

## Electronic Supplementary Information

### Highly efficient organic p-i-n photovoltaic cells based on tetraphenyldibenzoperiflантene and fullerene C<sub>70</sub>

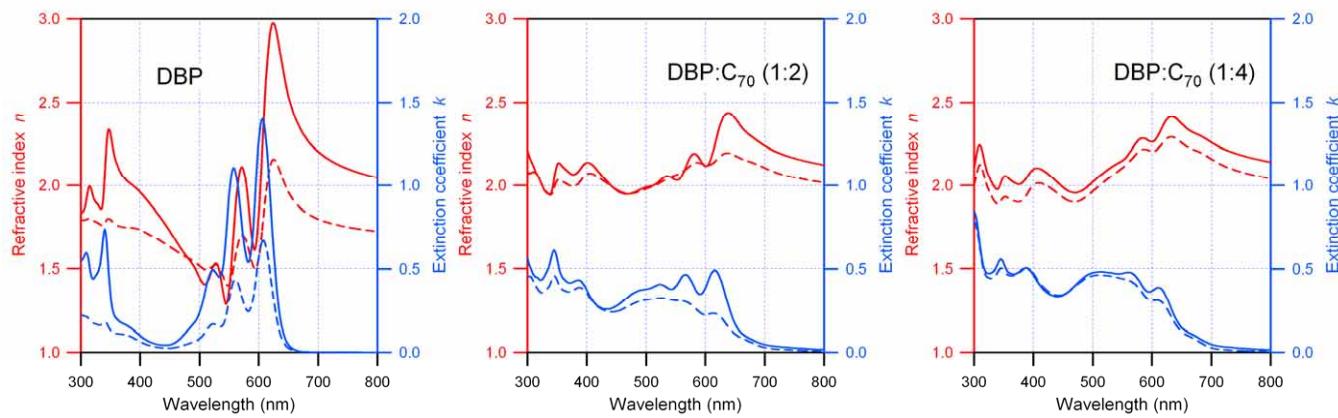
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**Fig. S1.** Comparison of anisotropic properties of DBP:C<sub>70</sub> films with blend ratios of (a) 1:0 (DBP neat film), also see Ref 20, (b) 1:2, and (c) 1:4.

One is 1:0 (DBP neat film), and the others are blend films with ratios of 1:2 and 1:4. All films show anisotropic properties, especially at the absorption wavelength of DBP around 615 nm, indicating that DBP molecules are horizontally oriented in all these films.

Although the anisotropy of the 1:4 film seems smaller than the 1:0 and 1:2 films, it is because DBP molecules having anisotropic orientation are highly diluted by C<sub>70</sub> molecules having isotropic orientation. (Ref 20. Sol. Energy Mater. Sol. Cells 2012, 98, 472.)

