Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic supplementary information

A pyrrolopyridazinedione-based copolymer for fullerene-free organic solar cells

Astrid-Caroline Knall,[a,b,*] Samuel Rabensteiner,[a] Sebastian Franz Hoefler,[a] Matiss Reinfelds,[a] Mathias Hobisch,[c] Heike M. A. Ehmann,[b] Nadiia Pastukhova,[d] Egon Pavlica,[d] Gvido Bratina,[d] Ilie Hanzu,[a] Shuguang Wen,[e] Renqiang Yang,[e] Gregor Trimmel,[a] and Thomas Rath[a,*]

[a] Institute for Chemistry and Technology of Materials (ICTM), NAWI Graz, Graz University of Technology, Stremayrgasse 9, 8010 Graz, Austria

[b] Anton Paar GmbH, Anton Paar Straße 20, 8054 Graz, Austria

[c] Institute of Paper, Pulp and Fibre Technology, Graz University of Technology, Inffeldgasse 23, 8010 Graz, Austria

[d] Laboratory of Organic Matter Physics, University of Nova Gorica, Vipavska 11c, 5270 Ajdovščina, Slovenia

[e] CAS Key Laboratory of Bio-based Materials, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, China

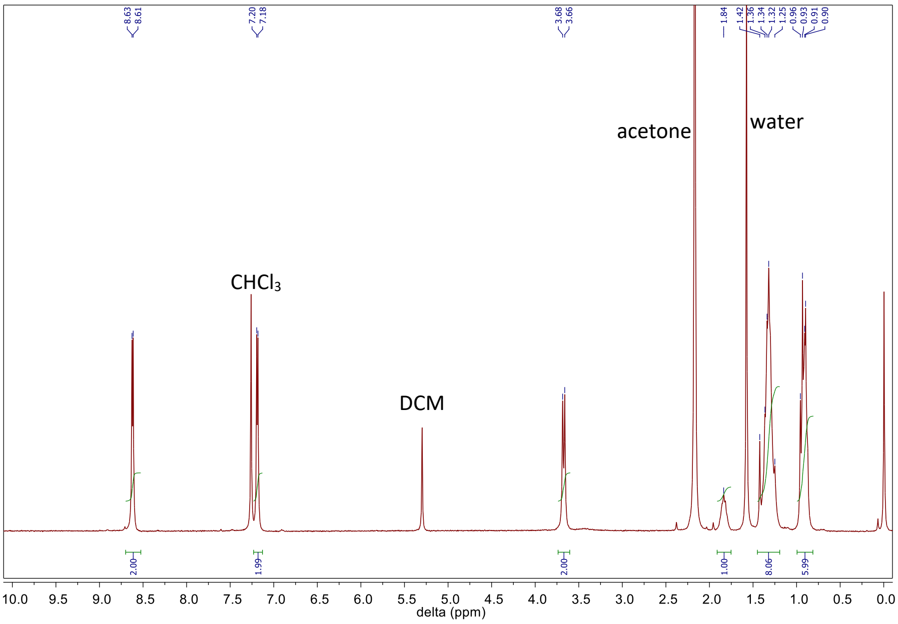

Fig. S1 ^{1}H-NMR spectrum of 1,4-bis(5-bromothiophen-2-yl)-6-(2-ethylhexyl)-5H-pyrrolo[3,4-d]pyridazine-5,7(6H)-dione (T-EHPPD-T monomer).

