

## Supporting Information for

# **Importance of Device Structure and Interlayer Design in Storage Stability of Naphthalene Diimide-based All-Polymer Solar Cells**

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**Keywords:** all-polymer solar cells, stability, burn-in degradation, storage lifetime, naphthalene diimide polymers, interlayers

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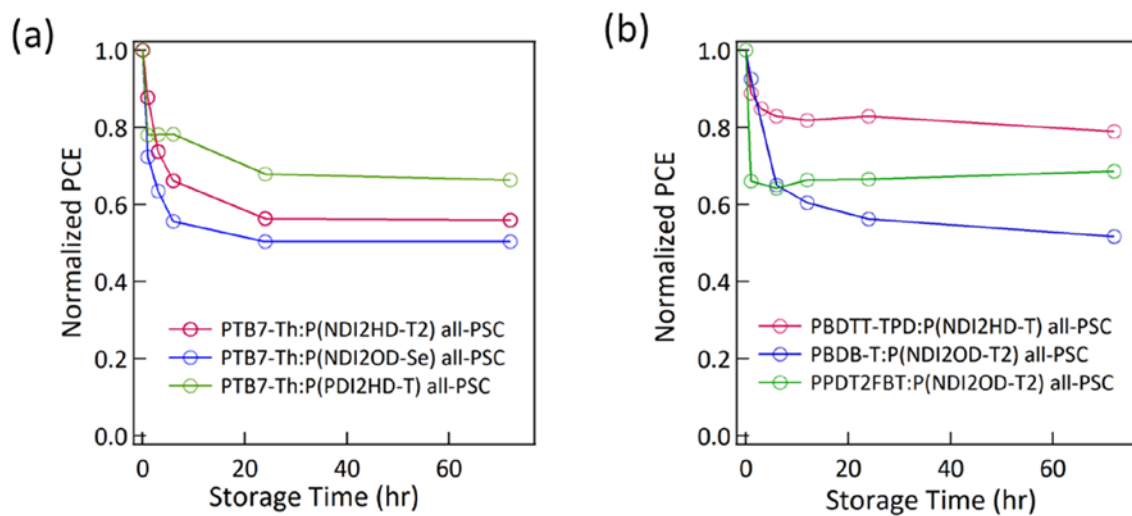
### Supplementary Fig. S1-5

- **Fig. S1:** Storage stability of various all-PSC systems.
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### Supplementary Table S1-2

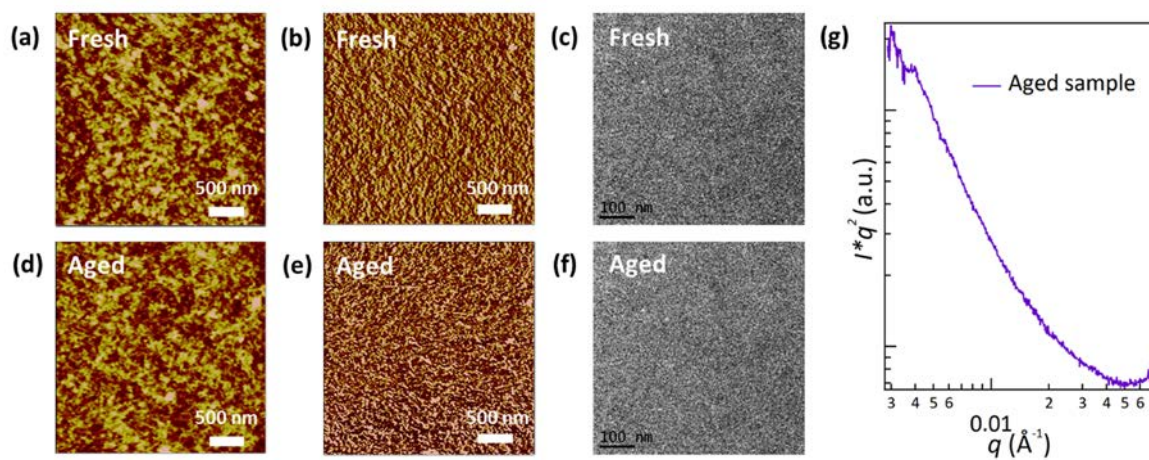
- **Table S1:** Performances of BHJ and bilayer all-PSCs as a function of storage.
- **Table S2:** Long-term storage stability of all-PSCs.

