

Effect of systematically tuning conjugated donor polymer LUMO levels via cyano substitution on OPV device performance

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Experimental

General: All solvents and chemicals, were purchased from Sigma-Aldrich and used without further purification. The polymers P(Ge-DTDCNBT)¹ and P(Ge-DTBT)² were prepared as reported. 5-Fluoro-4,7-dibromobenzo[c][1,2,5]thiadiazole³ and the donor monomer DTG² were also synthesised using literature procedures. Microwave reactions were performed in a Biotage initiator V 2.3 in constant temperature mode. **Nuclear magnetic resonance** (NMR) spectra were recorded on Bruker AV-400 (400 MHz) spectrometers in chloroform-*d* or TCE-*d*₂ solutions. Number-average (M_n) and weight-average (M_w) molecular weights were determined with an Agilent Technologies 1200 series **GPC** detected using the refractive index signal in chlorobenzene at 80°C using two PL mixed B columns in series, and calibrated against narrow polydispersity polystyrene standards. **UV-Visible absorption spectra** were measured using a Shimadzu UV-1800 UV-Vis Spectrophotometer. 16.6 mg/dm³ polymer solutions in chlorobenzene were used for solution spectra whilst 5 mg/ml polymer solutions in chlorobenzene were used to spin coat thin films. Solutions and films were not de-oxygenated for these measurements. **Ionisation potentials** were measured by Photo-electron Spectroscopy in Air (PESA) on a Riken Keiki AC-2 PESA spectrometer. Polymer thin films were prepared by spin-coating from 5 mg/ml polymer solutions in chlorobenzene onto glass substrates. The PESA samples were run with a light intensity of 5 nW and data processed with a power number of 0.5. **Density functional theory** using a B3LYP functional and basis set of 6-311G(d)⁴ was used to calculate the ground state geometries and electron density plots of monomers and trimer molecules. TD-DFT was used to calculate excited state (LUMO) energies. All calculations were carried out using

Gaussview 5.0.⁵ **Cyclic voltammograms** were recorded using a Metrohm Autolab PGStat101 Potentiostat/Galvanostat. The experimental set-up consisted of an Ag/Ag⁺ reference electrode, a platinum wire counter electrode and an FTO working electrode, all measurements were carried out under argon at room temperature (~25°C). Measurements of the polymers were done on spun-cast films in anhydrous, degassed solutions of acetonitrile with tetrabutylammonium hexafluorophosphate (0.1M) electrolyte. Thin films were spin coated onto FTO on glass substrate from a 5 mg/ml solution. A ferrocene internal standard was used to calibrate the results.

OFET device fabrication

Fabrication methods for OFET devices made from P(Ge-DTDCNBT) are reported in the literature.¹ Transistor characterization was carried out under nitrogen using a Keithley 4200 parameter analyzer. All films were prepared and characterized under inert atmosphere. Top gate/bottom contact devices were fabricated on glass substrates using Au (30 nm) source-drain electrodes and CYTOP dielectric. Devices made with P(Ge-DTBT) and P(Ge-DTCNBT) used Au electrodes treated with pentafluorobenzene thiol (PFBT) SAM to increase the work function, whilst devices made with P(Ge-DTDCNBT) used untreated gold electrodes. The channel width and length of the transistors are 1000 μm and 40 μm , respectively. All polymers were dissolved in chlorobenzene (5 mg/ ml) and spun cast at 2000 rpm from a hot solution for 60 s before being annealed at 160°C for 30 min. Mobility was extracted from the slope of $I_D^{1/2}$ vs. V_G .

OPV device fabrication

Fabrication methods for OPV devices made from P(Ge-DTBT) are reported in the literature.² ITO-coated glass substrates were washed by ultrasonication in acetone and isopropyl alcohol then dried before undergoing an oxygen plasma treatment. A thin layer of poly(3,4-ethylene-dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) was spin-coated onto the substrate and dried at 150°C for 30 minutes. The active layer, consisting of polymer (12 mg/ml of either P(Ge-DTCNBT) or P(Ge-DTDCNBT)) and PC₇₁BM (24 mg/mL) blend weight ratio 1:2 in *o*-DCB, was deposited by

spin-coating onto the PEDOT:PSS layer. Active layer thicknesses ranged from 110 nm to 155 nm. Solutions were heated to 90°C overnight to ensure dissolution. A Ca (30 nm)/Al (100 nm) cathode layer was then deposited by thermal evaporation under vacuum through a shadow mask to complete the BHJ cell. Current-voltage (J-V) characteristics were measured under AM1.5 solar illumination using a xenon lamp. Four devices were measured for each polymer and the average efficiency calculated.

