Electronic Supplementary Information (ESI)

BODIPY dyes with β -conjugation and their applications for high-efficiency inverted small molecule solar cells

Hsin-Yu Lin, Wei-Ching Huang, Yung-Chung Chen, Hsi
en-Hsin Chou, Chih-Yu Hsu, Jiann T. ${\rm Lin}^*,$ Hao-Wu
 ${\rm Lin}^*$

H.-Y. Lin, Prof. Dr. J. T. Lin Department of Chemistry, National Central University, Chungli, 320 Taiwan

W.-C. Huang, Prof. Dr. H.-W. Lin

Department of Materials Science and Engineering, National Tsing Hua University, Hsin Chu 300, Taiwan

Dr. Y.-C. Chen, Dr. H.-H. Chou, Dr. C.-Y. Hsu, Prof. Dr. J.-T. Lin

Institute of Chemistry, Academia Sinica, Nankang 115, Taipei, Taiwan

E-mail: jtlin@gate.sinica.edu.tw; hwlin@mx.nthu.edu.tw

Contents	Page
General information: Fig. S1	S2
Synthesis of materials: Scheme S1 and Scheme S2	S 3
UV-Visible of the dyes in THF solution and thin film: Fig. S2	S 7
Quantum chemistry computation	S 8
Computed energy states of the compounds in gas phase: Fig. S3	S 9
Selected frontier orbitals of the dyes: Fig. S4	S 10
Schematic division and dihedral angles of molecules: Fig. S5	S 11
Table S1. Calculated lower-lying transitions of the dyes.	S12
Cyclic voltammograms measurement: Fig. S6	S13
The atmospheric photoelectron spectrometer measurement: Fig. S7	S14
OPVs device fabrication and testing	S15
Device characteristics of normal and inverted solar cells: Fig. S8 and Table S2	S17
Device characteristics of t-FBF:PC71BM solar cells with different concentrations: Fig.	S18
S9 and Table S3	
SCLC mobility measurements: Fig. S10 and Fig. S11	S19
AFM phase images of dye:PC71BM (1:3;w/w) thin film: Fig. S12	S20
¹ H and ¹³ C spectra	S21
	(

General information:

Unless otherwise specified, all the reactions were performed under nitrogen atmosphere using standard Schlenk techniques. All solvents used were purified by standard procedures, or purged with nitrogen before use. ¹H NMR and ¹³C NMR spectra were taken on a Bruker AMX-400, Bruker AV-400 or Bruker AV-500 spectrometer using CDCl₃ or THF-*d*₈ as the solvent. Fast atom bombardment mass spectrometry (FABMS) analysis was performed on a JEOL Tokyo Japan JMS-700 mass spectrometer equipped with the standard FAB source. MALDI Matrix-assisted laser desorption ionization with time of flight (MALDI-TOF) mass spectra were recorded on a Voyager DE-PRO (Applied Biosystem, Houston, USA). Elemental analyses were performed on a Perkin–Elmer Model 2400 analyzer. Absorption spectra were recorded on a Dynamica DB-20 UV-Vis spectrophotometer. Fluorescence spectra were recorded on a Hitachi F-4500 Spectrophotometer. Cyclic voltammetry experiments were performed with a CHI-621B electrochemical analyzer. All measurements were carried out at room temperature with a conventional three electrode configuration consisting of a platinum working electrode, an auxiliary electrodes and a non-aqueous Ag/AgNO₃ reference electrode.

Organic films for atmospheric photoelectron spectrometer measurements were spin-coated on glass substrates. The HOMO levels of molecules were acquired with an atmospheric photoelectron spectrometer (*AC-2, Riken Keiki Co. Ltd.*). Atomic force microscopy (AFM) images were taken with *Veeco Nanoscope 3100* atomic force microscope. The film preparation conditions for the AFM measurements were kept the same as device fabrication for accurate comparison.



Fig. S1. Structure of BODIPY core.