## Storage stability of various all-PSC systems



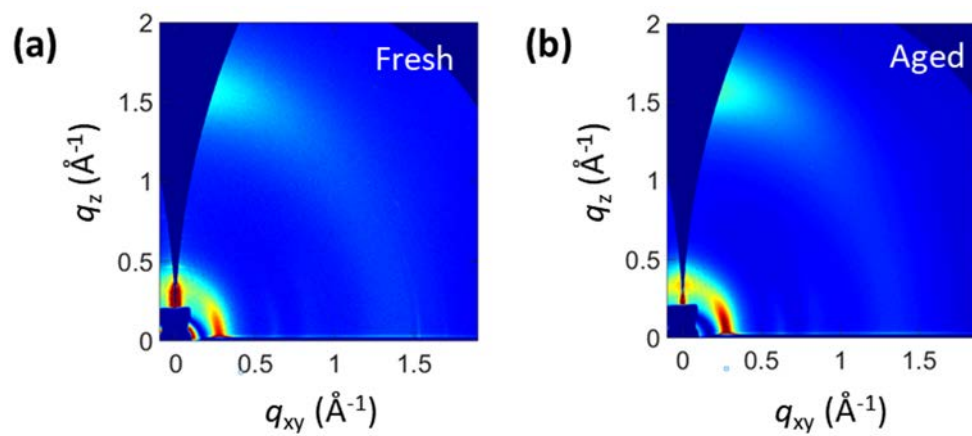
**Fig. S1.** (a) Storage lifetimes of PTB7-Th-based all-PSCs with different  $P_{AS}$ , P(NDI2HD-T2), P(NDI2HD-Se) and P(PDI2HD-T). (b) Storage lifetimes of NDI-based all-PSCs with different  $P_{DS}$ , PBDTT-TPD, PBDB-T and PPDT2FBT.

## Morphological change of all-PSCs after 24-hours storage



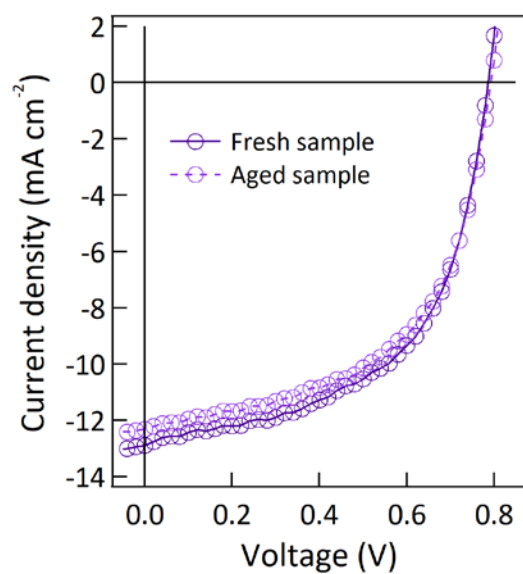
**Fig. S2.** AFM height and phase images of (a, b) fresh and (d, e) aged all-PSCs. TEM images of (c) fresh and (f) aged all-PSCs. (g) RSoXS profile of aged all-PSCs.

