Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

A Novel Bifunctional A-D-A Type Small Molecule for Efficient Organic Solar Cells

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1. Materials

Synthesis of DTF

4-hexyl-1-bromobenzene (1.09 g, 4.5 mmol) was dissolved in THF (20 mL) in a flask (100 mL) and the solution was flushed with nitrogen for 10 min. n-BuLi (1.65 mL, 4.1 mmol, 2.5 M in hexane) was added to the solution at –78 ° C and the mixture was kept at –78 ° C for 1 h. After compound 1 (0.52 g, 0.75 mmol) was added[1], the mixture was stirred at room temperature for 2 h and then the ice water was added into the mixture and extracted with diethyl ether. The organic layer was dried over with $MgSO_4$. The solvent was evaporated and the crude product was dissolved in chloroform (30 mL) in a flask (100 mL). Boron trifluoride (0.43 g, 3 mmol) was added and then the mixture was stirred at 40 ° C for 3 h. Then the ice water was added into the mixture and extracted with diethyl ether. The crude product was further purified by silica gel column with petroleum ether/dichloromethane (20:1) as the eluent to obtain a yellow solid (0.58 g, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (s, 2H), 7.29 (s, 2H), 7.17 (d, 2H), 7.06 (d, 4H), 6.95 (d, 4H), 6.91 (d, 2H), 2.44 (m, 8H), 1.90 (m, 4H), 1.48 (m, 8H), 1.21-1.01 (br, 48H), 0.81-0.70 (br, 18H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 156.14, 152.78, 151.02, 142.38, 141.40, 141.18, 139.20, 136.20, 128.25, 127.99, 127.22, 123.23, 117.47, 113.75, 62.66, 54.44, 40.66, 35.58, 31.83, 31.74, 31.31, 30.14, 29.29, 29.25, 29.20, 23.96, 22.62, 14.11..

Synthesis of DTF-2Sn

Compound DTF (0.38 g, 0.3 mmol) was dissolved in THF (10 mL) in a flask (50 mL) and the solution was flushed with nitrogen for 10 min. n-BuLi (0.42 mL, 1.05 mmol, 2.5 M in hexane) was added to the solution at –78 ° C and the mixture was kept at –78 ° C for 0.5 h and then was stirred at room temperature for 4 h. After trimethyltin chloride (1.2 mL, 1.2 mmol, 1 M in hexane) was added dropwise, the mixture was stirred at room temperature overnight. Then the ice water was added into the mixture and extracted with diethyl ether. The organic layer was dried over with MgSO4 and then the residue was recrystallized by ethyl alcohol to obtain a yellow solid (0.42 g, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (s, 2H), 7.27 (s, 2H), 7.19 (s, 2H), 7.06 (d, 8H), 6.95 (d, 8H), 2.45 (m, 8H), 1.88 (m, 4H), 1.47 (m, 8H), 1.21-0.99

(br, 48H), 0.81-0.60 (br, 18H), 0.29 (br, 18H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 156.8, 152.08, 149.89, 146.38, 141.66, 139.93, 139.78, 138.05, 134.94, 129.69, 127.13, 127.06, 116.51, 112.78, 61.24, 53.31, 39.63, 34.55, 30.80, 30.69, 30.23, 29.09, 28.17, 22.91, 21.57, 13.06.

DTF-Sn (75mg，0.05 mmol) and BR (77mg，0.2 mmol) were dissolved into 30 mL of toluene in a flask under nitrogen. The solution was flushed with nitrogen for 10 min, and 30 mg of Pd(PPh3)4 was added into the flask. The solution was flushed with nitrogen for an additional 25 min. Then, the reaction mixture was stirred for 24 h at 110 °C. The solvent was removed and the product was purified by flash column chromatography on silica gel from CH_2Cl_2 to yield **DTFBR** as a blue solid (80.5 mg , 88.2%). ^{1}H NMR (CDCl3, 500 MHz) δ 8.16 (2H, s), 7.97 (2H, d), 7.70 (2H, d), 7.56 (1H, s), 7.50 (2H,s), 7.21 (8H,d), 7.10(8H,d), 4.24(4H,dd), 2.56(8H,t) ,2.57 - 2.50 (8H, m), 2.00- 1.95 (4H, m), 1.61 - 1.49 (10H, m), 1.41 – 1.23 (46H, m), 0.86 (12H, t,), 0.79 (6H, t,). ^{13}C NMR ($CDCl_3$, 126 MHz) δ 193.01, 167.34, 157.25, 154.38, 153.26, 151.67, 145.89, 141.44, 140.28, 135.85, 130.08, 128.45, 126.92, 124.04, 117.59, 63.32, 54.43, 39.69, 35.47, 31.63, 29.15, 22.67, 14.02 .

