# **Supporting Information**

# Uphill and Downhill Charge Generation from Charge Transfer to Charge Separated States in Organic Solar Cells

Shahidul Alam<sup>1,2</sup>, Vojtech Nádaždy<sup>3,4</sup>, Tomas Vary<sup>5</sup>, Christian Friebe<sup>1,2</sup>, Rico Meitzner<sup>1,2</sup>, Johannes Ahner<sup>1,2</sup>, Aman Anand<sup>1,2</sup>, Safakath Karuthedath<sup>6</sup>, Catherine S. P. De Castro<sup>6</sup>, Clemens Göhler<sup>7</sup>, Stefanie Dietz<sup>8</sup>, Jonathan Cann<sup>15</sup>, Christian Kästner<sup>9</sup>, Alexander Konkin<sup>10</sup>, Wichard Beenken<sup>10</sup>, Arthur Markus Anton<sup>11,16</sup>, Christoph Ulbricht<sup>12</sup>, Andreas Sperlich<sup>8</sup>, Martin D. Hager<sup>1,2</sup>, Uwe Ritter<sup>10</sup>, Friedrich Kremer<sup>11</sup>, Oliver Brüggemann<sup>13</sup>, Ulrich S. Schubert<sup>1,2</sup>, Daniel A. M. Egbe<sup>14</sup>, Gregory C. Welch<sup>15</sup>, Vladimir Dyakonov<sup>8</sup>, Carsten Deibel<sup>7</sup>, Frédéric Laquai<sup>6</sup>, Harald Hoppe<sup>1,2</sup>

<sup>1</sup>Laboratory of Organic and Macromolecular Chemistry (IOMC), Friedrich Schiller University Jena, Humboldtstr. 10, D-07743 Jena, Germany

<sup>2</sup>Center for Energy and Environmental Chemistry Jena (CEEC Jena), Friedrich Schiller University Jena, Philosophenweg 7a, D-07743 Jena, Germany

<sup>3</sup>Institute of Physics, Slovak Academy of Sciences, Dúbravská cesta 9, 845 11 Bratislava, Slovak Republic <sup>4</sup>Centre for Advanced Material Application, Slovak Academy of Sciences, Dúbravská cesta 9, 845 11 Bratislava, Slovak Republic

<sup>5</sup>Faculty of Electrical Engineering and Information Technology, Slovak University of Technology, 812 19 Bratislava, Slovak Republic

<sup>6</sup>King Abdullah University of Science and Technology (KAUST), KAUST Solar Center (KSC), Physical Sciences and Engineering Division (PSE), Material Science and Engineering Program (MSE), Thuwal 23955-6900, Kingdom of Saudi Arabia

<sup>7</sup>Institute of Physics, Technische Universität Chemnitz, 09126, Cheminitz, Germany

<sup>8</sup>Experimental Physics VI, Julius Maximilian University of Würzburg, 97074 Würzburg, Germany

<sup>9</sup>Production Technology Group, Technische Universität Ilmenau, Gustav-Kirchhoff-Platz 2, Ilmenau, Germany

<sup>10</sup>Institute for Micro and Nanotechnologies, Technische Universität Ilmenau, Gustav-Kirchhoff-Str.7, D-98693 Ilmenau, Germany

<sup>11</sup>Peter Debye Institute for Soft Matter Physics, Universität Leipzig, 04103 Leipzig, Germany

<sup>12</sup>Linz Institute for Organic Solar Cells (LIOS), Johannes Kepler University Linz, Altenbergerstr. 69, 4040 Linz, Austria

<sup>13</sup>Institute of Polymer Chemistry, Johannes Kepler University Linz, Altenbergerstr. 69, 4040 Linz, Austria <sup>14</sup>Institute of Polymeric Materials and Testing, Johannes Kepler University, Altenbergerstr. 69, 4040 Linz, Austria

<sup>15</sup>Department of Chemistry, 731 Campus Place N.W., University of Calgary, Canada

<sup>16</sup>Department of Physics and Astronomy, The University of Sheffield, S102TN, Sheffield, United Kingdom

### **Corresponding author**

Shahidul Alam, Harald Hoppe E-mail: <u>shahidul.alam@uni-jena.de</u>, <u>harald.hoppe@uni-jena.de</u>

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### **1** Molecular structures

In **Figure S1**, schematic representation of the molecular structures of poly(*p*-phenylene-ethynylene)-*alt*-poly(*p*-phenylene-vinylene) (PPE-PPV) backbone known as **AnE-PV***stat*, fullerene derivatives [6,6]-phenyl-C61-butyric acid methyl ester (**PC**<sub>60</sub>**BM**), 3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2',3'-d']-s-indaceno[1,2-b:5,6-

b']dithiophene (ITIC) and three additional non-fullerene acceptors (NFAs) derived from perylene diimide (PDI) dimers PDI<sub>2</sub>Ac<sub>2</sub> (Pa2) ( $C_6H_{13} = n$ -hexyl), DPP-(Ac-PDI)<sub>2</sub> (DaP2) ( $C_6H_{13} = n$ -hexyl,  $C_8H_{17} = 2$ -ethylhexyl) and TII-(Ac-PDI)<sub>2</sub> (TaP2) ( $C_6H_{13} = n$ -hexyl,  $C_8H_{17} = 2$ -ethylhexyl), are shown.



**Figure S1:** Schematic representation of the molecular structure of AnE-PVstat ( $C_8H_{17} = n$ -octyl or 2ethylhexyl), PCBM, ITIC ( $C_6H_{13} = n$ -hexyl), PDI<sub>2</sub> $Ac_2$  (Pa2) ( $C_6H_{13} = n$ -hexyl), DPP-(Ac-PDI)<sub>2</sub> (DaP2) ( $C_6H_{13} = n$ -hexyl,  $C_8H_{17} = 2$ -ethylhexyl) and TII-(Ac-PDI)<sub>2</sub> (TaP2) ( $C_6H_{13} = n$ -hexyl,  $C_8H_{17} = 2$ ethylhexyl).

**Figure S2** illustrates the synthesis scheme for the preparation of the AnE-PV*stat* from comonomers, with octyloxy, and with 2-ethylhexyloxy side chains, by Horner-Wadsworth-Emmons polycondensation reaction<sup>1</sup>. The random incorporation of the comonomers yields a polymer with statistical successions of octyloxy and 2-ethylhexyloxy side chains.



*Figure S2:* Schematic representation of the polycondensation of two dialdehydes with two bisphosphonates (monomer ration: 1/1/1/1) yielding the statistical copolymer AnE-PVstat.

### 2 Current-voltage characteristics

In this section, I-V curves of the AnE-PV*stat*:NFA's (ITIC and PDI based) solar cells prepared in conventional architecture. **Figure S3** and **Figure S4** show the IV curves in semi-logarithmic scales in dark and under illumination. AnE-PV*stat*:PC<sub>60</sub>BM based solar cell is shown for comparison.



*Figure S3:* Semi-logarithmic dark I-V of AnE-PVstat:PC<sub>60</sub>BM, AnE-PVstat:ITIC and AnE-PVstat:PDI based NFA's solar cells in conventional architecture.



*Figure S4:* Semi-logarithmic light I-V of AnE-PVstat:PC<sub>60</sub>BM, AnE-PVstat:ITIC and AnE-PVstat:PDI based NFA's solar cells in conventional architecture.

# **3** Cyclic voltammetry

In order to estimate the HOMO and LUMO of the designated donor and acceptor material cyclic voltammetry (CV) measurements were conducted. The corresponding data are presented in this section. Two approaches to evaluate the obtained results are considered. Electrochemical bandgap in the CT-state is determined as the difference between HOMO of the donors and LUMO of the acceptor.



Figure S5: Oxidation and reduction potentials of AnE-PVstat determined by CV.



Figure S6: Oxidation and reduction potentials of PBDB-T determined by CV.



Figure S7: Oxidation and reduction potentials of PCDTBT determined by CV.



*Figure S8:* Oxidation and reduction potentials of PC<sub>60</sub>BM determined by CV.



*Figure S9:* Oxidation and reduction potentials of PC<sub>70</sub>BM determined by CV.



Figure S10: Oxidation and reduction potentials of ITIC determined by CV.

Table S1: F	HOMO-LUMO	energy values	determined by CV	<i>measurements</i>	and calculated	band gaps.
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Material	Oxidation		Reduction		HOMO	LUMO	Electrochemical
	onset	naak	onset	set peak	[eV]:	[eV]:	bandgap E <sub>G,EC</sub>
	onset	реак	onset		onset	onset	[eV]
AnE-PVstat	+0.24	+0.42	- 1.36	- 1.69	-5.24	-3.64	1.60
PBDB-T	+0.33	+0.76	-1.32	-1.55	-5.33	-3.68	1.65
PCDTBT	+0.14	+0.31	-1.47	-1.67	-5.14	-3.53	1.61
PC <sub>60</sub> BM	+1.07	+1.23	-1.09	-1.28	-6.07	-3.91	2.16
PC <sub>70</sub> BM	+1.00	+1.15	-1.09	-1.24	-6.00	-3.91	2.09
ITIC	+0.69	+0.84	-1.03	-1.17	-5.69	-3.97	1.72



Figure S11: Oxidation and reduction potentials of Pa2 determined by CV.