**Polymer packing structure of all-PSCs after 24-hours storage**



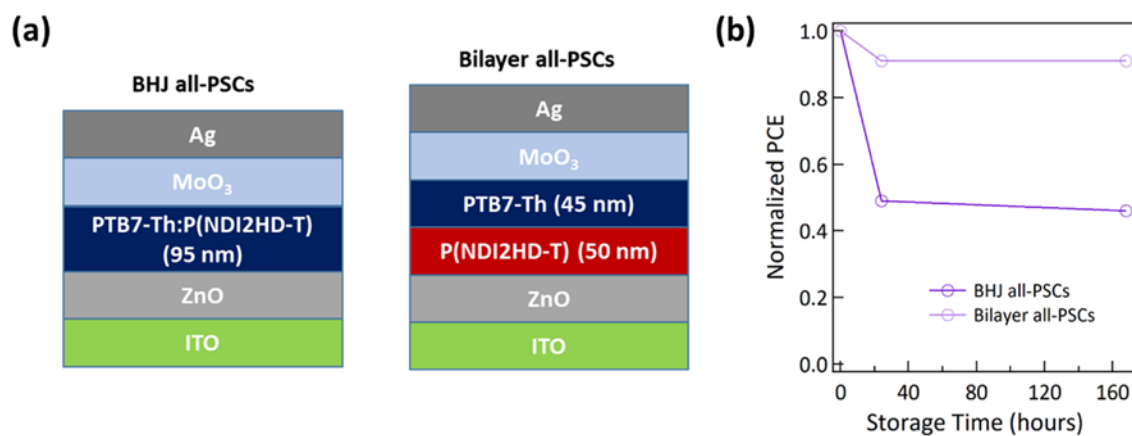
**Fig. S3.** 2D GIXS patterns of (a) fresh and (b) aged PTB7-Th:P(NDI2HD-T) all-PSCs.

## Device testing for checking morphological stability



**Fig. S4.** *J-V* curves of all-PSCs, where the Ag electrodes were deposited directly (fresh) or after 3 days (aged) from the active layer formation.

## Comparison on the storage stability of BHJ and bilayer all-PSCs



**Fig. S5.** Storage stability of BHJ and bilayer all-PSCs. To fabricate bilayer all-PSCs, PTB7-Th was floated onto water and transferred onto P(NDI2HD-T) layer.

**Table S1.** Photovoltaic parameters of BHJ and bilayer all-PSCs as a function of storage.

Devices	Storage (hr)	$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF	PCE (%)
BHJ all-PSCs	0	0.79	12.12	0.58	5.55
	24	0.77	6.93	0.51	2.72
	168	0.76	6.98	0.48	2.55
Bilayer all-PSCs	0	0.80	1.26	0.66	0.66
	24	0.80	1.20	0.63	0.60
	168	0.80	1.18	0.63	0.60

## Long-term storage stability of all-PSCs

**Table 1.** Photovoltaic parameters of all-PSCs as a function of storage time.

Inverted-type all-PSCs with a PEDOT:PSS passivation layer				
PTB7-Th:P(NDI2HD-T)	$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF	PCE (%)
0 hr	0.79	11.65	0.56	5.15
24 hr	0.78	11.35	0.54	4.78
168 hr	0.77	11.06	0.52	4.43
336 hr	0.77	10.80	0.51	4.24
1080 hr	0.76	11.02	0.50	4.15
PBDTT-TPD:P(NDI2HD-T)	$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF	PCE (%)
0 hr	1.03	10.01	0.57	5.88
24 hr	1.01	10.05	0.55	5.58
168 hr	0.99	10.26	0.54	5.48
336 hr	0.99	10.10	0.54	5.40
1080 hr	0.99	10.19	0.53	5.35
Normal-type all-PSCs with a PNDIT-F3N-Br polymer interlayer				
PTB7-Th:P(NDI2HD-T)	$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF	PCE (%)
0 hr	0.78	13.54	0.49	5.17
24 hr	0.78	13.05	0.48	4.89
168 hr	0.77	13.01	0.48	4.81
336 hr	0.77	13.72	0.46	4.86
1080 hr	0.76	13.33	0.45	4.52
PBDTT-TPD:P(NDI2HD-T)	$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF	PCE (%)
0 hr	1.07	10.69	0.65	7.42
24 hr	1.07	10.53	0.62	6.94
168 hr	1.06	10.42	0.62	6.85
336 hr	1.06	10.29	0.61	6.65
1080 hr	1.06	10.27	0.59	6.47