Supporting Information for

Boosting Photovoltaic Thermal Stability of Fullerene Bulk Heterojunction Solar Cells through Charge Transfer Interactions

Carr Hoi Yi Ho,^a Huanyang Cao,^b Yong Lu,^b Tsz-Ki Lau,^c Sin Hang Cheung,^a Ho-Wa Li,^d Hang Yin,^a Ka Lok Chiu,^a Lik-Kuen Ma,^a Yuanhang Cheng,^d Sai-Wing Tsang,^d Xinhui Lu,^c Shu Kong So,^{a,*} Beng S. Ong^{b,*}

^aDepartment of Physics and Institute of Advanced Materials, Hong Kong Baptist University, Kowloon Tong, Hong Kong.

^bResearch Centre of Excellence, Institute of Creativity and Department of Chemistry, Hong Kong Baptist University, Kowloon Tong, Hong Kong.

^cDepartment of Physics, The Chinese University of Hong Kong, Shatin, Hong Kong.

^dDepartment of Physics and Materials Science, City University of Hong Kong, Kowloon Tong, Hong Kong.

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Additive	Temperature (°C)	J _{sc} (mA/cm ²)	V _{oc} (V)	FF (%)	PCE (%)	Normalized PCE (%)
	RT	16.5	0.76	62	7.7	100
	50	15.5	0.76	59	6.9	90
	70	15.5	0.77	52	6.2	81
	100	14.5	0.77	47	5.3	69
PCFM	RT	15.5	0.76	68	8.0	100
PCFM	50	15.2	0.76	67	7.8	99
PCFM	70	14.8	0.76	68	7.7	97
PCFM	100	13.8	0.78	64	6.8	86
BDFB	RT	15.5	0.76	66	7.9	100
BDFB	50	15.6	0.77	65	7.8	100
BDFB	70	15.1	0.78	65	7.6	96
BDFB	100	15.6	0.78	60	7.3	93
TDFA	RT	16.4	0.75	63	7.8	100
TDFA	50	15.4	0.78	64	7.7	98
TDFA	70	15.4	0.78	60	7.2	93
TDFA	100	15.3	0.78	59	7.0	90

Table S1.Photovoltaic characteristics of BHJ-OSC devices different 9-fluorenylidene malononitrileadditives under various annealing temperatures for 20 hours.



Figure S1. *J-V* curves of PTB7:PC₇₁BM BHJ-OSCs with different 9-fluorenylidene malononitrile derivatives.

Additive used	LUMO of additive (eV)	J _{sc} (mA/cm ²)	V _{oc} (V)	FF (%)	PCE (%)
-		16.5	0.76	62	7.7
PCFM	-3.87	15.5	0.76	68	8.0
1-NPCFM	-4.13	13.0	0.75	63	6.1
2-NPCFM	-4.32	11.5	0.7	55	4.4

Table S2. Photovoltaic performance of PTB7:PC₇₁BM BHJ-OSCs with different 9-fluorenylidene malononitrile deriavtives.



Figure S2. External quantum efficiency spectra of PTB7:PC₇₁BM devices with and without BDFB additive.



Figure S3. Detailed photothermal deflection spectra of active layer BHJ films of PTB7:PC₇₁BM with and without BDFB additive at different annealing temperatures for 20 hours.

Sample	Increased trap density (cm ⁻³)
Without BDFB	$2.57 imes 10^{17}$
With BDFB	$2.50 imes 10^{16}$

Table S3. Calculated trap density increment upon thermally annealing at 100 °C for 20 hours according to PDS spectra.



Figure S4. 2D GIWAXS patterns of active layer BHJ films of PTB7:PC₇₁BM with and without BDFB additive before and after heating at 100 °C for ~20 hours.



Figure S5. Corresponding GIWAXS linecuts along (a) in-plane, and (b) out-of-plane directions.



Figure S6. 2D GIWAXS and 2D GISAXS patterns of active layer BHJ films of PTB7:PC₇₁BM with and without BDFB additive before and after heating at different temperatures for 20 hours.



Figure S7. Detailed GISAXS 2D linecut of active layer BHJ films of PTB7:PC₇₁BM (a) with and (b) without BDFB additive at different annealing temperatures for 20 hours.

