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From UV to Near-Infrared light detection: next generation photodetectors for imaging and biometric applications

Dr Nicola Gasparini

Department of Chemistry Imperial College London

Centre of Processable Electronics

n.gasparini@imperial.ac.uk

𝕏 @nicogaspa

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CPE Centre for Processable Electronics

The Gasparini group
Polina Jacoutot
Francesco Furlan
Tianyi Zhang
Zhuoran Qiao
Davide Nodari

Prof. Martin Heeney
Dr Julianna Panidi
Prof. James Durrant
Prof. Martyn McLachlan
Dr Artem Bakulin
Prof. Ji-Seon Kim

FAU

Prof. Christoph Brabec

UNIVERSITY OF OXFORD

Prof. Iain McCulloch

King Abdullah University of Science and Technology

Prof. Derya Baran
Prof. Thomas Anthopoulos
Dr Alberto Scaccabarozzi
Prof. Sahika Inal

POLITECNICO MILANO 1863

Prof. Giulio Cerullo
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TU Delft

Prof. Achilleas Savva

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Dr Christos Chochos

Swansea University Prifysgol Abertawe

Dr Armin Ardalan

Åbo Akademi University

Dr Oskar Sandberg

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UKRI Engineering and Physical Sciences Research Council

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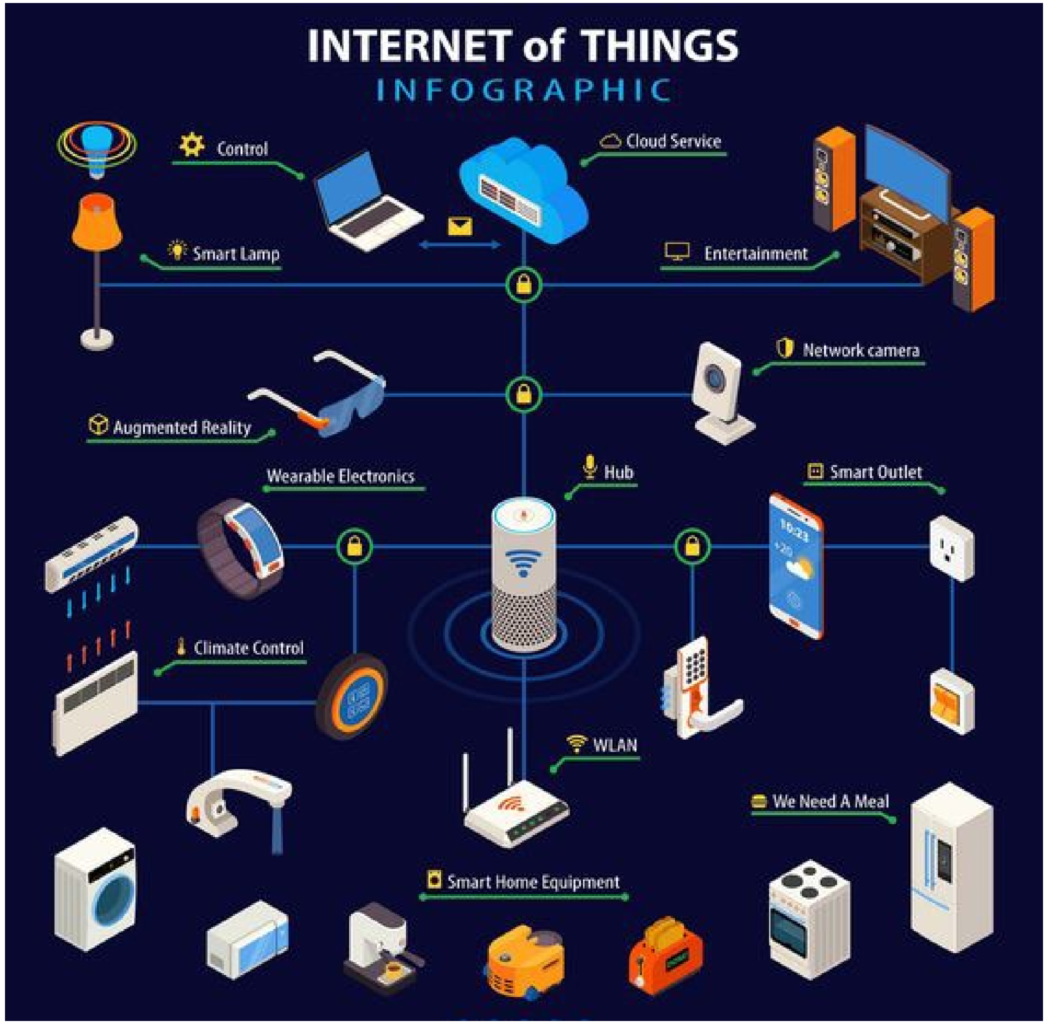
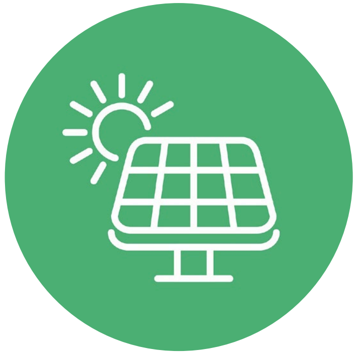
Internet of Things



Industrial IoT market size worldwide for 2025 predicted to be $111 billion!



Photovoltaics

Photodetectors

Healthcare sensors

State-of-the-art Inorganic PD Technologies

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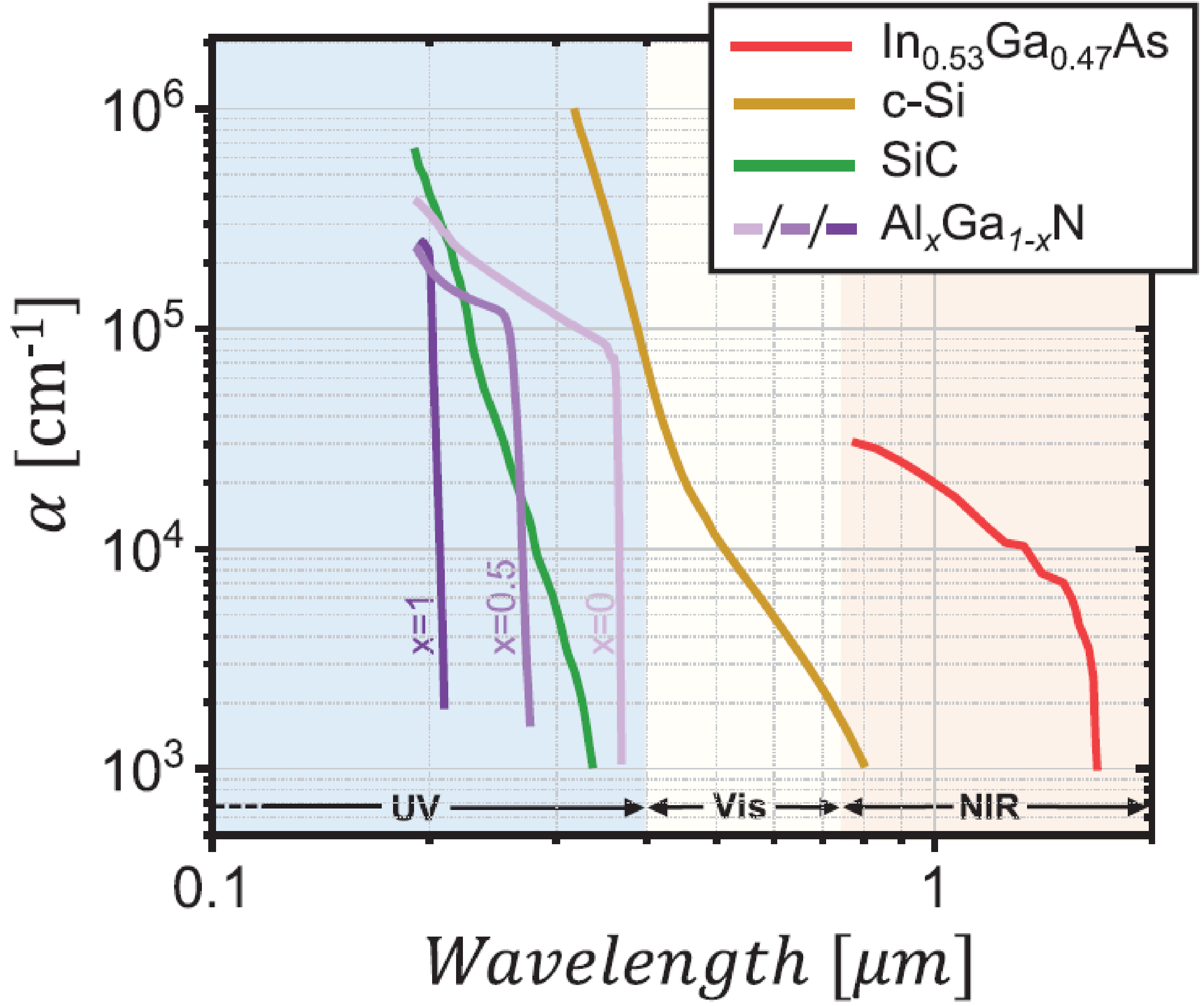

UV: **CsI** and **Cs_2Te** broadband photomultiplier tubes (PMTs) → bulky and fragile

Vis: **c-SI** and **III-V semiconductors** requires optical filtering for narrowband → fabrication complexity, high T processes

NIR: **InGaAs** broadband, input filtering through bulky diffraction gratings or interferometers → £££

Organic photovoltaics vs organic photodetectors

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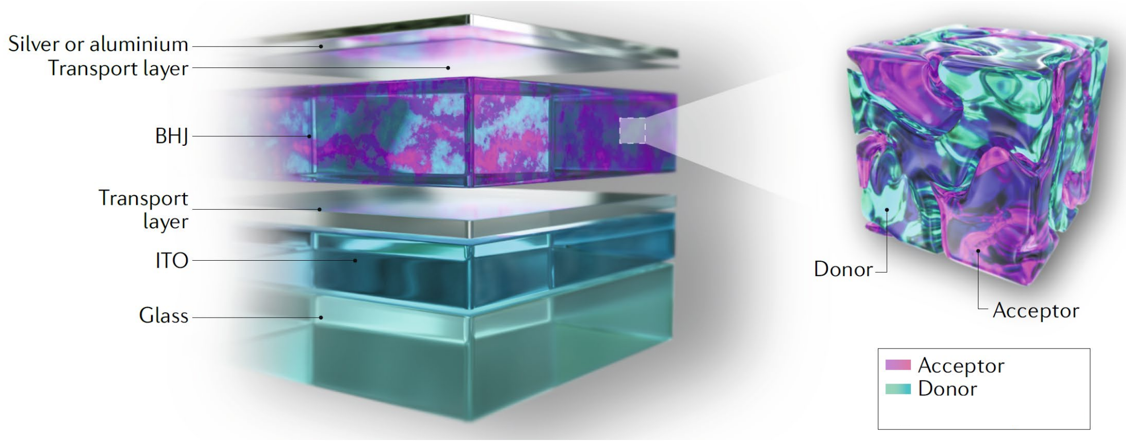
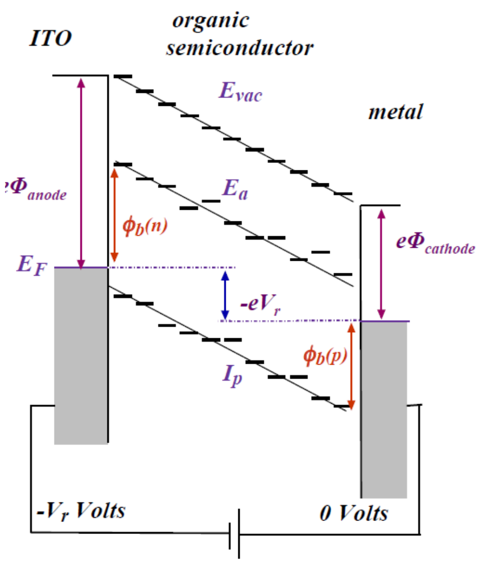
Similarities

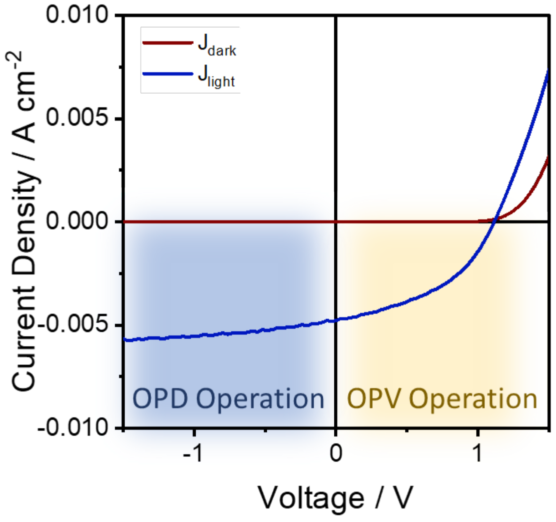
- Diode Architecture
- Necessity to extract current generated from light



Key Differences

- For Photovoltaics we maximise power output whereas for Photodetectors we want to simultaneously optimise responsivity, detectivity and speed of response
- Photovoltaics are operated at forward bias whereas photodetectors are operated at reverse bias





Figures of Merits

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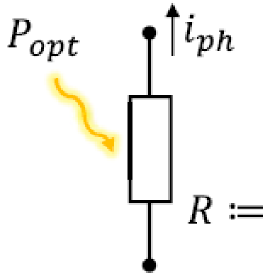
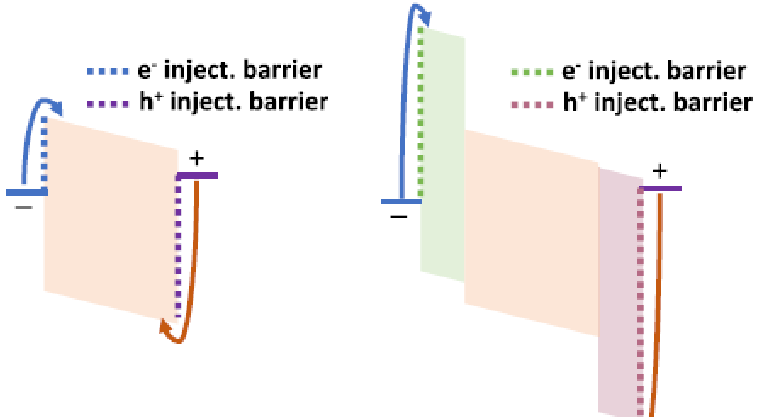
RESPONSIVITY (EQE)

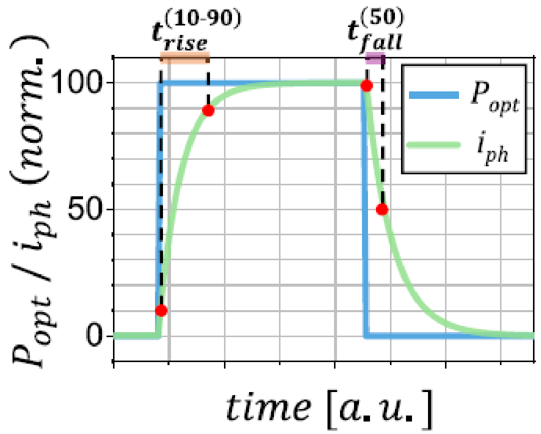


$$R \coloneqq \frac{i_{ph}}{P_{opt}}$$

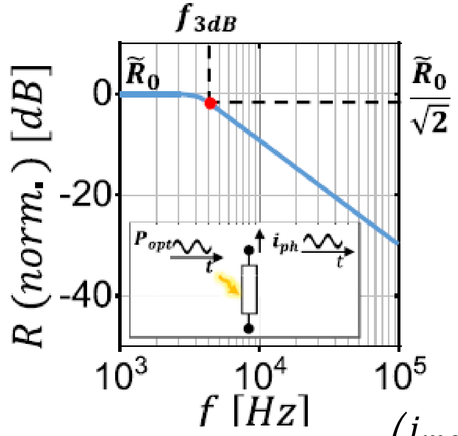
DARK CURRENT (Jd)



RISE/FALL TIMES

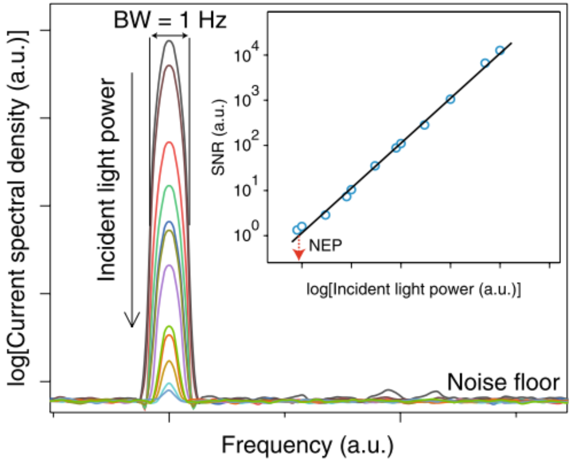


CUT-OFF FREQUENCY

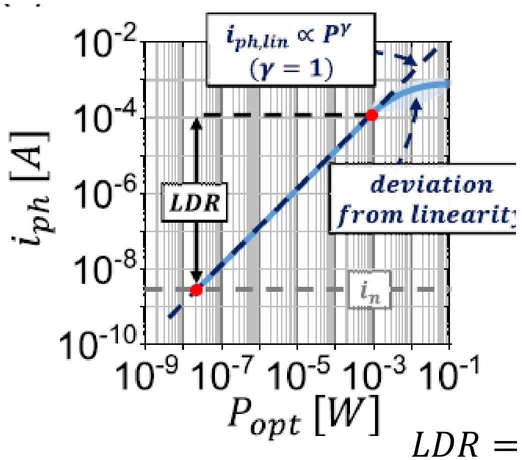


$$Damping = -20\log\left(\frac{i_{max}}{i_{freq}}\right)$$

NOISE EQUIVALENT POWER (NEP)



LINEAR DINAMIC RANGE (LDR)



$$LDR = 20\log\left(\frac{J_{max}}{J_{min}}\right)$$

Fang et al. *Nat. Phot.* 2109, **13,** 1.

Pecunia et al. *Organic Narrowband Photodetectors,* 2020

Specific Detectivity (D*)

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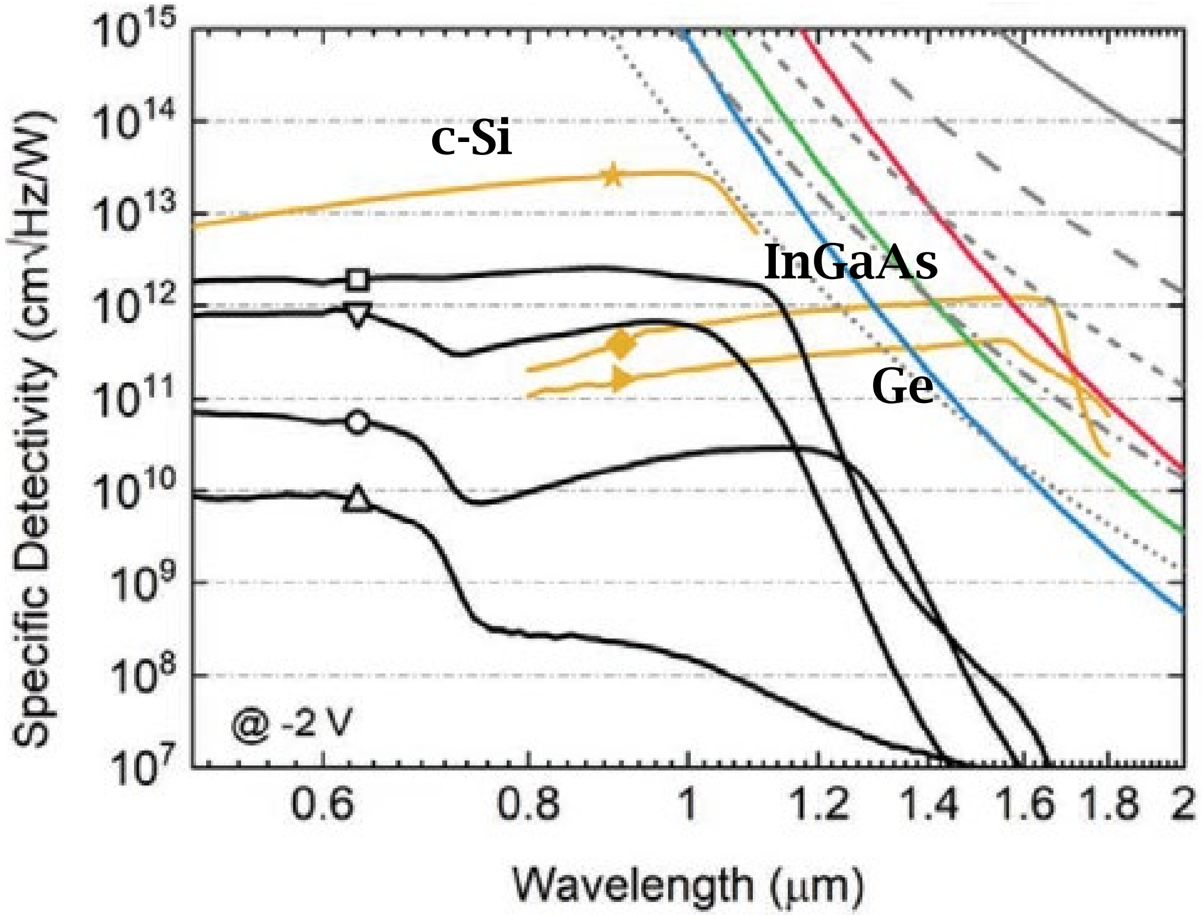

$$D^* = \frac{\sqrt{A\Delta f}}{NEP}$$

Adv. Mat. 2021, 32, 2003818.

Noise current

The noise describes the statistical fluctuations of the current over time i(t) around an average value i_{mean}. The root mean square value of this fluctuation is called noise current i_{noise}

$$i_{noise}(f) = \sqrt{i_{shot}^2 + i_{thermal}^2 + i_{1/f}^2(f)} \quad [A\,Hz^{-1/2}]$$

$$i_{shot} = \sqrt{2qi_{dark}} \quad [A\,Hz^{-1/2}]$$

Shot noise → represents fluctuations in the charge carrier distribution over time and space

$$i_{thermal} = \sqrt{4k_B T R_{shunt}^{-1}} \quad [A\,Hz^{-1/2}]$$

Thermal noise → results from thermal excitation of charge carriers

$$i_{1/f} \propto \frac{1}{f} \quad [A\,Hz^{-1/2}]$$

frequency-dependent sources, generation and recombination of electron-hole pairs.

Noise current

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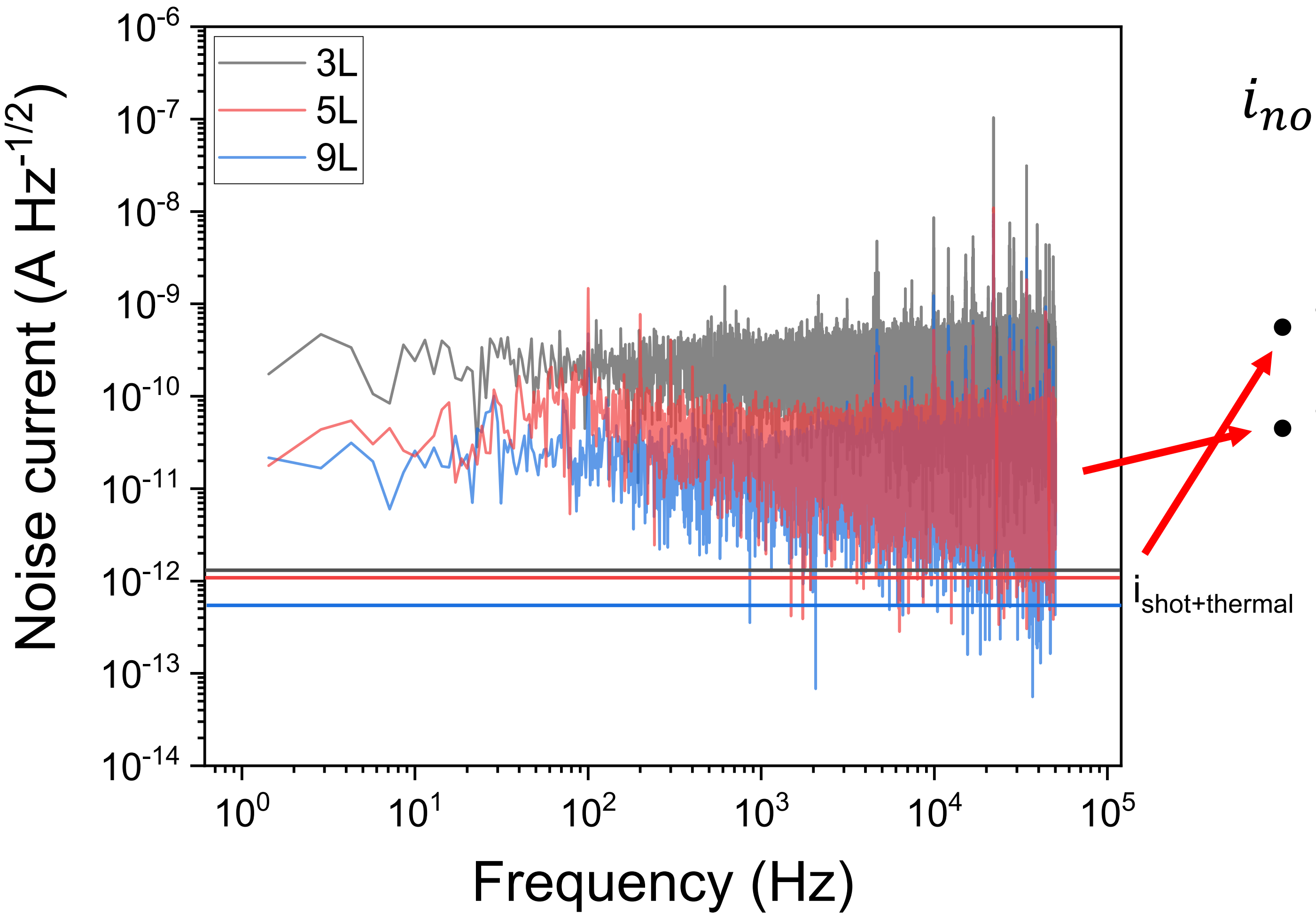

$$i_{noise}(f) = \sqrt{i_{shot}^2 + i_{thermal}^2 + i_{1/f}^2(f)}$$

- This is the **calculated noise**
- The **measured noise** is always higher because takes into account all the sources of the white noise that are not considered in the model

Current approaches for suppressing dark current

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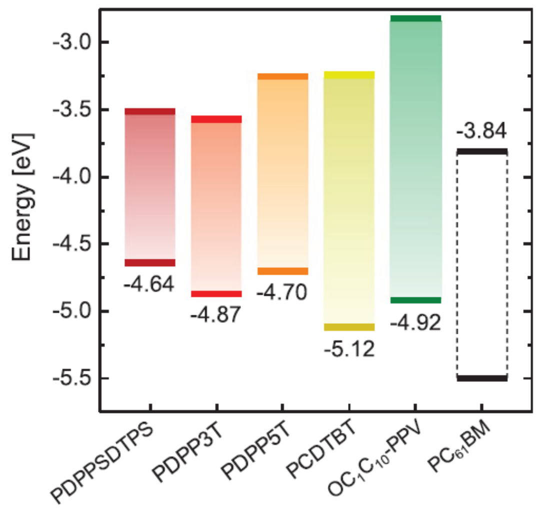
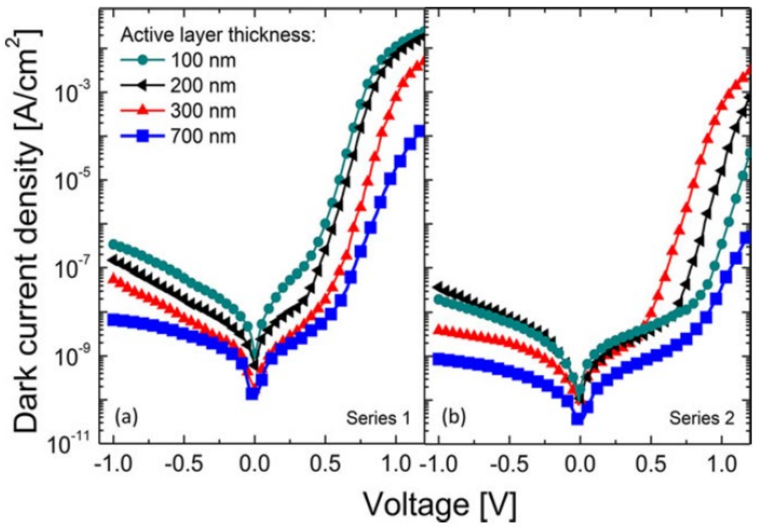
Materials energetics



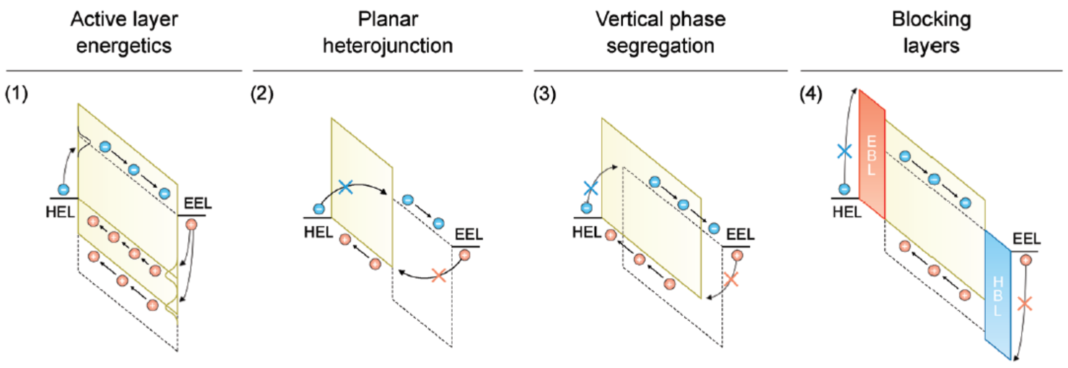
Adv. Optical Mater. 2020, 8, 1901568

Active layer thickness



Laser and Photonics Reviews. 2014, 8, 924.

Hole/Electron Blocking Layer



Adv. Funct. Mater. 2020, 30, 1904205

Infrared organic photodiodes

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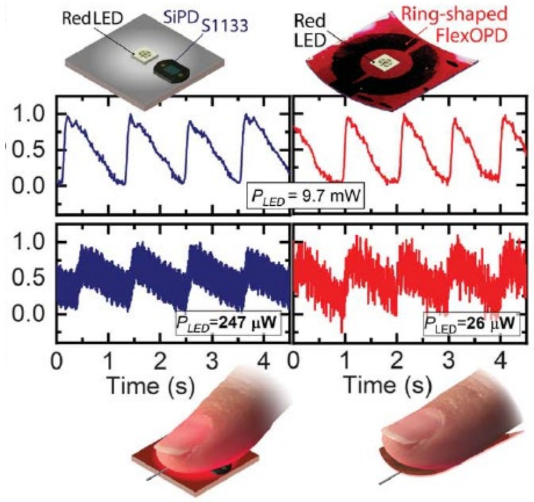
Why Infrared Photodetectors?

- Biological windows (NIR-II: 1000 – 1300 nm) and NIR-III: 1550 – 1870 nm), which offer deeper tissue penetration, improved image contrast and reduced photobleaching

- Night cameras

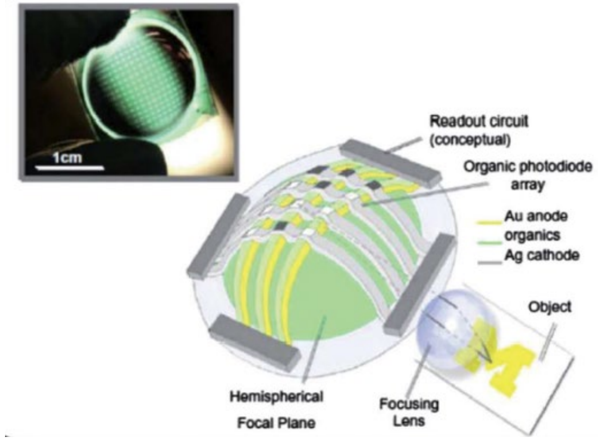
Why NIR-OPDs?:

- conformal coverage
- biocompatibility
- cooling requirements
- preferred choice for wearable health monitors

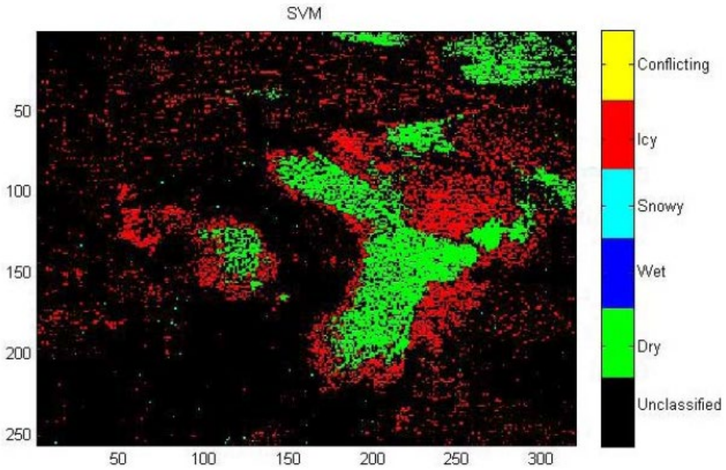


Wang et al. 2020

Khan et al. 2020



K.-H. Jeong, Science, 2006



Jonsson et al. 2015

Charge carrier mobility and lifetime

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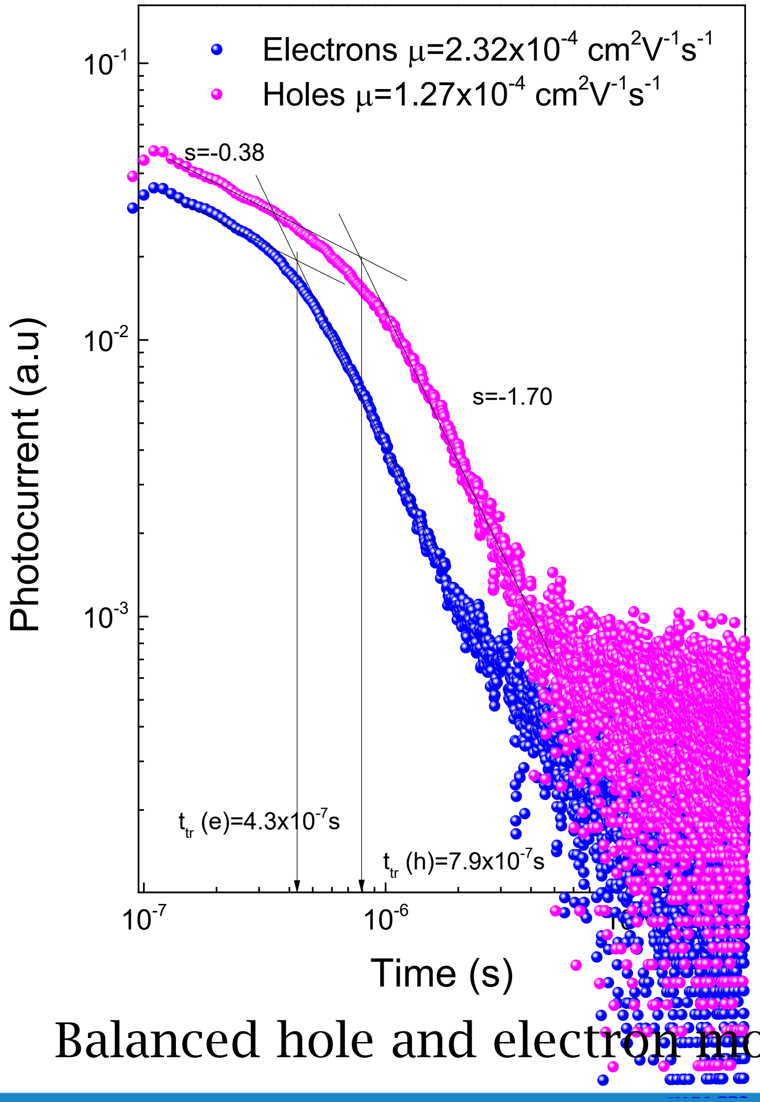
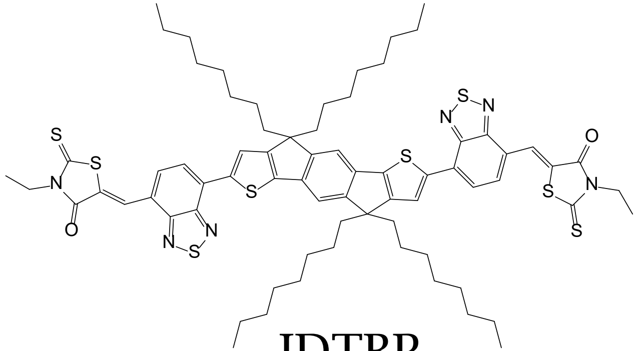
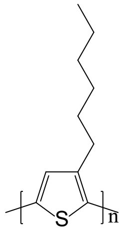
Time of flight



Balanced hole and electron mobility

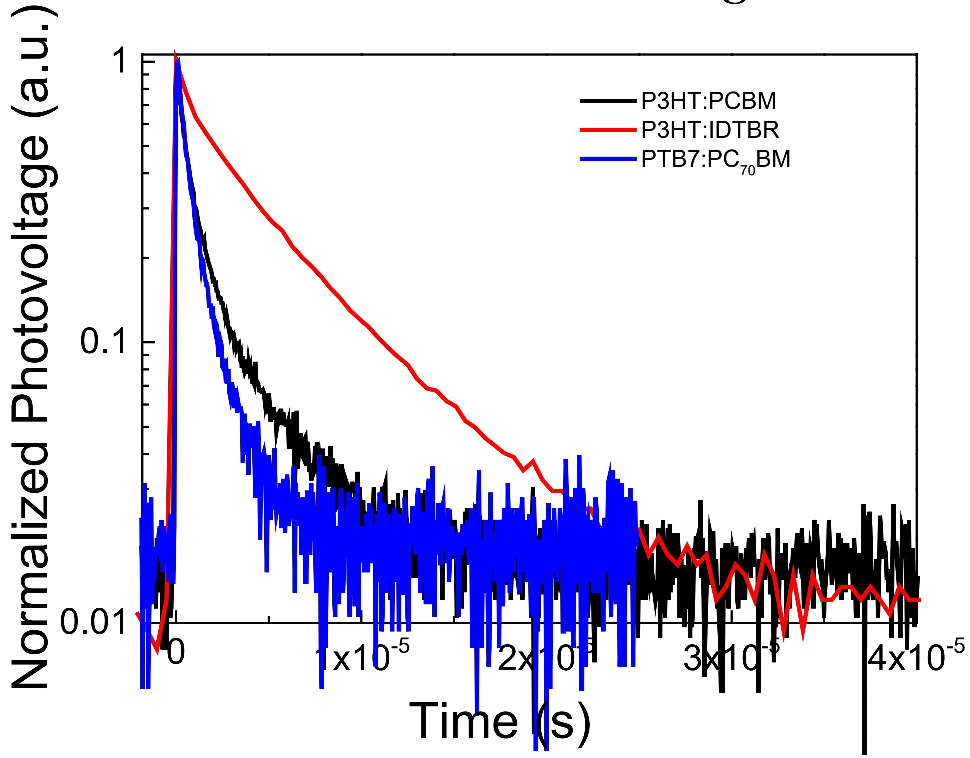


IDTBR



P3HT

Transient Photovoltage



Longer charge carrier lifetime in P3HT:IDTBR

Thickness dependent JVs

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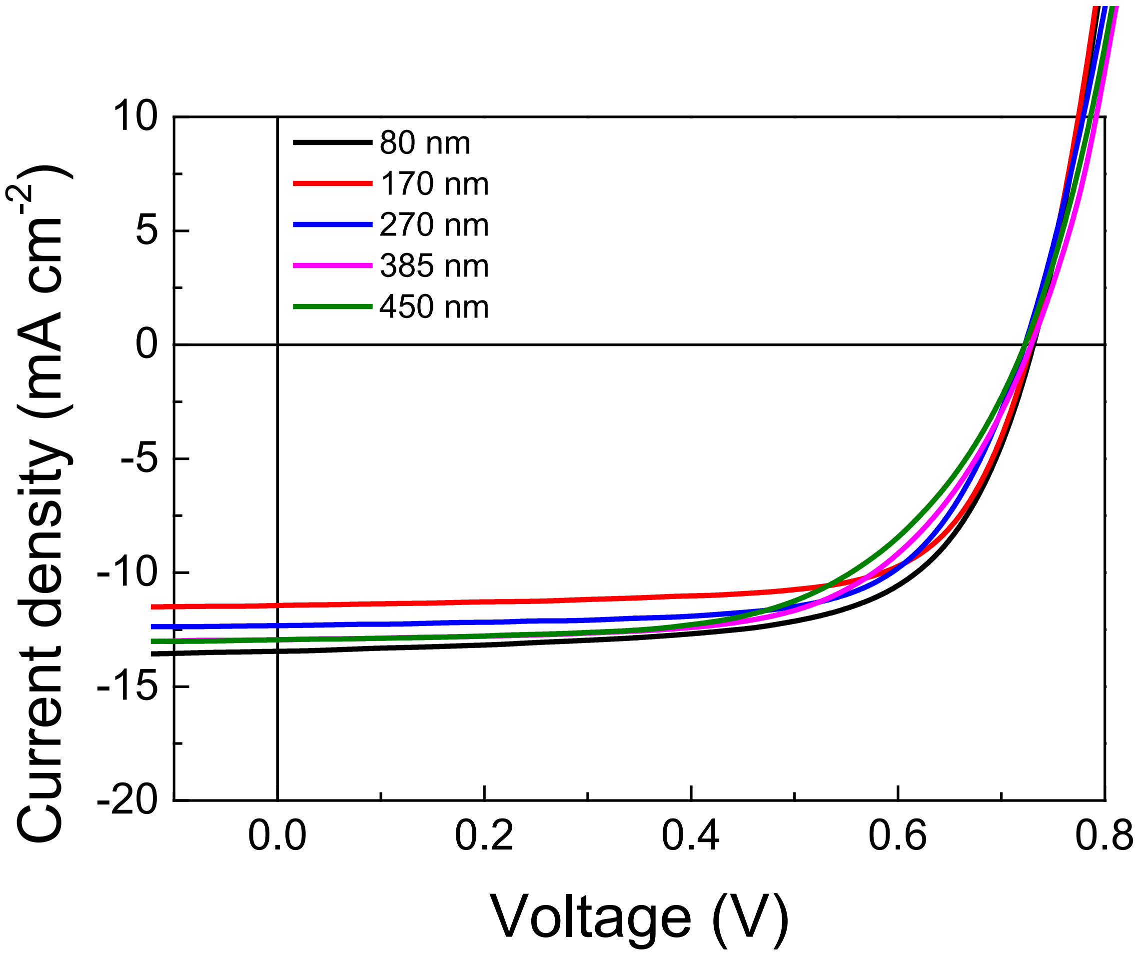
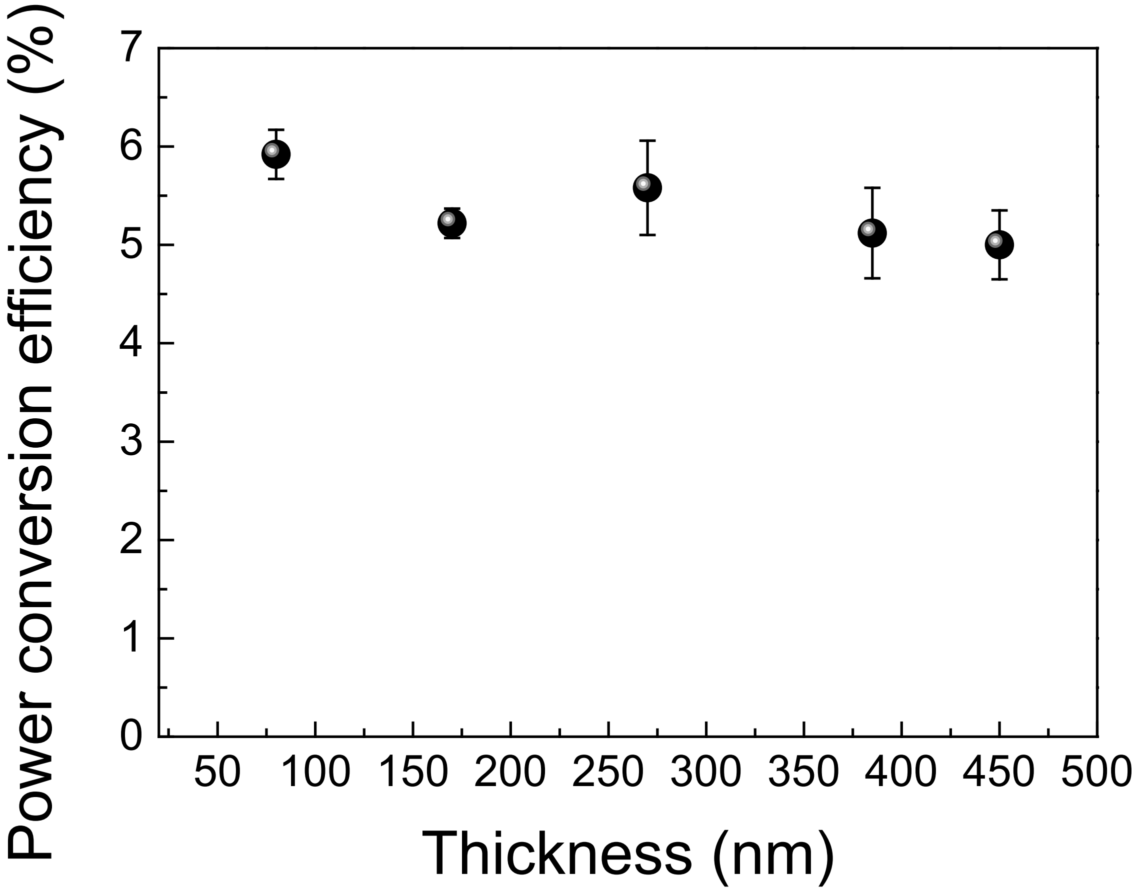
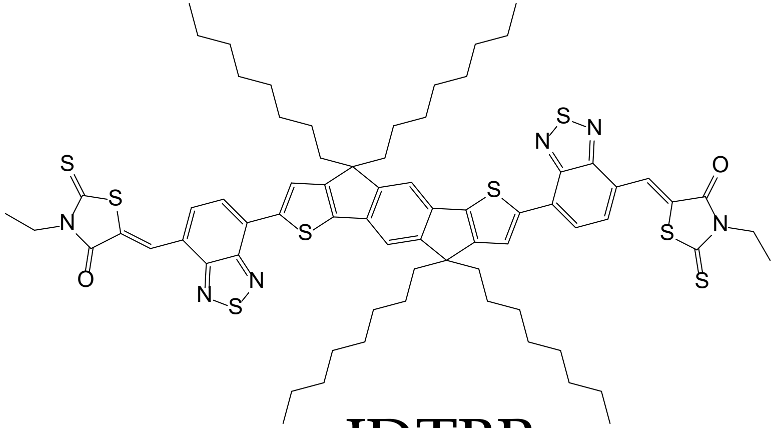


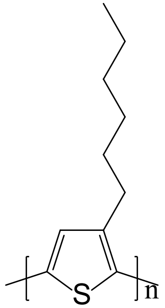


JVs and PD parameters

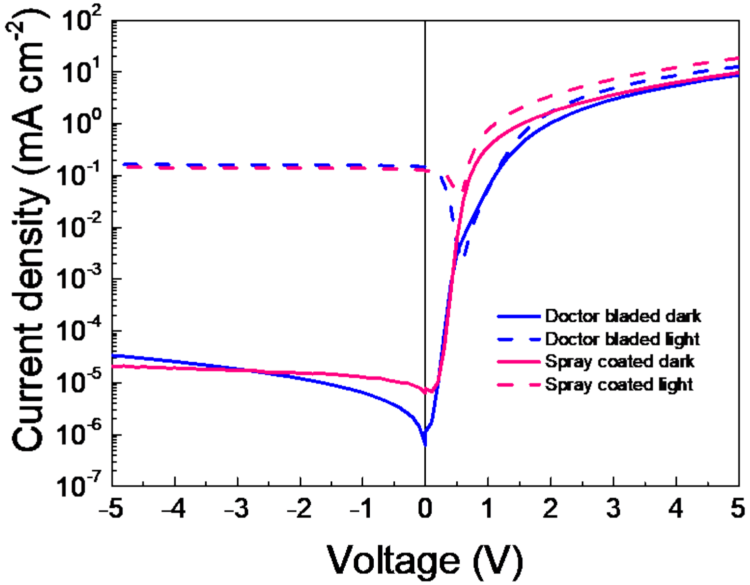
SIEMENS Imperial College London

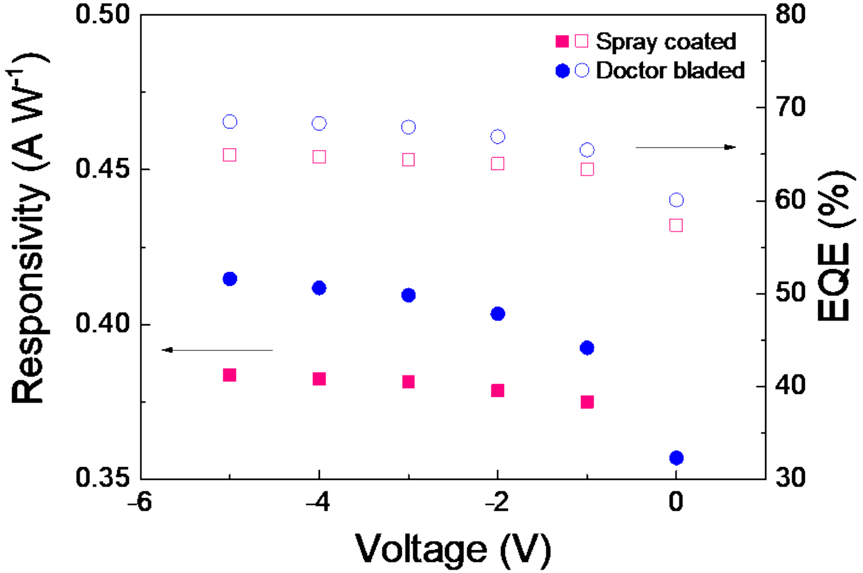


IDTBR



P3HT





			R [A W-1]	f_{-3dB} [Hz]	f_{-6dB} [Hz]
			0.42	52.6×10^3	141.9×10^3

Organic Photodetectors

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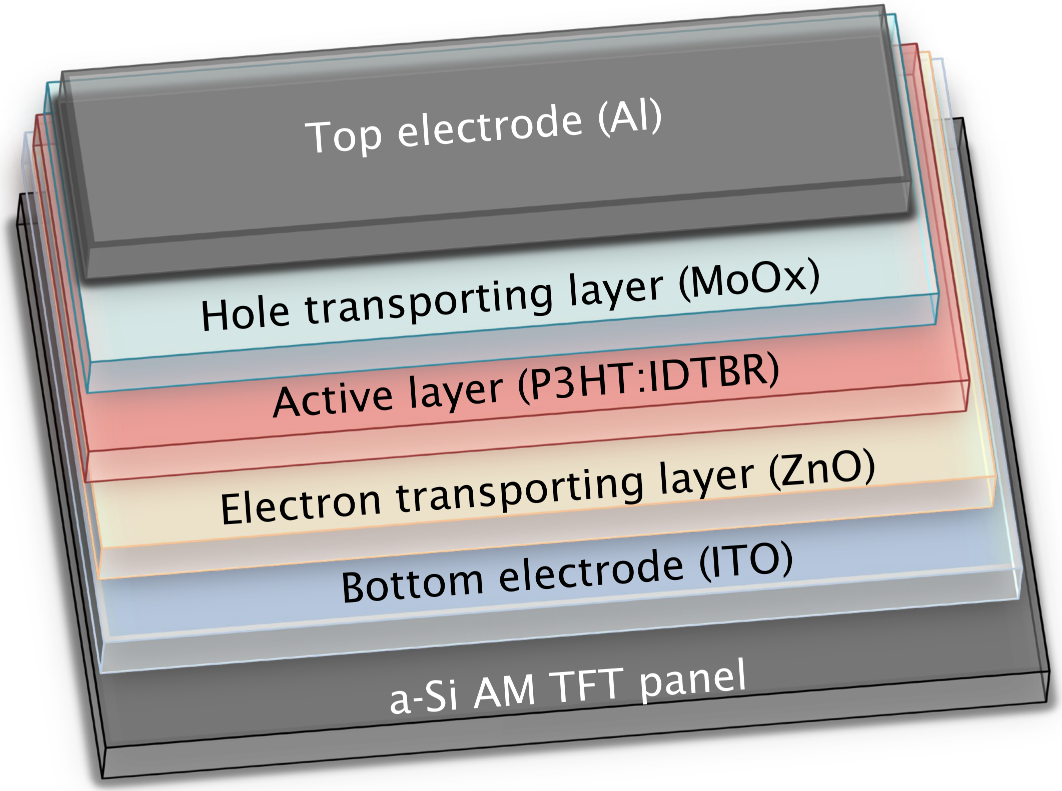

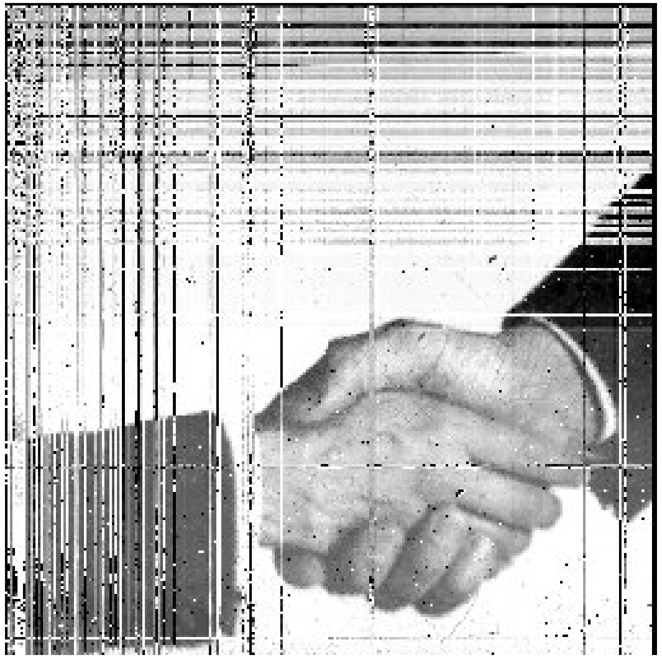

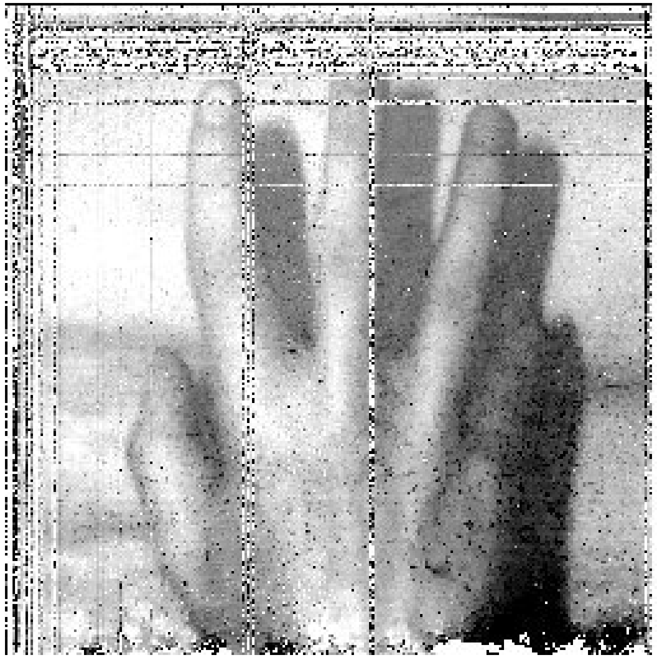

Gasparini et al. *Adv. Materials Techn.*, 2018, 1800104

Imager characteristics

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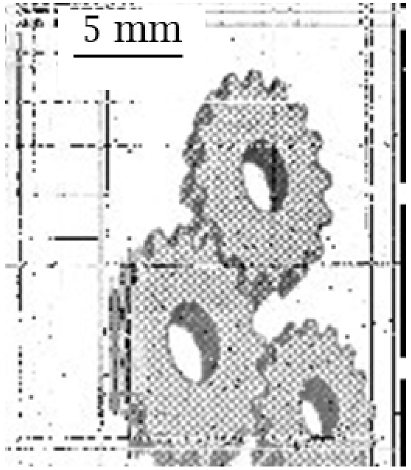
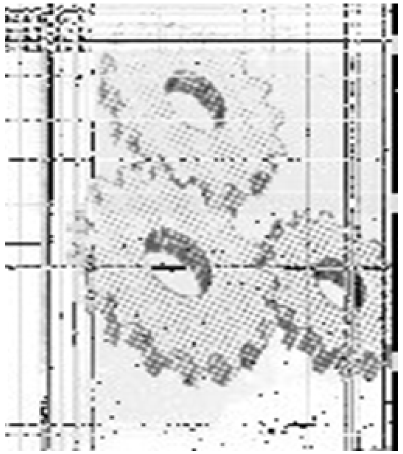
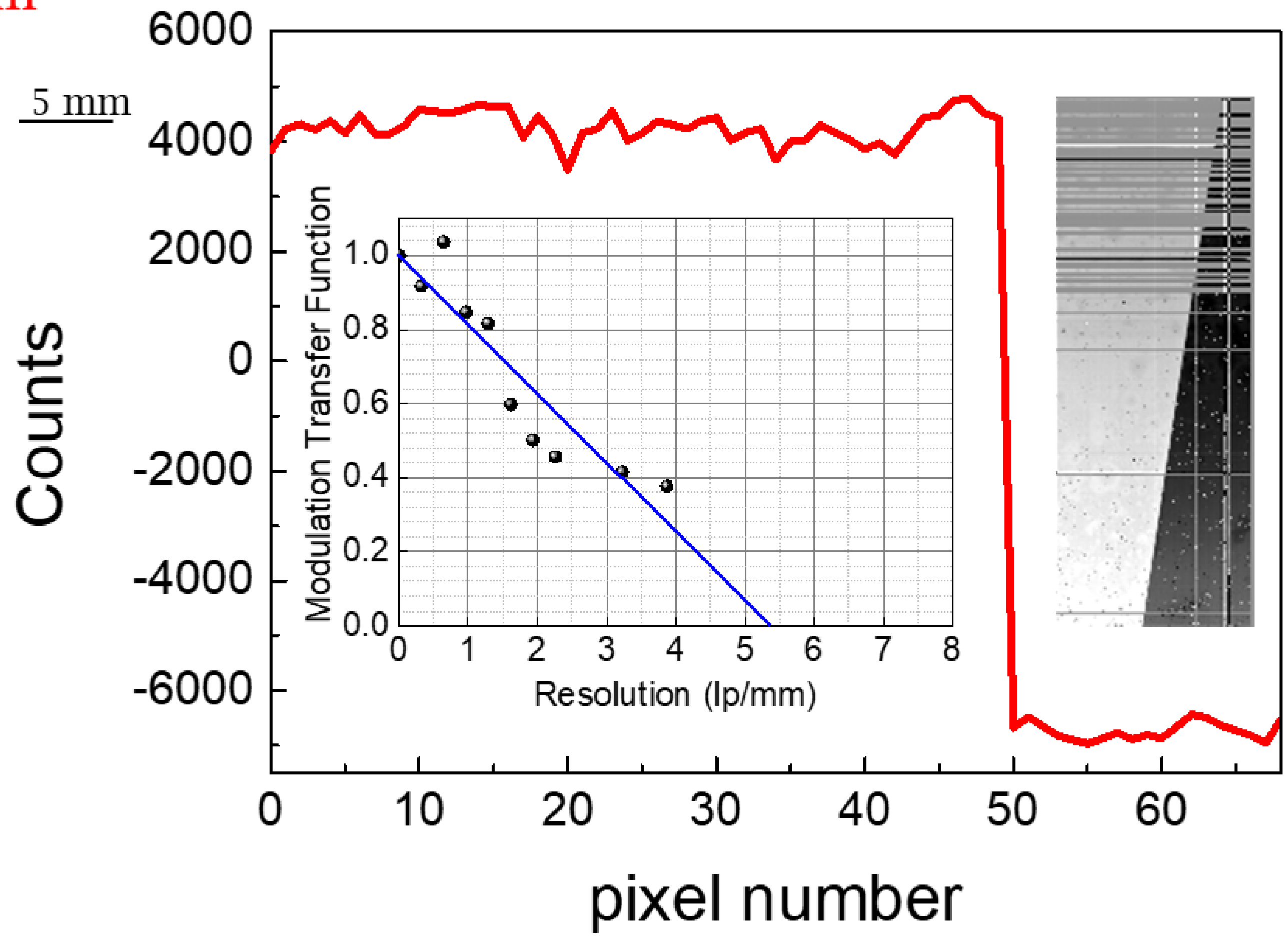
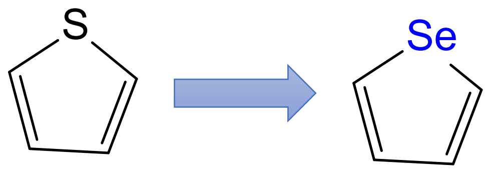




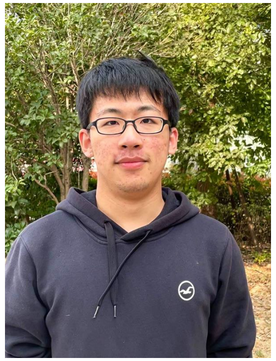


Selenium-Substituted NFA-IDSe



Lower aromatic stabilisation
Higher electron affinity
Increased polarisation

Reduced bandgap → red-shift absorption
Improved intermolecular interaction



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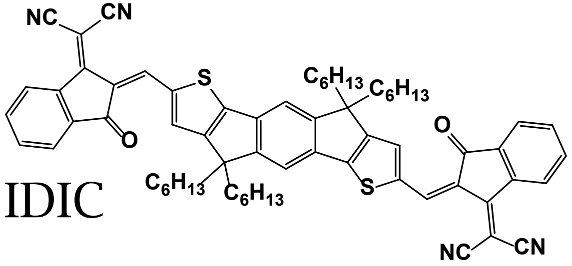
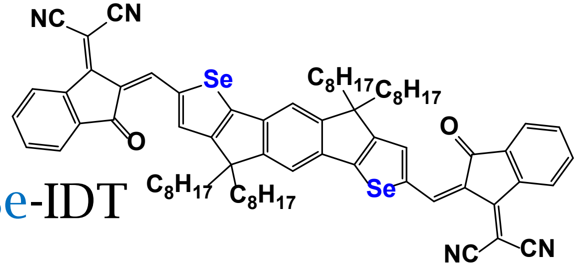
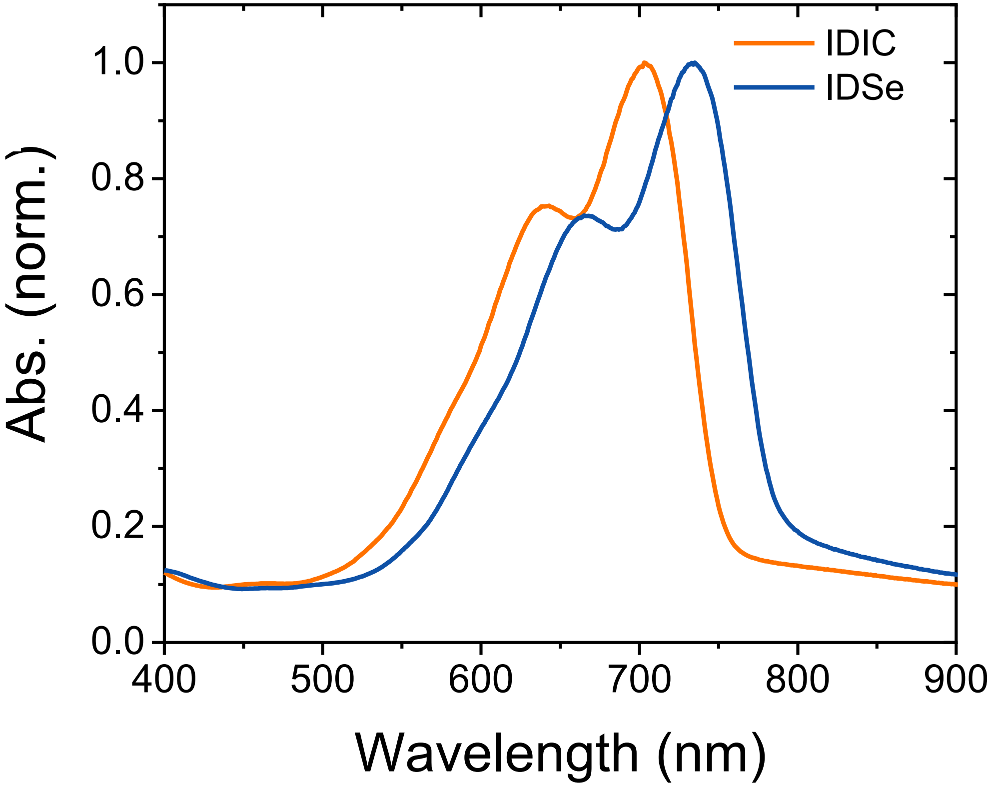
And the Heeney group



IDIC



Se-IDT



Qiao, … Gasparini. *Journal of Materials Chemistry C*, 2024

Selenium-Substituted NFA-IDSe

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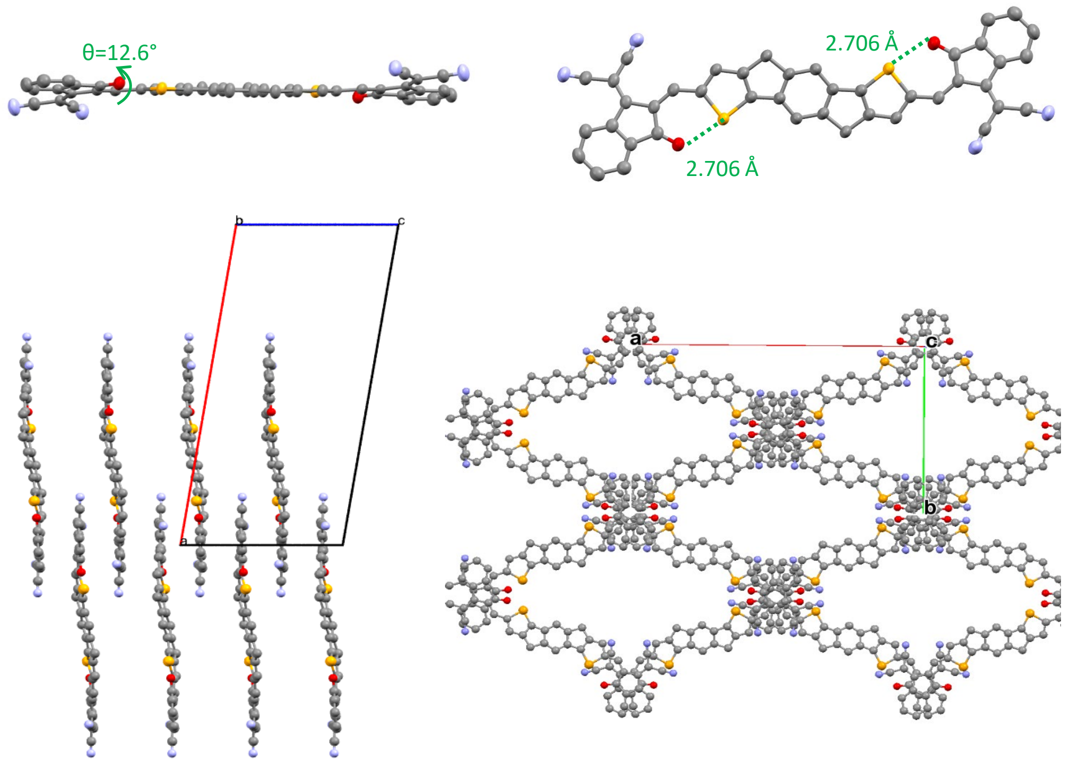
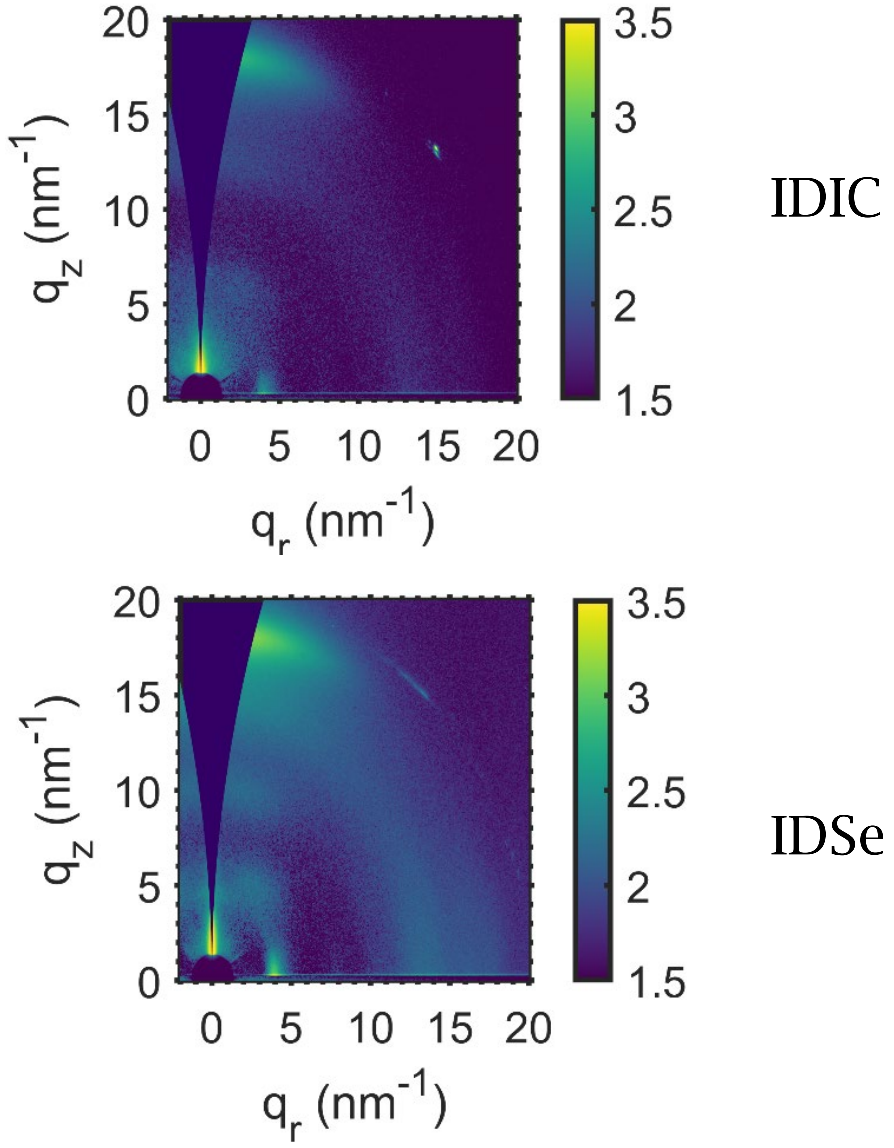
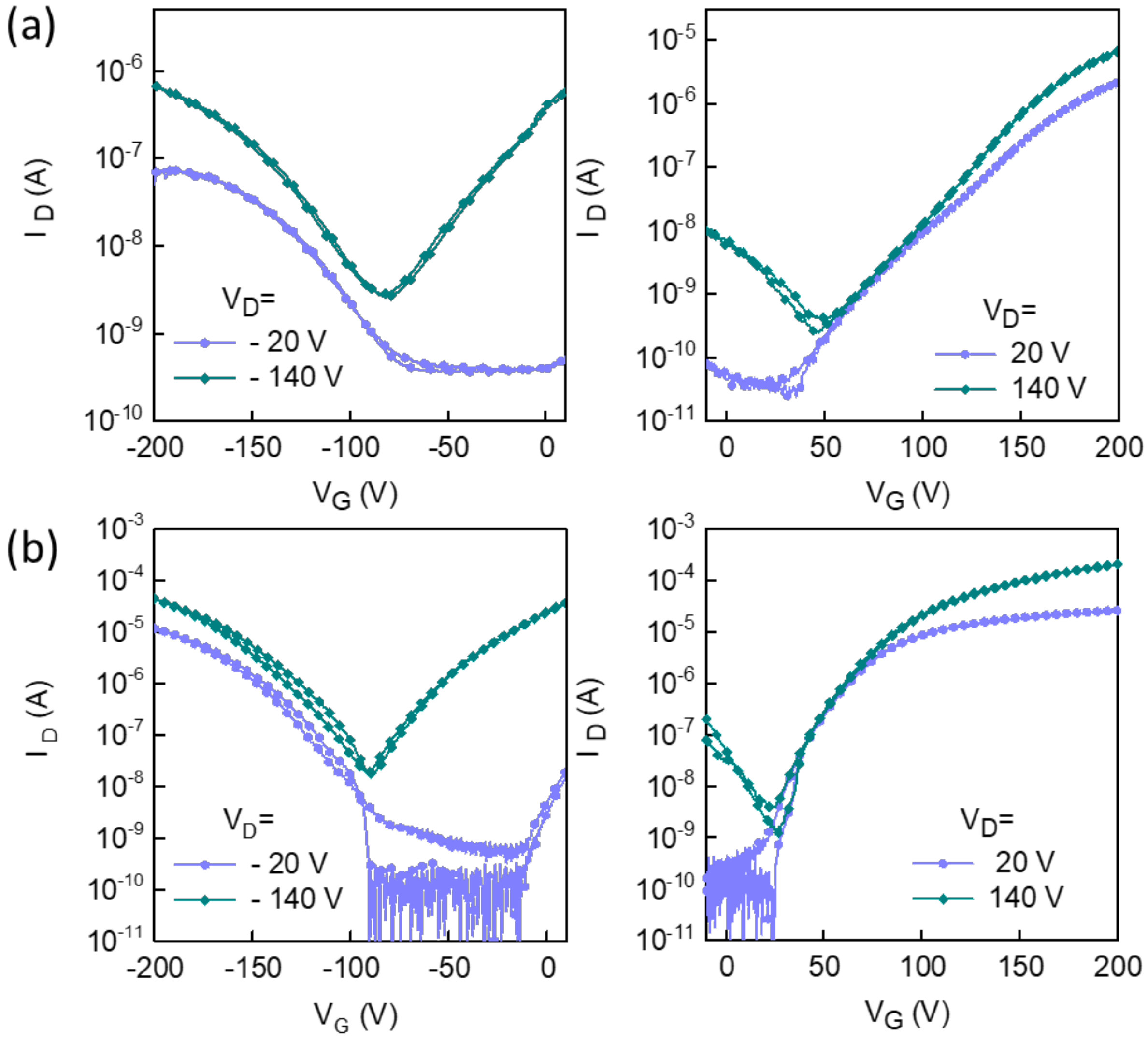




Charge carrier mobility



IDIC

$\mu_{electrons} = 0.002$ cm^2 V^{-1} s^{-1}

$\mu_{holes} = 0.009$ cm^2 V^{-1} s^{-1}

IDSe

$\mu_{electrons} = 0.16$ cm^2 V^{-1} s^{-1}

$\mu_{holes} = 0.22$ cm^2 V^{-1} s^{-1}

Selenium-Substituted NFA-IDSe

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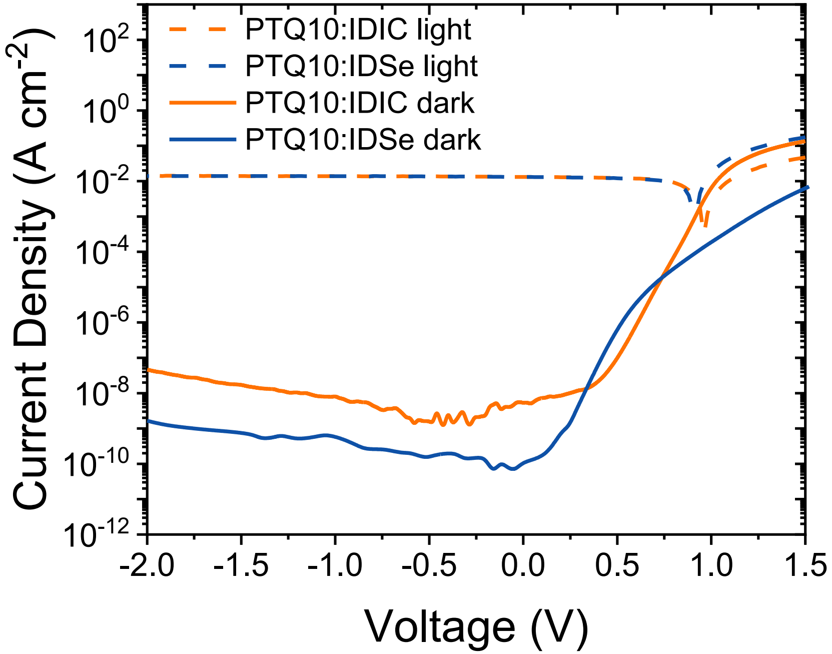
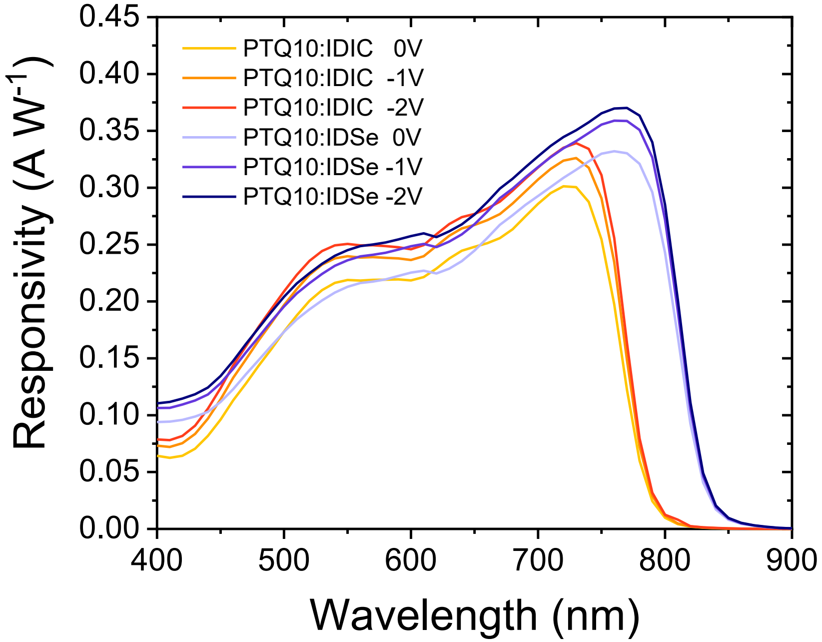
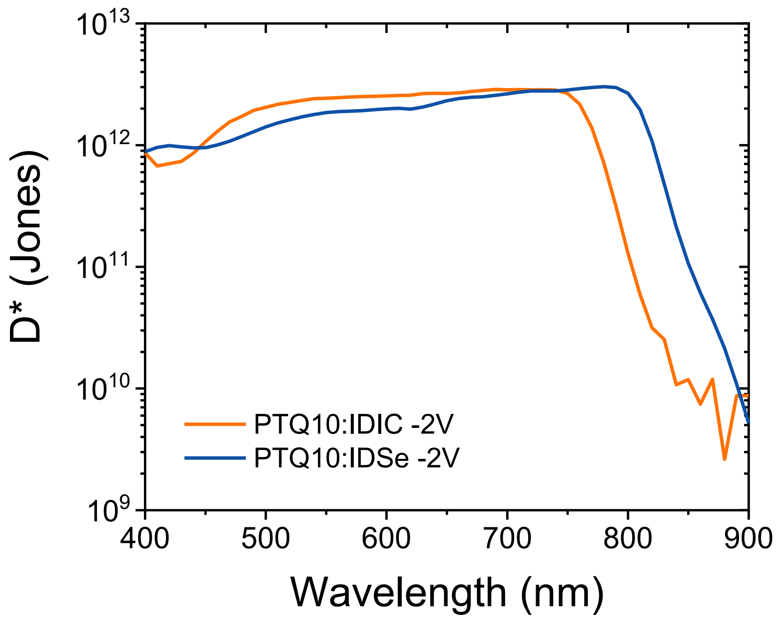
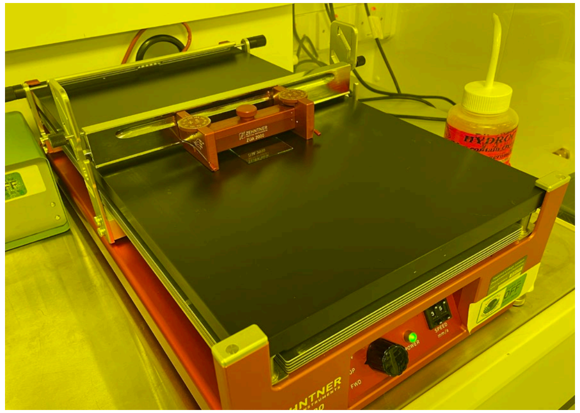




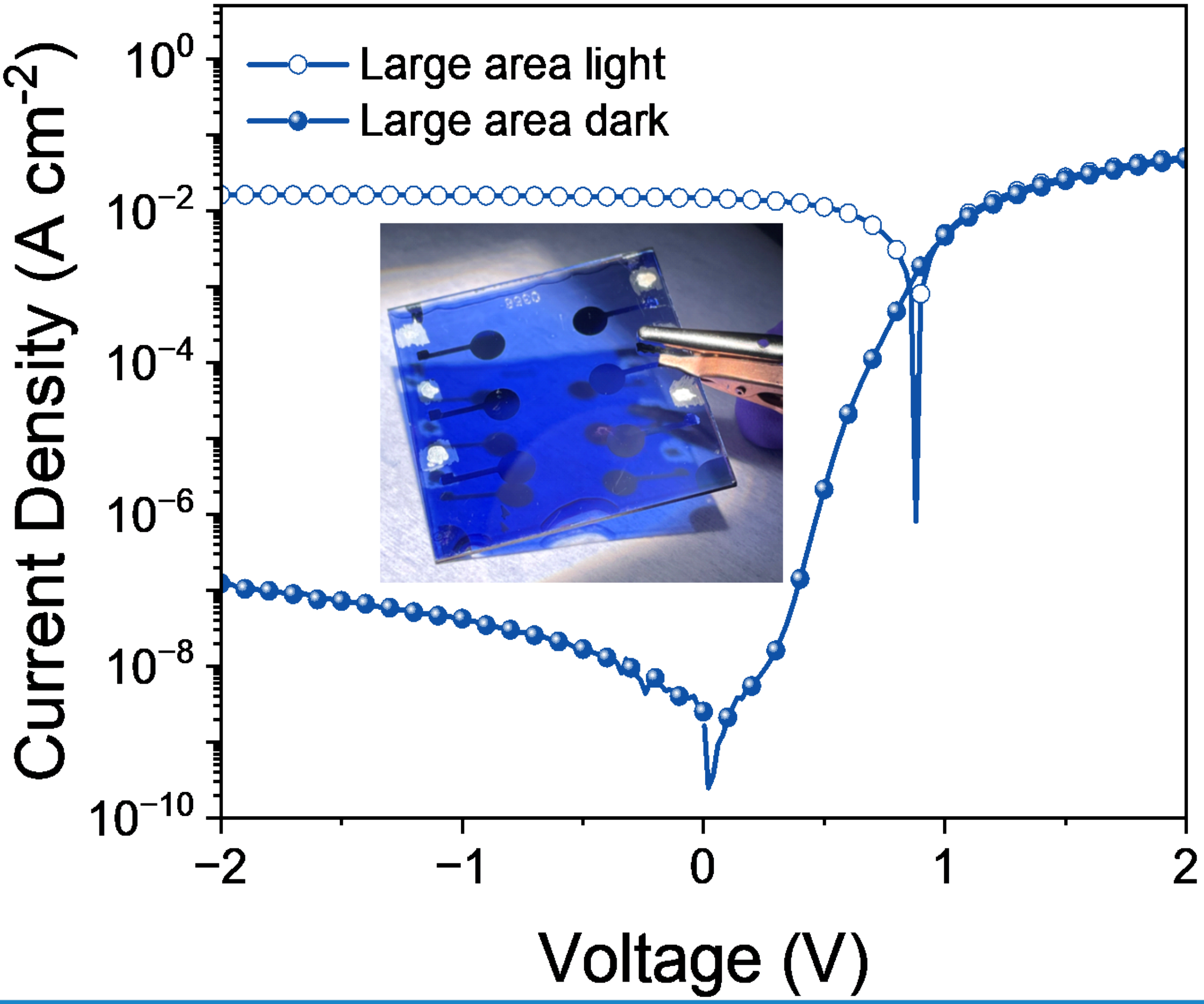


All figures of merit are higher in IDSe OPD

Blade coating- large-area device



	Dark current at -2V bias (A cm^{-2})
Large-area device	1.2×10^{-7}
Spin-coated device	1.7×10^{-9}



Ultra-low bandgap polymer for organic photodetector with high infrared detectivity

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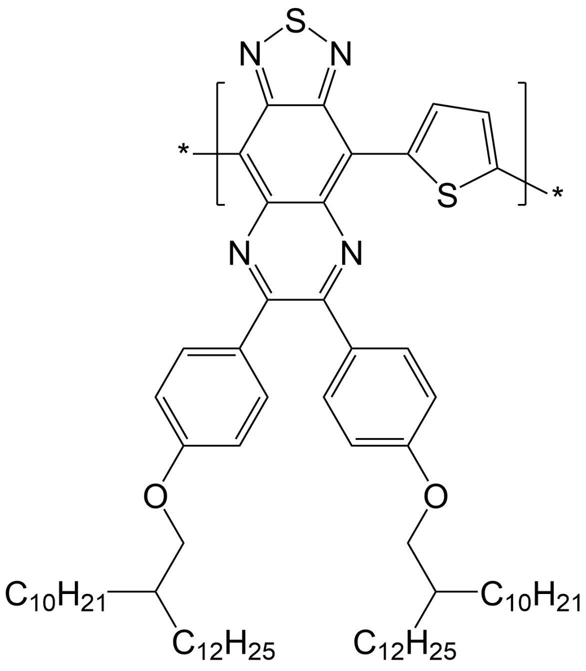
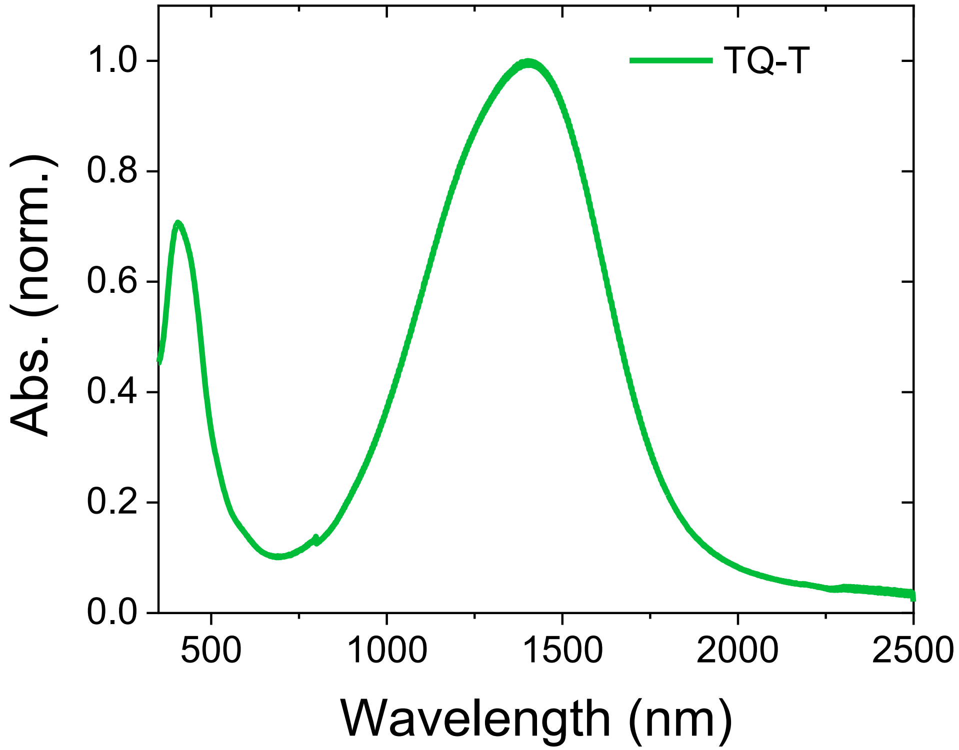


TQ-T



Jacoutot, …, Gasparini. *Small* 2022, 2200580

Ultra-low bandgap polymer for organic photodetector with high infrared detectivity

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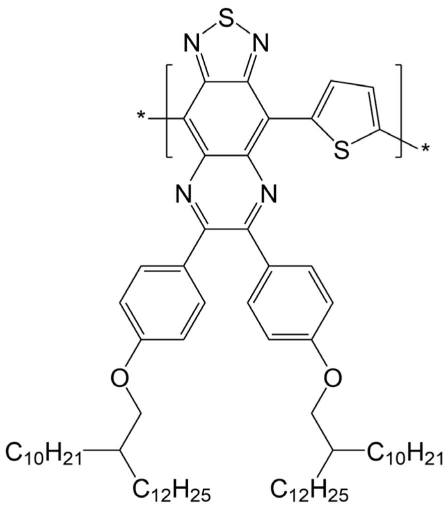
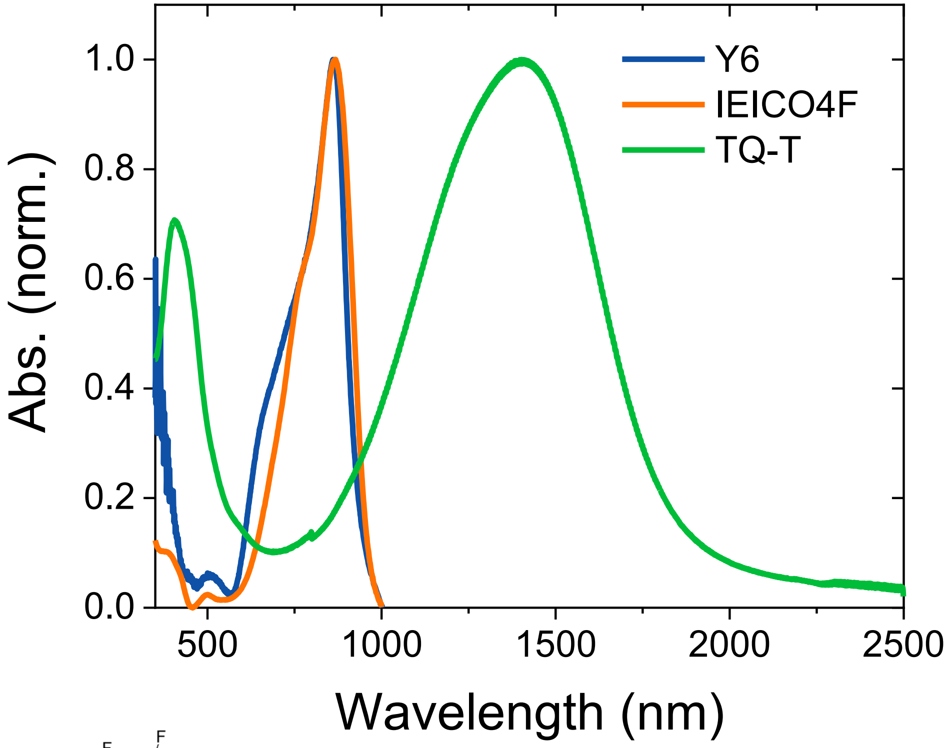
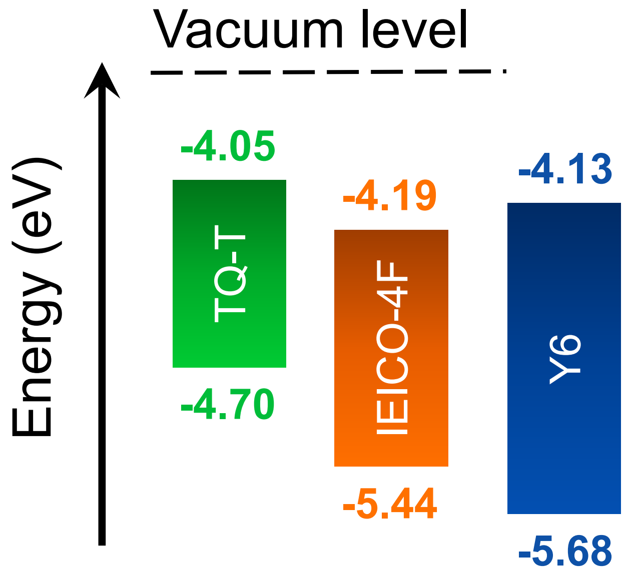
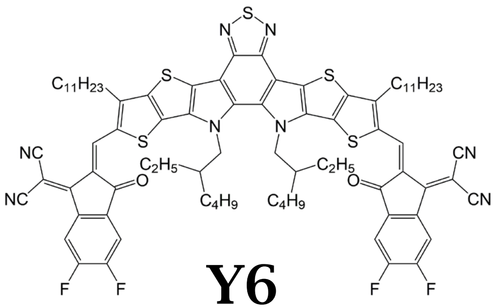


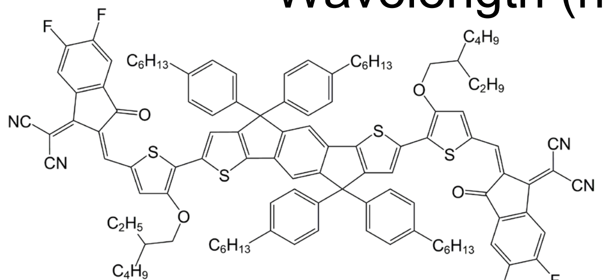
TQ-T







Y6



IEICO-4F

Figure of Merits

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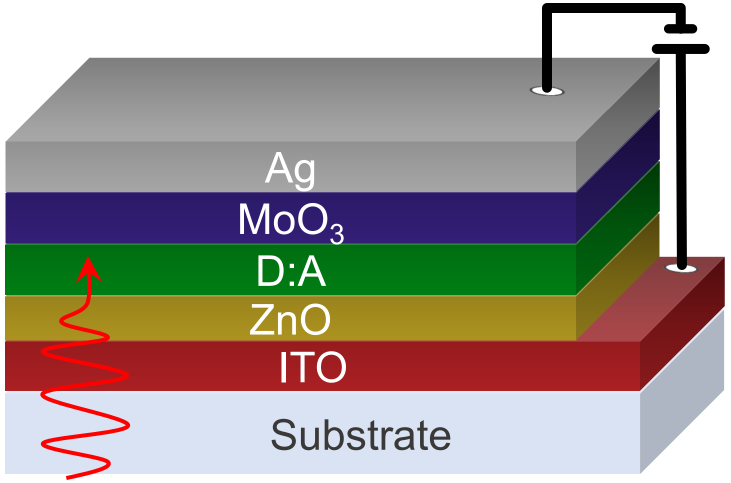
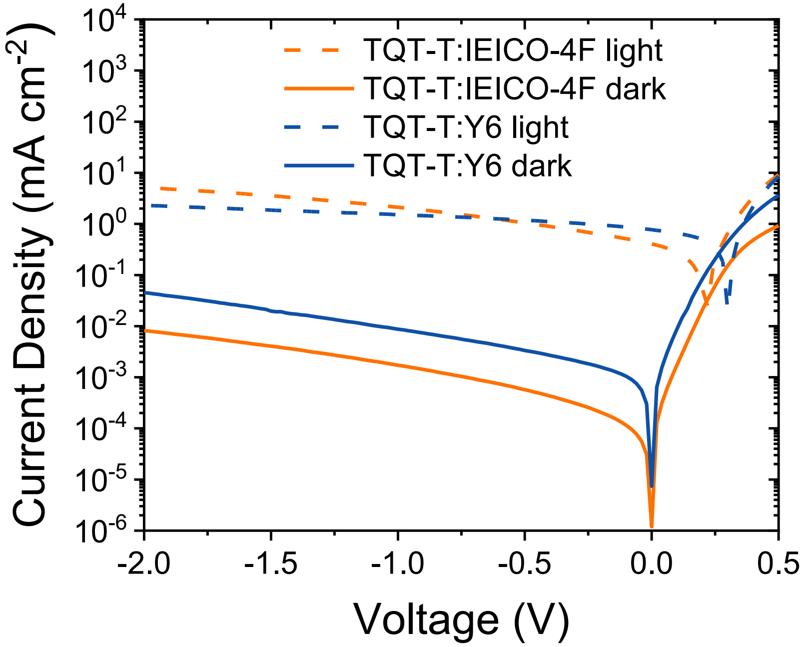
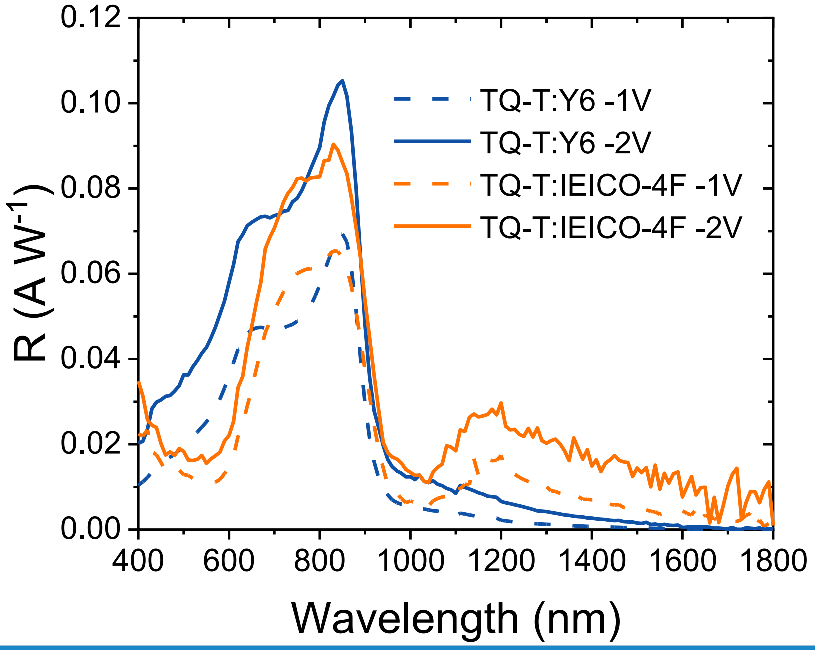




J_d at –2 V of 8.4×10^{-3} mA cm^{-2}

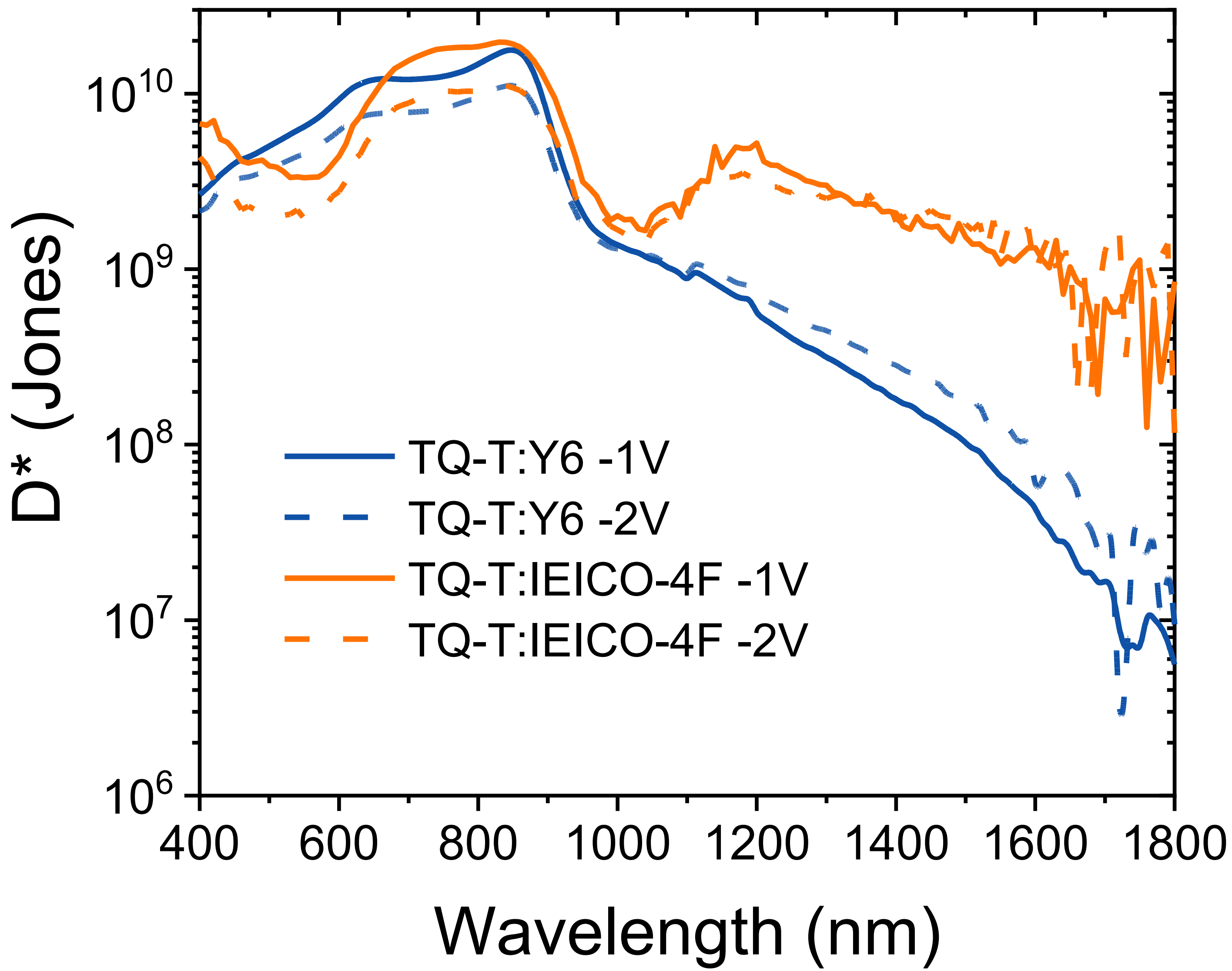


R at –2 V of 0.03 A W^{-1}
(EQE 2%)

Jacoutot, …, Gasparini. *Small* 2022, 2200580

Specific Detectivity

Imperial College London



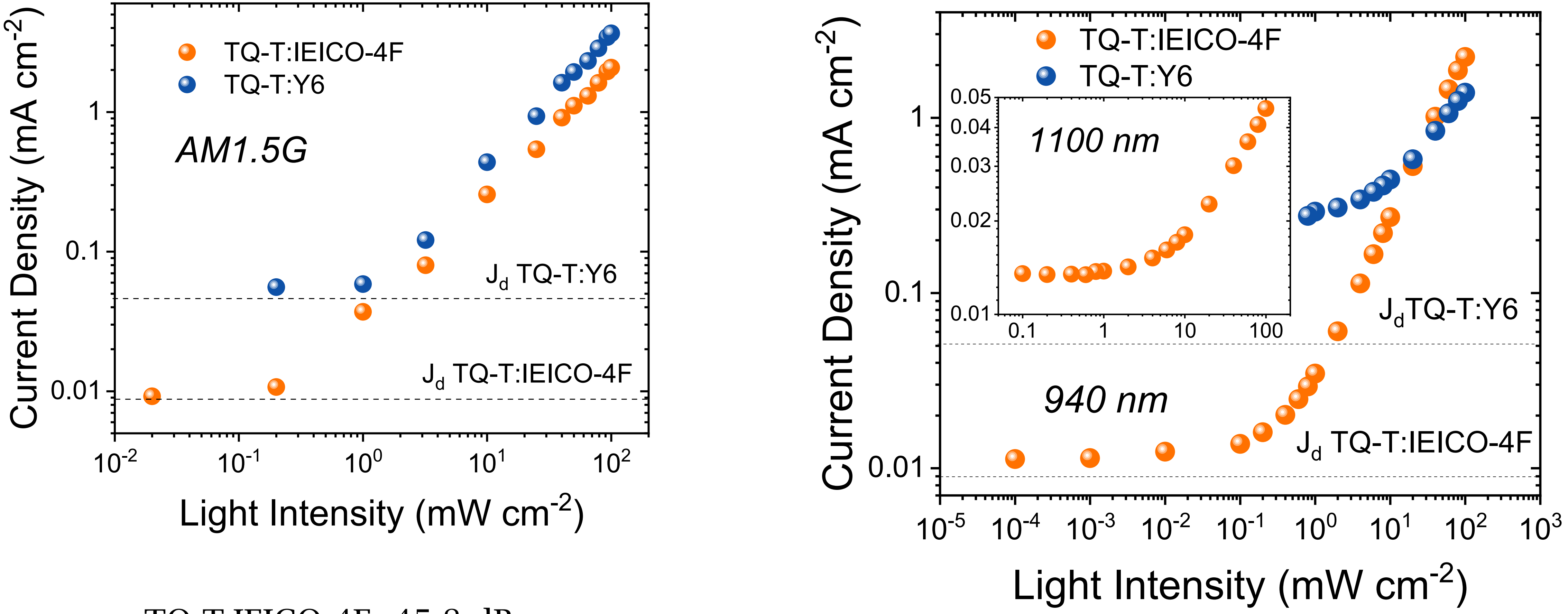
TQ-T:IEICO-4F OPD D* of 10^9–10^{10} Jones in the UV–Vis–NIR range

D* calculated from NEP and not Jd!

Jacoutot, …, Gasparini. *Small* 2022, 2200580

LDR

Imperial College London



TQ-T:IEICO-4F 45.8 dB

TQ-T:Y6 35.7 dB

Charge dynamics

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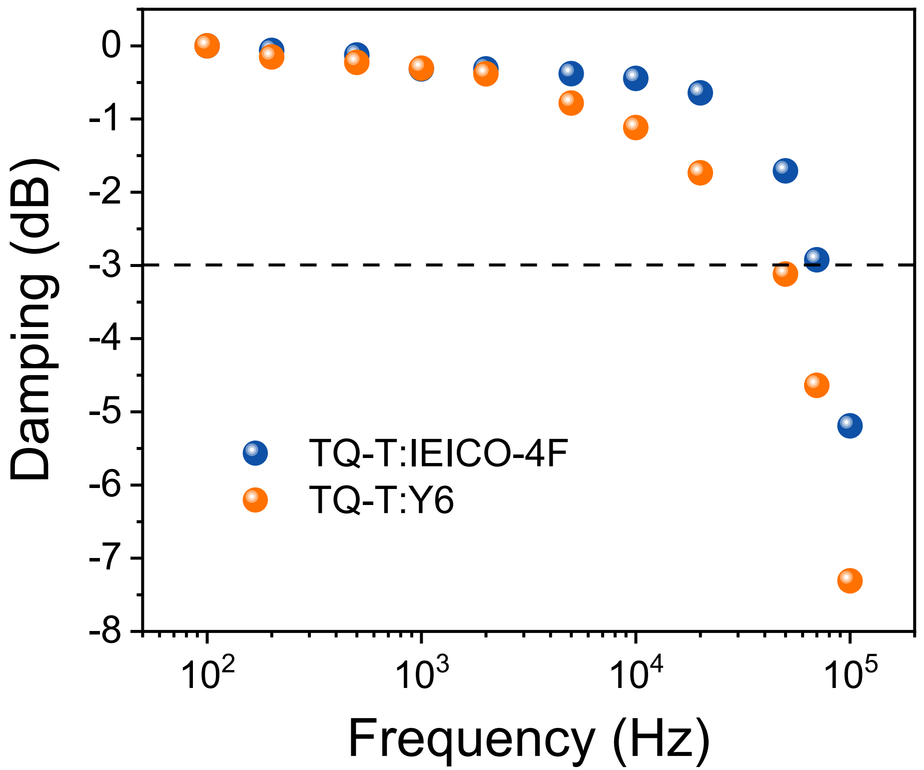
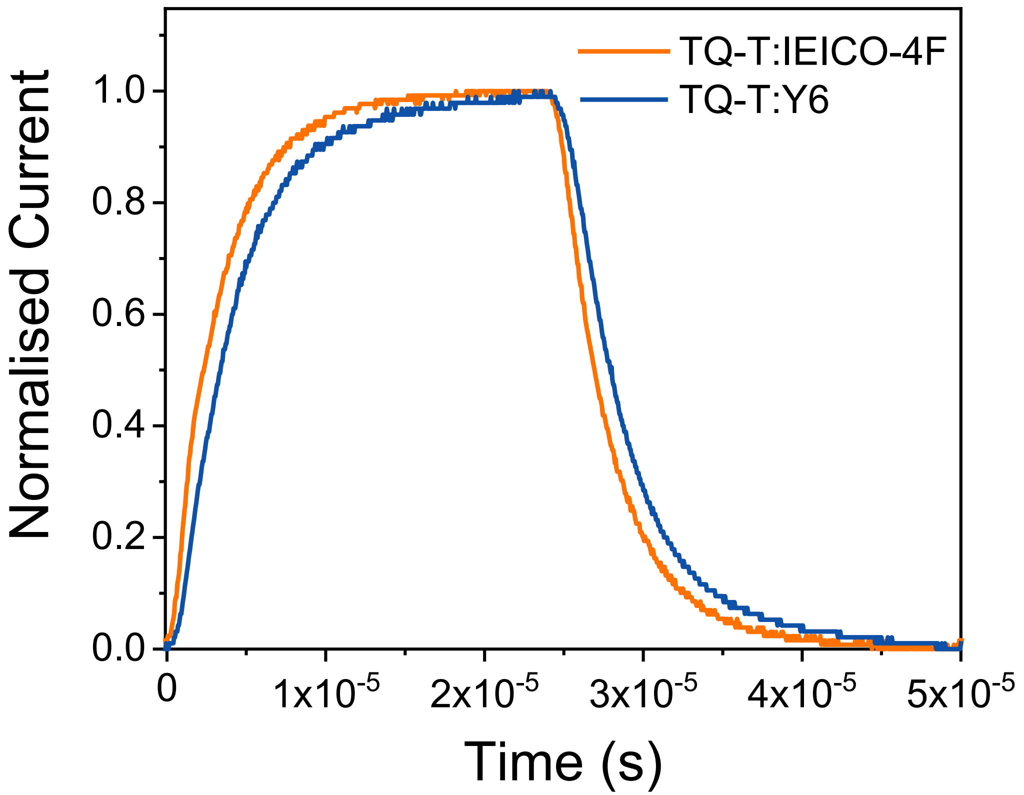




TQ-T:IEICO-4F 100 kHz

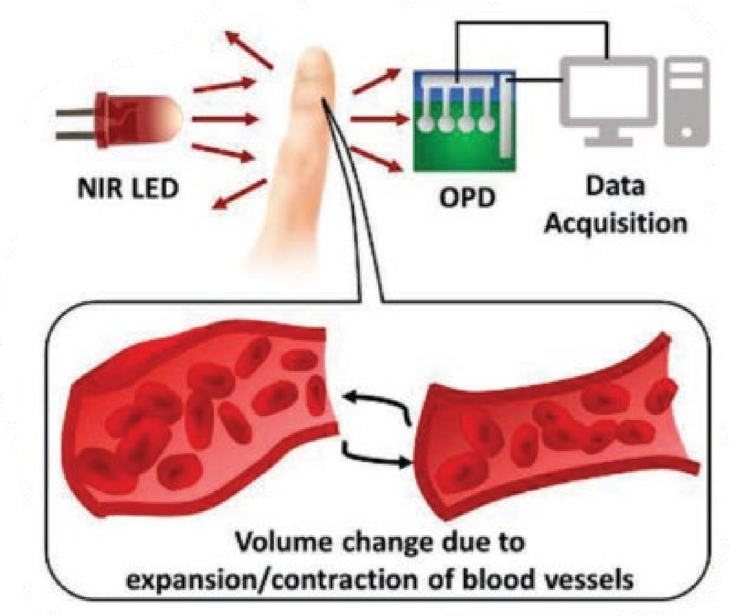
TQ-T:Y6 90 kHz

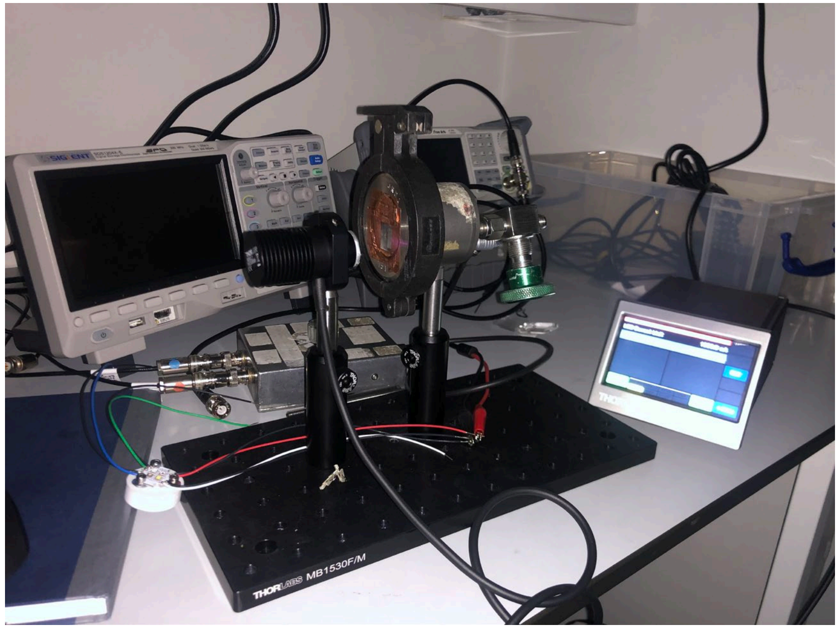
TQ-T:IEICO-4F rise/fall time 6.6/7.2 μs

TQ-T:Y6 rise/fall time 7.3/8.3 μs

Homemade Photoplethysmography setup

- **Photoplethysmography**: no-contact optical technique to detect volumetric changes in blood.
- Changes in absorbance → **direct current readout** from photodetector.





Jacoutot, …, Gasparini. *Small* 2022, 2200580

HB monitoring - comparison

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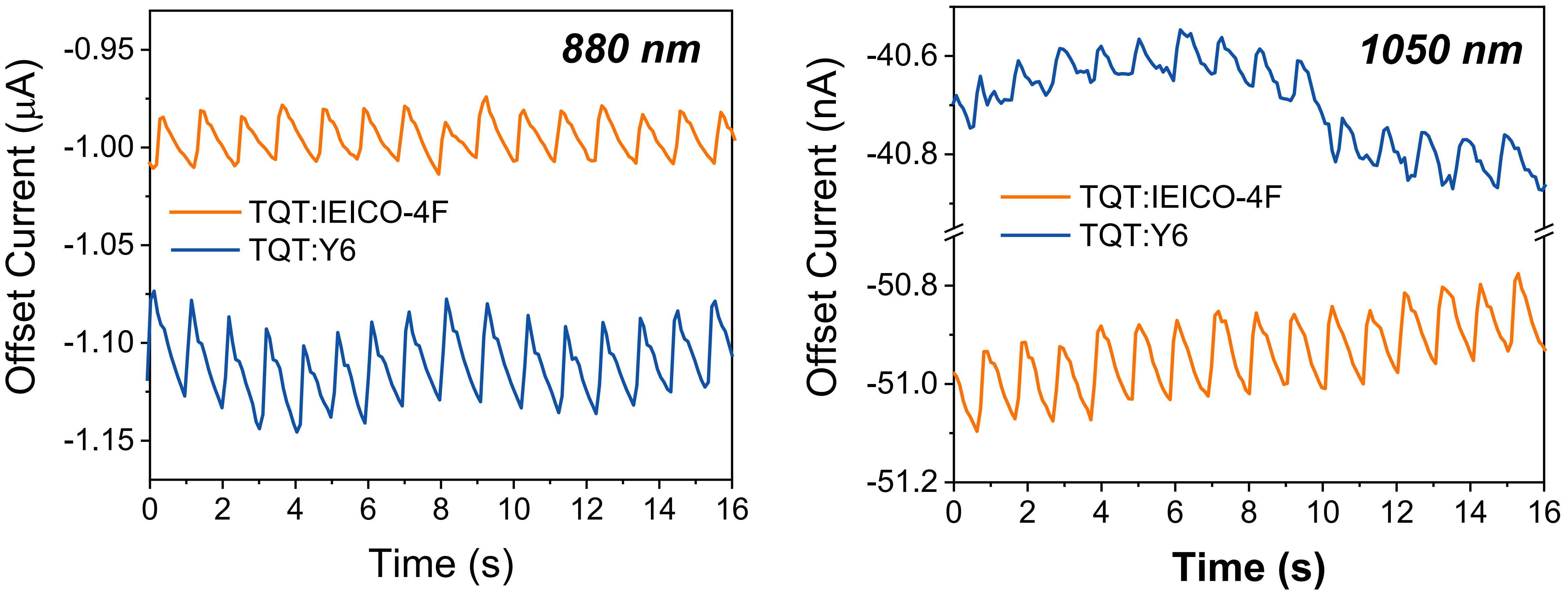
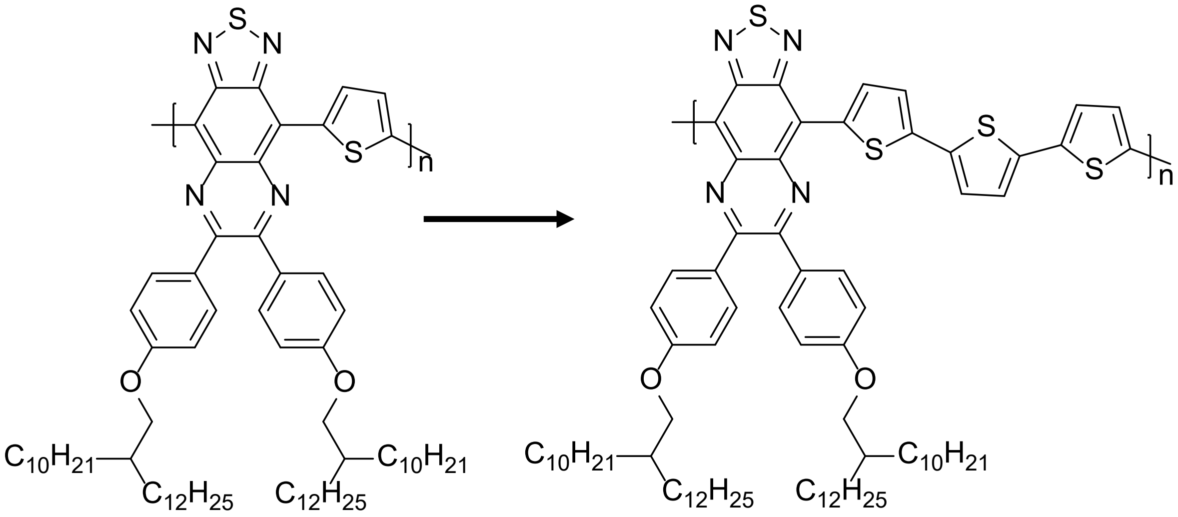


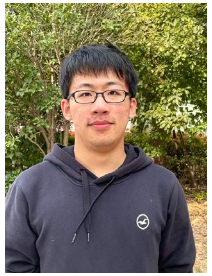
Jacoutot, …, Gasparini. *Small* 2022, 2200580

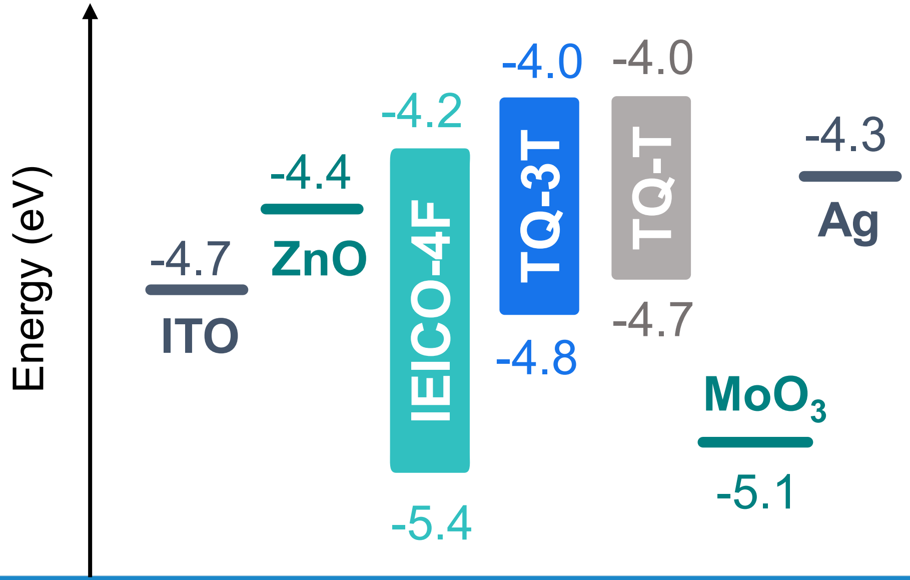
Tuning the polymer energetics

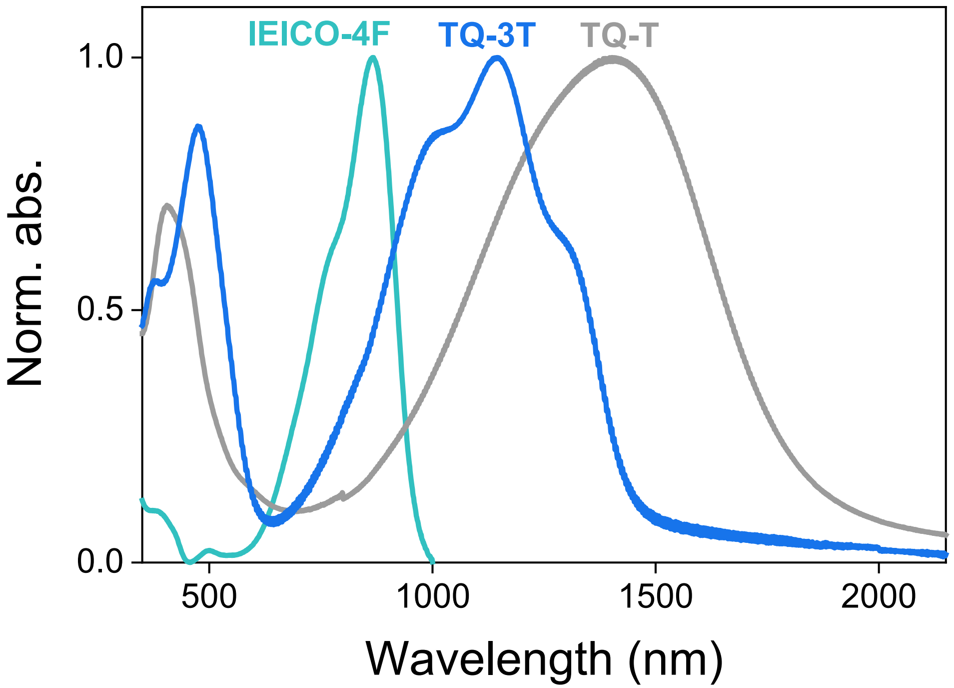
Imperial College London



TQ-T TQ-3T

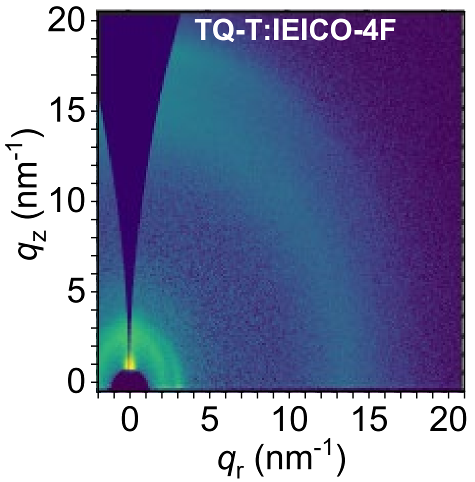


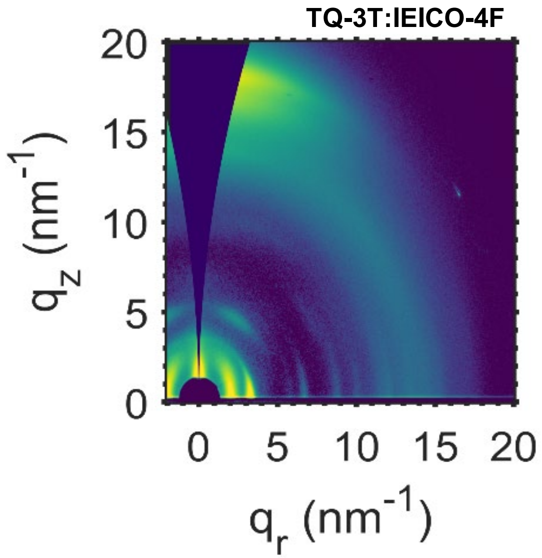


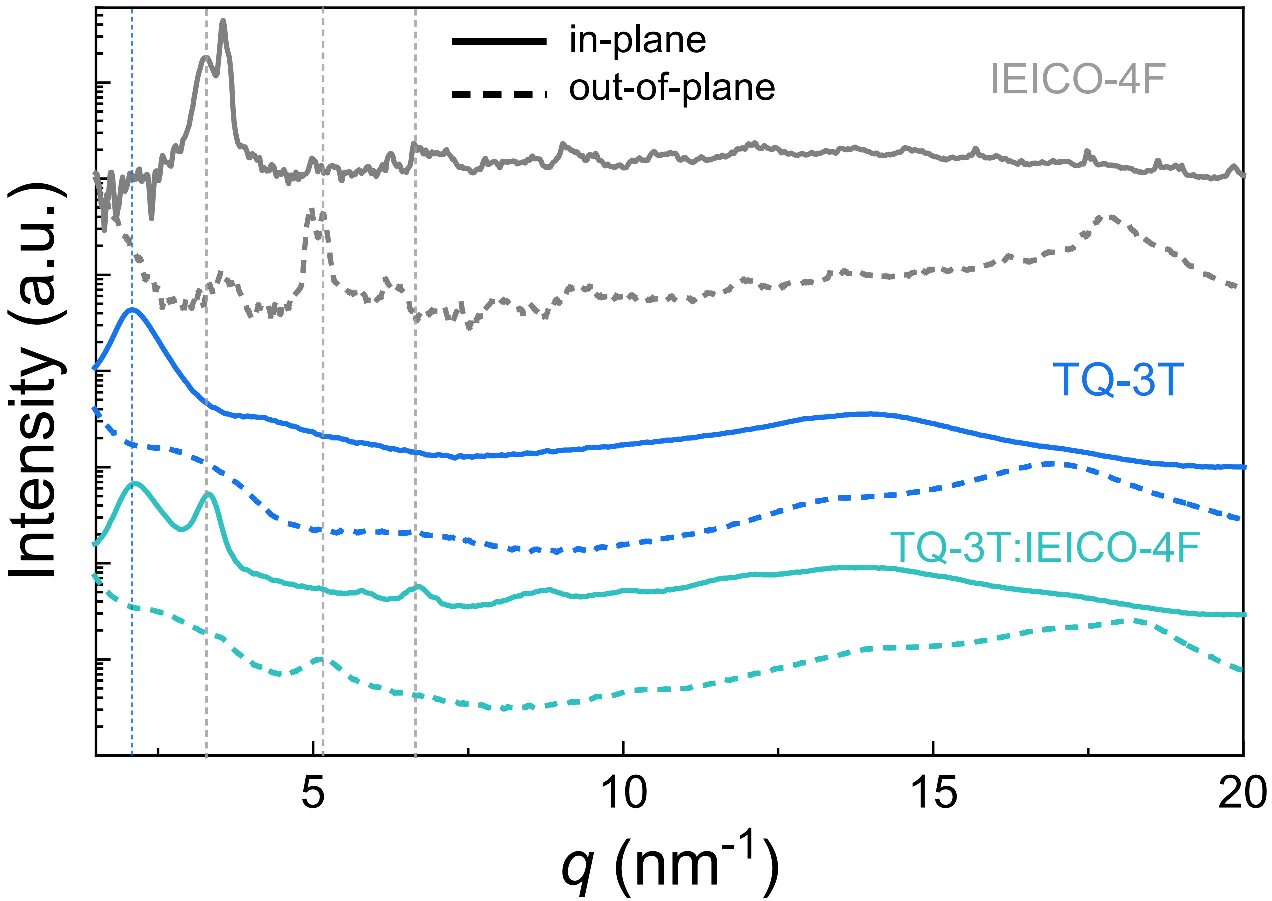


Tuning the polymer energetics and morphology

Imperial College London







Improved microstructure in TQ-3T:IEICO-4F

Device performances

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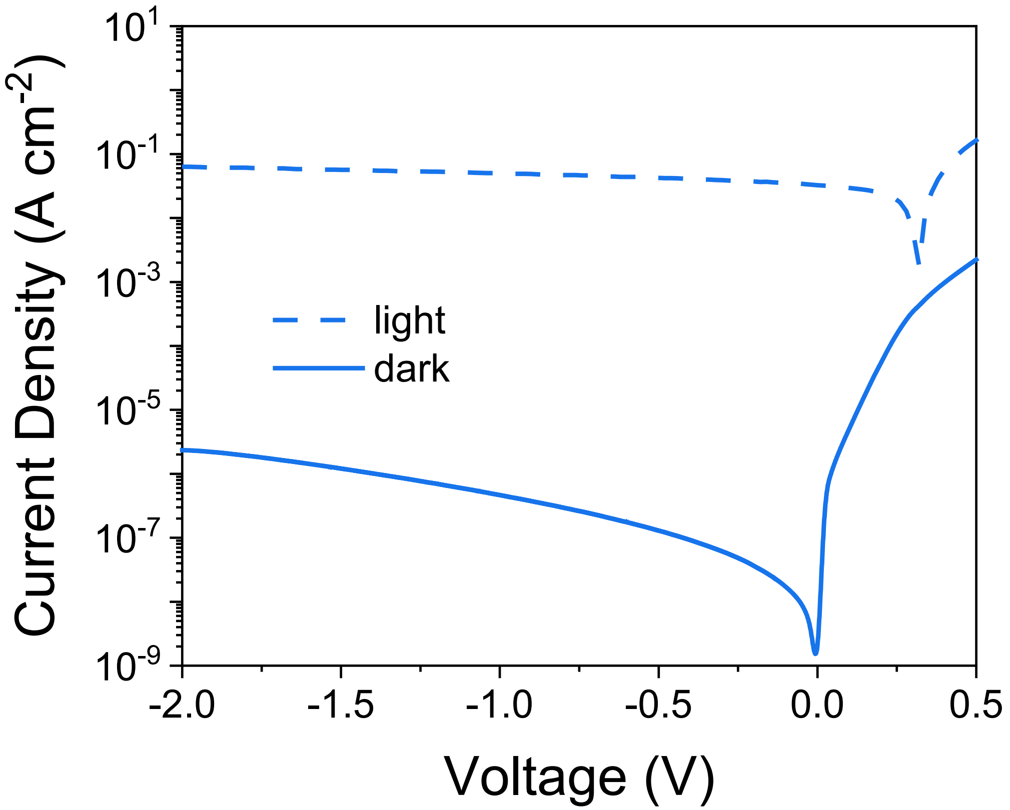
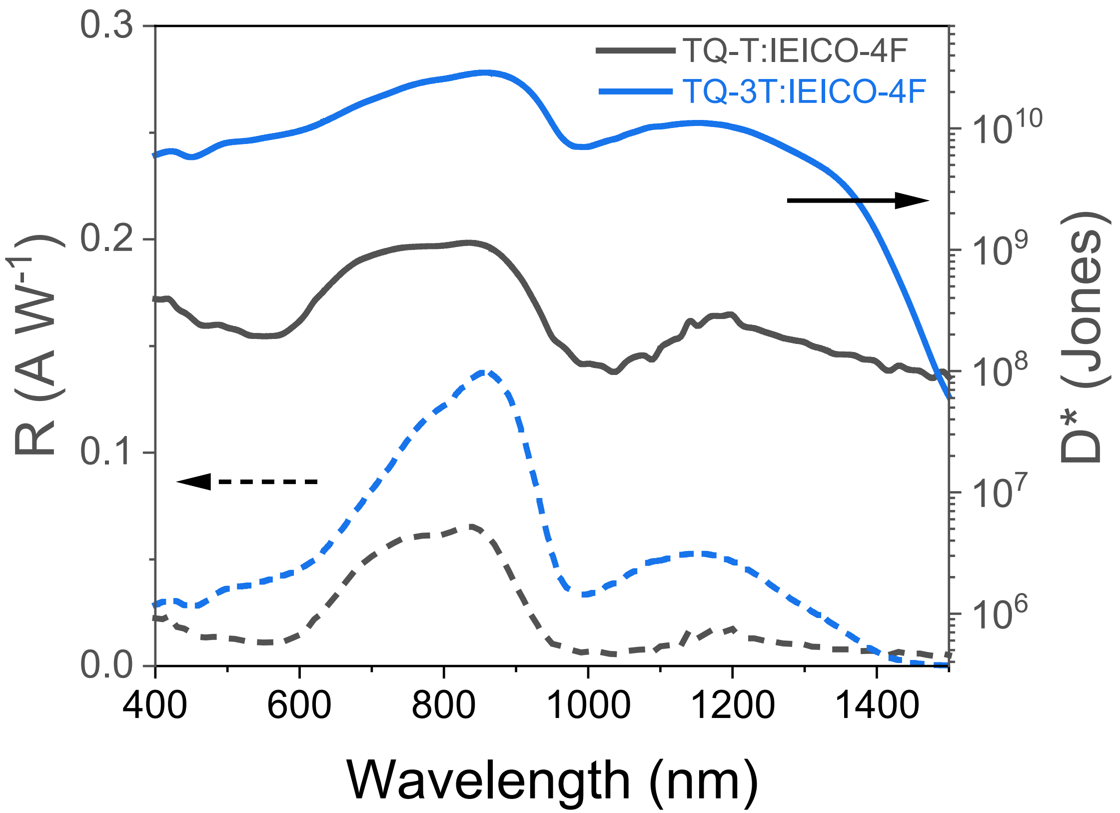


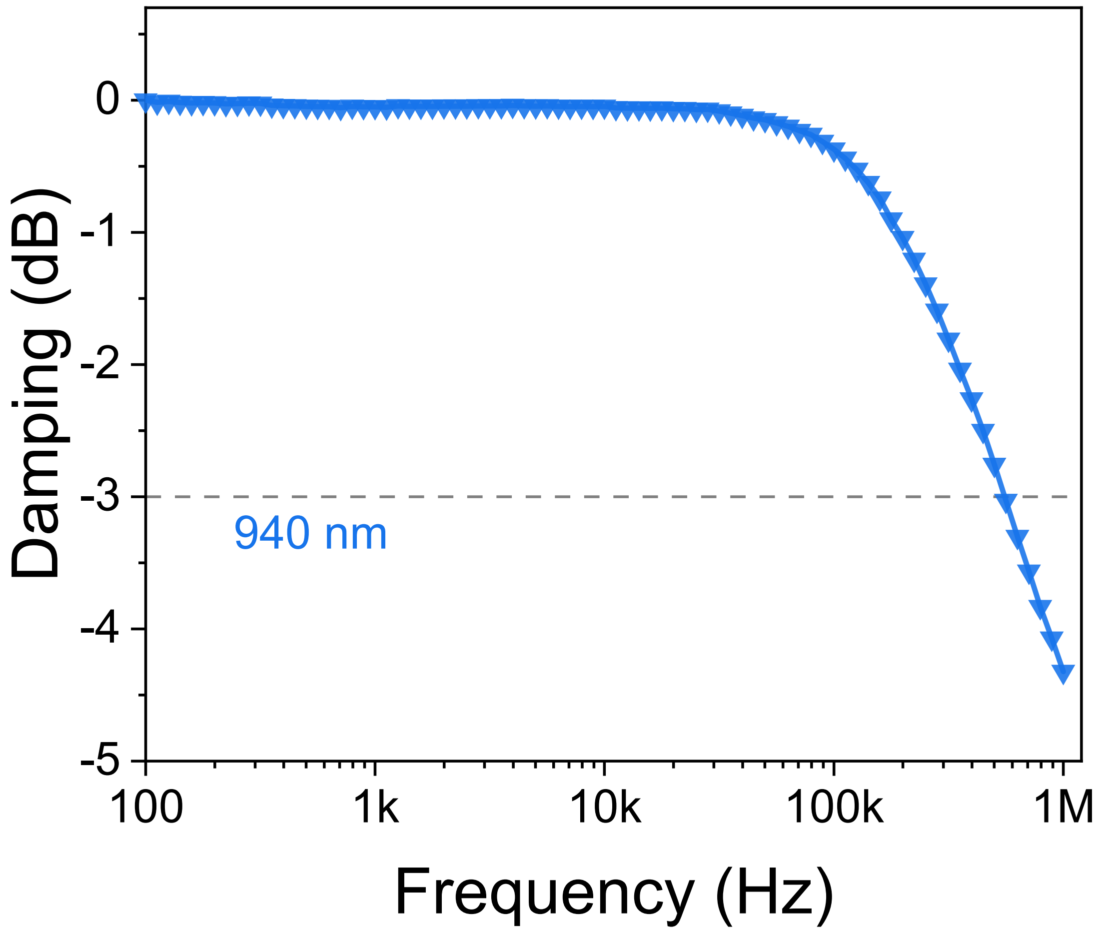


Jd reduced by 1 order of magnitude

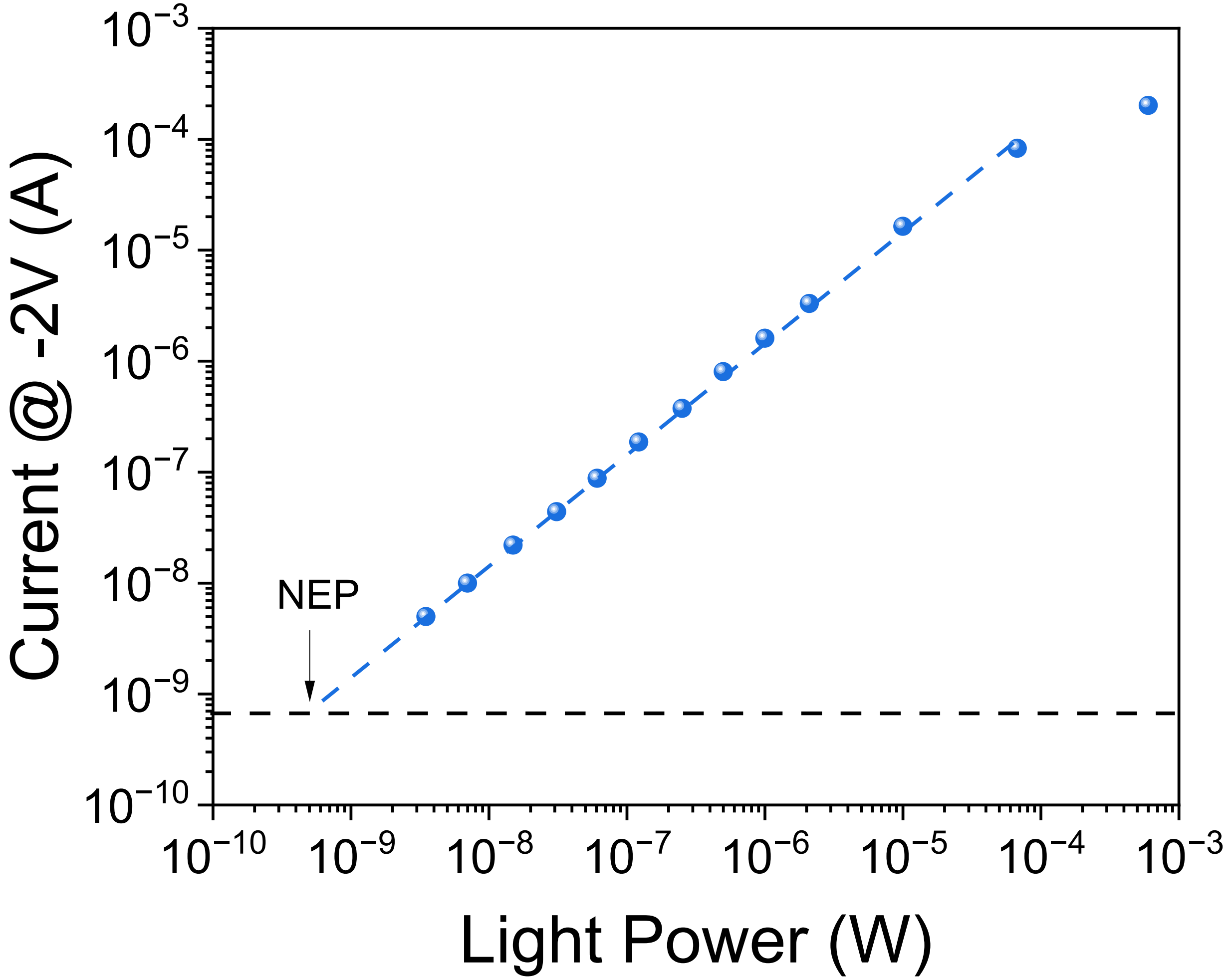
D* of 10^{10} Jones 400-1350 nm!

Device performances

Imperial College London



Cut-off frequency of >300 kHz



LDR = 84 dB

Real-world application

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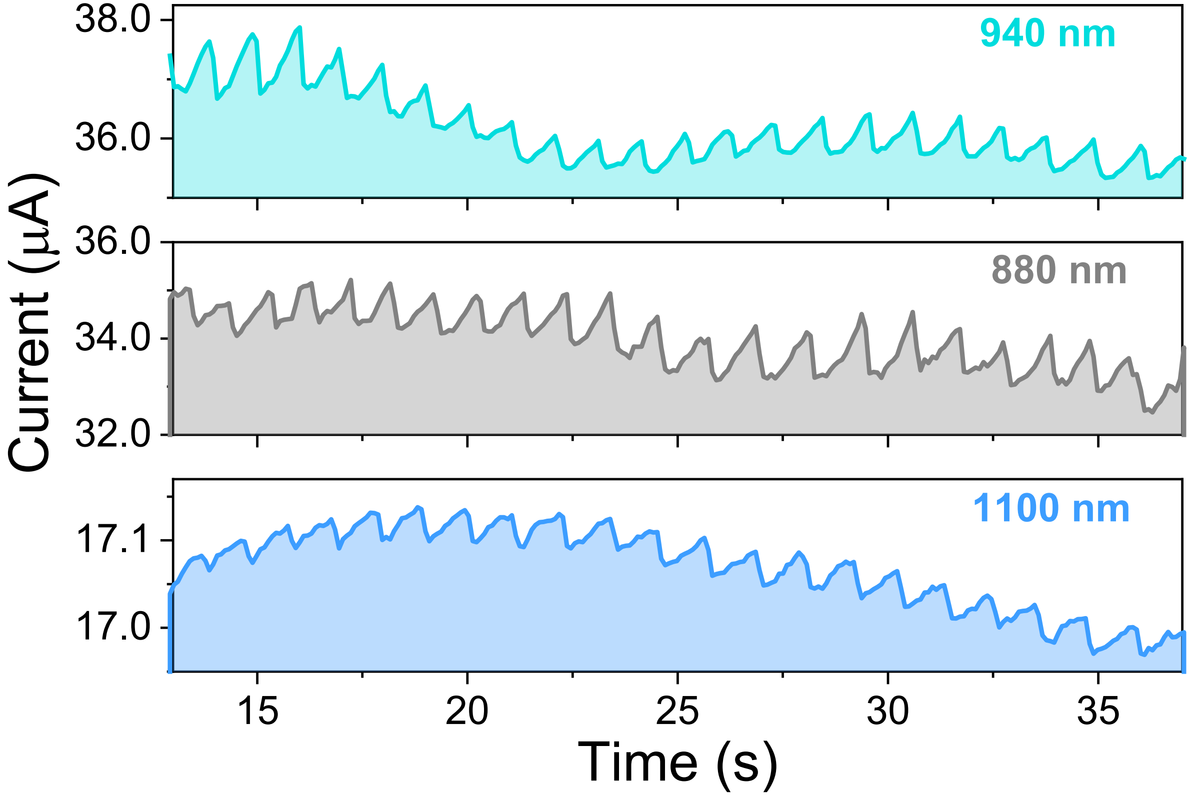
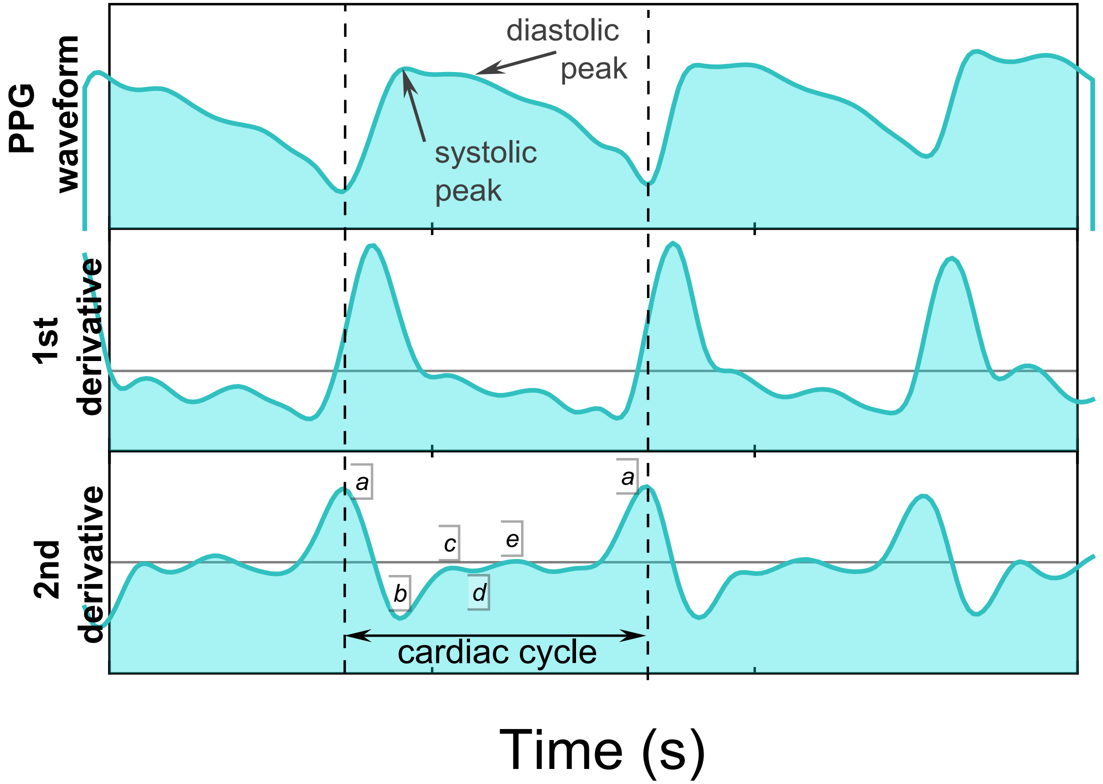
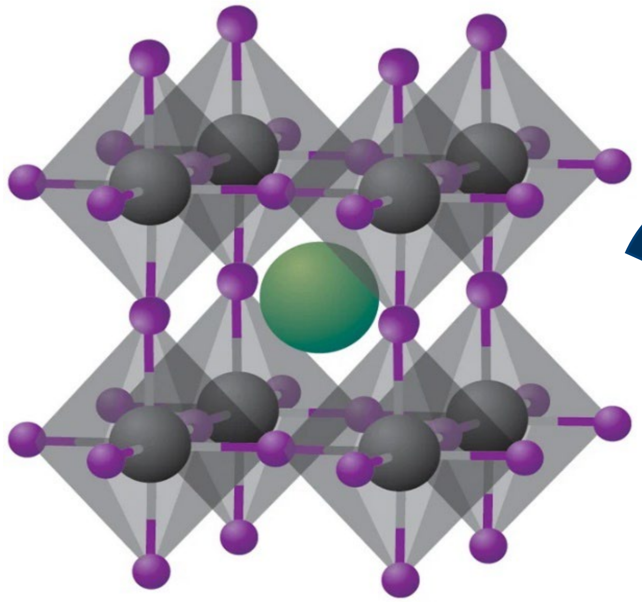




Jacoutot, ..., Gasparini. 2023, Science Advances 9 (23), eadh2694

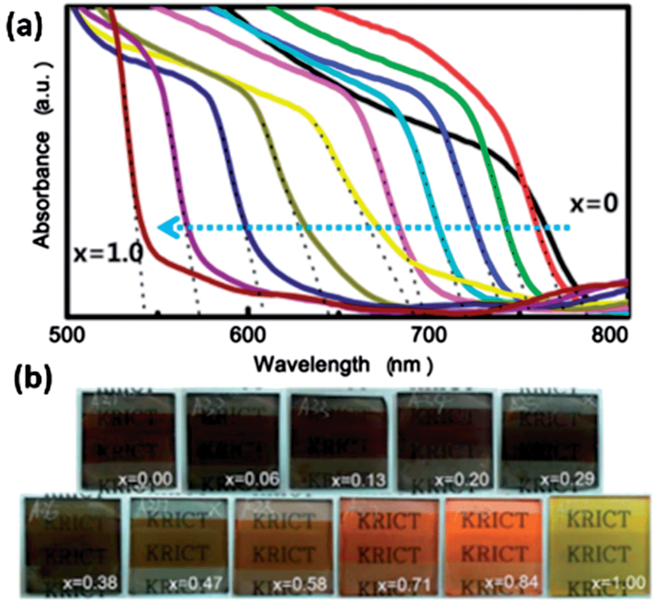
Perovskite Photodetectors

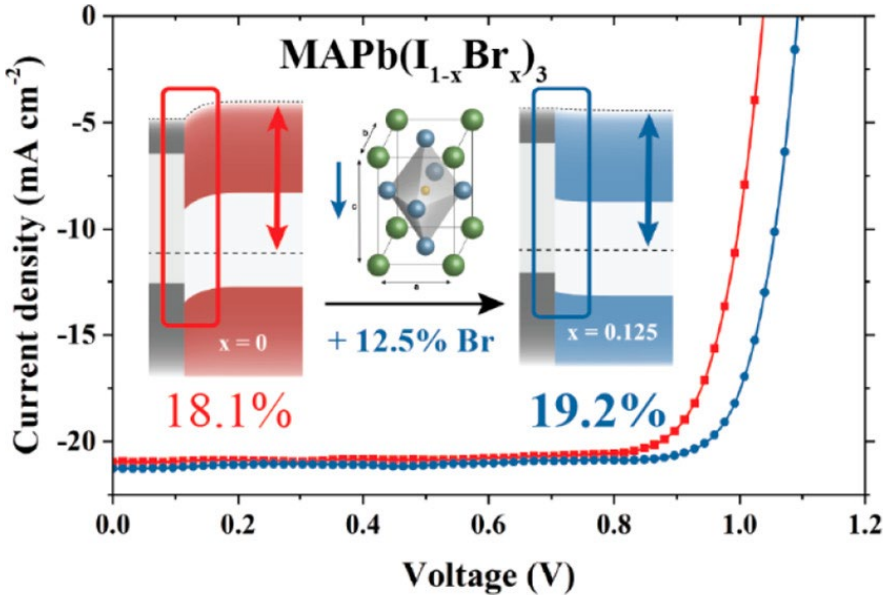
Imperial College London



ABX_3

A = monovalent organic cation
B = divalent metal cation
X = monovalent halogen anion





Tunable bandgap through halide engineering

Gao, Peng, et al. Energy & Environmental Science (2014)
Daboczi, Matyas, et al. ACS Energy Letters (2021)

Perovskite Photodetectors

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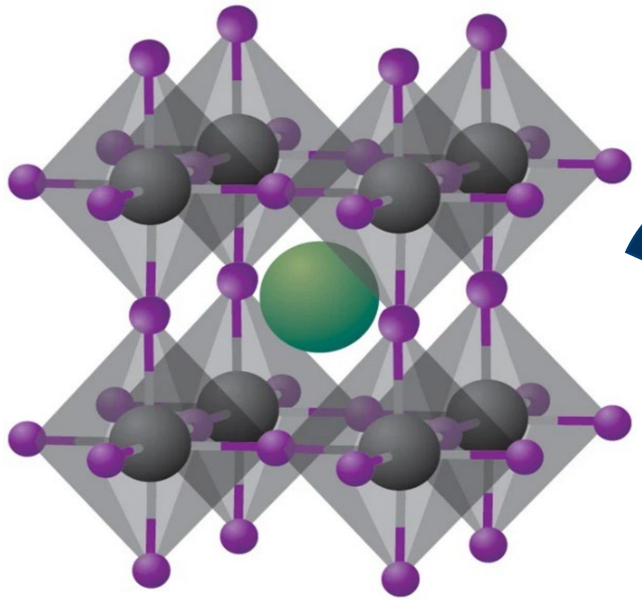
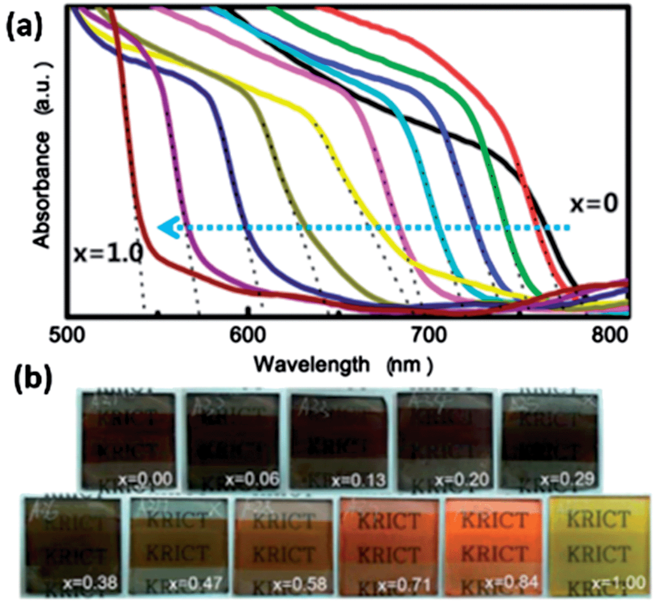
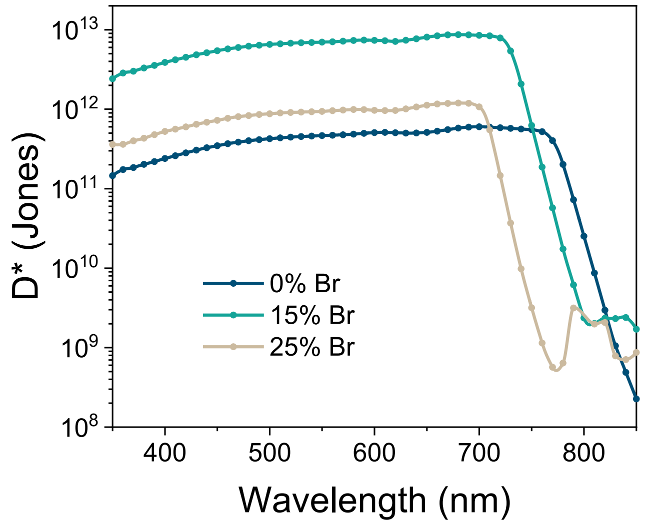


ABX$_3$

A = monovalent organic cation
B = divalent metal cation
X = monovalent halogen anion



Tunable bandgap through halide engineering



Gao, Peng, et al. Energy & Environmental Science (2014)
Daboczi, Matyas, et al. ACS Energy Letters (2021)

Reducing thermal charge generation: halide doping

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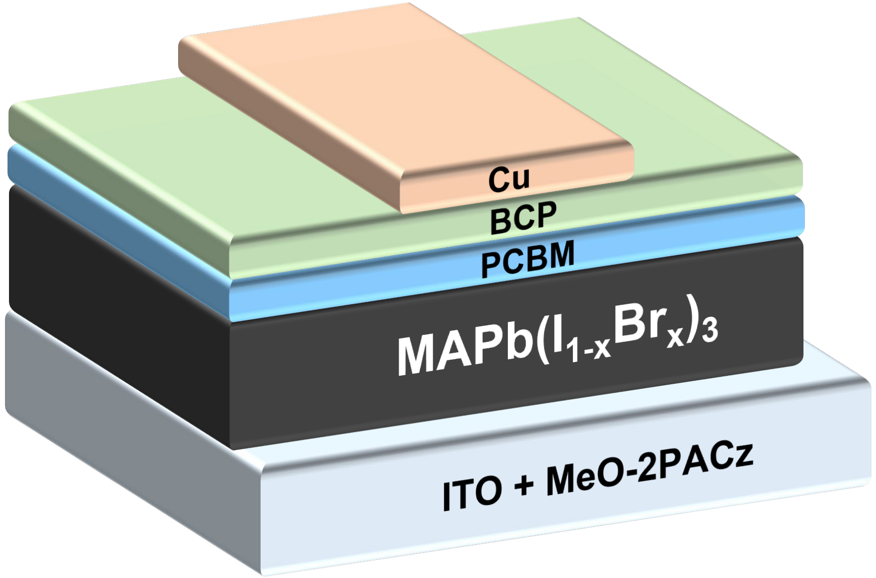
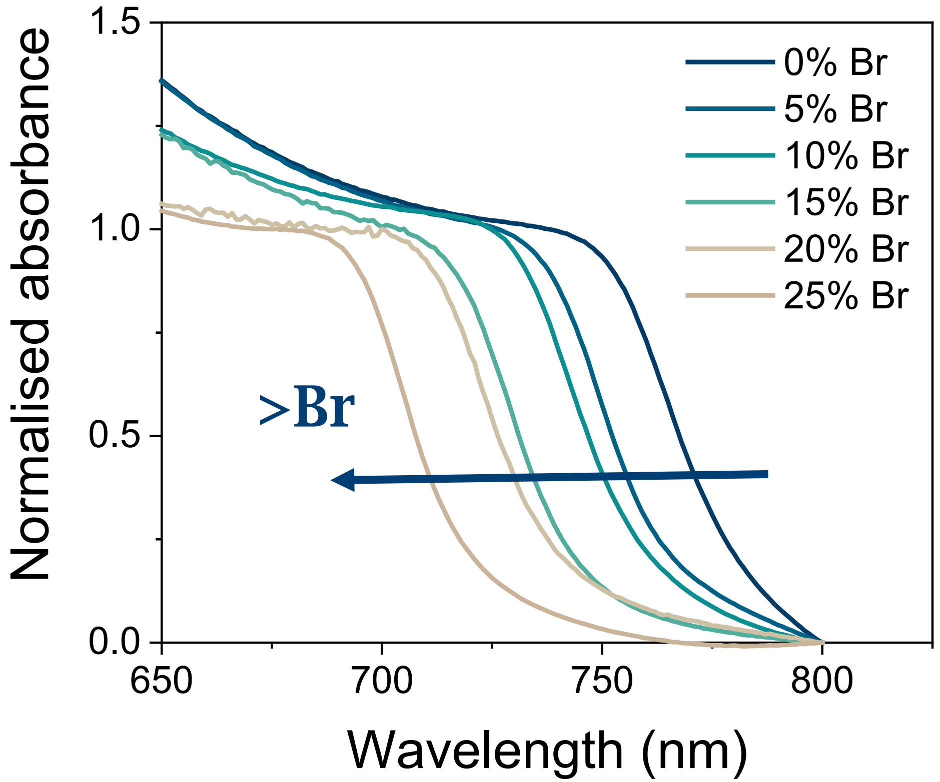
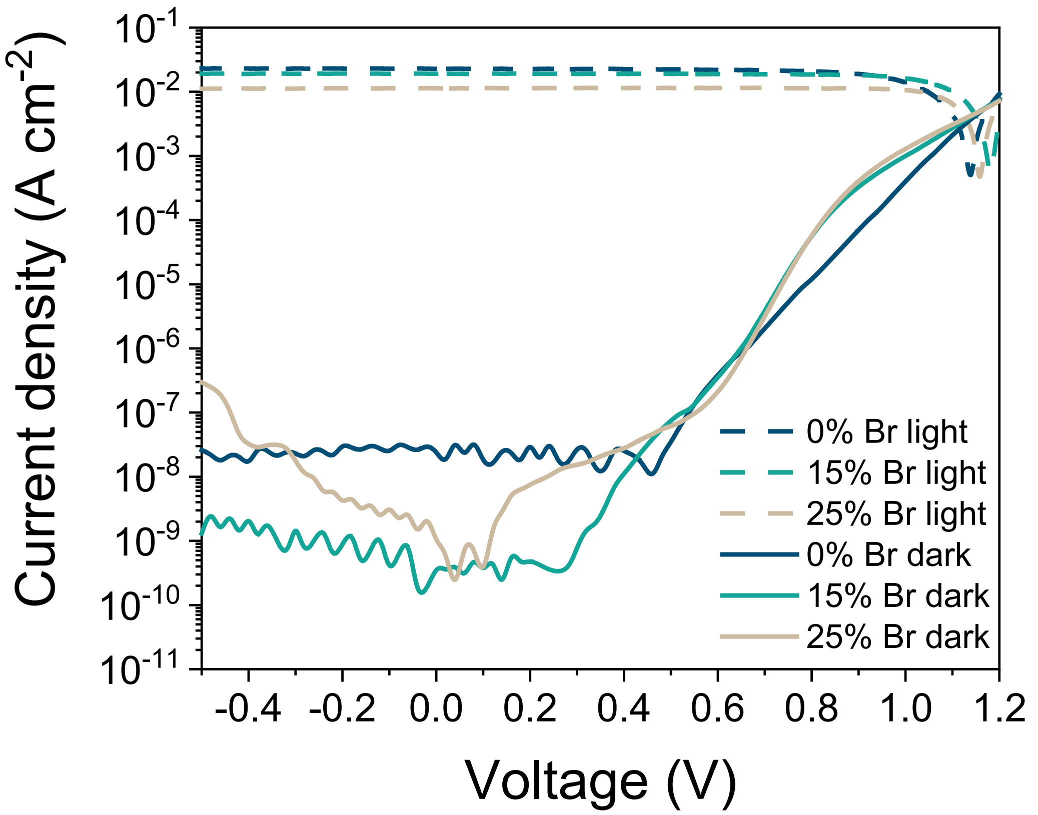


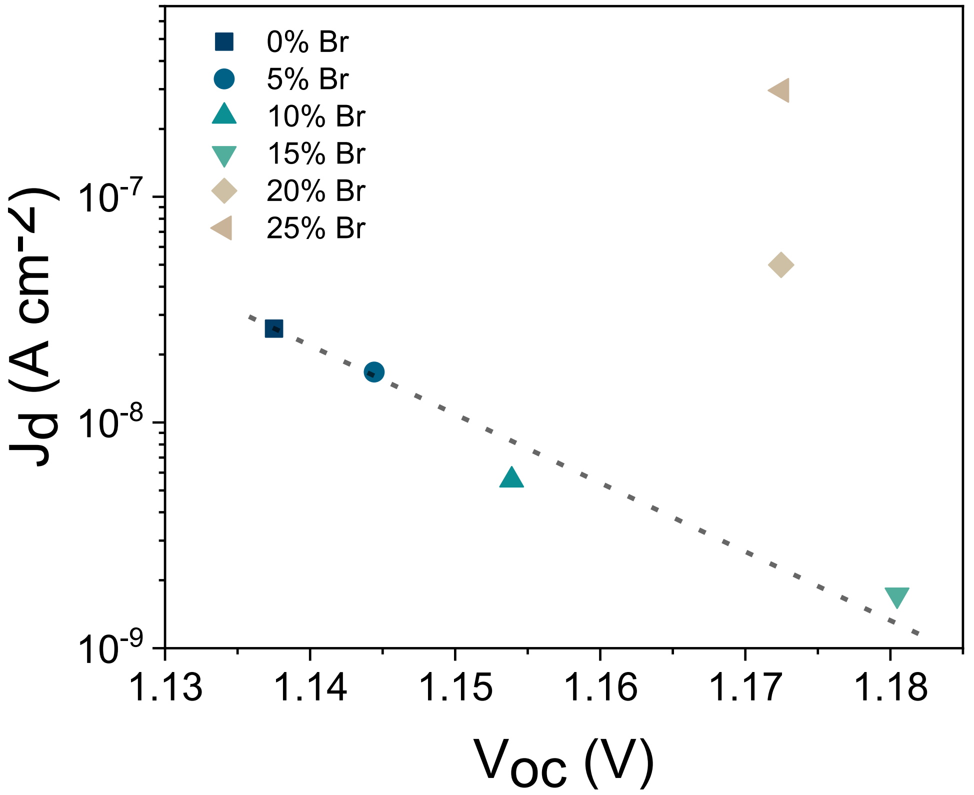
p-i-n structure



Nodari, Davide, et al. *Advanced Optical Materials* (2022): 2201816.

Dark current





	J_d $(A\ \mathrm{cm}^{-2})$ at -0.5V
0%Br	2.6×10^{-8}
15%Br	**1.3×10^{-9}**
25%Br	3.0×10^{-7}

Exponential relationship between J_d and V_{oc} over the 0-15% Br range

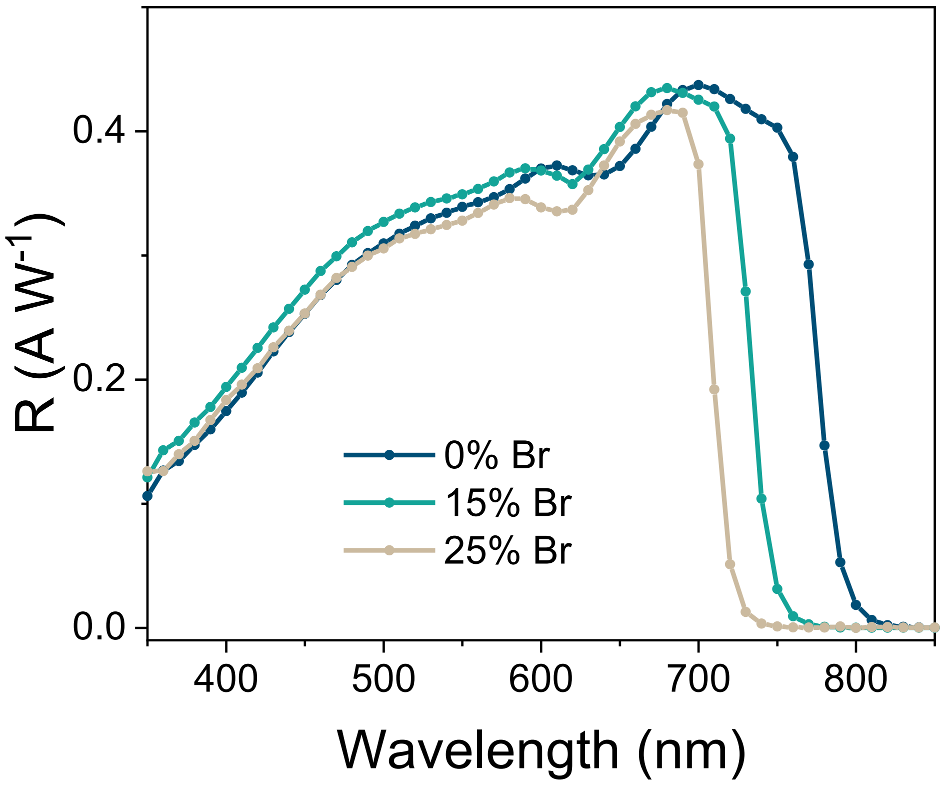
Similar behaviour as previously reported for organic PDs

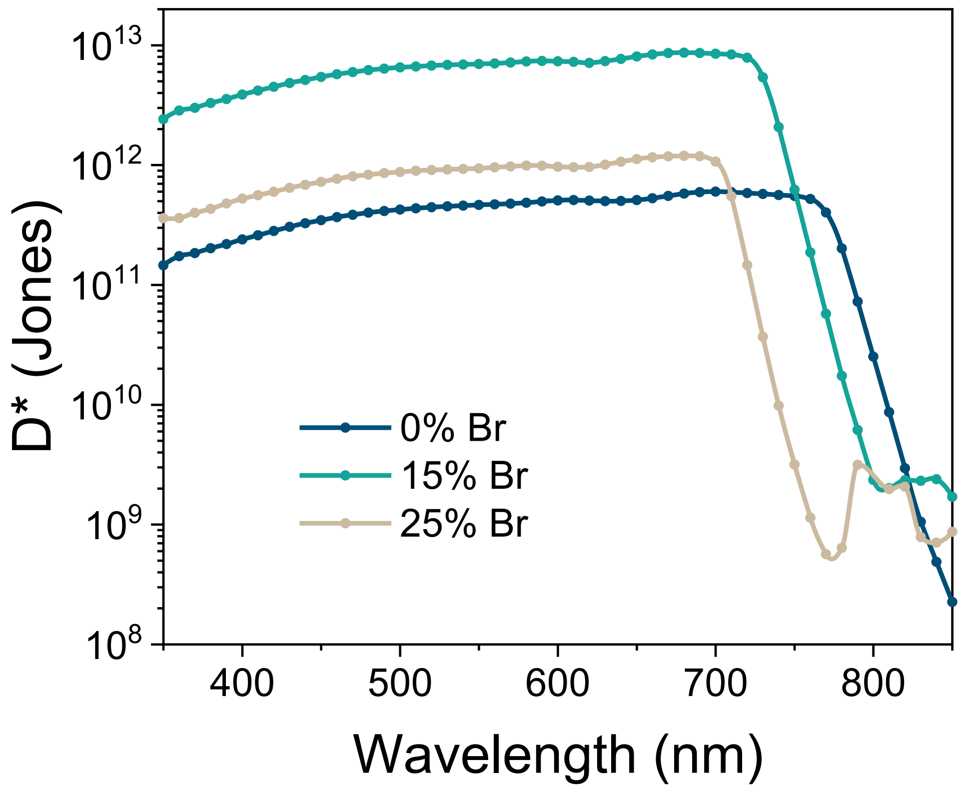
Responsivity and Detectivity

Imperial College London

$$SR(\lambda) = \frac{J_{ph}}{P_{in}} = EQE \cdot \frac{q\lambda}{hc} \quad [A\,W^{-1}]$$

$$D^*(f,\lambda) = \frac{SR(\lambda)\sqrt{A\Delta f}}{i_{noise}(f)} \quad [Jones]$$





Recombination investigation

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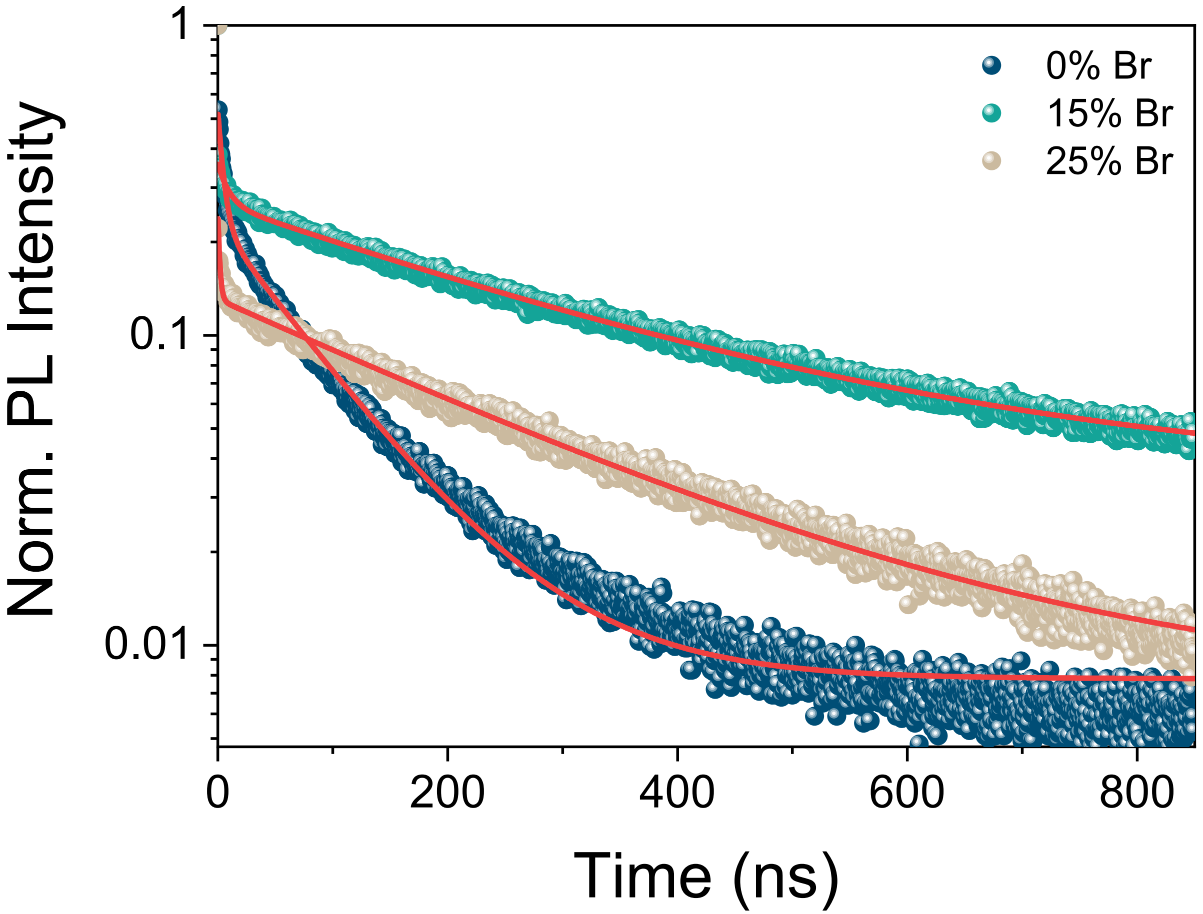
$\tau_{ave,0\%}$=80.28ns
$\boldsymbol{\tau_{ave,15\%}}$**=299.31ns**
$\tau_{ave,25\%}$=246.45ns



Long τ_{ave}represents suppressed non-radiative recombination pathways

Morphological analysis

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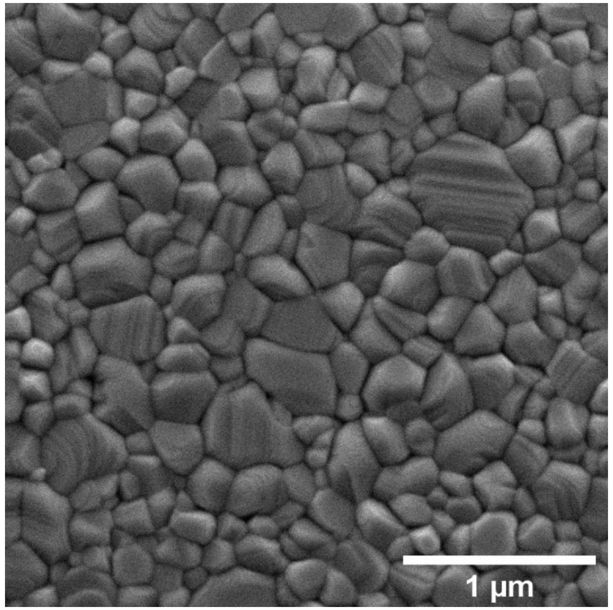

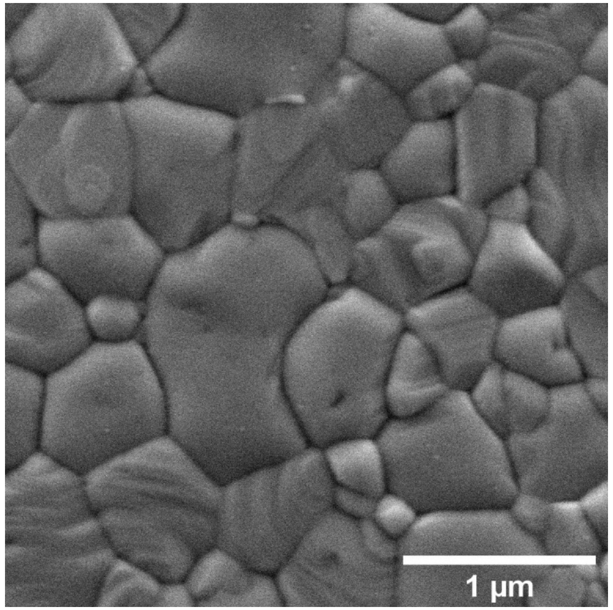

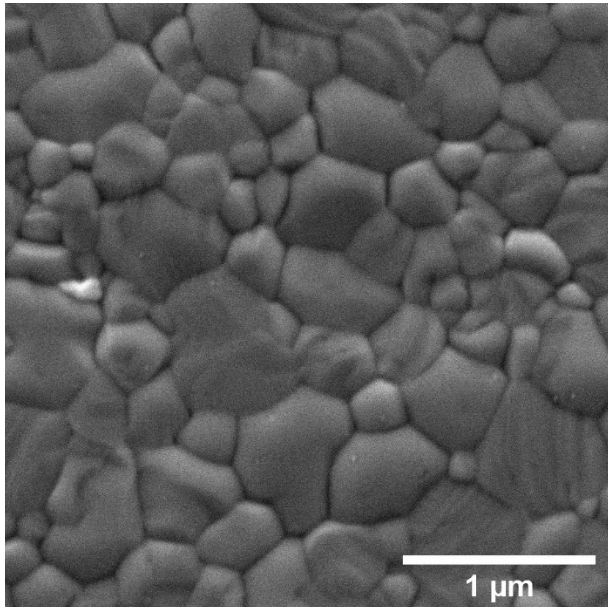

0% Br **15% Br** **25% Br**

Nodari, …, Gasparini *Advanced Optical Materials* (2022): 2201816.

Reducing Jd: Strain-induced α-phase stabilisation in FAPI-based Photodetectors

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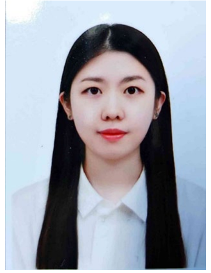
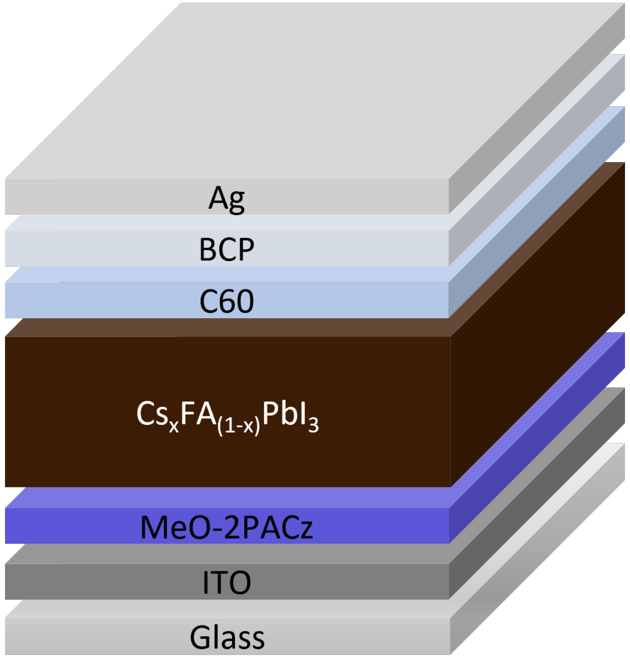
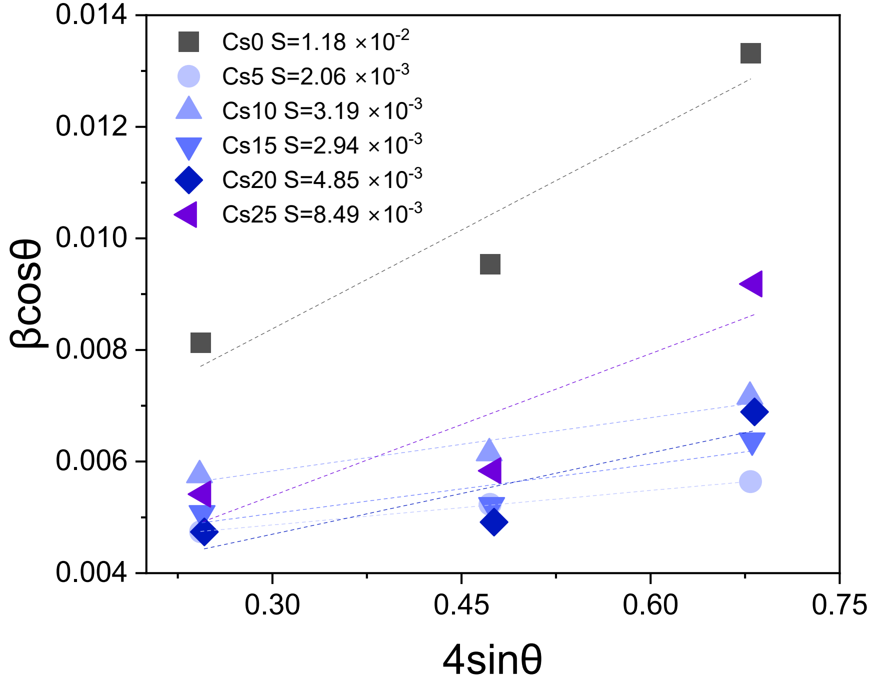
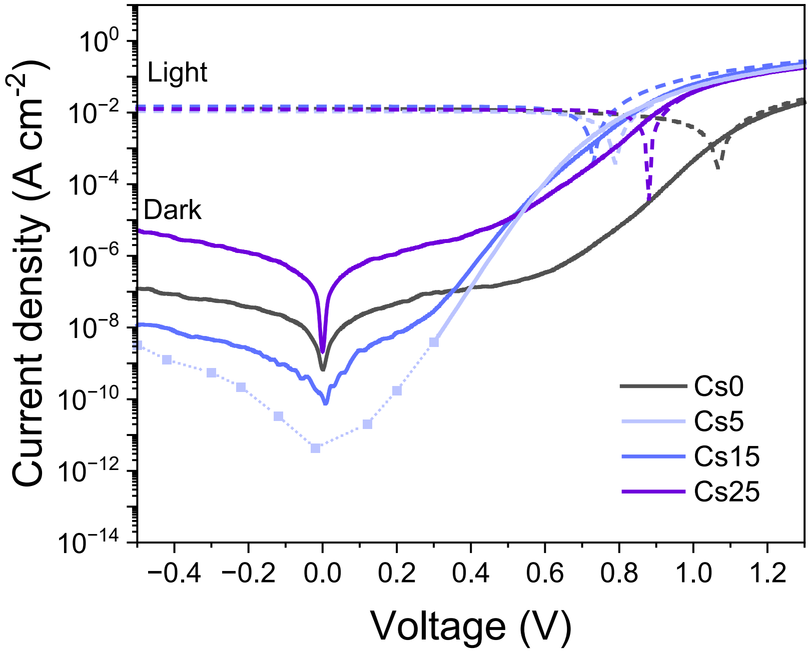






Williamson-Hall plots

Cs5 → reduction in lattice strain



Cs5 → lowest Jd

α-phase stabilisation

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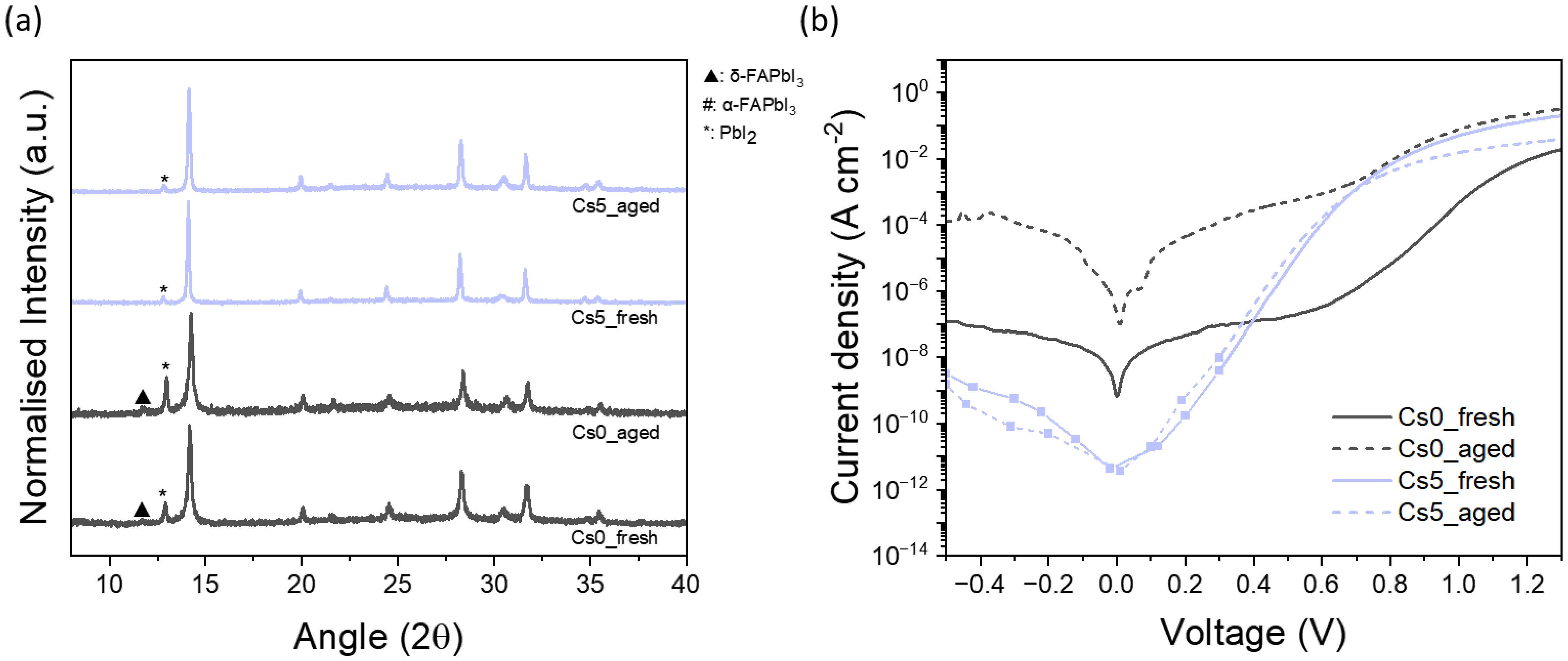

Long-term stability of Cs5-based PD

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Centre for Processable Electronics

Thank you for your attention

n.gasparini@imperial.ac.uk