Supporting Information

Light Induced Quasi-Fermi-Level Splitting in Molecular Semiconductor

Alloys

Nakul Jain^a, Rishabh Saxena^{a, #}, Sumukh Vaidya^a, Wenchao Huang^c, Adam Welford^c,

Christopher R McNeill^c and Dinesh Kabra^a*

^aDepartment of Physics, Indian Institute of Technology Bombay, Powai, Mumbai-400076, India.

^bDepartment of Electrical Engineering, Indian Institute of Technology Bombay, Powai, Mumbai-400076, India.

^cDepartment of Materials Science and Engineering, Monash University, Wellington Road, Clayton, VIC 3800 Australia

[#]Present address: Soft Matter Optoelectronics, University of Bayreuth, 95440 Bayreuth, Germany

dkabra@iitb.ac.in

This file contains

Figure S1 to Figure S10

Table S1 to Table S4

Materials and Device Fabrication-

Material PTB7-Th was purchased from 1-material. PCBM and ICBA were purchased from Solenne BV. All materials were used as received. An overall donor:acceptor ratio was fixed at 1:1.5 based on state-of-the-art devices. Six types of samples were made by changing the acceptor ratio in the donor material, namely 0% A₂, 10% A₂, 30% A₂, 60% A₂, 80% A₂ and 100% A₂. The total concentration of the material is chosen 25 mg in 1 mL of chlorobenzene with 3 vol% of DIO as additive. The device structure was chosen ITO/PEIE/BHJ/MoO₃/Ag. For mobility measurements, hole-only and electron-only devices were fabricated. The architecture for holeonly device was ITO/PEDOT:PSS/BHJ/Au and for electron-only device was ITO/PEIE/BHJ/Ca/Al. The devices were measured by In-house solar simulator with the use of AM1.5 filter and Keithley 2400 source meter. Bentham PVE300 which consists with Xenon and quartz halogen lamp was used to perform the sensitive EQE measurements. The intensity of the incident light was calibrated with the Si reference photodiode.

A ₁ :A ₂ ratio in D	$V_{OC}(V)$	J_{SC} (mA/cm ²)	FF (%)	PCE (%)
100:0	0.80	16.1	65.57	8.47
90:10	0.81	15.5	63.2	7.94
70:30	.82	14.8	59.6	7.24
40:60	0.86	12.2	52.5	5.49
20:80	0.89	11.8	51.1	5.37
0:100	1.01	12	51.2	6.19

Table S1- Solar cell parameters for different A1:A2 ratio in D.

Atomic Force Microscope-

The measurement was performed by Nanoscope IV multimode AFM from Veeco with $5\mu m \times 5\mu m$ window.



Figure S1- Surface morphology images of a) $D:A_1$, b) $D:A_1:A_2$ and, c) $D:A_2$ thin-films, corresponding roughness (r) is mentioned in the inset.

Sensitive photo-current spectroscopy-

Reduced EQE is plotted in figure S2, also shows the charge transfer region that is fitted with the equation S1 derived from the Marcus theory.¹ This equation provides the interfacial parameters such as diagonal bandgap, that is, E_{CT} and the reorganization energy (λ).

$$EQE_{CT} = \propto \frac{1}{E\sqrt{4\pi\lambda kT}} exp\left[-\frac{\left(E_{CT} + \lambda - E\right)^2}{4\lambda KT}\right]\dots\dotsS1$$

Where λ is the reorganization energy, E_{CT} is the diagonal bandgap, k is the Boltzmann constant and T is the temperature.



Figure S2- Reduced EQE spectrum, fitted with Marcus charge transfer equation S1 for different $A_1:A_2$ ratio in D.

Population Occupancy in Gaussian Disorder model-

Calculation of p/P_O :

The absorption length as a function of wavelength is given as:

$$A_L(\lambda) = \frac{A_{LO}}{A_S(\lambda)}......S2$$

where, A_{LO} is the absorption length of donor and A_S is the donor absorption spectrum (measured experimentally) as shown in Figure S4.

The absorption profile for the devices of thickness *d* is measured as:

The flux of photo generated holes is calculated by integrating the product of the solar spectrum and the obtained absorption profile,

$$\dot{p} = \frac{1}{d} \int \frac{AM1.5(\lambda).IQE.A(\lambda)}{E_{Ph}(\lambda)} d\lambda \dots S4$$

where, AM1.5 (λ) (mW/m²) is the conventional solar spectrum, IQE (no unit) is Internal Quantum Efficiency and E_{ph} (λ) is the photon energy in (eV or in W-sec).

The free hole carrier concentration is then measured as:

$$p = p \tau \dots S5$$

where, τ is the free carrier (hole) lifetime.



Figure S3- Transient photo voltage decay for different $A_1:A_2$ ratio in D for ternary BHJ OSCs, fitted with single exponential to calculate the life time of charge carriers. Extracted parameter is tabulated in Table S2.



Figure S4- Thin film absorption spectrum of PTB7-Th (D), used in equation S6.

