Supporting Information

The Role of Solvent Vapor Annealing in Highly Efficient Air-processed Small Molecule Solar Cells

Kuan Sun,*[a] Zeyun Xiao,[a] Eric Hanssen,[b] Michael F. G. Klein,[a] Henk H. Dam,[a] Marina Pfaff,[c] Dagmar Gerthsen,[c] Wallace W. H. Wong*[a] and David J. Jones*[a]

[a] *School of Chemistry, Bio21 Institute, The University of Melbourne, 30 Flemington Road, Parkville, Victoria 3010, Australia.*

[b] *Advanced Microscopy Facility, Bio21 Institute, The University of Melbourne, 30 Flemington Road, Parkville, Victoria 3010, Australia.*

[c] *Laboratory for Electron Microscopy (LEM), Karlsruhe Institute of Technology (KIT), Engesserstraße 7, Karlsruhe 76131, Germany.*

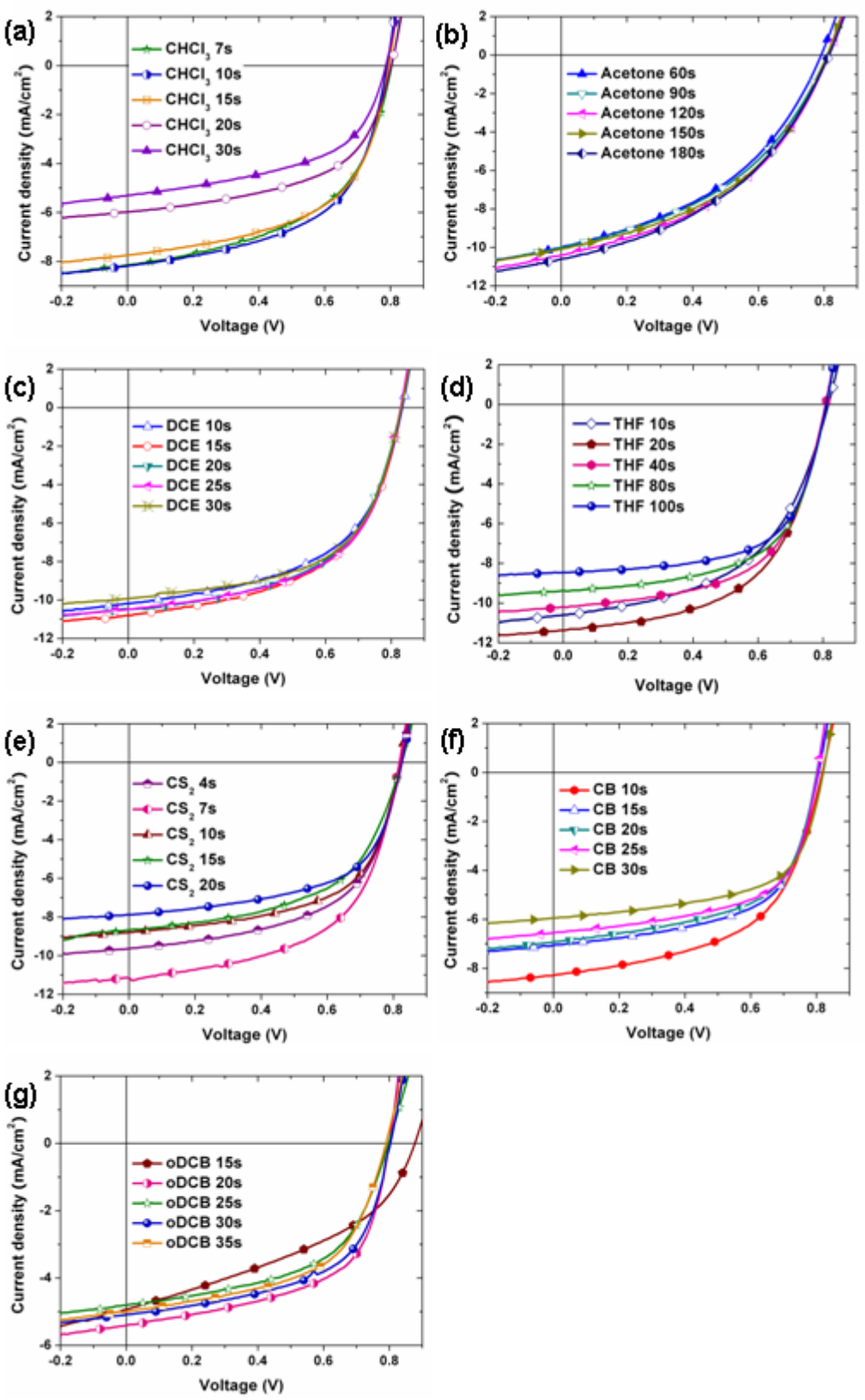

Figure S1. *J-V* curves of DPP(TBFu)$_2$:PC$_{71}$BM based OPVs after solvent vapor annealing (SVA) by (a) chloroform ($CHCl_3$), (b) acetone, (c) 1,2-dichloroethane (DCE), (d) tetrahydrofuran (THF), (e) carbon disulfide (CS_2), (f) chlorobenzene (CB) and (g) 1,2-dichlorobenzen (*o*DCB) after different treatment durations.

Table S1. OPV performance parameters of DPP(TBFu)$_2$:PC$_{71}$BM based OPVs after SVA by various solvents after different treatment durations.

