5th Physical Sensing and Processing Summer School, University of Bologna

Organic Semiconductors: New Frontiers in Radiation Detection

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Our Group and Location

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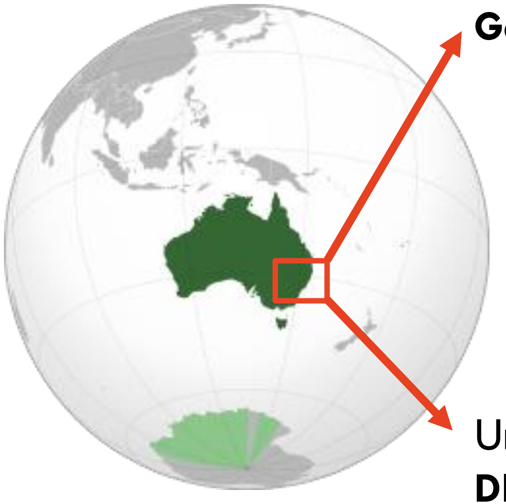

University of Sydney

Gadigal people of the Eora Nation

University of Wollongong

Dharawal Country

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Overview

1. Early Use of Ionizing Radiation and ‘Safety’
2. Introduction to Radiation Dosimetry
3. Basic Operation of Organic Semiconductors
4. New Frontiers in Radiation Detection with Organic Semiconductors

Early Use of Ionizing Radiation and 'Safety'

How the discovery of x-rays revolutionised medical treatment

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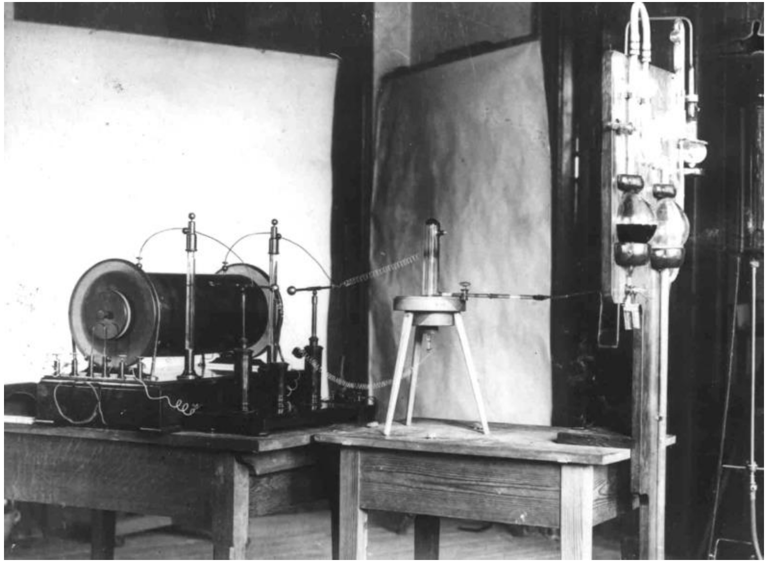
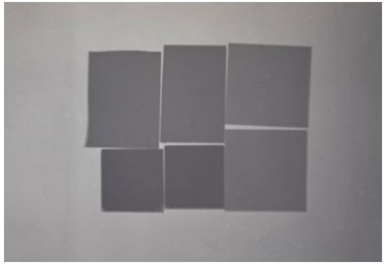
Wilhelm Röntgen
Born 1845 in Remscheid, Germany
PhD in Physics at University of Zurich

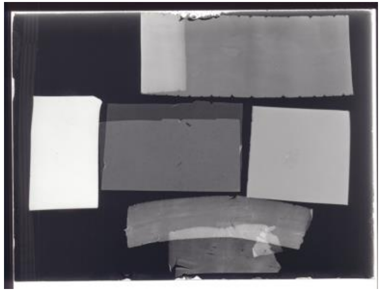
Discovery of X-Rays

Wilhelm Röntgen's Lab
Cathode Ray Tube
University of Würzburg, Germany



Röntgen found that objects of different thickness and material (platinium, lead, zinc and aluminium foil) interposed in the path of the rays showed variable transparency to them when recorded on a photographic plate.

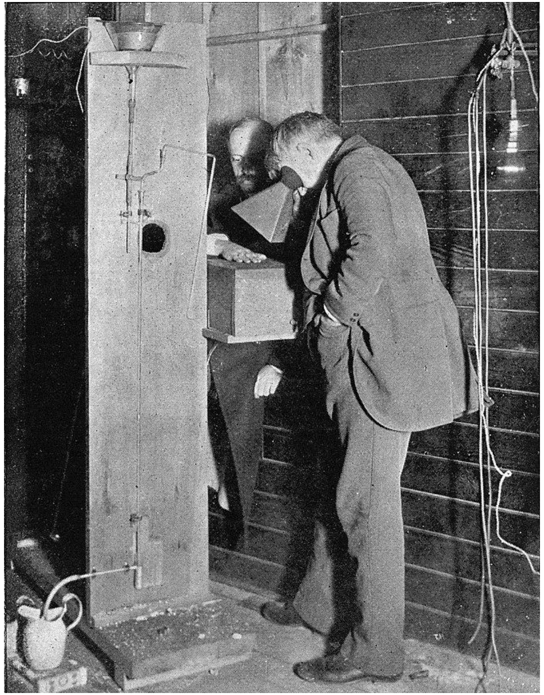




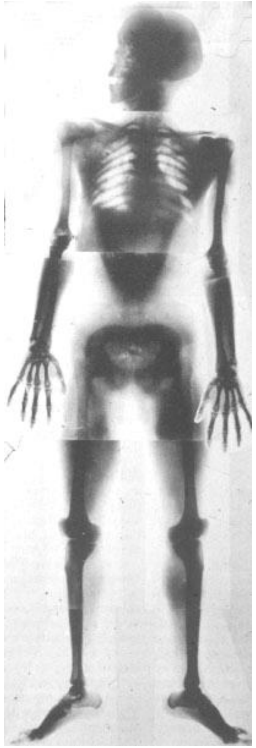
A Vision of Modern Diagnostics

- Birth of Radiography on December 22nd, 1895
- Radiograph of Rontgen's Wife, Anna's hand showing her wedding ring
- Rontgen called them **'X'**-rays to underline the fact that the nature of them was unknown
- Called Rontgen-rays in Europe

Science Phenomena to Surgical Tool



New York 1896
Public demonstration of x-rays
Thomas Edison examines Clarence Dally's hand

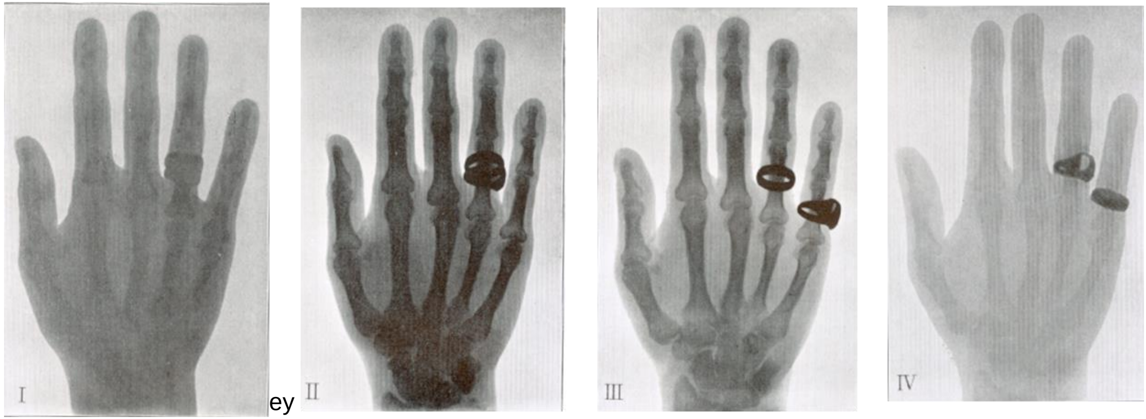


Germany 1896
First whole-body radiograph
Exposure: up to 60 min for head/pelvis

Radiology was recognized as a medical speciality after end WW1

Dangers of Radiology

- Effect of radiation exposure was not known and there was no way to monitor/measure exposure
- Doctors would use their hand to optimize x-ray image settings
- Treat superficial burns from x-rays like the sunburn from UV
- Amputated and preserved Hand of Dr. Paul Krause



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Introduction to Radiation Dosimetry

How we ensure the safe use of ionizing radiation in modern society

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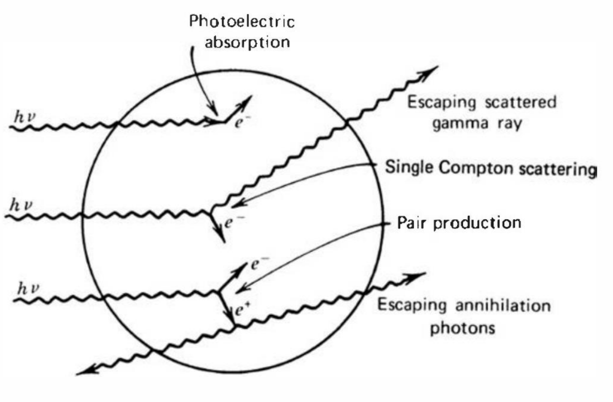
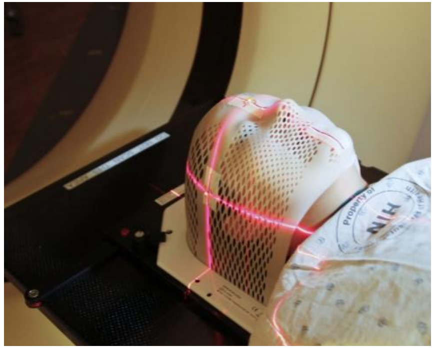
1. Interaction with x-rays



3. Medical Applications



2. Dosimeters

Units for Quantifying Ionizing Radiation

To ensure safe use of ionizing radiation we measure the amount of radiation a person is exposed to in units of radiation dose:

