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

3
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25 Research interest in new materials for X-ray detection is growing rapidly, driven by demand
26 from applications as diverse as fundamental materials science, medical imaging and
27 radiotherapy, space exploration, security and defence, personal wearable dosimeters, and
28 nuclear science.^[1-6] Current detectors utilize inorganic solid-state semiconductors such as
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
31 large-area pixelated arrays.^[7] Furthermore, these semiconductors are composed of heavier
32 elements, which exhibit much stronger X-ray attenuation than the lighter elements comprising
33 human tissue, resulting in perturbation of the X-ray beam. Consequently, their use for
34 medically relevant dosimetry or personal health monitoring requires complex, often unreliable
35 calibrations limiting their applications in radiotherapy or food sterilization.^[8] A new generation
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.

39

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
46 developments with selenium, perovskite, and organic materials have produced high
47 sensitivities ($S \sim 10^3 - 10^4 \mu\text{CGy}^{-1}\text{cm}^{-2}$),^[9-12] the thickness and crystallinity constraints mandate
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.

57

58 Organic semiconductors are a highly attractive pathway for creating devices that can
59 circumvent each of the above limitations. Their use has become ubiquitous in multidisciplinary
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
62 that enable cheap manufacturing onto flexible substrates at large scale.^[13-15] Such advantages
63 have seen organic electronic materials and devices excel across a vast number of applications,
64 including thin-film transistors,^[16] solar cells,^[17-20] sensors,^[21-22] visual displays,^[23-24] and
65 photodetectors.^[25] Critically, the density of thin solid films fabricated from organic
66 electroactive inks is very similar to that of human tissue, which has an approximate average
67 value of 1.10 g cm^{-3} , and a value of 1.07 g cm^{-3} for the soft tissues most often encountered in
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
71 have been found to be limited by low charge mobility (thus requiring application of bias
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

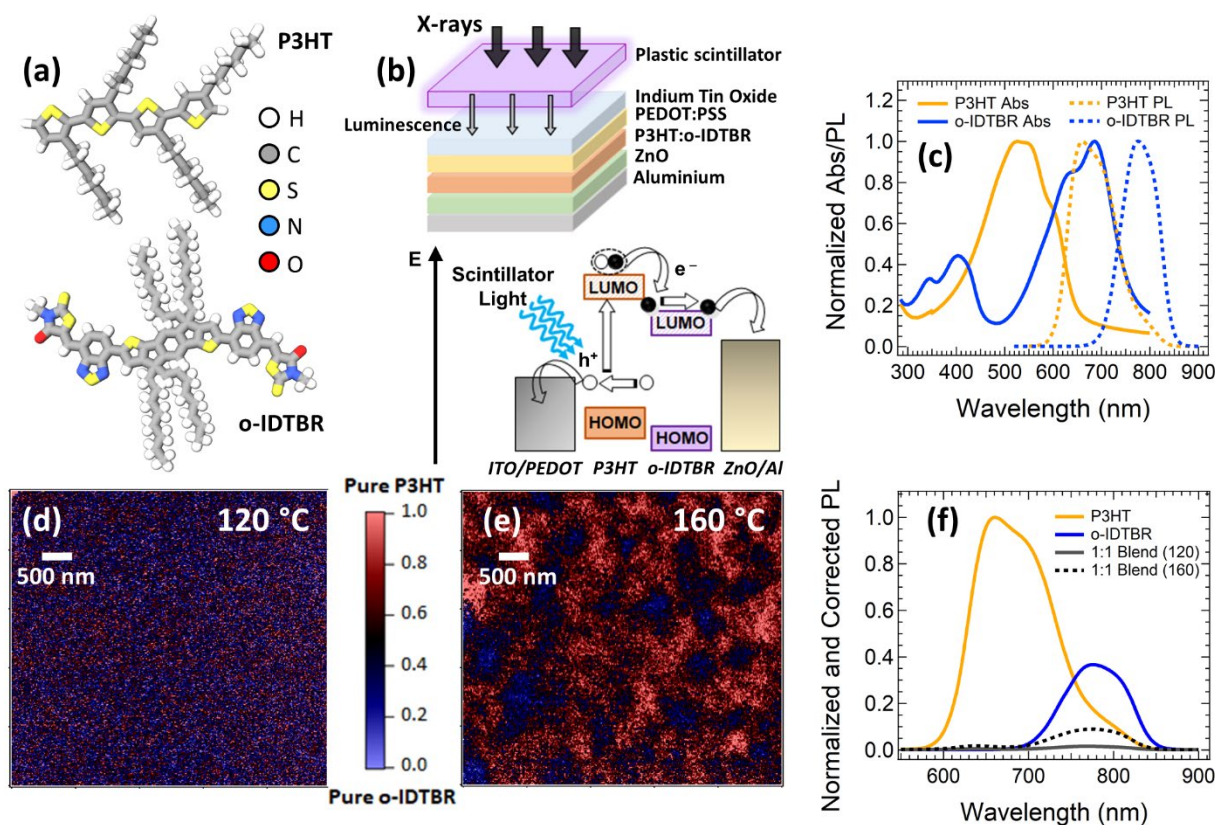
75 versatile coupling with luminescence from different organic scintillators. Critically, their
76 morphology and crystallinity can be controlled through synthetic chemical and device
77 fabrication routes. Creation of planar NFA molecular structures can induce a high packing
78 order, leading to both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