Figure S12: Oxidation and reduction potentials of DaP2 determined by CV.



Figure S13: Oxidation and reduction potentials of TaP2 determined by CV.

*Table S2:* HOMO-LUMO energy values determined by CV methods and calculated electrochemical bandgaps.

Material	Oxidation		Reduction		HOMO	LUMO	Electrochemical
	onset	naak	onset	naak	(eV):	(eV):	bandgap E <sub>G,EC</sub>
	onset	реак	onset	реак	onset	onset	(eV)
Pa2	+1.08	+1.31	-1.08	-1.28	-6.08	-3.92	2.16
DaP2	+0.53	+0.65	-1.09	-1.26	-5.53	-3.91	1.62
TaP2	+0.43	+0.56	-1.11	-1.28	-5.43	-3.89	1.54

## 4 Absorption (Abs.) and photoluminescence (PL)

### 4.1 Normalized absorption and photoluminescence for AnE-PVstat, PC<sub>60</sub>BM and NFA's

In this section, normalized absorption and photoluminescence spectra of all pristine and blend materials are depicted. Optical bandgap ( $E_{g,opt}$ ) is calculated from the normalized cross-section of absorption and photoluminescence spectra, shown in the inset of the graphs, all the values are summarized in **Tables S3 & S4.** 



Figure S14: Normalized absorption and photoluminescence spectra for pristine AnE-PVstat film.



*Figure S15:* Normalized absorption and photoluminescence spectra for pristine  $PC_{60}BM$  film.



*Figure S16: Normalized absorption and photoluminescence spectra for AnE-PVstat:PC*<sub>60</sub>*BM blend film.* 



Figure S17: Normalized absorption and photoluminescence spectra for pristine ITIC film.



Figure S18: Normalized absorption and photoluminescence spectra for AnE-PVstat:ITIC blend film.



Figure S19: Normalized absorption and photoluminescence spectra for pristine Pa2 film.



Figure S20: Normalized absorption and photoluminescence spectra for AnE-PVstat: Pa2 blend film.



Figure S21: Normalized absorption and photoluminescence spectra for pristine DaP2 film.



*Figure S22:* Normalized absorption and photoluminescence spectra for AnE-PVstat:DaP2 blend film.



Figure S23: Normalized absorption and photoluminescence spectra for pristine TaP2 film.



Figure S24: Normalized absorption and photoluminescence spectra for AnE-PVstat: DaP2 blend film.

Matarial	Optical bandgap E <sub>G,O*</sub> (eV)				
Material	Abs	PL	Abs/PL		
AnE-Pvstat			2.03		
PC <sub>60</sub> BM	1.68	1.76			
ITIC			1.61		
Pa2			2.03		
DaP2			1.61		
TaP2			1.48		
AnE-PVstat:PC <sub>60</sub> BM			2.05		
AnE-PVstat:ITIC			1.66		
AnE-PVstat:Pa2	1.98	1.59			
AnE-PVstat:DaP2			1.56		
AnE-PV <i>stat</i> :TaP2			1.45		

Table S3: Optical bandgap determined from the absorption and photoluminescence.

### 4.2 Norm. abs. and PL for PBDB-T, PBDB-T:PC<sub>70</sub>BM and PBDB-T:ITIC



Figure S25: Normalized absorption and photoluminescence spectra for pristine PBDB-T film.



*Figure S26: Normalized absorption and photoluminescence spectra for PBDB-T:PC*<sub>70</sub>*BM blend film.* 



Figure S27: Normalized absorption and photoluminescence spectra for PBDB-T:ITIC blend film.

### 4.3 Norm. abs. and PL for PCDTBT, PCDTBT:PC<sub>70</sub>BM and PCDTBT:ITIC



Figure S28: Normalized absorption and photoluminescence spectra for pristine PCDTBT film.



*Figure S29:* Normalized absorption and photoluminescence spectra for PCDTBT:PC<sub>70</sub>BM blend film.



*Figure S30:* Normalized absorption and photoluminescence spectra for PCDTBT:PC<sub>70</sub>BM blend film.

Table S4:	Optical	bandgap	determined	from th	e absorption	and photo	oluminescence.
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Matarial	Optical bandgap E <sub>G,O*</sub> (eV)				
Iviaterial	Abs	PL	Abs/PL		
PBDB-T			1.87		
PCDTBT			1.92		
ITIC			1.61		
PBDB-T: PC <sub>70</sub> BM			1.74		
PBDB-T: ITIC			1.67		
PCDTBT:PC <sub>70</sub> BM			1.81		
PCDTBT:ITIC			1.67		

# 5 Energy resolved electrochemical impedance spectroscopy (ER-EIS)

In this section, density of states (DOS) functions of pristine NFA's and AnE-PV*stat*:NFA's are shown. All the NFA's are investigated in two different substrates (glass/ITO and glass/ITO/ZnO), DOS for bare substrates are also shown in at first.

# 5.1 Density of states for bare substrates



Figure S31: Density of state (DOS) functions of bare Glass/ITO and Glass/ITO/ZnO substrates.

## 5.2 Density of states of pristine NFA's



*Figure S32:* ER-EIS measurements of NFA's. Density of state (DOS) functions of different non-fullerene acceptor films as measured by ER-EIS on glass/ITO substrates (left) and glass/ITO/ZnO substrates (right). Grey lines indicate the ER-EIS signals for the respective bare substrate.



Figure S33: Detail analysis of HOMO-LUMO values for AnE-PVstat and AnE-PVstat:NFA's blend.



**Figure S34:** ER-EIS measurements for AnE-PVstat: $PC_{60}BM$  and AnE-PVstat:NFA's. a) Density of state (DOS) functions of pristine AnE-PVstat and AnE-PVstat: $PC_{60}BM$ , AnE-PVstat:ITIC, AnE-PVstat:Pa2, AnE-PVstat:DaP2 and AnE-PVstat:TaP2 blends measured by ER-EIS.

# 5.4 Density of states of pristine PCBM



*Figure S35:* ER-EIS measurements data for pristine  $PC_{60}BM$  and  $PC_{70}BM$  film casted from different solvents.

From **Figure S35** as well as **Table S5** it is evident, that the solvent (system) from which the PCBM-film is cast largely impacts on the energy bandgap of the same.

Material	Solvent	НОМО	LUMO	Bandgap [eV]				
PC <sub>60</sub> BM	CB:CF	6.61	4.07	2.54				
PC <sub>60</sub> BM	CHCl <sub>3</sub> (CF)	6.35	4.33	2.02				
PC <sub>60</sub> BM	CB	6.16	4.19	1.97				
PC <sub>60</sub> BM	DCB	5.99	4.27	1.72				
PC <sub>70</sub> BM	CB	6.29	4.41	1.88				
PC <sub>70</sub> BM	CB:CF	6.38	4.29	2.09				
PC <sub>70</sub> BM	m-Xylene	6.07	4.31	1.76				

*Table S5:* HOMO and LUMO values obtained by ER-EIS on PC60BM and PC70BM, cast from different solvents.

# 5.5 Energy landscape analysis: AnE-PV*stat*:NFAs (PDI based)

Energy landscape of AnE-PV*stat*:NFA's (PDI based) and extracted charge transport gaps are shown in this section.



Figure S36: The evaluated energy landscape for AnE-PVstat, Pa2, and their blend.



Figure S37: The evaluated energy landscape for AnE-PVstat, DaP2, and their blend.



Figure S38: The evaluated energy landscape for AnE-PVstat, DaP2, and their blend.

**Table S6:** HOMO-LUMO values for pristine materials determined by ER-EIS method and calculated energy gaps ( $E_{G,DOS}$ ).

Materials	HOMO (eV)	LUMO (eV)	Energy Gap
			E <sub>G,DOS</sub> (eV)
AnE-PV <i>stat</i>	-5.44	-3.06	2.38
PC <sub>60</sub> BM	-6.55	-4.05	2.50
ITIC	-5.63	-4.00	1.63
Pa2	-5.97	-4.20	1.77
DaP2	-5.54	-4.15	1.39
TaP2	-5.52	-4.18	1.34
AnE-PV <i>stat</i> :PC <sub>60</sub> BM	-5.31	-4.19	1.12
AnE-PV <i>stat</i> :ITIC	-5.44	-3.54	1.90
AnE-PV <i>stat</i> :Pa2	-5.31	-3.81	1.50
AnE-PVstat:DaP2	-5.36	-3.50	1.86
AnE-PV <i>stat</i> :DaP2	-5.33	-3.67	1.66

# 5.6 Overview of DOS and open circuit voltage for indication of occupied states

The following graphs illustrate the resulting Fermi level splitting that have been overlaid in density of states diagram.





