## Supporting Information

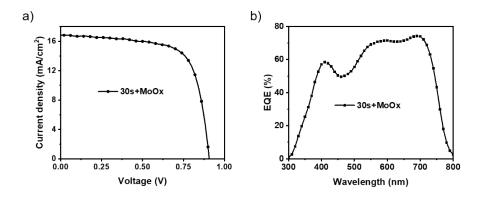
## Sequential molecular doping of non-fullerene organic solar cells without hole transport layers

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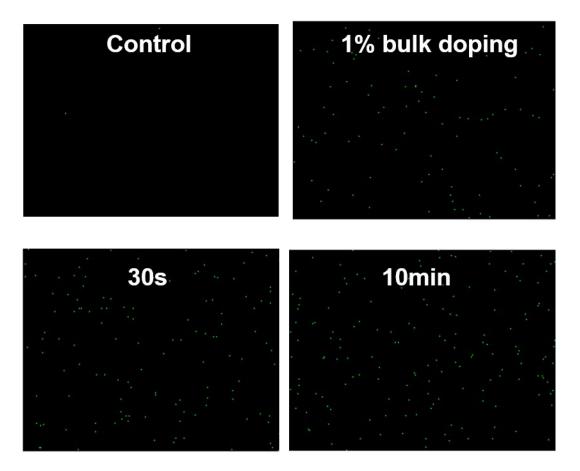
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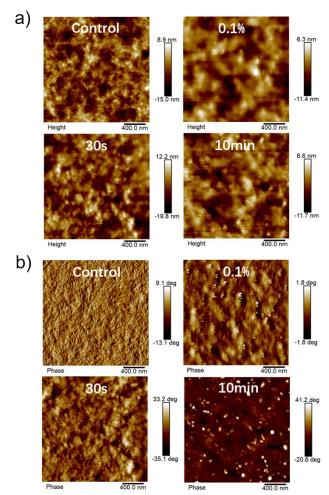
| Doping method     | HTL              | Doping condition | V <sub>oc</sub> (V) | J <sub>sc</sub> (mA/cm²) | FF (%) | PCE (%) |
|-------------------|------------------|------------------|---------------------|--------------------------|--------|---------|
| Bulk doping       | MoO <sub>x</sub> | 0%               | 0.89                | 16.61                    | 67.71  | 10.01   |
|                   |                  | 0.1%             | 0.89                | 16.10                    | 67.90  | 9.73    |
|                   |                  | 0.2%             | 0.89                | 15.67                    | 65.17  | 9.09    |
| Sequential doping | MoO <sub>x</sub> | 30 s             | 0.89                | 16.83                    | 71.16  | 10.66   |
|                   | w/o              | w/o              | 0.16                | 12.67                    | 42.09  | 0.85    |
|                   |                  | 0 s              | 0.87                | 16.28                    | 64.24  | 9.10    |
|                   |                  | 20 s             | 0.87                | 16.00                    | 68.34  | 9.51    |
|                   |                  | 40 s             | 0.87                | 17.01                    | 67.34  | 9.97    |
|                   |                  | 60 s             | 0.87                | 16.78                    | 65.20  | 9.52    |
|                   |                  | 80 s             | 0.87                | 16.06                    | 64.96  | 9.07    |



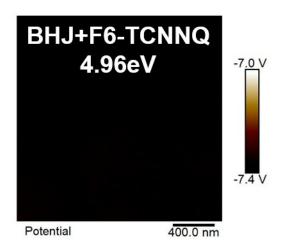
**Figure S1.** (a) Current density versus voltage (J-V) characteristics of sequential molecular doping device with MoOx after 30s penetration under AM 1.5 G solar irradiation. (b) EQE spectra of sequentially doped PBDBT:ITIC solar cells with MoOx after 30s penetration.



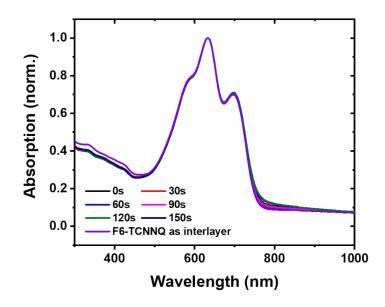
**Figure S2.** Elemental mapping of fluorine based on EDX analysis of PBDB-T:ITIC BHJ films with different doping methods.