Synthesis of materials:

4,4-Difluoro-1,3,5,7,8-pentamethyl-4-bora-3a,4a-diaza-*s*-indacene (**PMBDP**) were prepared by adopting published procedures,¹ and the preparation of 4,4-difluoro-1,3,5,7,8-pentamethyl-2,6-diiodo-4-bora-3a,4a-diaza-*s*-indacene (**I-PMBDP**) and 2,6-diacetyl-4,4-difluoro-1,3,5,7,8-pentamethyl-4-bora-3a,4a-diaza-*s*-indacene (**PMBDP**) will be described in detail (Scheme S1). **I-PMBDP** was used as the starting material for **FBF** and **2,7-CBC** and **PMBDP**' was used as the starting material for **t-FBF** and **t-2,7-CBC**.



Scheme S1

4,4-Difluoro-1,3,5,7,8-pentamethyl-2,6-diiodo-4-bora-3a,4a-diaza-*s***-indacene** (**I-PMBDP**). Iodic acid (1.76 g, 10.0 mmol) in 10 mL of water was added dropwise to the ethanol solution (100 mL) containing 4,4-difluoro-1,3,5,7,8-pentamethyl-4-bora-3a,4a- diaza-*s*-indacene (1.31 g, 5.0 mmol) and iodine (2.80 g, 11.0 mmol) over 30 minutes, the mixture was stirred for 1 h at 60 °C. After the reaction was complete, the mixture was filtered and the crude product was purified by washing with ethanol to yield a red product. Yield: 1.63 g (63%). ¹H NMR (CDCl₃, 400 MHz): δ 2.62 (s, 3 H), 2.60 (s, 6 H), 2.45 (s, 6 H). MS (FAB) m/z : 513.9 [M+H]⁺.

¹ a) M. Shah, K. Thangaraj, M.-L. Soong, L. T. Wolford, J. H. Boyer, I. R. Politzer, T. G. Pavlopoulos, *Heteroatom Chem.* **1990**, *1*, 389. b) J. H. Boyer, A. M. Haag, G. Sathyamoorthi, M. L. Soong, K. Thangarai, T. G. Pavlopoulos, *Heteroatom Chem.* **1993**, *4*, 39. c) S. Rihn, M. Erdem, A. De Nicola, P. Retailleau, R. Ziessel, Org. Lett. **2011**, *13*, 1916.

4,4-Difluoro-1,3,5,7,8-pentamethyl-2,6-bis(trimethylsilylacetyl)-4-bora-3a,4a-diaza-s-

indacene (TMS-PMBDP'). I-PMBDP (673 mg, 1.3 mmol), Pd(PPh₃)Cl₂ (46 mg, 0.05 mmol) and CuI (13 mg, 0.05 mmol) were added to a 100 mL of two-necked round-bottom flask under a nitrogen atmosphere. After adding anhydrous THF (20 mL), anhydrous diisopropylamine (20 mL) and trimethylsilylacetylene (0.60 mL, 4 mmol), the mixture was stirred at room temperature for 20 h. After the reaction was complete, the mixture was concentrated and then the crude product was purified by column chromatography on silica gel by eluting with hexane/dichloromethane (1:2) to yield a red solid. Yield: 464 mg (79%). ¹H NMR (CDCl₃, 400 MHz): δ 2.61 (s, 3 H), 2.58 (s, 6 H), 2.48 (s, 6 H), 0.24 (s, 18 H). MS (FAB) m/z : 454.2 [M+H]⁺.

2,6-Diacetyl-4,4-difluoro-1,3,5,7,8-pentamethyl-4-bora-3a,4a-diaza-s-indacene (PMBDP'). To a 100 mL flask containing a THF solution (50 mL) and **TMS-PMBDP'** (1.59 g, 3.5 mmol) prechilled to -78 °C was added dropwise a THF solution of tetrabutylammonium fluoride (14 mL, 14 mmol) via syringe under a nitrogen atmosphere. The reaction temperature was then brought to room temperature, and the mixture was stirred for 4 h. After the reaction was complete, the mixture was added water and the precipitate formed was filtered to give the desired product as a dark-red solid. Yield: 1.08 g (95%). ¹H NMR (CDCl₃, 400 MHz): δ 3.35 (s, 2 H), 2.63 (s, 3 H), 2.60 (s, 6 H), 2.51 (s, 6 H). (FAB) m/z : 310.1 [M+H]⁺.

FBF and **2,7-CBC** were synthesized by a similar procedure (Scheme S2), and only **FBF** will be described in detail.