SVA Treatment	V_{oc} [V]	J_{sc} [mA/cm^2]	*FF* [%]	PCE [%]
$CHCl_3$ 7s	0.8	8.15	52	3.4
$CHCl_3$ 10s	**0.79**	**8.18**	**55**	**3.57**
$CHCl_3$ 15s	0.8	7.74	55	3.42
$CHCl_3$ 20s	0.8	5.97	55	2.63
$CHCl_3$ 30s	0.79	5.3	52	2.19
Acetone 60s	0.79	10	42	3.32
Acetone 90s	0.81	9.99	42	3.41
Acetone 120s	0.81	10.4	43	3.64
Acetone 150s	0.81	10.09	44	3.56
Acetone 180s	0.81	10.6	42	3.64
DCE 10s	0.83	10.18	54	4.56
DCE 15s	0.83	10.8	54	4.86
DCE 20s	0.83	10.45	55	4.77
DCE 25s	**0.83**	**10.48**	**56**	**4.85**
DCE 30s	0.83	9.92	57	4.7
THF 10s	0.82	10.6	51	4.46
THF 20s	**0.81**	**11.37**	**55**	**5.11**
THF 40s	0.81	10.18	58	4.8
THF 80s	0.81	9.36	60	4.54
THF 100s	0.81	8.45	63	4.29
CS_2 4s	0.82	9.63	57	4.49
CS_2 7s	**0.82**	**11.15**	**56**	**5.16**
CS_2 10s	0.82	8.8	59	4.25
CS_2 15s	0.83	8.68	54	3.91
CS_2 $_2$0s	0.83	7.87	58	3.81
CB 10s	**0.82**	**8.29**	**55**	**3.72**
CB 15s	0.81	7.05	59	3.36
CB 20s	0.8	6.92	59	3.25
CB 25s	0.8	6.55	61	3.18
CB 30s	0.82	5.95	60	2.94
oDCB 15s	0.88	4.93	40	1.74
oDCB 20s	**0.8**	**5.41**	**56**	**2.44**
oDCB 25s	0.8	4.81	53	2.05
oDCB 30s	0.8	5.08	56	2.3
oDCB 35s	0.79	4.99	55	2.16

