

Effect of 4-biphenyl groups on the charge transport and photovoltaic properties of arylamine based push-pull systems

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NMR spectra

Figure S1. ^1H NMR (CDCl_3 , 300 MHz) spectrum of BPA-T-A.

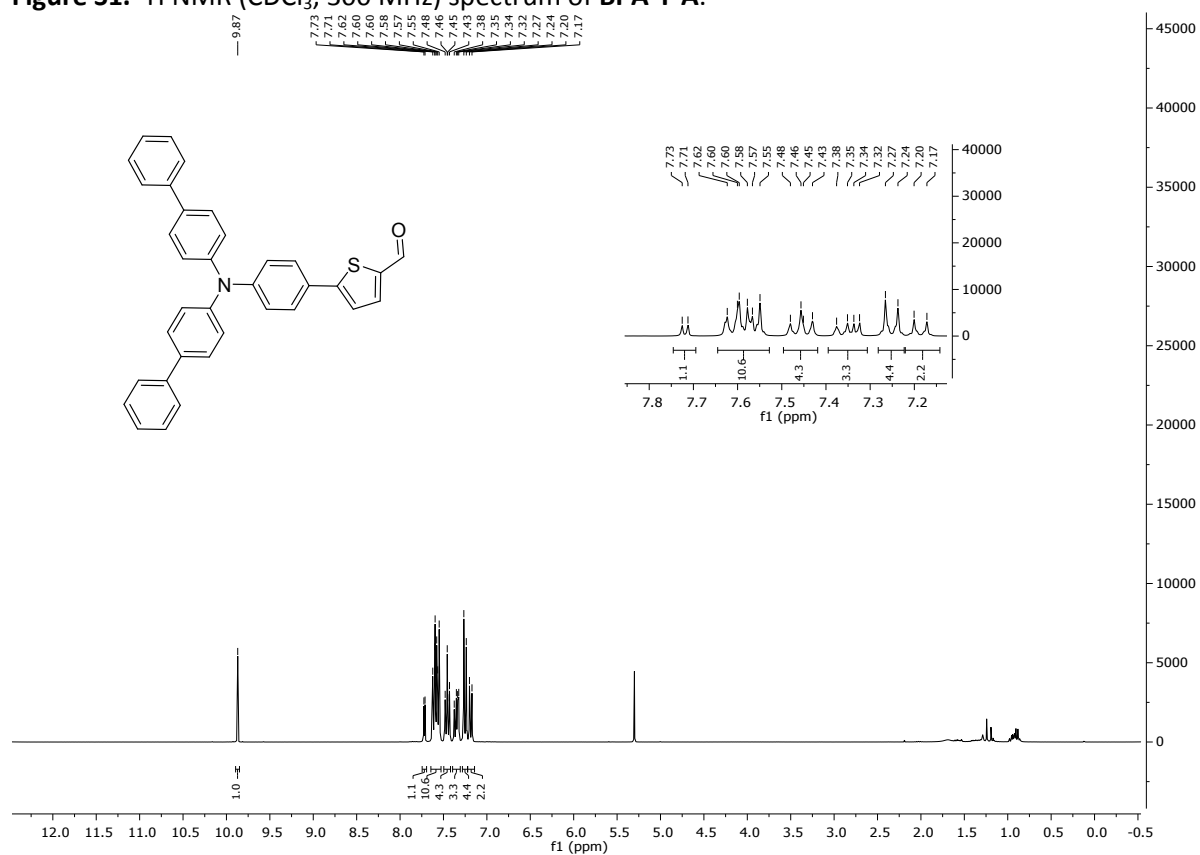


Figure S2. ^{13}C NMR (CDCl_3 , 75 MHz) spectrum of BPA-T-A.

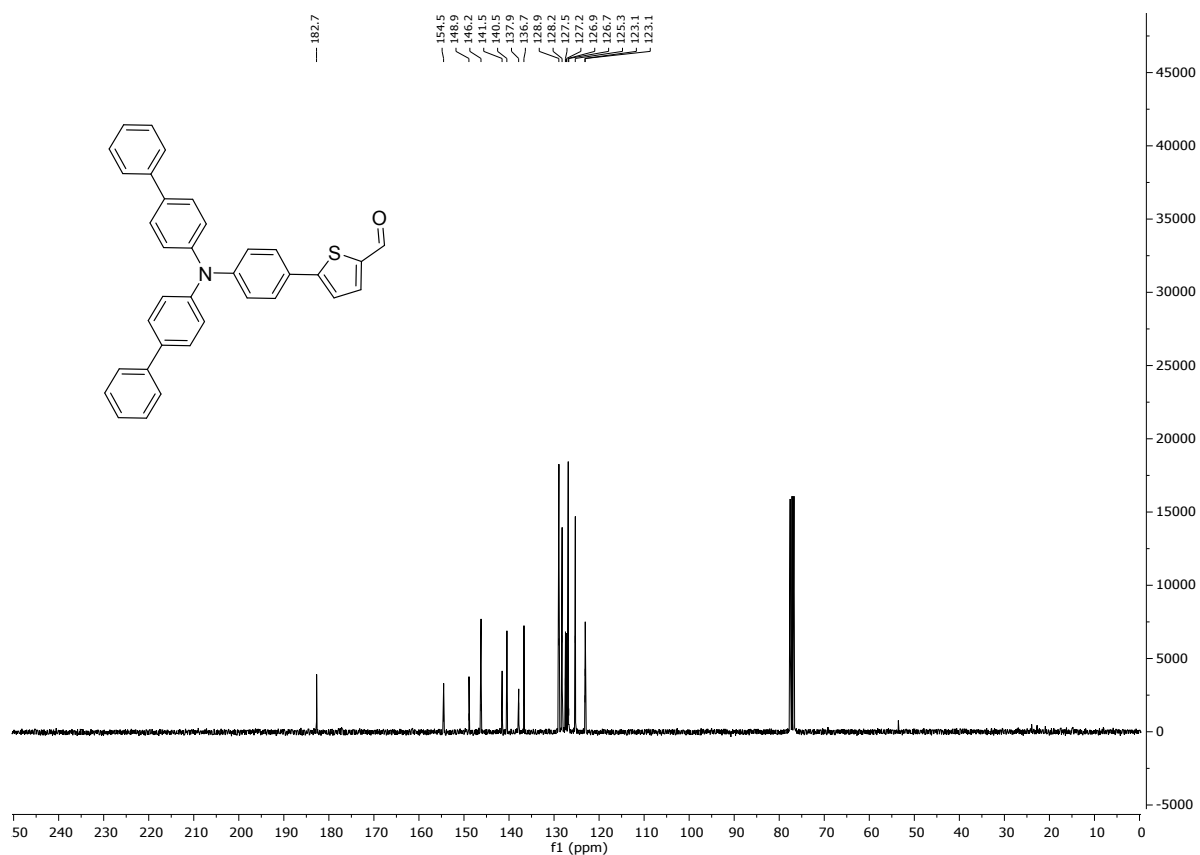


Figure S3. ¹H NMR (CDCl₃, 300 MHz) spectrum of BPA-BT-A.