Gray (Gy)	Unit of **absorbed** dose (D)	Amount of energy deposited by radiation in a **specific material*** such as human tissue
Sievert (Sv)	Unit of **equivalent** dose (H) Unit of **effective** dose (E)	Biological effect of absorbed dose by using a radiation weighting factor • H depends on the type of radiation incident on the body • E depends on the tissue sensitivity to certain organs Tells you the potential harm caused by radiation

$$D = \frac{\Delta E_D}{\Delta m} \quad \left[\frac{J}{kg}\right]$$

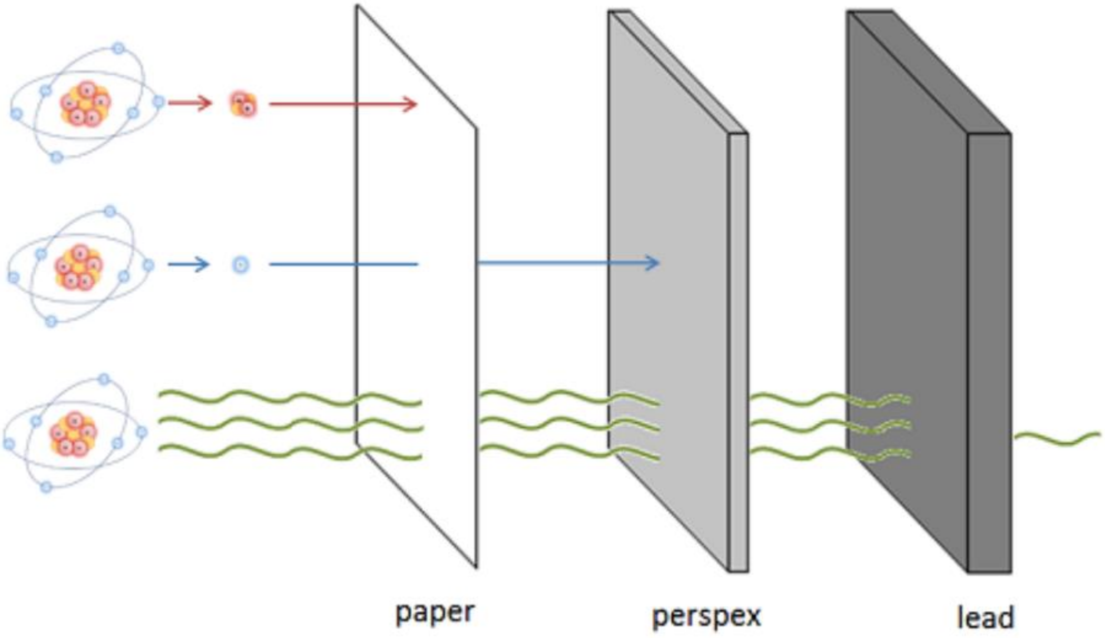
$$H = DQ$$

Types of Radiation

Alpha particles α

Beta particles β

Gamma rays γ

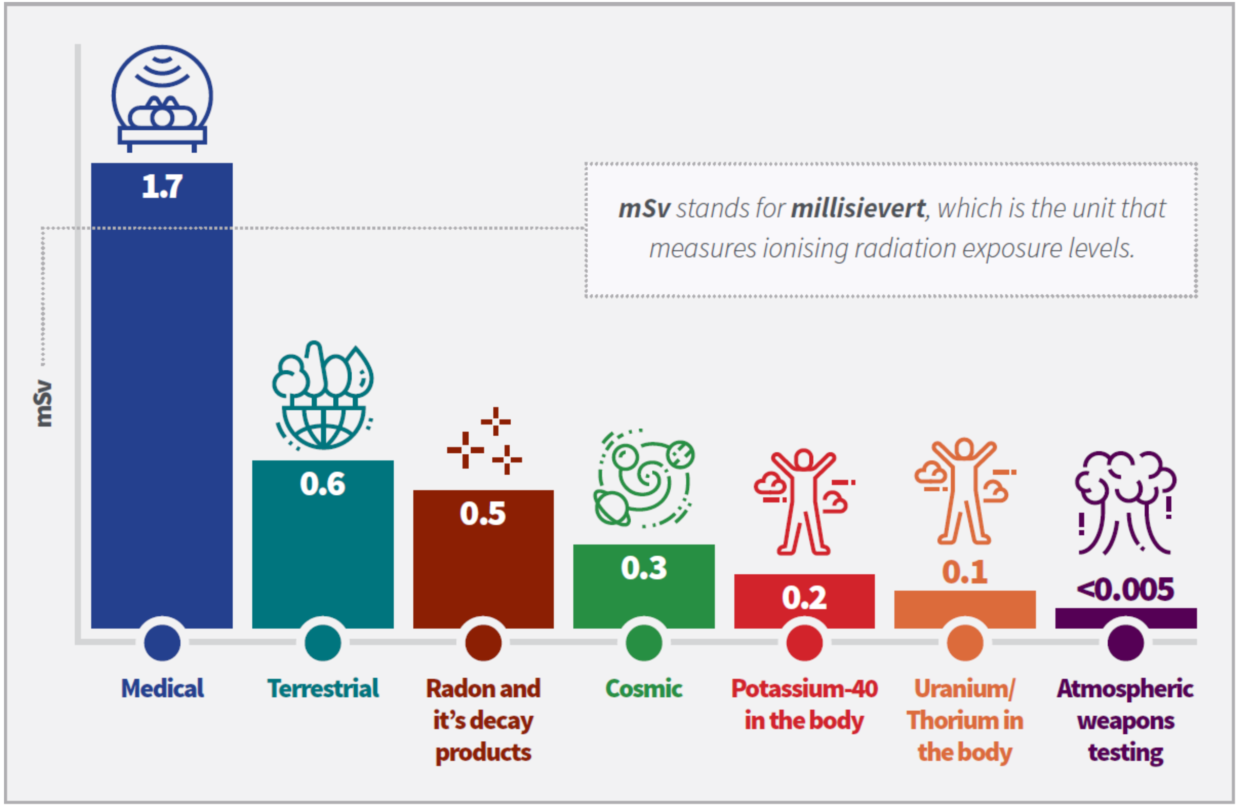


Sources of Exposure to Ionizing Radiation

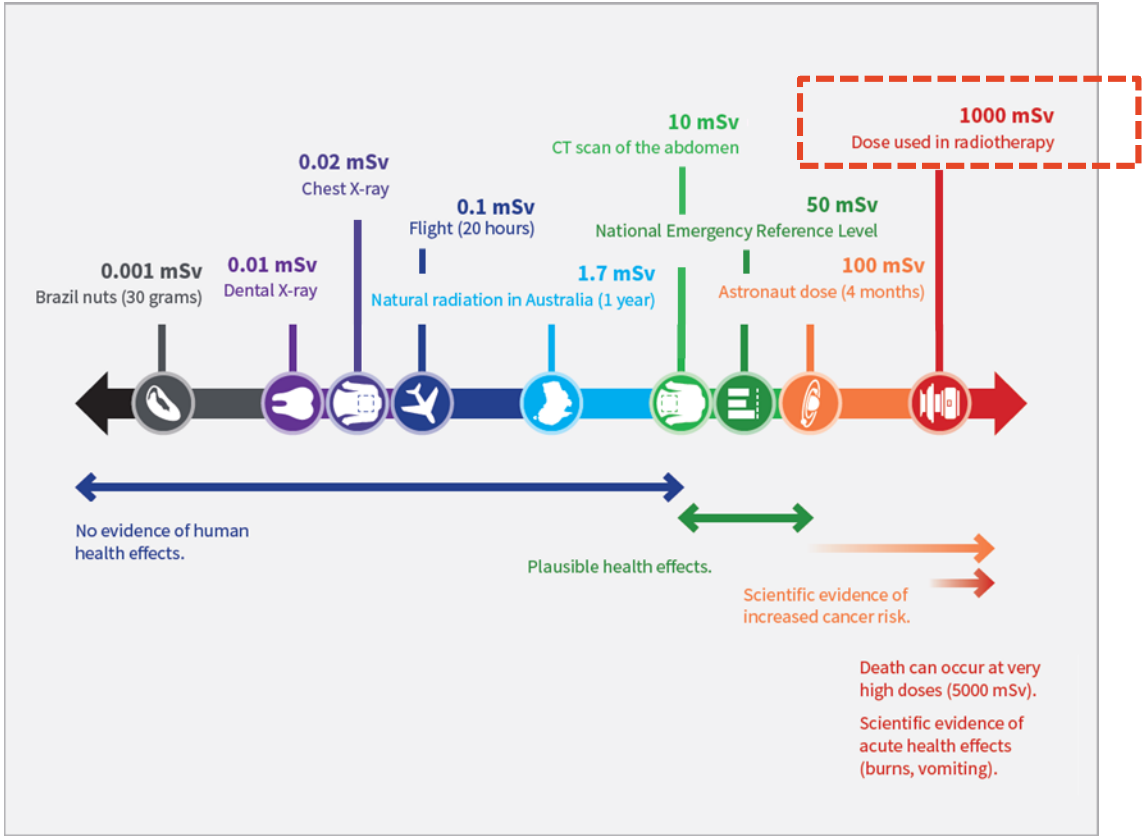
Public exposure limit is ~1 mSv

Occupational exposure limit for radiation workers including medical workers, airline crew, nuclear workers and miners may be higher

- Limit ~20 mSv per year, common recorded is 1-10 mSv per year



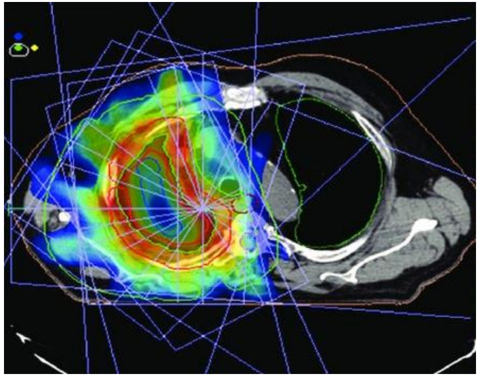
Highest Exposure to Ionizing Radiation



Radiation Therapy

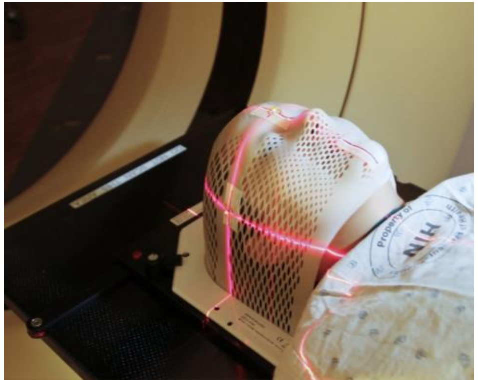
- 20M cancer patients per year; 50% need Radiotherapy
- Linear accelerator (LINAC) aims external beams of radiation from multiple directions to maximize dose to the tumor while minimizing dose to the normal cells/vital organs
- Dosimeters (radiation detectors) calibrate the beam **BEFORE** the patient enters
- Use lasers to align the patient

Treatment Plan



LINAC

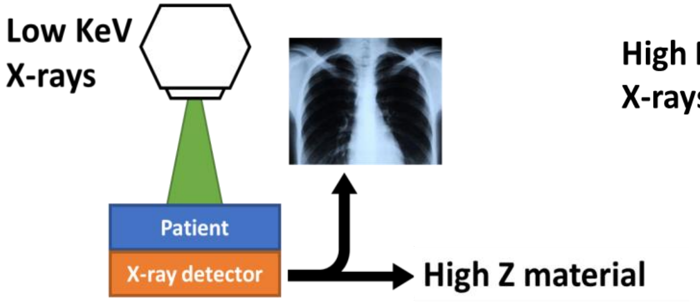
Patient Alignment

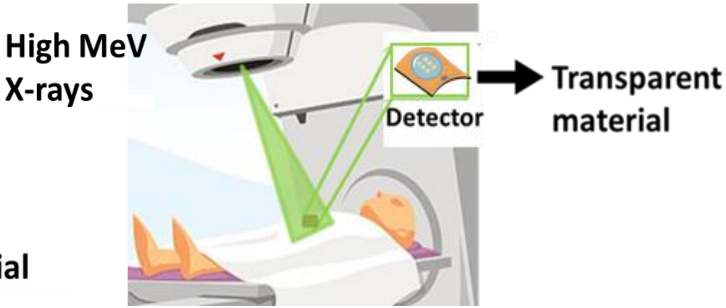


Medical Dosimetry

What is Dosimetry?	Measurement and assessment of radiation doses received by individuals or objects exposed to ionizing radiation
How is it achieved?	Passive dosimeters (film badges, TLDs) and Active dosimeters (silicon-based electronics)
Why in-vivo dosimetry?	Real-time feedback to instantaneously detect, evaluate, and correct for any deviations from the planned exposure; (ideally) without affecting the treatment plan.

