Supplementary information for:

Impact of the donor polymer on recombination via triplet excitons in a fullerene-free organic solar cell

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Contents

1. Synthetic procedure, characterization data and ^{1}H NMR spectrum for 2,4-diCN-Ph-DTTzTz

4,4'-{Thiazolo[5,4-d]thiazole-2,5-diyl-bis[4-(2-ethyl)hexylthiophene-5,2-diyl)}diisophthalonitrile (2,4-diCN-Ph-DTTzTz). 2,5-Bis[3'-(2''-ethyl)hexylthiophen-2'-yl]thiazolo[5,4-*d*]thiazole (100 mg, 0.188 mmol, 1 equiv), K_2CO_3 (39 mg, 0.283 mmol 1.5 equiv), $Pd(OAc)_2$ (1.0 mg, 5 µmol, 2 mol%), PCy_3HBF_4 (2.7 mg, 7.5 µmol, 4 mol%) and pivalic acid (5.7 mg, 0.057 mmol, 30 mol%) were weighed in air and placed in a microwave vial (10 mL) equipped with a magnetic stirring bar. 4-Bromoisophthalonitrile (82 mg, 0.396 mmol, 2.1 equiv) was added. The vial was purged with Ar and dry toluene (1 mL) was added. The reaction mixture was vigorously stirred under microwave irradiation at 180 °C for 4 h. The solution was then cooled down to room temperature and diluted with CH_2Cl_2 and H_2O. The aqueous phase was extracted with CH_2Cl_2. The organic fractions were combined and dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The obtained product mixture was separated by column chromatography (eluent gradient petroleum ether/$CHCl_3$ 4/1–1/1) to afford the pure mono- (15 mg, 11%) and disubstituted (128 mg, 87%; red solid) TzTz's. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 1.7, 0.6 Hz, 2H), 7.88 (dd, *J* = 8.3, 1.7 Hz, 2H), 7.81 (dd, *J* = 8.3, 0.6 Hz, 2H), 7.70 (s, 2H), 2.97 (d, *J* = 7.3 Hz, 4H), 1.91–1.75 (m, 2H), 1.52–1.37 (m, 8H), 1.36–1.20 (m, 8H), 0.98–0.85 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.9, 151.1, 144.0, 140.4, 138.2, 138.1, 136.1, 133.5, 130.1, 117.0, 116.6, 112.2, 110.9, 39.9, 34.9, 32.7, 28.8, 25.8, 23.2, 14.3, 10.7; UV-VIS ($CHCl_3$) λ_{max} (log ε) 448 nm (4.75).

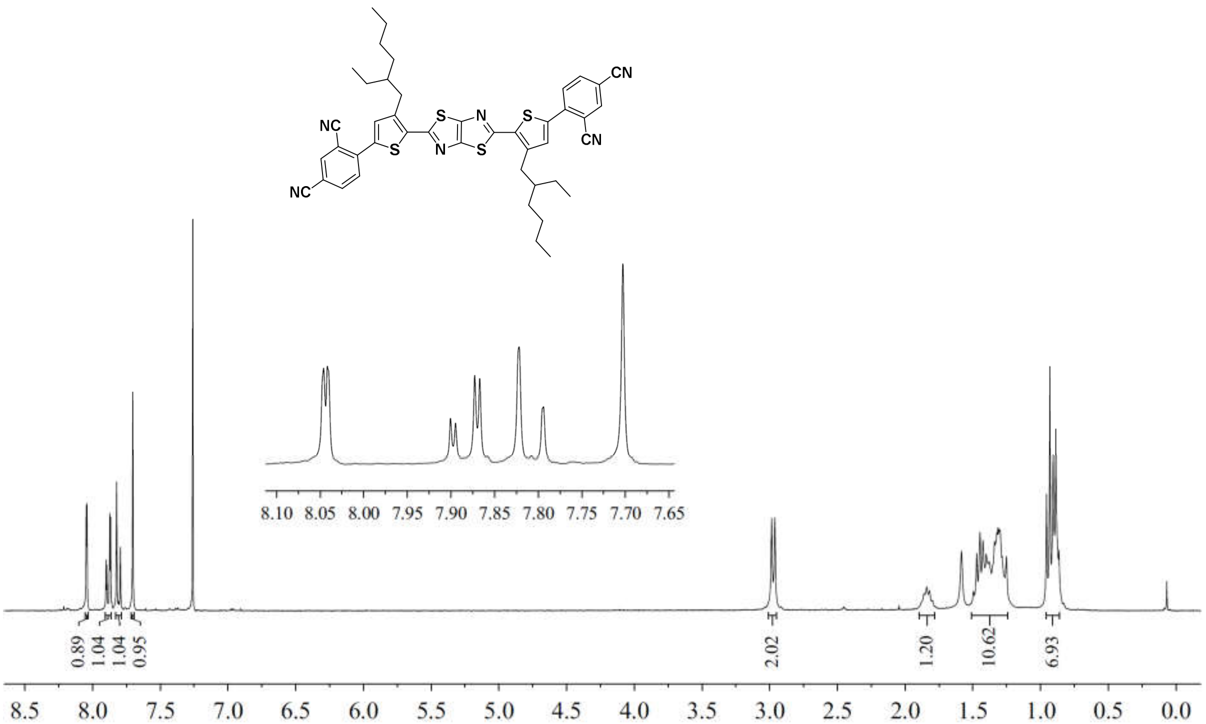

Fig. SI.1 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2,4-diCN-Ph-DTTzTz.

