Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Highly efficient fullerene and non-fullerene based ternary organic solar cells incorporating a new tetrathiocin-cored semiconductor

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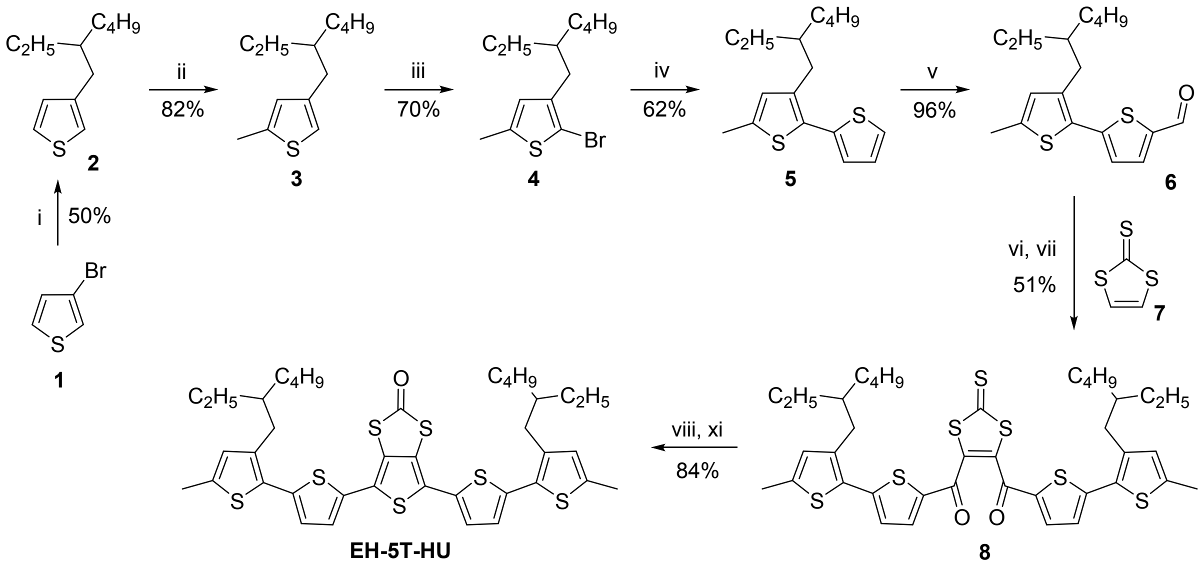
Synthetic procedures of all new compounds presented in the main manuscript

General

For all reactions carried out in anhydrous conditions, glassware was dried in an oven at 130°C. Reagents were purchased from commercial sources without further purification unless otherwise stated. Dry solvents were obtained from a solvent purification system (SPS 400 by Innovative Technologies) with an alumina drying agent. ^{1}H and ^{13}C NMR spectra were recorded on DRX 500 or AV3 400 at 500 and 125 MHz or 400 and 100 MHz, respectively. Chemical shifts are in ppm and *J* values are in Hz. Low resolution mass spectrometry (LRMS) was performed on a Shimadzu Axima-CFR spectrometer (MALDI). Elemental analyses were performed on a Perkin-Elmer 2400 analyser. Melting points were determined using a Stuart Scientific SMP1 Melting Point apparatus and are uncorrected.

Synthetic procedure for the synthesis of compound 1 in the main manuscript – EH-5T-HU

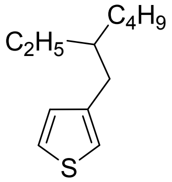
EH-5T-HU was prepared from 3-bromothiophene (**1**) by first appending the 2-ethylhexyl group *via* a Kumada coupling to give **2**. The 5-position of the thiophene ring was then capped with a methyl group utilising LiTMP to selectively lithiate the less hindered position, and trapping with methyl iodide to give **3**. After bromination with *N*-bromosuccinimide, **4** was coupled to tributyl(thiophen-2-yl)stannane giving the bithiophene system **5**, which was then formylated using DMF as a formyl cation equivalent. Vinylene trithiocarbonate (**7**) was then sequentially lithiated with LDA followed by addition of **6** to generate an intermediate diol that was quickly oxidised with MnO_2 to give **8**. The 1,3-dithiole-2-thione system was then transchalcogenated using $Hg(OAc)_2$ to give the carbonyl derivative, which underwent a Paal-Knorr thiophene synthesis with phosphorus pentasulfide to give **EH-5T-HU**.



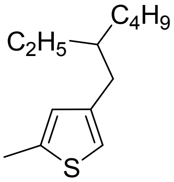
Scheme 1: Synthesis of **EH-5T-HU**. *Reagents and conditions*: i) $C_8H_{17}MgBr$, $Ni(dppp)Cl_2$, THF, reflux ii) LiTMP, THF, -80°C, then MeI iii) *N*-bromosuccinimide, $CHCl_3$/AcOH, r.t. iv) tributyl(thiophen-2-yl)stannane, $Pd(PPh_3)_4$, DMF, 150°C v) *n*-BuLi, THF, -80°C, then DMF vi) LDA, THF, -60°C vii) MnO_2, CH_2Cl_2 viii) $Hg(OAc)_2$, CH_2Cl_2/AcOH ix) P_2S_5 $NaHCO_3$, 1,4-dioxane.

Experimental

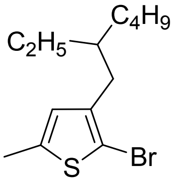
All reactions were performed under an inert atmosphere of nitrogen.



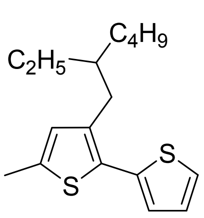
2-Ethylhexyl bromide (20.45 ml, 115 mmol) was added to magnesium turnings (2.91 g, 120 mmol) in anhydrous THF (15 ml), refluxed for 1 hr and then added drop-wise *via* cannula to a solution of 3-bromothiophene (8.91 ml, 92 mmol) and Ni(dppp)Cl_2 (0.25 g, 0.46 mmol) in anhydrous THF (50 ml). The reaction mixture was left to stir overnight, quenched with 2N HCl (30 ml) and extracted into diethyl ether (3 × 50 ml). The combined organic extracts were dried over anhydrous magnesium sulfate, concentrated under reduced pressure then purified *via* kugelrohr distillation (8 mbar, 115 - 120°C) followed by column chromatography (silica, hexane) to give 3-(2-ethylhexyl)thiophene (9.04 g, 50%) as a colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (1H, m, Th*H*), 6.91 (2H, m, Th*H*), 2.57 (2H, d, J = 7.0 Hz, ThCH_2), 1.56 (1H, m, C*H*), 1.28 (8H, m, CH_2), 0.89 (6H, m, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 129.0, 124.9, 120.8, 40.6, 34.5, 332.7, 29.1, 25.8, 23.2, 14.3, 11.0.