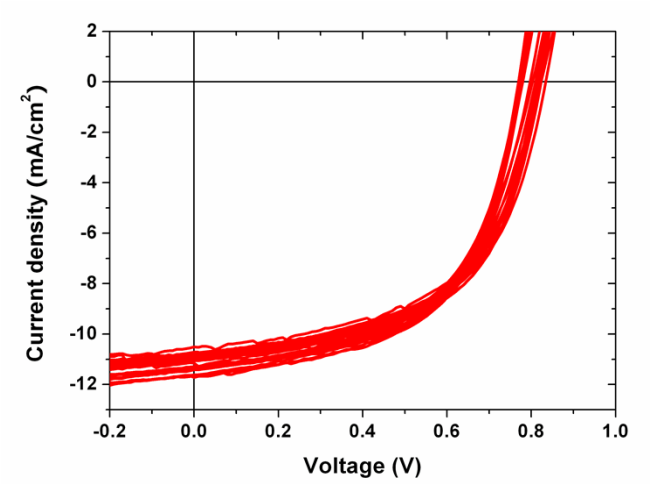

Figure S2. *J-V* curves of 24 DPP(TBFu)$_2$:PC$_{71}$BM based OPVs after SVA by THF or CS_2 fabricated from two batches of donor materials and five device batches by two individual researchers.

Table S2. OPV performance parameters of the 24 cells treated by THF or CS_2 and their average values and standard deviations.

Cell No.	V_{oc} [V]	J_{sc} [mA/cm^2]	*FF* [%]	PCE [%]
1	0.82	11.15	56	5.16
2	0.82	10.78	57	5.04
3	0.81	10.92	57	5.04
4	0.83	10.78	56	4.97
5	0.82	10.81	56	4.92
6	0.82	10.93	55	4.92
7	0.81	10.84	56	4.93
8	0.82	10.51	57	4.88
9	0.78	11.02	57	4.93
10	0.8	11.65	55	5.09
11	0.78	11.62	56	5.12
12	0.78	11.72	56	5.15
13	0.78	11.42	55	4.92
14	0.78	11.06	56	4.82
15	0.77	11.42	56	4.91
16	0.78	11.37	57	5.01
17	0.78	10.93	58	4.93
18	0.78	10.72	59	4.9
19	0.77	10.79	60	4.94
20	0.77	11.01	59	5
21	0.77	10.93	59	4.97
22	0.81	11.37	55	5.11
23	0.8	11.39	54	4.91
24	0.82	11.29	53	4.94
Average	**0.80±0.02**	**11.10±0.33**	**56±2**	**4.98±0.09**