*Figure S39:* ER-EIS data on the density of (electronic) states (DOS), including the lower and upper limit of CT-state energy, shown by color marked boxes. a) AnE-PVstat:PC<sub>60</sub>BM, b) AnE-PVstat:ITIC, c) PBDB-T:PC<sub>70</sub>BM, d)PBDB-T:ITIC, e)PCDTBT:PC<sub>70</sub>BM and f) PCDTBT:ITIC.

# 5.7 Arithmetic sum of single DOS and blend DOS

The following graphs illustrate the arithmetic sum of the individual DOS spectra that yields of blend. The arithmetic sum of DOS from pristine constituents nowhere co-insides with the bled DOS.



**Figure S40:** DOS of arithmetic of single materials (blue) and measured blend (brown) for a) AnE-PVstat:PC<sub>60</sub>BM, b) AnE-PVstat:ITIC, c) PBDB-T:PC<sub>70</sub>BM, d) PBDB-T:ITIC, e) PCDTBT:PC<sub>70</sub>BM and f) PCDTBT:ITIC blends determined by ER-EIS measurements.



*Figure S 41:* Determination of CT-state exciton binding energies from the difference between blend jDOS and its EQE onsets (in logarithmic scales) of the various donor acceptor bulk heterojunction blends.

### 5.9 DOS energy gaps, electronic gap and consolidated CT-energy



For the electronic gaps the reader is referred to section 6.2.

**Figure S42:** Compilation of energy levels for pristine materials in comparison to energy levels relevant for donor-acceptor blends. For single materials in increasing order the optical gap, DOS energy gap, and the electronic gap from the jDOS are depicted. For resulting blends, the consolidated CT-energy is compared to the jDOS gap. Note that optical gaps, electronic gaps, and CT-energies are shown without limiting generality centrosymmetric to the absolute energy values of DOS energy gaps.

### 5.10 Summary of HOMO and LUMO

**Table S7:** Highest occupied and lowest unoccupied molecular energy values for pristine and blend materials determined by ER-EIS method and calculated energy gaps; note that energy gaps for blends are so-called effective bandgaps, and may originate from an "effective semiconductor" based on  $HOMO_{Donor}$  and  $LUMO_{Acceptor}$ , or from one of the constituents alone.

Materials	HOMO	LUMO	DOS Energy gap
	[eV]	[eV]	E <sub>G,DOS</sub> [eV]
AnE-PV <i>stat</i>	-5.44	-3.06	2.38
PBDB-T	-5.35	-3.45	1.90
PCDTBT	-5.49	-3.57	1.92
PC <sub>60</sub> BM	-6.55	-4.05	2.50
PC <sub>70</sub> BM	-6.33	-4.38	1.95
ITIC	-5.63	-4.00	1.63
AnE-PVstat:PC <sub>60</sub> BM	-5.31	-4.19	1.12
AnE-PVstat:ITIC	-5.44	-3.54	1.90
PBDB-T:PC <sub>70</sub> BM	-5.47	-4.21	1.26
PBDB-T:ITIC	-5.31	-3.62	1.69 / <b>1.00 (FR)</b>
PCDTBT:PC <sub>70</sub> BM	-5.75	-4.21	1.54
PCDTBT:ITIC	-5.51	-3.59	1.92 / <b>1.51 (FR)</b>

Table S8: Analysis of effective bandgaps for photovoltaic blends, determined by ER-EIS method.

Materials	Expected bandgap ECEXP [eV]	Effective bandgap EC FFF [eV]	$\Delta E_G$ [meV]	Bandgap relation	Relative shift of effective bandgap
AnE-	1.39	1.12	-270	$E_{GEXP} > E_{GEFF}$	Shrinking
PVstat:PC60BM				_,	C
AnE-PVstat:ITIC	1.44	1.90	+460	$E_{G,EXP} < E_{G,EFF}$	Widening
PBDB-T:PC <sub>70</sub> BM	0.97	1.26	+290	$E_{G,EXP} < E_{G,EFF}$	Widening
PBDB-T:ITIC	1.35	1.69 /	+350 /	$E_{G,EXP} < E_{G,EFF}$	Widening /
		1.00 (FR)	-350	$E_{G,EXP} > E_{G,EFF}$	Shrinking
PCDTBT:PC <sub>70</sub> BM	1.11	1.54	+430	$E_{G,EXP} < E_{G,EFF}$	Widening
PCDTBT:ITIC	1.49	1.92 /	+430 /	$E_{G,EXP} < E_{G,EFF}$	Widening /
		1.51 (FR)	+20	$E_{G,EXP} \sim E_{G,EFF}$	Similar

**Table S7** summarizes the ER-EIS-extracted molecular energy levels defining the energy gap of individual materials and blends thereof, **Table S8** shows the analysis of the obtained effective bandgaps  $E_{g,eff}$  in comparison to the expected bandgaps  $E_{g,exp}$ . Note that in case of a Fano-resonance (FR) the character and energetics of the resulting effective bandgap may change in favor of photovoltaic operation.

### **6** Work function measurements

In order to obtain information about the work function of single and blend organic semiconductors in dependence on different types of metallic substrates, **AnE-PV***stat*, in combination with PC<sub>70</sub>BM and various **NFA's** spin coated films were measured by Kelvin Probe (KP) method on three different substrates. Work functions for bare substrates with native oxide layer were determined and the values are as follows: Glass/ITO (4.59 eV), glass/ITO/ZnO (4.53 eV) and glass/ITO/PEDOT:PSS (5.01 eV). The dotted lines indicate the work functions for bare substrates. It can be seen that, among all the acceptor materials, the work function of PC<sub>60</sub>BM follows the substrate work function also for ITO appropriately, but there are some major inconsistencies in the case of pristine NFAs except on glass/ITO/ZnO. Thus, Fermi level pinning does not show in all cases.



*Figure S43:* Work function of various materials on different substrate contacts. For comparison, the HOMO-LUMO values for the pristine AnE-PVstat,  $PC_{60}BM$  and NFA's determined by CV and ER-EIS are shown.


*Figure S44:* Work functions for various blends on different substrate contacts. HOMO-LUMO values for AnE-PVstat-based blends determined by ER-EIS and CV.

#### 6.1 Overview of electrochemical bandgap, optical bandgap and DOS energy gap

In this section an overview of electrochemical bandgap, optical bandgap and charge transport gap are presented. Electrochemical bandgaps are determined by CV measurement for all pristine materials. However, electrochemical bandgaps for blends are calculated from the difference between HOMO of the donor – LUMO of the acceptor, and that can be the upper limit of the open circuite voltage in the solar cell. Optical bandgaps are determined either from the inflection point of the absorption and/or photoluminescence, or from the corss section of both. Charge transport gaps are extrcated from the inflection point of the density of states measured by ER-EIS method.

*Table S9:* Evaluated electrochemical bandgap, optical bandgap and DOS energy gap of the pristine and blend materials.

	CV:	ER-EIS:	Optical	bandgap E <sub>G</sub>	<sub>,0*</sub> (eV)
Material	Electrochemical bandgap E <sub>G,EC</sub> (eV)	DOS energy gap E <sub>G,DOS</sub> (eV)	Abs	PL	Abs/PL
AnE-Pvstat	1.60	2.38			2.03
PC <sub>60</sub> BM	2.16	2.56	1.68	1.76	
ITIC	1.72	1.63			1.61
Pa2	2.16	1.77			2.03
DaP2	1.62	1.39			1.61
TaP2	1.54	1.34			1.48
AnE-PVstat:PC60BM	1.33	1.12			2.05
AnE-PV <i>stat</i> :ITIC	1.27	1.90			1.66
AnE-PV <i>stat</i> :Pa2	1.32	1.50	1.98	1.59	
AnE-PV <i>stat</i> :DaP2	1.33	1.86			1.56
AnE-PV <i>stat</i> :TaP2	1.35	1.66			1.45

	CV:	ER-EIS: DOS energy gap E <sub>G,DOS</sub> (eV)	<b>Optical bandgap</b> E <sub>G,O*</sub> (eV)		
Material	Electrochemical bandgap E <sub>G,EC</sub> (eV)		Abs	PL	Abs/PL
PBDB-T	1.65	1.90			1.87
PCDTBT	1.61	1.92			1.92
PC <sub>70</sub> BM	2.09	1.95			-
ITIC	1.72	1.63			1.61
PBDB-T: PC <sub>70</sub> BM	1.42	1.26			1.74
PBDB-T: ITIC	1.36	1.69			1.67
PCDTBT:PC <sub>70</sub> BM	1.23	1.54			1.81
PCDTBT:ITIC	1.17	1.92			1.67

### 6.2 Electronic bandgap from jDOS and optical bandgap

For calculation of the electronic bandgap, the joint density of states (jDOS) was obtained from a convolution of the ER-EIS determined density of states (DOS) for each individual material. Finally, the onset of the jDOS was evaluated with a tangent construction, which corresponds then to the electronic gap. Because this method has been applied for the electronic gap, also the optical gap was determined in the same manner. Meaning, the onset of the optical absorption spectrum, derived from transmission and reflection measurements, was evaluated with a tangent construction at the absorption onset and yielded the optical bandgap. From these to bandgaps, the exciton binding energies are readily calculated as the difference between the optical gap and the electronic gap <sup>2</sup>. The resulting values are summarized in **Table S7**.