2. Current density-voltage (J-V) curves for the polymer:2,4-diCN-Ph-DTTzTz solar cells

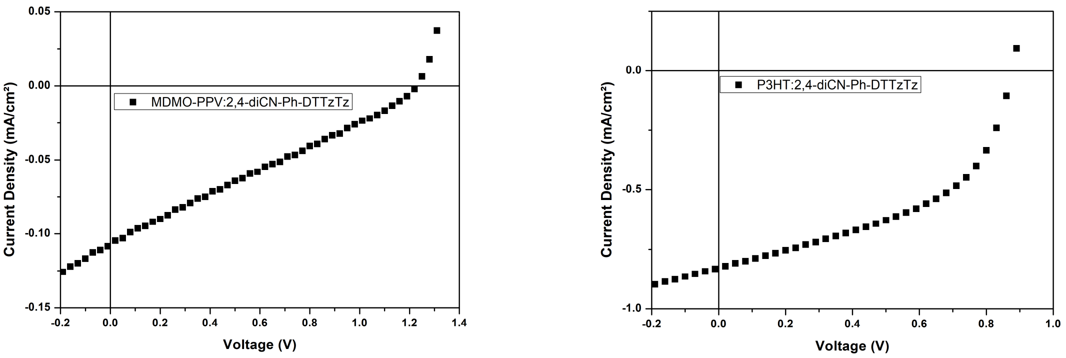

Fig. SI.2 J-V curves of solar cells based on (left) MDMO-PPV:2,4-diCN-Ph-DTTzTz and (right) P3HT:2,4-diCN-Ph-DTTzTz under the illumination of AM 1.5G.

Solar cells in standard architecture were prepared with a layout glass/ITO/PEDOT:PSS/blend/Ca/Al. Substrates with pre-patterned ITO on glass were purchased from Kintec (100 nm, 20 Ohm/sq) and cleaned through sonication in soap, deionized water, acetone and isopropyl alcohol before proceeding with the spin-coating of PEDOT:PSS (Heraeus Clevios AI 4083). The substrates were subsequently brought inside a N_2 filled glovebox and annealed during 10 min at 130 °C to remove residual humidity. All subsequent processing and characterization steps were conducted in inert atmosphere. Blend solutions were prepared with MDMO-PPV or P3HT as the donor polymer and 2,4-diCN-Ph-DTTzTz as the electron acceptor and spin-coated on top of the PEDOT:PSS layer. The best performances were obtained using a 2:1 ratio (wt/wt%) in chloroform and a total concentration of 6 mg/mL. Similar (very low) efficiencies were obtained for 1:1 blends. Finally, the Ca and Al top electrodes were deposited by vacuum deposition aiming at thicknesses of 30 and 80 nm, respectively, resulting in an active device area of 0.03 cm^2 through the use of shadow masks. Electrical characterization was carried out under illumination from a Newport class A solar simulator (model 91195A), calibrated with a silicon solar cell to give an AM 1.5G spectrum.