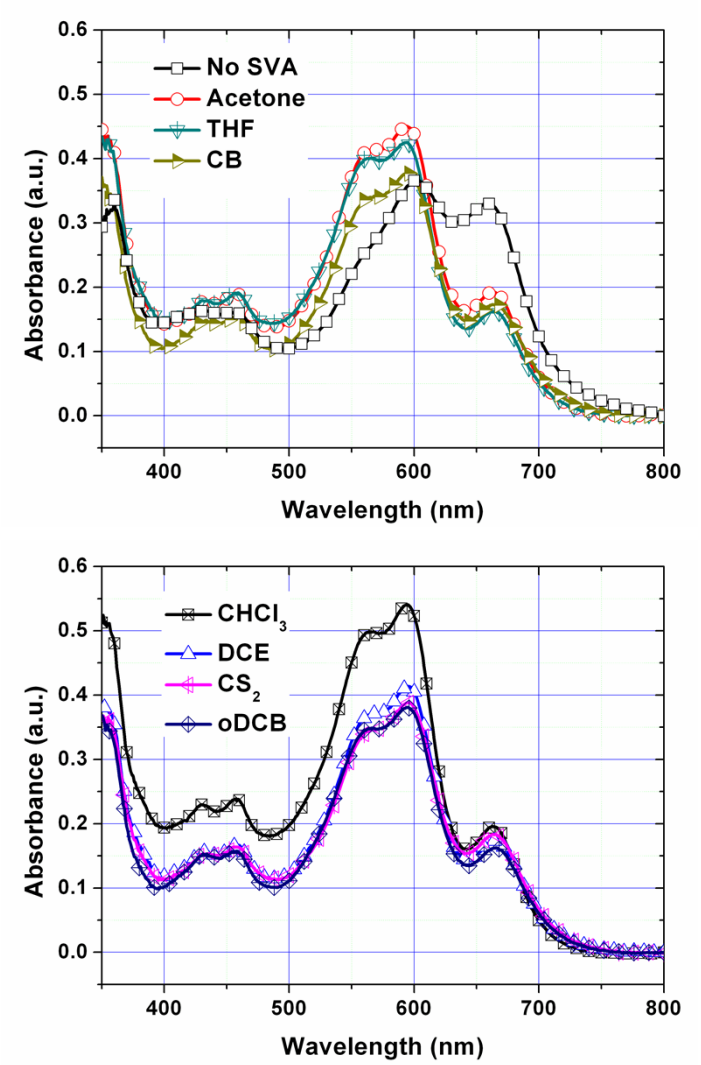

Figure S3. UV-Vis-NIR spectra of DPP(TBFu)$_2$:PC$_{71}$BM blend film without and with solvent vapor annealing (SVA) by different solvents.

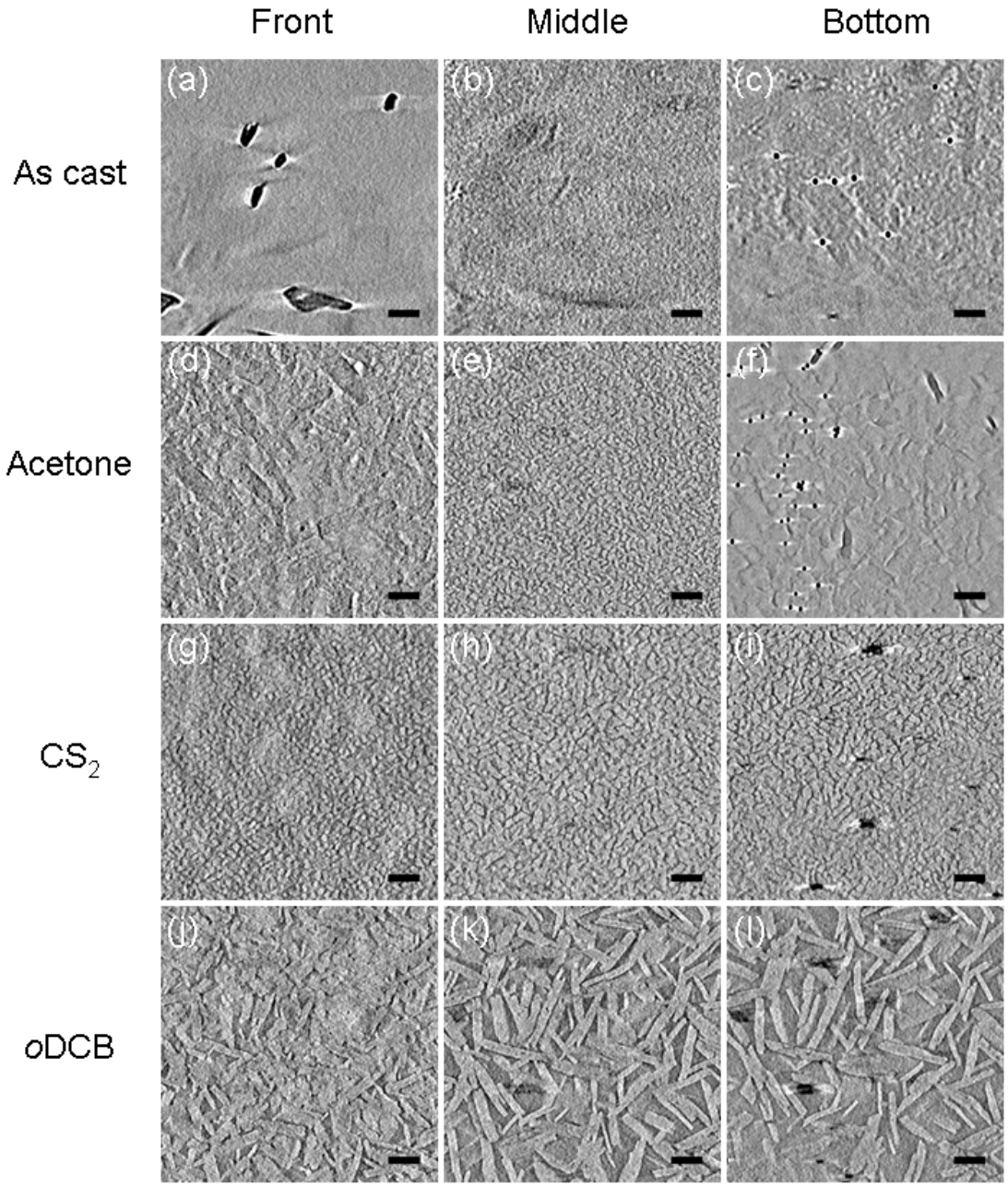

Figure S4. Slices taken out of a reconstructed volume of the DPP(TBFu)$_2$:PC$_{71}$BM blend film before (a, b, c) and after SVA by acetone (d, e, f), CS_2 (g, h, i) and *o*DCB (j, k, l). All slices are lying in the horizontal (X, Y) plane of the film but at different depth (Z location). The front surface is in contact with LiF/Al cathode for electron collection; and back surface is in contact with PEDOT:PSS/ITO anode for hole collection. The black dots in the last column are gold nanoparticles serve as fiducial markers. The scale bar is 100 nm.

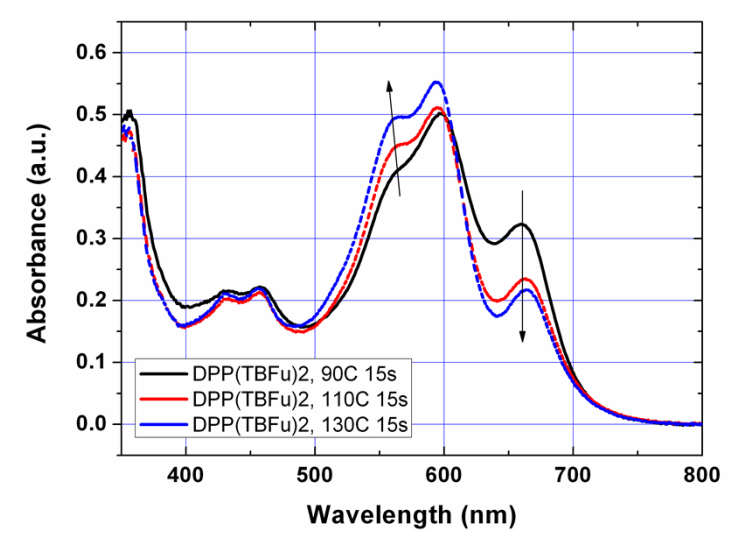

Figure S5. UV-Vis-NIR spectra of DPP(TBFu)$_2$:PC$_{71}$BM blend film after thermal annealing at different temperatures for 15 s.

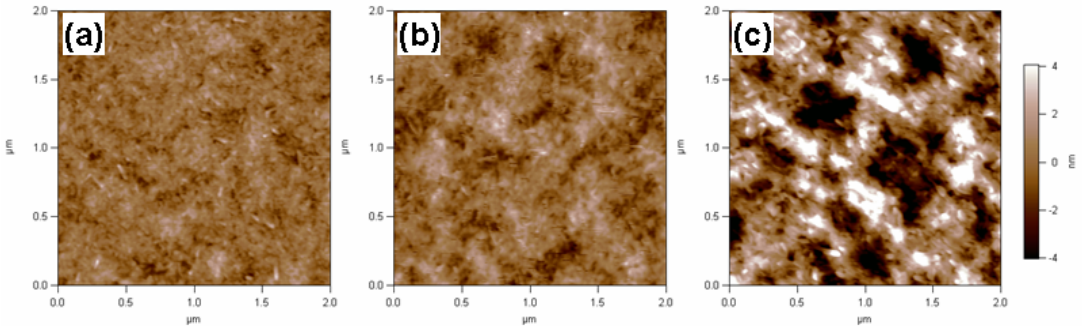

Figure S6. AFM topographic images of DPP(TBFu)$_2$:PC$_{71}$BM blend film after thermal annealing at (a) 90, (b) 110 and (c) 130 ^{o}C for 15 s. The height bar is 8 nm.