Imaging vs *in-vivo* Dosimetry:





Need for Innovative X-ray Detectors

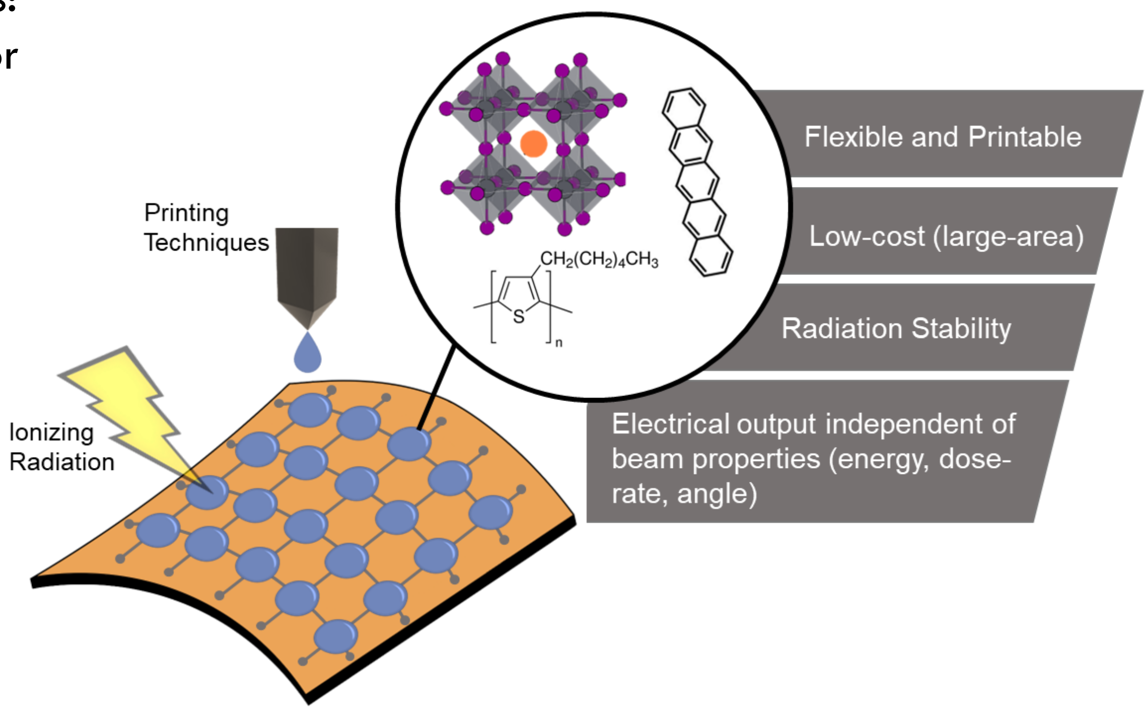
Advantages of current dosimeters:

- Well studied (and optimised for radiation detection)
- High spatial and temporal resolution
- High radiation stability
- Commercially available

Limitation of current dosimeters:

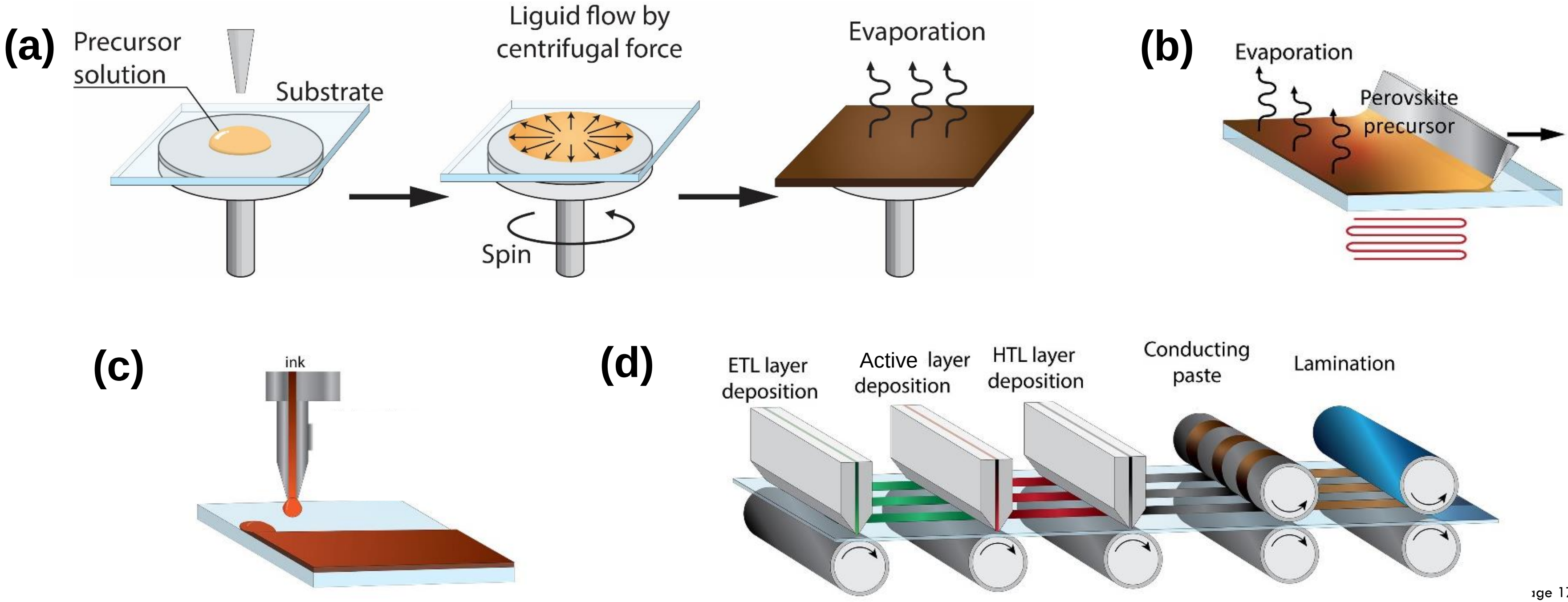
- Mechanically Rigid
- Expensive (large-area)
- Electrical output varies with beam properties

Material innovations needed:



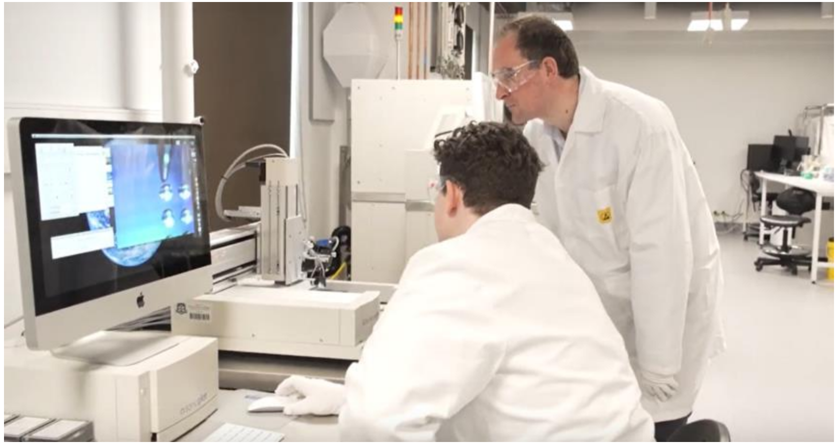
Next-Gen Materials for Radiation Detection

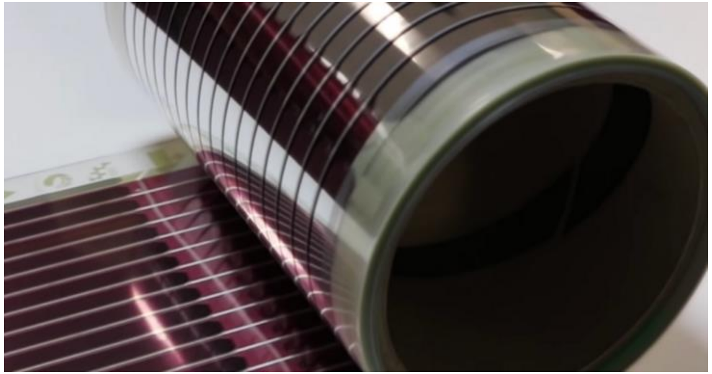
Solution processable electroactive inks can be printed onto flexible substrates with low-costs techniques: (**a**) spin-coating, (**b**) blading, (**c**) inkjet printing and (**d**) roll-to-roll printing

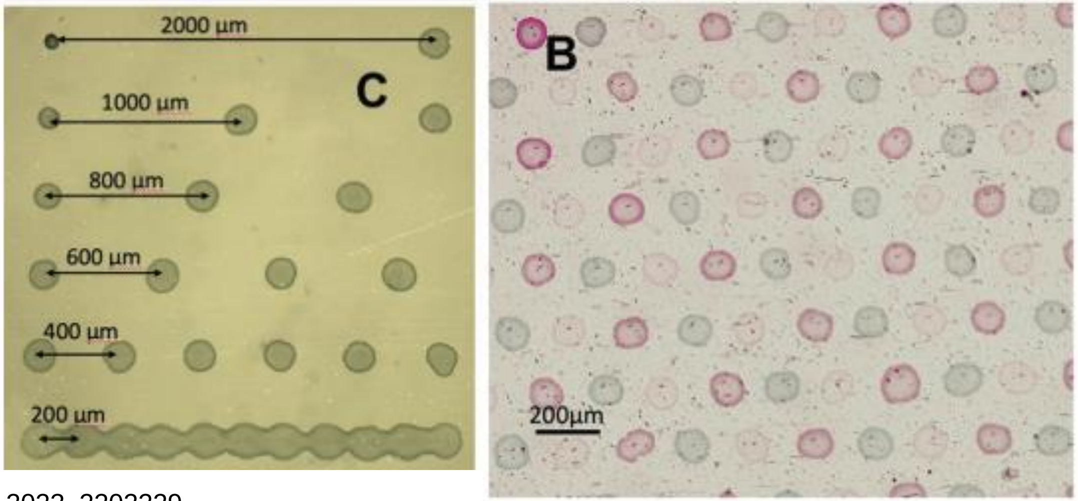


Example of Printability

- Organic semiconductors were Inkjet printed onto flexible Kapton substrates
- Droplets = 185 ± 30 μm







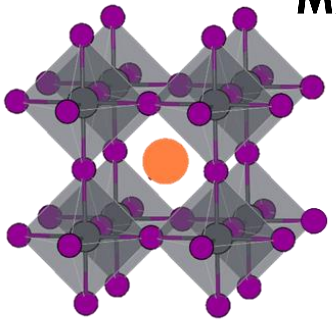
Sherwood CP, Crovador R, **Posar JA** et. al. *Adv. Mater. Interfaces* 2023, 2202229

Two Solution Processable Materials for Radiation Detection

Perovskites

- Lead, Iodide, bismuth and other heavy elements
- Well-defined crystal structure
- Excellent optical/electrical properties (high absorption coefficients and long carrier diffusion lengths)

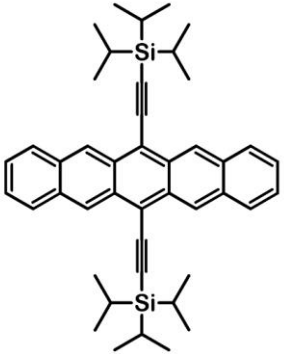
$MAPbI_3$



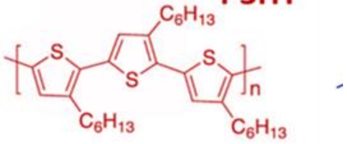
Organic Semiconductors

- Carbon, hydrogen and other light elements
- Disordered or amorphous structure
- Lower optical/electrical properties (low charge carrier mobilities)
- Mechanically flexible and highly compatible with low-cost techniques