Temperature dependent mobility-

The explicit dependence of mobility on temperature can be described by the following relation:

$$\mu(T) = \mu_0 \exp^{[i\sigma]} \left[-\frac{E_a}{kT} - C\left(\frac{\sigma}{kT}\right)^2 \right] \dots S6$$

Where μ_0 is the infinite temperature zero field mobility, E_a is the activation energy (related to polaronic disorder), σ is the width of the DOS (related to energetic disorder) and *C* quantifies the relative contribution of energetic and polaronic disorder. Bässler considered a value of C = 0.44 reflected pure energetic disorder ($E_a = 0$) ²and for a definite value of energetic disorder, Parris *et al.* considered C = 0.31 ³. To measure E_a by equation S6 for both holes and electrons, temperature dependent *J-V* measurements were performed on single carrier devices (Figure S5) with the measured *J-V* curves fitted using space charge limited current (SCLC) model to obtain the mobility values. The validity of equation S6 is confirmed by linear fit of the Poole-Frenkel term with 1/T and 1/T² (Figure S6 and Figure S7).



Figure S5- Temperature dependent dark J-V characteristics for hole-only a), b), c) and electrononly d), e), f) for D:A₁, D:A₂ and D:A₁:A₂ based devices, respectively and fitted with space charge limited current model.^{4,5}

Table S1- Room tempe	erature SCLC mobility	v extracted from	Figure S5.
----------------------	-----------------------	------------------	------------

Blend	$\mu_{\rm h} ({\rm cm}^2 {\rm V}^{-1} {\rm s}^{-1})$	$\mu_{e} (cm^{2}V^{-1}s^{-1})$
D:A ₁	2.8 x 10 ⁻⁴	2.6 x 10 ⁻⁵
D:A ₂	1.2 x 10 ⁻⁴	2 x 10 ⁻⁶
D:A ₁ :A ₂	2.1 x 10 ⁻⁴	1.5 x 10 ⁻⁵



Figure S6- A linear behavior of Poole-Frenkel term (β) from SCLC fitting with 1/T for D:A₁ (a,d), D:A₂ (b,e) and D:A₁:A₂ (c,f) based single-carrier devices to show the validity of equation S6. ⁶



Figure S7- A linear behavior of Poole-Frenkel term (β) from SCLC fitting with $1/T^2$ for D:A₁ (a,d), D:A₂ (b,e) and D:A₁:A₂ (c,f) based single-carrier devices to show the validity of equation S6.⁷



Figure S8- Mobility is plotted against $1/T^2$ for a), b) and 1/T for c), d) to determine the σ (Ea=0) and Ea (σ =0) for D:A₁, D:A₂ and D:A₁:A₂ based system using eqⁿ S6.

Table S2- Parameter used in population occupancy in Gaussian disorder model along with experimental V_{OC} to determine energetic disorder (σ).

Parameter	Value
Donor absorption length	50 nm
IQE	0.85
Device length	100 nm
DOS^8	$10^{26}/m^3$
Life time	
$D:A_1 \longrightarrow D:A_2$	1:1:1:1.5:1.9:1.7
0:10:30:60:80:100 %	(μs)
p/P _O (calculated)	6.07x10 ⁻³
Standard deviation	2.3x10 ⁻⁴

Table S3- Estimation of energetic disorder (σ) for D:A₁ and D:A₂ blend solar cell calculated from eqⁿ S6 by neglecting polaronic disorder (*E_a*).

	$\sigma_{\rm H} (E_{aH}=0)/{\rm meV}$	$\sigma_{\rm L} (E_{aL}=0)/{\rm meV}$
D:A ₁	63	78
D:A ₂	69	72
$D:A_1:A_2$	65	75

Grazing incidence wide-angle X-ray scattering (GIWAXS)-

Grazing-incidence wide-angle X-ray scattering (GIWAXS) experiments were conducted at the SAXS/WAXS beamline at the Australian Synchrotron⁵ using 15 keV photons, with the 2dimensional diffraction patterns collected by a Dectris Pilatus 2M detector. Images taken at the critical angle were used for further data analysis, with the critical angle identified by scanning the X-ray angle of incidence from 0° to 0.15° with intervals of 0.01°, as well as a separate measurement at high angle 0.2°. Before starting the measurement on a fresh sample with the predefined series of incident angles, the sample was leveled by iterating a beam alignment procedure, which involves coarse height scan, tiling angle scan and fine height scan subsequently. The X-ray exposure time was chosen as 1 s to maximize signal to noise ratio and in the same time minimize beam damage. Gapless mode of Pilatus 2M detector was utilized to eliminate the blank gap intrinsic to the detector. With the Pilatus 2D detector mounted within a vacuum flight tube, the samples were kept in air during GIWAXS measurement. Silver behenate was used as the diffraction standard to calibrate the physical dimension of detector-sample distance and beam center position. Data analysis is performed in Igor pro with a customized code Nika.⁹



Figure S9- Grazing incidence wide angle X-ray scattering (GIWAXS) profiles on a) $D:A_1$, b) $D:A_2$ and c) $D:A_1:A_2$ (1:0.5:0.5). Line profiles for all the three samples extracted from scattering profile d) in-plane and e) out-of-plane direction.

