

Supporting Information

Induced Crystallization of Perovskites by Perylene Underlayer For High-Performance Solar Cells

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KEYWORDS: perovskite solar cells; interface engineering; perylene underlayer; induced crystallization; stability.

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Table S1. A brief summary of the morphology and the crystallization controls of the perovskite films by different underlayers.

| Underlayer | Cell Configuration | J_{sc} (mA/cm ²) | V_{oc} (V) | FF | PCE (%) | Ref. |
|------------------------------|--|-----------------------------------|-----------------|------|--------------|--|
| P-type contact | NiO _x /MAPbI ₃ /PCBM | 16.27 | 0.88 | 0.63 | 9.1 | 2014 Angew. Chem. 126 , 12779 |
| | NiO _x /MAPbI ₃ /ZnO | 21.0 | 1.01 | 0.76 | 16.1 | 2016 Nat. Nanotechnol. 11 , 75 |
| | NiO+Cu/MAPb(I _{0.8} Br _{0.2}) ₃ /PCBM/C ₆₀ -bis | 18.50 | 1.11 | 0.72 | 15.0 | 2015, Adv. Mater. 27 , 695 |
| | rGO/MAPbI ₃ /PCBM/C ₆₀ /BCP | 14.81 | 0.95 | 0.71 | 10.8 | 2015 Nano Energy 12 , 96 |
| | NiMgLiO/MAPbI ₃ /PCBM/Ti(Nb)O _x | 20.62 | 1.07 | 0.75 | 16.2 | 2015, Science 350 , 944 |
| | Poly-TPD/MAPbI ₃ /PCBM/C ₆₀ /BCP | 22.0 | 1.10 | 0.69 | 15.3 | 2015 Adv. Energy Mater. 5 , 1401855 |
| | PTAA/MAPbI ₃ /PCBM/C ₆₀ /BCP | 22.0 | 1.07 | 0.77 | 18.12 | 2015 Nat. Commun. 6 , 7747 |
| | PTAA:F ₄ TCNQ/MAPbI ₃ /PCBM/C ₆₀ /BCP | 21.6 | 1.09 | 0.74 | 17.5 | 2015 Nano Energy 15 , 275 |
| Additive in PEDOT:PSS | PEDOT:PSS (DMSO additive)/MAPbI ₃ /PTCDI/Cr ₂ O ₃ /Cr | 17.5 | 0.93 | 0.80 | 12.5 | 2015, Nat. Mater. 14 , 1032 |
| Interfacial layer | PEDOT:PSS/Poly-TPD/MAPbI ₃ /PCBM | 16.12 | 1.05 | 0.67 | 12.0 | 2014 Nat. Photonics. 8 , 128 |
| | PEDOT:PSS/Perylene/MAPbI _{3-x} Cl _x /PCBM/Bphen | 22.61 | 0.98 | 0.77 | 17.0 | This work |