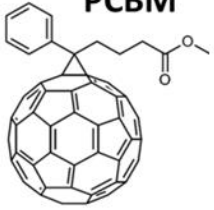
TIPS-pentacene



P3HT



PCBM



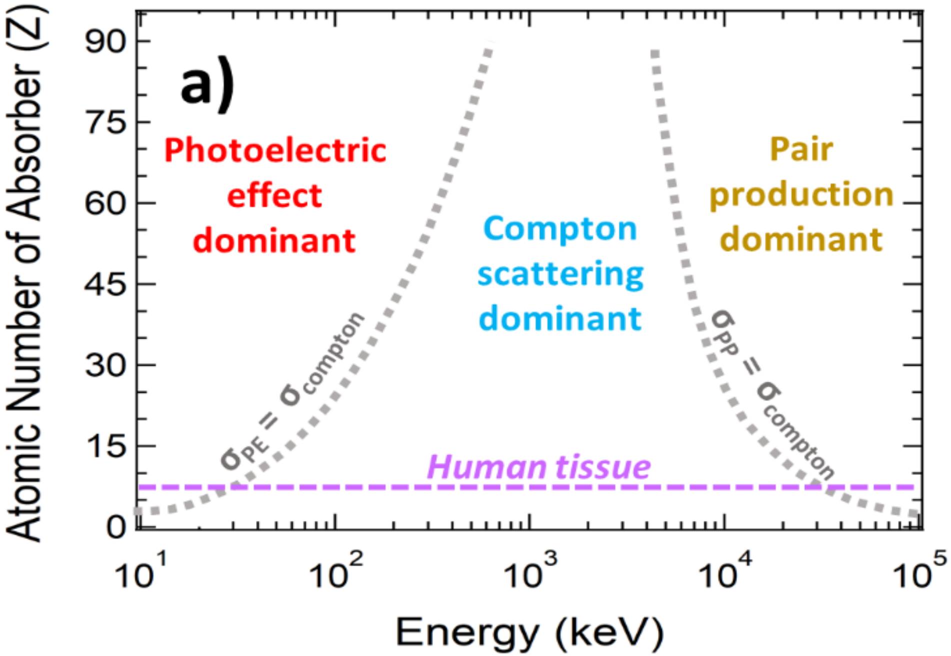
Interaction of Ionizing Radiation with Matter

- Why does the material of the radiation detector matter?

Novel Solution Processable Materials

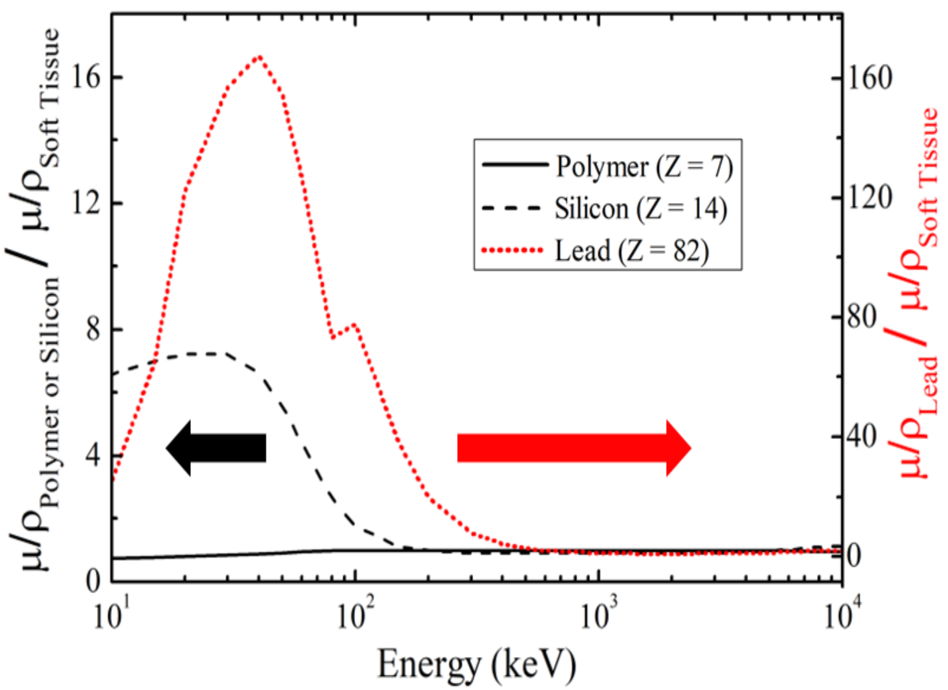
- Perovskites:
  - High-Z
  - Great for x-ray imaging

- Organic Semiconductors:
  - Low-Z matching human tissue
  - Great for **dosimetry**



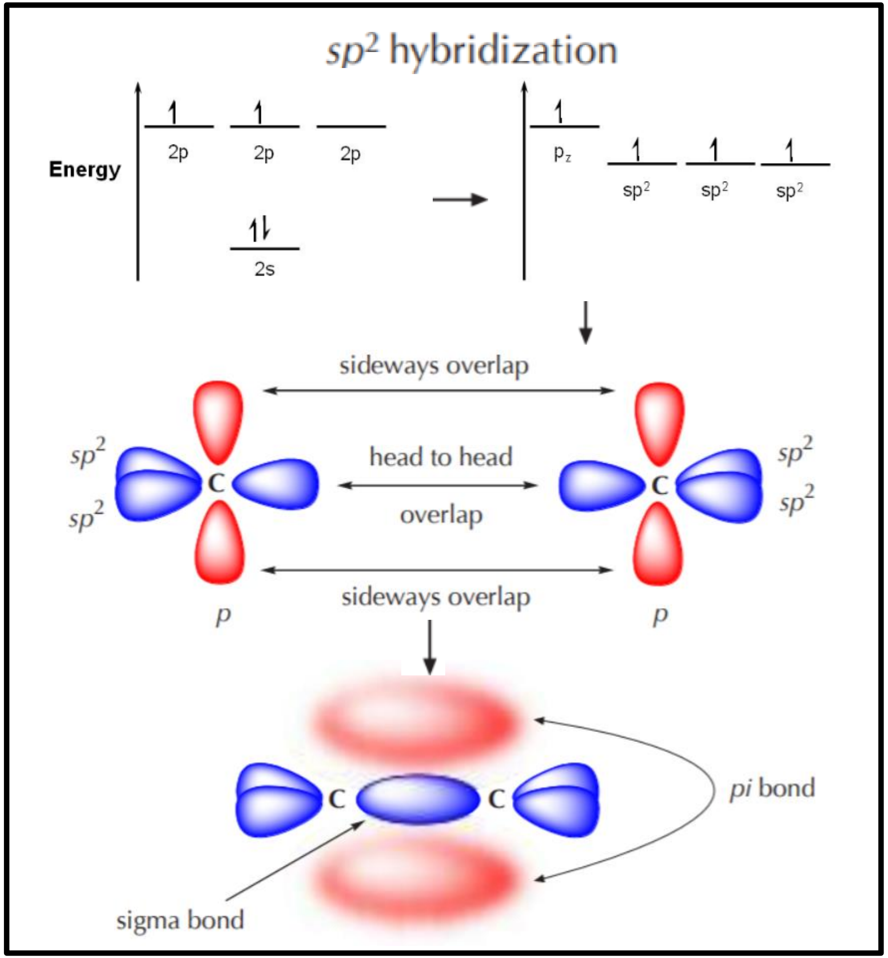
Impact of Detecting Material on Dosimetry

- **Aim of Dosimetry:** Measure the dose absorbed in the human body using a radiation detector
- But the dose absorbed varies depending on the atomic number of the material
- Need to calibrate the response of the detector to the human body
- **Benefit to carbon-based detectors**



Basic Operation of Organic Semiconductors

Why we need to develop new models for radiation detection



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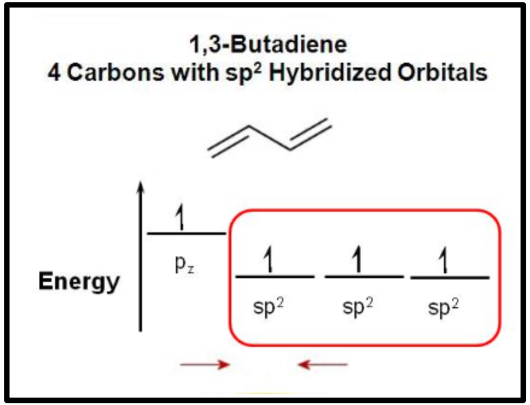
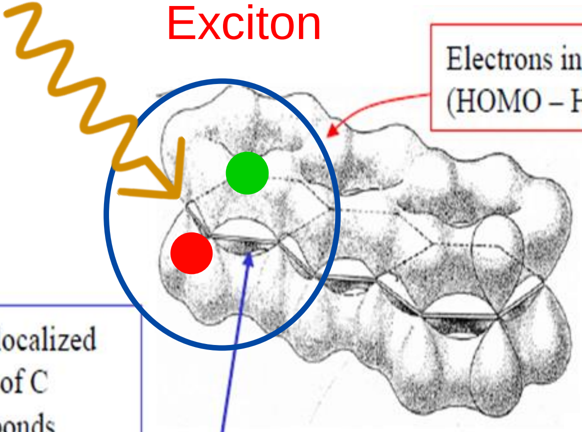
Molecular Structure of Organic Semiconductors



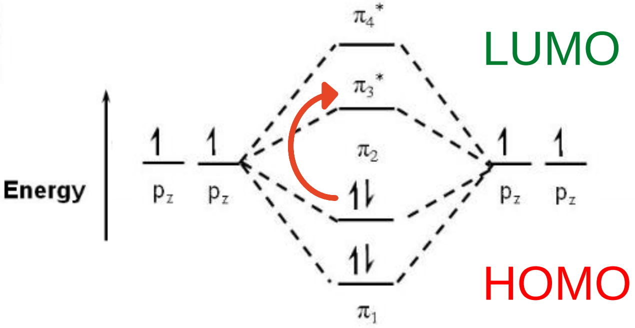
Exciton



Electrons in p_z orbitals (π electron) have higher energy (HOMO – Highest Occupied Molecular Orbital)

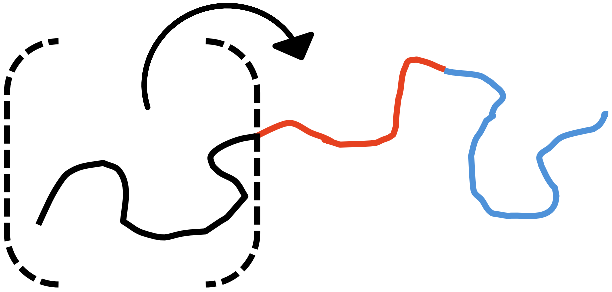
Electrons strongly localized between the nuclei of C partecipating to σ bonds

4 Frontier p_z Orbitals for π-Bonding



π electrons may easily be excited (LUMO – Lowest Unoccupied Mol. Orb.) and be "free" to move along the superposed p_z (π delocalization)

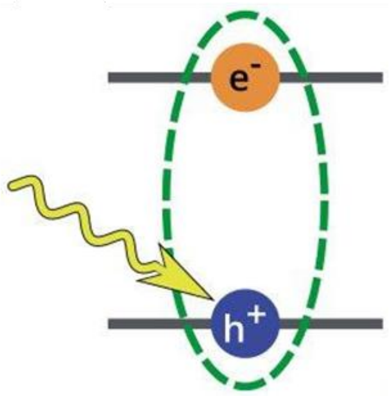
Charge Transport in Organic Semiconductors