Synthesis

5-fluoro-4,7-di(thiophen-2-yl)-2,1,3-benzothiadiazole. Literature compound.⁶

5-Fluoro-4,7-dibromobenzo[c][1,2,5]thiadiazole (0.857 g, 2.75 mmol), Pd(PPh₃)₄ (138 mg, 0.119 mmol), and a stirrer bar were added to a 20 mL high pressure microwave reactor vial. The vial was then sealed with a septum and flushed with argon before 2-thienylzinc bromide solution in THF (12.1 mL of a 0.5 M solution, 6.05 mmol) was added. The whole solution was then degassed again for 20 min before the reaction was heated to 100°C for 30 min in the microwave. After cooling, the reaction mixture was diluted with THF and passed through a silica plug (10×5×5 cm), with further washing with THF. After removal of the solvent under reduced pressure, the residue was recrystallized from acetone to afford the product as an orange solid (788 mg, 2.48 mmol). Yield 90%; ¹H NMR (400 MHz, CDCl₃) δ 8.25 (d, *J* = 3.7 Hz, 1H), 8.11 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.74 (d, *J* = 12.8 Hz, 1H), 7.56 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.50 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.26 – 7.22 (m, 1H), 7.21 (dd, *J* = 5.1, 3.7 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 158.98 (d, *J* = 254.0 Hz), 153.56 (d, *J* = 10.9 Hz), 149.86 (s), 138.07 (s), 132.60 (d, *J* = 5.4 Hz), 130.23 (d, *J* = 8.1 Hz), 128.51 (s), 128.25 (s), 128.07 (s), 128.02 (s), 127.36 (s), 126.01 (d, *J* = 11.3 Hz), 117.08 (d, *J* = 32.5 Hz), 111.32 (d, *J* = 15.3 Hz); ¹⁹F NMR (377 MHz, CDCl₃) δ -108.35 (d, *J* = 12.8 Hz); MS (EI): *m/z* = 318 [M⁺].

4,7-Bis(5-bromothiophen-2-yl)-5-fluoro-2,1,3-benzothiadiazole. Literature compound.⁶

To a solution of 5-fluoro-4,7-di-(thiophen-2-yl)-2,1,3-benzothiadiazole (207 mg, 0.65 mmol) in chloroform (60 mL) and acetic acid (10 mL) was added N-bromosuccinimide (NBS) (0.242mg, 1.37

mmol) and the reaction stirred in the absence of light for 16 h. The reaction mixture was then poured into a saturated solution of sodium sulfite to remove all residual bromine and extracted with chloroform. The organics were combined, dried (MgSO₄), filtered, and concentrated under reduced pressure. The residue was recrystallized from chloroform to afford the product as a red solid (251 mg, 0.53 mmol). Yield 81%; Mpt: 203°C; ¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, *J* = 4.1 Hz, 1H), 7.83 (d, *J* = 4.1 Hz, 1H), 7.72 (d, *J* = 12.9 Hz, 1H), 7.25 – 7.18 (m, 2H). ¹⁹F NMR (377 MHz, CDCl₃) δ -108.03 (d, *J* = 12.9 Hz); MS (EI): isotopic cluster at *m/z* = 476 [M⁺].

4,7-Bis(5-bromothiophen-2-yl)-5-cyano-2,1,3-benzothiadiazole

4,7-Bis(5-bromothiophen-2-yl)-5-fluoro-2,1,3-benzothiadiazole (312 mg, 0.655 mmol), KCN (55 mg, 0.852 mmol) and 18-crown-6 (22 mg, 0.085 mmol) were added to a round bottom flask before being flushed with Argon. Anhydrous THF (20 mL) and DMF (5 mL) was added and the mixture refluxed for 24 h. THF was removed under reduced pressure and the residue dissolved in DCM (100 mL) and washed with water (2 x 100 mL). The aqueous extracts were treated with ammonia solution (28%) to destroy any residual cyanide present. The organic extracts were dried (MgSO₄), filtered and concentrated under reduced pressure. The crude product was purified by recrystallization from chloroform to give a red powder (240 mg, 0.497 mmol). Yield: 76%; Mpt: 226-227°C; ¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 4.1 Hz, 1H), 7.96 (s, 1H), 7.83 (d, *J* = 4.1 Hz, 1H), 7.24 (d, *J* = 4.1 Hz, 1H), 7.20 (d, *J* = 4.1 Hz, 1H); ¹³C NMR (101 MHz, TCE-d₂) δ 152.60, 152.55, 138.56, 136.15, 131.33, 130.95, 130.41, 129.77, 128.55, 126.98, 126.28, 119.11, 117.95, 116.58, 108.95; IR (cm⁻¹): 2220.7 (CN); EI-HRMS (*m/z*): Calculated for C₁₅H₅N₃S₃Br₂ [M]⁺: 480.8012, found 480.8002

P(Ge-DTCNBT)

DTG (212 mg, 0.188 mmol), bis-Br(DTCNBT) (90.84 mg, 0.188 mmol), Pd₂(dba)₃ (3.44 mg, 0.004 mmol), P(o-tol)₃ (4.58 mg, 0.015 mmol) and a stirrer bar were added to a 2 mL high pressure microwave reactor vial. The vial was sealed with a septum and flushed with argon, before degassed chlorobenzene (1 mL) was added. The whole solution was then degassed for 20 min under argon and the argon inlet removed. The vial was heated to 100°C for 2 min, 140°C for 2 min, 160°C for 2 min,

180°C for 10 min and 200°C for 25 min. The polymer was cooled to RT and precipitated in methanol (100 mL), stirred for 30 min and filtered through a Soxhlet thimble. The polymer was extracted using Soxhlet apparatus (methanol, acetone, hexane, chloroform) under argon. The chloroform fraction was concentrated to ~60 mL in a round bottom flask, a solution of aqueous sodium diethyldithiocarbamate dihydrate solution (~100 mg in 60 mL) was then added. The round bottom flask was equipped with a reflux condenser and the mixture stirred vigorously at 60°C for 1 h to allow palladium extraction. The chloroform layer was then separated and washed with water (3 x 100 mL). The solution was then concentrated to ~8 mL, precipitated in methanol (100 mL) and filtered. This precipitation was repeated to yield the dark green polymer P(Ge-DTCNBT) (180 mg, yield: 85.4%) as long fibres. Chloroform fraction: M_n : 42.0 kDa, M_w : 109.2 kDa, M_n/M_w (\bar{D}): 2.6. ^1H NMR (400 MHz, TCE- d_2) δ 8.39 – 8.02 (m, 3H), 7.46 – 7.18 (m, 4H), 1.78 – 1.67 (m, 2H), 1.47 – 1.31 (m, 68H), 0.99 – 0.89 (m, 12H). Anal. Calcd. for $\text{C}_{63}\text{H}_{89}\text{GeN}_3\text{S}_5$ C 67.48, H 8.00, N 3.75; found: C 67.37, H 8.12, N 3.82.

References:

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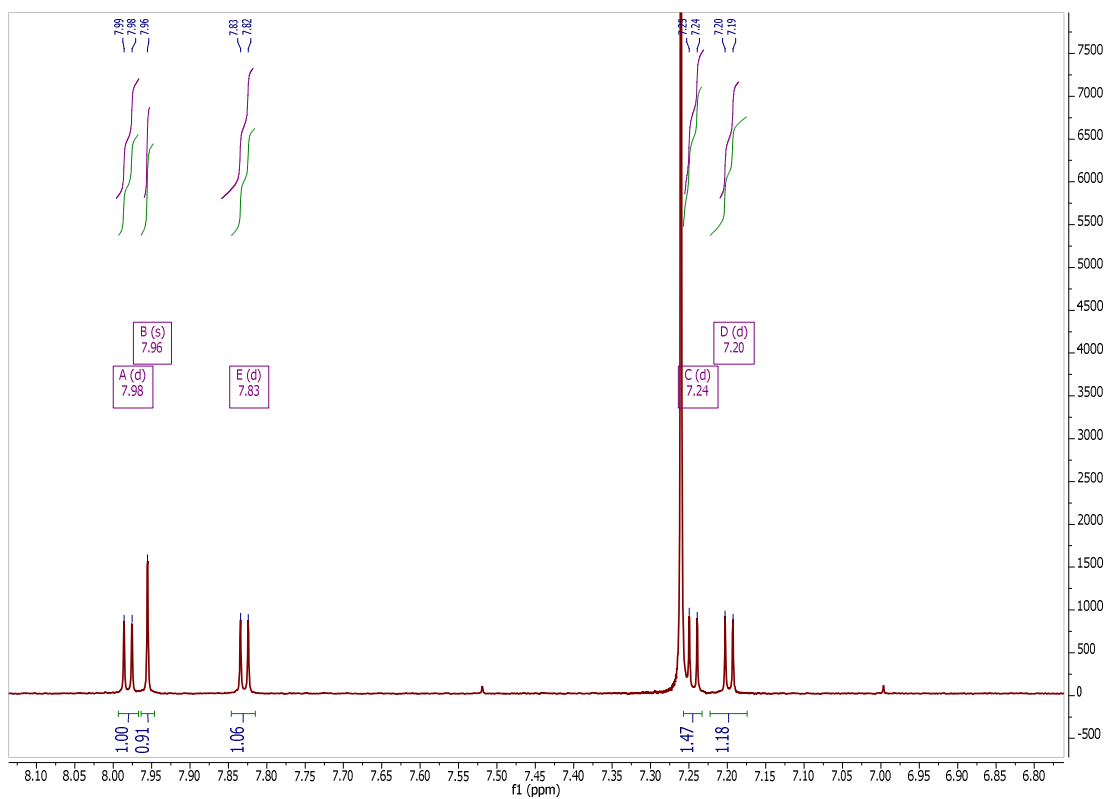


Figure S1: ¹H NMR of 4,7-Bis(5-bromothiophen-2-yl)-5-cyano-2,1,3-benzothiadiazole in CDCl₃

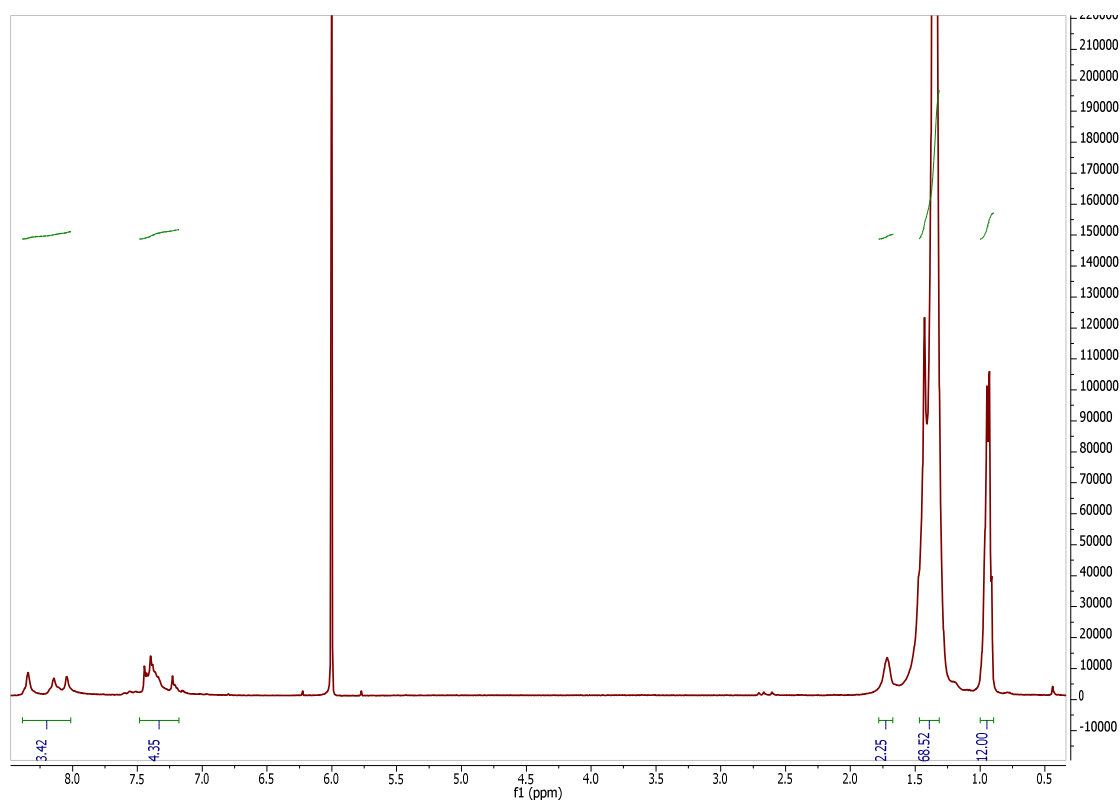


Figure S2: ^1H NMR of P(Ge-DTCNBT) in TCE-d_2

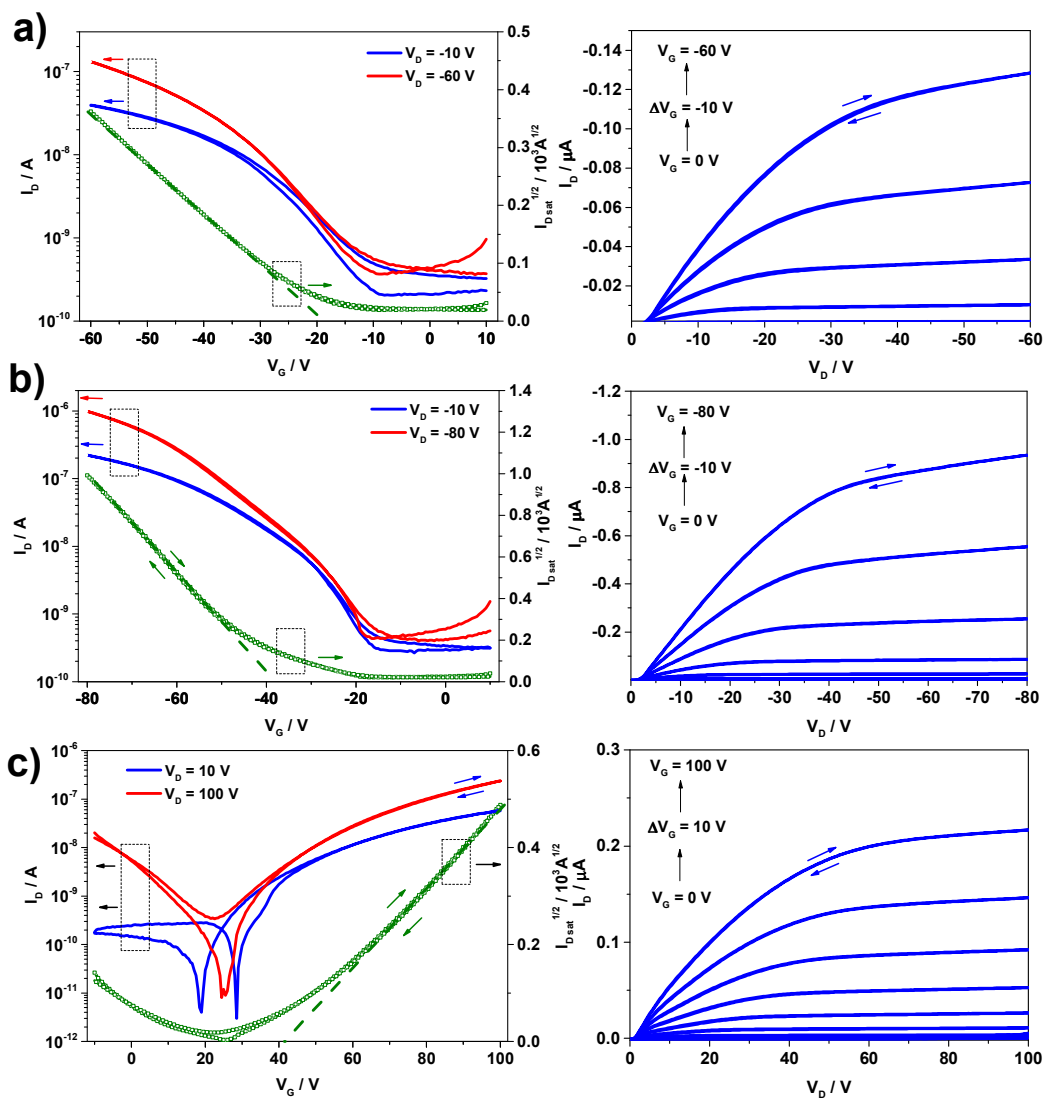


Figure S3: Transfer (left) and output (right) characteristics of (a) polymer P(Ge-DTBT), (b) polymer P(Ge-DTCNBT) and c) polymer P(Ge-DTDCNBT) in TG/BC device configuration.

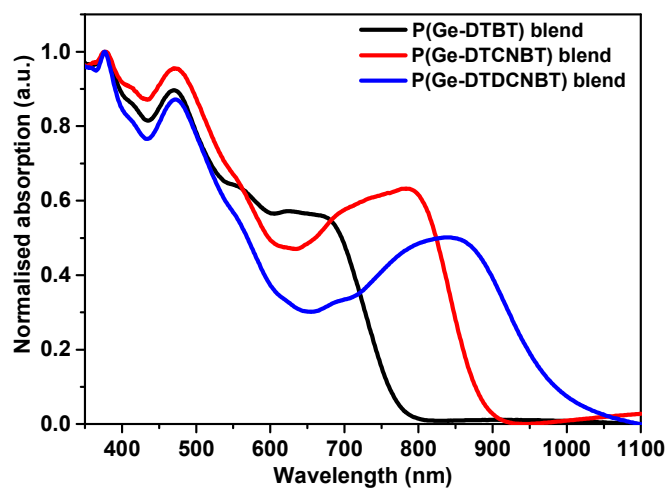


Figure S4: Optical absorption of blends (1:2 weight ratio of polymer:PC₇₁BM)

Transient absorption spectroscopy

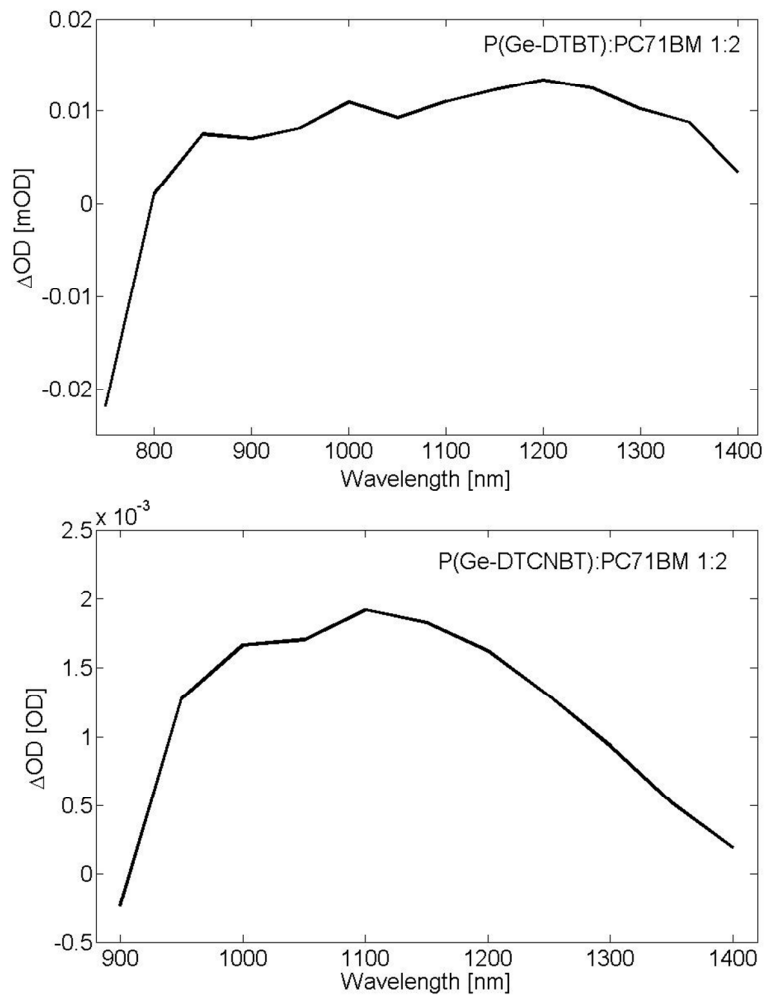


Figure S5. Transient absorption spectra recorded at 0.6 μs time delay of the blend films of P(Ge-DTBT):PC71BM (1:2) and P(Ge-DTCNBT):PC71BM (1:2). The P(Ge-DTBT):PC71BM (1:2) sample was excited with 660 nm $2.6 \mu\text{J}\cdot\text{cm}^{-2}$ laser pulse and the P(Ge-DTCNBT):PC71BM (1:2) with a 780 nm $12.3 \mu\text{J}\cdot\text{cm}^{-2}$ pulse. No signals were recorded for P(Ge-DTDCNBT):PC71BM (1:2) at these excitation densities.

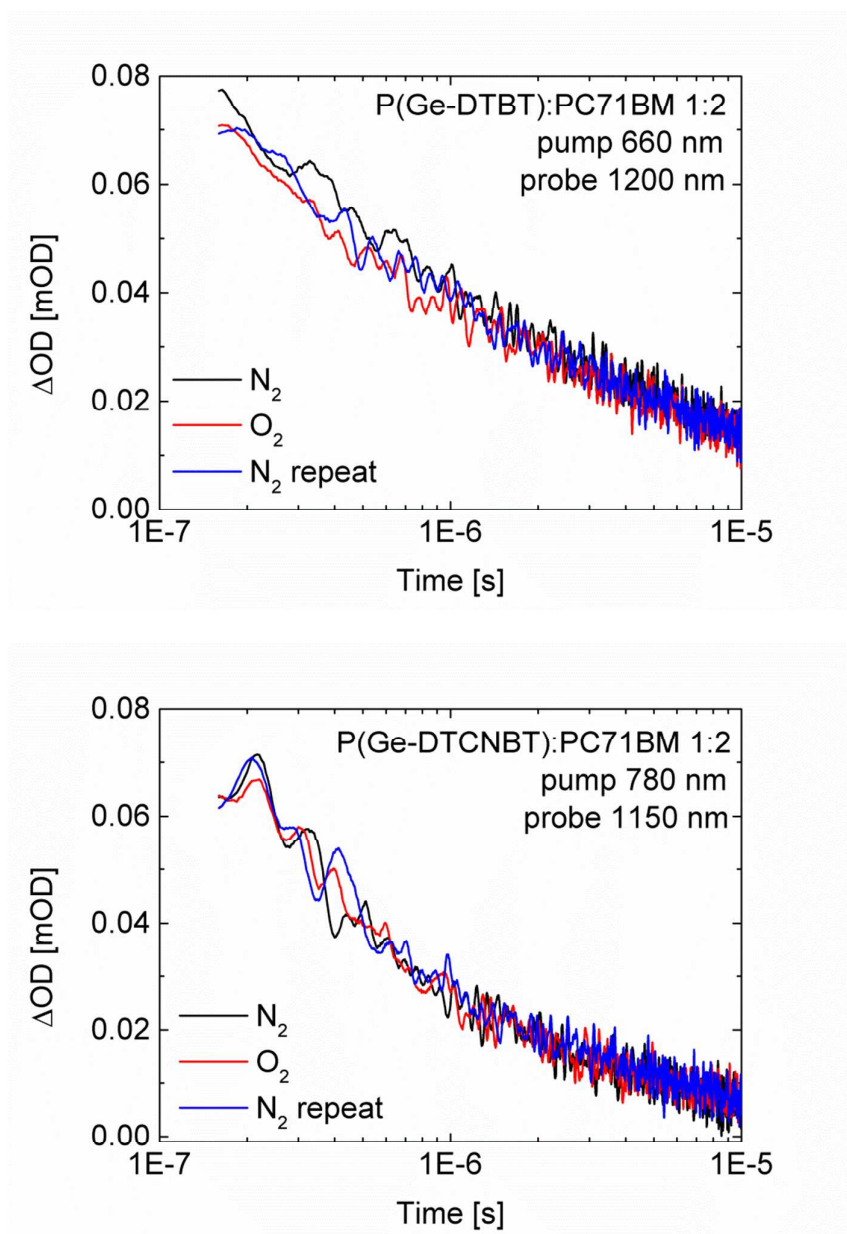


Figure S6. Transient absorption decays recorded under molecular oxygen and nitrogen atmosphere. The blend films of $(\text{Ge-DTBT}):PC_{71}BM$ (1:2) and $P(\text{Ge-DTCNBT}):PC_{71}BM$ (1:2) were excited with 660 nm $3.4 \mu\text{J}\cdot\text{cm}^{-2}$ and 780 nm $12.3 \mu\text{J}\cdot\text{cm}^{-2}$, correspondingly.

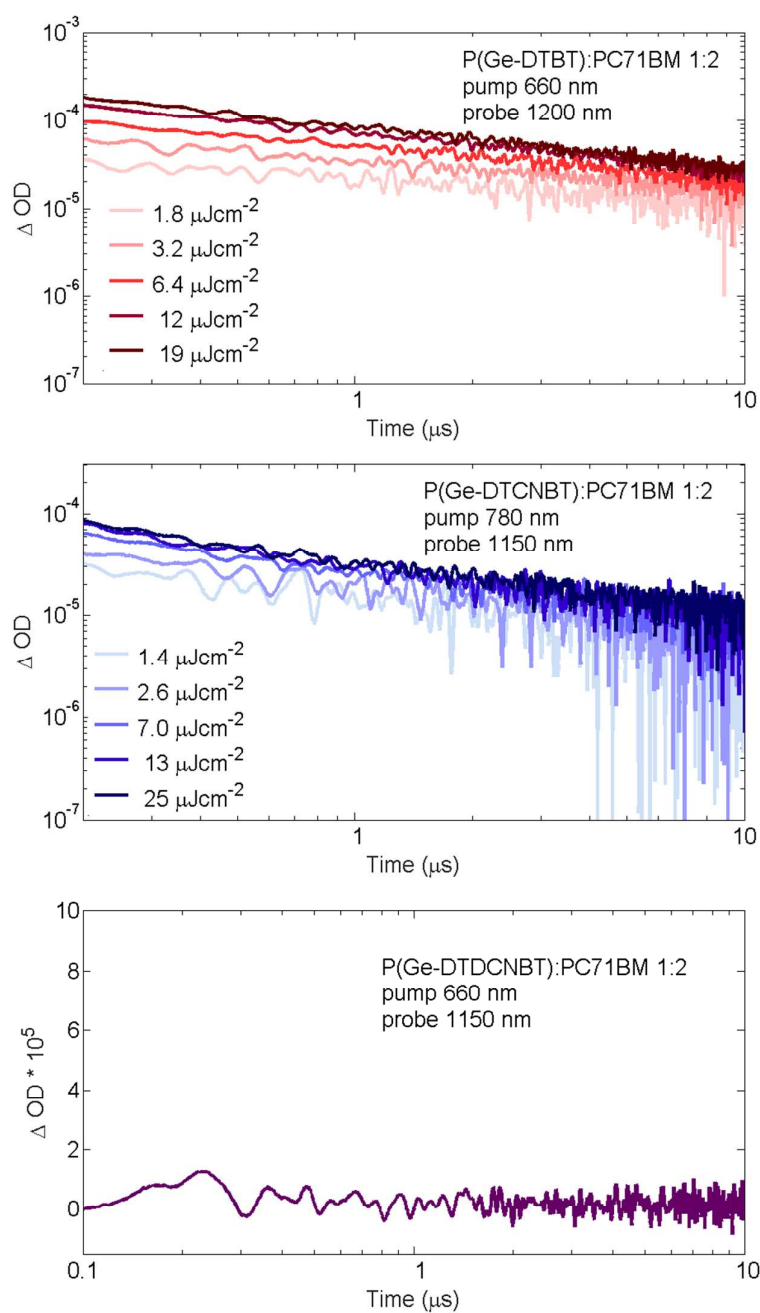


Figure S7. Transient absorption decays as a function of excitation density of P(Ge-DTBT):PC₇₁BM (1:2) and P(Ge-DTCNBT):PC₇₁BM (1:2). Samples were excited with 660 nm 2.6 $\mu J/cm^2$ and 780 nm 12.3 $\mu J/cm^2$ laser pulses, correspondingly. No signals were detected for P(Ge-DTDCNBT):PC₇₁BM (1:2) at excitation densities below 21 $\mu J/cm^2$ showing insignificant charge generation yields.

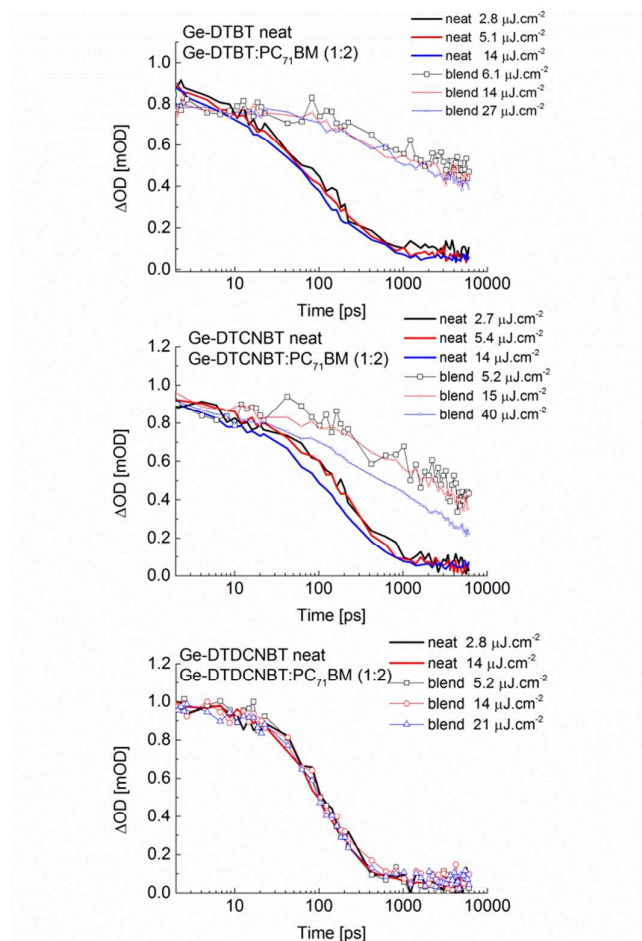


Figure S8. Transient absorption kinetics at 1200 nm of the neat polymer films: P(Ge-DTBT), P(Ge-DTCNBT) and P(Ge-DTDCNBT) and the blend films: (Ge-DTBT):PC₇₁BM (1:2), P(Ge-DTCNBT):PC₇₁BM (1:2) and P(Ge-DTDCNBT):PC₇₁BM (1:2) as a function of excitation density. The pump wavelengths are 660nm, 780 nm, 800 nm exciting at the lowest energy absorption maximum of the polymers. Kinetics show drastically different decay dynamics of the photoinduced absorption between neat polymers and blends. The weak intensity dependence of the decays allows us to estimate the exciton lifetimes of the neat polymer films.