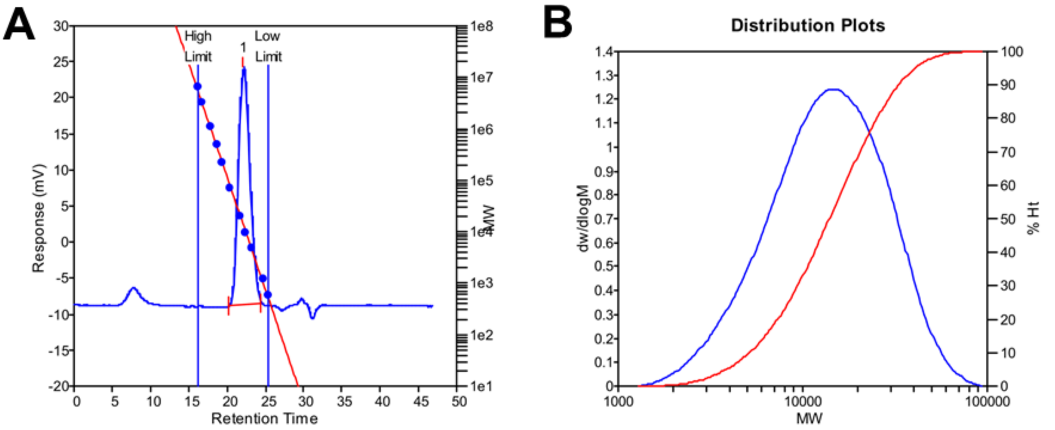

Fig. S2 (A) GPC chromatogram and (B) the corresponding distribution plots of T-EHPPD-T-EHBDT.

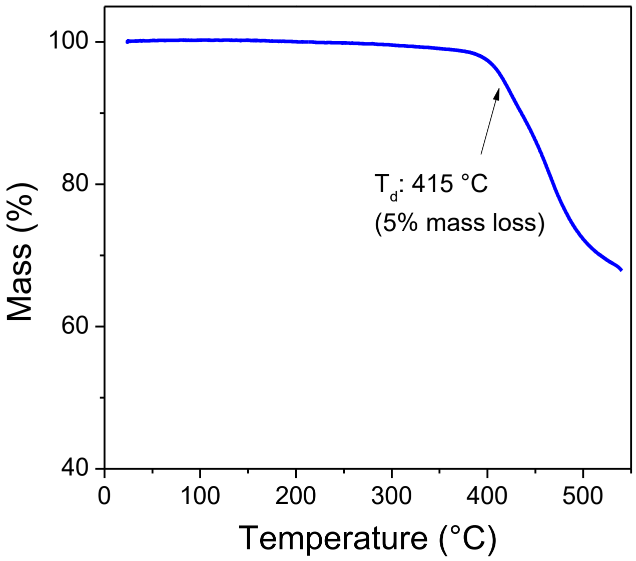

Fig. S3 Thermogravimetric analysis of the polymer T-EHPPD-T-EHBDT.

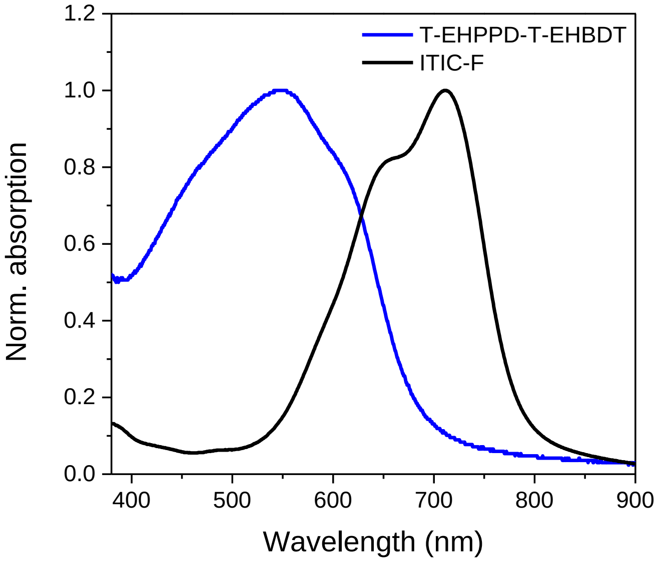

Fig. S4 Normalized UV-Vis absorption spectra of T-EHPPD-T-EHBDT and ITIC-F thin films.

Table S1 Characteristic parameters of the solar cells prepared with different layer thicknesses (D: donor, A: acceptor, L: absorber layer thickness). The average solar cell parameters have been calculated from the best four devices

D:A weight ratio	L (nm)	V_{OC} (V)	J_{SC} (mA/cm^2)	FF	PCE (%)
1:1	50 ± 5	0.74 ± 0.04	15.6 ± 0.8	0.49 ± 0.03	5.7 ± 0.4
	60 ± 5	0.78 ± 0.04	16.1 ± 0.2	0.58 ± 0.03	7.2 ± 0.4
	90 ± 10	0.78 ± 0.04	16.4 ± 0.7	0.46 ± 0.02	5.9 ± 0.4
	140 ± 10	0.74 ± 0.04	14.5 ± 0.6	0.39 ± 0.02	4.2 ± 0.3
1:1.5	50 ± 5	0.75 ± 0.04	16.2 ± 0.8	0.47 ± 0.03	5.7 ± 0.3
	60 ± 5	0.74 ± 0.04	15.7 ± 0.8	0.50 ± 0.03	5.9 ± 0.3
	95 ± 10	0.77 ± 0.04	15.8 ± 0.7	0.45 ± 0.03	5.5 ± 0.4
	140 ± 10	0.78 ± 0.04	12.4 ± 0.6	0.44 ± 0.02	4.1 ± 0.2