	Contr	ol	With BDFB		
	Room temp. 100°C		Room temp.	100°C	
amorphous phase (nm)	12.4	31.5	20.4	29.5	
$R_{g}PC_{71}BM$ (nm)	11.7	24.3	15.5	21.0	

Table S4. Fitted domain sizes from GISAXS intensity profiles along in-plane direction.



Figure S8. Thermal stability of photovoltaic characteristics of PTB7-Th:PC₇₁BM and P3HT:PC₆₁BM devices with and without BDFB additive as a function of temperature.



Figure S9. Thermal stability of photovoltaic properties of PTB7-Th:PC₇₁BM and P3HT:PC₆₁BM BHJ-OSC devices with and without BDFB additive.

System	Temp. (°C)	J _{sc} (mA/cm ²)	V _{oc} (V)	FF (%)	PCE (%)	Normalized PCE (%)
PTB7-Th	RT	16.5	0.83	62	8.5	100
PTB7-Th	50	15.7	0.81	60	7.6	90
PTB7-Th	70	15.1	0.83	59	7.4	87
PTB7-Th	100	15.9	0.82	51	6.6	77
PTB7-Th with BDFB	RT	16.6	0.81	63	8.5	100
PTB7-Th with BDFB	50	15.8	0.82	64	8.3	98
PTB7-Th with BDFB	70	15.7	0.82	62	8.0	95
PTB7-Th with BDFB	100	15.7	0.82	61	7.9	93
P3HT	RT	9.4	0.6	65	3.6	100
P3HT	50	9.9	0.59	64	3.7	103
P3HT	70	9.3	0.59	56	3.1	85
P3HT with BDFB	RT	10.0	0.59	61	3.6	100
P3HT with BDFB	50	10.2	0.59	62	3.7	103
P3HT with BDFB	70	9.9	0.58	63	3.6	101

Table S5. Photovoltaic properties of PTB7-Th:PC₇₁BM and P3HT:PC₆₁BM BHJ-OSC devices with and without BDFM additive at various annealing temperatures for 20 hours.

EXPERIMENTAL DETAILS

present studies are provided in Supplementary Information.

Materials:

Unless otherwise stated, commercially available chemicals and materials were purchased from Acros Organics, Aldrich Chemical Co., Alfa Aesar 1-Material, Nano-C, Sigma-Aldrich, Tokyo Chemical Industry Co., Luminescence Technology, Heraeus, or TCI Europe, and used as received without further purification. Methylene chloride was purified by distillation over CaH₂ and transferred under Nitrogen. CuPc was purchased from Sigma-Aldrich, and was purified by sublimation before use. Reaction temperatures are reported as the temperature of the bath surrounding the vessel unless otherwise stated. *Synthesis:* Detailed synthetic procedures for 9-fluorenylidene malononitrile derivatives utilized in the

Organic Solar cell fabrication:

A common BHJ-OSC device structure of ITO/PEDOT:PSS/PTB7:PC₇₁BM/LiF/Al was utilized for photovoltaic studies. ITO patterned glass substrate was first cleaned by deconex for 10 min at 120°C, and then cleaned by deionized water, acetone, and isopropanol in ultrasonic bath, followed by UV-ozone treatment. An anode buffer layer comprising of a 30-nm thick film of PEDOT:PSS was deposited on the UV-ozone treated substrate by spin coating, followed by annealing at 140°C for 10 min in air. The active layer coating solution was prepared by dissolving the donor polymer and fullerene acceptor in chlorobenzene. For the PTB7:PC₇₁BM and PTB7-Th:P₇₁BM coating solutions, 3 vol % of 1,8-diiodooctaone (DIO) processing additive was also added. The solution was stirred at 70°C overnight, filtered, and spin coated on the PEDOT:PSS-coated substrate in a glove box to form a ~100 nm active layer. The resulted active layer coating was annealed at 40°C in a glove box overnight, and then transported to a thermal evaporator for vacuum deposition of LiF (1 nm) and Al (130 nm) on the active layer. The experimental devices was characterized using AM 1.5G solar simulator with an intensity of 100 mW cm⁻².