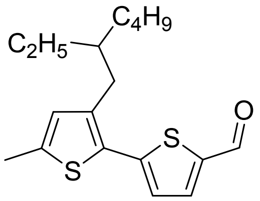
n-Butyllithium (28.2 ml, 2.35 M in hexanes, 67.8 mmol) was added drop-wise to a solution of tetramethylpiperidine (12.0 ml, 70.5 mmol) in anhydrous THF (50 ml) at -80°C and left to stir for 1 hr. The solution was then added slowly *via* cannula to a solution of 3-(2-ethylhexyl)thiophene (11.51 g, 58.9 mmol) in anhydrous THF (50 ml) at -80°C and left to stir for a further 1 hr. Iodomethane (7.34 ml, 117.8 mmol) was added and the solution left to stir overnight at room temperature, then quenched with water (50 ml) and extracted into diethyl ether (3 × 50 ml). The combined organic extracts were washed with water (30 ml), saturated $NaHCO_3$ solution (30 ml), water (30 ml), 2N HCl (30 ml) and brine (30 ml) then dried over anhydrous magnesium sulfate and concentrated under reduced pressure. The crude material was then run through a silica plug eluting with hexane and concentrated under reduced pressure to give 4-(2-ethylhexyl)-2-methylthiophene (10.8 g, 87%) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.67 (1H, m, Th*H*), 6.61 (1H, m, Th*H*), 2.51 (2H, d, *J* = 7.2 Hz, ThC*H₂*), 2.50 (3H, d, *J* = 0.8 Hz, ThC*H₃*), 1.57 (1H, m, C*H*), 1.33 (8H, m, C*H*$_2$), 0.93 (6H, m, C*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.9, 139.1, 127.3, 118.3, 40.4, 34.7, 32.7, 29.1, 25.7, 23.2, 15.5, 14.3, 11.0. LRMS (EI, *m/z*) calc. for $C_{13}H_{22}S$: 210 (M^+), found 211 $(M + H)^+$.



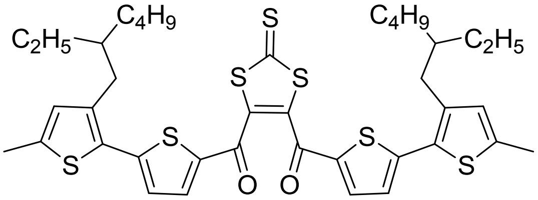
Under exclusion of light, N-bromosuccinimide (9.09 g, 51.1 mmol) was added to a solution of 5-methyl-3-(2-ethylhexyl)thiophene (10.74 g, 51.1 mmol) in chloroform (75 ml) and acetic acid (75 ml) and left to stir overnight. The resultant solution was then washed with water (3 × 50 ml) and neutralised with saturated $NaHCO_3$ solution before being dried over anhydrous magnesium sulfate and concentrated under reduced pressure. The crude product was then purified *via* kugelrohr distillation (6.67 mbar, 150 - 155°C) followed by a silica plug eluting with hexane to give 2-bromo-3-(2-ethylhexyl)-5-methylthiophene (10.1 g, 70%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.43 (1H, m, Th*H*), 2.41 (2H, d, *J* = 7.2 Hz, ThC*H₂*), 2.39 (3H, s, ThC*H*$_3$), 1.56 (1H, m, C*H*), 1.28 (8H, m, C*H*$_2$), 0.88 (6H, m, C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 139.2, 127.1, 105.9, 40.1, 33.9, 33.9, 32.6, 29.0, 25.8, 23.2, 14.3, 11.0. LRMS (EI, *m/z*) calc. for $C_{13}H_{21}SBr$: 289 (M^+), found 289 (M^+).



Tetrakis(triphenylphosphine)palladium (1.46 g, 0.50 mmol) was added to a degassed solution of 2-bromo-3-(2-ethylhexyl)-5-methylthiophene (7.30 g, 25.24 mmol) and 2-(tributylstannyl)thiophene (10.0 ml, 31.55 mmol) in anhydrous DMF (100 ml) and refluxed overnight. After cooling to room temperature, the solution was filtered through Celite washing through with diethyl ether. The filtrate was then treated with aqueous potassium fluoride solution (1 M, 130 ml), re-filtered through Celite, washed with saturated NH_4Cl solution (50 ml), dried over anhydrous magnesium sulfate and concentrated under reduced pressure. The crude product was then purified *via* column chromatography (silica, hexane) to give 3-(2-ethylhexyl)-5-methyl-2,2'-bithiophene (4.40 g, 62%) as a colourless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.25 (1H, m, Th*H*), 7.03 (2H, m, Th*H*), 6.56 (1H, m, Th*H*), 2.60 (2H, d, J = 7.6 Hz, ThC*H₂*), 2.44 (3H, d, J = 1.2 Hz, ThC*H₃*), 1.59 (1H, m, C*H*), 1.26 (8H, m, C*H*₂), 0.83 (6H, m, C*H*₃); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1, 138.0, 136.8, 128.9, 128.7, 127.3, 125.9, 125.0, 40.4, 33.5, 32.7, 28.8, 25.9, 23.2, 15.4, 14.3, 10.9. LRMS (EI, *m/z*) calc. for $C_{17}H_{24}S_2$: 293 (M^+), found 293 (M^+).

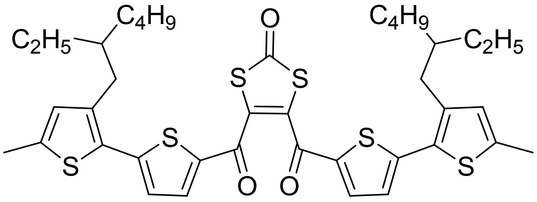


n-Butyllithium (7.50 ml, 2.35 M in hexanes, 17.6 mmol) was added drop-wise to a solution of 3-(2-ethylhexyl)-5-methyl-2,2'-bithiophene (4.63 g, 15.8 mmol) in anhydrous THF (60 ml) at -80°C. After stirring at -80°C for 2 hrs, anhydrous DMF (2.45 ml, 31.6mmol) was added, the resultant solution stirred at -80 °C for 1 hr, then left acquire room temperature and stir overnight. The reaction was then poured into water (200 ml), extracted into ethyl acetate (3 × 80 ml), washed with brine (50 ml), dried over anhydrous magnesium sulfate and concentrated under reduced pressure. The crude product was then purified *via* column chromatography (silica, 1:1 hexane:chloroform) to give 3'-(2-ethylhexyl)-5'-methyl-[2,2'-bithiophene]-5-carbaldehyde (4.89 g, 96%). as an orange oil. ^1H NMR (400 MHz, $CDCl_3$) δ 9.86 (1H, s, C*HO*), 7.67 (1H, d, J = 4.0 Hz, Th*H*), 7.10 (1H, d, J = 4.0 Hz, Th*H*), 6.61 (1H, m, Th*H*), 2.67 (2H, d, *J* = 7.2 Hz, ThC*H*$_2$), 2.46 (3H, d, *J* = 1.2 Hz, ThC*H*$_3$), 1.63 (1H, m, C*H*), 1.28 (8H, m, C*H*$_2$), 0.84 (6H, m, C*H*$_3$); ^{13}C NMR (100 MHz, CDCl$_3$) δ 182.8, 147.4, 141.9, 141.7, 140.5, 137.0, 129.8, 127.9, 126.0, 40.3, 34.0, 32.6, 28.8, 25.9, 23.2, 15.5, 14.3, 10.9; LRMS (MALDI, *m/z*) calc. for $C_{18}H_{24}OS_2$: 321 (M^+), found 320 $(M - H)^+$.