81

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
87 thickness for controlling radiolucency, enabling operation as a transparent dosimeter for
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.

94

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



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Figure 1: (a) Geometry optimized quantum chemical models of P3HT and o-IDTBR chemical 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. The lower part of the figure shows the photodetector current transduction mechanism in 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 of a blended P3HT:o-IDTBR film annealed at 120 °C for 10 minutes, and (e) 160 °C for 10 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) and o-IDTBR (blue) films with blended films annealed at 120 °C for 10 minutes (grey) and 160 °C for 10 minutes (black and dashed) after fabrication.

116 value of 1.10 g cm^{-3} , and a value of 1.07 g cm^{-3} for the soft tissues most often encountered in
 117 medical dosimetry. Solid films cast from these organic semiconductors had mass densities of
 118 1.04 g cm^{-3} for P3HT and 1.06 g cm^{-3} for o-IDTBR, highlighting their suitability for tissue-
 119 equivalent X-ray detection. Complete organic photodetectors fabricated using a 1:1 blend of
 120 P3HT:o-IDTBR for charge generation, PEDOT:PSS and ZnO for charge selective transport
 121 layers to prevent interfacial recombination, and ITO and aluminium electrodes (Figure 1b)

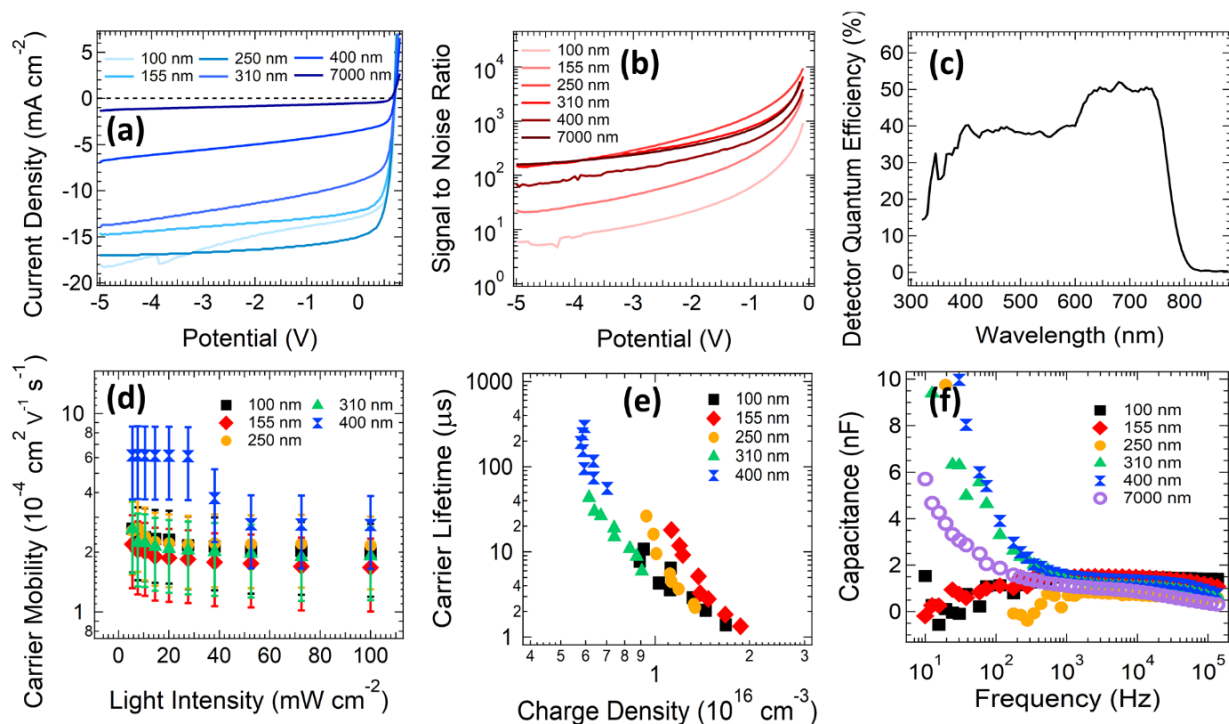
122 exhibited a mass density of 1.18 g cm^{-3} , confirming an excellent tissue equivalency for the fully
123 fabricated organic photodetectors. Since many of these materials are solutions, they can be
124 printed into a multilayer stack onto ITO-coated (120 nm) glass or ITO-coated flexible plastic
125 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
128 vacuum deposition of a thin (100 nm) aluminium layer. Therefore, the entire device represents
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
134 applications requiring exposure to radiation without perturbing the energy fluence of the
135 radiation.