Charge transport measurements:

The device structure for charge transport measurement was similar to that of BHJ-OSC devices.¹ For the electron-only devices, the PEDOT:PSS layer was replaced by a 50 nm aluminum film serving as a hole blocking layer. For hole-only devices, after the active layer was annealed overnight, the sample was transferred to a high vacuum system for thermal co-evaporation of a 10 nm spiro-TPD:CuPc electron blocking and trapping layer.² The deposition rates of spiro-TPD and CuPc were 4.9 Å/s and 0.1 Å/s respectively. After device fabrication, the device was put in an Oxford cryostat with a pressure of less than 20 mTorr for measurement.

Photothermal deflection spectroscopy (PDS):

For PDS measurements, thin films of active layer on quartz were utilized. The measurement was carried out in a standard setup consisting of 1 kW Xenon arc lamp and a 1/4 m grating monochromator (Oriel) as the tunable light source. The pump beam was modulated at 13 Hz by a mechanical chopper before irradiating on the sample. Perfluorohexane was used as the deflection fluid. A Uniphase HeNe laser was directed parallel to polymer sample surface as the probe laser. A quadrant cell (United Detector Technology) was used as the position sensor for monitoring the photothermal deflection signal of the

probe beam. The output of the detector was fed into a lock-in amplifier (Stanford Research, Model SR830) for phase-sensitive measurements. All PDS spectra were normalized to the incident power of the pump beam. Detailed experimental setup was previously reported.³

Grazing incidence X-ray scattering:

BHJ-OSC active layer (~100 nm) was spin coated on top of PEDOT:PSS pre-coated silicon dioxide wafer for measurements. The grazing incidence wide angle and small angle X-ray scattering measurements (GIWAXS and GISAXS) were carried out at BL23A1 of National Synchrotron Radiation Research Center, Hsinchu. The energy of the X-ray source was 10 keV (wavelength of 1.24 Å) and the incident angle was 0.15°.

SYNTHESIS

Materials and Instruments. Commercially available chemicals were obtained from Acros Organics. Aldrich Chemical Co., Alfa Aesar and TCI Europe and used without further purification. CH₂Cl₂ was purified by distillation over CaH₂ and transferred under Nitrogen. Reaction temperatures are reported as the temperature of the bath surrounding the vessel unless otherwise stated. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Ultrashield 400 Plus NMR spectrometer. Chemical shifts (δ) are quoted in ppm downfield of tetramethylsilane and were referenced to the solvent peak (for CDCl₃, ¹H NMR: 7.26 ppm, ¹³C NMR: 77.16 ppm, for DMSO-*d*₆, ¹H NMR: 2.50 ppm, ¹³C NMR: 39.52 ppm and for CD₂Cl₄, ¹H NMR 5.91 ppm, ¹³C NMR: 74.20 ppm). Coupling constants (J) are quoted in Hz, and the following abbreviations were used: s: singlet, bs: broad signal, d: doublet, t: triplet, q: quartet, m: multiplet. UV-vis spectra were recorded on a HP 8453 UV-vis spectrophotometer with Temperature Controller 89090A. Photoluminescence (PL) spectra were recorded on a PerkinElmer LS 55 Fluorescence Spectrometer. Cyclic voltammentry (CV) measurements were recorded on a CHI 600 Electrochemical Workstation. All CV measurements were carried out at room temperature with a conventional three-electrode configuration under nitrogen atmosphere. The electrochemical cyclic was performed in a $0.1 \text{ mol} \cdot L^{-1}$ tetrabutylammonium hexafluorophosphate voltammetry (Bu₄NPF₆)/dichloromethane (DCM) solution with a scan speed of 0.1 V·s⁻¹. A Pt disk embedded in Teflon was used as the working electrode. The surface was polished before use. A Pt wire and Ag/AgCl were used as the counter and reference electrodes, respectively. A ferrocene/ferrocenium (Fc/Fc⁺) redox couple was used as an external standard. The concentration of small molecule solution was 1.0×10^{-3} mol·L⁻¹ in DCM for CV measurement.



Reaction conditions: (i) isopentanol, conc. H_2SO_4 , toluene /reflux; (ii) malononitrile, morpholine / methanol, reflux; (iii) 65% HNO₃/80 °C; (iv) fuming HNO₃, conc. $H_2SO_4/25$ °C; (v) SOCl₂ /reflux; (vi) 2,4-diethyl-1,5-pentanediol, Et₃N, CH₂Cl₂ / 25 °C; (vii) triethanolamine, Et₃N, CH₂Cl₂ /25 °C.

