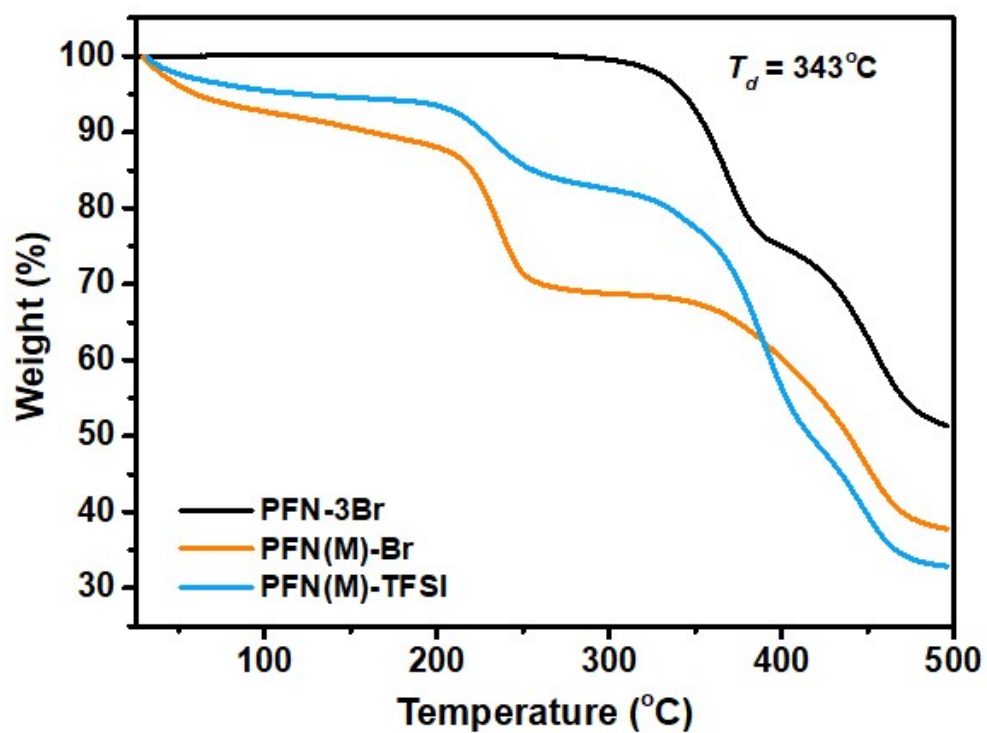
**Figure S5.** Thermogravimetric analysis (TGA) of each polymer (PFN-3Br, PFN(M)-Br and PFN(M)-TFSI) under $N_2$.
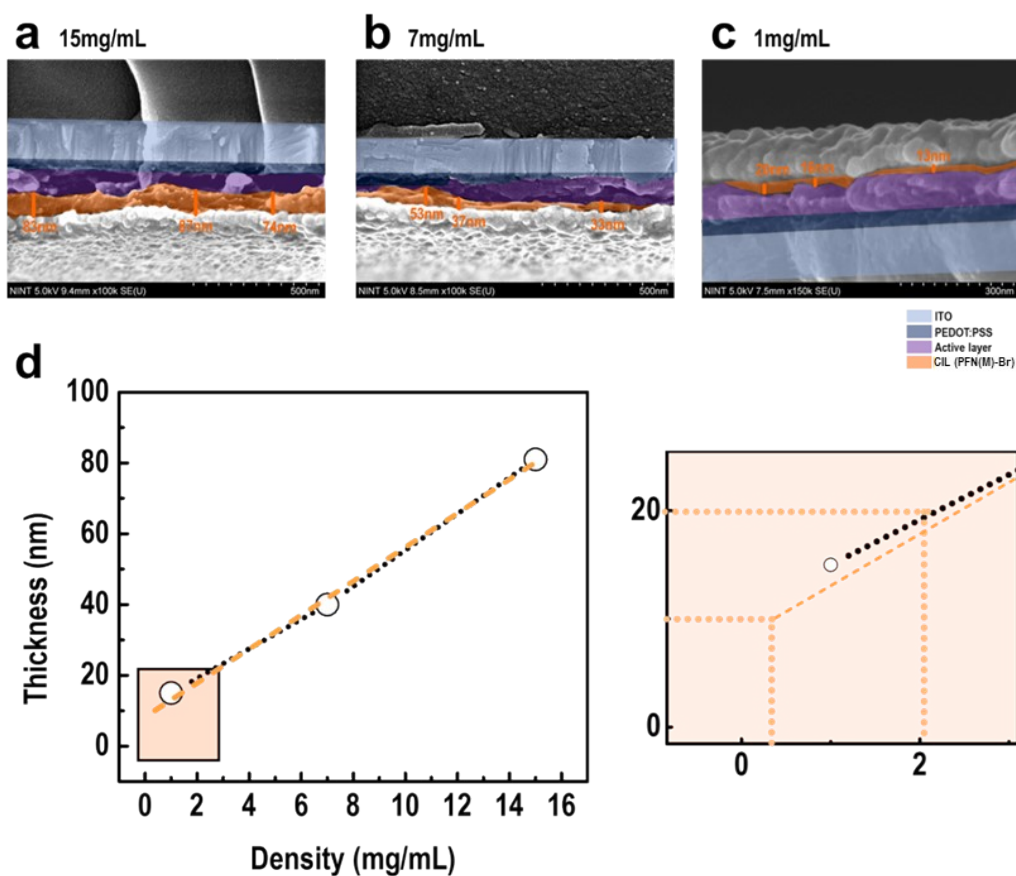
**Figure S6.** Cross-section SEM image of the architecture. (ITO/PEDOT:PSS/PM6:Y6 BHJ/CIL/Ag) CIM film was spin coated on BHJ active layer, by 3000rpm 30s with **(a)** 15mg/mL **(b)** 7mg/mL and **(c)** 1mg/mL of PFN(M)-Br in MeOH. **(d)** Thickness graph according to the solution density and the values of thickness were extracted from the cross-section SEM images. The estimated thicknesses of thin film (from ~5nm to ~20nm) were extracted using the linear fit.