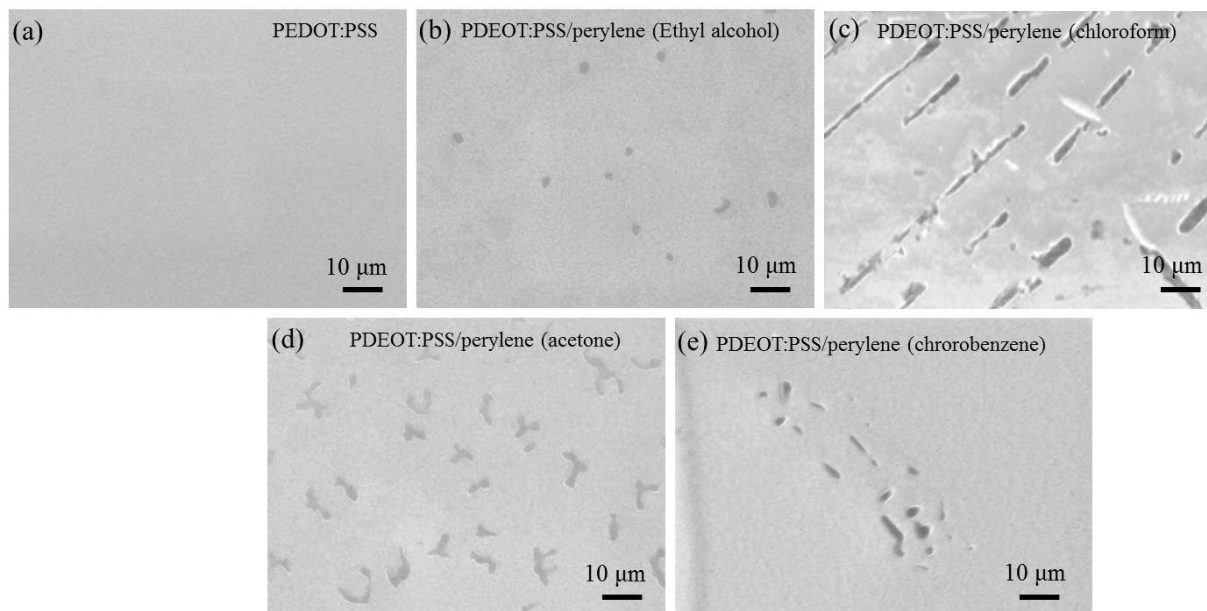


Figure S1. SEM images of (a) pristine PEDOT:PSS, (b) PEDOT:PSS/perylene (Ethyl alcohol), (c) PEDOT:PSS/perylene (chloroform), (d) PEDOT:PSS/perylene (Acetone), and (e) PEDOT:PSS/perylene (chlorobenzene) with fixed concentration of 1 mg/mL.

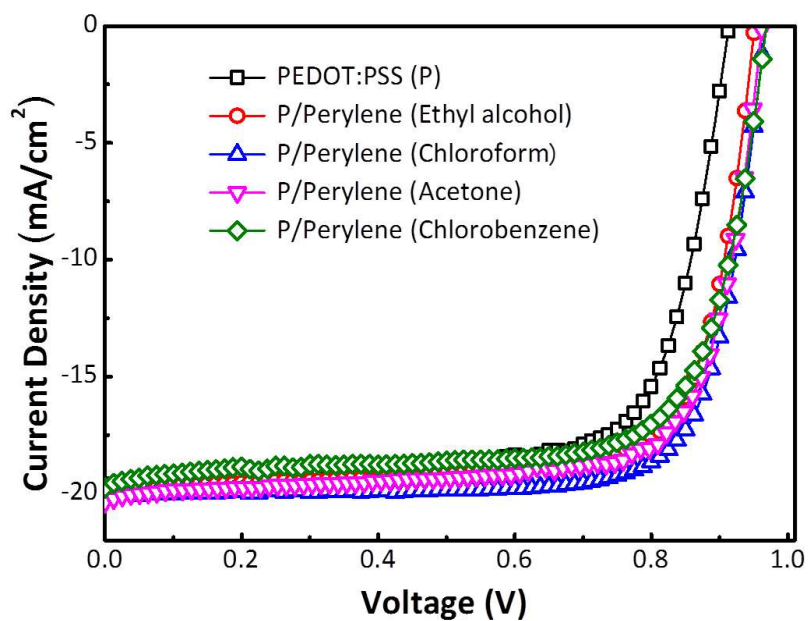


Figure S2. J - V curves of PHJ PSCs based on perylene layers with different solvent and fixed concentration of 1 mg/mL measured under simulated AM 1.5 sunlight of 100 mW/cm².