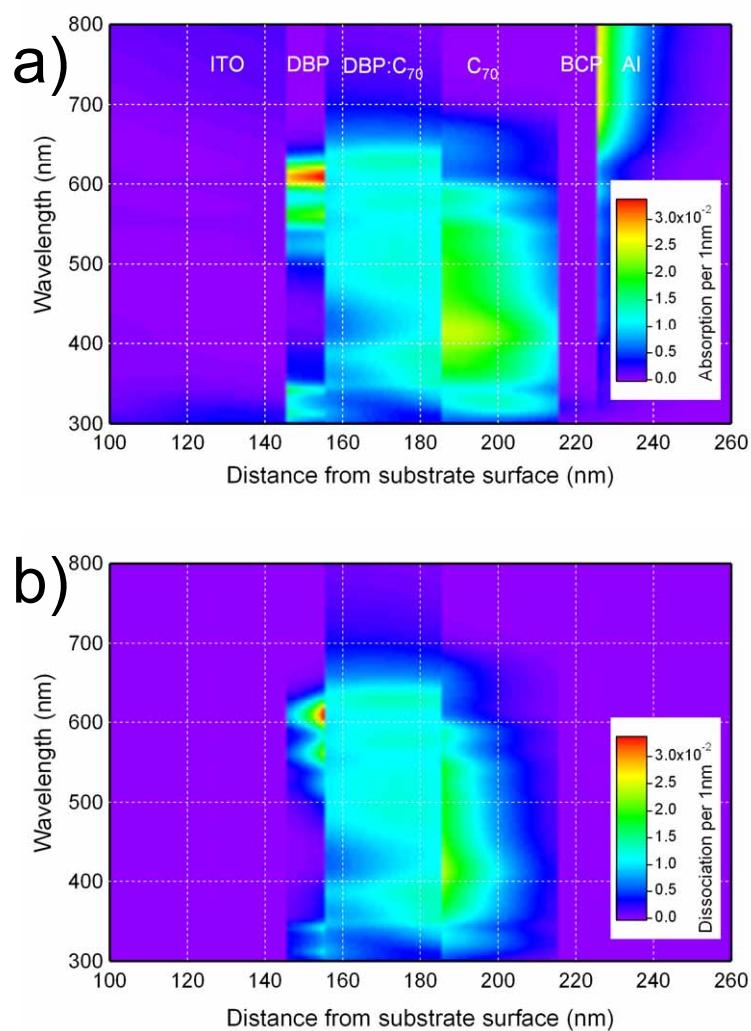
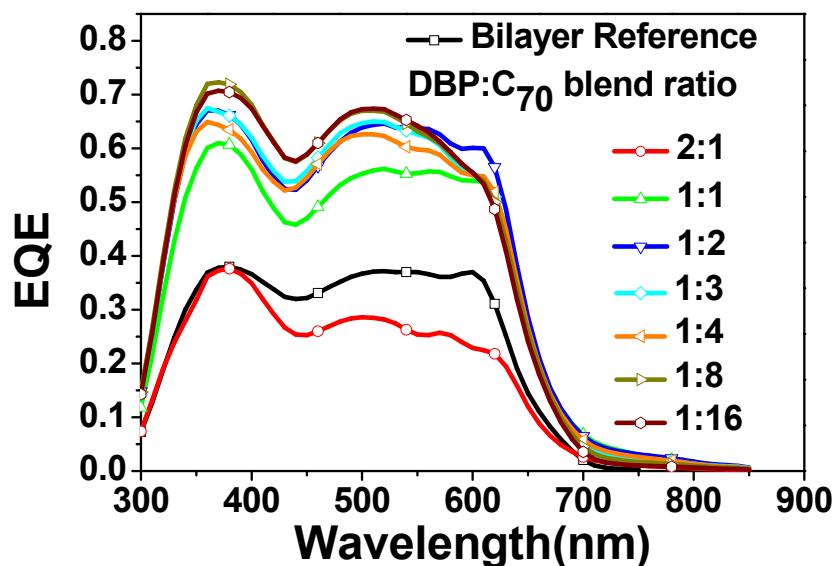
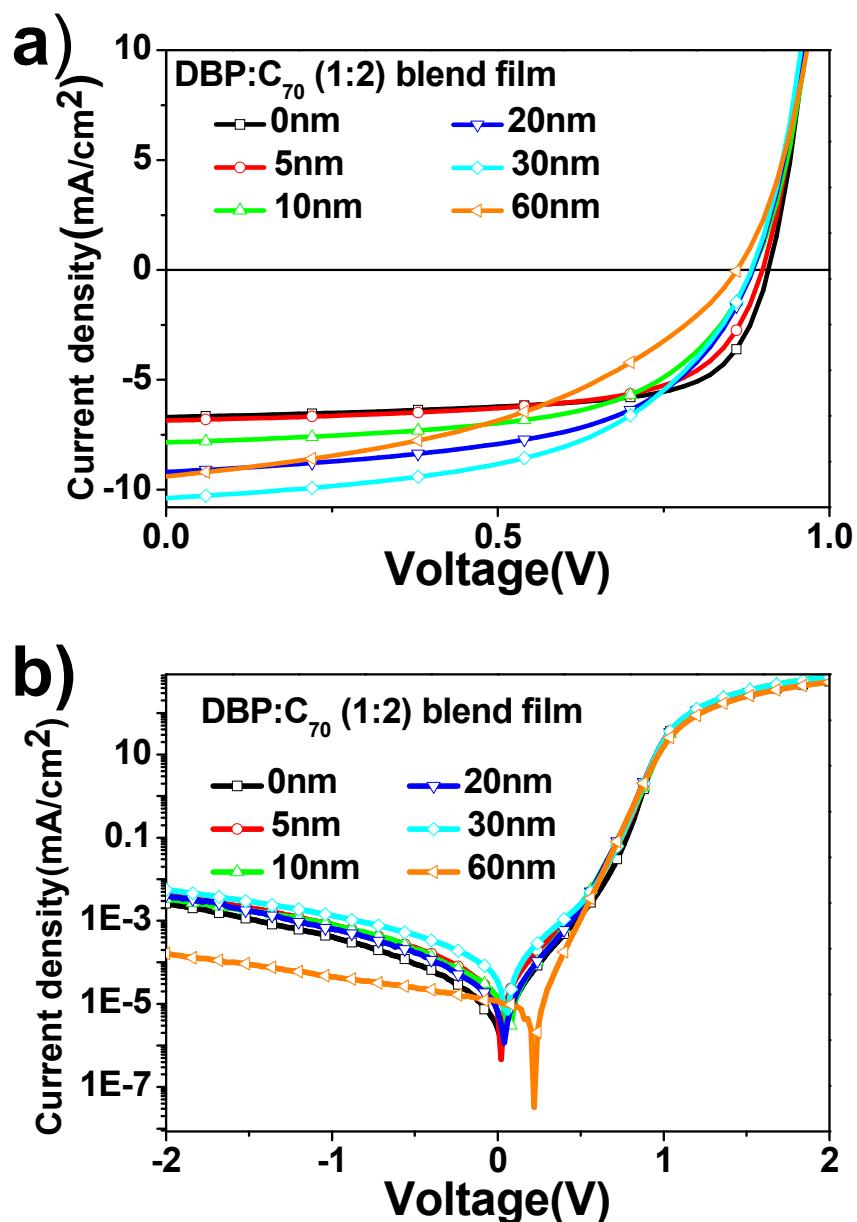