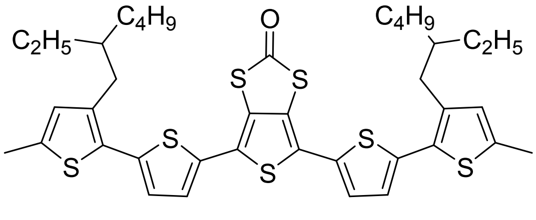


Lithium diisopropylamide solution (3.00 ml, 1.90 M in THF/heptanes/ethyl benzene, 5.60 mmol) was added drop-wise to a solution of 1,3-dithiole-2-thione (0.76 g, 5.60 mmol) in anhydrous THF (60 ml) at -60°C and left to stir for 20 min before a solution of 3'-(2-ethylhexyl)-5'-methyl-[2,2'-bithiophene]-5-carbaldehyde in anhydrous THF (40.0 ml, 0.14 mM, 5.60 mmol) was added and left to stir for a further 20 min at -60°C. A second equivalent of lithium diisopropylamide solution (3.00 ml, 1.90 M, 5.60 mmol) was added drop-wise, left to stir for 20 min then the solution was cooled to -80ºC whereupon a second equivalent of 3'-(2-ethylhexyl)-5'-methyl-[2,2'-bithiophene]-5-carbaldehyde solution (anhydrous THF) (40.0 ml 0.14 mM, 5.60 mmol) was added. After stirring for a further 20 min at -60°C, the solution was allowed to warm to room temperature, before being poured into saturated $NaHCO_3$ solution (280 ml) to which potassium bromide (28 g) was added. The mixture was extracted into ethyl acetate (3 × 200 ml) and the combined organic extracts dried over anhydrous magnesium sulfate and concentrated under reduced pressure to give a dark oil. The crude material (6.00 g) was immediately dissolved in dichloromethane (120 ml) to which manganese (IV) oxide (10 fold w/w excess, 60 g) was added, stirred at room temperature for 1 min and then run through a silica plug eluting with dichloromethane. All product containing washings were combined, concentrated under reduced pressure and then purified *via* column chromatography (silica, 5:2 hexane:CH_2Cl_2) to give (2-thioxo-1,3-dithiole-4,5-diyl)bis((3'-(2-ethylhexyl)-5'-methyl-[2,2'-bithiophen]-5-yl)methanone) (2.99 g, 51%) as a viscous deep red oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.61 (2H, d, *J* = 4.0 Hz, Th*H*), 7.03 (2H, d, *J*

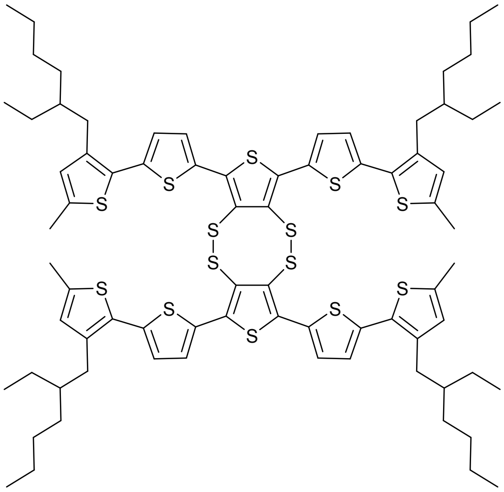
= 4.0 Hz, ThH), 6.58 (2H, m, ThH), 2.58 (4H, d, J = 7.2 Hz, ThCH_2), 2.43 (6H, d, J = 0.8 Hz, ThCH_3), 1.57 (2H, m, CH), 1.23 (16H, m, CH_2), 0.82 (12H, m, CH_3); ^{13}C NMR (100 MHz, CDCl$_3$) δ 208.0, 175.3, 150.0, 144.4, 142.4, 141.3, 139.9, 136.2, 130.0, 127.8, 126.0, 40.2, 34.2, 32.7, 28.8, 25.9, 23.1, 15.5. 14.1, 10.8. LRMS (MALDI, *m/z*) calc. for $C_{39}H_{46}O_2S_7$: 771 (M^+), found 772 $(M + H)^+$.



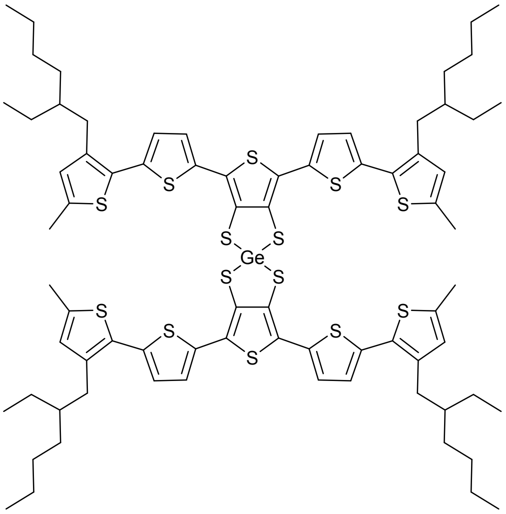
Mercury (II) acetate (1.73 g, 5.40 mmol) was added to a solution of (2-thioxo-1,3-dithiole-4,5-diyl)bis((3'-(2-ethylhexyl)-5'-methyl-[2,2'-bithiophen]-5-yl)methanone) (2.99 g, 3.90 mmol) in dichloromethane (120 ml) and acetic acid (40 ml) and left to stir for 24 hrs at room temperature. The resultant suspension was run through a silica plug eluting with dichloromethane, washed with water (3 × 200 ml), neutralised with saturated NaHCO$_3$ solution (200 ml), dried over anhydrous magnesium sulfate and concentrated under reduce pressure to give (2-oxo-1,3-dithiole-4,5-diyl)bis((3'-(2-ethylhexyl)-5'-methyl-[2,2'-bithiophen]-5-yl)methanone) (2.84 g, 97%) as a viscous deep red oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.58 (2H, d, J = 4.0 Hz, ThH), 7.02 (2H, d, J = 4.4 Hz, ThH), 6.57 (2H, m, ThH), 2.57 (4H, d, J = 7.2 Hz, ThCH_2), 2.43 (6H, d, J = 0.4 Hz, ThCH_3), 1.57 (2H, m, CH), 1.23 (16H, m, CH_2), 0.82 (12H, m, CH_3); ^{13}C NMR (100 MHz, CDCl$_3$) δ 187.4, 466.5, 149.6, 142.2, 141.1, 140.2, 136.0, 135.5, 129.9, 127.8, 125.9, 40.2, 34.2, 32.7, 28.8, 25.8, 23.1, 15.5, 14.1, 10.8. LRMS (MALDI, *m/z*) calc. for $C_{39}H_{46}O_3S_6$: 755 (M^+), found 754 $(M - H)^+$.



A mixture of (2-oxo-1,3-dithiole-4,5-diyl)bis((3'-(2-ethylhexyl)-5'-methyl-[2,2'-bithiophen]-5-yl)methanone) (2.84 g, 3.80 mmol), sodium hydrogen carbonate (1.58 g, 18.8 mmol) and phosphorus pentasulfide (8.36 g, 18.8 mmol) in anhydrous 1,4-dioxane (100 ml) was heated to 60°C then the temperature was gradually increased to 90°C over the course of 30 min. The reaction was then left to stir for 3 hrs at 90°C before cooling to room temperature. Water (100 ml) was slowly added and the resulting suspension refluxed for 1 hr then left to stir at room temperature overnight before being filtered and washed with water (300 ml) and cold methanol (200 ml). The crude solid was collected, dissolved in the minimum amount of hot ethanol and allowed to cool overnight. The resultant precipitate was filtered, washed with cold methanol and dried overnight in a desiccator to give 4,6-bis(3'-(2-ethylhexyl)-5'-methyl-[2,2'-bithiophen]-5-yl)thieno[3,4-d][1,3]dithiol-2-one (2.40 g, 87%) as an orange/red solid (mp 99 – 101°C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (2H, d, $J = 4.0$ Hz, Th*H*), 7.00 (2H, d, $J = 3.6$ Hz, Th*H*), 6.56 (2H, s, Th*H*), 2.62 (4H, d, $J = 7.2$ Hz, ThCH_2), 2.44 (6H, s, ThCH_3), 1.61 (2H, m, C*H*), 1.28 (16H, m, CH_2), 0.84 (12H, m, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.9, 139.0, 138.1, 133.6, 129.5, 127.9, 126.5, 125.7, 125.5, 124.2, 40.5, 33.8, 32.8, 29.0, 25.9, 23.3, 15.6, 14.4, 11.0; LRMS (MALDI, *m/z*) calc. for $C_{39}H_{46}O_2S_7$: 755 (M^+), found 754 $(M - H)^+$.