Table S2. Cell parameters of PHJ PSCs based on perylene layers with different solvent and fixed concentration of 1 mg/mL.

| Underlayer | J_{sc} (mA/cm ²) | V_{oc} (V) | FF (%) | PCE (%) |
|------------------------------------|--------------------------------|--------------|--------|---------|
| PEDOT:PSS | 19.73 | 0.91 | 72 | 12.93 |
| PEDOT:PSS/Perylene (Ethyl alcohol) | 20.02 | 0.94 | 73 | 13.73 |
| PEDOT:PSS/Perylene (Chloroform) | 20.09 | 0.96 | 77 | 14.85 |
| PEDOT:PSS/Perylene (Acetone) | 20.36 | 0.95 | 74 | 14.31 |
| PEDOT:PSS/Perylene (Chlorobenzene) | 19.44 | 0.96 | 72 | 13.43 |

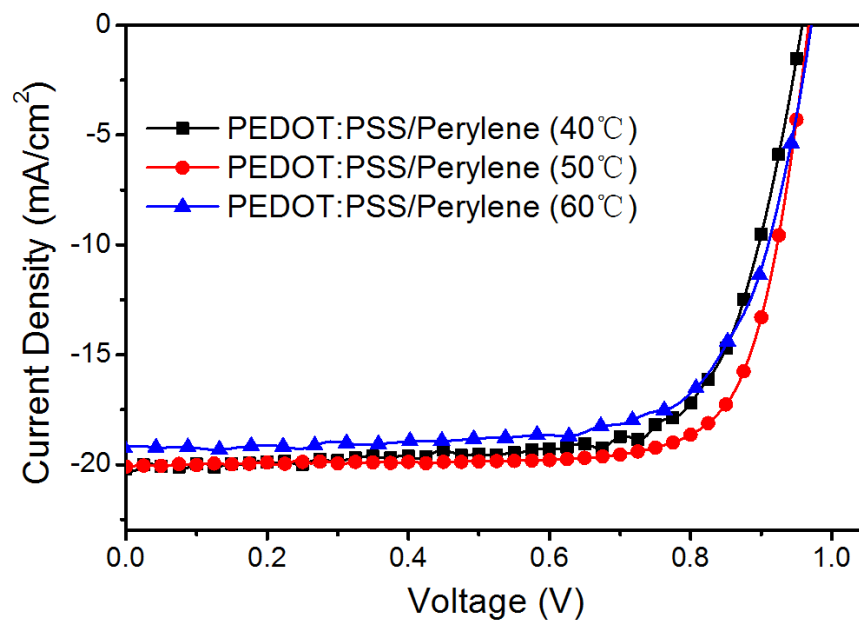


Figure S3. *J-V* curves of PHJ PSCs based on perylene (4 mg/mL) layers with different annealing temperatures measured under simulated AM 1.5 sunlight of 100 mW/cm².

Table S3. Cell parameters of PHJ PSCs based on perylene layers with different annealing temperature.

| Underlayer | J_{sc} (mA/cm ²) | V_{oc} (V) | FF (%) | PCE (%) |
|----------------------------|--------------------------------|--------------|--------|---------|
| PEDOT:PSS/Perylene (40 °C) | 0.96 | 20.20 | 72 | 13.93 |
| PEDOT:PSS/Perylene (50 °C) | 0.96 | 20.09 | 77 | 14.85 |
| PEDOT:PSS/Perylene (60 °C) | 0.97 | 19.16 | 73 | 13.48 |

Table S4. The film coverage of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskites with different underlayers.

| Samples | Total pixel | Cover pixel | Coverage (%) |
|---|----------------|----------------|-----------------|
| ITO/ $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ | 67902 | 47123 | 69.4 |
| ITO/perylene/ $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ | 68852 | 56114 | 81.5 |
| ITO/PEDOT:PSS/ $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ | 68542 | 62853 | 91.7 |
| ITO/PEDOT:PSS/perylene/ $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ | 66895 | 63015 | 94.2 |

The total pin-holes' area (or non-covered area) in the active surface area of all samples were calculated by using the method reported in the ref: T. Matsushima *et al.*, *J. Mater. Chem. A* **2015**, 3, 17780.

This method separates the RGB tricolor gray value from the picture, so the area covered by perovskite was determined by measuring the proportion of every perovskite pixel. The coverage can be calculated by image pixels' regional distribution. Here we used photoshop CS5 software to calculate the image pixels.