*Figure S45:* Joint density of states (*jDOS*) calculated by the convolution of ER-EIS data for AnE-PVstat.



*Figure S46: Joint density of states (jDOS) calculated by the convolution of ER-EIS data for PBDB-T.* 



Figure S47: Joint density of states (jDOS) calculated by the convolution of ER-EIS data for PCDTBT.



*Figure S48:* Joint density of states (jDOS) calculated by the convolution of ER-EIS data for  $PC_{60}BM$ .



*Figure S49:* Joint density of states (jDOS) calculated by the convolution of ER-EIS data for PC<sub>70</sub>BM.



Figure S50: Joint density of states (jDOS) calculated by the convolution of ER-EIS data for ITIC.

### 6.2.2 Optical bandgap from absorption edge



*Figure S51:* Optical band gap determined from the absorption onset for AnE-PVstat.



Figure S52: Optical band gap determined from the absorption onset for PBDB-T.



*Figure S53:* Optical band gap determined from the absorption onset for PCDTBT.



*Figure S54:* Optical band gap determined from the absorption onset for  $PC_{60}BM$ .



*Figure S55:* Optical band gap determined from the absorption onset for  $PC_{70}BM$ .



*Figure S56:* Optical band gap determined from the absorption onset for  $PC_{70}BM$ .

### 6.3 Exciton binding energy from optical and electronic bandgap

*Table S10:* Electronic gap determined from ER-EIS method, extracted optical bandgap from absorption edge and calculated exciton binding energy.

Materials	Electronic gap	Optical	Exciton binding energy
	[eV]	bandgap	E <sub>EB</sub>
		[eV]	[eV]
AnE-PVstat	2.60	1.92	0.68
PBDB-T	2.12	1.77	0.35
PCDTBT	2.11	1.87	0.24
PC <sub>60</sub> BM	2.94	2.00	0.94
PC <sub>70</sub> BM	2.50	1.68	0.82
ITIC	1.72	1.44	0.28

### 6.4 Electronic bandgap from joint density of states (jDOS) of blends



*Figure S57:* Joint density of states (jDOS) calculated by the convolution of ER-EIS data for AnE-PVstat:PC<sub>60</sub>BM blends.



**Figure S58:** Joint density of states (jDOS) calculated by the convolution of ER-EIS data for AnE-PVstat:ITIC blends.



*Figure S59:* Joint density of states (jDOS) calculated by the convolution of ER-EIS data for PBDB- $T:PC_{60}BM$  blends.



*Figure S60:* Joint density of states (jDOS) calculated by the convolution of ER-EIS data for PBDB-T:ITIC blends.



*Figure S61:* Joint density of states (jDOS) calculated by the convolution of ER-EIS data for  $PCDTBT:PC_{60}BM$  blends.



*Figure S62:* Joint density of states (jDOS) calculated by the convolution of ER-EIS data for PCDTBT:ITIC blends.

Table S11: Electronic gap of the blends determined from ER-EIS method

Materials	Electronic gap
	[eV]
AnE-PVstat:PC <sub>60</sub> BM	1.37
AnE-PVstat:ITIC	2.29
PBDB-T:PC <sub>70</sub> BM	2.21
PBDB-T:ITIC	1.97 & 1.00 (FR)
PCDTBT:PC <sub>70</sub> BM	2.16
PCDTBTT:ITIC	2.07 & 1.45 (FR)

### 7 CT-state energy

CTE-EL and PL spectra were taken as is and a multiple peak fit was performed by applying the least possible number of Voigt functions (convolution of Gaussian and Lorentzian line shape functions) to simulate the experimental spectra. Fittings were done with Peak Analysis Pro in Origin Pro. Subsequently, transitions of polymer, acceptor and CTE were localized by comparing them with the EL/PL spectra of the pristine materials.

# 7.1 CTE-EL and DOS energy gap



Figure S63: CTE-EL energy and DOS energy gap for PBDB-T:ITIC.



Figure S64: CTE-EL energy and DOS energy gap for PCDTBT:ITIC.

# 7.2 CTE-PL and transport gap



*Figure S65: CTE-PL energy and DOS energy gap for PBDB-T:PC*<sub>70</sub>*BM.* 



*Figure S66: CTE-PL energy and DOS energy gap for PCDTBT:ITIC.* 



*Figure S67: CTE-PL energy and DOS energy gap for PCDTBT:PC*<sub>70</sub>*BM.* 



8 CTE-PL and transport gap for AnE-PV*stat*:NFAs (PDI based) Photon Energy, *hv* [eV]

Figure S68: CTE-PL energy and DOS energy gap for AnE-PVstat: Pa2.



*Figure S69: CTE-PL energy and DOS energy gap for AnE-PVstat:DaP2.* 



Figure S70: CTE-PL energy and DOS energy gap for AnE-PVstat: TaP2.

Materials	Measurement method	CTE 1	CTE 2	CTE 3	CTE 4
		[eV]	[eV]	[eV]	[eV]
PBDB-T:ITIC	EL	1.55	1.39	1.28	1.22
PCDTBT:ITIC	EL	1.61	1.46	1.32	
PBDB-T:PC <sub>70</sub> BM	PL		1.72	1.49	1.33
PCDTBT:ITIC	PL	1.61	1.46	1.31	1.11
PCDTBT:PC <sub>70</sub> BM	PL	1.96	1.74	1.49	1.12
AnE-PVstat:Pa2	PL	1.53	1.44	1.32	1.23
AnE-PVstat:DaP2	PL	1.48	1.41	1.32	1.24
AnE-PVstat:TaP2	PL	1.44	1.36	1.29	1.22

# 9 Determination of sub-bandgap EQE

**Table S13:** Overview of  $E_{CTE}$  of sub-bandgap EQE CTE transition or Urbach energies  $E_U$ , with confidence intervals of one standard deviation.

Photovoltaic blends	CTE-Subgap EQE	E <sub>CTE-EQE</sub> [eV]	Exponential Urbach Tail	Urbach Energy [meV]
AnE-PVstat:PC <sub>60</sub> BM	$\checkmark$	1.51		
AnE-PVstat:ITIC		-	$\checkmark$	32.4
PBDB-T:PC <sub>70</sub> BM	√	1.42		
PBDB-T:ITIC		-	$\checkmark$	28.3
PCDTBT:PC <sub>70</sub> BM	√	1.48		
PCDTBT:ITIC		-	√	33.5

**Table S14:** Overview of  $E_{CTE}$  of sub-bandgap EQE CTE transition or Urbach energies  $E_U$ , with confidence intervals of one standard deviation.  $E_{CTE}$  values in brackets were determined from an alternative linear regression recently published by Tvingstedt et al.

Photovoltaic blends	CTE-Subgap EQE	E <sub>CTE-EQE</sub> [eV]	Exponential Urbach Tail	Urbach Energy [meV]
AnE-	$\checkmark$	1.51		
PVstat:PC <sub>60</sub> BM		(1.53 +/- 0.09)		
AnE-PVstat:ITIC		-	$\checkmark$	32.4
				32.4 +/- 0.5
PBDB-T:PC <sub>70</sub> BM	$\checkmark$	1.42		
		(1.45 +/- 0.07)		
PBDB-T:ITIC		-	$\checkmark$	28.3
				28.35 +/- 0.24
PCDTBT:PC <sub>70</sub> BM	$\checkmark$	1.48		
		(1.49 +/- 0.11)		
PCDTBT:ITIC		-	$\checkmark$	33.5
				33.5+/-0.7

## The fitting routines CT Energy fitting from photovoltaic subgap EQE

Method 1 (original):

•

- Nonlinear least-square fitting of a reduced Gaussian distribution to the CT part of the subgap EQE spectrum
- Levenberg-Marquard algorithm
- Fit limits and starting values chosen "by hand"

$$EQE_{PV,CT} = \frac{A}{E\sqrt{4\pi\lambda k_B T}} \exp\left(-\frac{(E_{CT} + \lambda - E)^2}{4\lambda k_B T}\right)$$

- Amplitude A, Energy E, Reorganisation Energy  $\lambda$ , CT Energy  $E_{CT}$ , thermal Energy  $k_B T$
- Pros: direct model-to-data fit

Fitting equation:

• Cons: We cannot determine a fitting error, as numerical methods for their determination only apply for functions with linear fitting coefficients. For a non-linear, reduced Gaussian function,

they are not reliable -> so, don't believe the errors for method 1, they are probably much higher in reality.