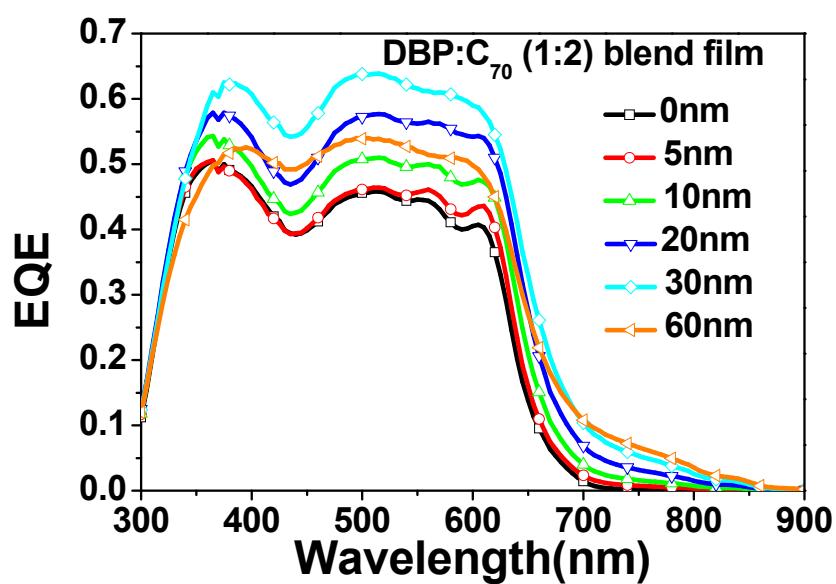
Fig. S2. 2D absorption profiles of the OPV device under AM1.5G illumination. a) overall absorption and b) effective absorption contributing to photogeneration.