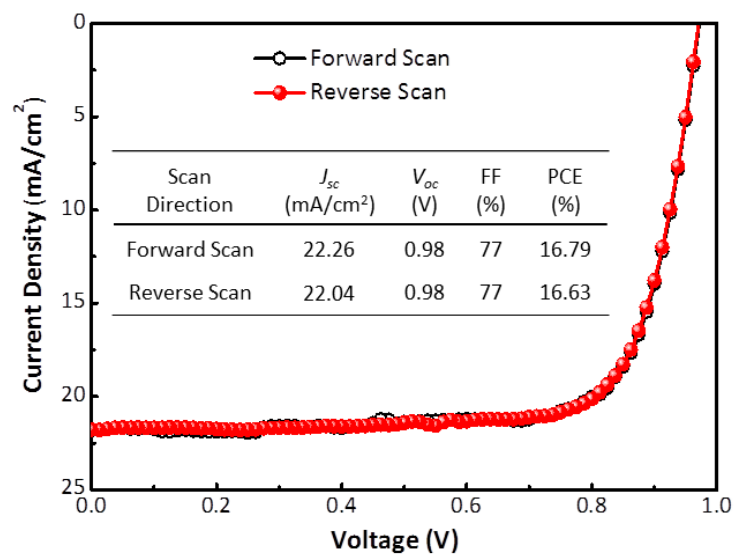


Figure S4. Forward and reverse scans of J - V curves of PHJ PSCs based on perylene deposited from 4 mg/mL solution. The inset is the table of key cell parameters.

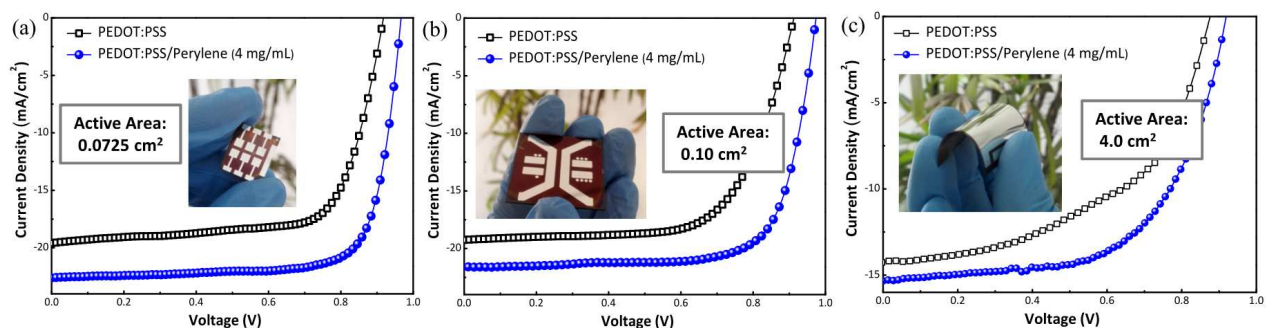


Figure S5. J - V curves of PEDOT:PSS and PEDOT:PSS/Perylene based PHJ PSCs with active area of (a) 0.0725 cm^2 , (b) 0.10 cm^2 , and (c) 4.0 cm^2 .

Table S5. Cell parameters of PEDOT:PSS and PEDOT:PSS/Perylene based PHJ PSCs with different active area.

| Device | J_{SC} (mA/cm ²) | V_{OC} (V) | FF | PCE (%) |
|--|--------------------------------|--------------|----|---------|
| PEDOT:PSS (0.0725 cm^2) | 19.61 | 0.91 | 71 | 12.67 |
| PEDOT:PSS/Perylene (0.0725 cm^2) | 22.61 | 0.98 | 77 | 17.06 |
| PEDOT:PSS (0.10 cm^2) | 19.29 | 0.91 | 67 | 11.67 |
| PEDOT:PSS/Perylene (0.10 cm^2) | 21.80 | 0.97 | 74 | 15.75 |
| PEDOT:PSS (4.0 cm^2) | 14.22 | 0.87 | 52 | 6.43 |
| PEDOT:PSS/Perylene (4.0 cm^2) | 15.33 | 0.91 | 60 | 8.47 |