2. Figures and tables

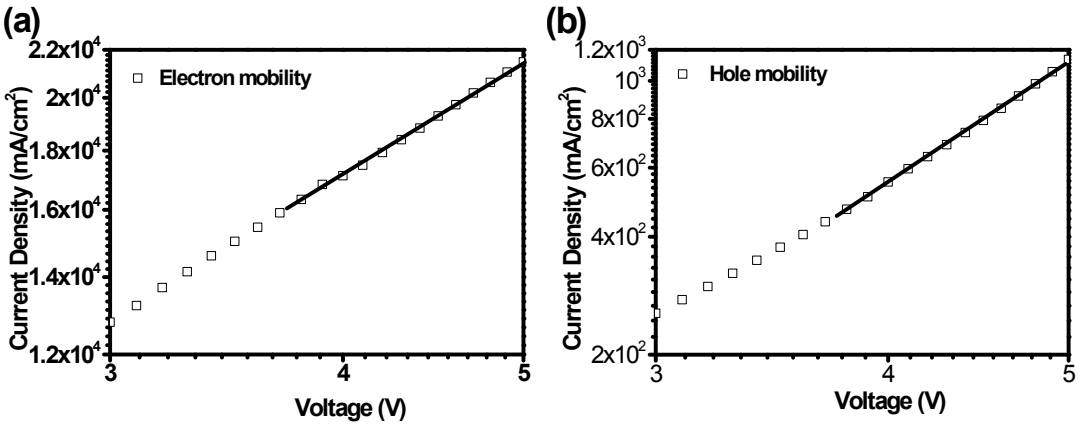

Fig. S1 Space-charge-limited current (SCLC) fittings of the electron-only(a) and hole-only(b) device based on **DTFBR**.

Table S1. Charge transfer properties of **DTFBR**.

Sample	Hole mobility (10^{-4}cm^2 V^{-1} s^{-1})[a)]	Electron mobility (10^{-4}cm^2 V^{-1} s^{-1}) [a)]
DTFBR	2.21±0.04	0.90±0.04

[a)] The average values are calculated from five devices.

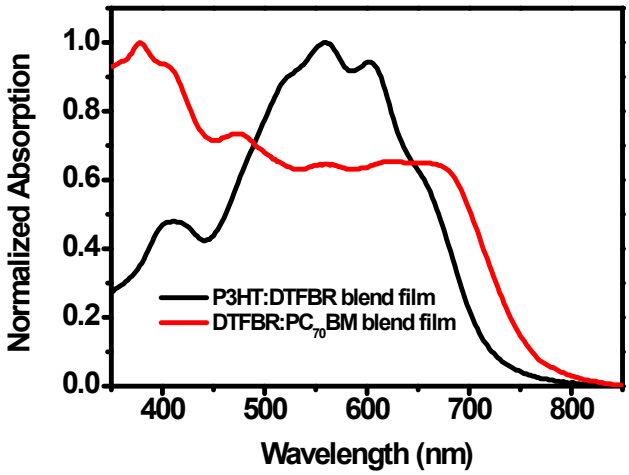

Fig. S2 Normalized UV-vis spectra of P3HT:**DTFBR** and **DTFBR**:$PC_{71}BM$ blend films.