Freshly prepared sodium methoxide solution (0.744 M in anhydrous methanol, 0.61 ml, 0.453 mmol) was added drop-wise to a solution of 4,6-bis(3'-(2-ethylhexyl)-5'-methyl-[2,2'-bithiophen]-5-yl)thieno[3,4-d][1,3]dithiol-2-one (0.114 g, 0.151 mmol) in anhydrous THF (20 ml) at room temperature under nitrogen. After refluxing for 15 mins, the dark solution was cooled to room temperature before iodine solution (0.0965 M in anhydrous THF, 1.88 ml, 0.181 mmol) was added drop-wise to give a red/orange solution. After stirring at room temperature for 1 hr, the reaction was quenched with aqueous sodium thiosulfate solution (10 ml), poured into water (100 ml) and extracted into CH_2Cl_2 (3 × 50 ml). The combined organic extracts were washed with water, dried over anhydrous magnesium sulfate and concentrated under reduced pressure. The resulting crude red solid was dissolved in CH_2Cl_2 and run through a short silica plug eluting with CH_2Cl_2. All coloured material was collected and combined then concentrated to approximately 5 ml and precipitated with methanol (100 ml) to give an orange precipitate, which was collected *via* filtration and dried under vacuum to give **EH-5T-TTC** (0.070 g, 64 %) as a red solid (mp 142 - 144°C). ^1H NMR (600 MHz, $CDCl_3$) δ 7.41 (4H, d, J = 3.8 Hz, ThH), 7.03 (4H, d, J = 3.8 Hz, ThH), 6.59 (4H, s, ThH), 2.69 (8H, dd, J = 7.1, 1.9 Hz, CH_2), 2.47 (12H, s, ThCH_3), 1.64 (4H, m, CH), 1.34 – 1.23 (32H, br m, CH_2), 0.83 (24H, m, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.0, 139.9, 139.8, 138.7, 133.6, 132.5, 129.4, 128.4, 128.2, 125.6, 40.4, 33.9, 32.7, 28.8, 25.9, 23.2, 15.5, 14.3, 10.9; LRMS (MALDI, *m/z*) calc. for $C_{76}H_{92}S_{14}$ (M^+): 1452.33, found 1453.06; Elemental analysis, calc: C 62.79, H 6.38, found: C 62.80, H 6.14. T_d 318 °C.



Sodium methoxide solution (0.876 M in anhydrous methanol, 1.37 ml, 1.20 mmol) was added dropwise to a solution of 4,6-bis(3'-(2-ethylhexyl)-5'-methyl-[2,2'-bithiophen]-5-yl)thieno[3,4-d][1,3]dithiol-2-one (0.302 g, 0.400 mmol) in anhydrous THF (50 ml) at room temperature. After refluxing for 15 mins, the dark solution was cooled to room temperature and freshly prepared (under an inert atmosphere) germanium (IV) bromide solution (0.167 M in anhydrous THF, 1.32 ml, 0.220 mmol) added dropwise. The resultant orange solution was stirred for 45 mins at room temperature, then quenched with 2N HCl

(3 ml), poured into water (100 ml) and extracted into CH_2Cl_2 (3 × 75 ml). The combined organic extracts were washed with water (2 × 100 ml) dried over anhydrous magnesium sulfate and concentrated under reduced pressure to give an orange/red oil. The crude product was dissolved in CH_2Cl_2 and run through a short silica plug before concentrating to dryness. The residue was then dissolved in hot hexane (150 ml), filtered whilst hot and left to cool in the freezer overnight. The resultant precipitate was collected, washed with cold hexane (2 × 50 ml) and dried under high vacuum in a dessicator to give **EH-5T-Ge** (0.203 g, 66%) as an orange solid (mp 83 - 85 °C). ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 (4H, d, $J = 3.9$ Hz, Ar*H*), 7.00 (4H, d, $J = 3.9$ Hz, Ar*H*), 6.57 (4H, s, Ar*H*), 2.65 (8H, m, CH_2), 2.44 (12H, s, $ArCH_3$), 1.63 (4H, m, CH_2), 1.30 (32H, m, CH_2), 0.86 (24H, m, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6, 138.6, 137.5, 134.6, 129.3, 128.8, 128.3, 126.5, 126.1, 125.9, 40.5, 33.8, 32.8, 28.9, 25.8, 23.3, 15.3, 14.3, 10.9; LRMS (MALDI, *m/z*) calc. for $C_{76}H_{92}GeS_{14}$: 1526.25, found 1526.79 (M^+); Elemental analysis, calc: C 59.78, H 6.07, found: C 59.94, H 5.87. T_d 383 °C.

Single crystal X-ray diffraction

A suitable crystal for **EH-5T-TTC** was selected and data collected following a standard method[i], on a Rigaku AFC12 goniometer at 100K equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E-Superbright molybdenum anode generator with VHF Varimax optics (70μm focus).

Cell determination and data collection were carried out using CrystalClear[ii], with data reduction, cell refinement and absorption correction carried out using CrysAlisPro[iii]. Within Olex2[iv], the structures were solved using SHELXT[v] and refinement using SHELXL[vi].

Crystal data for **EH-5T-TTC** : $C_{76}H_{92}S_{14}$, $M_r = 1454.33$, red plate, monoclinic, $P2_1/c$, a = 16.8658(8) Å, b = 24.1932(7) Å, c = 9.1640(5) Å, $\beta = 100.116(5)^\circ$, $\alpha = \gamma = 90^\circ$, $V = 3681.1(3)$ Å^3, $T = 100(2)$ K, $Z = 2$, $Z' = 0.5$, $\mu(\mathrm{MoK}_\alpha) = 0.455$ mm^{-1}, 52641 reflections measured, 8374 unique ($R_{int} = 0.0725$). $R1 = 0.0688$, $wR2 = 0.1716$ [$F^2 > 2\sigma(F^2)$], $R1 = 0.1299$, $wR2 = 0.2043$ (all data).