Method 2:

•

• Numerical recalculation of the subgap EQE spectrum, so that the Gaussian distribution resolves into a straight line

$$\frac{d}{dE}\ln\left(EQE_{PV}(E)\times E\right) = \frac{E_{CT}+\lambda}{2\lambda k_BT} - \frac{E}{2\lambda k_BT} = B - C \times E$$

• This line is then fitted by linear regression (which is the mathematically sound method).

λ

• 
$$\lambda$$
 is extracted from C, and  $E_{CT}$  from  $\frac{B}{C}$ 

- Pros: it is much easier to fit a line (set the correct fitting range etc.), we get good estimates for the parameter range (errors), which can further be transformed to parameters errors for  $\lambda$  and  $E_{CT}$
- Cons: requires numerical deviation, which may be influenced by noise (so pre-averaging may be required)

Urbach Energy and Gap Fitting from subgap EQE spectra

• Fit of a straight line to  $\ln (EQE_{PV}(E,T))$  in the exponential tail region, and average value of the "pre-gap" plateau (to determine cross-point with exponential tail)

*Table S15:* Overview of  $E_{CTE}$  of sub-bandgap EQE CTE and reorganization energies evaluated by two different methods.

	PBDB-T:PC <sub>70</sub> BM		AnE-PVsta	AnE-PVstat:PC <sub>60</sub> BM		C:PC <sub>70</sub> BM
	Method 1	Method 2	Method 1	Method 2	Method 1	Method 2
E <sub>CT</sub>	1.423 eV +/- 15 meV	1.45 eV +/- 70 meV	1.508 eV +/- 5 meV	1.53 +/- 90 meV	1.481 +/- 6 meV	1.49 eV +/- 110 meV
$\lambda_{CT}$	480 +/- 60 meV	390 +/- 15 meV	220 +/- 40 meV	288 +/- 13 meV	332 +/- 30 meV	303 +/- 16 meV
	AnE-PVs	tat:ITIC	PCDTB	T:ITIC	PBDB-	T:ITIC
E <sub>U</sub>	32.4 +/- 0	0.5 meV	33.5 +/-	0.7 meV	28.35 +/-	0.24 meV
E <sub>gap</sub>	1.67 eV +/- 50 meV		1.67 eV +	/- 60 meV	1.662 +/-	- 27 meV

# **10** Electron spin resonance

In this section, electron spin resonance (ESR) signals for AnE-PV*stat*,  $PC_{60}BM$  and ITIC as single species in frozen solutions and in films are shown.



*Figure S71: X-band LESR spectra of pristine AnE-PVstat in the frozen liquid solution, and solid film state recorded at 77 K temperature.* 



*Figure S72:* X-band LESR spectra of pristine  $PC_{60}BM$  in the frozen liquid solution, and solid film state recorded at 77 K temperature.



*Figure S73:* X-band LESR spectra of pristine ITIC in the frozen liquid solution, and solid film state recorded at 77K temperature.

# **11** Transient absorption



*Figure S74: Ps-ns TA spectra of AnE-PVstat:ITIC (1.29 \muJ/cm2) after excitation wavelength at 700 nm (short delay). Right: Charge carrier dynamics probed in the spectral window of 2.05-2.37 eV.* 



*Figure S75:* The comparison of the TA signal at 5 ns to the TA signal at 500 fs. Fast decay of the excited states leads to significant geminate recombination in the AnE-PVstat:ITIC blends.

# 12 Jablonski diagram



**Figure S76:** Jablonski diagram of occupied states and observed transitions detected by ODMR in the blend systems of a) AnE-PVstat: $PC_{60}BM$  and b) AnE-PVstat:ITIC. Occupied states and possible transitions are represented by solid lines and arrows, while improbable ones are represented by dotted lines and arrows, respectively. The intended steps to the generation to free charge carriers are first charge transfer from acceptor or donor to an interfacial CT state, followed by potentially thermally activated ( $k_BT$ ) charge separation (blue).

# **13** Density functional theory (DFT)



**Figure S77:** Frontier molecular orbitals of ITIC displayed as isosurface for  $|\psi_{MO}|=0.02$  with their energies as calculated by DFT using the hybrid functional B3LYP and the Gaussian basis-set 6-311G\*\*.



**Figure S78:** Frontier molecular orbitals of the model PV-AnE-PV oligomer displayed as isosurface for  $|\psi_{MO}|=0.02$  with their energies as calculated by DFT using the hybrid functional B3LYP and the Gaussian basis-set 6-311G(2d,p).

# 14 Infrared transition moment orientational analysis

#### 14.1 Experimental

FTIR spectra were recorded in transmission mode with a spectral resolution of 2 cm<sup>-1</sup> by means of a Bio-Rad FTS 6000 FTIR spectrometer equipped with an UMA-500 infrared microscope and a liquid nitrogencooled Mercury Cadmium Telluride (MCT) detector (Kolmar Technologies). Sample films were prepared by spin coating on an IR-transparent barium fluoride substrate, for pristine materials 3.6 wt.-% material was dissolved in chlorobenzene (CB) and spin casted with 800 rpm spin frequency. In case of blend, donor:acceptor ratio was 1:1, yielded final concentration of 1.8 wt.-% of each component in the blend.

In order to examine IR-TMOA measurements, the collimated IR beam was transmitted through the sample film while a set of different polarizer positions  $\varphi$  was scanned and a home built tilting device kept the film fixed at a constant inclination  $\vartheta$  (**Figure S77**). After one set of polarization angles was scanned through at one fixed inclination the sample was tilted further to the next inclination angle, affecting the projection of the transition dipole moment onto the plane of polarization. Due to systematically scanning the IR absorption depending on the polarization *and* inclination, the tensor of absorption can be evaluated in 3-dimensional space and the principal axes and principal values of absorption can be determined. A representative sketch of the measurement geometry is provided in **Figure S77**. A detailed description and applications can be found in the literature<sup>3-6</sup>.

In the case of the examined samples it appeared that all studied transition moments (TMs) are rotationally symmetric distributed with respect to the film normal (z-axis). In this case we can simplify the analysis. One principal axis of absorption is identical with the z-axis, whereas the remaining other two principal axes (x and y axes) are parallel to the film. Hereafter we denote the principal value of absorption parallel to the film normal and parallel to the film plane as  $A_{\perp} (=A_z)$  and  $A_{\parallel} (=1/2 \cdot (A_x + A_y))$ , respectively. Because of the rotational symmetry, the TMs can be modeled as equally distributed on the surface of a cone centered at the z-axis and exhibiting an opening angle  $\Theta$ , given by

$$\cos \Theta = \sqrt{\frac{A_{\perp}}{A_{\perp} + 2A_{\parallel}}}$$



**Figure S79:** (a) Measurement geometry of an IR-TMOA experiment. The sample film supported though a  $BaF_2$  substrate is inclined at an angle  $\Im$  while at the same time the polarization dependence of the projection of the transition dipole moments onto the plane of polarization ( $\varphi$ ) is measured. Because the sample-fixed coordinate system (x,y,z) is tilted relative to the laboratory frame (x',y',z'), the transition dipole moment tensor can be determined for different molecular moieties in 3-dimensional space . (b) As a consequence of symmetry, the IR-active transition moments (TMs) can be modeled as equally distributed on the surface of a cone with an opening angle  $\Theta$  centered along the z-axis.

As a consequence of the small film thickness, spectral distortion from atmospheric water and interference effects from parallel surfaces are more pronounced than for thicker films. Thus, adequate filtering was necessary (**Figure S78 a**). Because the spectral region of the C=O stretching vibration (**Figure S78 c**) is overlapping with the region where atmospheric water is absorbing, removing of the water spikes and filtering was necessary. In contrast, C=N stretching absorbs at higher wavenumbers where interference from parallel surfaces is less pronounced and no interfering from atmospheric water occurs. Thus, the raw data could be used for analyzing this spectral region.



**Figure S80:** (a) Infrared spectra of AnE-PVstat:ITIC at normal incidence ( $\mathcal{G} = 0^\circ$ ,  $\varphi = 0^\circ$ ). (b) The  $C \equiv N$  stretching vibration is not affected by absorption of atmospheric water or interference from parallel surfaces, and thus the raw data can be used. (c) The region of C=O stretching absorption overlaps with that of absorption of atmospheric water, which is why filtering was applied (Savitzky-Golay: polynomial of degree three, windows of 11 points). Only where necessary corrected data is used for analysis; otherwise raw data is employed.

#### 14.1.1 CN stretching

In the spectra of samples containing ITIC a narrow absorption band is visible at around 2220 cm<sup>-1</sup>, which arises from the absorption of the symmetric and antisymmetric C=N stretching mode<sup>7</sup>. Simulations (ORCA program package<sup>8-9</sup>, B3LYP functional, 6-31G(2d2p) basis set<sup>10-19</sup>) predict that the high frequency peak ( $\bar{\nu} = 2218 \text{ cm}^{-1}$ ) contributing to this band arises from the symmetric C=N stretching vibration v<sub>s</sub>(C=N), whereas the low-frequency peak ( $\bar{\nu} = 2208 \text{ cm}^{-1}$ ) is caused by the antisymmetric stretching mode v<sub>as</sub>(C=N) (**Figure S79**). The shoulder at the low-frequency side is probably resulting from a combination of conjugated CC stretching vibrations from aromatic rings<sup>7</sup>.