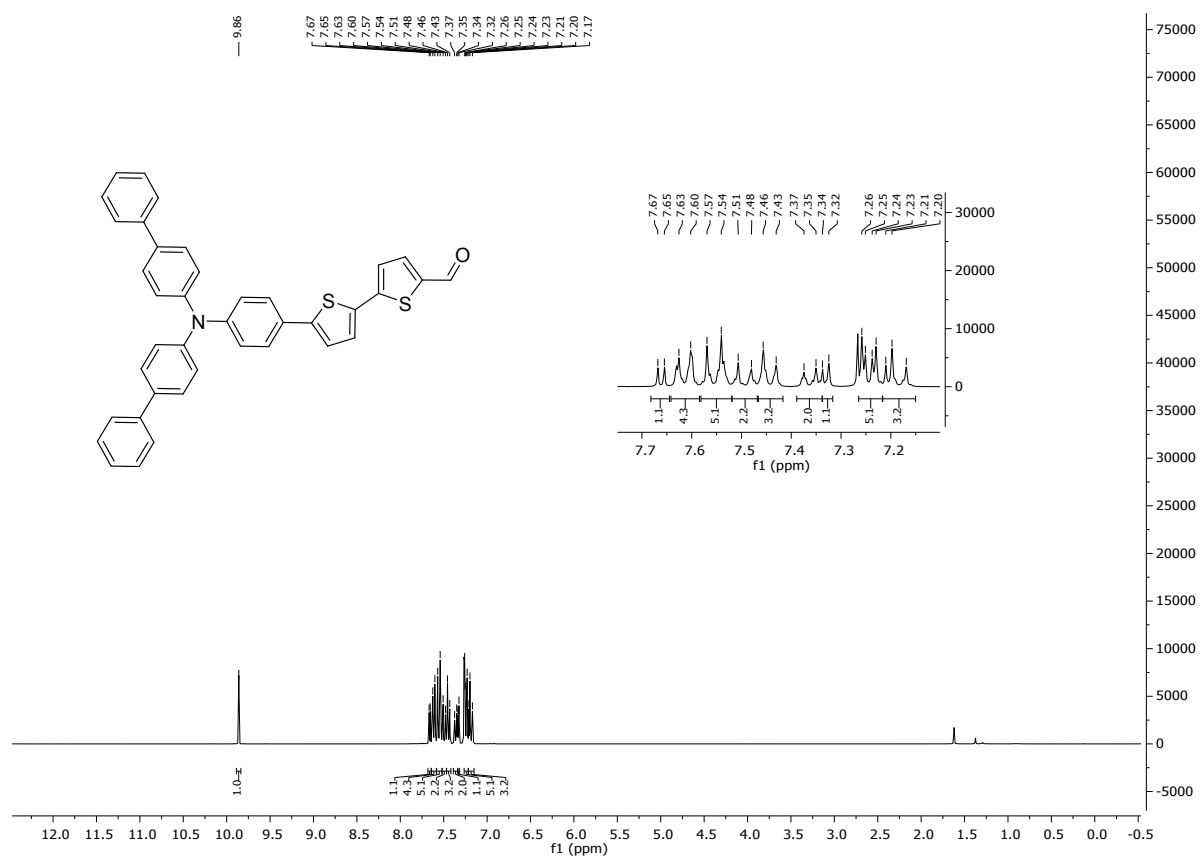


Figure S4. ¹³C NMR (CDCl₃, 75 MHz) spectrum of BPA-BT-A.