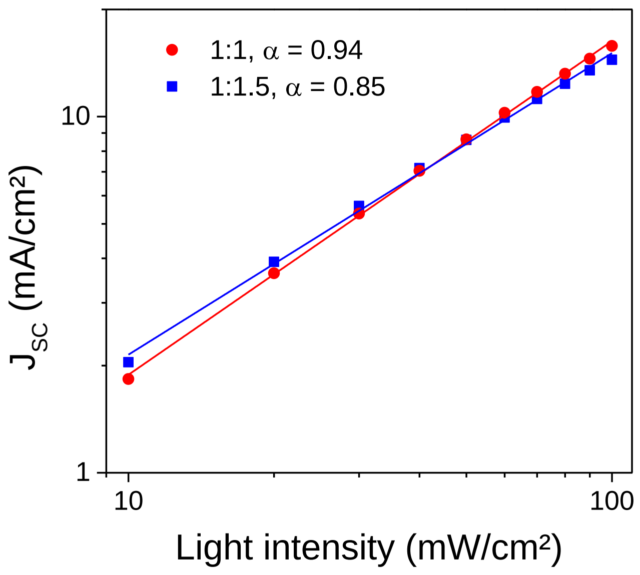

Fig. S5 Dependence of the J_{SC} on the light intensity.

Determination of the SCLC charge carrier mobility of the blend films

In addition to the OFET-based mobility measurements, an analysis of the dark current in the organic solar cells was performed to obtain the SCLC charge carrier mobility of the blend films. The j-V characteristics used for the analysis are presented in Fig. S6.

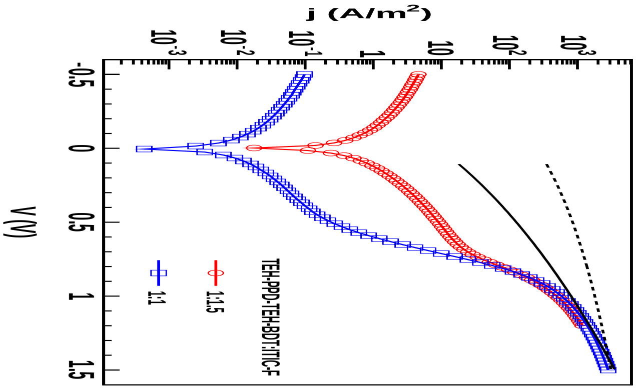

Fig. S6 j-V characteristics measured in the dark of solar cells with polymer:ITIC-F weight ratios of 1:1 and 1:1.5.

Since the anode (ZnO/ITIC-F) and cathode (T-EHPPD-T-EHBDT/MnO_3) interfaces represent a low injection barrier for electrons and holes, respectively, the observed j-V dependence is limited by the bimolecular recombination. Due to the low film thickness (L = 60 nm), the transit time of injected carriers is presumably shorter than the dielectric relaxation time. Therefore, the current density can be described as:[1,2]

$$j = 2\varepsilon_r\varepsilon_0 \frac{(V - V_{bi})^2}{L^3} \sqrt{\frac{\beta_L}{\beta}\mu_h\mu_e}$$

where (ε_0) is the vacuum permittivity and ε_r is a relative permittivity taken as 3. The externally applied bias voltage (V) is reduced by the built-in voltage (V_{bi}), which we found to be -0.60 ± 0.02 V in this case. β and β_L are the bimolecular and Langevin recombination rates, respectively. However, in the case when one of the injection barriers is limiting carrier injection, j is not limited by bimolecular recombination. Therefore, the observed j-V dependence can be interpreted in terms of the space-charge limited current (SCLC) model of Murgatroyd and Gill:[3,4]

$$j = \frac{9}{8}\varepsilon_r\varepsilon_0 \frac{(V - V_{bi})^2}{L^3}\mu(V) \quad \mu(V) = \mu_0 \exp\left(0.891\gamma\sqrt{\frac{V - V_{bi}}{L}}\right)$$