Scheme S1. Syntheses of 9-fluorenylidene malononitrile derivatives.

iso-Pentyl 9-fluorenone-4-carboxylate (1).

The intermediate (1) was prepared in accordance with the procedure of US patent (US4,562,132; Dec. 31, 1985) as follows:

In a 100 mL round-bottomed flask equipped with a Dean-stark apparatus and a water condenser, were placed 9-fluorenone-4-carboxylic acid (1.0 g, 4.46 mmol), isopentyl alcohol (7.863 g, 89.2 mmol), conc. sulfuric acid (0.05 mL) and toluene (20 mL). The mixture was magnetically stirred and refluxed for 24 h before cooling to room temperature. After the reaction, the reaction mixture was evaporated under reduced pressure in the presence of NaHCO₃ (0.1 g). Subsequently, methylene chloride (100 mL) was added and the resulting solution was washed with dilute aq. NaHCO₃ solution (2 times) and with water (2 times), and dried with anhydrous MgSO₄. This was followed by filtration and evaporation under reduced pressure to give the crude product which was purified by flash chromatography on silica gel with hexane/ethyl acetate (volume ratio 15/1) as the eluent to afford a yellow oil (1.27 g, 97 %).

¹H NMR (400 MHz, CDCl₃) δ 8.25 (d, *J* = 7.8 Hz, 1H), 7.89 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.77 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.66 (ddd, *J* = 7.3, 1.2, 0.6 Hz, 1H), 7.47 (td, *J* = 7.7, 1.3 Hz, 1H), 7.30 (dd, *J* = 7.9, 7.3 Hz, 1H), 7.47 (td, *J* = 7.4, 1.3 Hz, 1H), 7.49 (dd, *J* = 7.4, 1.4 Hz), 7.49 (dd, *J* = 7.4 Hz), 7.49 (dd, J = 7.4 Hz), 7.49 (dd, J

2H), 4.42 (t, *J* = 6.8 Hz, 2H), 1.79 (tt, *J* = 12.9, 6.5 Hz, 1H), 1.69 (dt, *J* = 7.0, 3.5 Hz, 2H), 0.98 (d, *J* = 6.5 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 192.93, 166.73, 143.97, 143.19, 135.99, 135.56, 135.11, 134.41, 129.76, 128.61, 127.28, 127.14, 126.26, 124.07, 64.34, 37.36, 25.24, 22.56.

HRMS-MALDI (m/z): $[M + 1]^+$ calcd for C₁₉H₁₈O₃ 295.1329; found 295.1893

[4-iso-Pentoxycarbonyl-9-fluorenylidene]malononitrile, PCFM (I).

The conversion of (1) to the corresponding malononitrile (I) was prepared in accordance with the procedure of US patent (US4,562,132; Dec. 31, 1985) as follows:

A mixture of isopentyl 9-fluorenone-4-carboxylate (1) (1.2607 g, 4.28 mmol), methanol (15 mL), malononitrile (0.8488 g, 12.85 mmol) and 1 drop of morpholine was magnetically stirred and refluxed in a 50 mL 2-neck round-bottomed flask equipped for 24 h. After cooling to room temperature, the solid precipitate in the reaction mixture was filtered, washed twice with methanol, once with water, and dried in vacuo at 50 °C for 10 h. The crude product was recrystallized from acetone and methanol to yield an orange solid, m.p., $126 \sim 127$ °C (1.31 g, 89.3%).

¹H NMR (400 MHz, CDCl₃) δ 8.59 (dd, *J* = 7.9, 0.9 Hz, 1H), 8.46 (d, *J* = 7.9 Hz, 1H), 8.19 (d, *J* = 7.8 Hz, 1H), 7.85 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.51 (td, *J* = 7.7, 1.0 Hz, 1H), 7.41 – 7.33 (m, 2H), 4.45 (t, *J* = 6.8 Hz, 2H), 1.80 (tt, *J* = 12.7, 6.5 Hz, 1H), 1.71 (q, *J* = 6.8 Hz, 2H), 1.00 (d, *J* = 6.5 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 166.87, 160.42, 141.22, 140.82, 135.83, 135.70, 135.18, 134.71, 129.94, 129.15, 128.63, 128.24, 126.68, 126.14, 113.58, 113.50, 76.16, 64.77, 37.40, 25.30, 22.62.