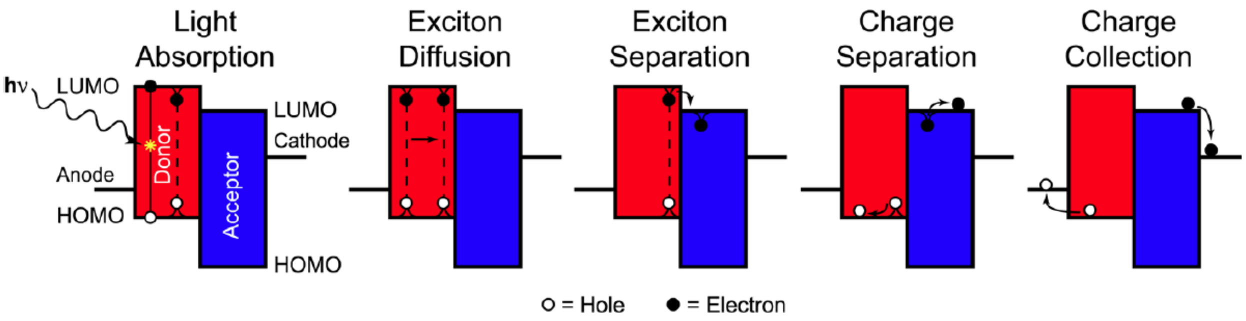


Known transport mechanism for **optical** excitation in OSCs:

- Charges are “sticky” (excitons)
- Need multiple materials to create free charge with complex nanostructures to maximize interfacial area
- **Charges ‘hop’ across segments of the polymer chain**

- **Unknown** charge transport mechanism for x-rays (direct ionization)
- **Cannot use** models developed for silicon radiation detectors

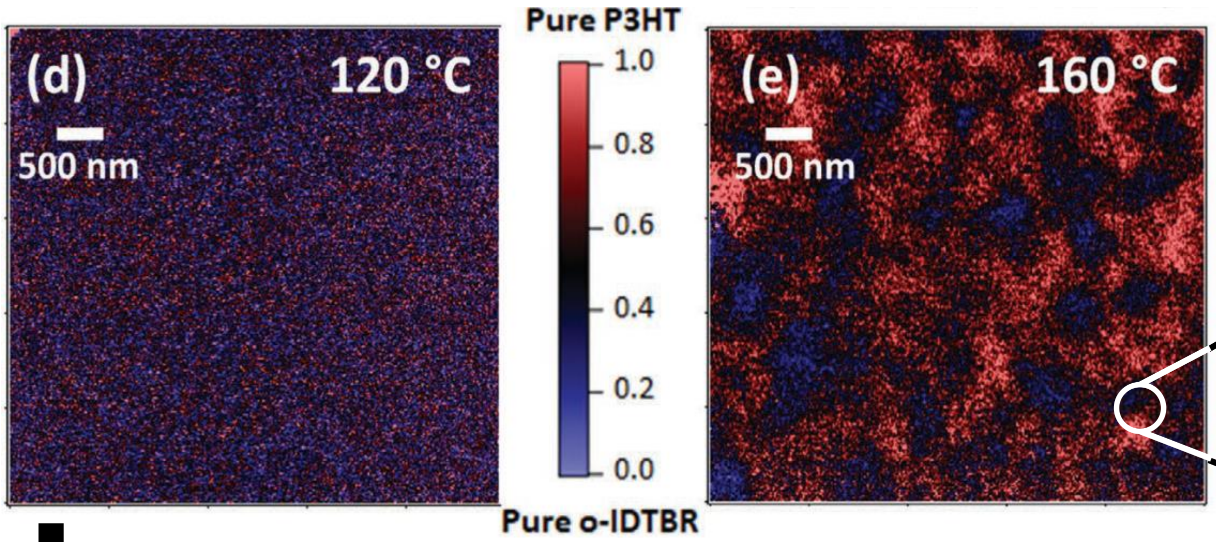


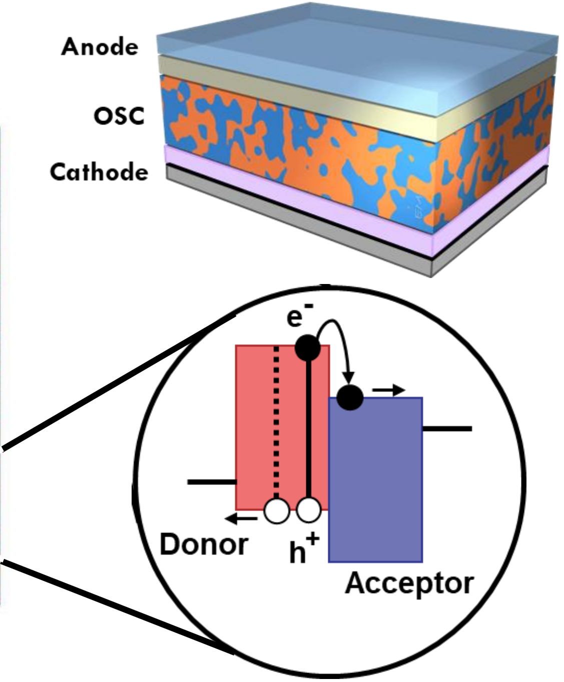


BHJ Morphology Optimization

- **Exciton diffusion length ~ 20 nm**

Polymer Scanning Transmission X-Ray Microscopy (STXM)



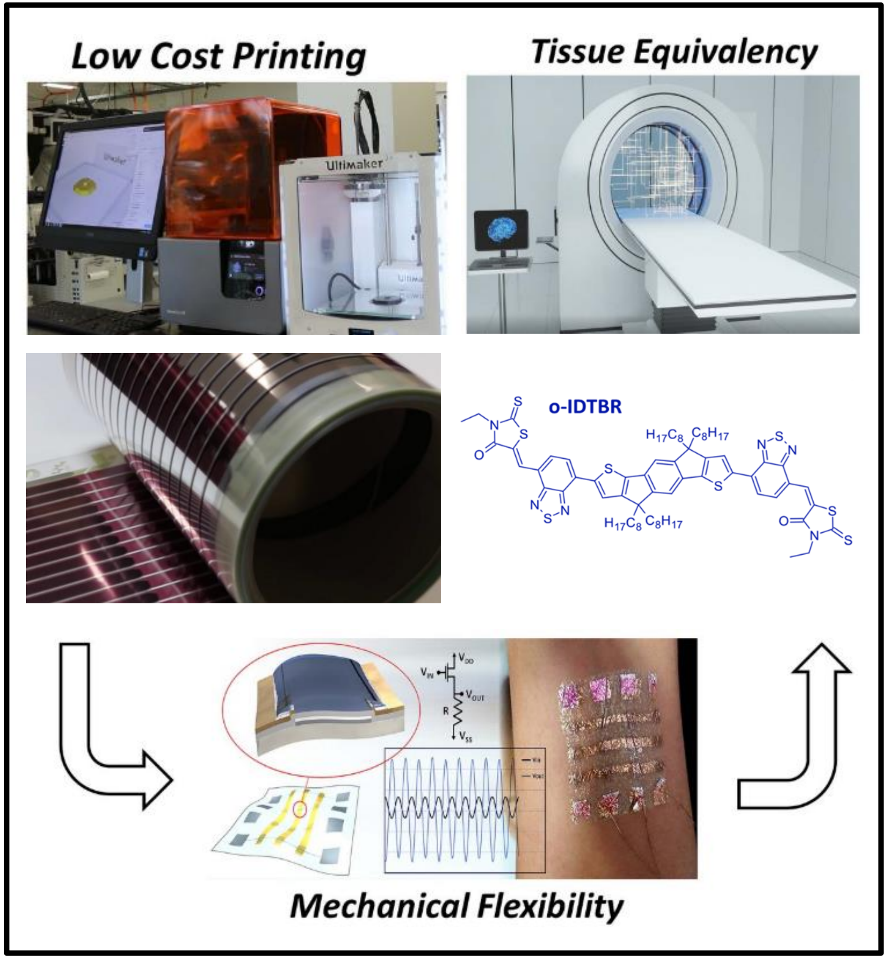


Results in improved electrical performance to <u>detect ionizing radiation</u>

J.A. Posar et. al. *Adv. Mater. Technol.* 2021, 2001298, doi: 10.1002/admt.202001298

Organic Semiconductors

New Frontiers in Radiation Detection



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Clinical Measurements

- Illawarra Cancer Care Centre, Wollongong Hospital
- Linear accelerator (LINAC):
    - 6 MV pulsed x-rays (3.6 μs)
    - Rotates around the patient to treat all body sites with specific techniques such as I/VMRT, IGRT or SBRT
- Orthovoltage:
    - 50 to 200 keV x-rays
    - Treat skin cancers in sensitive locations, nose, eyelids or ears

Direct and Indirect Detection

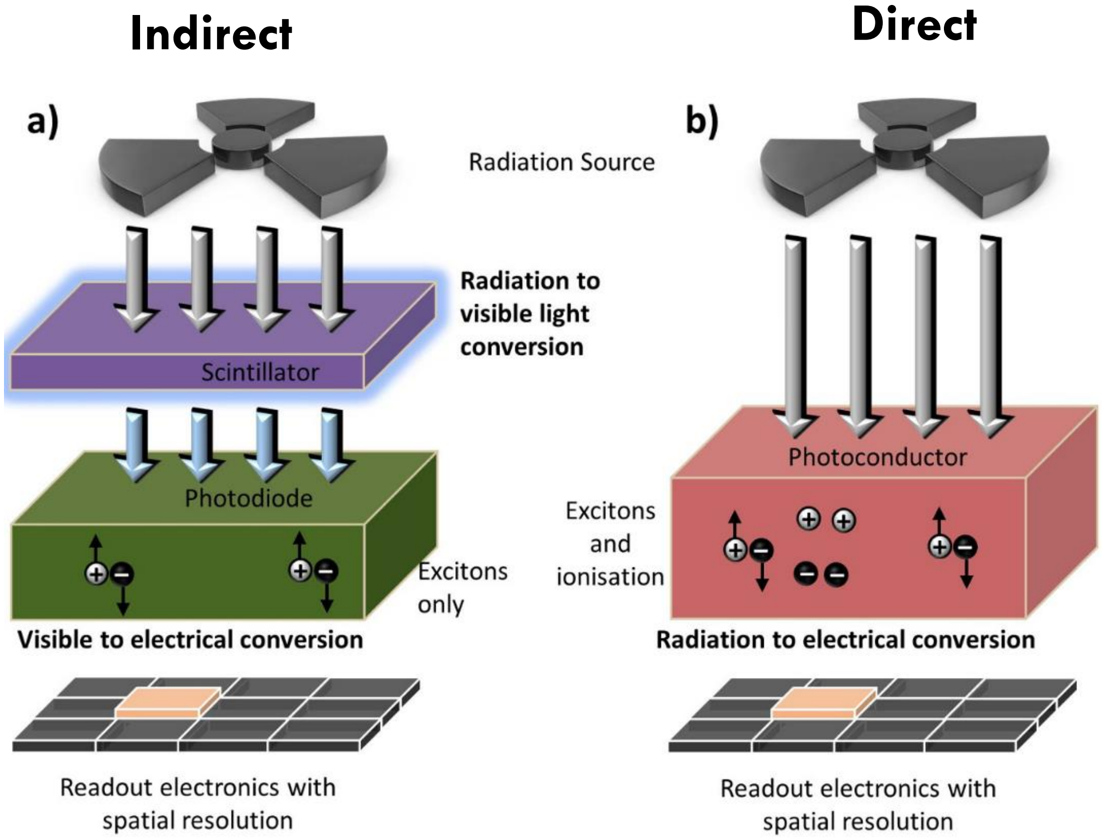
Direct Detection

– Requires a material with both a strong x-ray absorption and high electrical performance

Indirect Detection:

– Range of scintillator materials with different shapes/sizes/forms, efficiencies, optical wavelengths emission, decay times to match the application