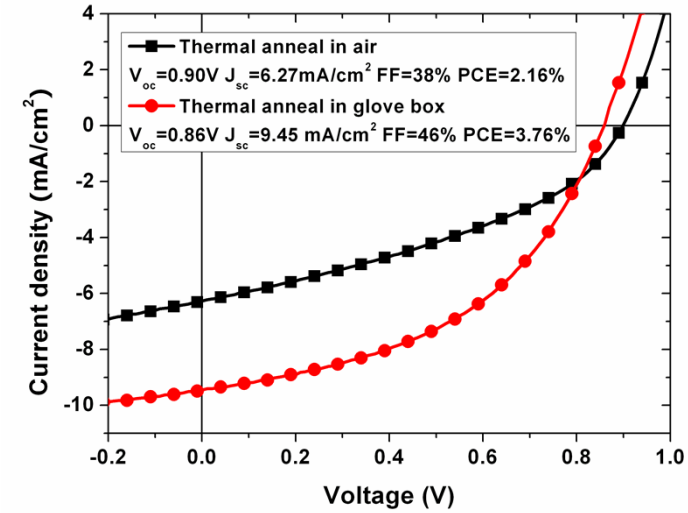

Figure S7. *J-V* curves of OPV devices that were thermally annealed at 110 ^{o}C for optimal durations of 15 s in air or 13 min in a glove box filled with dry nitrogen gas.

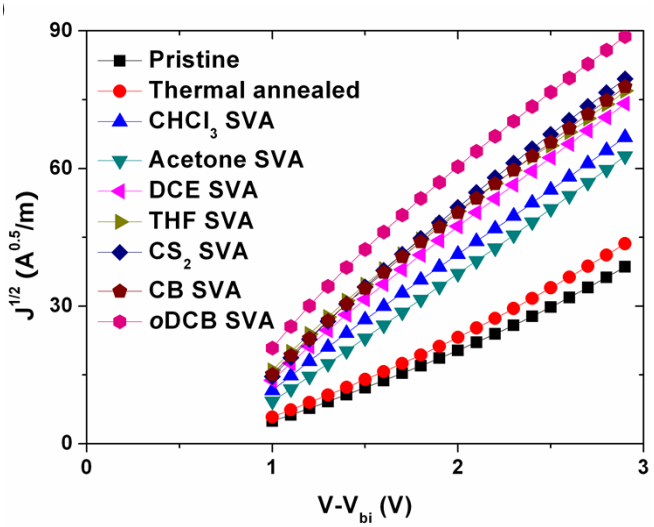

Figure S8. $J^{1/2}$-V plots of the dark currents of hole-only devices before and after thermal annealing or solvent vapor annealing (SVA) by different solvents.

Table S3. Hole mobilities determined by SCLC method of DPP(TBFu)$_2$:PC$_{71}$BM thin films before and after thermal annealing or solvent vapor annealing.

Treatment[a)]	Treatment duration [s]	Hole mobility [cm^2/(V·s)]
None		2 x 10^{-4}
Thermal annealing[b)]	15	2 x 10^{-4}
THF[a)]	20	6 x 10^{-4}
CS_2[a)]	5	7 x 10^{-4}
CB[a)]	10	6 x 10^{-4}
*o*DCB[a)]	20	7 x 10^{-4}
$CHCl_3$[a)]	10	5 x 10^{-4}
Acetone[a)]	120	5 x 10^{-4}
DCE[a)]	25	6 x 10^{-4}

[a)] Solvent vapor annealing; [b)] thermal annealing at 110 °C in air.