**Figure S81:** The  $C \equiv N$  stretching band at different inclination angles ( $9 = 60^\circ$ ,  $30^\circ$ , and  $0^\circ$ ) and polarization angles ( $\varphi = 0^\circ$ : s-polarization;  $\varphi = 90^\circ$ : p-polarization) along with the individual peaks (modeled as Gaussians) contributing to this band.



*Figure S82:* Inclination and polarization-dependent absorption of the symmetric  $C \equiv N$  stretching mode  $(v_s(C \equiv N), \overline{v} = 2218 \text{ cm}^{-1}, \text{ orange squares})$  and the absorption of the fitted model distribution of TMs (red line).

**Table S16:** Parameters extracted from IR-TMAO for  $v_s(C \equiv N)$  and the derived inclination of the TMs. The wavenumber-specific refractive index of the BaF<sub>2</sub> substrate is assumed as n = 1.47 according to Querry<sup>20</sup>. The inclination is accurate up to  $\pm 3^{\circ}$ .

Principal value of absorption	
$A_x$	$0.09\pm0.01$
$A_y$	$0.08\pm0.01$
$A_z$	$0.03\pm0.01$
A <sub>II</sub>	$0.08\pm0.01$
$A_{\perp}$	$0.03\pm0.01$
Inclination of TMs	75°
Θ	(73° - 78°)



line).

**Table S17:** Parameter extracted from IR-TMAO for  $v_{as}(C \equiv N)$  and the derived inclination of the TMs. The wavenumber-specific refractive index of the BaF<sub>2</sub> substrate is assumed as n = 1.47 according to Querry<sup>20</sup>. The inclination is accurate up to  $\pm 3^{\circ}$ .

Principal value of	
absorption	
$A_{x}$	$0.03\pm0.01$
$A_y$	$0.03\pm0.01$
$A_z$	$0.01\pm0.01$
$A_{\parallel}$	$0.03 \pm 0.01$
$A_{\perp}$	$0.01\pm0.01$
Inclination of TMs	90°
Θ	

#### 14.1.2 CO stretching

In the IR spectra, a narrow peak is evident at  $\bar{\nu} = 1702 \ cm^{-1}$  which arises from the absorption of the C=O group in ITIC (**Figure S78**). It is modeled with a single pseudo-Voigt function; a slightly asymmetric Gaussian is employed as auxiliary peak (**Figure S82**). Referred to the literature, peaks originating from C=O stretching are generally narrow, even when the C=O group is incorporated into hydrogen bonding. Thus, we exclude C=O stretching as the origin of the broad auxiliary peak.



**Figure S84:** The C=O stretching band at different inclination angles ( $9 = 60^\circ$ ,  $30^\circ$ , and  $0^\circ$ ) and polarization angles ( $\varphi = 0^\circ$ : s-polarization;  $\varphi = 90^\circ$ : p-polarization) along with the individual peaks contributing to this band. Peaks modeled as a pseudo-Voigt or a slightly asymmetric Gaussian.



*Figure S85:* Inclination and polarization-dependent absorption of the C=O stretching mode (v(C=O),  $\bar{v} = 1702 \text{ cm}^{-1}$ , green squares) and the absorption of the fitted model distribution of TMs (red line).

**Table S18:** Parameters extracted from IR-TMAO for v(C=O) and the derived inclination of the TMs. The wavenumber-specific refractive index of the BaF<sub>2</sub> substrate is assumed as n = 1.46 according to Querry<sup>20</sup>. The inclination is accurate up to  $\pm 3^{\circ}$ .

$0.21\pm0.01$
$0.21\pm0.01$
$0.04\pm0.01$
$0.21\pm0.01$
$0.04\pm0.01$
83°
(80° – 86°)

#### 14.1.3 Ring stretching

When comparing spectra of AnE-PV*stat*:ITIC with that of PBDB-T:ITIC we noticed a signal at around  $\bar{\nu} \approx 1500$  and  $1200 \text{ cm}^{-1}$  arising solely from AnE-PV*stat*. (Figure S84 a and Figure S86 a). Simulations (ORCA program package<sup>8-9</sup>, B3LYP functional, 6-31G(2d,2p) basis set<sup>10-19</sup>) predict that these peaks originate from C-O-C stretching and ring bending modes in the direction along the 1-4-positions at the 1,4-bis(octyloxy)benzene. In addition, these peaks correlate with the absorption of 1,4-di(methoxy)benzene<sup>21</sup>.



**Figure S86:** (a) Spectra of AnE-PVstat:ITIC and PBDB-T:ITIC ( $9 = 0^\circ$ ,  $\varphi = 0^\circ$ ) scaled accordingly in order to assign the peaks at  $\overline{\nu} = 1503 \text{ cm}^{-1}$  as arising from AnE-PVstat. (b) Fit as a sum of Gaussians.



 $\overline{\nu} = 1503 \text{ cm}^{-1}$ , olive squares) and the absorption of the fitted model distribution of TMs (red line).

**Table S19:** Parameters extracted from IR-TMAO for the ring stretching mode at  $\overline{v} = 1503 \text{ cm}^{-1}$  and the derived inclination of the TMs. The wavenumber-specific refractive index of the BaF<sub>2</sub> substrate is assumed as n = 1.45 according to Querry<sup>20</sup>. The inclination is accurate up to  $\pm 5^{\circ}$ .

Principal value of	
absorption	
$A_{x}$	$0.21\pm0.01$
$A_y$	$0.19\pm0.01$
$A_z$	$0.01\pm0.02$
$A_{\parallel}$	$0.20\pm0.01$
$A_{\perp}$	$0.01\pm0.02$
Inclination of TMs	87°
Θ	



*Figure S88:* (a) Spectra of AnE-PVstat:ITIC and PBDB-T:ITIC ( $\mathcal{G} = 0^\circ$ ,  $\varphi = 0^\circ$ ) scaled accordingly in order to assign peaks at around  $\bar{\nu} \approx 1200 \text{ cm}^{-1}$  as arising from AnE-PVstat. (b) Fit as a sum of Gaussians.



 $\bar{\nu} = 1184 \text{ cm}^{-1}$ , dark cyan squares) and the absorption of the fitted model distribution of TMs (red line).

**Table S20:** Parameters extracted from IR-TMAO for the ring stretching mode at  $\overline{\nu} = 1184 \text{ cm}^{-1}$  and the derived inclination of the TMs. The wavenumber-specific refractive index of the BaF<sub>2</sub> substrate is assumed as n = 1.44 according to Querry<sup>20</sup>. The inclination is accurate up to  $\pm 5^{\circ}$ .

Principal value of	
absorption	
$A_{x}$	$0.06\pm0.01$
$A_y$	$0.04\pm0.01$
$A_z$	$0.01\pm0.01$
$A_{\parallel}$	$0.05\pm0.01$
$A_{\perp}$	$0.01\pm0.01$
Inclination of TMs	90°
Θ	



*Figure S90:* Inclination and polarization-dependent absorption of the ring stretching mode ( $\bar{\nu} = 1204 \text{ cm}^{-1}$ , dark cyan squares) and the absorption of the fitted model distribution of TMs (red line).

**Table S21:** Parameters extracted from IR-TMAO for the ring stretching mode at  $\overline{v} = 1204 \text{ cm}^{-1}$  and the derived inclination of the TMs. The wavenumber-specific refractive index of the BaF<sub>2</sub> substrate is assumed as n = 1.44 according to Querry<sup>20</sup>. The inclination is accurate up to  $\pm 5^{\circ}$ .

Principal value of	
absorption	
$A_x$	$0.63\pm0.01$
$A_y$	$0.59\pm0.01$
$A_z$	$0.06\pm0.04$
$A_{\parallel}$	$0.61\pm0.01$
$A_{\perp}$	$0.06\pm0.01$
Inclination of TMs	86°
Θ	

As a consequence of the greater integrated absorbance of the peak at  $\overline{\nu} = 1204 \ cm^{-1}$  compared to the peak at  $\overline{\nu} = 1184 \ cm^{-1}$ , we assess the inclination of the TMs determined on the basis of the first vibration as more trustworthy than the inclination determined in the basis of the second vibration.

#### 14.1.4 Anthracene deformation

When comparing spectra of AnE-PV*stat*:ITIC with that of PBDB-T:ITIC we noticed a signal at  $\bar{\nu} = 1423 \ cm^{-1}$  arising solely from AnE-PVstat (**Figure S89a**). Simulations (ORCA program package<sup>8-9</sup>, B3LYP functional, 6-31G(2d,2p) basis set<sup>10-19</sup>) predict that this peak originates from anthracene deformation. The TM of this vibration is oriented parallel to the anthracene plane and perpendicular to the polymer backbone<sup>22-23</sup>. In addition, these peaks correlate with the absorption of 9,10-dimethylanthracene and 9,10-bis(phenylmethyl)-anthracene<sup>24-25</sup>.