3. UV-VIS absorption of the polymer:2,4-diCN-Ph-DTTzTz blend films

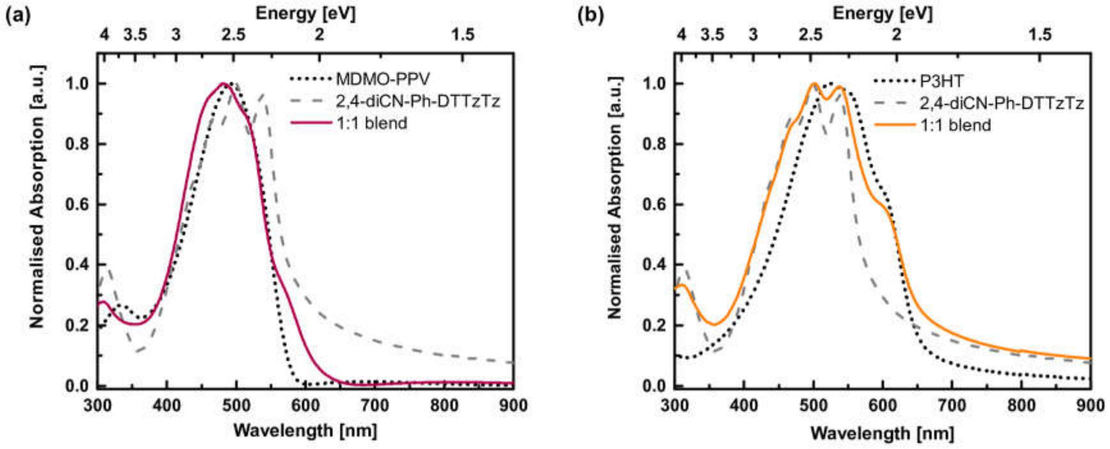

Fig. SI.3 Normalised absorption spectra of spin-coated films of blends of (a) MDMO-PPV:2,4-diCN-Ph-DTTzTz and (b) P3HT:2,4-diCN-Ph-DTTzTz and the corresponding pure donor and acceptor components.

The absorption spectra of the blends can be roughly interpreted as a superposition of the absorption bands of the individual components. However, in the blend with MDMO-PPV we find that the long-wavelength tail due to diffuse scattering from ordered 2,4-diCN-Ph-DTTzTz domains is completely absent. Hence aggregation of the 2,4-diCN-Ph-DTTzTz molecule seems to be strongly suppressed in this blend, suggesting either a very intimately mixed blend or strong molecular interactions between the polymer and the acceptor molecules. The different packing of 2,4-diCN-Ph-DTTzTz molecules in this blend also results in a slight blueshift of the 2,4-diCN-Ph-DTTzTz absorption with respect to the pristine film. In the blend with P3HT these effects are not observed, suggesting stronger ordering of the 2,4-diCN-Ph-DTTzTz domains in these films.

4. Optical bandgap of 2,4-diCN-Ph-DTTzTz

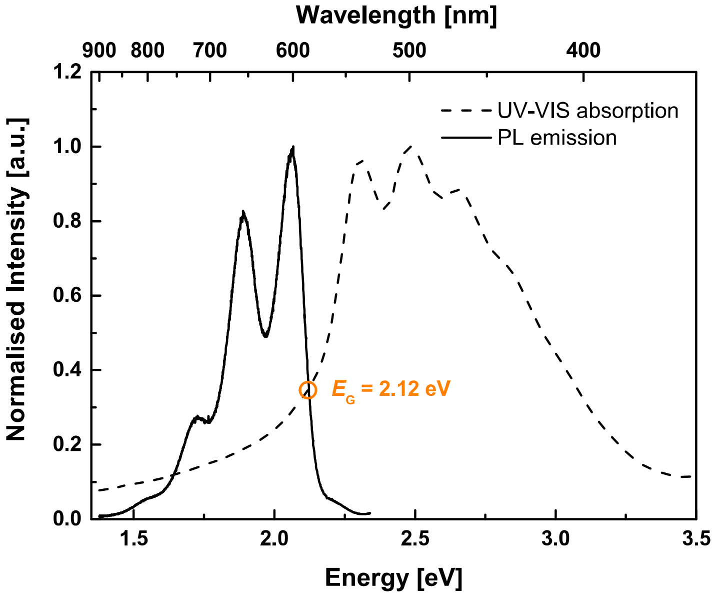

Fig. SI.4 Normalised absorption (dashed line) and PL emission (solid line) spectra of a spin-coated 2,4-diCN-Ph-DTTzTz film. The intersection between the spectra used to determine the optical band gap is indicated in orange.

The strong tendency for crystallization of the 2,4-diCN-Ph-DTTzTz molecular acceptor in spin-coated films resulted in a long-wavelength tail in the absorption spectrum due to diffuse scattering. Hence, the absorption onset is ill-defined and the optical gap of the 2,4-diCN-Ph-DTTzTz acceptor was instead determined from the intersection of the normalized absorption and PL spectra, as shown in Fig. SI.4. This approach has been shown to yield a more reliable estimation of the band gap in disordered semiconductors.[1]