Scheme S2

FBF. A mixture of 7-(5-(tributylstannyl)thiophen-2-yl)-9,9-dihexyl-*N*,*N*-diphenyl-9*H*- fluoren-2amine (3.68 g, 4.0 mmol), **I-PMBDP** (514 mg, 1 mmol), Pd(PPh₃)₂Cl₂ (21 mg, 0.03 mmol), PPh₃ (9 mg) and DMF (30 mL) in a one-necked round bottom flask was refluxed for 18 h. The reaction was quenched by addition of water and the crude product was extracted with dichloromethane. The organic extract was dried over anhydrous MgSO₄ and pumped dry to yield purple syrup. It was purified by column chromatography on silica gel using hexanes/dichloromethane mixture (2:1 by vol.) as the eluent. Yield: 684 mg (48%). ¹H NMR (CDCl₃, 400 MHz): δ 7.60–7.51 (m, 8 H), 7.36 (d, *J* = 3.6 Hz, 2 H), 7.24–7.21 (m, 8 H), 7.10 (m, 10 H), 7.01–6.97 (m, 6 H), 6.89 (d, *J* = 3.6 Hz, 2 H), 2.73 (s, 3 H), 2.62 (s, 6 H), 2.48 (s, 6 H), 1.95–1.80 (m, 8 H), 1.13–1.10 (m, 8 H), 1.10–1.05 (m, 16 H), 0.77 (t, *J* = 7.0 Hz, 12 H), 0.75–0.67 (m, 8 H). ¹³C NMR (CDCl₃, 400 MHz): δ 153.8, 152.5, 151.7, 148.2, 147,5, 146.1, 142.4, 140.9, 138.8, 136.0, 132.4, 129.4, 126.5, 124.9, 126.5, 124.9, 124.1, 123.8, 123.0, 122.8, 120.6, 119.9, 119.7, 119.5, 55.4, 40.5, 31.7, 29.8, 24.0, 22.8, 17.7, 15.9, 14.3, 13.7. HR-MS (FAB) m/z: 1427.8688 [M+H]⁺. Anal. Calcd for C₉₆H₁₀₃BF₂N₄S₂: C, 80.87; H, 7.28; N, 3.93. Found: C, 80.62; H, 7.37; N, 4.12.

2,7-CBC. (Yield : 35%). ¹H NMR (CDCl₃, 400 MHz) : δ 7.96 (d, *J* = 8.4 Hz, 2 H), 7.90 (d, *J* = 8.4 Hz, 2 H), 7.53 (d, *J* = 1.2 Hz, 2 H), 7.48 (dd, *J* = 1.2; 8.4 Hz, 2 H), 7.40 (d, *J* = 3.6 Hz, 2 H), 7.26-7.22 (m, 8 H), 7.13 (d, *J* = 8.4 Hz, 8 H), 7.08 (d, *J* = 1.6 Hz, 2 H), 7.00 (t, *J* = 7.4 Hz, 4 H), 6.96 (dd, *J* = 1.6 Hz; 8.4 Hz, 2 H), 6.91 (d, *J* = 3.6 Hz, 2 H), 4.15 (t, *J* = 6.8 Hz, 2 H), 2.74 (s, 3 H), 2.64 (s, 6 H), 2.50 (s, 6 H), 1.79-1.74 (m, 4 H), 1.28-1.22 (m, 12 H), 0.88-0.81 (m, 6 H). ¹³C NMR (THF-*d*₈, 400 MHz): δ 154.1, 149.6, 147.6, 147.5, 144.2, 143.5, 142.5, 139.6, 134.4, 133.5, 132.3, 130.4, 130.1, 127.1, 124.8, 124.1, 123.8, 123.4, 121.8, 121.0, 120.0, 118.4, 118.3, 106.4, 43.4, 32.7, 29.9, 27.8, 23.6, 17.9, 15.9, 14.6, 13.8.