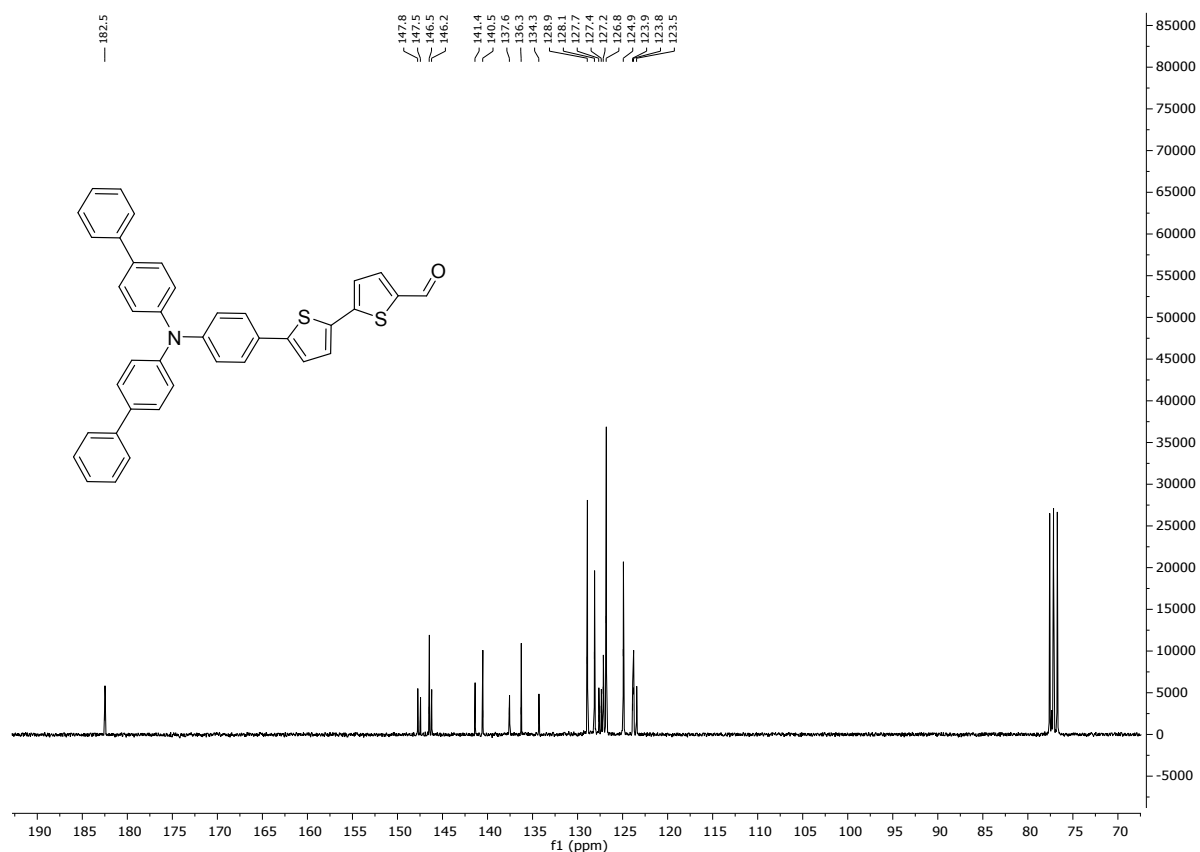


Figure S5. ¹H NMR (CDCl₃, 300 MHz) spectrum of BPA-T-DCV.

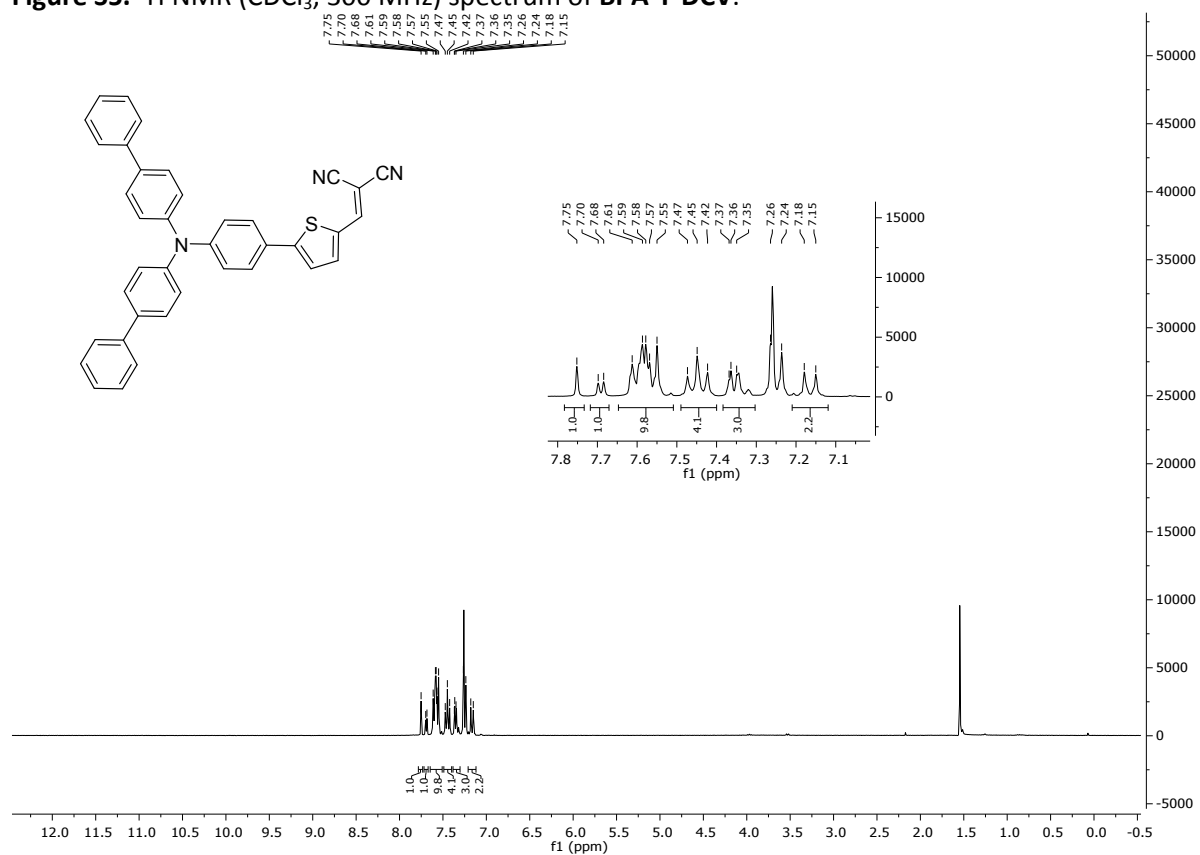


Figure S6. ¹³C NMR (CDCl₃, 75 MHz) spectrum of BPA-T-DCV.