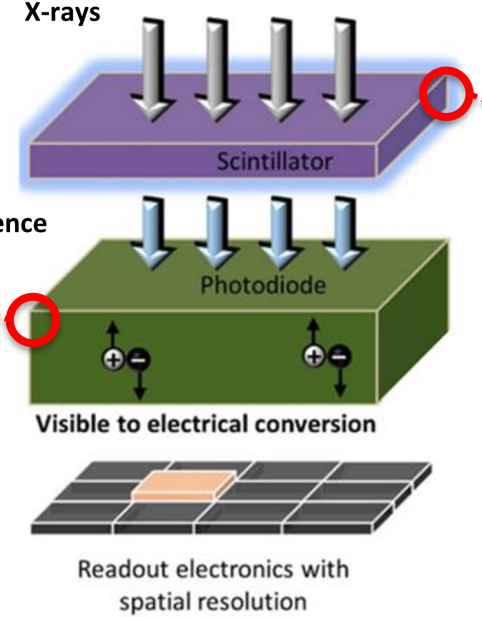
– Known transport mechanism for **optical** excitation in organic semiconductors



Indirect Detection with Organic Materials

Organic Semiconductors

- Tissue equivalent
- Low x-ray attenuation
- High visible absorption with **known photophysics**
- **Unknown** radiation tolerance



Organic Scintillators

- Transfer x-ray to visible
- Tissue equivalent
- Used to profile radiation treatment fields
- High radiation tolerance

2. Sensitivity

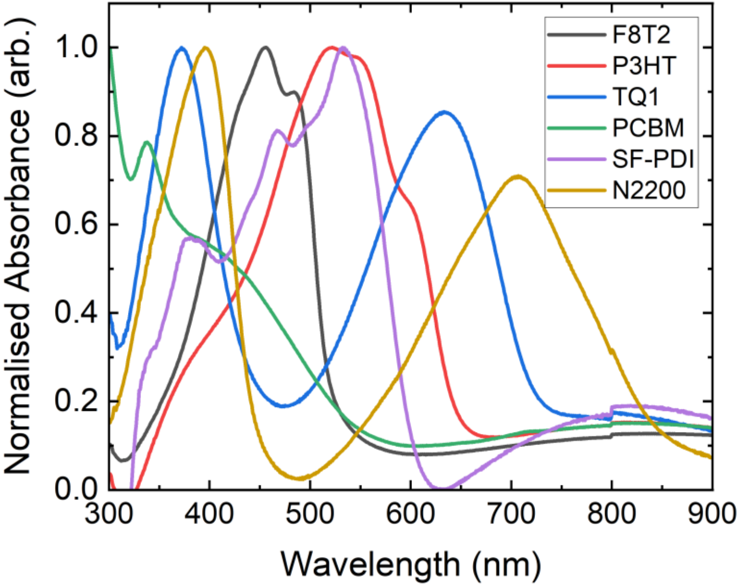
50 keV X-ray Source

Scintillator	Yield (ph/MeV)	Sensitivity (pC/cGy)	Tissue Equivalent
Organic	10,150	51	Yes
Inorganic	33,200	$22x10^3$	No

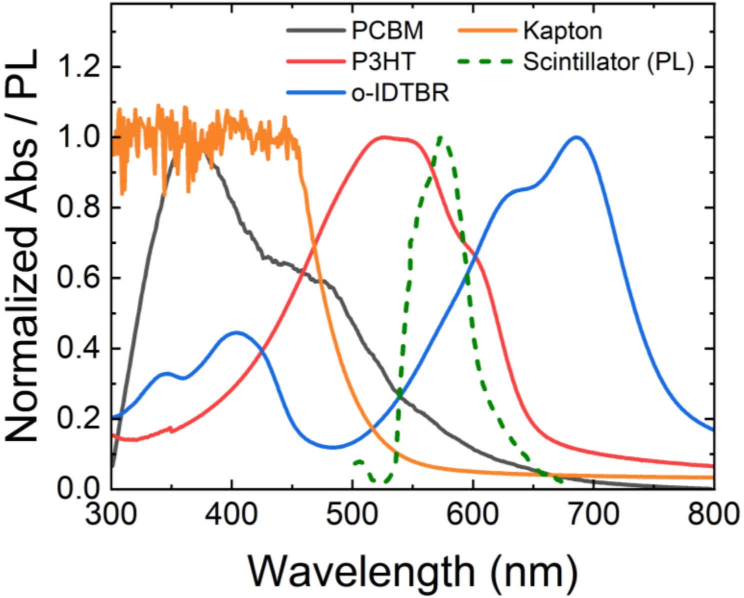
J.A. Posar et. al. *Flex. Print. Electron.* **6** (2021) 043005

Indirect Detection with Organic Materials

Organic semiconductors can be tuned to absorb specific visible wavelengths



Comparison to a red emitting scintillator



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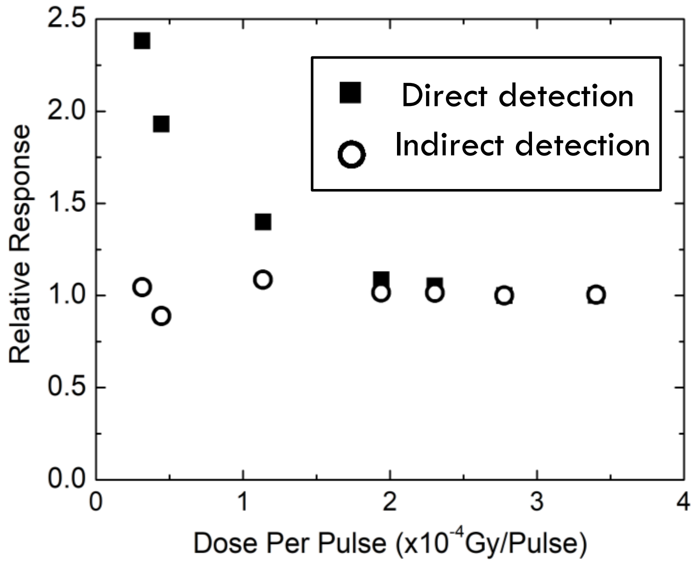
Dose-Rate Dependence (Direct vs Indirect Detection)

Dose rate [Gy/s]:

- how quickly the radiation dose is deposited in a given area/volume
- Can vary during treatment/across the treatment volume
- Impacts treatment time and has radiobiological effects

A dose-rate dependent detector will **under/over-estimate the dose deposited** impacting:

- Dosimetry of treatment volume in RT
- Contract in x-ray imaging



Dose-rate dependence is observed in organic semiconductors **only when used as direct radiation detectors**

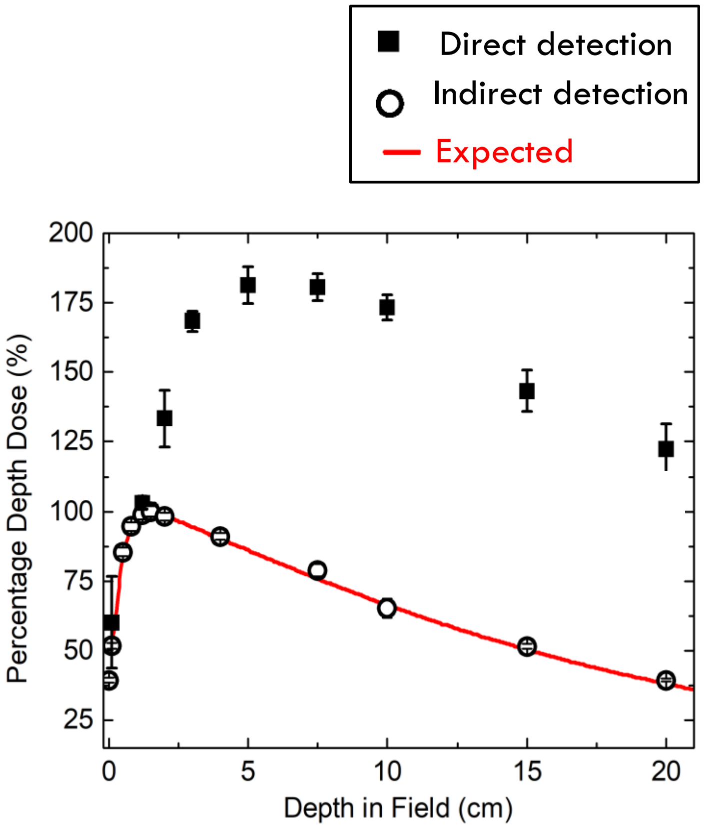
J.A. Posar et. al. *Med. Phys.* **47** (8) (2020) 3658-3668

Dose Deposited in Depth

Percentage Depth Dose Curve (PDD):

- Provides valuable information about the radiation dose delivered by a treatment beam as a function of depth in a patient's body
- PDD decreases with depth due to the inverse square law and attenuation of the radiation beam (solid red line in plot)

A dose-rate dependent detector will **under/over-estimate the dose deposited** as a function of depth within the patient where the tumor is located



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A Flexible X-ray Detector for In-vivo Dosimetry

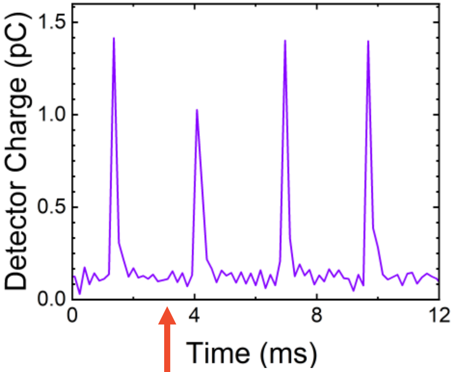
In-vivo dosimetry requires a detector to sit on the patient during treatment:

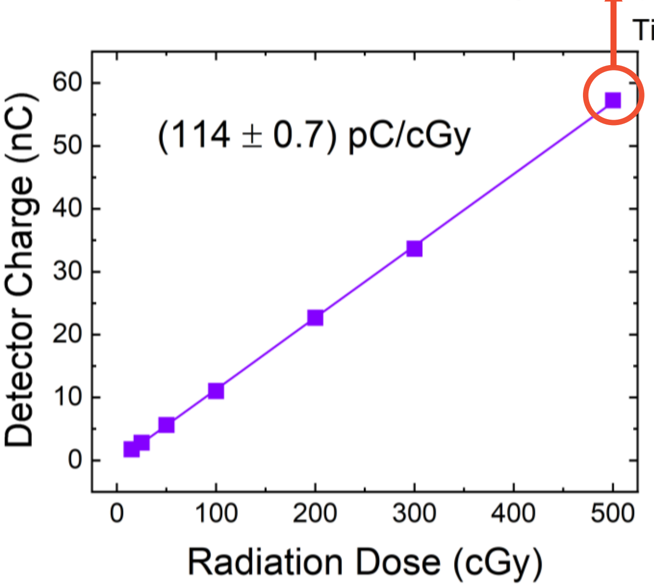
- X-ray sensitivity vs transparency

Organic Detector:

- X-ray transmission is **99.6%**
- Sensitivity is **linear with dose** (114 pC/cGy)
- Fast temporal resolution to resolve the **LINACs pulsed output** matching Silicon