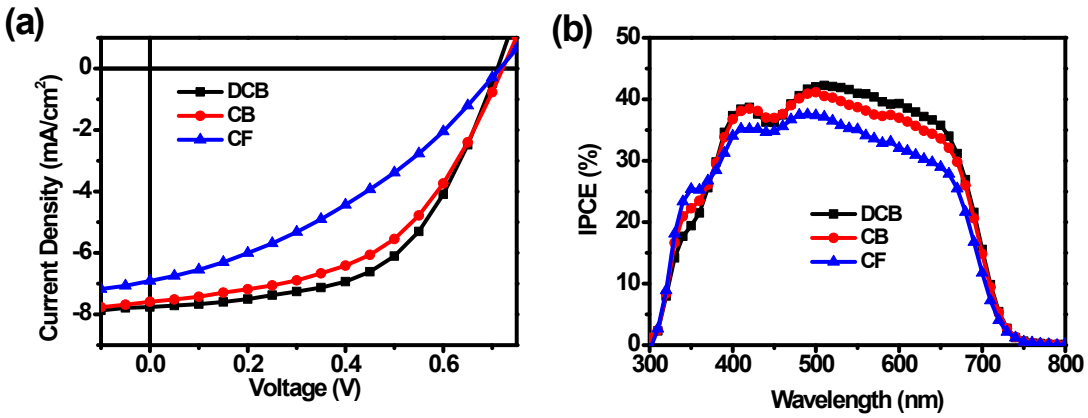

Fig. S3 (a) *J-V* and (b) IPCE cures of devices based on P3HT:**DTFBR** active layer in different solvent (the weight ratio of D:A is 1:1).

Table S2. Photovoltaic parameters of devices based on P3HT: **DTFBR** active layer in different solvent (the weight ratio of D:A is 1:1).

Ratio of D:A (w/w)	Solvent	V_{OC} (V)	J_{SC} (mAcm^{-2})	FF	PCE[a)] (%)	PCE^{max} (%)
1:1	DCB	0.71±0.01	7.47±0.14	0.53±0.02	2.82±0.08	3.06
	CB	0.71±0.01	7.44±0.16	0.49±0.01	2.63±0.10	2.77
	CF	0.71±0.01	6.83±0.11	0.35±0.01	1.70±0.08	1.78

[a)] The average values are calculated from ten devices.

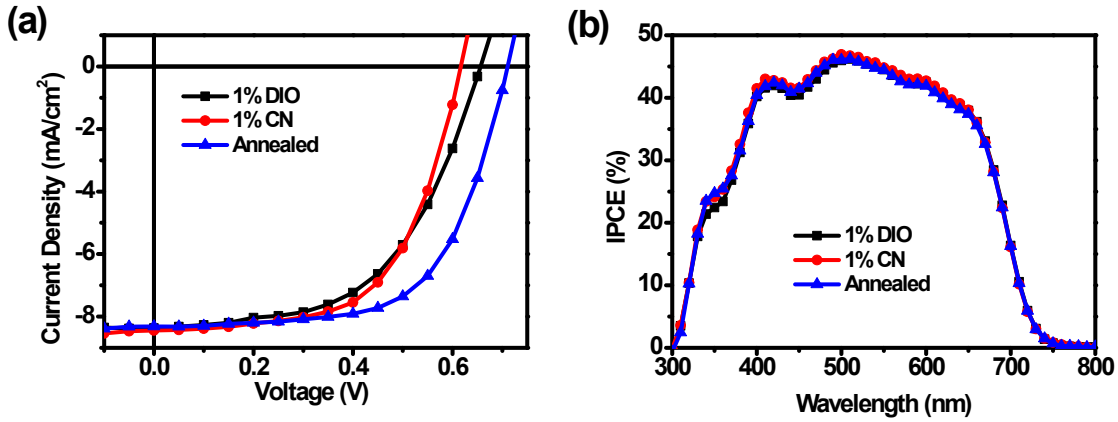

Fig. S4 (a) *J-V* and (b) IPCE cures of devices based on P3HT:**DTFBR** active with different process condition (the weight ratio of D:A is 1:1).

Table S3. Photovoltaic parameters of devices based on P3HT:**DTFBR** active layer with different process condition (the weight ratio of D:A is 1:1).

Ratio of D:A (w/w)	Process condition	V_{OC} (V)	J_{SC} (mAcm^{-2})	FF	PCE[a)] (%)	PCE^{max} (%)
1:1	1% DIO	0.66±0.01	8.06±0.31	0.54±0.01	2.87±0.12	2.99
	1% CN	0.62±0.01	8.35±0.11	0.58±0.01	2.99±0.07	3.11
	Annealed	0.71±0.01	8.15±0.13	0.62±0.01	3.56±0.07	3.68

a) The average values are calculated from ten devices.