Mass (FAB, m/z): 1259.58 [M+H]⁺. Anal. Calcd for C₈₂H₇₇BF₂N₆S₂ : C, 78.20 ; H, 6.16; N, 6.67. Found: C, 78.48 ; H, 6.35 ; N, 6.66.

t-FBF and **t-2,7-CBC** were synthesized by a similar procedure (Scheme S2), and only **t-FBF** will be described in detail.

t-FBF. 9,9-Dihexyl-7-(5-iodothiophen-2-yl)-*N*,*N*-diphenyl-9*H*-fluoren-2-amine (2.84 g, 4 mmol), **PMBDP'** (310 m g, 1.0 mmol), Pd(PPh₃)₂Cl₂ (35 mg, 0.05 mmol) and CuI (10 mg, 0.05 mmol) were added to a 100 mL two-necked round-bottom flask under a nitrogen atmosphere. After adding 25 mL of anhydrous THF and 25 mL of anhydrous diisopropylamine, the mixture was stirred at room temperature for 20 h. After the reaction was complete, the reaction mixture was concentrated. The product was purified by silica gel column chromatography using hexanes/dichloromethane (3:1 by vol.) as the eluent to yield a deep-blue solid. Yield: 1.07 g (73 %). ¹H NMR (CDCl₃, 400 MHz): δ 7.58 (d, *J* = 7.6 Hz, 2 H), 7.53 (d, *J* = 8.4 Hz, 4 H), 7.47 (s, 2H), 7.25–7.21 (m, 12 H), 7.11–7.09 (m, 10 H), 7.00 (t, *J* = 7.6 Hz, 6 H), 2.68 (m, 9 H), 2.57 (s, 6 H), 1.93–1.79 (m, 8 H), 1.13–1.08 (m, 16 H), 1.08–1.04 (m, 16 H), 0.77 (t, *J* = 7.0 Hz, 12 H), 0.76–0.67 (m, 8 H). ¹³C NMR (CDCl₃, 400 MHz): δ 157.2, 152.6, 151.8, 148.2, 147.6, 147.0, 142.6, 141.9, 141.4, 135.8, 133.0, 132.3, 131.9, 129.4, 125.1, 124.1, 123.7, 122.8, 122.1, 120.7, 120.1, 119.8, 119.4, 116.2, 89.9, 86.4, 55.4, 40.5, 31.7, 29.8, 24.0, 22.8, 17.2, 16.4, 14.2, 13.9. Mass (MALDI, m/z): 1473.7800 [M+H]⁺. Anal. Calcd for C₁₀₀H₁₀₃BF₂N₄S₂: C, 81.49; H, 7.04; N, 3.80. Found: C, 81.39; H, 7.15; N, 3.79.

t-2,7-CBC. (Yield : 52%). ¹H NMR (CDCl₃, 400 MHz) : 7.95 (d, J = 8.4 Hz, 2 H), 7.89 (d, J = 8.4 Hz, 2 H), 7.49 (s, 2 H), 7.43 (dd, J = 1.2; 8.4 Hz, 2 H), 7.29–7.22 (m, 12 H), 7.14 (d, J = 7.6 Hz, 8 H), 7.07 (d, J = 1.6 Hz, 2 H), 7.00 (t, J = 7.2 Hz, 4 H), 6.95 (dd, J = 1.6; 8.4 HZ, 4 H), 4.13 (t, J = 6.8 Hz, 4 H), 2.68 (s, 6 H), 2.66 (s, 3 H), 2.56 (s, 6 H), 1.77–1.74 (m, 4 H), 1.35–1.15 (m, 12 H), 0.82 (t, J = 6.8 Hz, 6 H). ¹³C NMR (CDCl₃, 500 MHz) : δ 157.1, 148.4, 147.5, 146.8, 142.5, 141.9, 141.4, 133.0, 132.3, 130.7, 129.4, 124.2, 123.2, 123.0, 122.8, 122.1, 121.2, 120.4, 118.5, 117.7, 117.5, 116.1, 105.9, 105.0, 90.0, 86.4, 43.1, 31.7, 29.0, 27.0, 22.7, 16.4, 14.2, 13.9. Mass (MALDI, m/z): 1307.58 [M+H]⁺. Anal. Calcd for C₈₆H₇₇BF₂N₆S₂ : C, 79.00 ; H, 5.94 ; N, 6.43. Found : C, 79.08 ; H, 6.00 ; N, 6.40.



Fig. S2. UV-Visible of the dyes in THF solution and thin film.

