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## Polymer Photodetectors for Printable, Flexible and Fully Tissue Equivalent X-Ray Detection with Zero-Bias Operation and Ultrafast Temporal Responses

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25 Research interest in new materials for X-ray detection is growing rapidly, driven by demand from applications as diverse as fundamental materials science, medical imaging and 26 radiotherapy, space exploration, security and defence, personal wearable dosimeters, and 27 nuclear science.<sup>[1-6]</sup> Current detectors utilize inorganic solid-state semiconductors such as 28 29 silicon, selenium or cadmium zinc telluride. However, X-ray detectors fabricated from these 30 materials are expensive to manufacture and cannot be easily fabricated into flexible sensors or large-area pixelated arrays.<sup>[7]</sup> Furthermore, these semiconductors are composed of heavier 31 elements, which exhibit much stronger X-ray attenuation than the lighter elements comprising 32 33 human tissue, resulting in perturbation of the X-ray beam. Consequently, their use for medically relevant dosimetry or personal health monitoring requires complex, often unreliable 34 calibrations limiting their applications in radiotherapy or food sterilization.<sup>[8]</sup> A new generation 35 36 of materials for X-ray sensing must therefore be envisaged, combining a tissue equivalent 37 response with other ideal properties such as mechanical flexibility, low operating power 38 requirements and real-time response rates.

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40 Photoactive materials can be fabricated into either direct or indirect X-ray detectors. Direct 41 detectors absorb X-rays and convert them into an electrical signal in a single photoconductor, 42 whilst indirect detectors employ a scintillator to first convert X-rays to optical photons that are 43 subsequently coupled into a secondary photodetector. Direct detectors face higher design 44 constraints as the photoconductive materials must have both a high thickness for strong X-ray 45 absorption and a high crystallinity for good charge carrier mobility. Thus, whilst recent developments with selenium, perovskite, and organic materials have produced high 46 sensitivities (S  $\sim 10^3 - 10^4 \ \mu CGy^{-1} cm^{-2}$ ),<sup>[9-12]</sup> the thickness and crystallinity constraints mandate 47 48 complex manufacturing and prevent radiation transmission, precluding their use in many 49 applications. Indirect detectors offer more design flexibility, with the scintillator and 50 photodetector able to be independently optimized for X-ray absorption and charge carrier 51 extraction, respectively. Consequently, indirect X-ray detectors have been the more widely 52 adopted industrial architecture. However, state-of-the-art materials – including thallium-doped 53 cesium iodide (CsI:Tl), terbium-doped gadolinium oxysulfide (GOS:Tb) or perovskite 54 nanocrystals coupled to silicon photodetectors – are not tissue equivalent and require 55 substantial bias voltages. Some of these materials also exhibit relatively slow response times 56 due to delayed scintillator photoluminescence.

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58 Organic semiconductors are a highly attractive pathway for creating devices that can

circumvent each of the above limitations. Their use has become ubiquitous in multidisciplinary 59 60 materials science due to the ability to tune their optoelectronic properties through simple wet 61 chemistry procedures. They are also solution-processable, forming printable electroactive inks that enable cheap manufacturing onto flexible substrates at large scale.<sup>[13-15]</sup> Such advantages 62 63 have seen organic electronic materials and devices excel across a vast number of applications, including thin-film transistors,<sup>[16]</sup> solar cells,<sup>[17-20]</sup> sensors,<sup>[21-22]</sup> visual displays,<sup>[23-24]</sup> and 64 photodetectors.<sup>[25]</sup> Critically, the density of thin solid films fabricated from organic 65 electroactive inks is very similar to that of human tissue, which has an approximate average 66 value of 1.10 g cm<sup>-3</sup>, and a value of 1.07 g cm<sup>-3</sup> for the soft tissues most often encountered in 67 68 medical dosimetry. These materials are therefore uniquely capable of tissue equivalent X-ray 69 attenuation and electrical conductivity. Whilst organic semiconductors have been trialled as 70 both photodetectors for indirect X-ray detection and photoconductors for direct detection, they have been found to be limited by low charge mobility (thus requiring application of bias 71 72 voltages), very slow response times (thus limiting real-time X-ray detection) and poor 73 photostability. These limitations can be addressed using the recent evolution of non-fullerene 74 acceptors (NFAs). NFAs are broad spectrum light absorbers, a property which can also enable

versatile coupling with luminescence from different organic scintillators. Critically, their morphology and crystallinity can be controlled through synthetic chemical and device fabrication routes. Creation of planar NFA molecular structures can induce a high packing order, leading to both higher carrier mobility<sup>[26-27]</sup> and enhanced stability against high energy irradiation.<sup>[28]</sup> Combination of NFAs with a donor polymer creates a photodetector with a builtin electric field, thereby circumventing the requirement for an external bias to extract charge.