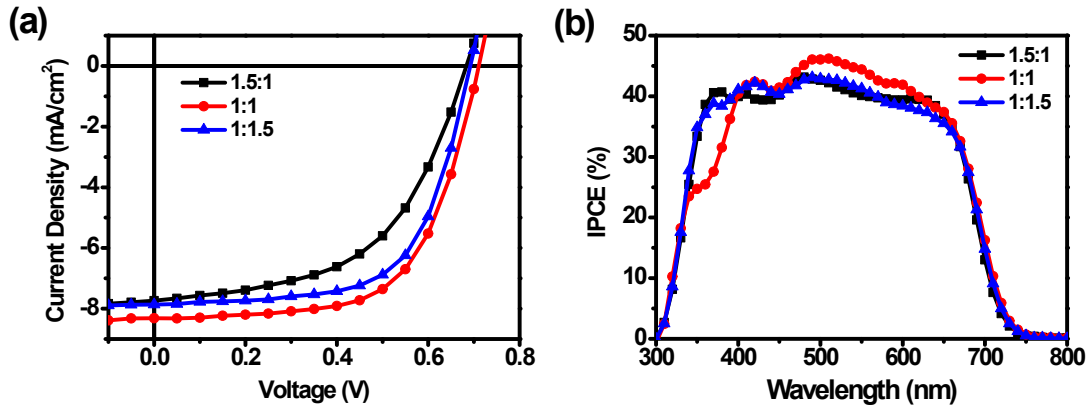

Fig. S5 (a) *J-V* and (b) IPCE cures of devices based on P3HT:**DTFBR** active layer in different blend weight ratios (the blend film was annealed at 100℃ for 10 min) .

Table S4. Photovoltaic parameters of devices based on P3HT: **DTFBR** active layer in different blend weight ratios (the blend film was annealed at 100℃ for 10 min).

Ratio of D:A (w/w)	V_{OC} (V)	J_{SC} (mAcm^{-2})	FF	PCE[a)] (%)	PCE^{max} (%)
1.5:1	0.67±0.01	7.61±0.08	0.53±0.01	2.70±0.06	2.80
1:1	0.71±0.01	8.15±0.13	0.62±0.01	3.56±0.07	3.68
1:1.5	0.69±0.01	7.72±0.19	0.63±0.01	3.37±0.07	3.44

a) The average values are calculated from ten devices.

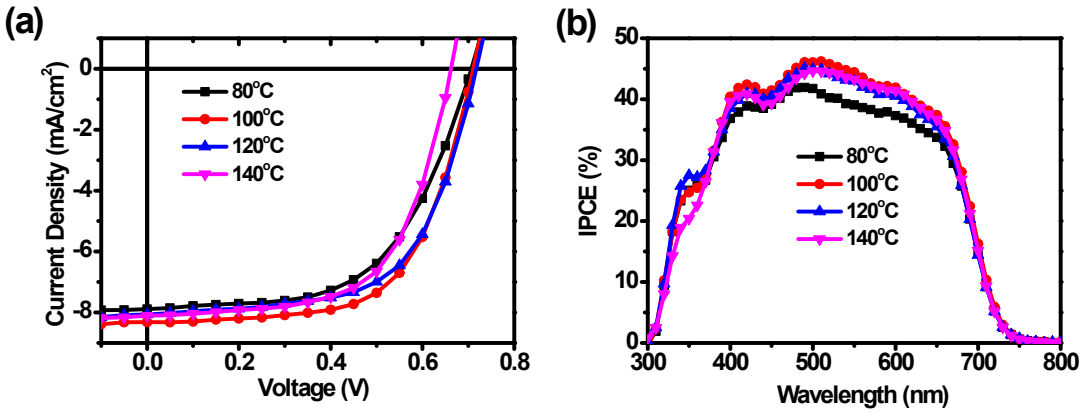

Fig. S6 (a) *J-V* and (b) IPCE cures of devices based on P3HT: **DTFBR** active layer with different annealing temperature .

Table S5. Photovoltaic parameters of devices based on P3HT: **DTFBR** active layer with different annealing temperature.