Supplementary Figures

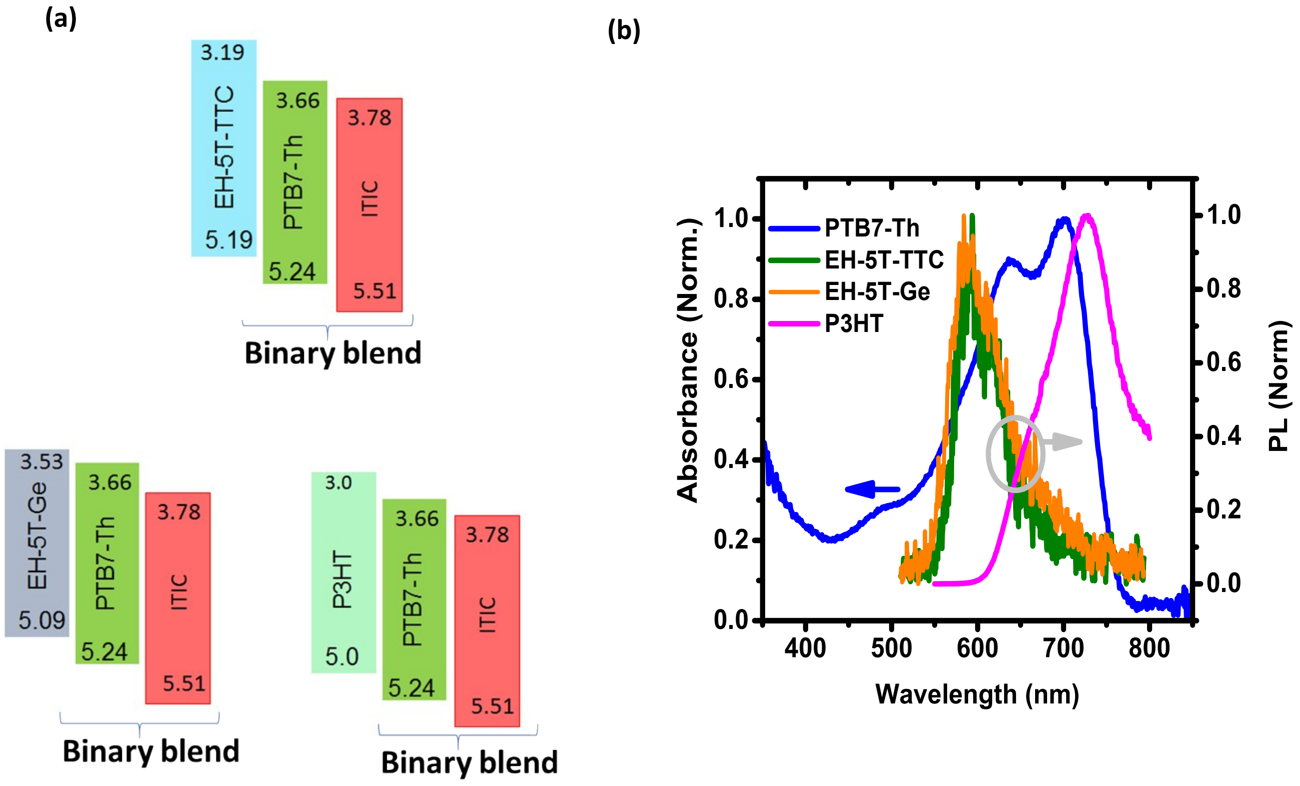


Figure S1. (a) Energy level diagram of the binary blend components and the ternary components. (b) The spectral overlap between the UV-Vis absorption spectra of **PTB7-Th** and the photoluminescence spectra of the ternary donor components.

(a)

(b)

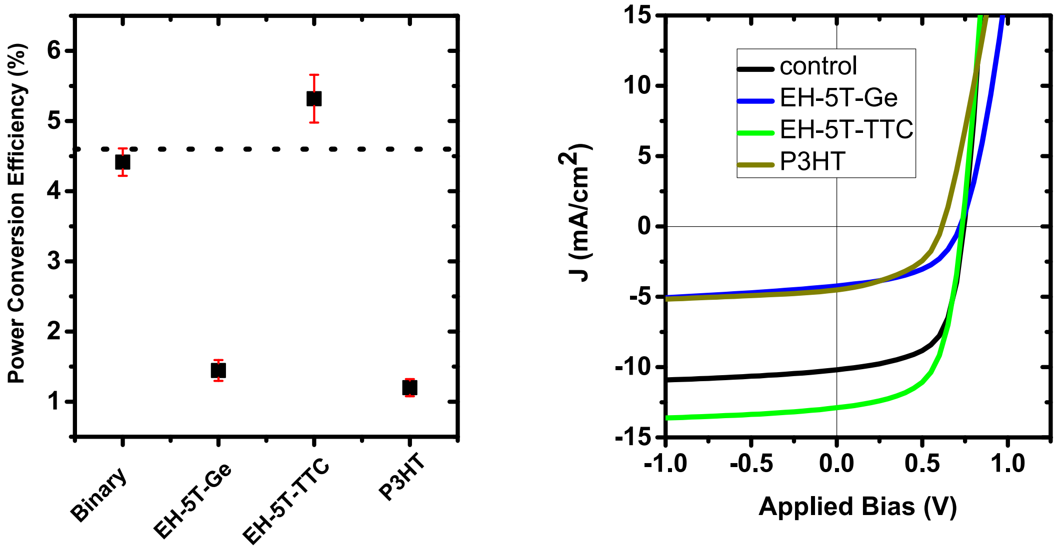


Figure S2. (a) Comparison of PCE and (b) J-V characteristics of the of binary **PTB7-Th:ITIC** and ternary blend systems.

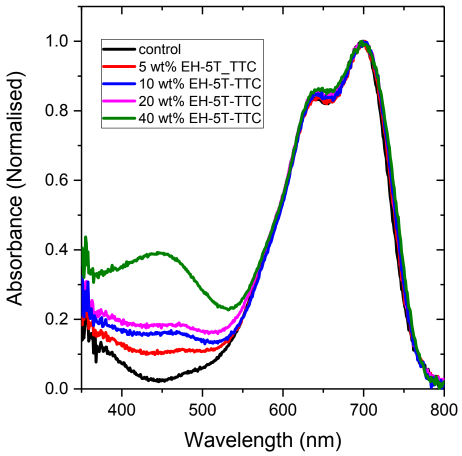


Figure S3. UV-Vis absorption spectra of the **PTB7-Th:ITIC** as a function of different **EH-5T-TTC** content.

Table S1. Photovoltaic performance parameters of the binary **PTB7-Th:EH-IDTBR** and **PTB7-Th:EH-IDTBR:EH-5T-TTC** blend systems. J_{sc} estimated from EQE spectra is also shown.

EH-5T-TTC (wt%)	**Jsc/(EQE) (mA/cm^2)**	**Voc (V)**	**FF (%)**	**Rsh (Ωcm^2)**	**Rs (Ωcm^2)**	**PCE (%) avg**	**PCE best (%)**
0	12.81±0.27 (13.5±0.4)	1.02±0.01	56.7±0.5	594±68	1.66±0.35	7.46±0.17	7.82
10	15.35±0.39 (15.5±0.5)	0.965±0.005	59.7±0.77	736±172	1.35±0.20	8.84±0.27	9.19