No bias applied



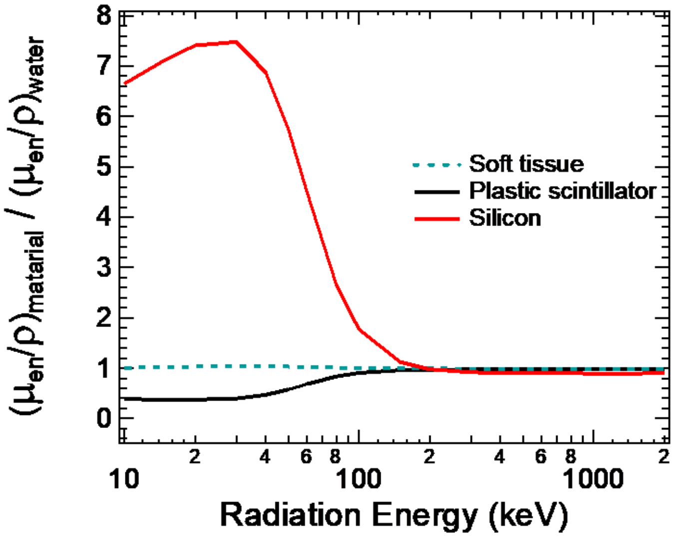


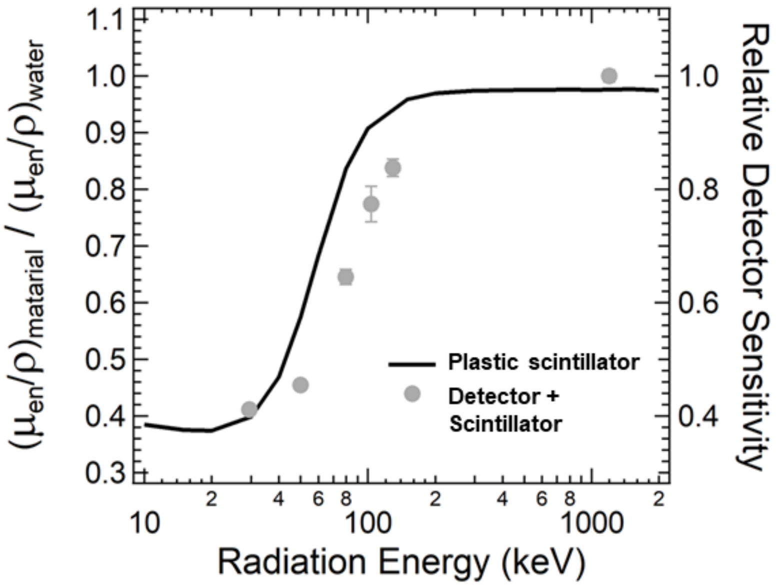
M.J. Large, **J.A. Posar** et. al. *ACS Appl. Mater. Interfaces* 2021, 13(48), p5770

Energy Dependence

A tissue equivalent detector has a response that matches the human body:

- Example is the response to energy when normalised to soft tissue
- Plastic scintillators are termed tissue equivalent





Energy Dependence impacts detection of **radiation fields with mixed energy** e.g., Image Guided Radiation Therapy

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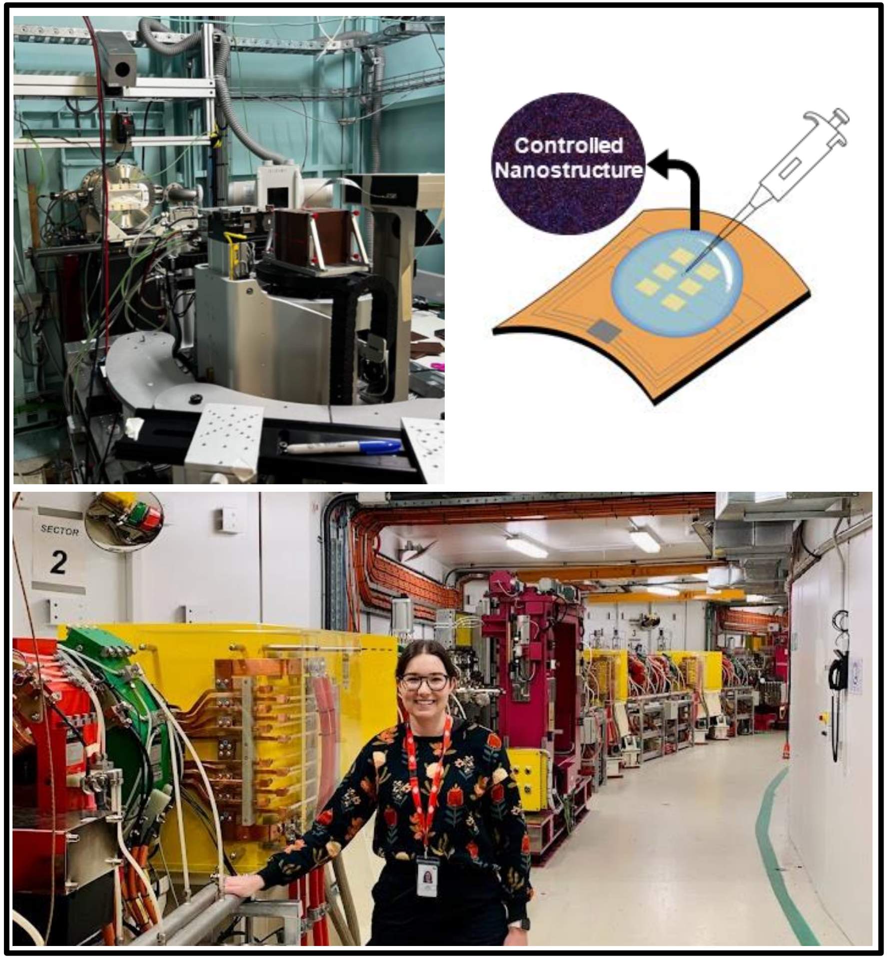
Novel Radiation Treatment Modalities



Using organic semiconductors to safety treat untreatable tumours

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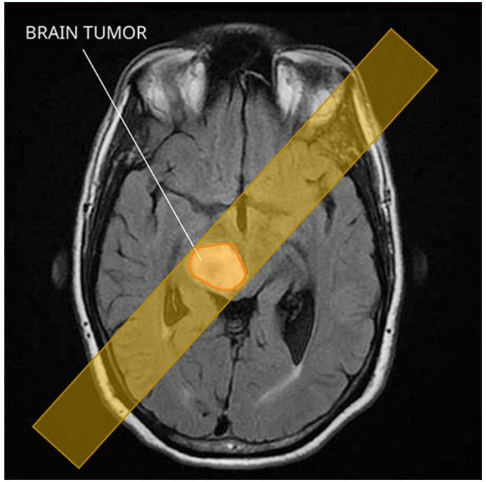
Microbeam Radiation Therapy

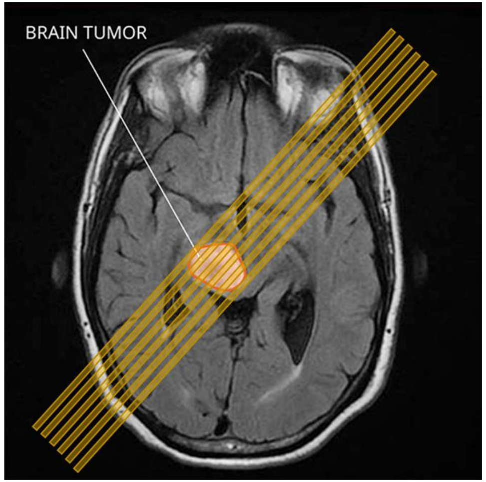
RT treats 50% of cancer patients, however the large variety of tumor sizes/locations present a challenge to safely directing external beams to small target volumes while avoiding normal tissue and vital organs:

- Glioblastoma multiforme (brain tumor) is resistance to conventional therapy leading to exceptionally poor prognosis (5% of patients survive 5 years following diagnosis)

Microbeam Radiation Therapy is a novel form of spatially fractionated RT with extremely high dose-rates

- Clinical research shows that normal tissue can recover from MRT whilst cancerous cells are destroyed





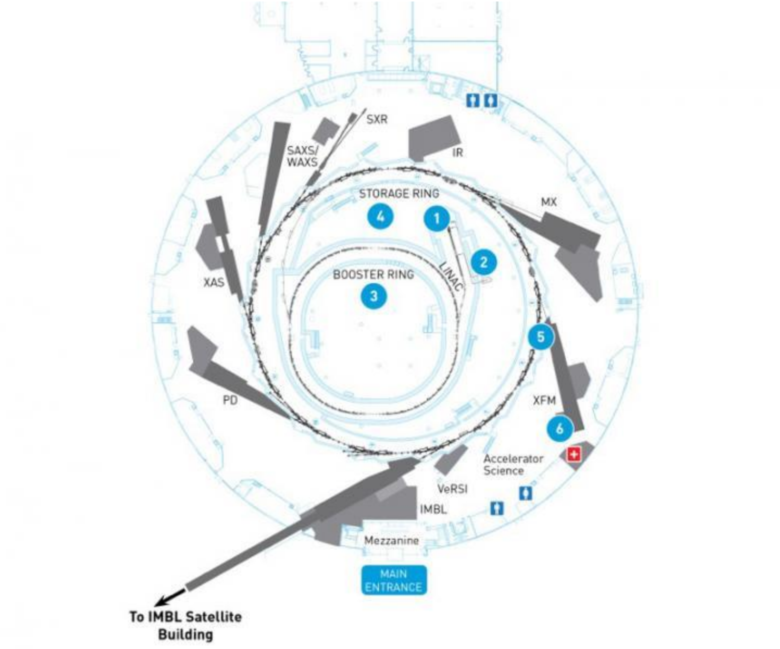
Synchrotron Sources

- MRT uses **<u>synchrotron-generated</u>** x-ray microbeams
- Only two sources in the world capable of generating MRT fields:
  - European Synchrotron Radiation Facility (ESRF)
  - **Australian Synchrotron**

Synchrotron Radiation:

1. Electrons accelerated to 99.9997% of the speed of light (LINAC)
2. Energy increased from 100 MeV to 3,000 MeV (3 GeV) in ~half a second (booster ring)
3. As the electrons are deflected through the magnetic field created by the magnets, they give off synchrotron radiation (storage ring)

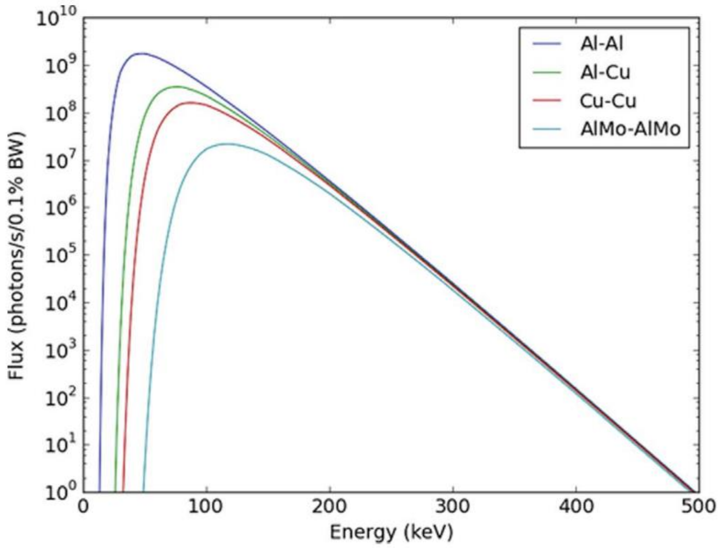
- Flux 1000x higher than conventional RT (dose rate= 3.6kGy/s)