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82 In this work we report the first ever demonstration of a printed X-ray detector that is fully tissue 83 equivalent, has a rapid (sub-microsecond) response and exhibits good sensitivity at zero-bias 84 operation. This performance is achieved by coupling an RP400 plastic scintillator with a 85 photodiode composed of donor polymer P3HT and NFA o-IDTBR to create an indirect X-ray 86 detector. We optimize fabrication conditions to provide both high carrier mobility and tuneable thickness for controlling radiolucency, enabling operation as a transparent dosimeter for 87 88 wearable applications. Operation of the device with no external bias exhibits good sensitivity 89 and a remarkably fast temporal response for X-ray detection, comparable to that of biased 90 silicon photodetectors. The X-ray detecting materials system can be printed into flexible 91 devices with pixel sizes of 60 µm that exhibit exceptional stability against aging degradation, 92 repeated bending, and high irradiation doses – demonstrating a pathway for scalable production 93 of large-area detector arrays.

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Figure 1a shows geometry optimized chemical structures determined from quantum chemical modelling of the organic semiconductors. Both P3HT and o-IDTBR, like most organic semiconductors, consist predominantly of hydrogen and carbon with functional groups of other light elements; a similar elemental composition to human tissue. Since X-ray attenuation is determined by the electron densities of a material, achieving tissue equivalent X-ray detection requires the density of materials to be equivalent to human tissue, which has an approximate



![](_page_6_Figure_1.jpeg)

103 Figure 1: (a) Geometry optimized quantum chemical models of P3HT and o-IDTBR chemical 104 structure. (b) The device architecture employed for the organic photodetector devices (that are the focus of this investigation) and the indirect X-ray detection experiments using a scintillator. 105 106 The lower part of the figure shows the photodetector current transduction mechanism in 107 response to luminescence from a scintillator. (c) UV-visible absorbance (solid) and photoluminescence (dashed) spectra for P3HT (orange) and o-IDTBR (blue). (d) STXM map 108 109 of a blended P3HT:o-IDTBR film annealed at 120 °C for 10 minutes, and (e) 160 °C for 10 110 minutes after fabrication. Red pixels indicate pure P3HT phases and blue pixels indicate pure o-IDTBR phases. (f) A comparison of the photoluminescence spectra for pure P3HT (orange) 111 112 and o-IDTBR (blue) films with blended films annealed at 120 °C for 10 minutes (grey) and 113 160 °C for 10 minutes (black and dashed) after fabrication.

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- 115

value of 1.10 g cm<sup>-3</sup>, and a value of 1.07 g cm<sup>-3</sup> for the soft tissues most often encountered in medical dosimetry. Solid films cast from these organic semiconductors had mass densities of 1.04 g cm<sup>-3</sup> for P3HT and 1.06 g cm<sup>-3</sup> for o-IDTBR, highlighting their suitability for tissueequivalent X-ray detection. Complete organic photodetectors fabricated using a 1:1 blend of P3HT:o-IDTBR for charge generation, PEDOT:PSS and ZnO for charge selective transport layers to prevent interfacial recombination, and ITO and aluminium electrodes (Figure 1b)

exhibited a mass density of 1.18 g cm<sup>-3</sup>, confirming an excellent tissue equivalency for the fully 122 123 fabricated organic photodetectors. Since many of these materials are solutions, they can be 124 printed into a multilayer stack onto ITO-coated (120 nm) glass or ITO-coated flexible plastic 125 anodes. This structure consists of a 40 nm hole-transporting PEDOT:PSS film, followed by 126 deposition of the photoactive P3HT:o-IDTBR blend films (variable thickness) onto which a 30 127 nm ZnO electron transporting film is deposited. The device structure is then completed by vacuum deposition of a thin (100 nm) aluminium layer. Therefore, the entire device represents 128 129 one of the first reported examples of a flexible X-ray detecting device with a fully tissue-130 equivalent response which can be fabricated with inexpensive printing technologies. These 131 features are critical requirements for wearable detectors for safety and medical applications, 132 since the device not only conforms to and provides a radiation response equivalent to the human 133 body, but the low cross-section for X-ray absorption allows radiation transmission for applications requiring exposure to radiation without perturbing the energy fluence of the 134 radiation. 135

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P3HT exhibits a single broad absorption between 450 nm and 600 nm, whilst o-IDTBR shows 137 138 both a blue (300-400 nm) and red absorption peak (550-750 nm) in comparison (Figure 1c). 139 Collectively, the P3HT:o-IDTBR films exhibit optical absorption spanning the range of 300-750 nm, providing substantial versatility for coupling with X-ray absorbing scintillators. The 140 141 photoluminescence spectra exhibit Stokes shifts of ~120 nm for each semiconductor, a signal 142 which can be monitored to measure the extent of free charge generation efficiency in the blended film. The HOMO and LUMO energy levels of the materials are offset, allowing 143 144 excitons generated in the low dielectric constant organic materials to be spontaneously 145 dissociated into free charges at the material interfaces through a built-in electric field without the need for external bias, a process which causes quenching of the photoexcited states.<sup>[29]</sup> 146