*Figure S91:* (a) IR spectra of AnE-PVstat:ITIC and PBDB-T:ITIC ( $9 = 0^\circ$ ,  $\varphi = 0^\circ$ ) scaled accordingly in order to assign the peak at  $\overline{\nu} = 1423 \text{ cm}^{-1}$  as arising from AnE-PVstat. (b) Fit as a sum of Gaussians.

![](_page_70_Figure_5.jpeg)

 $\bar{\nu} = 1423 \text{ cm}^{-1}$ , dark blue squares) and the absorption of the fitted model distribution of TMs (red line).

**Table S22:** Parameters extracted from IR-TMAO for the ring stretching mode at  $\overline{v} = 1423 \text{ cm}^{-1}$  and the derived inclination of the TMs. The wavenumber-specific refractive index of the BaF<sub>2</sub> substrate is assumed as n = 1.45 according to Querry<sup>20</sup>. The inclination is accurate up to  $\pm 5^{\circ}$ .

Principal value of	
absorption	
$A_{x}$	$0.06\pm0.01$
$A_{\gamma}$	$0.05\pm0.01$
$A_z$	$0.03\pm0.01$
$A_{\parallel}$	$0.05\pm0.01$
$A_{\perp}$	$0.03\pm0.01$
Inclination of	71°
TMs Θ	

We would like to bring to the readers' notice that the angle of inclination of a particular TM represents an *averaged* value over all molecules exhibiting the vibrational mode according to the TM. Because there is only one anthracene part within one repeat unit, the angle of inclination describes the tilt of the anthracene part. In contrast, there are three 1,4-disubstituted benzene rings within one repeat unit, and thus this angle of inclination represents an average value over all three rings. Therefore, a potential tilt between the rings can easily induce a difference between the inclination of the anthracene part and the averaged inclination of the benzene rings. Because of this fact we focus on the anthracene vibration at  $\bar{\nu} = 1423 \text{ cm}^{-1}$  for discussing a potential alignment (cf. **13.4 Discussion and Summary**).

In order to determine the inclination of the anthracene moiety in the direction along the polymer backbone, we are seeking for a vibrational mode with a TM parallel to the backbone. However, an absorption band of such a mode cannot be isolated within the IR spectrum, because of the similarity of the different materials of the blend. Instead, we make use of a combined deformation of the anthracene part and adjacent benzene rings (simulation: ORCA program package<sup>8-9</sup>, B3LYP functional, 6-31G(2d,2p) basis set<sup>10-19</sup>) giving rise to an absorption band at around  $\bar{\nu} \approx 1030 \text{ cm}^{-1}$  (Figure S91 a). The TM of this mode is oriented parallel to the polymer backbone. IR-TMOA reveals that all 3 peaks contributing to this band are oriented parallel to the film plane ( $\Theta = 90^\circ$ , Table S21).


*Figure S93:* (a) IR spectra of of AnE-PVstat:ITIC and PBDB-T:ITIC ( $9 = 0^\circ$ ,  $\varphi = 0^\circ$ ) scaled accordingly in order to assign the band at around  $\bar{\nu} \approx 1030 \text{ cm}^{-1}$  as arising from AnE-PVstat. (b) Fit of this band as a sum of Gaussians.



*Figure S94:* Inclination and polarization-dependent absorption (sum of the three peaks) of the anthracene and benzene deformation band ( $\overline{\nu} \approx 1030 \text{ cm}^{-1}$ , brown squares) and the absorption of the fitted model distribution of TMs (green line).

**Table S23:** Parameters extracted from IR-TMAO for the deformation vibrations at around  $\bar{\nu} \approx 1030 \text{ cm}^{-1}$  and the derived inclinations of the TMs. The wavenumber-specific refractive index of the BaF<sub>2</sub> substrate is assumed as n = 1.43 according to Querry<sup>20</sup>. The inclination is accurate up to  $\pm 5^{\circ}$ .

Principal value of	$\bar{\nu} = 1019 \ cm^{-1}$	$\bar{\nu} = 1031 \ cm^{-1}$	$\bar{\nu} = 1044 \ cm^{-1}$
absorption			
$A_{x}$	$0.03\pm0.01$	$0.14\pm0.01$	$0.04\pm0.01$
$A_y$	$0.03\pm0.01$	$0.14\pm0.01$	$0.05\pm0.01$
$A_z$	$0.01\pm0.01$	$0.01\pm0.01$	$0.01\pm0.01$
$A_{\parallel}$	$0.03\pm0.01$	$0.14\pm0.01$	$0.04\pm0.01$
$A_{\perp}$	$0.01\pm0.01$	$0.01\pm0.01$	$0.01\pm0.01$
Inclination of TMs	90°	90°	<u>90</u> °
Θ			

## 14.2 PBDB-T:ITIC

Similar to the case of AnEPV*stat*:ITIC, the spectra of PBDB-T:ITIC have to be corrected for interference caused by parallel surfaces and absorption from atmospheric water (**Figure S93**). Only where necessary corrected data is used for analysis; otherwise raw data is employed.



**Figure S95:** Infrared spectra of PBDB-T:ITIC at normal incidence ( $9 = 0^\circ$ ,  $\varphi = 0^\circ$ ). Because of the small film thickness, interference effects appear in the raw data (Savitzky-Golay: polynomial of degree three, windows of 11 points).

#### **CN** stretching

Similar to the case of AnE-PV*stat*:ITIC a narrow absorption band at around 2220 cm<sup>-1</sup> is visible for PBDB-T:ITIC. It arises from the absorption of the symmetric and antisymmetric C=N stretching mode<sup>7</sup> at  $\bar{\nu} = 2218 \ cm^{-1} (v_s(C=N))$  and  $\bar{\nu} = 2212 \ cm^{-1} (v_{as}(C=N))$ , respectively (**Figure S94**). The shoulder at the low-frequency side is probably resulting from combination of conjugated CC stretching vibrations from aromatic rings<sup>7</sup>.



**Figure S96:** The  $C \equiv N$  stretching band at different inclination angles ( $9 = 60^\circ$ ,  $30^\circ$ , and  $0^\circ$ ) and polarization angles ( $\phi = 0^\circ$ : s-polarization;  $\phi = 90^\circ$ : p-polarization) along with the individual peaks (modeled as Gaussians) contributing to this band.



*Figure S97:* Inclination and polarization-dependent absorption of the symmetric  $C \equiv N$  stretching mode  $(v_s(C \equiv N), \overline{\nu} = 2218 \text{ cm}^{-1}, \text{ orange squares})$  and the absorption of the fitted model distribution of TMs (red line).

**Table S24:** Parameters extracted from IR-TMAO for  $v_s(C \equiv N)$  and the derived inclination of the TMs. The wavenumber-specific refractive index of the BaF<sub>2</sub> substrate is assumed as n = 1.47 according to Querry<sup>20</sup>. The inclination is accurate up to  $\pm 3^{\circ}$ .

Principal value of	
absorption	
$A_{x}$	$0.09\pm0.01$
$A_y$	$0.09\pm0.01$
$A_z$	$0.03\pm0.01$
$A_{\parallel}$	$0.09\pm0.01$
$A_{\perp}$	$0.03\pm0.01$
Inclination of TMs	78°
Θ	(76° - 80°)



**Figure S98:** Inclination and polarization-dependent absorption of the antisymmetric  $C \equiv N$  stretching mode  $(v_{as}(C \equiv N), \bar{\nu} = 2212 \text{ cm}^{-1}, \text{ orange squares})$  and the absorption of the fitted model distribution of TMs (red line).

**Table S25:** Parameters extracted from IR-TMAO for  $v_{as}(C \equiv N)$  and the derived inclination of the TMs. The wavenumber-specific refractive index of the BaF<sub>2</sub> substrate is assumed as n = 1.47 according to Querry<sup>20</sup>. The inclination is accurate up to  $\pm 3^{\circ}$ .

Principal value of	
absorption	
$A_x$	$0.11\pm0.01$
$A_y$	$0.10\pm0.01$
$A_z$	$0.01\pm0.06$
$A_{\parallel}$	$0.11 \pm 0.01$
$A_{\perp}^{"}$	$0.01 \pm 0.05$
Inclination of TMs	90°
Θ	

### 14.2.1 CO stretching

In the IR spectra of PBDB-T:ITIC two narrow peaks are evident at  $\bar{\nu} = 1703$  and 1648 cm<sup>-1</sup> (Figure S93), which originate from the absorption of the C=O group in ITIC and PBDB-T, respectively<sup>7</sup>. They are modeled through pseudo-Voigt functions and a slightly asymmetric Gaussian as an auxiliary peak (Figure S97, compare with Figure S82).