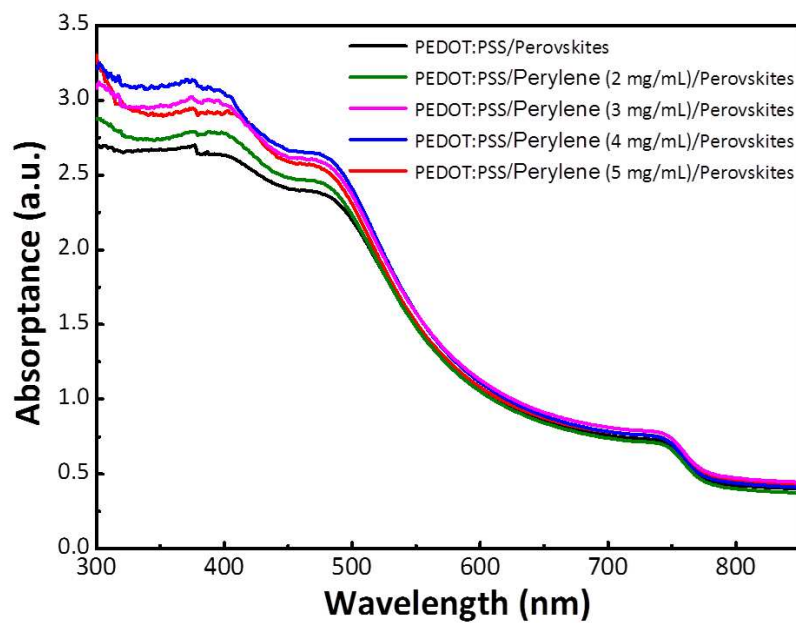


Figure S6. Absorption spectra of CH₃NH₃PbI_{3-x}Cl_x perovskite films deposited on PEDOT:PSS and PEDOT:PSS/perylene with different concentration.

Table S6. Electrical impedance spectroscopy (EIS) parameters of PEDOT:PSS and PEDOT:PSS/perylene (4 mg/mL) based PHJ PSCs.

| | PEDOT:PSS | PEDOT:PSS/perylene |
|-------------------|----------------------|----------------------|
| | Based Device | Based Device |
| $R_s (\Omega)$ | 62.3 | 31.2 |
| $R_{CT} (\Omega)$ | 1356 | 957 |
| C (F) | 2.3×10^{-6} | 2.3×10^{-6} |

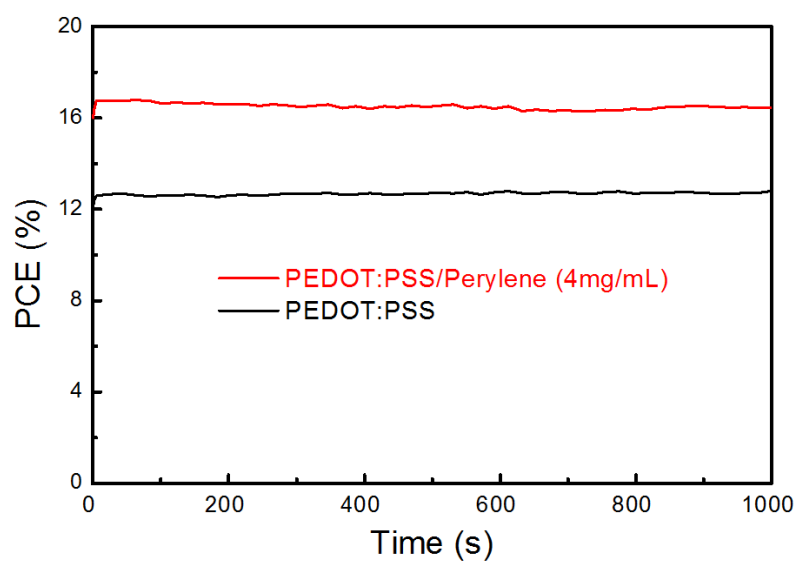


Figure S7. Steady state power conversion efficiency (PCE) operated at the maximum power point of PHJ PSCs using PEDOT:PSS and PEDOT:PSS/perylene as the underlayers.