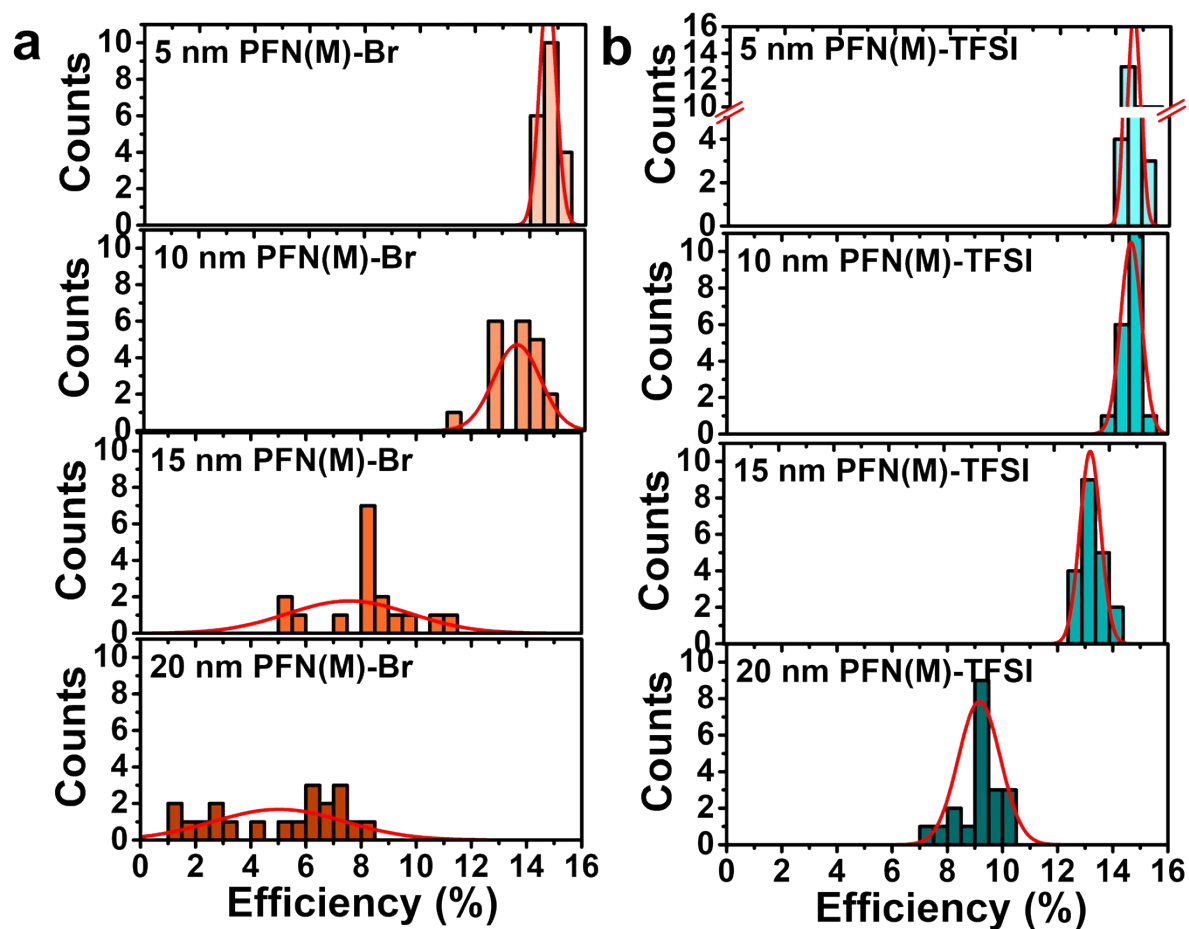
**Figure S7.** The histogram for power conversion efficiency of different 20 devices, which used **(a)** PFN(M)-Br or **(b)** PFN(M)-TFSI as cathode interlayer (CIL), according to the CIL thickness in a range of 5 nm to 20 nm.
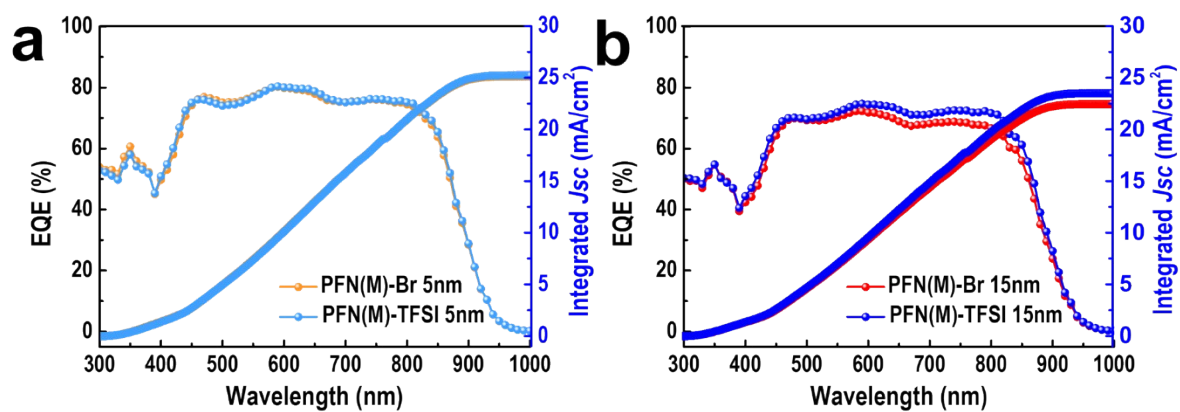
**Figure S8.** The results of external quantum efficiency measurement on the condition of **(a)** 5 nm and **(b)** 15 nm thickness of PFN(M) series CIM.