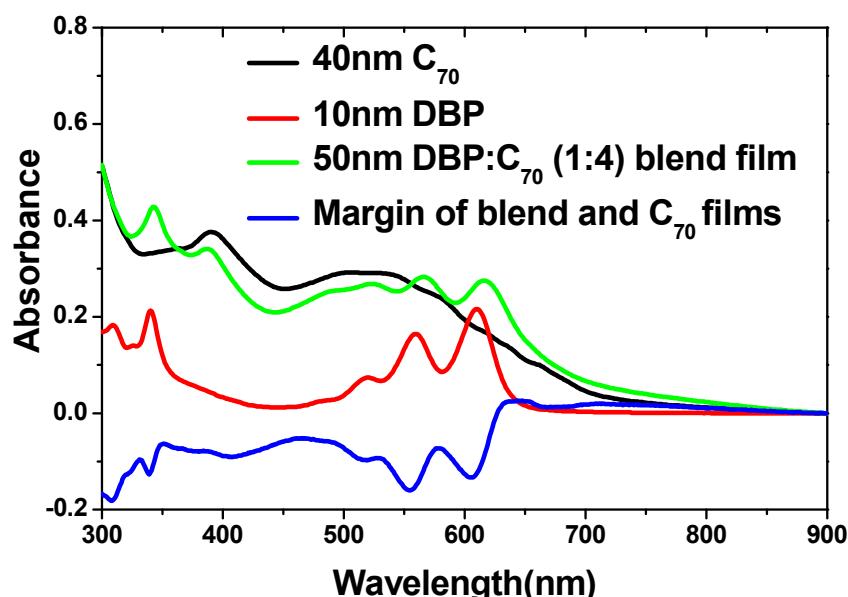
**Fig. S3.** EQE of the devices with a structure of ITO/DBP(10 nm)/DBP:C<sub>70</sub>(1:2, 30 nm)/C<sub>70</sub>(30 nm)/BCP(10 nm)/Al, in which D/A ratios vary from 2:1 to 1:16.



**Fig. S4** J-V characteristics of p-i-n cells with various thickness of i-layer (DBP:C<sub>70</sub>, 1:2) from 0 nm to 60 nm, (a) under illumination of 1 sun AM1.5G, and (b) in dark.



**Fig. S5.** EQE from OPV cells with a structure of ITO/DBP(10 nm)/DBP:C<sub>70</sub> (X nm)/C<sub>70</sub>(30 nm)/BCP(10 nm)/Al. The i-layer thickness (X nm) changed from 0 nm to 60 nm.



**Fig. S6.** Absorption of 40 nm  $C_{70}$ , 10 nm DBP, 50 nm 1:4 DBP: $C_{70}$  blend films. Since absorption of DBP goes to near zero beyond 700 nm, the absorption margin of the DBP: $C_{70}$  blend and  $C_{70}$  films represents a new absorption band in the wavelength range of 700 nm-800 nm. This band is ascribed to ground-state charge transfer formation between DBP and  $C_{70}.\beta$

**Table SI** Fitted data of  $R_{sh}$  and  $R_s$  of p-i-n cells, (ITO/DBP(10 nm)/DBP:C<sub>70</sub> (1:2, Y nm)/C<sub>70</sub>(30 nm)/BCP(10 nm)/Al, with different thickness of blend films (DBP:C<sub>70</sub>=1:2)

**(a)** Dark-state

Blend film (nm)	$R_{sh}(\Omega\text{cm}^2)$	$R_s(\Omega\text{cm}^2)$
0	$7.72 \times 10^5$	3.48
5	$4.53 \times 10^5$	3.17
10	$5.87 \times 10^5$	2.67
20	$4.83 \times 10^5$	3.13
30	$3.57 \times 10^5$	2.74
60	$1.23 \times 10^7$	3.63

**(b)** Light-state

Blend film (nm)	$R_{sh}(\Omega\text{cm}^2)$	$R_s(\Omega\text{cm}^2)$
0	$2.41 \times 10^3$	3.46
5	$4.87 \times 10^3$	3.15
10	$2.61 \times 10^3$	2.64
20	$1.98 \times 10^3$	3.14
30	$1.71 \times 10^3$	2.71
60	$0.88 \times 10^3$	3.56