136
137 P3HT exhibits a single broad absorption between 450 nm and 600 nm, whilst o-IDTBR shows
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-
140 750 nm, providing substantial versatility for coupling with X-ray absorbing scintillators. The
141 photoluminescence spectra exhibit Stokes shifts of $\sim 120 \text{ nm}$ for each semiconductor, a signal
142 which can be monitored to measure the extent of free charge generation efficiency in the
143 blended film. The HOMO and LUMO energy levels of the materials are offset, allowing
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
146 the need for external bias, a process which causes quenching of the photoexcited states.^[29]

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 ~ 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.

167

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



172
 173 **Figure 2:** (a) Current density-voltage curves for P3HT:o-IDTBR photodetectors with
 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
 176 optical to electrical conversion as a function of wavelength in the 250 nm device, (d) Charge
 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
 185 signal-to-noise ratios (SNRs) of 10³ to 10⁴ at bias voltages below -0.5 V for film thicknesses
 186 of 250 nm to 7 μm (Figure 2b). These values are equivalent to state-of-the-art silicon
 187 photomultiplier detectors, but without requiring the same high bias voltages (> 25 V) as
 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

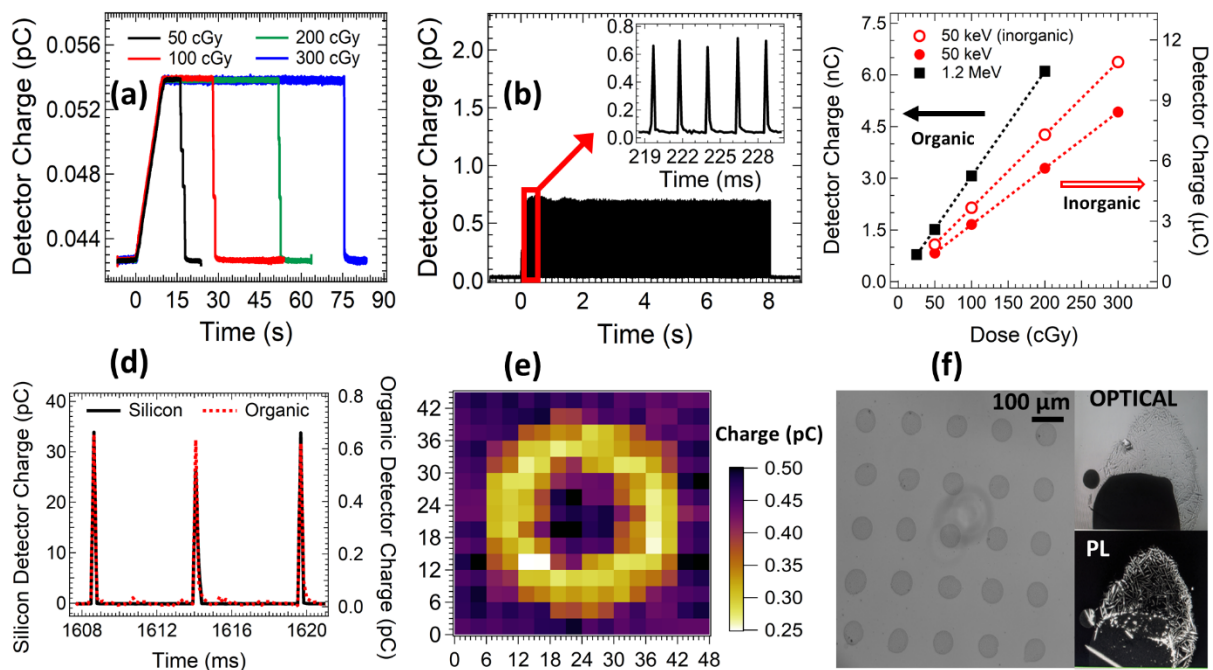
192 and 600 nm (Figure 2c), a spectral range which covers the luminescence light outputs of the
193 vast majority of commercially available X-ray scintillators (vide infra).