HRMS-MALDI (m/z): $[M + 1]^+$ calcd for C₂₂H₁₈N₂O₂ 342.1363; found 342.1350.

7-Nitro-9-fluorenone-4-carboxylic acid (2).

A suspension of 9-fluorenone-4- carboxylic acid (2.0 g, 8.92 mmol) in 65% nitric acid (75 mL) was heated at 80° C. for 18 h, and then cooled to room temperature. The reaction mixture was poured into a stirring ice-water mixture, and the resulting precipitate was collected by filtration, washed with water and ether to give the product as a yellow solid (1.31 g, 54.6%).

¹H NMR (400 MHz, DMSO- d_6) δ 13.95 (s, 1H), 8.55 – 8.45 (m, 2H), 8.23 (d, J = 2.0 Hz, 1H), 8.07 (dd, J = 7.8, 1.1 Hz, 1H), 7.91 (dd, J = 7.3, 1.1 Hz, 1H), 7.62 (t, J = 7.6 Hz, 1H).

¹³C NMR (100 MHz, DMSO-*d*₆) δ 189.89, 167.57, 148.26, 147.90, 140.47, 136.78, 135.55, 134.80, 131.11, 130.35, 129.39, 127.27, 126.81, 118.03.

HRMS-MALDI (*m/z*): [M + Na] calcd for C₁₄H₇NO₅Na 292.0216; found 292.0231.

iso-Pentyl 7-nitro-9-fluorenone-4-carboxylate (3).

Esterification of 7-nitro-9- fluorenone-4-carboxylic acid (2) (0.7 g, 2.6 mmol) was conducted according to the procedure for intermediate (1). The crude ester was purified by recrystallization from methylene chloride and isopropanol to afford a yellow solid, m.p., $135 \sim 136$ °C (0.86 g, 97.3%).

¹H NMR (400 MHz, CDCl₃) δ 8.59 (d, J = 8.5 Hz, 1H), 8.48 (d, J = 2.2 Hz, 1H), 8.38 (dd, J = 8.5, 2.3 Hz, 1H), 8.08 (dd, J = 7.9, 1.2 Hz, 1H), 7.93 (dd, J = 7.4, 1.2 Hz, 1H), 7.51 (t, J = 7.6 Hz, 1H), 4.47 (t, J = 6.8 Hz, 2H), 1.82 (tt, J = 12.7, 6.4 Hz, 1H), 1.73 (q, J = 6.8 Hz, 2H), 1.01 (d, J = 6.5 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 190.39, 166.22, 148.81, 148.51, 142.14, 136.98, 136.35, 135.50, 130.55, 129.95, 128.54, 128.00, 127.34, 118.97, 64.89, 37.39, 25.34, 22.64.

HRMS-MALDI (m/z): $[M + 1]^+$ calcd for C₁₉H₁₇NO₅ 340.1179; found 340.1116.

[7-Nirto-4-isopentoxycarbonyl-9-fluorenylidene]malononitrile, 1-NPCFM (II).

The conversion of isopentyl 7-nitro-9-fluorenone-4-carboxylate (3) (339.3 mg, 1 mmol) to the corresponding malononitrile was carried out in accordance with the procedure for **PCFM** (I). The ester was purified by flash chromatography on silica gel with hexane/ethyl acetate (volume ratio 5/1) as the eluent to afford a yellow solid, m.p., $177 \sim 178$ °C (260 mg, 67.1%).

¹H NMR (400 MHz, CDCl₃) δ 9.33 (d, *J* = 2.0 Hz, 1H), 8.72 (dd, *J* = 7.9, 0.9 Hz, 1H), 8.54 (d, *J* = 8.7 Hz, 1H), 8.40 (dd, *J* = 8.7, 2.1 Hz, 1H), 8.03 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.56 (t, *J* = 7.9 Hz, 1H), 4.48 (t, *J* = 6.8 Hz, 2H), 1.81 (dq, *J* = 19.2, 6.5 Hz, 1H), 1.73 (q, *J* = 6.7 Hz, 2H), 1.01 (d, *J* = 6.5 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 166.23, 157.71, 148.50, 145.83, 139.15, 136.62, 136.57, 135.50, 130.45, 129.65, 129.58, 129.41, 126.94, 121.10, 112.84, 112.63, 78.97, 65.22, 37.36, 25.33, 22.62.

HRMS-MALDI (m/z): $[M + 1]^+$ calcd for C₂₂H₁₇N₃O₄ 387.1214; found 387.1200.

2,7-Dinitro-9-fluorenone-4-carboxylic acid (4).

The dinitro intermediate (4) was prepared in accordance with the procedure of US patent (US4,474,865; Oct 2, 1984) as follows:

Red fuming nitric acid (60 mL) was added dropwise to 9-fluorenone-4-carboxylic acid (2.24 g, 10 mmol) in a 100 ml round-bottom flask at room temperature over a period of 2 min. This was followed by dropwise addition of conc. sulfuric acid (1 mL) over a period of 1 min. The resulting mixture was stirred at room temperature for 10 min and then poured slowly into ice cold water with constant stirring. The solid product was collected by filtration, washed with 5% aq. hydrochloric acid solution, and then dried in a vacuum at 60 °C for 24 h to give the product as a yellow solid (2.67 g, 85.0%).

¹H NMR (400 MHz, DMSO- d_6) δ 14.18 (s, 1H), 8.66 (d, J = 1.6 Hz, 1H), 8.51 (s, 2H), 8.35 (d, J = 1.5 Hz, 1H), 8.24 (s, 1H).

¹³C NMR (100 MHz, DMSO-*d*₆) δ 187.52, 165.70, 148.98, 148.33, 145.81, 145.21, 136.98, 135.75, 131.06, 130.60, 130.18, 128.30, 120.74, 118.38.

iso-Pentyl 2,7-dinitro-9-fluorenone-4-carboxylate (5).

Esterification of 2,7-dinitro -9-fluorenone-4-carboxylic acid (4) (2 g, 6.37 mmol) was conducted in accordance with the procedure for intermediate (1). The ester was purified by recrystallization from methylene chloride and isopropanol to give a yellow solid, m.p., $132\sim133$ °C (1.84 g, 75.3%).

¹H NMR (400 MHz, CDCl₃) δ 8.95 (d, J = 2.3 Hz, 1H), 8.80 (d, J = 8.6 Hz, 1H), 8.71 (d, J = 2.3 Hz, 1H), 8.60 (d, J = 2.2 Hz, 1H), 8.50 (dd, J = 8.6, 2.3 Hz, 1H), 4.54 (t, J = 6.8 Hz, 2H), 1.89 – 1.74 (m, 3H), 1.03 (d, J = 6.4 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 187.88, 164.41, 149.73, 148.83, 146.93, 146.44, 137.79, 136.40, 131.75, 130.45, 129.50, 128.99, 122.21, 119.61, 65.90, 37.30, 25.38, 22.64.

HRMS-MALDI (m/z): $[M + 1]^+$ calcd for $C_{19}H_{16}N_2O_7$ 385.1030; found 385.1051.

[2,7-Dinitro-4-isopentoxycarbonyl-9-fluorenylidene]malononitrile, 2-NPCFM (III).

The conversion of iso-pentyl 2,7-dinitro-9-fluorenone-4-carboxylate (5) (0.9 g, 2.34 mmol) to the corresponding malononitrile was carried out in accordance with the procedure for PCFM (I). The

compound was purified by flash chromatography on silica gel with hexane/ethyl acetate (volume ratio 5/1) as the eluent to afford a bright yellow solid, m.p., 170-171 °C (0. 75 g, 74.2%).

¹H NMR (400 MHz, CDCl₃) δ 9.56 (d, J = 2.0 Hz, 1H), 9.43 (d, J = 2.0 Hz, 1H), 8.89 (d, J = 2.0 Hz, 1H), 8.74 (d, J = 8.7 Hz, 1H), 8.50 (dd, J = 8.7, 2.1 Hz, 1H), 4.55 (t, J = 6.8 Hz, 2H), 1.87 – 1.73 (m, 3H), 1.03 (d, J = 6.4 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 164.47, 155.31, 149.43, 148.38, 143.84, 143.53, 137.74, 136.42, 131.12, 130.03, 129.97, 128.58, 123.59, 121.35, 112.09, 112.01, 81.51, 66.21, 37.28, 25.37, 22.61.

HRMS-MALDI (m/z): $[M + 1]^+$ calcd for C₂₂H₁₆N₄O₆ 433.1143; found 433.1119.

(4-Carboxy-9-fluorenylidene)malononitrile (6).

The intermediate (6) was prepared in accordance with the procedure of US patent (US4,562,132; Dec. 31, 1985) as follows:

9-Fluorenone-4-carboxylic acid (5.0 g, 22.3 mmol), methanol (90 mL), malononitrile (4.42 g, 66.9 mmol) and 2 drops of morpholine were added to a 250 mL round-bottomed flask equipped with a reflux condenser. The reaction mixture was magnetically stirred and refluxed for 48 h. Subsequently, the reaction mixture was cooled to room temperature and the orange solid product was filtered off. The crude product was stirred in boiling methanol (30 mL) for half an hour, and filtered hot, washed with methanol (3 mL), and then dried in vacuo at 60 °C for 12 h to provide 5.47g of orange solid product (yield 90.2%).

¹H NMR (400 MHz, DMSO- d_6) δ 13.83 (s, 1H), 8.35 (dd, J = 7.9, 0.7 Hz, 1H), 8.24 (d, J = 7.8 Hz, 1H), 8.11 (d, J = 7.8 Hz, 1H), 7.85 (dd, J = 7.8, 0.8 Hz, 1H), 7.60 (td, J = 7.7, 0.9 Hz, 1H), 7.53 – 7.43 (m, 2H).

¹³C NMR (100 MHz, DMSO-*d*₆) δ 168.04, 158.85, 139.99, 139.03, 135.17, 135.08, 134.88, 134.02, 129.84, 129.11, 129.07, 127.89, 125.76, 125.33, 113.64, 76.24.

(4-Chloroformyl-9-fluorenylidene)malononitrile (7).

The chloroformyl intermediate (7) was prepared in accordance with the procedure of US patent (US4,562,132; Dec. 31, 1985) as follows:

A mixture of (4-carboxy-9- fluorenylidene)malononitrile (6) (5.47 g, 20.1 mmol) and thionyl chloride (50 mL) in a 100 mL round-bottomed flask equipped with a reflux condenser was magnetically stirred and refluxed under N_2 for 6 h. As the reaction proceeded, the reaction mixture turned brownish in color and became dark brown at the end of the reaction. The cooled reaction mixture was evaporated at reduced pressure to give a solid residue. Dichloroethane (60 mL) was added and the resulting solution was evaporated under reduced pressure to remove trace thionyl chloride. The crude product was recrystallized from methyl chloride/hexane to give an orange solid after drying in vacuo at 40 °C for 12 h (5.44 g, 93.0%).

¹H NMR (400 MHz, DMSO-*d*₆) δ 8.32 (dd, *J* = 7.9, 0.8 Hz, 1H), 8.21 (d, *J* = 7.8 Hz, 1H), 8.10 (d, *J* = 7.7 Hz, 1H), 7.84 (dd, *J* = 7.8, 0.8 Hz, 1H), 7.59 (td, *J* = 7.7, 0.9 Hz, 1H), 7.46 (dt, *J* = 15.2, 4.4 Hz, 2H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 167.93, 158.81, 139.97, 139.07, 135.22, 135.07, 134.84, 133.96, 129.82, 129.04, 127.88, 125.72, 125.36, 113.60, 76.14.

1,4-Bis(9-dicyanomethelenefluorene-4-carboxy)-2,3-diethylbutane, BDFB (IV).

A solution of 2,4-diethyl-1,5-pentanedinol (DL- and meso- mixture) (160.3 mg, 1.00 mmol) and trimethylamine (247.1 mg, 2.44 mmol) in dry methyl chloride (3 mL) was added dropwise to a solution of (4-chloroformyl-9-fluorenylidene)malononitrile (7) (646.0 mg, 2.22 mmol) in dry methyl chloride (15 mL) in a 50 mL round-bottomed flask at room temperature under N₂ atmosphere. The resulting reaction mixture was magnetically stirred at room temperature overnight. After the reaction, the mixture was washed with dilute aq. NaHCO₃ solution (3 times) and then water (2 times), dried with anhydrous MgSO₄, and filtered. The filtrate was evaporated under reduced pressure to give the crude product which was purified by flash chromatography on silica gel with hexane/methyl chloride (volume ratio 1/2) as the eluent to afford an orange solid, m.p., 131-132 °C (354.0 mg, 52.9%).