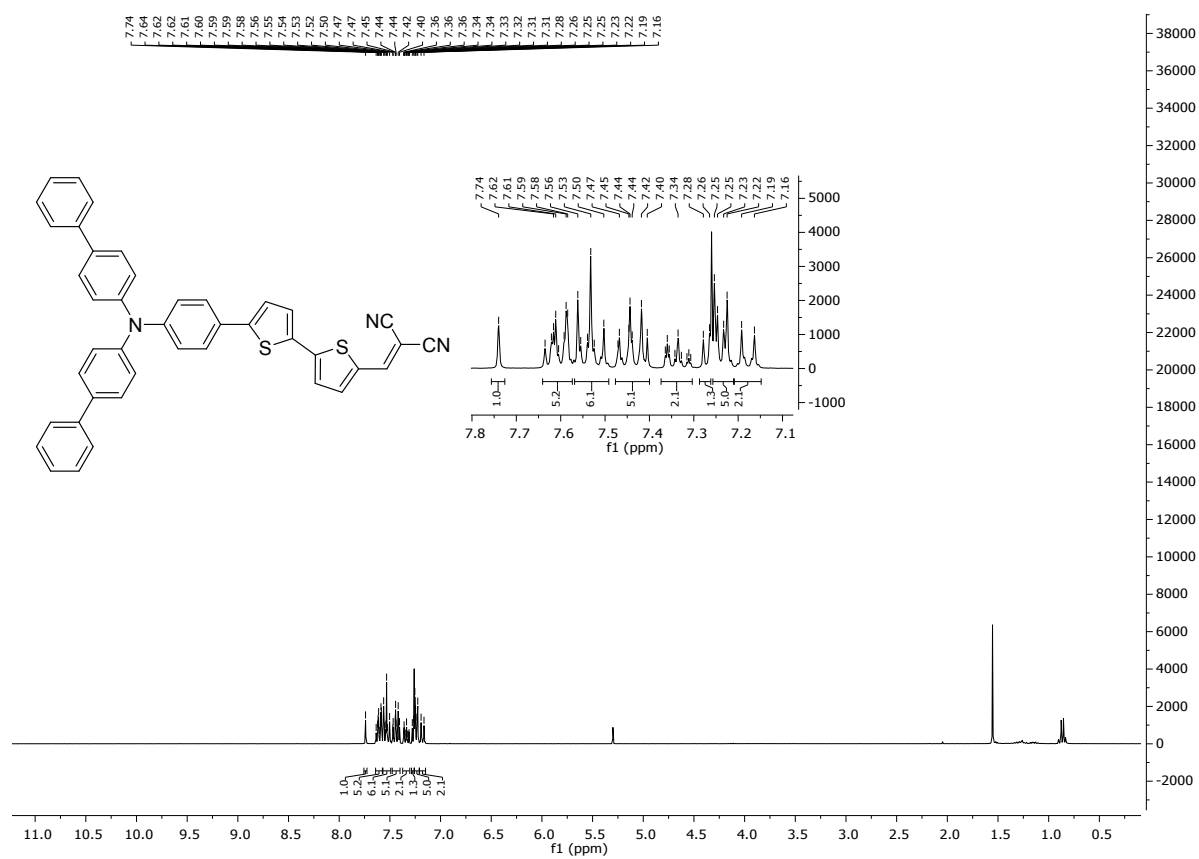
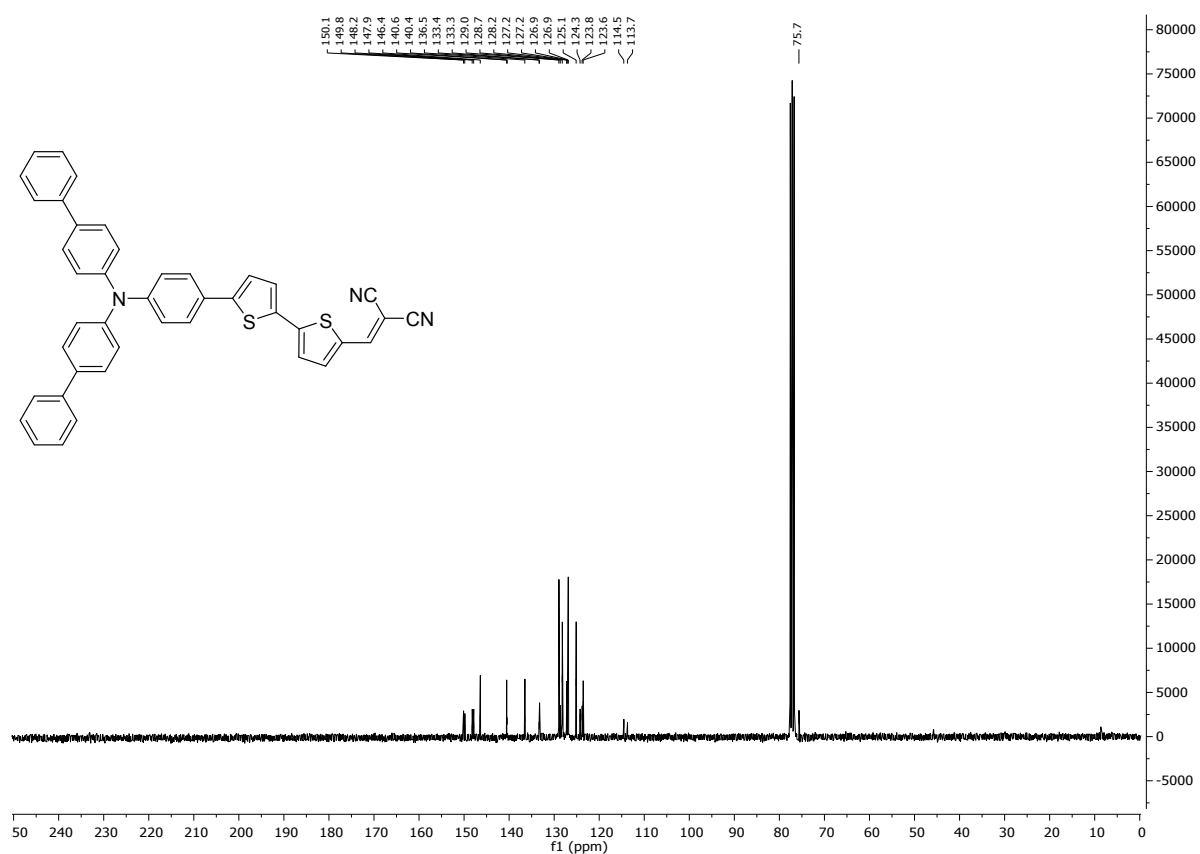