147 Smaller pure material domains promote this charge generation process, however larger and 148 more crystalline domain sizes are typically advantageous for fast carrier transport through the 149 film. To optimise the internal blend nanostructure, films were subjected to various thermal 150 treatments to induce crystallinity and domain size changes. The size of material phases was 151 determined using scanning X-ray transmission microscopy (STXM) measurements performed 152 at the Advanced Light Source (ALS) synchrotron, while the charge generation efficiency was 153 monitored by comparing the residual photoluminescence in the blended films to that of the 154 individual materials. STXM provides high-resolution (~25 nm) imaging with chemical 155 sensitivity to collect X-ray maps of the blend morphology. A range of different thermal post-156 treatment conditions were trialled with annealing at 120 °C for 10 minutes found to produce 157 the best films, which exhibited strongly intermixed morphology below the resolution limit of 158 the technique (Figure 1d). Photoluminescence in these blended films was negligible, with a 159 calculated quantitative charge generation yield of 98% (Figure 1f), whilst the fine structure of 160 the absorbance spectrum suggests some crystallinity. Increasing the annealing temperature to 161 enhance polymer crystallinity caused gross phase segregation, where the individual domain 162 sizes became much larger than the  $\sim 20$  nm exciton diffusion length (Figure 1e). This 163 segregation resulted in poorer exciton dissociation, with the generation yield decreased to 72% 164 as determined from photoluminescence quenching (Figure 1f). Fabrication conditions 165 producing the optimized nanoscale morphology were utilised for the remainder of the study to 166 maximize sensitivity for X-ray detection.

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Figure 2a shows the current density–voltage (J-V) characteristics of photodetector devices with P3HT:o-IDTBR thicknesses ranging from 100 nm to 7  $\mu$ m. For thicknesses above 100 nm, the data reveals nearly complete charge extraction at ultra-low (and even zero) applied bias, with minimal differences in the photocurrent extracted in passive mode (0 V) and at -5 V bias. This

![](_page_9_Figure_0.jpeg)

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Figure 2: (a) Current density-voltage curves for P3HT:o-IDTBR photodetectors with 173 174 thicknesses between 100 nm and 7000 nm. (b) Photocurrent to dark current signal to noise 175 ratios for devices as a function of the applied bias. (c) The detector quantum efficiency for optical to electrical conversion as a function of wavelength in the 250 nm device, (d) Charge 176 177 carrier mobility in photodetectors as a function of their light intensity at various thicknesses. 178 (e) Charge carrier lifetime as a function of the photogenerated charge density in photodetectors. 179 (f) Photodetector capacitance as a function of perturbation AC voltage frequency for 180 photodetectors operating under illumination without any DC bias voltage. 181

182 result demonstrates that these printable P3HT:o-IDTBR devices are extremely efficient at 183 extracting generated charges without requiring external bias, a key advantage in wearable 184 electronic devices. Comparing the photocurrent to the dark current demonstrates exceptional signal-to-noise ratios (SNRs) of  $10^3$  to  $10^4$  at bias voltages below -0.5 V for film thicknesses 185 of 250 nm to 7 µm (Figure 2b). These values are equivalent to state-of-the-art silicon 186 photomultiplier detectors, but without requiring the same high bias voltages (> 25 V) as 187 188 inorganic semiconductors. Light absorption was found to be maximized after a thickness of 189 250 nm had been reached (Figure S1), corresponding with the thickness value that produced 190 the best optical-to-electrical power conversion efficiency (Table S2). The quantum efficiency 191 for converting optical photons into current was constant at a value of ~40% between 400 nm

and 600 nm (Figure 2c), a spectral range which covers the luminescence light outputs of the
vast majority of commercially available X-ray scintillators (vide infra).