	In-plane (100)					Out-of-plane (010)				
Blend	q (Å-1)	d (Å)	Area (a.u.)	FWHM (Å ⁻¹)	CL (nm)	q (Å ⁻¹)	d (Å)	Area (a.u.)	FWHM (Å ⁻¹)	CL (nm)
D:A ₁	0.296 ± 0.001	20.7 ± 0.1	91 ± 1	0.0504 ± 0.0004	12.2 ± 0.1	1.576 \pm 0.001	3.89 ± 0.01	6.8 ± 0.5	0.115 ± 0.004	5.3 ± 0.2
D:A ₂	0.295 ± 0.001	20.8 ± 0.1	30 ± 1	0.0531 ± 0.0005	11.6 ± 0.1	1.642 ± 0.006	3.74 ± 0.01	4 ± 1	0.19 ± 0.02	$\begin{array}{c} 3.2 \pm \\ 0.3 \end{array}$
D:A ₁ :A ₂	0.295 ± 0.001	20.8 ± 0.1	20.3 ± 0.4	0.0546 ± 0.0005	11.2 ± 0.1	$ \begin{array}{c} 1.585 \\ \pm \\ 0.001 \end{array} $	3.87 \pm 0.01	6.6± 0.2	$\begin{array}{c} 0.170 \pm \\ 0.002 \end{array}$	3.6 ± 0.1

Table S4- Summary of key crystallographic parameters extracted from the GIWAXS data (Figure S9) via peak fitting.

Flow Chart-

In order to clarify this detailed model, a flow chart is prepared to guide the readers.



Figure S10- Flow chart of study on ternary alloy molecular semiconductors for photovoltaic.

References

1.

1

81, 125204 (2010). 2 H. Bässler, physica status solidi (b) 175, 15 (1993). 3 P. E. Parris, V. M. Kenkre, and D. H. Dunlap, Physical review letters 87, 126601 (2001). N. Mott, New York (1940). 5 N. Chandrasekaran, E. Gann, N. Jain, A. Kumar, S. Gopinathan, A. Sadhanala, R. H. Friend, A. Kumar, C. R. McNeill, and D. Kabra, ACS applied materials & interfaces 8, 20243 (2016). P. Murgatroyd, Journal of Physics D: Applied Physics 3, 151 (1970). 7 T. Kreouzis, D. Poplavskyy, S. Tuladhar, M. Campoy-Quiles, J. Nelson, A. Campbell, and D. Bradley, Physical Review B 73, 235201 (2006). 8 P. K. Nayak, G. Garcia-Belmonte, A. Kahn, J. Bisquert, and D. Cahen, Energy & Environmental Science 5, 6022 (2012). 9 J. Ilavsky, Journal of Applied Crystallography 45, 324 (2012). A. Singareddy and P. R. Nair, 36th European Photovoltaic Solar Energy conference and 2. *Exhibition*, 2019, 3-936338-60-4, 80-82 3. Mott N F and Gurney R W 1940 Electronic Processes in Ionic Crystals (Oxford: Oxford University Press) 4. N. Chandrasekaran, E. Gann, N. Jain, A. Kumar, S. Gopinathan, A. Sadhanala, R. H. Friend, A. Kumar, C. R. McNeill, D. Kabra, ACS Appl. Mater. Interfaces, 2016, 8, 20243-20250. 5a. Murgatroyd, P. N., J. Phys. Appl. Phys. 1970, 3 (2), 308.

Yang, Liqiang, et al. Journal of the American Chemical Society 134.12 (2012): 5432-5435.

K. Vandewal, K. Tvingstedt, A. Gadisa, O. Inganäs, and J. V. Manca, Physical Review B

5b. T. Kreouzis, D. Poplavskyy, S. M. Tuladhar, M. Campoy-Quiles, J. Nelson, A. J. Campbell, and D. D. C. Bradley, *PHYSICAL REVIEW B* 73, 235201, (2006).

6. Nayak, P. K.; Garcia-Belmonte, G.; Kahn, A.; Bisquert, J.; Cahen, D., *Energy & Environmental Science* **2012**, *5* (3), 6022-6039.

7. N. M. Kirby, S. T. Mudie, A. M. Hawley, D. J. Cookson, H. D. T. Mertens, N. Cowiesona, V. Samardzic-Bobana, *Journal of Applied Crystallography* **2013**, 46, 1670-1680.

8. T. Basel, U. Huynh, T. Zheng, T. Xu, L. Yu, and Z. V. Vardeny, *Adv. Funct. Mater.* **25**, 1895 (2015).

9. A. Dey, A. Rao, and D. Kabra, *Advanced Optical Materials* **5** (2017).

10. J. Ilavsky, *Journal of Applied Crystallography* **2012**, 45, 2, 324-328.