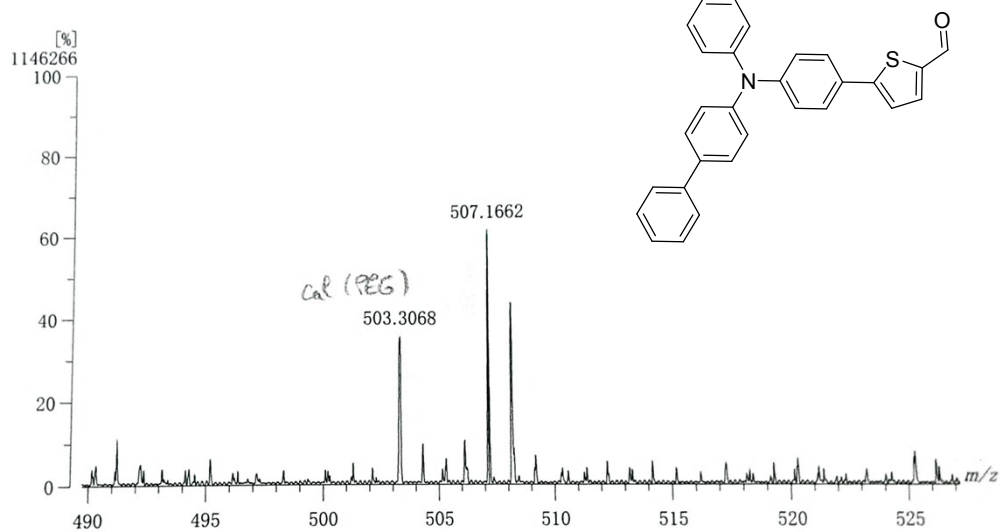
Figure S8. ^{13}C NMR (CDCl_3 , 75 MHz) spectrum of **BPA-BT-DCV**.



HRMS Spectra

Figure S9. HRMS (FAB+) of **BPA-T-A**. Calculated for $\text{C}_{35}\text{H}_{25}\text{NOS}$ 507.1651, found 507.1662.

[Mass Spectrum]
 Data : pj263-FAB+argon001 Date : 23-Feb-2018 14:27
 RT : 5.80 min Scan# : (30,33)
 Elements : C 40/0, H 49/0, N 1/0, O 1/0, S 1/0
 Mass Tolerance : 1000ppm, 1mmu if $m/z > 1$
 Unsaturation (U.S.) : -0.5 - 50.0



Observed m/z	Int%	Err[ppm / mmu]	U.S. Composition
1 507.1662	61.67	+1.0 / +0.5	25.0 C35 H25 N O S

Figure S10. HRMS (EI) of **BPA-BT-A**. Calculated for $C_{39}H_{27}NOS_2$ 589.1529, found 589.1529.

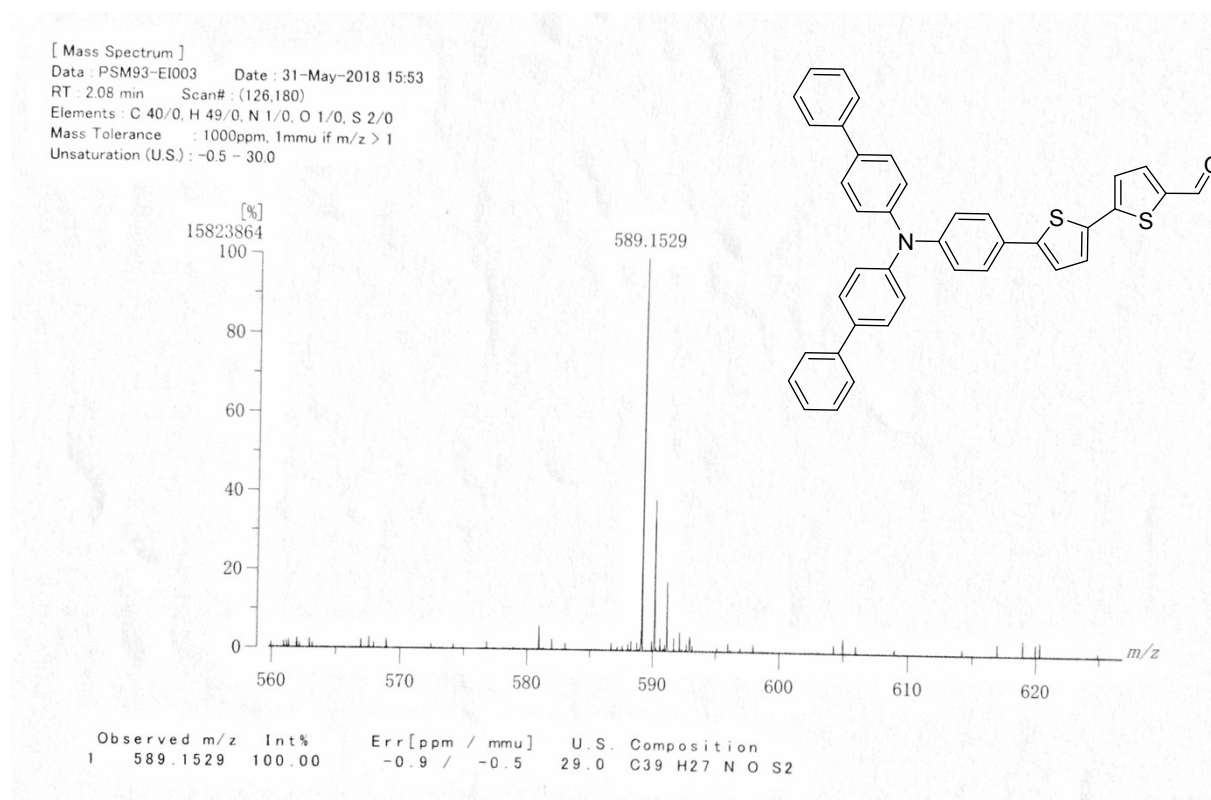


Figure S11. HRMS (FAB+) of **BPA-T-DCV**. Calculated for $C_{38}H_{25}N_3S$ 555.1764, found 555.1765.

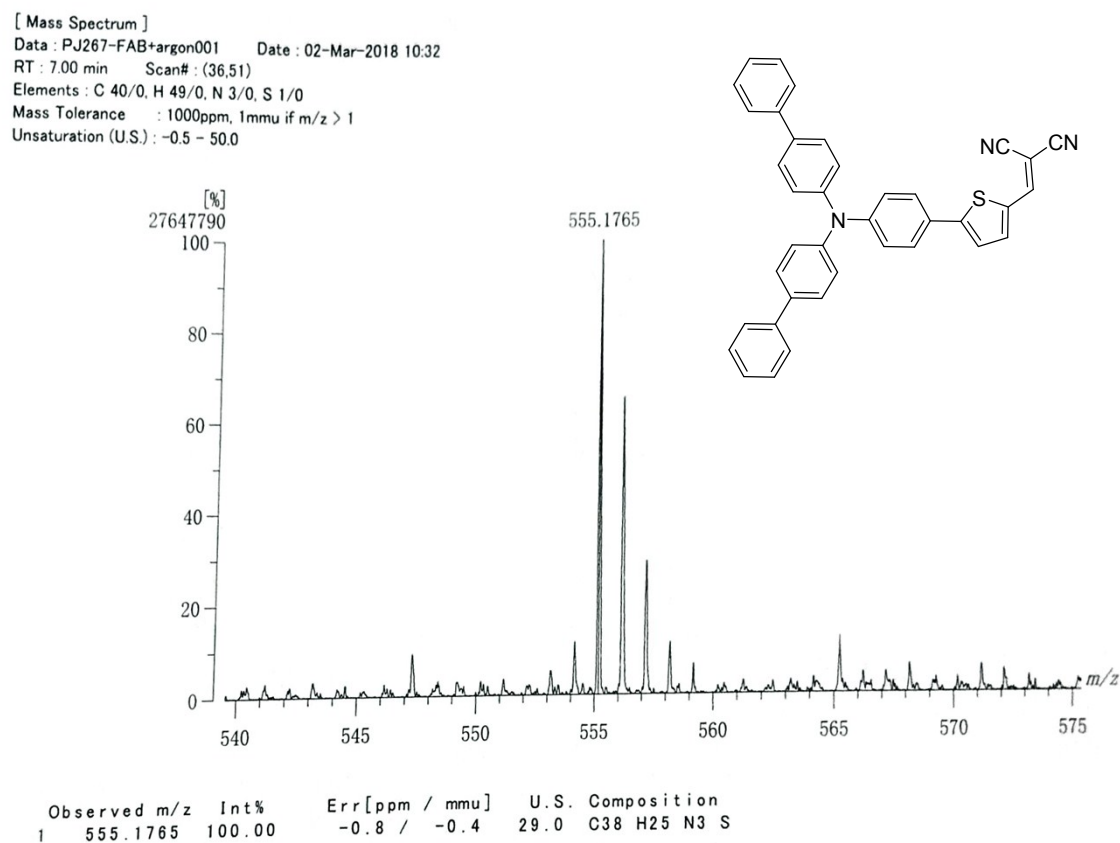
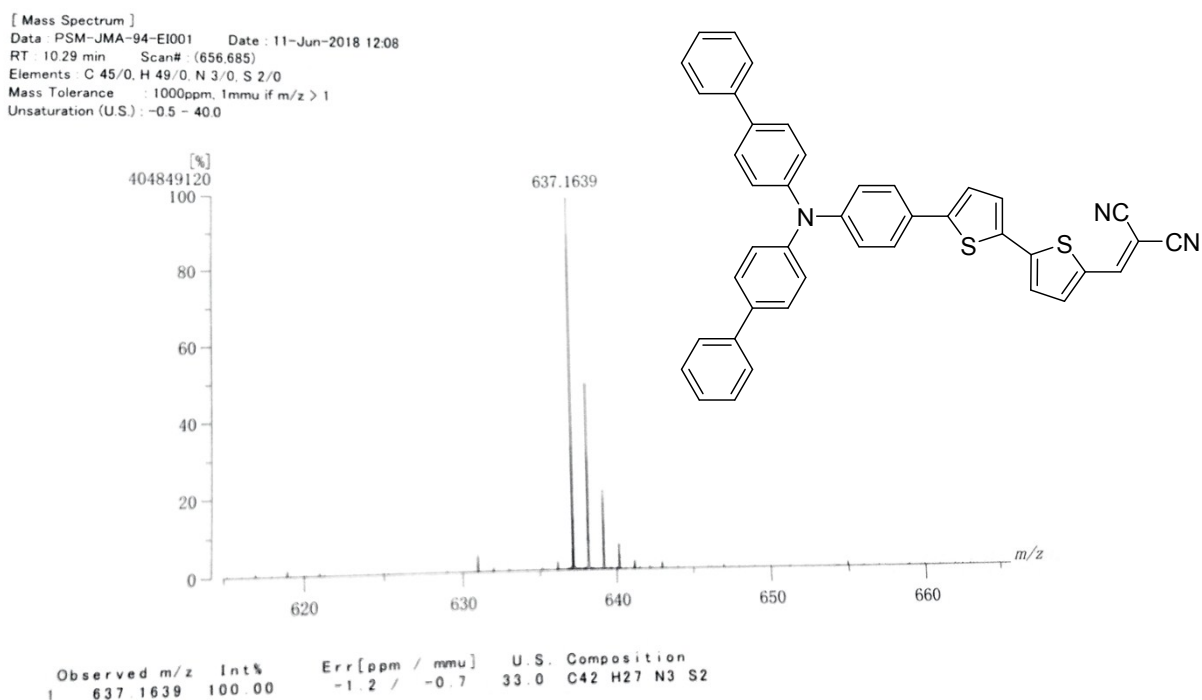


Figure S12. HRMS (EI) of **BPA-BT-DCV**. Calculated for $C_{42}H_{27}N_3S_2$ 637.1641, found 637.1639.



Photoelectron spectroscopy in air

Figure S13. Photoelectron Spectroscopy in Air (PESA) spectrum of **BPA-T-DCV** on a spun-cast thin film.

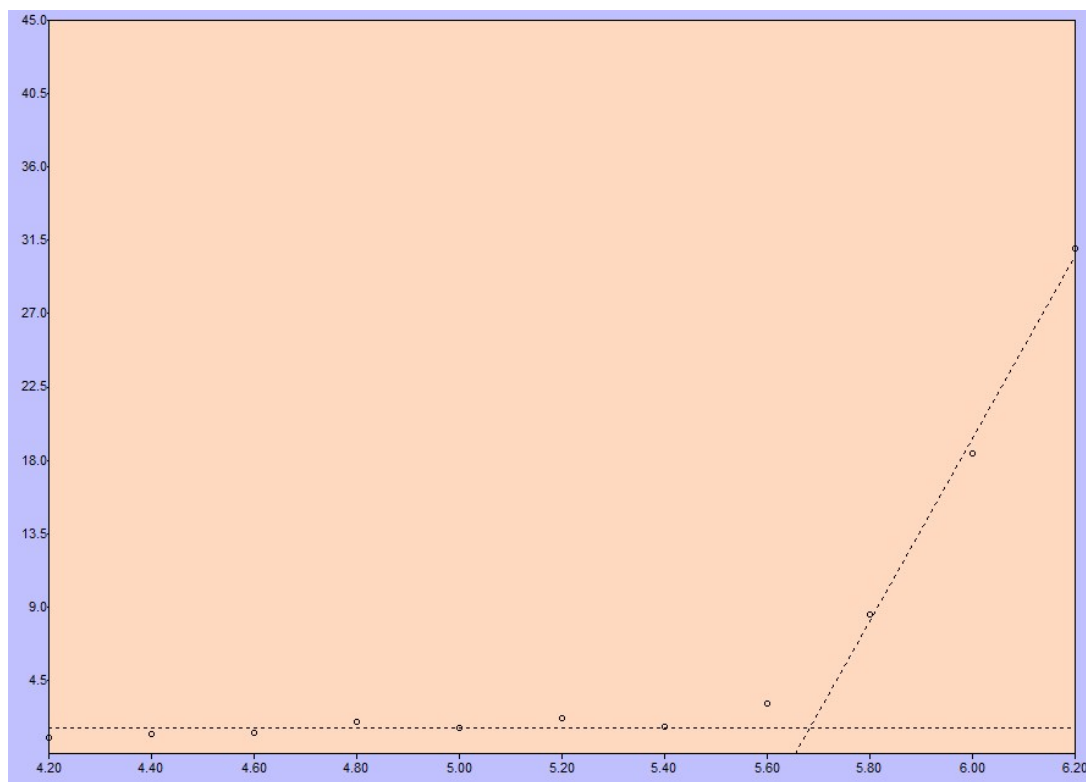
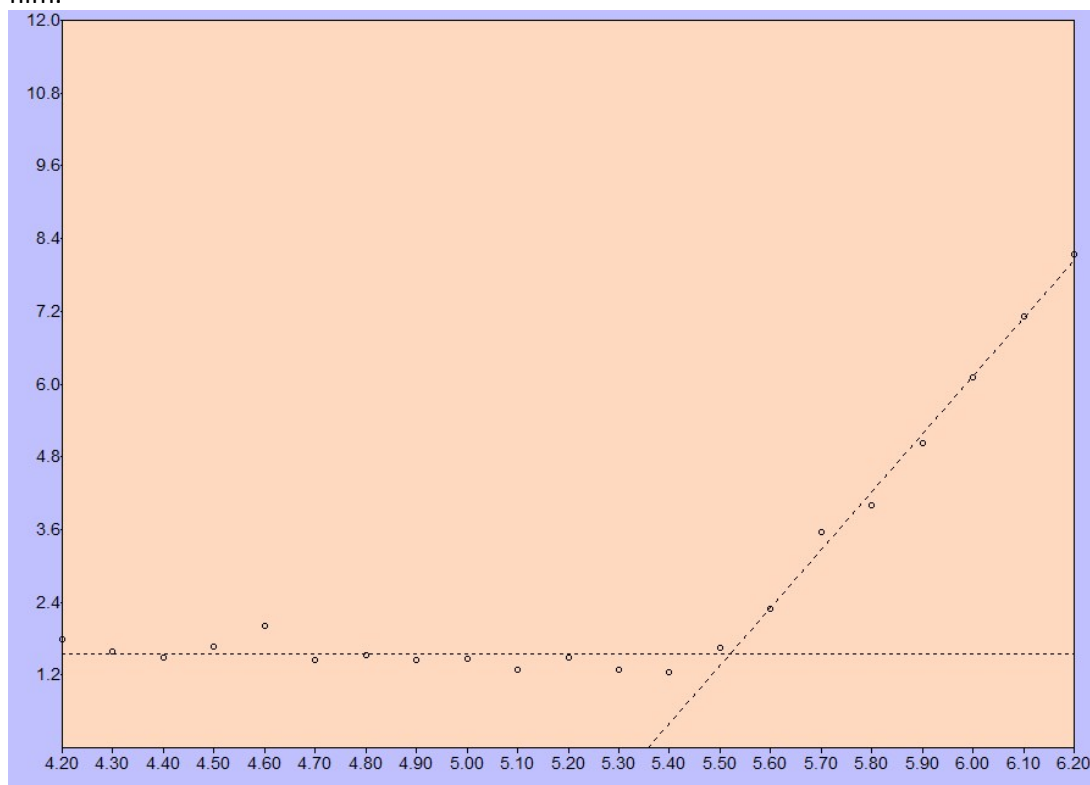


Figure S14. Photoelectron Spectroscopy in Air (PESA) spectrum of **BPA-BT-DCV** on a spun-cast thin film.



DFT calculations

Figure S15. DFT optimized geometries.

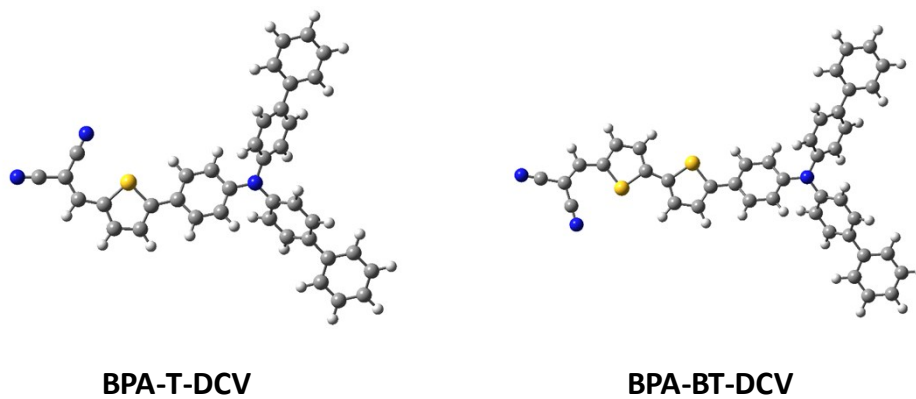


Figure S16. TD-DFT simulated spectra.

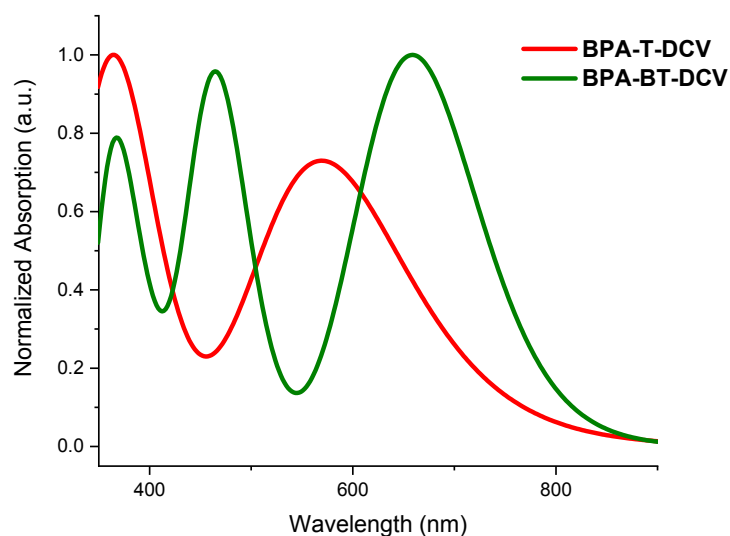


Table S1. Contribution of optical transitions obtained from TD-DFT calculations at B3LYP/311G(d) level.

Compound	λ_{maxABS}	Major contribution	Minor contribution
BPA-T-DCV	569	HOMO->LUMO	-
	382	HOMO-1->L(72%)	HOMO->L+1(28%)
	351	HOMO->LUMO+1	-
	338	HOMO->L+2(55%)	H-1->L+1(9%), H-3->L(36%)
BPA-BT-DCV	659	HOMO->LUMO	-
	465	HOMO-1->L(77%)	HOMO->L+1(23%)
	392	HOMO->L+1(71%)	H-1->L(15%), H-3->L(14%)
	364	HOMO->L+2	-

Device characterization

Figure S18. J-V (left) and EQE (right) curves of planar-heterojunction OSCs fabricated with **BPA-T-DCV** using two donor thicknesses, 6 nm (red) and 10 nm (blue), and the same device architecture as in the manuscript. They were recorded in the dark (dashed lines) and under AM 1.5 illumination at 100 mW.cm⁻² (full lines).

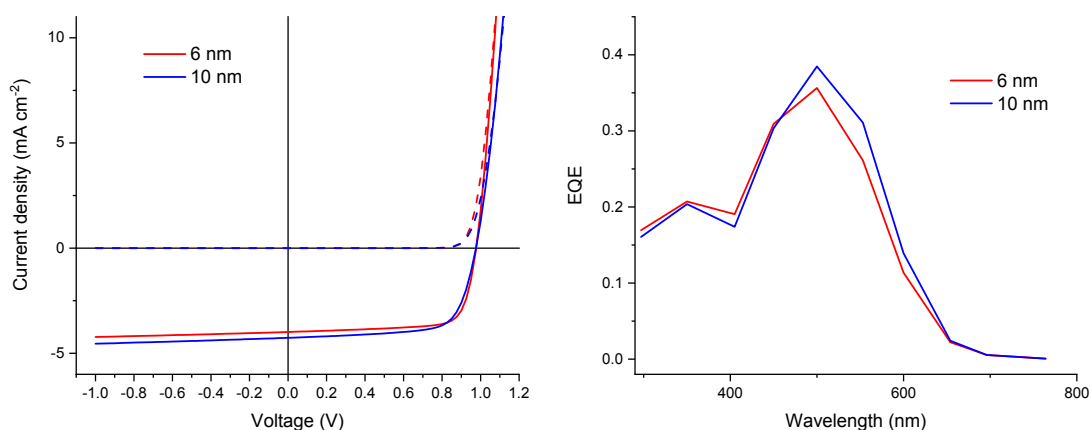


Figure S18. J-V (left) and EQE (right) curves of planar-heterojunction OSCs fabricated with **BPA-BT-DCV** using two donor thicknesses, 6 nm (red) and 10 nm (blue), and the same device architecture as in the manuscript. They were recorded in the dark (dashed lines) and under AM 1.5 illumination at 100 mW.cm⁻² (full lines).

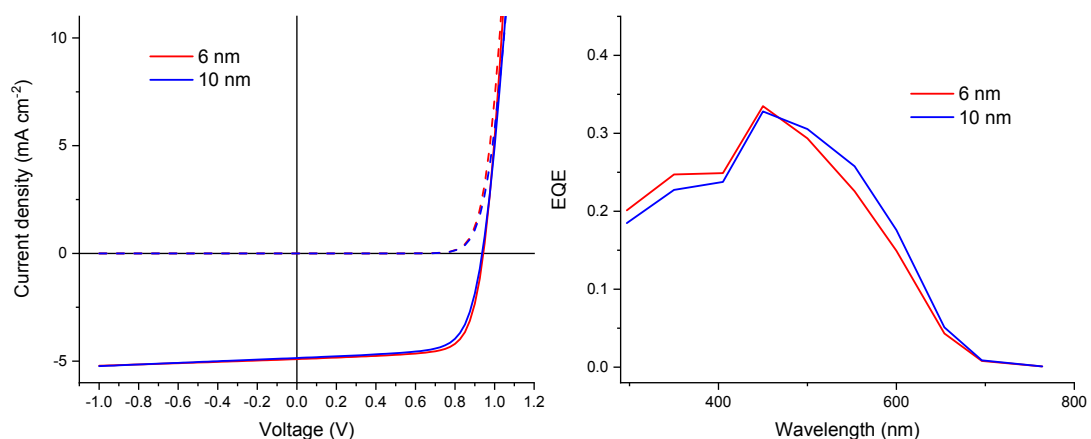


Table S2. Organic solar cell device parameters of **BPA-T-DCV** and **BPA-BT-DCV** using two different donor thicknesses and the same device architecture as in the manuscript.

Molecule	D thickness (nm)	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE (%)
BPA-T-DCV	6 nm	4.0	0.98	75	2.95
	10 nm	4.3	0.98	71	2.98
BPA-BT-DCV	6 nm	4.9	0.94	73	3.34
	10 nm	4.9	0.94	71	3.25