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195 Charge carrier dynamics were measured to provide comprehensive insight into material 196 nanostructure and aid in optimizing their performance in a coupled indirect X-ray detection system. The device charge carrier mobility was determined to be between 2-3 x  $10^{-4}$  cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> 197 from current transients using photo-CELIV measurements (Figure S1), with this mobility 198 199 invariant for all thicknesses up to 400 nm (Figure 2d). The photo-CELIV technique produces 200 an ambipolar mobility influenced by both hole and electron transport, however, this mobility 201 value is dominated by the faster carrier for imbalanced transport, which has been reported to be the holes for this P3HT:o-IDTBR system in previous studies.<sup>[30]</sup> The increase in photoactive 202 layer thickness from 400 nm to 7000 nm substantially increased the series resistance of the 203 204 devices, resulting in a significant increase in the RC time constant of the devices (from <500 205 ns to 2.2 µs, see Table S1). The longer RC time constant prevented accurate current extraction 206 and mobility determination in these thicker 7000 nm films, as the device response became 207 slower than the lifetime of charges (Figure 2e). Consequently, photophysical parameters extracted from the transient measurements have not been plotted for this thickness in Figures 208 209 2d, e and f. The carrier mobility determined for the P3HT:o-IDTBR system is an order of 210 magnitude higher than that previously observed in organic polymer systems that have been trialled as photodetectors for X-ray detection (P3HT:PCBM =  $4.4 \times 10^{-5} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ ), thus 211 allowing improved performance and detection sensitivity.<sup>[31]</sup> Indeed the P3HT:o-IDTBR 212 213 devices fabricated here have the highest photocurrents reported for any organic photodetector 214 systems employed for indirect detection of X-rays. The enhanced carrier mobility is attributed 215 to the combination of the highly planar o-IDTBR acceptor with a P3HT donor that exhibits 216 high regioregularity along the thiophene sidechains (Figure 1a), promoting the formation of 217 highly ordered crystalline domains that provide higher charge carrier mobility. The charge 218 carrier lifetime was found to vary between 1 and 100 µs depending on the photoinduced charge 219 density (light intensity) and film thickness (with increasing charge density causing a greater 220 concentration of charge carriers and thus faster recombination (Figure 2e). However, the 221 gradient of the lifetime vs charge density plots were not affected by the thickness of the 222 photoactive materials within the range of 100 nm to 400 nm, suggesting that the recombination 223 rate is unaffected by device thickness, and thus implying that the nanoscale morphology of the 224 blends does not meaningfully change over this thickness range. The distribution of charge 225 trapping states within the blend morphology was investigated by electrochemical impedance 226 spectroscopy, with devices operating under illumination at short circuit perturbed by a small 227 AC voltage to determine how carriers within the device respond. As presented in Figure 2f, all 228 mobile charges – which are detected by their characteristic response to faster probe perturbation 229 frequencies  $(10^3-10^4 \text{ Hz})$  – were extracted efficiently for all thicknesses, resulting in only the 230 geometric device capacitance. However, more deeply trapped charges, which respond when the perturbation frequency is lowered to less than  $10^2$  Hz, became trapped inside devices for 231 film thicknesses between 310 nm and 7 µm, as determined by the rapidly increasing 232 233 capacitance at these lower frequencies. This result implies that operation without external bias 234 will not efficiently extract photoinduced charges for device thicknesses exceeding 310 nm, 235 providing an upper bound on the photodetector thickness for zero-bias operation. This value 236 precludes the use of these particular organic semiconductors as direct X-ray detectors, as this 237 low thickness would result in a lower sensitivity (vide infra). Consequently, these thin organic 238 films are highly compatible with creation of a flexible, radiolucent material system for the 239 photodetector component of an indirect X-ray detector. These photodetectors can be operated 240 without external bias but still achieve fast temporal responses, as the carriers are only required to transit distances of less than 0.3  $\mu$ m.<sup>[30, 32]</sup> We note that there have been other reports of 241

- organic semiconductors used as direct X-ray detectors with high sensitivities, however, these
   devices do not produce any X-ray detection without external power.<sup>[11-12, 33]</sup>
- 244

Complete X-ray detectors were fabricated by coupling the P3HT:o-IDTBR photodetectors with a 2 mm thick plastic scintillator to absorb X-rays and produce visible light with a peak at 425 mm (Figure S4). The mass density of the plastic scintillator is 1.023 g cm<sup>-3</sup>, with an electron density of  $3.33 \times 10^{22}$  cm<sup>-3</sup>, compared to values of 1.07 g cm<sup>-3</sup> and  $3.34 \times 10^{22}$  cm<sup>-3</sup>, respectively, for soft tissue. Thus the addition of the plastic scintillator enables the device to maintain its

![](_page_12_Figure_4.jpeg)

Figure 3: (a) Indirect detection of  $\langle E \rangle = 50$  keV X-rays at various cumulative doses, and (b) 252 253  $\langle E \rangle = 1.2$  MeV X-rays using a 2 mm plastic scintillator coupled to the P3HT:o-IDTBR 254 photodetectors. The inset in (b) presents an expanded view to show the resolution of individual 255 3.6 µs pulses. (c) The coupled X-ray detection system response as a function of radiation dose 256 at 50 keV (red) and 1.2 MeV (black). The response of the photodetector coupled with a 2 mm 257 LYSO inorganic scintillator is shown in open red circles for reference purposes. (d) A 258 comparison of the temporal response for detection of 3.6  $\mu$ s pulses at  $\langle E \rangle = 1.2$  MeV for silicon 259 (black) and the coupled organic X-ray detector (red dashed). (e) An X-ray image of a standard metal washer acquired with the organic X-ray detector under the 50 keV X-ray beam. (f) An 260 image of an inkjet-printed array of scintillator dots deposited onto organic photodetectors with 261 262 pixel pitch of 120 µm. Zoomed in optical and photoluminescence (PL) microscope images of 263 a single pixel show quenching of the photoluminescence in the area of overlap between the scintillator and the photodetector, indicating normal operation of the coupled detection system 264 265 in the printed array.

tissue equivalent X-ray attenuation properties.<sup>[34]</sup> The electrical response to X-ray irradiation 266 was measured in zero-bias operation for both low (keV) and high (MeV) X-ray energies to 267 explore the organic material applicability across a range of applications. The low energy 268 269 response was investigated with X-rays produced from a clinical X-ray tube radiating a dispersive X-ray beam with mean energy of  $\langle E \rangle = 50$  keV. The tube required a long ramp time 270 271  $(\sim 10 \text{ s})$  to reach the maximum machine rate output, which was detected by the coupled scintillator/photodiode system as shown in Figure 3a by the rising edge of the detector charge 272 273 profile. The electrical response increased linearly with the X-ray dose deposited from 50 cGy 274 to 300 cGy (Figure 3c).

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276 Each profile in Figure 3a was repeated three times, showing exceptional reproducibility (error 277 bars in Figure 3c, defined as one standard deviation, are smaller than the marker size). The 278 sensitivity for X-ray detection, calculated from the gradient of the data in Figure 3c, was determined to be 1.6 x  $10^4 \ \mu CGy^{-1}cm^{-3}$ . This value is somewhat lower than other organic X-279 280 ray detection systems, though remains noteworthy as it is obtained without any bias and 281 matches that of state-of-the-art amorphous selenium direct detectors used in current medical imaging technologies (~1 x  $10^{-4} \mu CGy^{-1} cm^{-3}$ ). Furthermore, the sensitivity was found to be 282 283 restricted by the plastic scintillator required for full tissue equivalency rather than the intrinsic photodetector performance. The RP400 plastic scintillator generates a relatively low light yield 284 (9,200 photons MeV<sup>-1</sup>) and has a limited emission spectral overlap with the photodetector 285 286 absorption (Figure 1c and S4) in comparison to inorganic scintillators. Coupling the photodetector to an inorganic LYSO (Lutetium-yttrium oxyorthosilicate) scintillator, which is 287 employed in existing reference technologies and has both a higher light yield of 33,200 photons 288 MeV<sup>-1</sup> and a broader spectral overlap between the scintillator emission and the P3HT:o-IDTBR 289 absorption in the range of 500-600 nm, produces a sensitivity of 3.6 x 10<sup>7</sup> µCGy<sup>-1</sup>cm<sup>-3</sup>, a value 290

more than three orders of magnitude higher than that produced with the plastic scintillator and 291 292 equivalent to the best indirect X-ray detecting sensitivities reported with organic photodetectors.<sup>[35-36]</sup> The response to high energy X-rays produced from a Varian Clinac® 293 21iX linear accelerator operating at 6 MV ( $\leq E \geq 1.2$  MeV) used for radiotherapy treatment of 294 cancer showed similar sensitivity to that observed in the lower energy keV X-rays, but with a 295 296 completely different temporal response. The electrical output was again found to be linear with increasing X-ray dose, with a calculated sensitivity of  $3.4 \times 10^4 \,\mu\text{CGy}^{-1}\text{cm}^{-3}$  with the plastic 297 298 scintillator and a response that saturated our detector with the inorganic LYSO scintillator. We 299 also monitored the transmission of the photodetector and scintillator to high and low energy X-300 rays beams (Figure S5 and Table S2). The native transmission of the photodetector was 301 extremely high 99.8% ( $\pm 0.1\%$ ) under the 6 MV linac beam, dropping slightly to 84.9% ( $\pm 0.2\%$ ) 302 for the low energy X-rays, likely due to stronger interactions with the ITO-glass substrate at 303 lower energies. Addition of the scintillator decreased transmission by 0.2% for high energy and 304 1.5% for low energy X-rays. These results confirm the high radiolucency of these devices and 305 their applicability for wearable dosimetry applications.

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307 Of particular interest, the detection response for the MeV X-rays shows a remarkably fast 308 temporal resolution. The linear accelerator is a pulsed radiation source with a pulse width of 309 3.6 µs and an instantaneous dose delivery of 270 µGy per pulse. Figure 3b shows that the tissue 310 equivalent X-ray detectors can resolve each individual pulse generated from the linear accelerator, and rapidly discharges completely following each pulse. This result confirms that 311 312 the temporal response of this organic photodetector is at least an order of magnitude faster than 313 that typically reported for other organic semiconductor systems. A comparison of the timing 314 response of the organic device with a state-of-the-art silicon radiation detector in Figure 3d 315 shows negligible differences in the risetime and discharge performance between these two

316 technologies, indicating that both sensors can follow the time structure of these fast X-ray pulses with similar performance, though direct comparison of the respective limiting time 317 responses would require a faster pulsed energy source. These results show for the first time that 318 319 judicious material choice and optimisation of organic semiconductor device architecture 320 produces organic photodetector devices that can follow the temporal profile of fast pulsed Xray sources, in contrast to previously reported limitations with low carrier mobilities.<sup>[26]</sup> The 321 322 increased mobility enabling an organic photodiode that can follow the pulsed X-ray beam profile with similar performance to silicon is supported by consideration of the carrier transit 323 324 time as an approximation for temporal response. The transit time of carriers through the film is given by  $t_{tr} = \frac{L}{v}$ , where L is the photoactive film thickness and v the carrier velocity. Since 325 the carrier velocity is related to mobility according to  $v = \mu E_{bi}$ , where  $\mu$  is the mobility and  $E_{bi}$ 326 327 is the magnitude of the built-in field created by the asymmetric electrode work functions, calculated here as  $E_{bi} = \frac{V_{oc}}{L}$  where  $V_{oc}$  is the open circuit voltage, the transit time is related to 328 mobility according to  $t_{tr} = \frac{L^2}{\mu V_{oc}}$ . For a 250 nm film, using the  $\mu$  (increased by an order of 329 330 magnitude compared to previous organic blends) and  $V_{oc}$  values for these photodetectors 331 extracted from Figure 2, a transit time of 1.9 µs is calculated, in agreement with the measured charge extraction times in Figure S3 and confirming the organic photodiodes can respond to 332 333 the fast X-ray beam pulses without delay. To test the applicability of the device in standard X-334 ray detection applications, multiple 2 x 2 mm pixels were used to acquire a 2D X-ray scan of a flat aluminium annulus-shaped washer. The X-ray image shows high contrast (Figure 3e), 335 336 with the spatial resolution limited only by the photodetector pixel dimensions. The successful acquisition of an X-ray image demonstrates the functionality of the new P3HT:o-IDTBR 337 338 photodetector. Further attention can now be directed at improving the device design and 339 manufacture to optimise performance.

340

341 Figure 3f shows an image of organic photoactive materials printed into a pixelated array 342 covered with a second layer of a printable organic scintillator (1-phenyl-3-mesityl-2-343 pyrazoline) to create 60 µm electroactive dots with a centre-to-centre pixel pitch of 120 µm. 344 This result demonstrates the ability to produce detectors that have 2D detection properties, with 345 a spatial resolution of the same order as state-of-the-art inorganic detection arrays (typically 98 346 µm pitch), but with the enticing ability to scale the detector array quickly and cheaply to much 347 larger sizes than current X-ray arrays are capable of achieving. The functionality of the printed array was investigated with optical and photoluminescence microscopy, focusing on a pixel 348 349 where the scintillator (light colour in optical image) is deliberately offset from the organic 350 photodetector (dark colour). The photoluminescence microscopy confirms the scintillator is 351 highly fluorescent, however, this fluorescence disappears in regions of the printed pixel where 352 the scintillator overlaps with the photodetector. This result could simply be attributed to 353 absorbance of the emitted light from the photodetector materials, or alternatively, could also 354 arise from loss of fluorescence in the scintillator due to efficient transfer of the optical energy 355 to the organic photodetector component as we have observed in similar materials systems.<sup>[37]</sup> 356 Whilst the former explanation does not provide insight into device functionality, the latter 357 explanation would be indicative of a fully functional organic indirect X-ray detection system 358 that can be fabricated with inexpensive printing techniques into spatially resolved flexible 359 arrays. This ability to form thin flexible arrays is highly advantageous for wearable dosimetry 360 applications where the target area shifts due to the movement of the human body.

![](_page_17_Figure_0.jpeg)

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Figure 4: (a) An illustration of the three different degradation mechanisms to which the flexible organic photodetectors were subjected. (b) Detector photocurrent as a function of time. (c) Detector photocurrent as a function of the number of repeated bend cycles (red) around a radius of 1 cm. The control data for an unbent sample is shown in black. (d) The current densityvoltage curves for photodetectors before (black) and after (red) 5kGy irradiation from a <sup>60</sup>Co source.

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370 The stability of the flexible X-ray photodetectors was assessed against 3 different degradation 371 mechanisms; time, repeated mechanical flexing, and large radiation doses (Figure 4a). The 372 organic materials were protected from air and water using a flexible barrier film composed of 373 polyethylene terephthalate (PET) stacks integrated with a commercial UV and moisture barrier 374 (Amcor UB4) and barrier resin glue to minimize oxidation of the semiconductors in the 375 sensitive volume. PET films are known to exhibit scintillation with a deep blue photon emission, potentially overlapping with that of the RP400 plastic scintillator employed in the 376 devices.<sup>[38]</sup> We have extensively characterised the influence of these barrier films on the 377 sensitivity and radiation hardness of organic photodiodes elsewhere, confirming that they have 378 minimal effects on both parameters.<sup>[39]</sup> No degradation in performance was observed after 379 380 encapsulation for up to 1000 hours, within the measurement error margin of 4% (Figure 4b). Photodetector performance was tested with a voltage cycle between +1V and -5V every day 381 382 for the first 5 days, then every 100 hrs thereafter. Light intensity during measurements was 100

mWcm<sup>-2</sup>, with a total light exposure time of approximately 1 hour over the testing period, 383 384 followed by storage in a dark, air permeable environment. This intense level of light exposure 385 is orders of magnitude higher than that produced from the plastic scintillator under X-ray exposure, providing an accelerated testing platform that implies a long device shelf-life under 386 387 continuous operation. The stability of the photodetector current output during repeated bending 388 cycles was tested by preparing new encapsulated devices with similar organic materials 389 prepared using home-made synthesis procedures to fit the flexible testing apparatus. Devices 390 were taken from flat to a bend radius of 1 cm and monitoring performance after every 100 391 cycles, was tested by assembling new form similar materials. is shown in Figure 4c. The 392 photocurrent output decreased by a total of 12% after 1000 bending cycles, confirming the high 393 stability of the organic photodetectors against mechanical stress. No visual evidence of 394 interfacial fracture was observed in any of the samples measured. Finally, the stability of the 395 photodetector to harsh irradiation conditions was investigated, a property for which previous 396 studies have found organic semiconductors have particularly poor performance. Dosimeters 397 for medical applications may be exposed to X-ray doses as high as 500 Gy per year and are 398 expected to perform with minimal degradation. Plastic scintillators, such as the one used in this 399 study, have been extensively characterized for high energy physics applications and proven to 400 exhibit high radiation hardness, with less than 8% variation in their light yields up to an irradiation of 10 kGy.<sup>[40-41]</sup> Therefore, the P3HT:o-IDTBR photodetector response was 401 402 characterized independently after irradiation with a cobalt-60 gamma source up to a total 403 irradiation dose of 5 kGy (approximately equivalent to a 5 year working lifetime in high dose 404 applications, and 10 years in medical imaging). A decrease in the photocurrent output of 22% 405 was observed for zero-bias operation after 5 kGy of irradiation (Figure 4d). This result is 406 exceptional for organic semiconductors, representing not only the first report on the effect of 407 ionizing radiation for organic non-fullerene acceptor materials, but also one of the best 408 radiation hardness results reported, with less than half the degradation of other solution-based organic semiconductors at the same level of irradiation.<sup>[42]</sup> This result substantiates one of the 409 rationales for employing the planar NFA material o-IDTBR, which was a suspected increased 410 411 resistance to radiation-induced degradation. The suspected origin of the enhanced radiation 412 tolerance is the strong degree of planarity in the molecular structure of o-IDTBR. Recent work 413 has found that these non-fullerene acceptor molecules undergo a photoinduced conformational 414 change as a key initiator of photooxidation and subsequent degradation, further reporting that 415 if this planarity was frozen by the use of molecular interactions or structure it would be possible to inhibit the degradation.<sup>[43]</sup> Furthermore, the optical-to-electrical conversion efficiency of 416 417 photodetectors fabricated with the NFA were already greater than any other reported polymer-418 based materials employed in X-ray detecting systems, showing at least double the initial performance of other systems such as P3HT:PCBM, F8BT:PDI or TFB:PDI.<sup>[44]</sup> Thus the 419 420 performance of the P3HT:o-IDTBR photodetectors not only make them the most efficient 421 polymer-based organic materials used in indirect X-ray detectors by up to an order of 422 magnitude after irradiation, but they also maintain a higher performance after irradiation than 423 any other pristine non-irradiated polymer-based devices have ever achieved.

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425 To conclude, we have demonstrated a new printable organic material combination for the 426 photodetector component of an indirect X-ray detection system. The device exhibits 427 exceptional optical-to-electrical conversion efficiency as a photodetector, with higher 428 performance than any other reported printable organic systems and the unique ability to operate 429 efficiently with zero external bias. Complete X-ray detectors fabricated by coupling the 430 photodiode with a plastic scintillator are amongst the first flexible and fully tissue equivalent 431 X-ray detectors capable of operating without external bias. The X-ray performance is energy 432 independent between 50 keV and 1.2 MeV, with a detection sensitivity that is equivalent to

433 inorganic direct X-ray detectors for the pulsed beams monitored and the fastest temporal 434 response ever reported for organic indirect X-ray detectors. The materials can be printed into a 435 pixelated array to provide high spatial resolution and demonstrate major improvements in both 436 radiation hardness and temporal response compared to other organic materials. The device is also shown to be highly stable with respect to time, mechanical flexing and large radiation 437 438 doses. The new materials and fully tissue equivalent X-ray detectors we report here provide a device that is capable of being a stable, printable, flexible, and tissue equivalent detector with 439 440 high radiolucency for wearable applications where simultaneous monitoring and transmission 441 of the X-ray absorbed dose in the human body is required.

442

## 443 **Experimental**

444 Device Fabrication: ITO-coated glass and ITO-PET substrates were employed as anodes after 445 cleaning by successive ultrasonication in acetone, isopropyl alcohol and deionized water, 446 followed by 15 min of UV-ozone treatment. PEDOT:PSS suspensions (Heraeus) were filtered 447 (0.45-um), deposited onto electrodes by spin-coating at 4000 rpm for 90 s, then annealed at 448 140 °C for 30 min, producing 40 nm films. P3HT:o-IDTBR films (1:1 ratio) were deposited from 10 mg mL<sup>-1</sup>, 18 mg mL<sup>-1</sup> and 30 mg mL<sup>-1</sup> solutions in chloroform by spin-coating in a 449 450 glove box at a variety of speeds to obtain the desired thickness, followed by drying at 70 °C for 4 min. Zinc oxide (10 mg mL<sup>-1</sup> in acetone) was deposited at 5000 rpm for 50 s, followed 451 by drying at 80 °C for 2 min, producing 40 nm films. A 100 nm aluminum metal contact was 452 thermally evaporated (Angstrom Amod) in a vacuum with a chamber pressure of  $2 \times 10^{-6}$  Torr 453 and area of 4 mm<sup>2</sup>, followed by annealing of the completed devices at 120 °C for 10 min. The 454 455 devices were encapsulated by a barrier film (Amcor; UB4 + UV) and epoxy glue (DELO 456 LP655) with a 30 s exposure under a UV lamp to seal the device.

458 Optoelectronic Characterization: J-V measurements were performed in the dark and under an 459 AM1.5 white light spectrum using a Keithley 2400 sourcemeter. External Quantum Efficiency 460 (EQE) measurements were achieved using illumination from a mechanically chopped 100 W quartz tungsten halogen lamp passed through an Oriel Cornerstone 130 monochromator 461 462 Photocurrent responses were measured with a digitizing lock-in amplifier and referenced to a 463 calibrated silicon diode. UV-vis absorbance spectra were measured using the Cary 6000i UV-464 vis Spectrophotometer with a Diffuse Reflectance Accessory (DRA-1800), with the defined 465 thicknesses of the sensitive volume spun on quartz slides. Photoluminescence spectra were 466 acquired using a Varian Cary Eclipse fluorescence spectrophotometer with an excitation 467 wavelength of 400 nm.

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469 X-Ray Response Characterization: X-ray characterization was achieved at the Illawarra Cancer 470 Care Centre at Wollongong Hospital, Australia. The device was attached to a thin PCB probe 471 and read out using a custom-designed data acquisition system based on a DDC264 chip in 472 passive mode. A 2 mm thick plastic scintillator (Rexon; RP400) was coupled to the back of the 473 device with coupling grease (RX-688) and wrapped in Teflon tape to reduce reflections. Two 474 beam sources were used: (a) a Gumlay orthvotage X-ray tube with a broad 100 kVp spectrum  $(\langle E \rangle = 50 \text{ keV})$ , with the device at surface and 30 cm from the source, and (b) a Varian Clinac® 475 476 21iX linear accelerator (Varian Medical Systems, Palo Alto, USA) pulsed radiation source 477 producing 6 MV photons ( $\langle E \rangle = 1.2 \text{ MeV}$ ) with a pitch of 3.6 µs and repetition rate of 360 Hz, 478 with an instantaneous dose rate of 2.5 kGy/min. The device for source (b) was placed at a 479 source-to-surface distance of 100 cm at a sample depth of 1.5 cm in a water-equivalent plastic 480 phantom.

482 Charge Carrier Dynamics: Photo-CELIV, TPV and impedance measurements were performed 483 using the commercially available PAIOS 2 system (Fluxim AG). For carrier transport and 484 recombination data, a light pulse from a white LED (Cree, xp-g) was used to generate charges whilst a compensating offset voltage held the device at open circuit. The end of the light pulse 485 was simultaneous with the application of either a linearly increasing voltage (photo-CELIV) or 486 487 square-step voltage (TPV) to extract photogenerated charges. The current transients were 488 recorded by the integrated PAIOS hardware. The impedance response was measured over the 489 range of 10 Hz to 1 MHz with an oscillation amplitude of 30 mV. The impedance was recorded 490 under dark and illuminated conditions at 0 V applied bias (short circuit conditions).

491

492 STXM Microscopy: STXM measurements were performed on beamline 5.3.2.2 at the ALS 493 synchrotron. Samples were prepared for STXM measurements by spin coating 2.5 µL of 494 nanoparticle ink onto low stress silicon nitride (Si<sub>3</sub>N<sub>4</sub>) membrane windows with silicon dioxide coating (window dimensions  $0.25 \times 0.25 \text{ mm}^2$ , window thickness 15 nm, silicon frame 495 dimensions  $5 \times 5$  mm<sup>2</sup>, purchased from Norcada, Canada) at 3000 rpm, 1 min, low acceleration 496 497 of 112 rpm/s. Samples were air dried at room temperature. The samples on Si<sub>3</sub>N<sub>4</sub> windows 498 were loaded in the STXM sample chamber and rastered with respect to the X-ray beam. The 499 STXM sample chamber was backfilled with helium (0.33 atm). The transmitted X-ray beam is 500 detected by a scintillator and a photomultiplier tube. The STXM Fresnel zone plate had an 501 outer most zone width of 25 nm, setting the spatial resolution limit of the measurement. A 502 careful selection of the photon energy for each X-ray (NEXAFS) spectrum was performed, 503 establishing orthogonal energies to uniquely identify both P3HT and o-IDTBR. Singular value 504 decomposition was used to fit a sum of the pristine material NEXAFS spectra to the measured 505 blend spectrum of the nanoparticles – at each pixel – in the STXM images. The aXis2000 506 package was used to perform image analysis of STXM maps.

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