Quantum chemistry computation:

The computation were performed with Q-Chem 4.0 software.² Geometry optimization of the molecules were performed using hybrid B3LYP functional and 6-31G* basis set. For each molecule, a number of possible conformations were examined and the one with the lowest energy was used. The same functional was also applied for the calculation of excited states using time-dependent density functional theory (TD–DFT). There exist a number of previous works that employed TD–DFT to characterize excited states with charge-transfer character.³ In some cases underestimation of the excitation energies was seen.⁴ Therefore, in the present work, we use TD–DFT to visualize the extent of transition moments as well as their charge-transfer characters, and avoid drawing conclusions from the excitation energy.

² Y. Shao, L. Fusti-Molnar, Y. Jung, J. Kussmann, C. Ochsenfeld, S. T. Brown, A. T. B.Gilbert, L. V. Slipchenko, S. V. Levchenko, D. P. O'Neill, R. A. DiStasio Jr., R. C. Lochan, T. Wang, G. J. O. Beran, N. A. Besley, J. M. Herbert, C. Y. Lin, T. Van Voorhis, S. H. Chien, A. Sodt, R. P. Steele, V. A. Rassolov, P. E. Maslen, P. P. Korambath, R. D. Adamson, B. Austin, J. Baker, E. F. C., Byrd H. Dachsel, R. J. Doerksen, A. Dreuw, B. D. Dunietz, A. D. Dutoi, T. R. Furlani, S. R. Gwaltney, A. Heyden, S. Hirata, C.-P. Hsu, G. Kedziora, R. Z. Khaliullin, P. Klunzinger, A. M. Lee, M. S. Lee, W. Liang, I. Lotan, N. Nair, B. Peters, E. I. Proynov, P. A. Pieniazek, Y. M. Rhee, J. Ritchie, E. Rosta, C. D. Sherrill, A. C. Simmonett, J. E. Subotnik, H. L. Woodcock III, W. Zhang, A. T. Bell, A. K. Chakraborty, D. M.Chipman, F. J. Keil, A. Warshel, W. J. Hehre, H. F. Schaefer III, J. Kong, A. I. Krylov, P. M. W. Gill, M. Head-Gordon, Z. Gan, Y. Zhao, N. E. Schultz, D. Truhlar, E. Epifanovsky, M. Oana, R. Baer, B. R. Brooks, D. Casanova, J.-D. Chai, C.-L. Cheng, C. Cramer, D. Crittenden, A.Ghysels, G. Hawkins, E. G. Hohenstein, C. Kelley, W. Kurlancheek, D. Liotard, E. Livshits, P. Manohar, A. Marenich, D. Neuhauser, R. Olson, M. A. Rohrdanz, K. S. Thanthiriwatte, A. J. W. Thom, V. Vanovschi, C. F. Williams, Q. Wu, Z.-Q. You, E. Sundstrom, J. Parkhill, K. Lawler, D. Lambrecht, M. Goldey, R. Olivares-Amaya, Y. Bernard, L. Vogt, M. Watson, J. Liu, S. Yeganeh, B. Kaduk, O. Vydrov, X. Xu, I. A. Kaliman, C. Zhang, N. Russ, I. Y. Zhang, W. A. Goddard III, N. Besley, A. Ghysels, A. Landau, M. Wormit, A. Dreuw, M. Diedenhofen, A. Klamt, A. W. Lange, D. Ghosh, D. Kosenkov, D. Zuev, J. Deng, S. and Small, Q-Chem, Ρ. Mao, Υ. C. Su D. Version 4.0. http://www.achem.com/BetaQChem4DemoRequest.html. Q-Chem Inc. 2011. Pittsburgh, PA. ³ a) H. M. Vaswani, C.-P. Hsu, M. Head-Gordon, G. R. Fleming, J. Phys. Chem. B 2003, 107, 7940. b) Y. Kurashige, T. Nakajima, S. Kurashige, K. Hirao, Y. Nishikitani, J. Phys. Chem. A

^{2007, 111, 5544.}

⁴ a) N. Hirata, J.-J. Lagref, E. J. Palomares, J. R. Durrant, M. K. Nazeeruddin, M. Grätzel, M.; D. Di Censo, *Chem. Eur. J.* **2004**, *10*, 595. b) J. R. Durrant, S. A. Haque, E. Palomares, *Chem. Commun.* **2006**, 3279. c) A. Dreuw, M. Head-Gordon, *J. Am. Chem. Soc.* **2004**, *126*, 4007.

Computed energy states of the compounds in gas phase:



Fig. S3. Computed energy states of the compounds in gas phase.

Selected frontier orbitals of the dyes:



Fig. S4. Selected frontier orbitals of the dyes.

Schematic division and dihedral angles of molecules:



Fig. S5. Schematic division and dihedral angles of molecules.

	state	excitation ^b	_{cal,} eV	f^{c}		state	excitation ^b	$_{cal,}eV$	f^{c}
t-FBF	S_1	$\mathrm{H} \rightarrow \mathrm{L} \ (96\%)$	1.88	0.92	FBF	\mathbf{S}_1	H → L (97%)	2.06	0.28
	S_2	H1 \rightarrow L (99%)	2.01	0.01		\mathbf{S}_2	$\mathrm{H1} \rightarrow \mathrm{L}~(98\%)$	2.11	0.01
	S_3	$\mathrm{H2} \rightarrow \mathrm{L} \ (94\%)$	2.28	0.48		S ₃	$\mathrm{H2} \rightarrow \mathrm{L} \ (89\%)$	2.53	0.66
t-2,7-CBC	S ₁	$\mathrm{H} \rightarrow \mathrm{L} \ (96\%)$	1.85	0.90	2,7-CBC	\mathbf{S}_1	$\mathrm{H} \rightarrow \mathrm{L} \ (96\%)$	2.02	0.33
	S_2	H1 \rightarrow L (98%)	1.97	0.01		\mathbf{S}_2	$\mathrm{H1} \rightarrow \mathrm{L}~(97\%)$	2.08	0.00
	S_3	$\mathrm{H2} \rightarrow \mathrm{L}~(94\%)$	2.26	0.54		S_3	$\mathrm{H2} \rightarrow \mathrm{L}~(90\%)$	2.51	0.64

Table S1. Calculated lower-lying transitions of the dyes.^a

^{*a*}Results are based on gas-phase TD-DFT calculation. ^{*b*}H = HOMO, L = LUMO, H1 = The next highest occupied molecular orbital, or HOMO – 1, H2 = HOMO – 2. In parentheses is the population of a pair of MO excitations. ^{*c*}Oscillator strength.

Cyclic voltammograms measurement:



Fig. S6. (Upper) cyclic voltammograms and (lower) differential pulse voltammograms of the dyes in dichloromethane.

The atmospheric photoelectron spectroscopy measurement:



Fig. S7. The atmospheric photoelectron spectroscopy spectra of t-FBF, FBF, t-2,7-CBC, and 2,7-CBC.

OPVs device fabrication and testing:

The inverted orange solar cells were fabricated on indium tin oxide (ITO) coated glass substrates with a sheet resistance of ~10 Ω /sq. ITO were cleaned in an ultrasonic bath with deionized water, acetone, and methanol for 15 min, respectively. The Ca layer was deposited on ITO glass substrates in high vacuum chamber with base pressure $\sim 5 \times 10^{-7}$ Torr, and the rate of deposition was performed at rate of $1 \sim 2$ Å s⁻¹ with the substrate held at room temperature. A blend solution of solar active materials BODIPY dye and PC₇₁BM (purchased from Nano-C) was prepared using chloroform as solvent with BODIPY dye:PC₇₁BM ratio of 1:3 (w/w). The active layer was spin-coated (1500 rpm, 50 s) on top of the Ca modified ITO substrate in a glove box under the anhydrous nitrogen atmosphere, and the thicknesses were controlled by concentration from 15 mg/ml to 35 mg/ml. The samples were then transferred to vacuum chamber for MoO_3 and Ag deposition. The rates of deposition for MoO_3 and the Ag top electrode were ~1 Å s⁻¹ and ~4 Å s⁻¹, respectively. All the transfer processes were done in inert atmosphere without exposure to air. All devices in this study were with structure: ITO (150 nm)/Ca (1 nm)/BODIPY dye:PC₇₁BM (66 nm ~ 172 nm)/MoO₃ (7 nm)/Ag (150 nm). The active area of the cells had an average size of 5 mm² (intersect area between Ag cathode and ITO anode) and were carefully measured device-by-device using calibrated optical microscope. Devices were encapsulated using a UV-cured sealant (Everwide Chemical Co., Epowide EX) and a cover glass under the anhydrous nitrogen atmosphere after fabrication and were measured in air. Current densityvoltage characteristics were measured with a SourceMeter Keithley 2400 under illumination of AM1.5G solar light from a xenon lamp solar simulator (Abet Technologies). The incident light intensity was calibrated as 100 mW/cm² using a NREL-traceable KG5 filtered Si reference cell. The external quantum efficiency (EQE) spectra were taken by illuminating chopped monochromatic light with a continuous-wave bias white light (from halogen lamp, intensity ~ 100 mW/cm²) on the solar cells. The photocurrent signals were extracted with lock-in technique using

a current preamplifier (*Stanford Research System*) followed by a lock-in amplifier (*AMETEK*). The EQE measurement is fully computer controlled and the intensity of monochromatic light is carefully calibrated with NIST-traceable optical power meter (*Ophir Optronics*). Organic films for absorption spectroscopy and ellipsometry measurements were spin-coated on fused silica substrates. Absorption spectra were acquired with spectrometer (*Thermo Spectronic*) and ellipsometry measurements were carried out with *J. A. Woollam Inc. V-VASE* variable-angle spectroscopic ellipsometer. The electron and hole mobilities for the BODIPY dye:PC₇₁BM blended films were carried out by using SCLC method. The hole only device was configured as follows: ITO/MoO₃ (1 nm)/BODIPY dye:PC₇₁BM (~100 nm)/MoO₃ (10 nm)/Al (80 nm), while the electron only device was configured as follows: ITO/Mg (5 nm)/BODIPY dye:PC₇₁BM (~100 nm)/Ca (5 nm)/Al (80 nm). Current density-voltage characteristics of SCLC devices were also measured with a *SourceMeter Keithley* 2400.

Device characteristics of normal and inverted solar cells:



Fig. S8. *J-V* characteristics of **t-FBF**:PC₆₁BM and **t-FBF**:PC₇₁BM solar cells. The normal device structure is: ITO/PEDOT:PSS (40 nm)/**t-FBF**:PC₆₁BM/LiF (1 nm)/Al (120 nm).

device	$V_{\rm oc}$ (V)	J_{sc} (mA/cm ²)	FF	η (%)
Normal ^a	1.004	4.16	0.323	1.35
Inverted ^a	0.967	4.35	0.353	1.50
Inverted ^b	0.988	8.25	0.395	3.22

Table S2. Performance parameters of devices:

^{*a*} **t-FBF**:PC₆₁BM (1:4; w/w) as the active layer. ^{*b*} **t-FBF**:PC₇₁BM (1:3; w/w) as the active layer.





Fig. S9. (a) *J-V*, dark current curves and (b) EQE spectra at various concentrations based on the t-FBF:PC₇₁BM (1:3; w/w) as the active layer.

as the active layer.						
concentration	Thickness (nm)	$V_{\rm oc}$ (V)	J_{sc} (mA/cm ²)	FF	η (%)	
35 mg / 1 mL	172	0.967	5.45	0.323	1.70	
25 mg / 1mL	111	0.975	6.17	0.353	2.12	
20 mg / 1 mL	87	0.984	7.11	0.377	2.64	
15 mg / 1 mL	66	0.988	8.25	0.395	3.22	

Table S3. Device parameters at various concentrations based on the **t-FBF**:PC₇₁BM (1:3; w/w) as the active layer.

SCLC mobility measurements:



Fig. S10. Zero-field electron (solid symbol) and hole (open symbol) mobilities of the dyes:PC₇₁BM (1:3; w/w) active layer



Fig. S11. Field dependent electron and hole mobilities of the dyes:PC₇₁BM (1:3; w/w) active layer.

AFM phase images of dye:PC₇₁BM (1:3;w/w) thin film:



Fig. S12. AFM phase images (250 × 250 nm²) (a) **t-FBF**:PC₇₁BM (1:3; w/w) (b) **FBF**:PC₇₁BM (1:3; w/w) (c) **t-2,7-CBC**:PC₇₁BM (1:3; w/w) (d) **2,7-CBC**:PC₇₁BM (1:3; w/w) at the same concentration (15 mg/ 1 mL)



S21