194

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
197 system. The device charge carrier mobility was determined to be between $2-3 \times 10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$
198 from current transients using photo-CELIV measurements (Figure S1), with this mobility
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
202 be the holes for this P3HT:o-IDTBR system in previous studies.^[30] The increase in photoactive
203 layer thickness from 400 nm to 7000 nm substantially increased the series resistance of the
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
208 extracted from the transient measurements have not been plotted for this thickness in Figures
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
211 trialled as photodetectors for X-ray detection (P3HT:PCBM = $4.4 \times 10^{-5} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$), thus
212 allowing improved performance and detection sensitivity.^[31] Indeed the P3HT:o-IDTBR
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 Hz) – were extracted efficiently for all thicknesses, resulting in only the
230 geometric device capacitance. However, more deeply trapped charges, which respond when
231 the perturbation frequency is lowered to less than 10^2 Hz, became trapped inside devices for
232 film thicknesses between 310 nm and 7 μm , as determined by the rapidly increasing
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
241 to transit distances of less than 0.3 μm .^[30, 32] We note that there have been other reports of

242 organic semiconductors used as direct X-ray detectors with high sensitivities, however, these
 243 devices do not produce any X-ray detection without external power.^[11-12, 33]
 244
 245 Complete X-ray detectors were fabricated by coupling the P3HT:o-IDTBR photodetectors with
 246 a 2 mm thick plastic scintillator to absorb X-rays and produce visible light with a peak at 425
 247 nm (Figure S4). The mass density of the plastic scintillator is 1.023 g cm⁻³, with an electron
 248 density of 3.33x10²² cm⁻³, compared to values of 1.07 g cm⁻³ and 3.34x10²² cm⁻³, respectively,
 249 for soft tissue. Thus the addition of the plastic scintillator enables the device to maintain its
 250



251

252 **Figure 3:** (a) Indirect detection of $\langle E \rangle = 50$ keV X-rays at various cumulative doses, and (b)
 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 μ s 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 μ 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
 260 metal washer acquired with the organic X-ray detector under the 50 keV X-ray beam. (f) An
 261 image of an inkjet-printed array of scintillator dots deposited onto organic photodetectors with
 262 pixel pitch of 120 μ m. 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
 264 scintillator and the photodetector, indicating normal operation of the coupled detection system
 265 in the printed array.