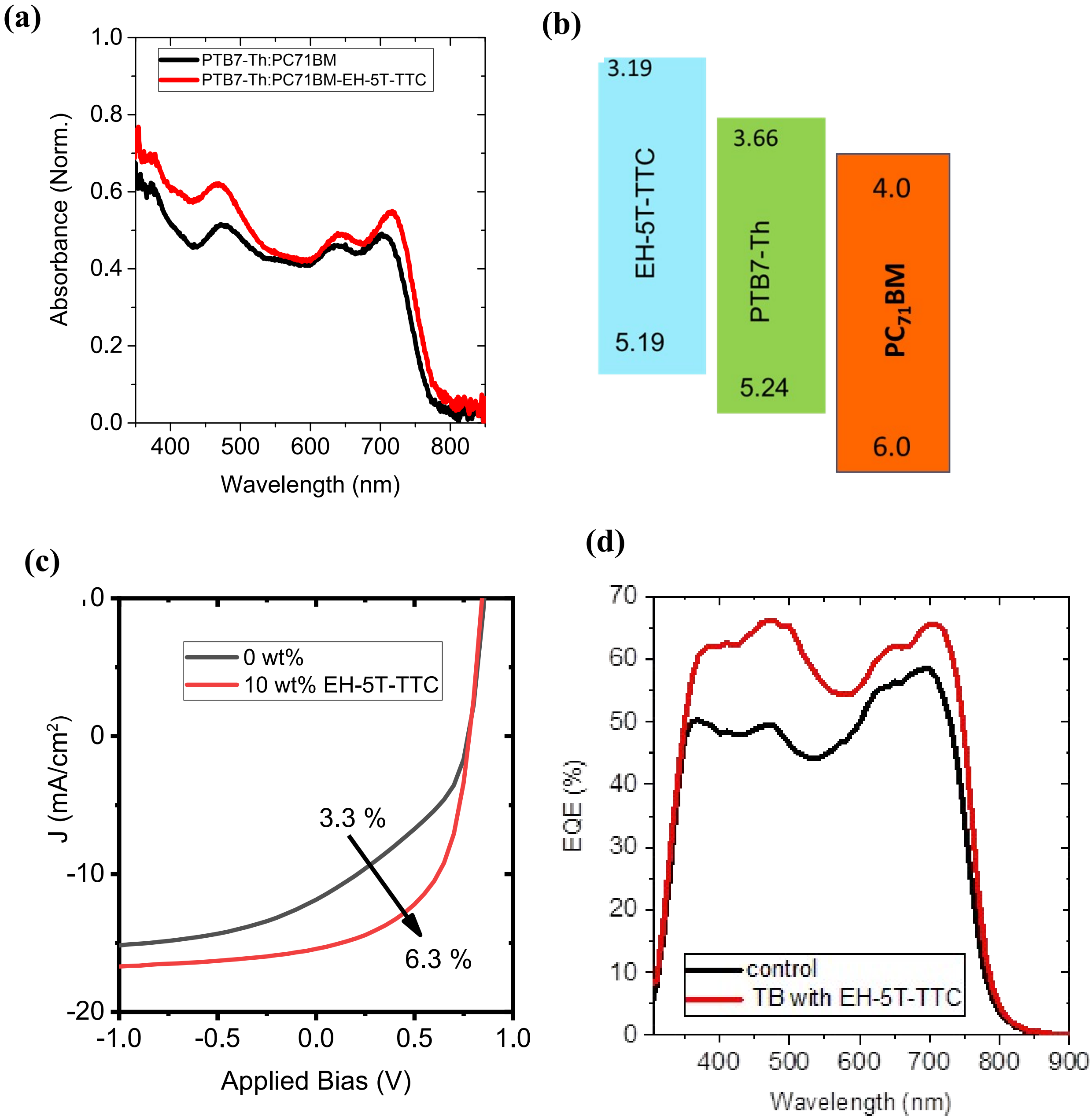
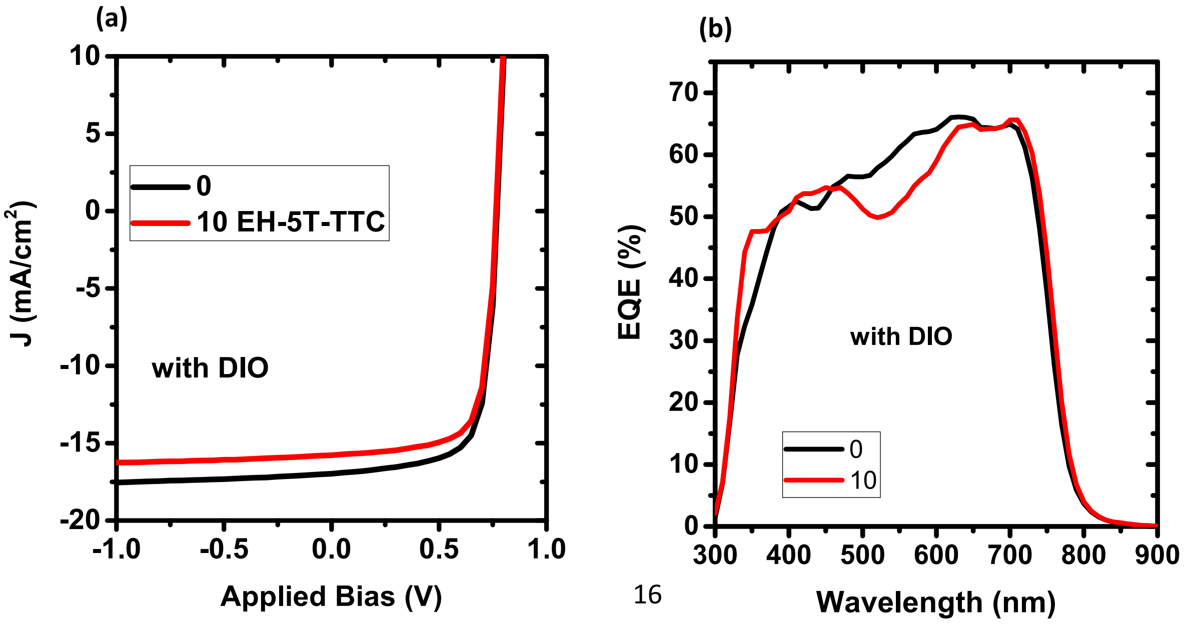


Figure S4. (a) Absorption spectra of the binary **PTB7-Th:PC$_{71}$BM** and ternary **PTB7-Th:PC$_{71}$BM:EH-5T-TTC**; (b) energy level diagram of the three components in the blend system: (c) *J-V* characteristics of the best ternary OPV devices; (d) the EQE spectra of the binary and ternary blend systems compared.

Table S2. Photovoltaic performance parameters of the binary **PTB7-Th:PC$_{71}$BM** and **PTB7-Th:PC$_{71}$BM:EH-5T-TTC** blend systems. J$_{sc}$ estimated from EQE spectra is also shown.

DIO	EH-5T-TTC (wt%)	J$_{sc}$/(EQE) (mA/cm^2)	V$_{oc}$ (V)	FF (%)	Rsh (Ωcm^2)	Rs (Ωcm^2)	PCE (%) avg	PCE best (%)
No	0	11.4±0.3 (12.3±0.3)	0.770±0.009	36.5±0.4	137±4.5	2.4±0.5	3.2±0.1	3.36
No	10	15.0±0.2 (14.9±0.4)	0.778±0.004	52.0±0.6	370±33	2.0±0.2	6.09±0.24	6.31
Yes	0	16.3±0.95 (16.8±0.5)	0.772±0.003	71.9±0.6	1200±468	1.11 0.22	9.02±0.45	9.42
Yes	10	15.2±0.7 (16.4±0.5)	0.769±0.004	72.7±0.5	1480±553	1.12±0.26	8.50±0.35	8.82

Figure S5. (a) *J-V* characteristics and the corresponding (b) EQE spectra of the **PTB7-Th:PC$_{71}$BM** and **PTB7-Th:PC$_{71}$BM:EH-5T-TTC** in the presence of DIO additive.



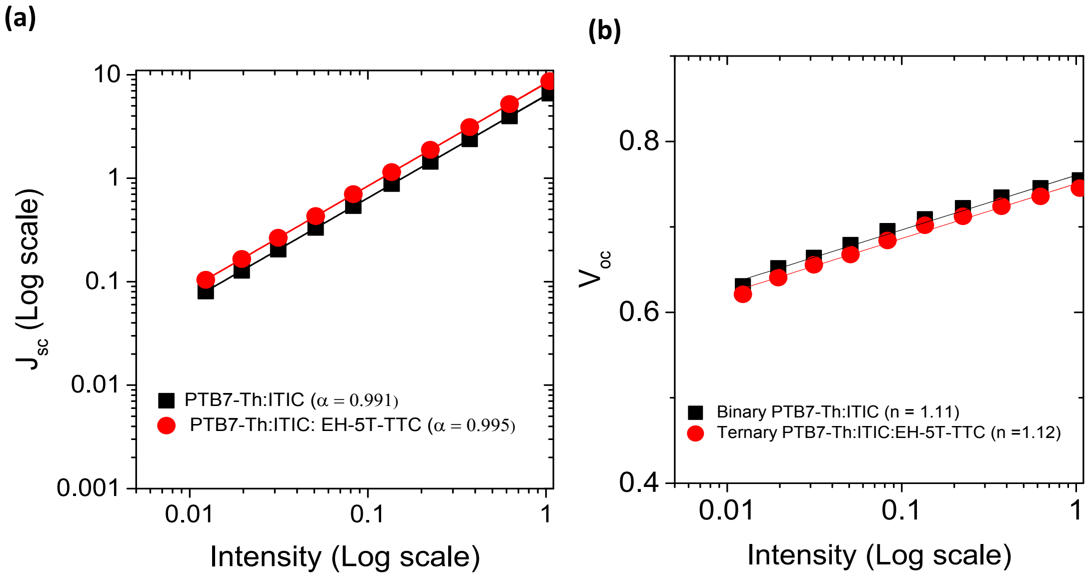


Figure S6. Variation of (a) *Jsc* and (b) *Voc* as a function of light intensity for binary **PTB7-Th: ITIC** blend and **EH-5T-TTC: PTB7-Th: ITIC** ternary blend**.**