**Figure S99:** The C=O stretching bands at different inclination angles ( $9 = 60^\circ$ ,  $30^\circ$ , and  $0^\circ$ ) and polarization angles ( $\varphi = 0^\circ$ : s-polarization;  $\varphi = 90^\circ$ : p-polarization) along with the individual peaks (modeled as pseudo-Voigt profiles, PsdVoigt) contributing to both bands.



 $\bar{v} = 1703 \text{ cm}^{-1}$ , green squares) in ITIC along with the absorption of the fitted model distribution of TMs (red line).

**Table S26:** Parameters extracted from IR-TMAO for v(C=O) in ITIC and the derived inclination of the TMs. The wavenumber-specific refractive index of the BaF<sub>2</sub> substrate is assumed as n = 1.46 according to Querry<sup>20</sup>. The inclination is accurate up to  $\pm 3^{\circ}$ .

Principal value of absorption	
- A <sub>x</sub>	$0.28\pm0.01$
$A_y$	$0.27\pm0.01$
Az	$0.01\pm0.02$
$A_{\parallel}$	$0.28\pm0.01$
$A_{\perp}$	$0.01\pm0.02$
Inclination of TMs	90°
Θ	



**Table S27:** Parameters extracted from IR-TMAO for v(C=O) in PBDB-T and the derived inclination of the TMs. The wavenumber-specific refractive index of the BaF<sub>2</sub> substrate is assumed as n = 1.46 according to Querry<sup>20</sup>. The inclination is accurate up to  $\pm 3^{\circ}$ .

Principal value of	
absorption	
A <sub>x</sub>	$0.29\pm0.01$
$A_y$	$0.28\pm0.01$
$A_z$	$0.01\pm0.03$
$A_{II}$	$0.29 \pm 0.01$
$A_{\perp}^{"}$	$0.01 \pm 0.03$
Inclination of TMs	90°
Θ	

#### 14.3 Discussion and summary

In order to calculate the inclination of the indanone plane its molecular structure has been simulated by means of the ORCA program package with B3LYP functional and 6-31G(2d,2p) basis set (**Figure S 97 a**)<sup>8-19</sup>. First, we defined *vector 1* ( $v_1$ ) as a unit vector parallel to the TM of  $v_s(C=N)$  and *vector 2* ( $v_2$ )as a unit vector parallel to the TM of v(C=O). The direction of  $v_1$  is given through the sum of the two vectors connecting atoms 21 with 23 and 22 with 24 (angle bisector of the C=N bonds), whereas the direction of  $v_1$  is given through the vector connecting atoms 11 and 15 (C=O bond). On the basis of the scalar product of  $v_1$  and  $v_2$ ,

 $v_1 \cdot v_2 = |v_1| |v_2| \cos{(\omega)}$ 

with  $|v_1|$ ,  $|v_2|$ , and  $\omega$  as the length of  $v_1$  and  $v_2$  and the angle between these two vectors, respectively, we calculated an angle of  $\omega$ =139° between  $v_1$  and  $v_2$  (Figure S100 b).

Second, we calculated the normal vector of the indanone plane (n) making use of the vector cross product of  $v_1$  and  $v_2$ ,

$$n = v_1 \times v_2$$

and spherical coordinates ( $r_1$ ,  $\Phi_1$ ,  $\Theta_1$ ,  $r_2$ ,  $\Phi_2$ ,  $\Theta_2$ ), with  $r_i$  as the length of vector i,  $\Phi_i$  the polar angle and  $\Theta_i$  the azimuthal angle of vector i<sup>26</sup>. We can identify the particular azimuthal angles as the inclination angles of the TMs (**Table S 10, S 12, S 18, S 20**) and the polar angles are either 0° or 139°. Furthermore, we set the length of the vectors equal to 1, because we are only interested in the direction of the plane's normal vector.



*Figure S102:* (*a*) *Simulated structure of the indanone unit (B3LYP, 6-31G(2d,2p) with atom numbers indicated) and (b) scheme of vectors 1 and 2 used in order to calculate the indanone plane's normal vector.* 

In the case of the transition moments (TMs) originating from vibrations at ITIC in AnE-PV*stat*:ITIC,  $v_s(C\equiv N)$  exhibits an angle of 15° to the substrate ( $\Theta = 75^\circ$ , **Figure S101**), whereas v(C=O) shows an angle of 7° to the substrate ( $\Theta = 83^\circ$ ). As a consequence of the symmetry of absorption, we cannot separate between an upward ( $\Theta > 0$ ) or downward orientation ( $\Theta < 0$ ) of a transition moment. Thus, we distinguish

between all four possible cases, as stated in **Table S26**. Two cases become evident, the normal vector of the indanone plane is inclined either by 29° relative to the film normal (*z* axis) or by 16°, which indicates that the indanone plane is tilted by 29° or 16° out of the film plane (*x-y* plane), respectively. Having the inclination of the anthracene unit ( $\Theta = 19^\circ$ ) and the fast geminate recombination in mind, the value of  $\Theta = 16^\circ$  is most likely and supported by results from other measurements, whereas the value of  $\Theta = 29^\circ$  can be neglected.

$\Theta_1$ [°]	$\Theta_2$ [°]	Inclination of
		indanone plane [°]
+75	+83	29
-75	+83	16
+75	-83	16
-75	-83	29

**Table S28:** Calculated inclination of the indanone plane's normal vector in dependence of the particular inclination angles of the TMs.

Concerning the anthracene deformation, the inclination of the TM perpendicular to the backbone resulted in  $\Theta = 71^{\circ}$ , which means this TM is tilted by 19° relative to the substrate (**Figure S101**). On the other hand, the combined deformation vibration of the anthracene and 1,4-disubstituted benzene rings at around  $\bar{\nu} \approx 1030 \text{ cm}^{-1}$  with the TM along the backbone resulted in a flat-on alignment ( $\Theta = 90^{\circ}$ ) of this TM. Thus, the anthracene plane is tilted by 19° relative to the substrate, and consequently the molecular planes formed through the indanone and the anthracene parts are *parallel* within the measurement accuracy.

For the ring stretching vibrations at the 1,4-disubstituted benzene rings in AnE-PV*stat*, the TMs are inclined at 4° relative to the substrate ( $\Theta = 86^\circ$ ). Because of the greater integrated absorbance, we focus on the TMs of the vibration at  $\overline{\nu} = 1204 \ cm^{-1}$  and neglect the TMs of the vibration at  $\overline{\nu} = 1184 \ cm^{-1}$ . Moreover, one repeat unit comprises 3 different 1,4-disubstituted benzene rings. Thus, the inclination we measured is influenced through the particular inclination of each of these rings, which explains the difference to the orientation of the anthracene or indanone plane.



*Figure S103:* Inclination of the examined TMs (solid arrows) and indicated planes' normal vectors (dotted arrows) for AnE-PVstat:ITIC. v(C=O): green solid,  $v_s(C=N)$ : orange solid, indanone plane: red dotted, anthracene deformation: blue solid, anthracene plane: blue dotted, v(COC): cyan solid, 1,4-disubstituted benzene ring plane: cyan dotted.

In the case of PBDB-T:ITIC, the TMs of  $v_s(C=N)$  and v(C=O) exhibit an angle of 12° and 0° to the substrate ( $\Theta = 78^\circ$  and 90°), respectively (**Figure S102**). Thus, the normal vector of the indanone plane is inclined by 18° relative to the film normal, which is tantamount with the tilt of the indanone plane relative to the film plane. Since one TM is parallel to the substrate ( $\Theta = 90^\circ$ ), all possible cases of an upward or downward orientation of the other TM results in the same inclination of the indanone plane (**Table S27**). On the other hand, the inclination of the TMs connected to v(C=O) in PBDB-T amount 90°. This indicates a flat on orientation of this unit.

 $\Theta_1$ [°]	$\Theta_2 [\circ]$	Inclination of
 		indanone plane [°]
 +78	+90	18
-78	+90	18
+78	-90	18
-78	-90	18

*Table S29:* Calculated inclination of the indanone plane's normal vector in dependence of the particular inclination angles of the TMs.



**Figure S104:** Inclination of the examined TMs (solid arrows) and indicated planes' normal vectors (dotted arrows) for PBDB-T:ITIC. v(C=O): green solid,  $v_s(C\equiv N)$ : orange solid, indanone plane: red dotted, v(C=O): blue solid, PBDB-T plane: blue dotted.

In summary, the indanone part in ITIC and the anthracene part in AnE-PVstat are in parallel alignment ( $\Theta = 16^{\circ}$  vs. 19°), whereas the indanone part in ITIC and PBDB-T are tilted ( $\Theta = 18^{\circ}$  vs. 0°). As a consequence,  $\pi - \pi$  stacking is hindered in PBDB T:ITIC, which allows for percolation pathways. In AnE-PV*stat*:ITIC, instead, donor and acceptor molecules undergo  $\pi - \pi$  stacking which is in agreement with the parallel orientation of the distinct subunits determined individually by means of IR-TMOA and experimental findings as the pronounced donor quenching or the fast geminate recombination. Thus, the interpretation of the intermixing of donor and acceptor molecules is highly supported.

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