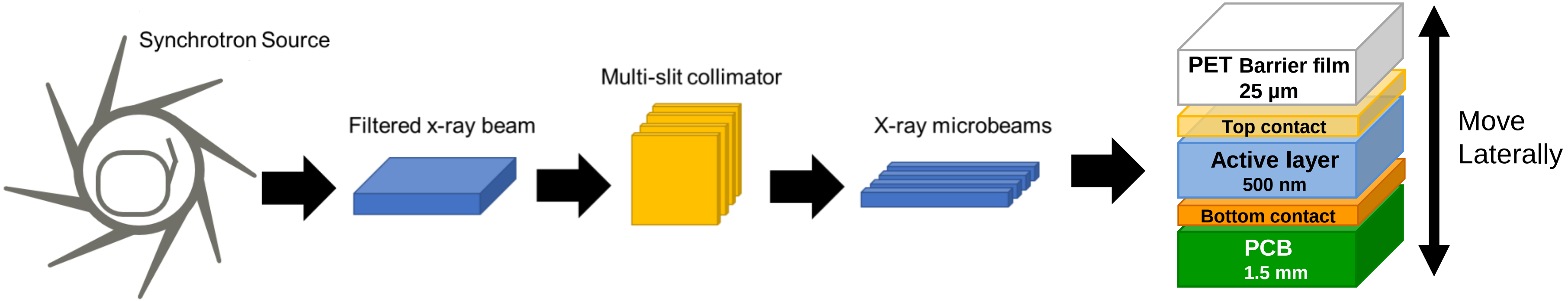


MRT Dosimetry

- Before clinical implementation, all RTs require routine quality assurance to ensure treatment efficacy and patient safety

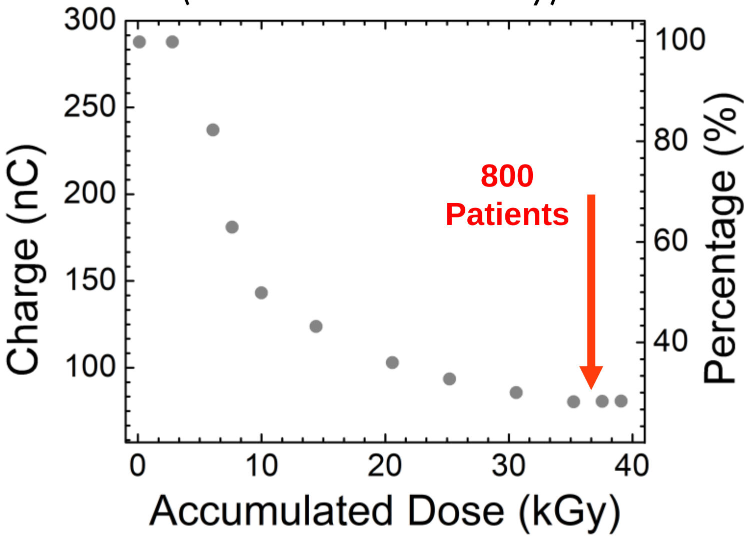
- Unique challenges for MRT dosimetry:
  - Radiation Tolerance (Flux 1000x higher)
  - Spatial Resolution (50 μm beams)



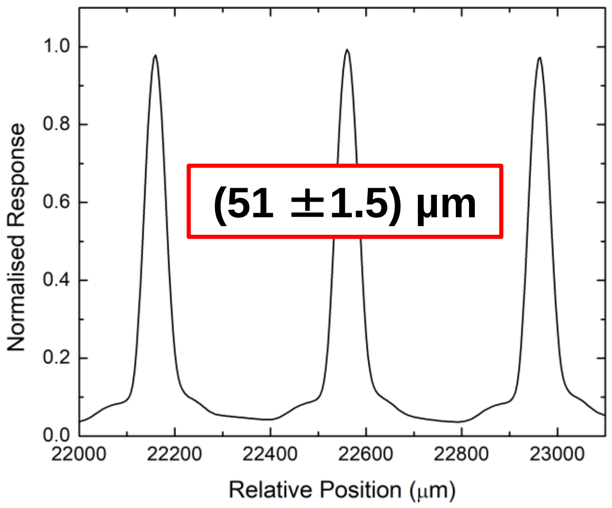


MRT Dosimetry with Organic Semiconductors

Radiation Damage
(Stabilised after 35 kGy)



Reconstruction of Microbeams
(Highest dose-rate beam 3.6 kGy/s)



J.A. Posar et. al. *J. Synchrotron Rad*. 2021, 28, p1444, doi: 10.1107/S1600577521006044

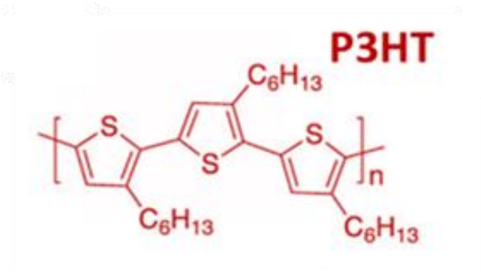
Radiation Hardness

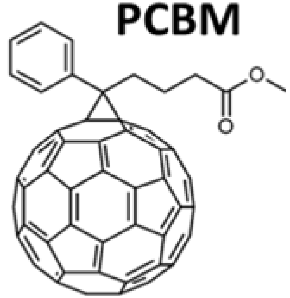
Radiation hardness is necessary for:

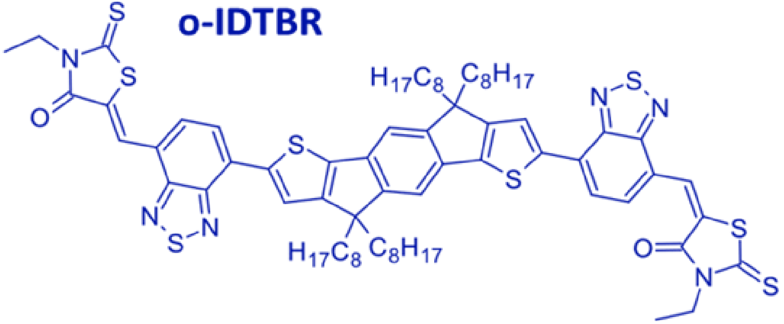
- Measurement accuracy and reliability
- Longevity and stability

Unknown radiation damage mechanism in organic semiconductors:

- Is there a correlation between material structure and radiation stability?
- Planar structure of o-IDTBR exhibits higher photostability compared to PCBM*







*J. Luke et. al. *Adv. Energy Mater.* **2019**, 9, 1803755

Insights into Radiation Damage

P3HT:o-IDTBR vs P3HT:PCBM

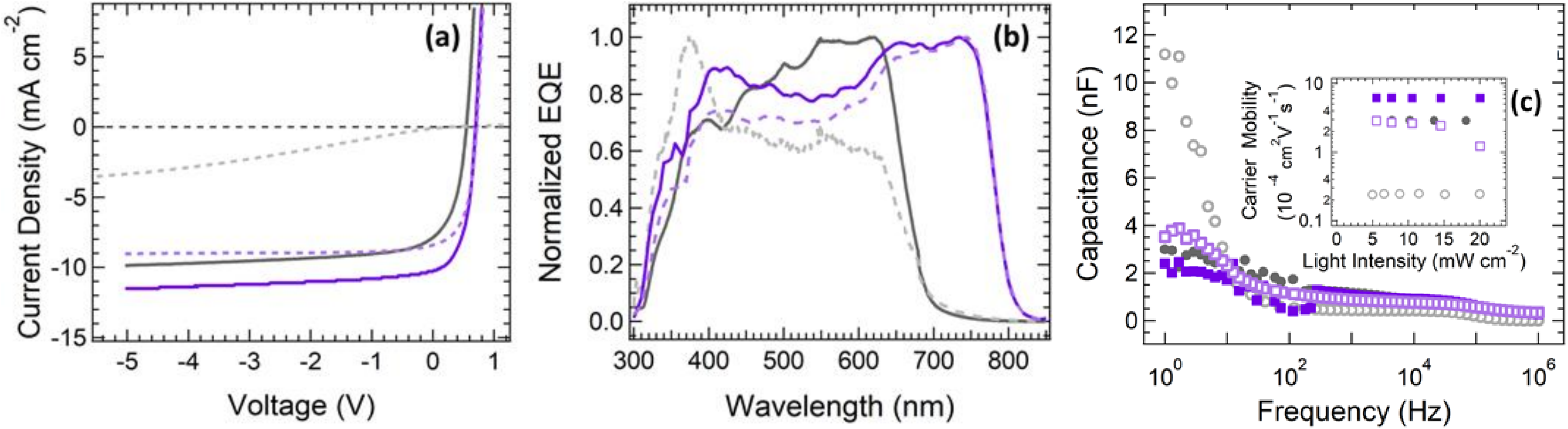
P3HT:o-IDTBR	P3HT:PCBM
■ Pristine	● Pristine
□ Irradiated	○ Irradiated

Degradation occurs in P3HT:

⟶Deep trapping sites

⟶Unique features of planar o-IDTBR improve radiation stability

Radiation Exposure > 10 kGy



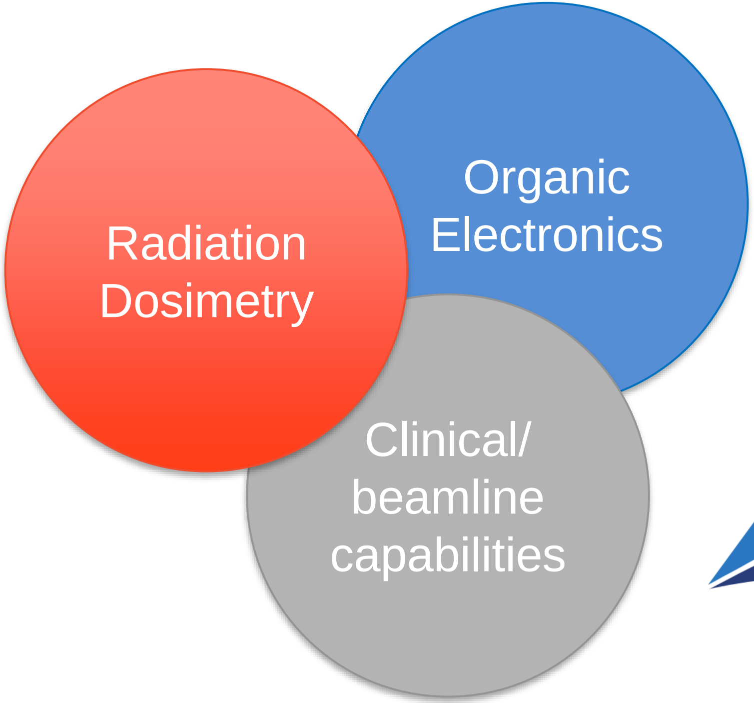
M.J. Large, **J.A. Posar** et. al. *ACS Appl. Mater. Interfaces* 2021, 13(48), p5770

Lecture Summary

- Active monitoring ***(in-vivo dosimetry)*** during Radiation Therapy is necessary to guarantee safe treatment however it requires innovative material solutions
- Radiation detection for dosimetry has unique challenges where detectors must have:
  - High spatial and temporal resolution
  - Flexible, large-area and low-cost manufacturing
  - Radiation hardness
  - Electrical output independent of beam properties (energy, dose-rate and angle) termed tissue-equivalent
- Solution processable semiconducting materials are a potential solution to fabricate flexible, large-area and low-cost radiation detectors
- Organic semiconductors exhibit unique material properties for dosimetry, particularly:
  - Carbon-based composition that permits a tissue-equivalent response
  - Simple material tunability to optimize the absorption properties and radiation hardness
  - However, before widespread use we must understand the charge transport mechanism under ionizing radiation fields and develop a model for radiation hardness to further optimize their performance

Collaborative Effort

Researchers with expertise in:



Thank you for you attention

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- Deutsches Rontgen-Museum https://roentgenmuseum.de/en/home-en/

Interaction of Ionizing Radiation with Matter

Very quick overview of the different interaction processes: