Supporting Information

Energy-Level Modulation of Coumarin-Based Molecular donors for Efficient All Small Molecule Fullerene-Free Organic Solar Cells

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Experimental

1. Experimental Section

Materials. All reagents and solvent used for synthesis were purchased from Spectrochem and Loba chemicals were of the highest available purity and were used without further purification. Spectroscopic grade solvents purchased from Spectrochem (India) were used for UV-vis and fluorescence measurements. 4-Diethylaminosalicylaldehyde and triphenylamine were purchased from sigma-aldrich. 3-acetyl-7-(diethylamino)-2H-chromen-2-one was synthesized following the literature procedure published earlier.¹ 4-(Diphenylamino)benzaldehyde was synthesized in accordance to previously published literature.² poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), Poly[(9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN), BThIDT-Cl and Y6 (also called as BTP-4F) were purchased from OSSILA, UK. All materials were used as received without purification. **Methods**. The optical properties of the synthesized compound were investigated by UVvis with Simadzu UV-2450 spectrophotometer. Steady-state fluorescence measurements were performed with a Hitachi F-7000 (Japan) spectrofluorometer using a 1 cm \times 1 cm quartz cuvette. Excitation and emission slits with a nominal band pass of 5 nm were used for all measurements. The synthesized compound shows good solubility in organic solvents but partially soluble in non-polar solvents like Hexane. Cyclic voltammetry (CV) analysis was carried out by employing 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆) in DCM as the supporting electrolyte in the three-electrode cell using a Pt disc acting as the working electrode, Pt wire as the counter electrode and Ag/Ag⁺ as the reference electrode.

NMR spectra were recorded on a Avance III 400 MHz Bruker spectrometer (¹H NMR: 400 MHz, ¹³C NMR: 100 MHz) at 25 °C unless otherwise noted. Chemical shift values (δ) are expressed in parts per million using residual solvent protons (¹H NMR, δ H = 7.26 for CDCl₃; ¹³C NMR, δ C = 77.0 for CDCl₃ as internal standard. The splitting patterns are designated as follows: s (singlet), d (doublet), t (triplet), and m (multiplet). Melting points were determined using a Mettler Toledo DSC 823 e and were not corrected. Preparative column chromatography was performed on glass columns packed with silica gel (particle size 60-120 µm. TLC was performed using manually coated silica gel 60 TLC plates. Mass spectrum (HRMS) was measured in Waters Xevo G2-S QTOF with UPLC.



Scheme S1. Synthesis of coumarin-triphenylamine conjugate C2.

Synthesis of 7-(diethylamino)-3-(3-(4-(diphenylamino)phenyl)acryloyl)-2H-chromen-2one (C2). A mixture of 0.5g (1.83 mmol) of 3-acetyl-7-(diethylamino)-2H-chromen-2-one 3 and 0.474g (1.83 mmol) of (4-(diphenylamino)benzaldehyde 5 was taken in a round bottom flask containing ethanol then a catalytic amount (2-3 drops) of piperidine was added. A sharp change in color from yellow to orange was observed and refluxed for 8 hours at a temperature of 80 °C. The mixture was cooled and the resulting solid was filtered and purified by column chromatography using silica in mixture of dichloromethane:petroleum ether (2:5) as eluent to obtain the desired product C2 as orange red solid. (yield = 70%). MP. 230 °C, ¹H NMR (400 MHz, CDCl₃, ppm) δ : 1.25 (t, 6H), 3.46 (q, 4H), 6.49 (d, 1H, J = 2.3 Hz), 6.62 (dd, 1H, J = 9.0, 2.5 Hz), 7.01 (d, 2H, J = 8 Hz), 7.09 (t, 2H, J = 7.3 Hz), 7.14 (dd, 4H, J = 8, 0.9 Hz), 7.27-7.32 (m, 4H), 7.42 (d, 1H, J = 8 Hz), 7.53 (d, 2H, J = 8 Hz), 7.80 (d, 1H, J = 16 Hz), 8.02 (d, 1H, J = 16 Hz), 8.55 (s,1H). ¹³C NMR (400 MHz, CDCl₃, ppm) δ : 12.45, 45.13, 96.59, 108.64, 109.73, 121.65, 122.37, 123.89, 125.33, 128.56, 129.42, 130.01, 131.68, 143.28, 146.90, 148.47, 149.84, 152.78, 158.56, 160.91, 186.35. TOF (HRMS) m/z: 515.6221 (M⁺ + H) (calcd. for C₃₄H₃₀N₂O₃ 514.6250).

2. Device Fabrication and Characterization

We have fabricated the OSCs employing a conventional type device with structure of ITO/PEDOT:PSS/active layer/PFN/Al. indium tin oxide (ITO) coated glass substrates were cleaned sequentially with detergent, deionized water, acetone and isopropyl alcohol for 20 min, respectively in ultrasonication bath, an dried on hot vacuum oven for 30 min. The PEDOT:PSS layer was deposited by spin coating the Al 4083 solution onto the ITO substrates for 40 s at 3000 rpm and the films were annealed at 120°C for 15 min. The active layer blend solution (C1 and C2 as donor and BThIND-Cl and Y6 as acceptor) using chloroform as solvent (total concentration of 16 mg/mL, was spin coated at 2500 rpm for 40s, on the top of the active layer with film thickness of 95 \pm 5 nm. The weight ratio between the donor and acceptor was varied from 1:0.4 to 1:1.6. The optimized active layers were further subjected to solvent vapor annealing via exposing the thin films with THF environment for 40 s. PFN interlayer solution was prepared in methanol with concentration of 1 mg/mL was stirred for 1 hr. at room temperature. The PFN interlayer was deposited onto the top of active layer by spin coating the solution for 40s at 3000 rpm. Finally, 100 nm thick aluminum (Al) electrode was deposited on the top of PFN layer vis thermal evaporation at pressure less than 10-5 Torr). The ternary devices were fabricated in same manner as employed for binary devices. We have varied the weight ratio between the two acceptor and kept the concentration of donor constant. The effective area of the devices is 0.16 cm^2 . The current -voltage (*J-V*) characteristics of the final OSCs were performed by Keithley 2400 SMU and solar simulator under light irradiation of 100 mW/cm², which is provided by 150 W Xe arc lamp and fileted by an air mass 1.5 G filter. The external quantum efficiency (EQE) spectra of OSCs were recorded using Bentham EQE measurement system.

The electron and hole mobility for the active layers were estimated via fabrication of the electron only (ITO/Al/active layer/Al) and hole only (ITI/PEDOT:PSS/active layer/Al) devices, respectively and measured the dark current-voltage characteristics of these devices and fitting the data with space charge limited current (SCLC) model.

The transient photocurrent (TPC) and transient photovoltage (TPV) curves were measured by connecting the devices to an oscilloscope with 1 M Ω and 40 Ω input impedance for TPV and TPC, respectively, and exposing the devices with an excitation pulse from a laser (700 nm) with pulse duration < 10 ns and frequency of 10 kHz.



Figure S1. TGA thermograms of the donor molecules measured under N_2 , conditions: N_2 flow, 50 mL/min; heating rate, 10 °C/min.



Figure S2. Absorption and emission C1 and C2 in chloroform solution and thin film.



Figure S3. Cyclic voltammograms of C1 and C2 films on a Pt electrode in 0.1 mol $L^{-1}Bu_4NPF_6$ in CH₃CN solution, scan rate = 200 mV, absolute energy level of Fc⁺/Fc set as -5.1 eV below vacuum.



Figure S4. (a) PL spectra of pristine BThIND-Cl and blend of C2:BThIND-Cl in thin film. (b) PL spectra of pristine Y6 and blend of C2:Y6 in thin film.



Figure S5. Absorption spectra of blend films of C1 and C2 donors with acceptors BThIND-Cl and Y6.



Figure S6. (a) Absorption spectra of Y6 and emission of BThIND-Cl to show the overlap region for FRET. (b) Solid state photoluminescence spectra of pristine acceptors and their blend excited at 760 nm.



Figure S7. Dark current-voltage characteristics of (a) hole only devices and (b) electron only devices for optimized binary and ternary active layers.



Figure S8. ¹H NMR (400 MHz) Spectra of C2. (*Solvent peak)



Figure S9. C₁₃ NMR (400 MHz) Spectra of C2.



Figure S10. High resolution mass spectrum of C2.

Table S1. Photovoltaic parameters of the OSCs based on C1:BThIND-Cl with different weight ratios using chloroform as solvent.

Weight ratio	J _{SC} (mA cm ⁻²)	$V_{\rm OC}$ (V)	FF	PCE (%)
1:0.4	6.31	0.97	0.41	2.51
1:0.8	7.85	0.98	0.44	3.38
1:1.2	8.79	0.99	0.46	4.00
1:1.5	9.54	0.99	0.49	4.63
1:1.6	9.03	0.99	0.46	4.11

Table S2. Photovoltaic parameters of the OSCs based on C2:BThIND-Cl with differentweight ratios using chloroform as solvent.

Weight ratio	J _{SC} (mA cm ⁻²)	$V_{\rm OC}$ (V)	FF	PCE (%)
1:0.4	6.75	1.03	0.45	3.13
1:0.8	7.79	1.04	0.47	3.81
1:1.2	8.35	1.05	0.50	4.38
1:1.5	9.98	1.06	0.51	5.40
1:1.6	9.31	1.05	0.49	4.79

Weight ratio	$J_{\rm SC}$ (mA cm ⁻²)	$V_{\rm OC}$ (V)	FF	PCE (%)
1:0.4	7.58	0.76	0.44	2.53
1:0.8	8.41	0.77	0.46	2.98
1:1.2	9.95	0.78	0.50	3.88
1:1.5	10.86	0.79	0.51	4.38
1:1.6	10.21	0.79	0.49	3.95

Table S3. Photovoltaic parameters of the OSCs based on C1:Y6 binary blend with different weight ratios using chloroform as solvent.

Table S4. Photovoltaic parameters of the OSCs based on C2:Y6 binary blend with different weight ratios using chloroform as solvent.

Weight ratio	J _{SC} (mA cm ⁻²)	$V_{\rm OC}$ (V)	FF	PCE (%)
1:0.4	7.82	0.75	0.45	2.64
1:0.8	8.83	0.76	0.47	3.15
1:1.2	10.82	0.78	0.50	4.22
1:1.5	11.04	0.79	0.51	4.45
1:1.6	10.56	0.79	0.48	4.00

Table S5. Photovoltaic parameters of the ternary OSCs based on C1:BThIND-CI:Y6 ternary blend with different weight ratios of BThIND-Cl and Y6 using chloroform as solvent.

Weight ratio	$J_{\rm SC}$ (mA cm ⁻²)	$V_{\rm OC}$ (V)	FF	PCE (%)
0.1:1.4	16.87	0.86	0.54	7.83
0.2:1.3	17.92	0.82	0.56	8.23
0.3:1.2	18.42	0.84	0.58	8.97
0.4:1.1	18.02	0.85	0.57	8.73
0.6:0.9	17.45	0.87	0.55	8.35

Table S6. Photovoltaic parameters of the ternary OSCs based on C2:BThIND-CI:Y6 ternary blend with different weight ratios of BThIND-CI:Y6 using chloroform as solvent.

Weight ratio	J _{SC} (mA cm ⁻²)	$V_{\rm OC}$ (V)	FF	PCE (%)
0.1:1.4	17.45	0.91	0.57	9.05
0.2:1.3	18.42	0.93	0.59	10.11
0.3:1.2	19.38	0.96	0.61	11.35
0.4:1.1	18.76	0.98	0.60	11.03
0.6:0.9	18.04	1.0	0.58	10.46

Weight ratio	$J_{\rm SC}$ (mA cm ⁻²)	$V_{\rm OC}$ (V)	FF	PCE (%)
10 s	18.96	0.83	0.61	9.60
20 s	19.42	0.81	0.65	10.22
30 s	19.76	0.79	0.69	10.77
40 s	20.09	0.79	0.71	11.27
50 s	19.74	0.77	0.68	10.34

Table S7. Photovoltaic parameters of the ternary OSCs based on SVA treated C1:BThIND-Cl:Y6 (1:0.3:1.2) ternary blend with different exposure time in THF environment.

Table S8. Photovoltaic parameters of the ternary OSCs based on SVA treated C2:BThIND-Cl:Y6 (1:0.3:1.2) ternary blend with different exposure time in THF environment.

Weight ratio	J _{SC} (mA cm ⁻²)	$V_{\rm OC}$ (V)	FF	PCE (%)
10 s	19.08	0.96	0.68	12.46
20 s	19.56	0.94	0.69	12.69
30 s	20.07	0.92	0.71	13.11
40 s	20.38	0.91	0.73	13.54
50 s	19.74	0.89	0.71	12.47

References

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