5. Comparison room-temperature PL and EL spectrum MDMO-PPV:2,4-diCN-Ph-DTTzTz device

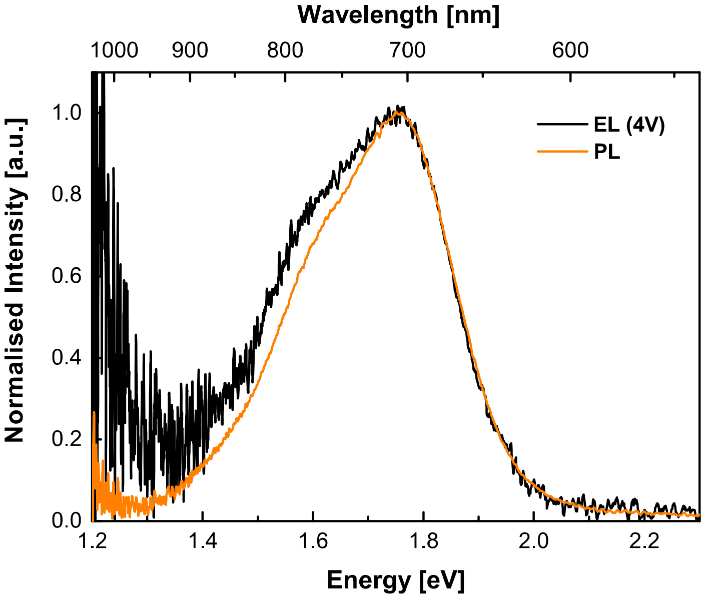

Fig. SI.5 Normalised PL (orange) and EL (black) emission spectra of the MDMO-PPV:2,4-diCN-Ph-DTTzTz device, both recorded at room-temperature. The forward voltage of 4 V was applied to the device for the EL experiment.

In order to confirm the assignment of the redshifted PL in the MDMO-PPV:2,4-diCN-Ph-DTTzTz blend film to CT state emission, we directly compare the room-temperature PL and EL emission of a solar cell based on this blend in Fig. SI.5. The close similarity between EL and PL spectra indicate that emission indeed occurs from the same CT states.

6. Phosphorescence and lowest triplet state energy of 2,4-diCN-Ph-DTTzTz

Phosphorescence spectra were recorded using pulsed laser excitation and time-gated detection to eliminate overlap with long-wavelength PL contributions. Pulsed excitation at 532 nm (2.33 eV) was achieved using the second harmonic output of a Q-switched Nd:YAG laser (Quanta-Ray INDI, Spectra Physics) operating at a pulse rate of 20 Hz. The pulse length was 5 – 8 ns and the laser fluence was kept at 0.6 mJ/cm^2 per pulse. A 1064 nm band reject filter eliminated residual first harmonic contributions from the laser beam before impinging on the sample. Backscattered luminescence from the sample was passed through an f = 30 cm grating monochromator before detection by a Si photodiode (response time 200 ns). A digital storage oscilloscope allowed registration of the time-dependent signal following the laser pulse. To maximise the phosphorescence yield, the thin film sample was cooled to 8 K using a liquid He cryostat.

The spectrum shown in Fig. SI.6 was obtained after integrating the time-domain signals over a window of 3 – 7 µs after the laser pulse. After 3 µs, all direct fluorescence of the 2,4-diCN-Ph-DTTzTz acceptor has decayed and the spectrum can be safely assigned to phosphorescence from triplet states. The lowest triplet state energy was determined from a Gaussian fit of the maximum, resulting in E_T = 1.48 eV. The small peak at λ = 1064 nm is caused by residual first harmonic output of the frequency-doubled Nd:YAG laser.

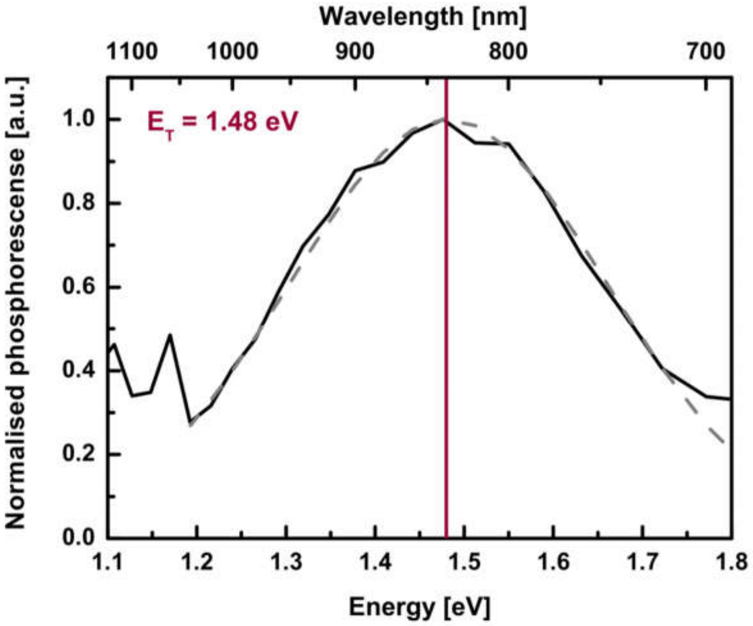

Fig. SI.6 Phosphorescence spectrum of a spin-coated 2,4-diCN-Ph-DTTzTz film recorded at 8 K. The Gaussian fit of the peak maximum is shown with a dashed grey line.

References

1 Y. Wang, D. Qian, Y. Cui, H. Zhang, J. Hou, K. Vandewal, T. Kirchartz and F. Gao, *Adv. Energy Mater.*, 2018, **8**, 1801352.