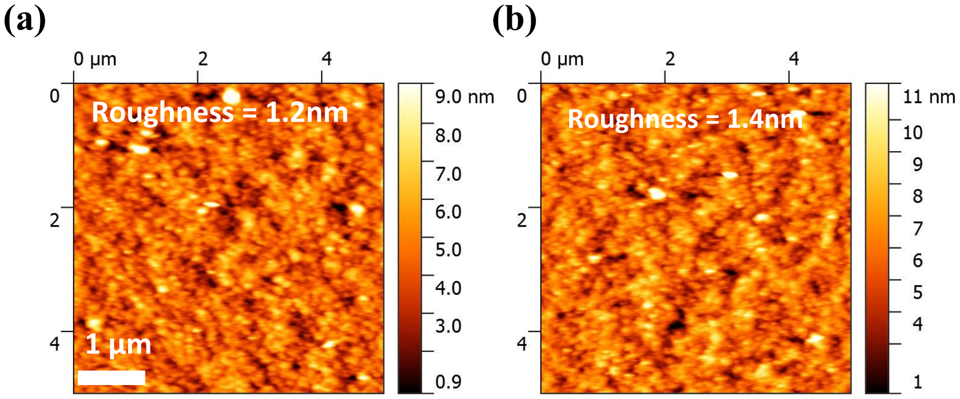


Figure S7. Atomic force microscopy images of the (a) **PTB7-Th:ITIC** and (b) **PTB7-Th:ITIC:EH-5T-TTC** blend films

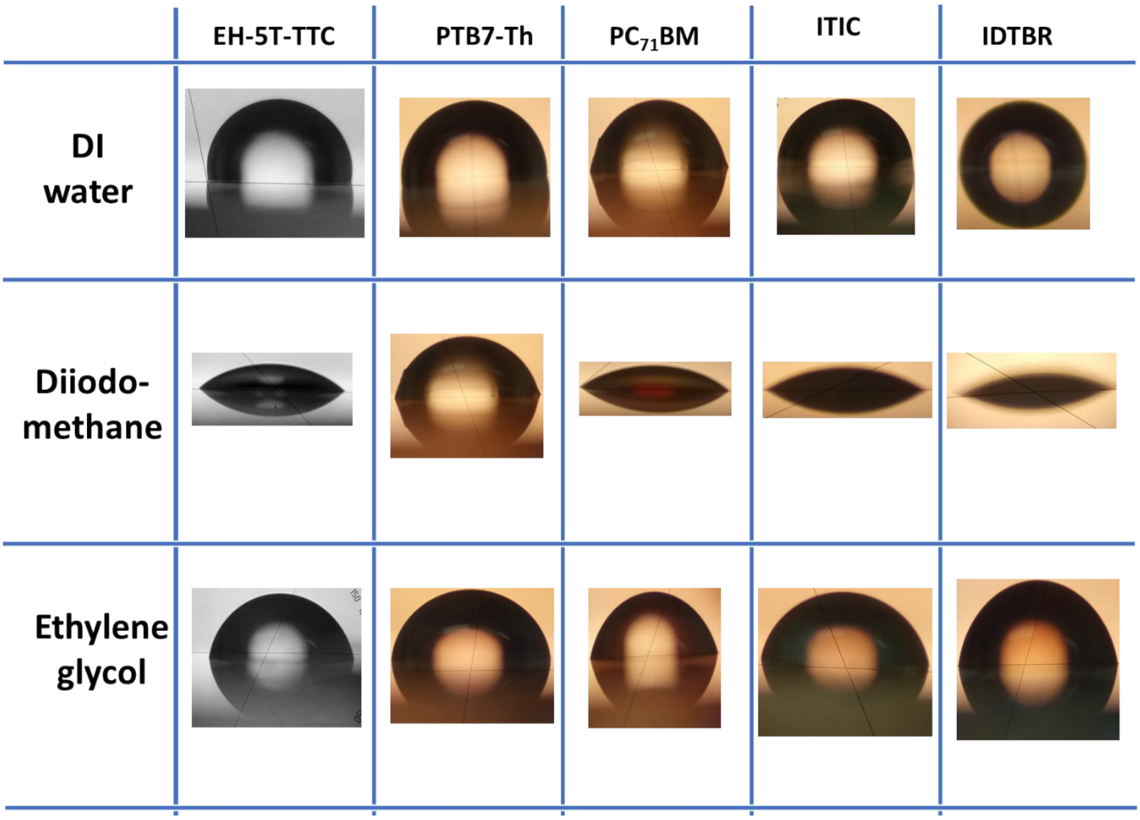


Figure S8. Contact angle measurement of the each of the donor and acceptor components for three different solvents. These contact angle measurements have been used for the surface energy calculations.

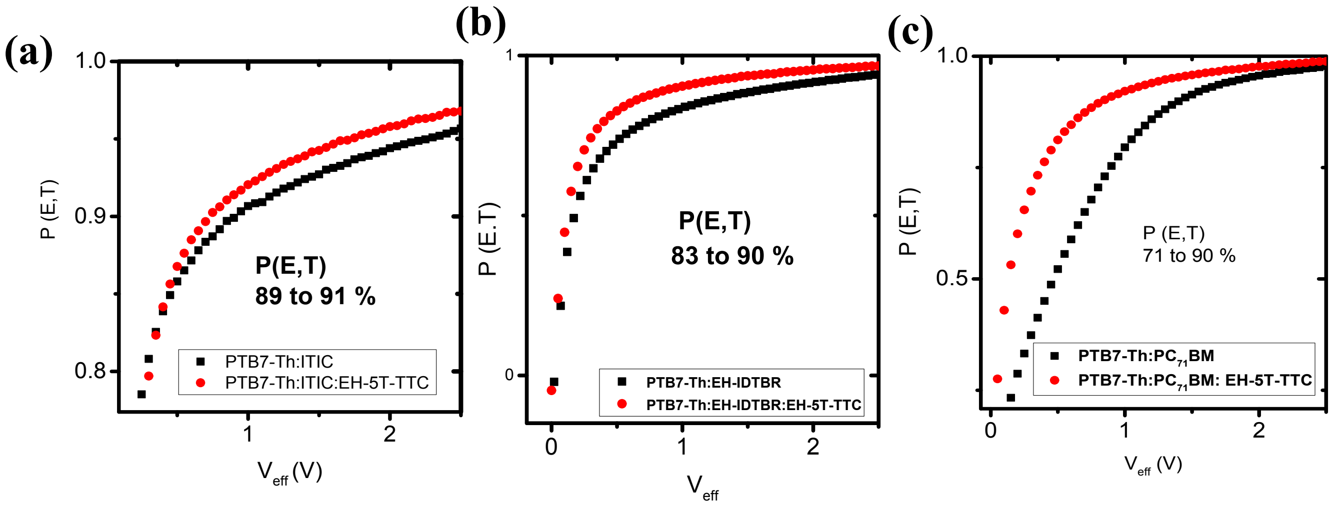


Figure S9. Comparison of the exciton dissociation probability of binary and ternary blends of (a) **PTB7:ITIC** (b) **PTB7-Th:EH-IDTBR** and **(c)**, **PTB7-Th:PC$_{71}$BM with** EH-5T-TTC

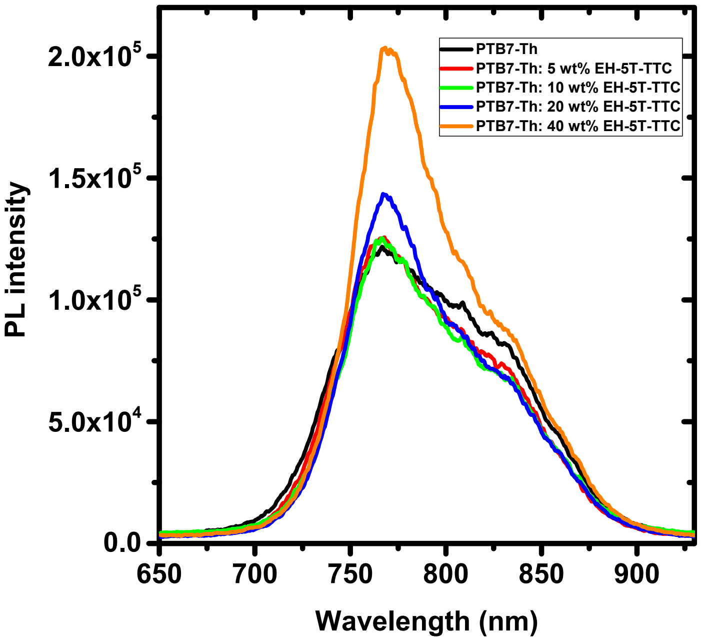


Figure 10. Photoluminescence spectra of **PTB7-Th** and blends of **PTB7-Th:EH-5T-TTC**.

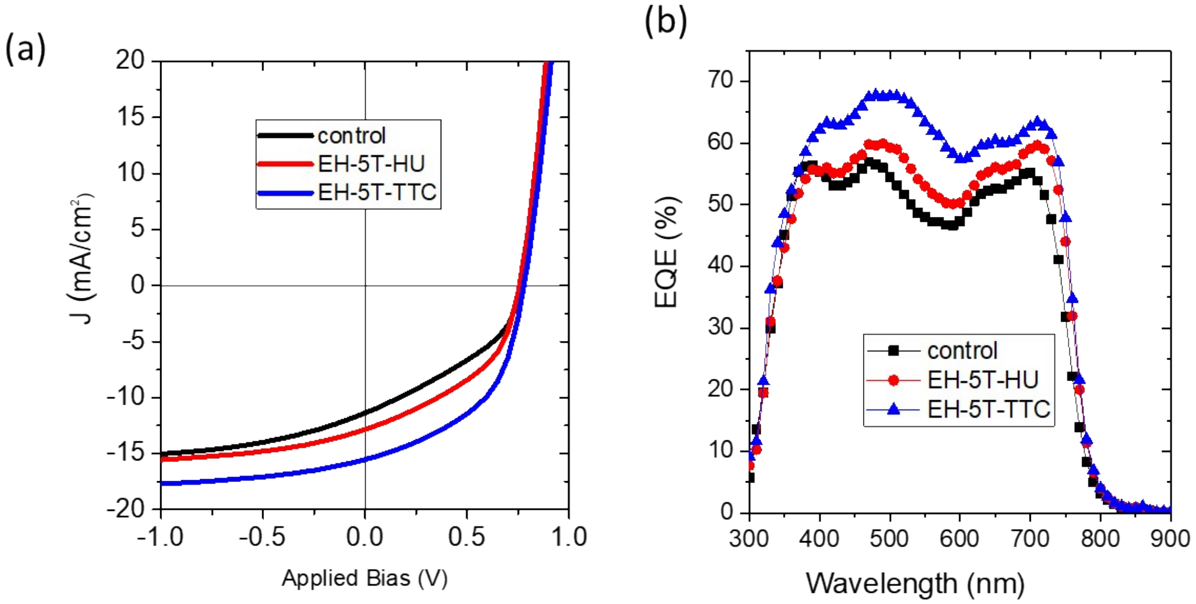


Figure S11: Photovoltaic performance parameters of the binary **PTB7-Th:PC$_{71}$BM** and ternary blend systems using **EH-5T-HU** and **EH-5T-TTC**.

Table S3. Photovoltaic performance parameters of the binary **PTB7-Th:PC$_{71}$BM** and ternary blend systems using **EH-5T-HU** and **EH-5T-TTC**. The average values of the device characteristics are given throughout, alongside their standard deviation, and the highest recorded PCE values are recorded in the final column. J$_{sc}$ estimated from EQE spectra is also shown

Blend	**Jsc (mA/cm^2)**	**Voc (V)**	**FF (%)**	**Rs (Ohmcm^2)**	**Rsh (Ohmcm^2)**	**PCE (%)**	**PCE (%)**
PTB7-Th: PC$_{71}$BM	10.6 ±0.48 (12.5±0.3)	0.770 ±0.005	37.9 ±0.34	2.64 ±0.51	136 ±4	3.1±0.14	3.33
PTB7-Th:PC$_{71}$BM:EH-5T-HU	12.2 ±0.4 (13.6±0.4)	0.756 ±0.013	43.5 ±0.71	2.41 ±0.61	183 ±13	4.02±0.20	4.26
PTB7-Th:PC$_{71}$BM:EH-5T-TTC	14.7 ±0.5 (15.2±0.5)	0.771 ±0.007	49.1 ±0.6	2.18 ±0.49	232.4 ±20.9	5.60±0.20	5.89

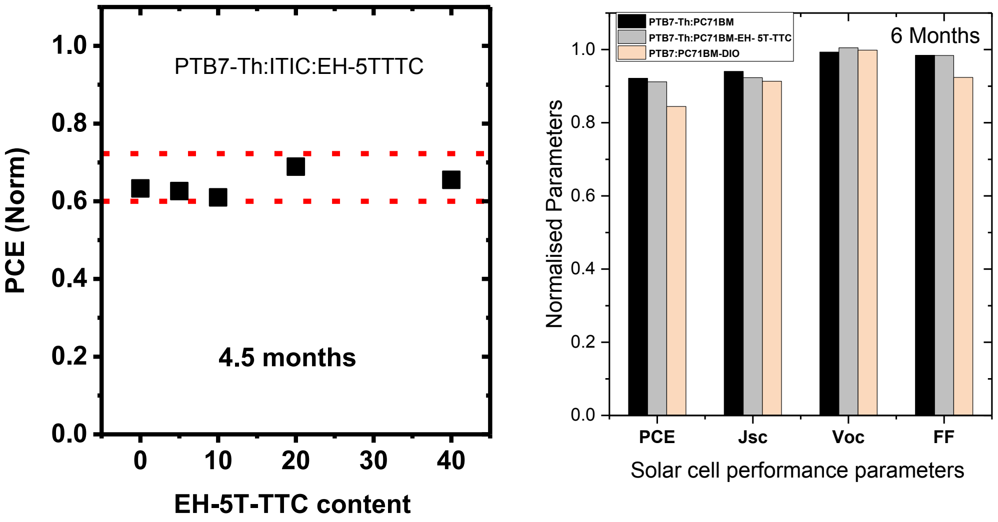


Figure S12. Shelf life of encapsulated ternary and binary solar cells under ambient conditions

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[ii] *CrystalClear-SM Expert 3.1 b 27*, Rigaku Corporation, The Woodlands, Texas, U.S.A., (2008-2014).

[iii] *CrysAlisPro Version 1.171.39.9g* Rigaku Oxford Diffraction, Yarnton, Oxford, UK (2015)

[iv] O.V. Dolomanov and L.J. Bourhis and R.J. Gildea and J.A.K. Howard and H. Puschmann, *J. Appl. Cryst.*, **2009**, *42*, 339-341.

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[vi] Sheldrick, G.M., *Acta Cryst*, **2015**, *C71*, 3-8