¹H NMR (400 MHz, CDCl₃) δ 8.58 – 8.36 (m, 2H), 8.14 (m, 1H), 7.77 (m, 1H), 7.43 (m, 1H), 7.37 – 7.14 (m, 2H), 4.50 – 4.18 (m, 2H), 1.93 (m, 1H), 1.66 – 1.37 (m, 4H), 1.00 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 166.63, 166.37, 160.02, 159.78, 141.34, 140.61, 140.50, 135.86, 135.72, 135.50, 135.12, 135.05, 134.62, 134.50, 129.99, 129.96, 129.18, 129.01, 128.56, 128.39, 127.90, 127.72, 126.62, 126.52, 126.34, 126.23, 113.49, 113.46, 113.39, 113.33, 76.28, 76.26, 68.29, 67.96, 36.86, 36.62, 32.95, 32.91, 31.72, 24.74, 24.59, 22.79, 14.25, 11.28, 11.16.

HRMS-MALDI (*m/z*): [M +Na] calcd for C₄₃H₃₂N₄O₄Na 691.2315; found 691.2340.

Tris(9-dicyanomethelenefluorene-4-carboxyethyl)amine, TDFA (V).

A solution of triethanolamine (83.5 mg, 0.56 mmol) and trimethylamine (198.1 mg, 1.96 mmol) in dry methyl chloride (3 mL) was added dropwise to a solution of (4-chloroformyl-9-fluorenylidene)malononitrle (7) (569.1 mg, 1.96 mmol) in dry methyl chloride (15 mL) in a 50 mL round-bottomed flask at room temperature under N₂. The resulting reaction mixture was magnetically stirred at room temperature overnight. After the reaction, the mixture was washed with dilute aq. NaHCO₃ solution (3 times) and then water (2 times), dried with anhydrous MgSO₄, and filtered. The filtrate was evaporated under reduced pressure to give the crude product which was purified by flash chromatography on silica gel with hexane/methyl chloride (volume ratio 1/2) as the eluent to afford an orange solid, m.p., 129-130 °C (276.4 mg, 54.2%).

¹H NMR (400 MHz, $C_2Cl_4D_2$) δ 8.23 (s, 2H), 7.99 (d, J = 7.1 Hz, 1H), 7.70 (d, J = 6.9 Hz, 1H), 7.45 – 7.16 (m, 2H), 7.07 (s, 1H), 4.43 (s, 2H), 3.07 (s, 2H).

 ^{13}C NMR (100 MHz, C_2Cl_4D_2) δ 166.28, 160.01, 141.39, 140.49, 136.13, 135.61, 135.43, 134.44, 130.24, 129.18, 128.67, 127.40, 126.65, 126.55, 113.68, 113.61, 75.96, 63.90, 53.59.

HRMS-MALDI (m/z): [M +]⁺ calcd for C₅₇H₃₃N₇O₆ 911.2487; found 911.2497.



Figure S10. Normalized UV-vis absorption spectra of 9-fluorenylidene malononitrile derivatives in methylene solutions.



Figure S11. Cyclic voltammetry (CV) of 9-fluorenylidene malononitrile derivatives in dichloromethane solutions (at 1.0×10^{-3} mol L⁻¹, with 0.1 mol L⁻¹ Bu₄NPF₆ as the supporting electrolyte) at a scan rate of 100 mV s⁻¹.

		solution		cyclic voltammetry		
Small molecules	λ_{\max} (nm)	λ_{onset} (nm)	E_{g}^{opt} (eV)*	$E_{\rm red}^{\rm onset}$ (eV)	E _{LUMO} (eV)	$E_{\rm HOMO}$ (eV)**
PCFM (I)	349	387	3.20	-0.46	-3.87	-7.07
1-NPCFM (II)	348	388	3.20	-0.19	-4.13	-7.33
2-NPCFM (III)	365	385	3.22	-0.03	-4.32	-7.54
BDFB (IV)	351	395	3.14	-0.49	-3.86	-7.00
TDFA (V)	352	395	3.14	-0.58	-3.77	-6.91

* Optical band gap.

** Calculated from the difference of LUMO energy level and optical band gap.

 Table S4. Optical and electrochemical properties of small molecules.

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