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

275

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
279 determined to be $1.6 \times 10^4 \mu\text{CGy}^{-1}\text{cm}^{-3}$. This value is somewhat lower than other organic X-
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
282 imaging technologies ($\sim 1 \times 10^4 \mu\text{CGy}^{-1}\text{cm}^{-3}$). Furthermore, the sensitivity was found to be
283 restricted by the plastic scintillator required for full tissue equivalency rather than the intrinsic
284 photodetector performance. The RP400 plastic scintillator generates a relatively low light yield
285 ($9,200$ photons MeV^{-1}) and has a limited emission spectral overlap with the photodetector
286 absorption (Figure 1c and S4) in comparison to inorganic scintillators. Coupling the
287 photodetector to an inorganic LYSO (Lutetium-yttrium oxyorthosilicate) scintillator, which is
288 employed in existing reference technologies and has both a higher light yield of $33,200$ photons
289 MeV^{-1} and a broader spectral overlap between the scintillator emission and the P3HT:o-IDTBR
290 absorption in the range of 500-600 nm, produces a sensitivity of $3.6 \times 10^7 \mu\text{CGy}^{-1}\text{cm}^{-3}$, a value

291 more than three orders of magnitude higher than that produced with the plastic scintillator and
292 equivalent to the best indirect X-ray detecting sensitivities reported with organic
293 photodetectors.^[35-36] The response to high energy X-rays produced from a Varian Clinac®
294 21iX linear accelerator operating at 6 MV ($\langle E \rangle = 1.2$ MeV) used for radiotherapy treatment of
295 cancer showed similar sensitivity to that observed in the lower energy keV X-rays, but with a
296 completely different temporal response. The electrical output was again found to be linear with
297 increasing X-ray dose, with a calculated sensitivity of $3.4 \times 10^4 \mu\text{CGy}^{-1}\text{cm}^{-3}$ with the plastic
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.

306

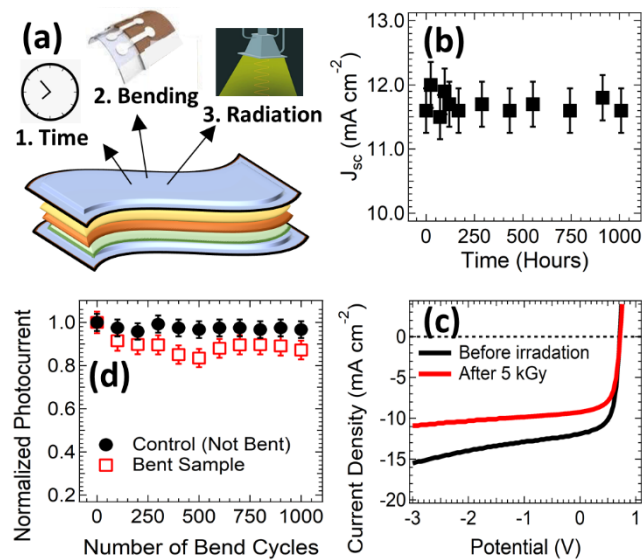
307 Of particular interest, the detection response for the MeV X-rays shows a remarkably fast
308 temporal resolution. The linear accelerator is a pulsed radiation source with a pulse width of
309 $3.6 \mu\text{s}$ and an instantaneous dose delivery of $270 \mu\text{Gy}$ per pulse. Figure 3b shows that the tissue
310 equivalent X-ray detectors can resolve each individual pulse generated from the linear
311 accelerator, and rapidly discharges completely following each pulse. This result confirms that
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
317 pulses with similar performance, though direct comparison of the respective limiting time
318 responses would require a faster pulsed energy source. These results show for the first time that
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 X-
321 ray sources, in contrast to previously reported limitations with low carrier mobilities.^[26] The
322 increased mobility enabling an organic photodiode that can follow the pulsed X-ray beam
323 profile with similar performance to silicon is supported by consideration of the carrier transit
324 time as an approximation for temporal response. The transit time of carriers through the film
325 is given by $t_{tr} = \frac{L}{v}$, where L is the photoactive film thickness and v the carrier velocity. Since
326 the carrier velocity is related to mobility according to $v = \mu E_{bi}$, where μ is the mobility and E_{bi}
327 is the magnitude of the built-in field created by the asymmetric electrode work functions,
328 calculated here as $E_{bi} = \frac{V_{oc}}{L}$ where V_{oc} is the open circuit voltage, the transit time is related to
329 mobility according to $t_{tr} = \frac{L^2}{\mu V_{oc}}$. For a 250 nm film, using the μ (increased by an order of
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 μ s is calculated, in agreement with the measured
332 charge extraction times in Figure S3 and confirming the organic photodiodes can respond to
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
335 a flat aluminium annulus-shaped washer. The X-ray image shows high contrast (Figure 3e),
336 with the spatial resolution limited only by the photodetector pixel dimensions. The successful
337 acquisition of an X-ray image demonstrates the functionality of the new P3HT:o-IDTBR
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
348 array was investigated with optical and photoluminescence microscopy, focusing on a pixel
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.^[37]
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.