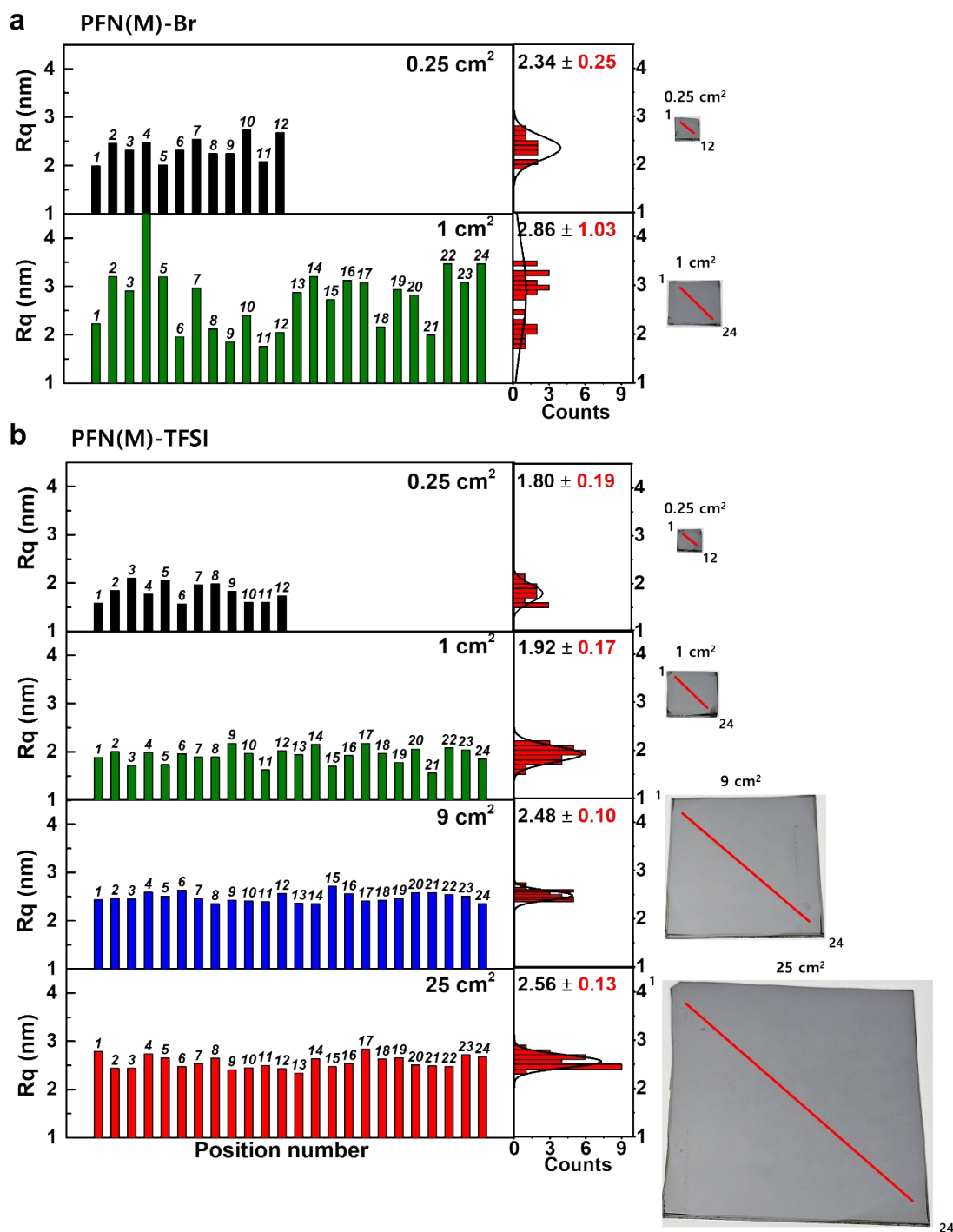
**Figure S9.** The raw data of $R_q$ at 24 measurement points along diagonal line on **(a)** the PFN(M)-Br and **(b)** PFN(M)-TFSI films in the area from 0.25 to 100 cm$^2$.
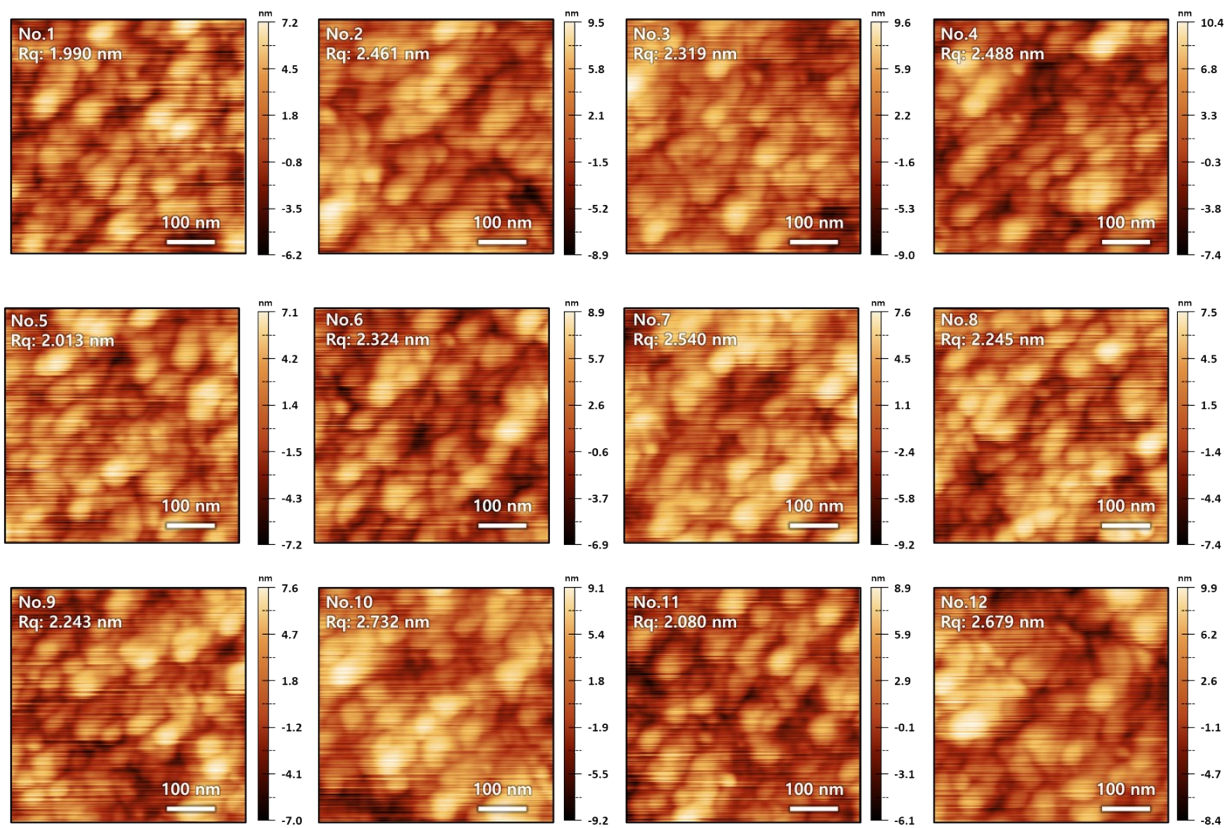
**Figure S10.** AFM image measuring 12 points diagonally of the PFN(M)-Br over an area of 0.25 cm$^2$.
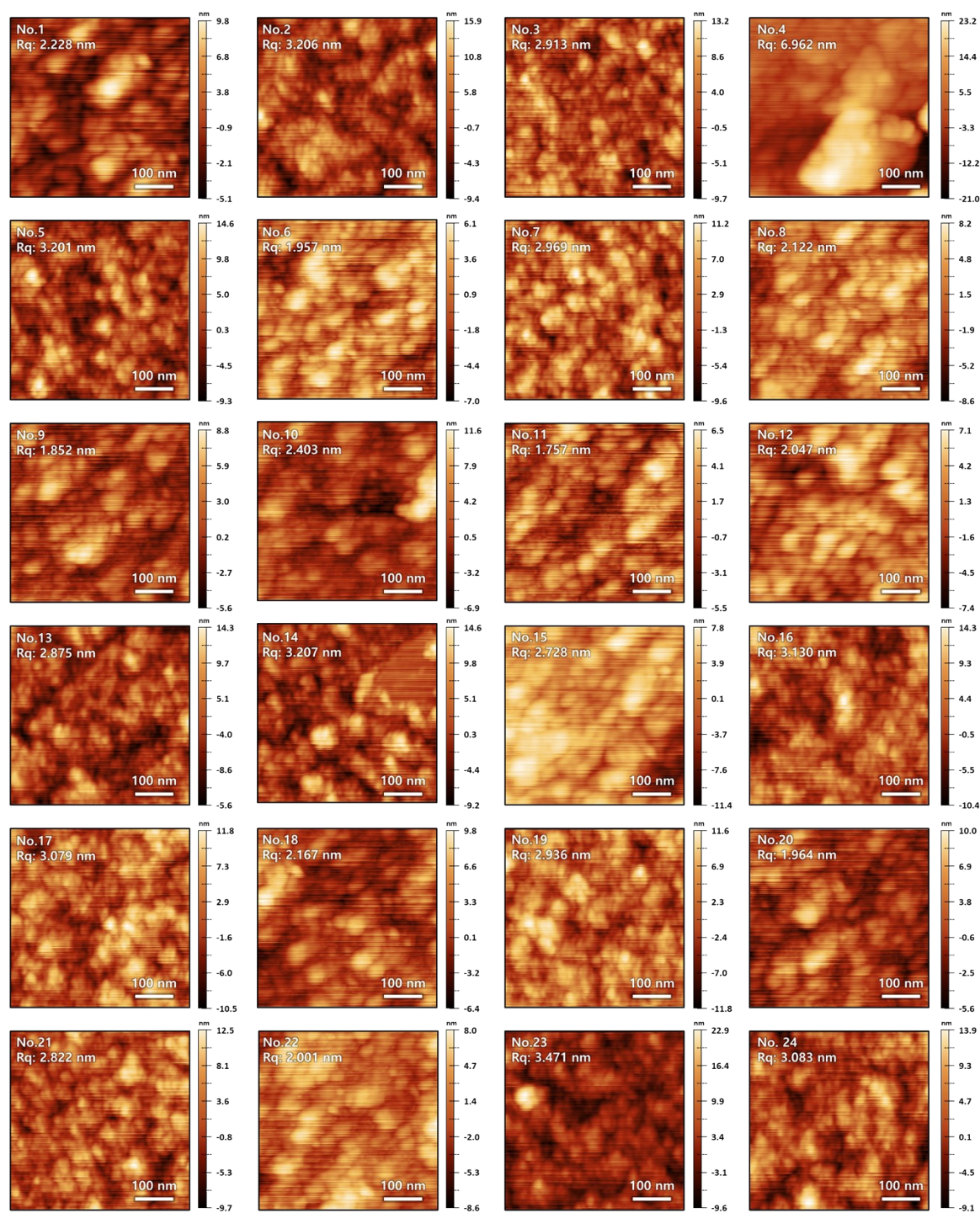
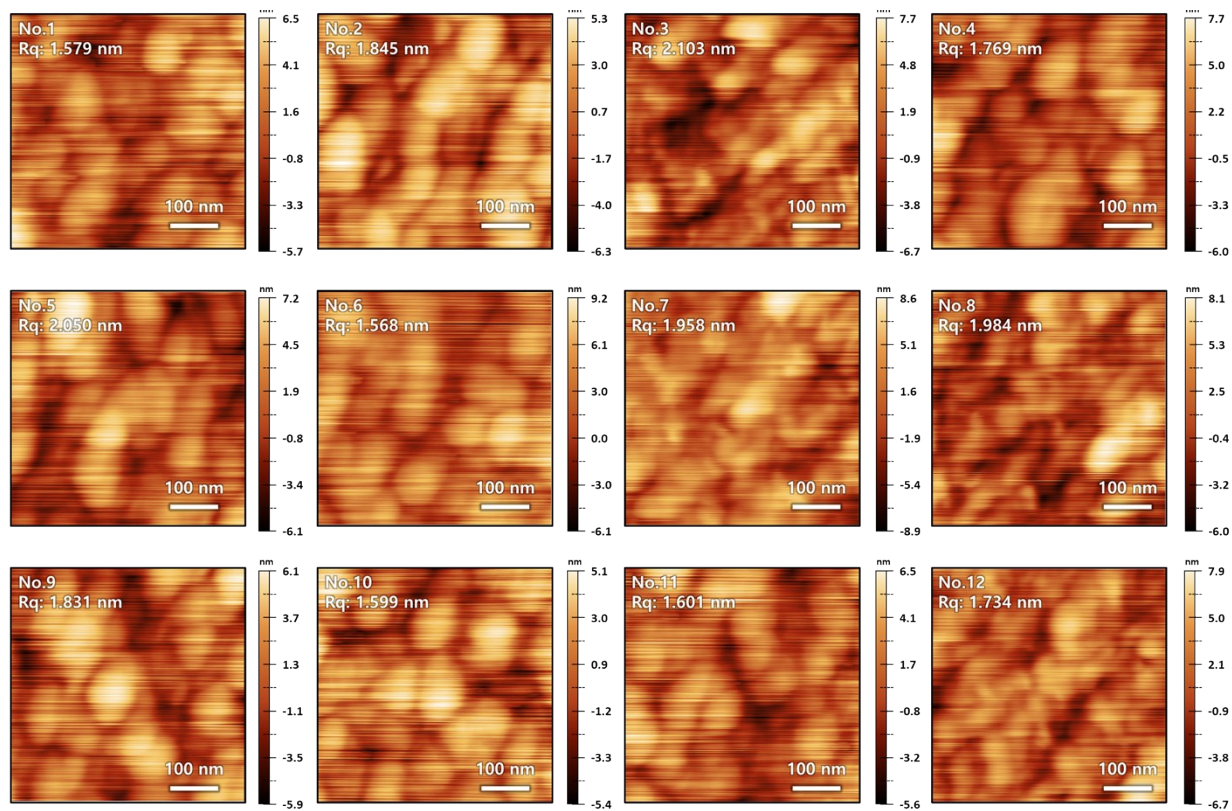**Figure S11.** AFM image measuring 24 points diagonally of the PFN(M)-Br over an area of 1 cm$^2$.

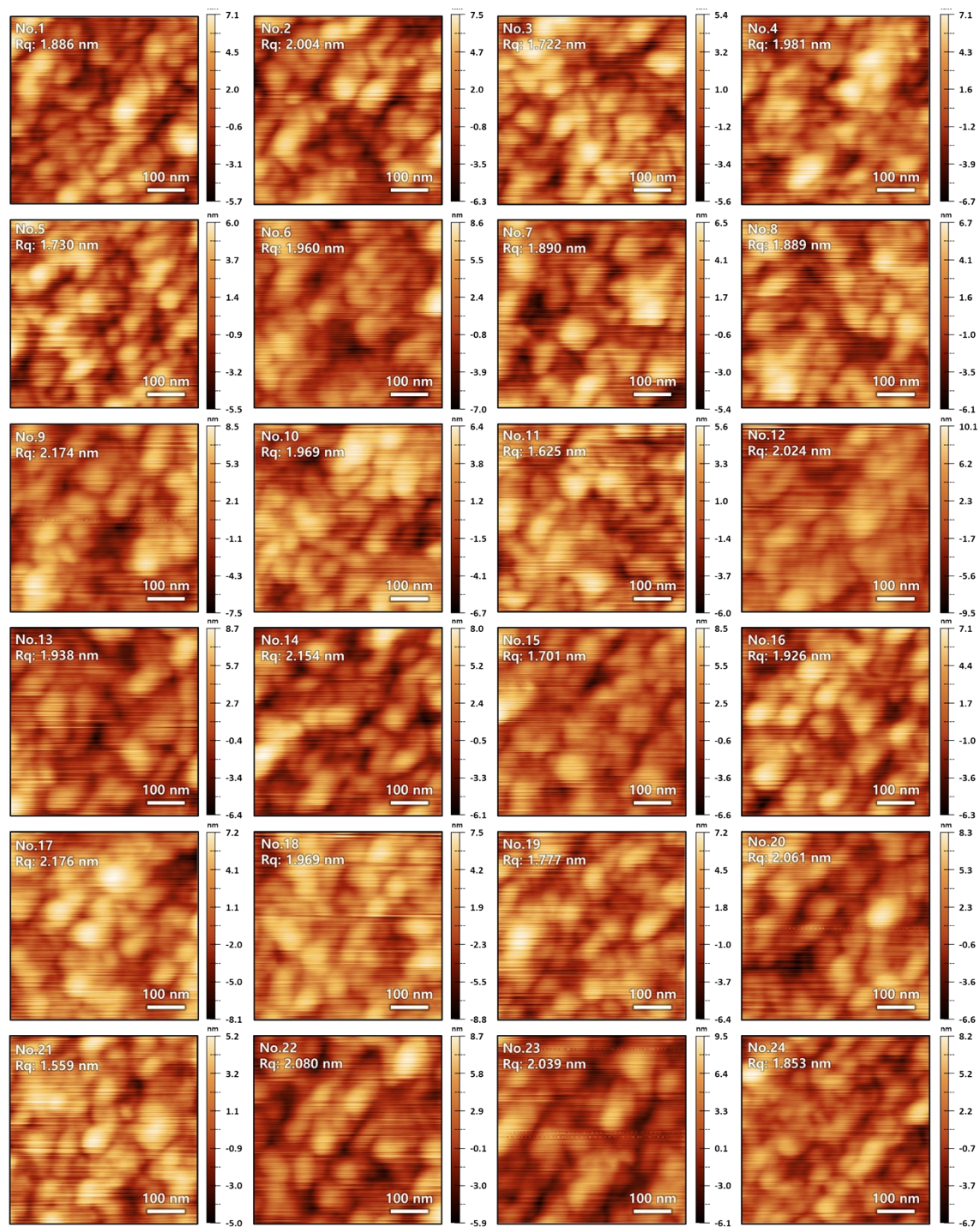**Figure S12.** AFM image measuring 12 points diagonally of the PFN(M)-TFSI over an area of 0.25 cm$^2$.

**Figure S13.** AFM image measuring 24 points diagonally of the PFN(M)-TFSI over an area of 1 cm$^2$.
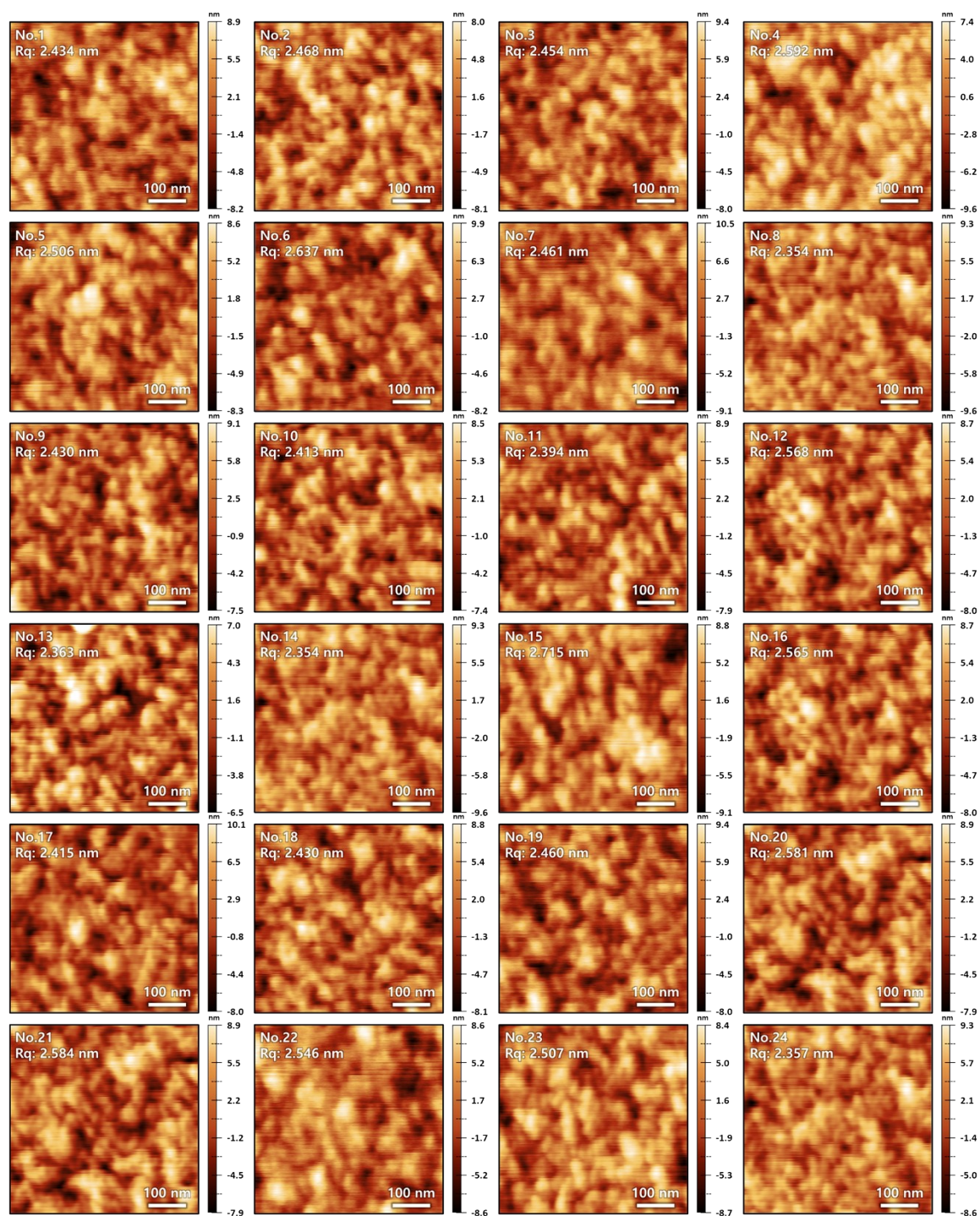
**Figure S14.** AFM image measuring 24 points diagonally of the PFN(M)-TFSI over an area of 9 cm$^2$.
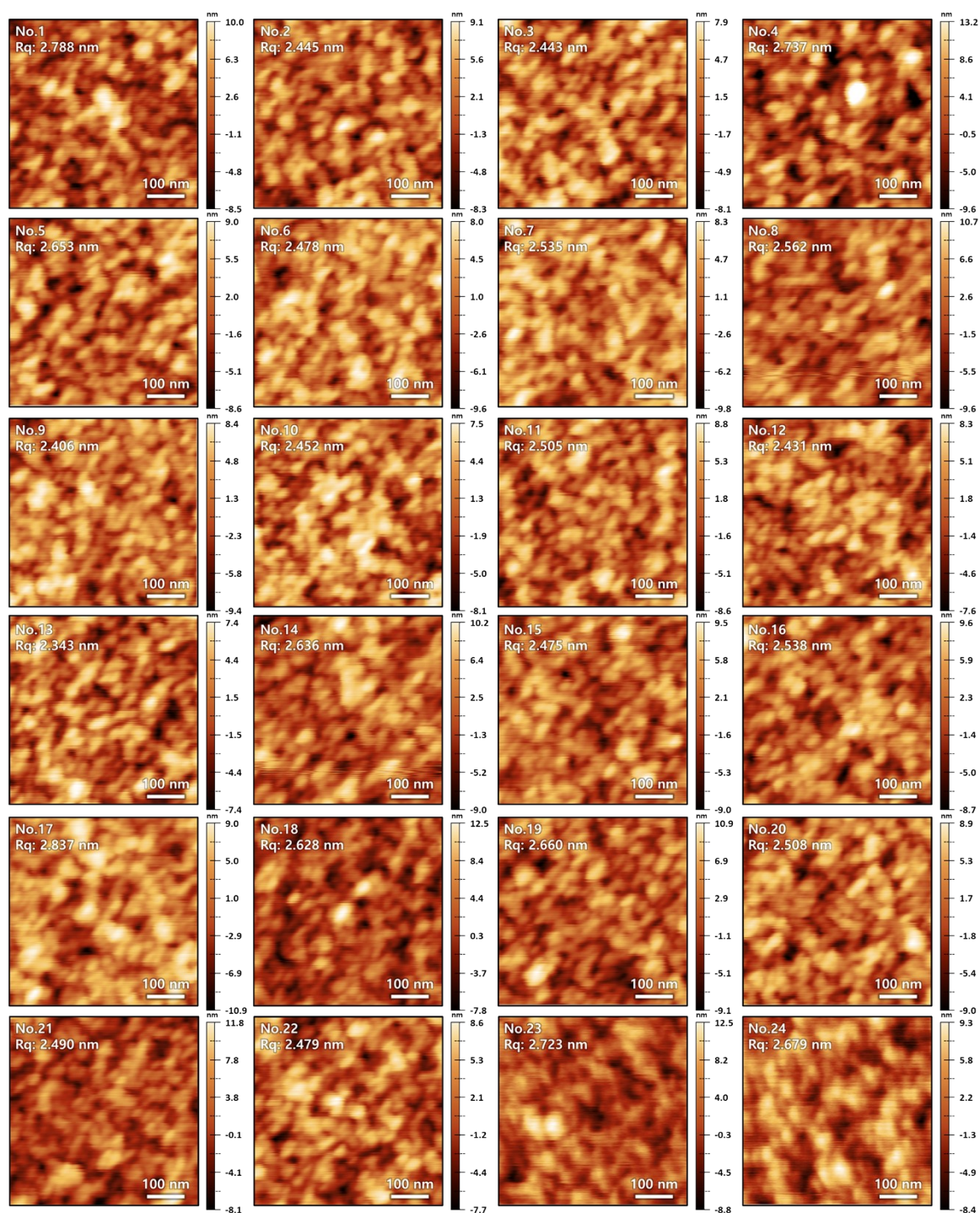
**Figure S15.** AFM image measuring 24 points diagonally of the PFN(M)-TFSI over an area of 25 cm$^2$.
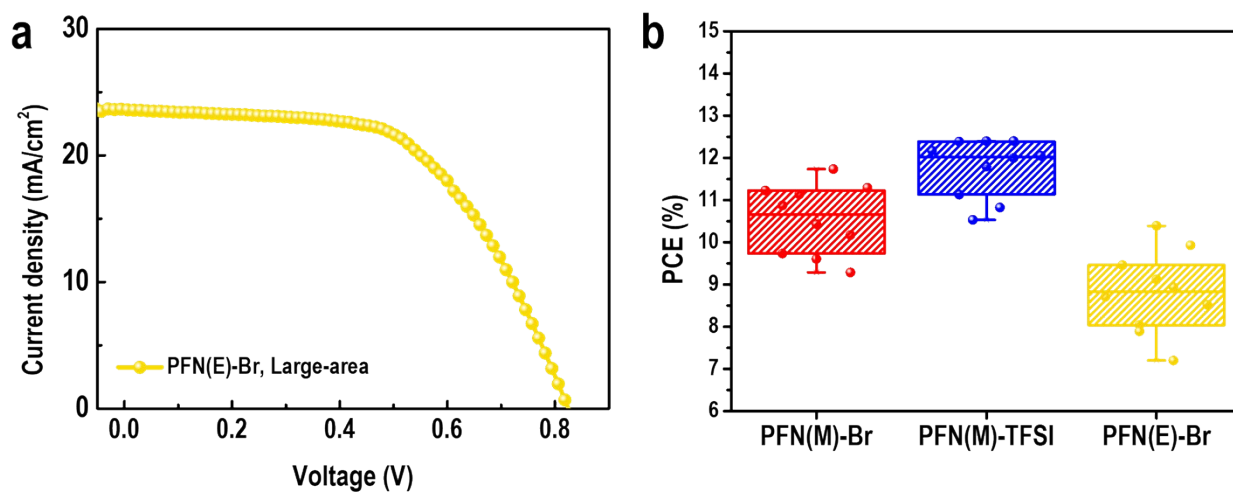
**Figure S16. (a)** The J-V curve of large-area devices, which applied PFN(E)-Br as CIL, and **(b)** the histograms of power conversion efficiency for 10 different devices.
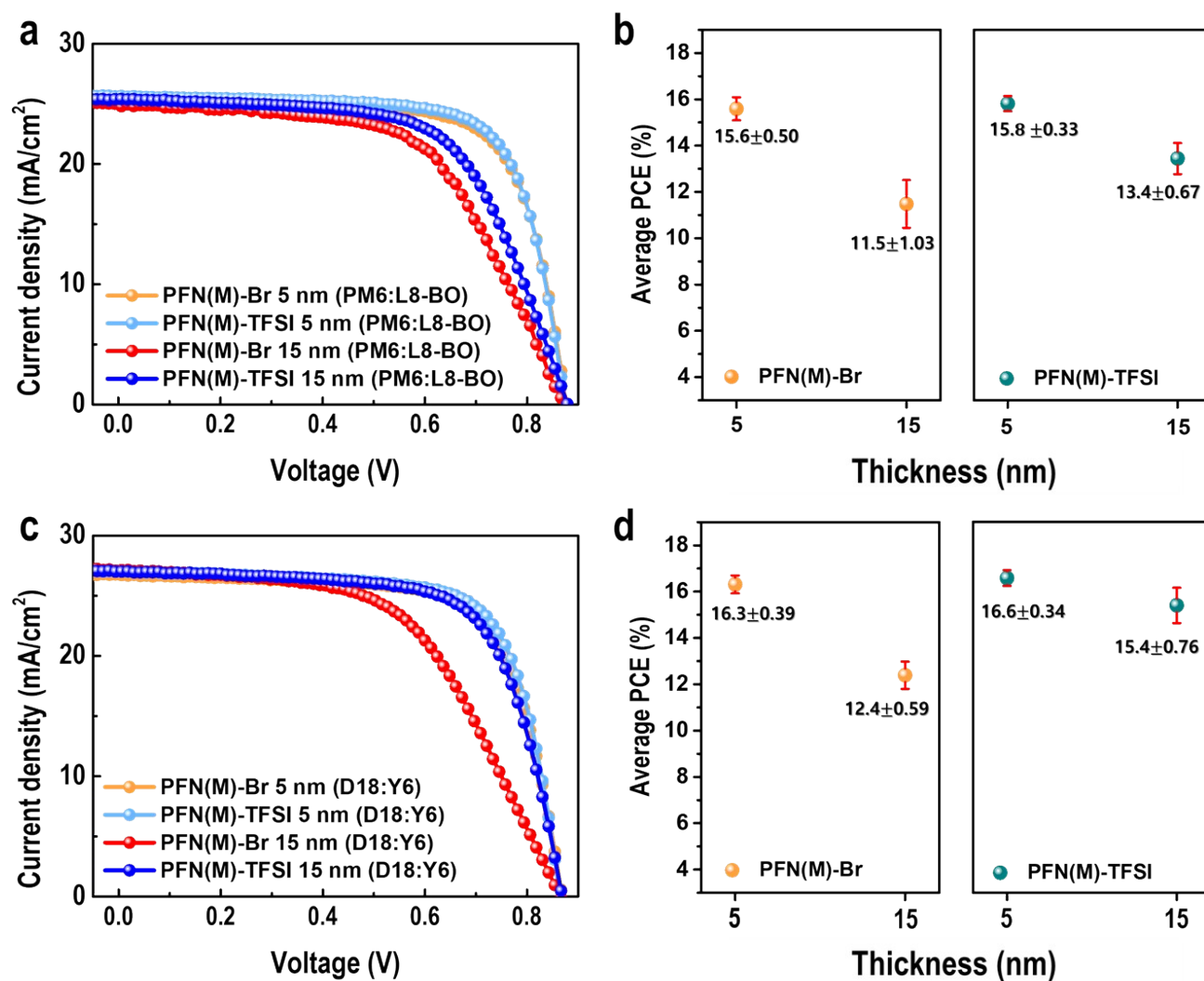
**Figure S17.** The J-V curve for the maximum power conversion efficiency at the thickness of 5 nm and 15 nm for PFN(M)-Br and PFN(M)-TFSI CIL in **(a)** PM6:L8-BO and **(c)** D18:Y6 based OPV. Device efficiency distribution with average efficiency and standard deviation value for 15 different devices. **(b)** PM6:L8-BO and **(d)** D18:Y6 based OPV.

**Table S1.** Alpha step results of cathode interlayer thickness according to precursor concentration of cathode interlayer material and spin-coating conditions.

| Condition | 0.5 mg/ml_dynamic | | 0.5 mg/ml_static | | 1 mg/ml_static | | 2 mg/ml_static | |
|---|---|---|---|---|---|---|---|---|
| Material | PFN(M)-Br | PFN(M)-TFSI | PFN(M)-Br | PFN(M)-TFSI | PFN(M)-Br | PFN(M)-TFSI | PFN(M)-Br | PFN(M)-TFSI |
| 1 | 5.0 nm | 5.0 nm | 9.3 nm | 11.6 nm | 14.6 nm | 15.7 nm | 18.3 nm | 19.2 nm |
| 2 | 5.5 nm | 4.9 nm | 11.9 nm | 10.8 nm | 14.2 nm | 17.2 nm | 20.4 nm | 19.5 nm |
| 3 | 3.4 nm | 4.5 nm | 10.7 nm | 10.1 nm | 17.8 nm | 16.1 nm | 20.7 nm | 19.9 nm |
| 4 | 4.7 nm | 5.5 nm | 8.8 nm | 9.2 nm | 17.6 nm | 14.1 nm | 20.1 nm | 20.2 nm |
| 5 | 6.6 nm | 5.4 nm | 9.0 nm | 8.9 nm | 12.7 nm | 14.2 nm | 19.2 nm | 19.4 nm |
| Average | 5.04 nm | 5.06 nm | 9.94 nm | 10.12 nm | 15.38 nm | 15.46 nm | 19.74 nm | 19.64 nm |

**Table S2**. The summary of J-V curve results with power conversion efficiency and device parameters of PFN(M)-Br, PFN(M)-TFSI and PFN(E)-Br employed devices with active area of 1.12 cm$^2$.

| CIM | $J_{SC}$[a] [mA/cm$^2$] | $V_{OC}$[b] [V] | FF[c] [%] | PCE[d] [%] |
|---|---|---|---|---|
| PFN(M)-Br | 24.6 | 0.81 | 58.7 | 11.74 |
| PFN(M)-TFSI | 24.5 | 0.81 | 62.7 | 12.44 |
| PFN(E)-Br | 22.6 | 0.83 | 56.4 | 10.58 |

[a]Short circuit current density ; [b]Open circuit voltage ; [c]Fill factor; [d]Best power conversion efficiency.

**Table S3**. The summary of J-V curve results with power conversion efficiency and device parameters of PFN(M)-Br and PFN(M)-TFSI employed devices with diverse active layer.

| Active layer | CIM | Thickness | $J_{SC}$[a] [mA/cm$^2$] | $V_{OC}$[b] [V] | FF[c] [%] | PCE[d] [%] |
|---|---|---|---|---|---|---|
| PM6:L8-BO | PFN(M)-Br | 5nm | 25.4 | 0.88 | 72.0 | 16.09 |
| | | 15nm | 25.0 | 0.88 | 55.7 | 12.25 |
| | PFN(M)-TFSI | 5nm | 25.6 | 0.88 | 72.8 | 16.40 |
| | | 15nm | 25.4 | 0.88 | 62.9 | 14.06 |
| D18:Y6 | PFN(M)-Br | 5nm | 26.8 | 0.87 | 71.1 | 16.58 |
| | | 15nm | 26.8 | 0.87 | 55.1 | 12.92 |
| | PFN(M)-TFSI | 5nm | 27.0 | 0.87 | 72.0 | 16.91 |
| | | 15nm | 27.0 | 0.87 | 69.2 | 16.26 |

[a]Short circuit current density ; [b]Open circuit voltage ; [c]Fill factor; [d]Best power conversion efficiency.