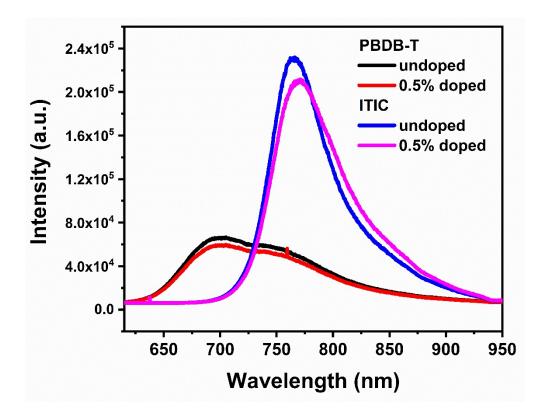
**Figure S3.** (a) Topographic and (b) phase images of pristine, bulk doped (0.1%) and sequentially doped (30 s and 10 min) PBDB-T:ITIC BHJ films.



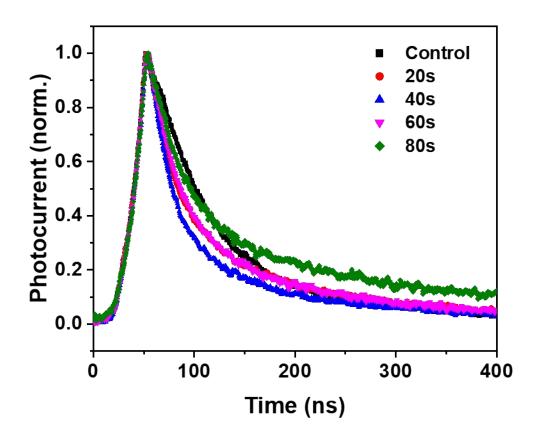
**Figure S4.** 2D mapping of the surface potential attained by scanning Kelvin probe microscopy for BHJ film spun-coat with F6-TCNNQ solution (conc. = 1.5 mg/mL).



**Figure S5.** Absorption spectra of PBDB-T:ITIC BHJ films in different sequential doping conditions.



**Figure S6.** Steady-state photoluminescence (PL) spectra of undoped and F6-TCNNQ doped PBDB-T or ITIC films in different conditions.



**Figure S7.** Transient photocurrent (bias = 0 V) decay traces of sequentially doped PBDBT:ITIC solar cells without MoOx under 488 nm excitation.

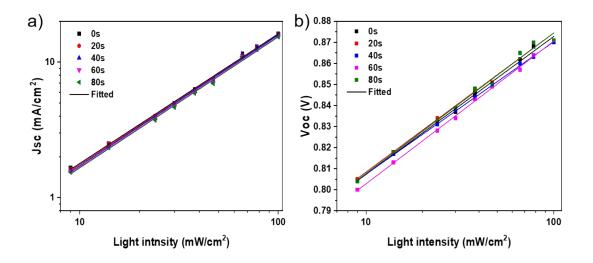
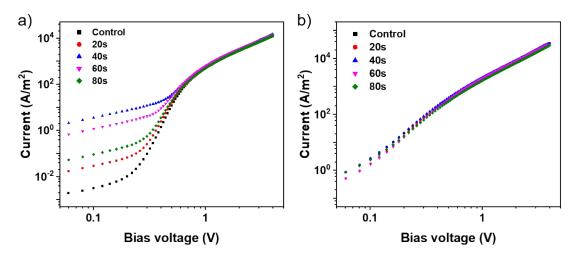


Figure S8. Short-current  $(J_{SC})$  and open-circuit voltage  $(V_{OC})$  versus light intensity characteristics.

| Doping condition | Slope of $J_{\rm SC}$<br>vs. $P_{\rm light}$ | Slope of $Vo_{\rm C}$ vs.<br>$P_{\rm light} (k_{\rm B}T/q)$ |
|------------------|--|---|
| 0 s              | 0.956  | 1.109   |
| 20 s             | 0.958  | 1.119   |
| 40 s             | 0.966  | 1.065   |
| 60 s             | 0.966  | 1.130   |
| 80 s             | 0.966  | 1.148   |
|                  |  |   |

Table S2. Extracted slopes of  $J_{\rm SC}$  vs.  $P_{\rm light}$  and  $V_{\rm OC}$  vs.  $P_{\rm light}$  characteristics.



**Figure S9.** Dark *J-V* characteristics of (a) hole-only devices based on the structure of ITO/PEDOT:PSS/doped BHJ/Au and (b) electron-only devices based on the structure of ITO/ZnO/doped BHJ/ BCP/Al. The active layers are PBDB-T:ITIC blend films in different doping conditions.