Annealing temperature (℃)	V_{OC} (V)	J_{SC} (mAcm^{-2})	FF	PCE[a)] (%)	PCE^{max} (%)
80	0.70±0.01	7.66±0.13	0.56±0.01	3.06±0.08	3.14
100	0.71±0.01	8.15±0.13	0.62±0.01	3.56±0.07	3.68
120	0.72±0.01	7.93±0.11	0.62±0.01	3.51±0.02	3.55
140	0.67±0.01	7.84±0.15	0.60±0.02	3.15±0.13	3.33

[a)] The average values are calculated from ten devices.

The optimization process of the device based on **DTFBR:**$PC_{71}BM$ active layer:

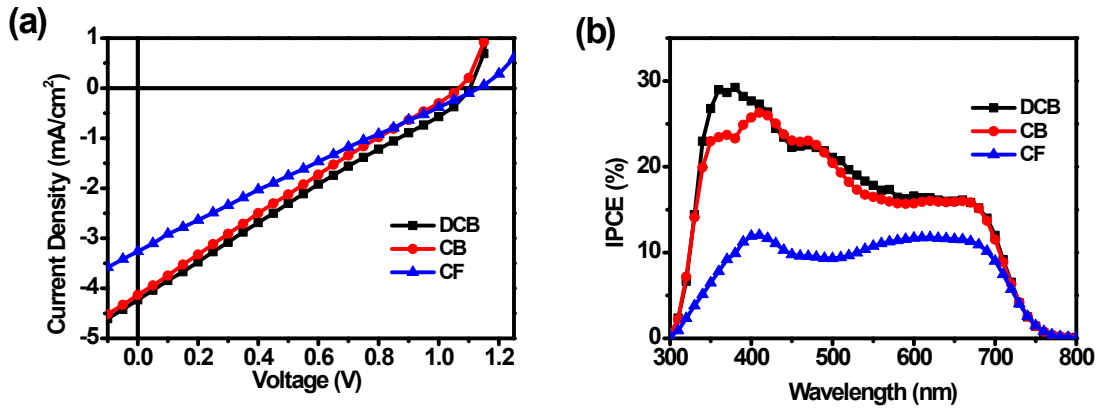

Fig. S7 (a) *J-V* and (b) IPCE cures of devices based on **DTFBR:**$PC_{71}BM$ active layer in different solvent (the blend weight ratio of D:A is 1:1).

Table S6. Photovoltaic parameters of devices based on **DTFBR:**$PC_{71}BM$ active layer in different solvent (the blend weight ratio of D:A is 1:1)

Ratio of D:A (w/w)	Solvent	V_{OC} (V)	J_{SC} (mAcm^{-2})	FF	PCE[a)] (%)	PCE^{max} (%)
1:1	DCB	1.09±0.03	4.13±0.08	0.24±0.01	1.10±0.08	1.16
	CB	1.07±0.04	4.01±0.08	0.24±0.01	1.03±0.02	1.06
	CF	1.08±0.01	2.42±0.04	0.25±0.01	0.65±0.02	0.68

[a)] The average values are calculated from ten devices.

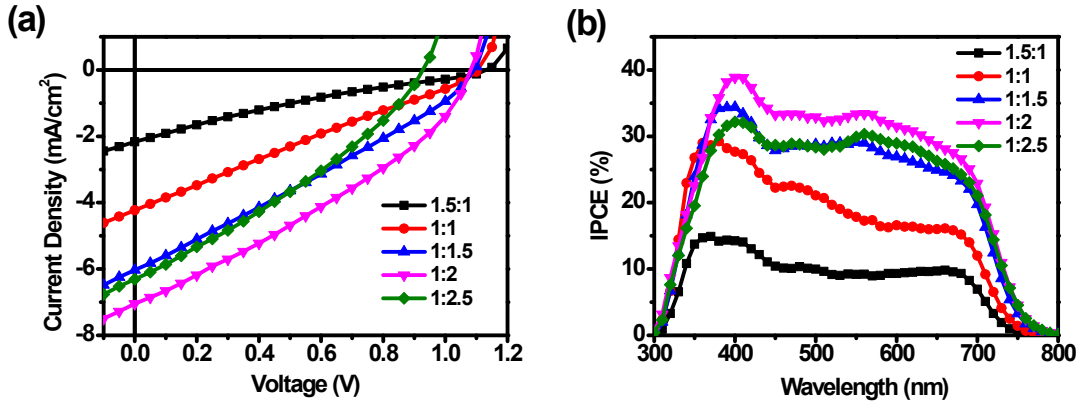

Fig. S8 (a) *J-V* and (b) IPCE cures of devices based on **DTFBR:** $PC_{71}BM$ active layer in different blend weight ratio.