361



362

363 **Figure 4:** (a) An illustration of the three different degradation mechanisms to which the
 364 flexible organic photodetectors were subjected. (b) Detector photocurrent as a function of time.
 365 (c) Detector photocurrent as a function of the number of repeated bend cycles (red) around a
 366 radius of 1 cm. The control data for an unbent sample is shown in black. (d) The current density-
 367 voltage curves for photodetectors before (black) and after (red) 5kGy irradiation from a ^{60}Co
 368 source.

369

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
 376 emission, potentially overlapping with that of the RP400 plastic scintillator employed in the
 377 devices.^[38] We have extensively characterised the influence of these barrier films on the
 378 sensitivity and radiation hardness of organic photodiodes elsewhere, confirming that they have
 379 minimal effects on both parameters.^[39] No degradation in performance was observed after
 380 encapsulation for up to 1000 hours, within the measurement error margin of 4% (Figure 4b).
 381 Photodetector performance was tested with a voltage cycle between +1V and -5V every day
 382 for the first 5 days, then every 100 hrs thereafter. Light intensity during measurements was 100

383 mWcm⁻², with a total light exposure time of approximately 1 hour over the testing period,
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
386 exposure, providing an accelerated testing platform that implies a long device shelf-life under
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
401 irradiation of 10 kGy.^[40-41] Therefore, the P3HT:o-IDTBR photodetector response was
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
409 organic semiconductors at the same level of irradiation.^[42] This result substantiates one of the
410 rationales for employing the planar NFA material o-IDTBR, which was a suspected increased
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
416 to inhibit the degradation.^[43] Furthermore, the optical-to-electrical conversion efficiency of
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
419 performance of other systems such as P3HT:PCBM, F8BT:PDI or TFB:PDI.^[44] Thus the
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.

424

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
437 also shown to be highly stable with respect to time, mechanical flexing and large radiation
438 doses. The new materials and fully tissue equivalent X-ray detectors we report here provide a
439 device that is capable of being a stable, printable, flexible, and tissue equivalent detector with
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- μm), 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
449 from 10 mg mL⁻¹, 18 mg mL⁻¹ and 30 mg mL⁻¹ solutions in chloroform by spin-coating in a
450 glove box at a variety of speeds to obtain the desired thickness, followed by drying at 70 °C
451 for 4 min. Zinc oxide (10 mg mL⁻¹ in acetone) was deposited at 5000 rpm for 50 s, followed
452 by drying at 80 °C for 2 min, producing 40 nm films. A 100 nm aluminum metal contact was
453 thermally evaporated (Angstrom Amod) in a vacuum with a chamber pressure of 2×10^{-6} Torr
454 and area of 4 mm², followed by annealing of the completed devices at 120 °C for 10 min. The
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.

457

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
461 quartz tungsten halogen lamp passed through an Oriel Cornerstone 130 monochromator
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.

468

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 orthovoltage X-ray tube with a broad 100 kVp spectrum
475 ($\langle E \rangle = 50$ keV), with the device at surface and 30 cm from the source, and (b) a Varian Clinac®
476 21iX linear accelerator (Varian Medical Systems, Palo Alto, USA) pulsed radiation source
477 producing 6 MV photons ($\langle E \rangle = 1.2$ MeV) with a pitch of 3.6 μ s 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.

481

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
485 whilst a compensating offset voltage held the device at open circuit. The end of the light pulse
486 was simultaneous with the application of either a linearly increasing voltage (photo-CELIV) or
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_3N_4) membrane windows with silicon dioxide
495 coating (window dimensions $0.25 \times 0.25 \text{ mm}^2$, window thickness 15 nm, silicon frame
496 dimensions $5 \times 5 \text{ mm}^2$, purchased from Norcada, Canada) at 3000 rpm, 1 min, low acceleration
497 of 112 rpm/s. Samples were air dried at room temperature. The samples on Si_3N_4 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.

507

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