which is an extended version of the Mott-Gurney law to account for the electric field dependence of the mobility ($\mu(V)$). In the model, the mobility is represented as a product of zero-field mobility (μ_0) and the exponential term including the parameter γ. In Fig. S7, we show j as a function of externally applied bias voltage (V) by red open circles. j is linearly increasing with V below 0.2 V. The corresponding slope of the j-V characteristics (dashed blue line and right axis) is approximately 1. In contrast, above 0.2 V, j exhibits a rapid increase, which is a typical trap-filling effect. The slope in this voltage region reaches a value between 16 and 17 in Fig. S7A (blend ratio = 1:1) and a value between 10 and 11 in Fig. S7B (blend ratio = 1:1.5). For higher bias, the slope drops towards 2, which is a fingerprint of the Mott-Gurney law. Therefore, the model was used to estimate V_{bi}, μ_0 and γ in the bias above 1 V.[5] The resulting parameters are presented in Table S2.

Table S2 Parameters obtained based on the above described model

blend ratio	V_{bi} (V)	μ_0 (cm^2/Vs)	γ (m$^{1/2}$/V$^{1/2}$)
1:1	-0.587	2.9 x 10^{-8}	1.4 x 10^{-3}
1:1.5	-0.602	5.6 x 10^{-10}	2.2 x 10^{-3}

The parameters display a significant variation, which results from the analysis in a relatively narrow voltage range. Therefore, we calculated the SCLC mobility in the blend layer at a bias voltage of 1.2 V. The corresponding mobility is 2.8 x 10^{-5} cm^2/Vs and 2.7 x 10^{-5} cm^2/Vs for the 1:1 and the 1:1.5 blend, respectively. In case of double-injection, the geometric average of mobility $\sqrt{\mu_h \mu_e}$ is found to be 1.6 x 10^{-5} cm^2/Vs multiplied by a factor $\sqrt{\beta/\beta_L}$. Regarding the latter, it was found to be a fraction of unity in fullerene-based solar cells.[6] However, recent kinetic Monte Carlo simulations predict that the recombination rate decreases with time.[7] Hence, it is significantly higher for non-thermalized injected carriers. In our case with reduced layer thickness, the injected carriers are presumably non-thermalized. Therefore, we assume that the recombination rate is of the order of Langevin type and hence the geometric average of the mobility is in the order of 10^{-5} cm^2/Vs.

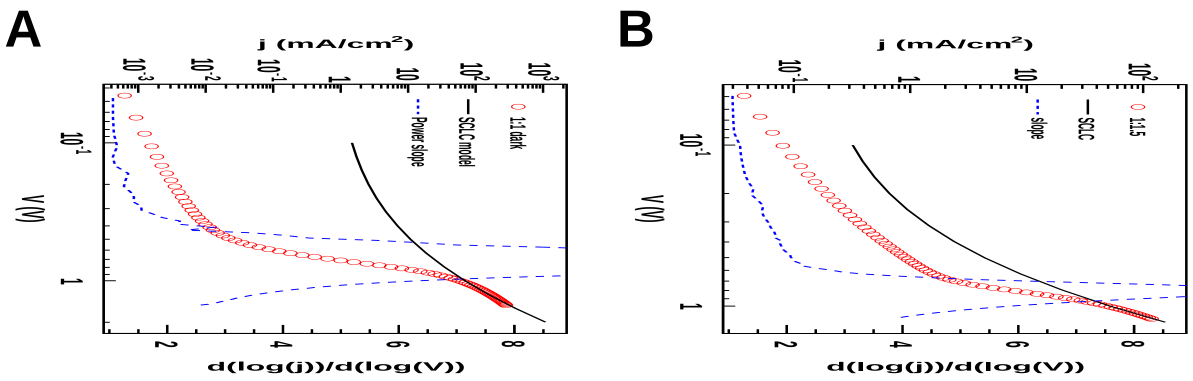

Fig. S7 Hole-only current density as a function of applied bias voltage of the blend films in a double-logarithmic plot (A: 1:1 blend ratio; B: 1:1.5 blend ratio). Measurements (open red circles) and SCLC model (black solid line) obtained with a least-square-method in the range above 1 V. The power slope of the measurements is presented with a dashed blue line and the corresponding scale on the right axis.

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