Table S7. Photovoltaic parameters of devices based on **DTFBR:**$PC_{71}BM$ active layer in different blend weight ratio.

Ratio of D:A (w/w)	V_{OC} (V)	J_{SC} (mAcm^{-2})	FF	PCE[a)] (%)	PCE^{max} (%)
1.5:1	1.12±0.01	2.08±0.15	0.21±0.01	0.49±0.03	0.51
1:1	1.09±0.03	4.13±0.08	0.24±0.01	1.10±0.08	1.16
1:1.5	1.06±0.04	5.97±0.19	0.28±0.01	1.74±0.09	1.88
1:2	1.08±0.01	6.94±0.10	0.32±0.01	2.42±0.07	2.50
1:2.5	0.92±0.01	6.07±0.08	0.31±0.01	1.74±0.07	1.85

[a)] The average values are calculated from ten devices.

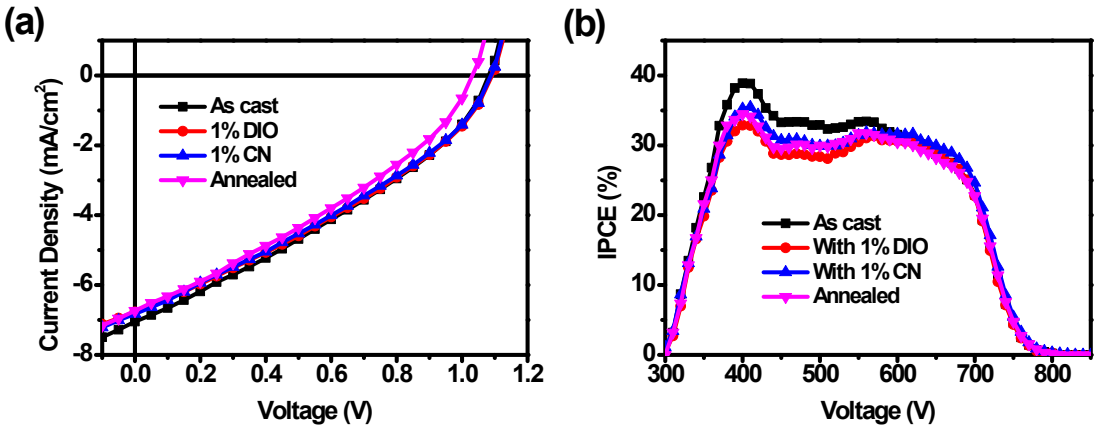

Fig. S9 (a) *J-V* and (b) IPCE cures of devices based on **DTFBR:** $PC_{71}BM$ active layer processed in different condition.

Table S8. Photovoltaic parameters of devices based on **DTFBR:**$PC_{71}BM$ active layer processed in different condition.

Process condition	V_{OC} (V)	J_{SC} (mAcm^{-2})	FF	PCE[a)] (%)	PCE_{max} (%)
As cast	1.08±0.01	6.94±0.10	0.32±0.01	2.42±0.07	2.50
1% DIO	1.08±0.01	6.70±0.09	0.33±0.01	2.41±0.10	2.47
1% CN	1.07±0.01	6.88±0.10	0.32±0.01	2.32±0.09	2.43
Annealed	1.03±0.01	6.77±0.06	0.32±0.01	2.25±0.02	2.28

[a)] The average values are calculated from ten devices.

Table S9. Photovoltaic parameters of devices with different active layer.

Active layer	V_{OC} (V)	J_{SC} (mAcm^{-2})	FF	PCE (%)
PBDB-T:DTFBR	1.04	7.00	0.55	3.97
PTB7-Th:DTFBR	1.03	8.10	0.36	2.97
DTFBR:ITIC	1.00	0.36	0.19	0.07
DTFBR	0.763	6.72×10^{-2}	0.24	0.01

3. Reference

1 C. Y. Chang, Y. J. Cheng, S. H. Hung, J. S. Wu, W. S. Kao, C. H. Lee and C. S. Hsu, *Adv. Mater.*, 2011, **24**, 549-553.