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## Millimeter-Scale Unipolar Transport in High Sensitivity Organic-Inorganic Semiconductor X-Ray Detectors

K. D. G. Imalka Jayawardena, Hashini M. Thirimanne, Sandro Francesco Tedde, Judith E. Huerdler, Andrew J. Parnell, R. M. Indrachapa Bandara, Christopher A. Mills, and S. Ravi P. Silva

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# Millimeter-Scale Unipolar Transport in High Sensitivity Organic-Inorganic Semiconductor X-Ray Detectors

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## 20 21 **ABSTRACT** 22 23

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26 Hybrid inorganic-in-organic semiconductors are an attractive class of materials for  
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29 optoelectronic applications. Traditionally, the thicknesses of organic semiconductors are  
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32 kept below 1 micron due to poor charge transport in such systems. However, recent work  
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35 suggests that charge carriers in such organic semiconductors can be transported over  
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38 centimeter length scales opposing this view. In this work, a unipolar X-ray photoconductor  
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41 based on a bulk heterojunction architecture, consisting of poly(3-hexylthiophene), a C70  
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44 derivative and high atomic number bismuth oxide nanoparticles operating in the 0.1 – 1  
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47 mm thickness regime is demonstrated, having a high sensitivity of  $\sim 160 \mu\text{CmGy}^{-1}\text{cm}^{-3}$ .  
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54 The high performance enabled by hole drift lengths approaching a millimeter facilitates a  
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3 device architecture allowing a high fraction of the incident X-rays to be attenuated. An X-  
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7 ray imager is demonstrated with sufficient resolution for security applications such as  
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10 portable baggage screening at border crossings and public events and scalable medical  
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14 applications.  
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## 23 **KEYWORDS**

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28 detectors, direct conversion, radiation, inorganics, organics  
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50 Due to their low cost and solution processible nature, organic semiconductors based  
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53 on conjugated polymers and small molecules have been proposed for energy harvesting  
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3 applications,<sup>1-3</sup> light emitting devices.<sup>4</sup> In addition to the applications highlighted above,  
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6 organic semiconductor based devices as well as inorganic-organic hybrid devices are  
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10 gaining attention for the detection of ionizing radiation.<sup>5,6</sup> The first reported inorganic  
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14 nanomaterials used for sensitization of organic semiconductor devices for ionizing  
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17 radiation can be traced to the work of Intaniwet *et al.*<sup>7</sup> where bismuth oxide nanoparticles  
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20 (Bi<sub>2</sub>O<sub>3</sub> NPs) were incorporated into a *p*-type poly(triaryl amine) matrix for detection of  
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24 ionizing radiation based on a mono-carrier device architecture. The versatility of the  
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28 concept was further examined through variation of the high atomic number (Z) NP and  
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31 the organic semiconductor used.<sup>8</sup> In addition to the above developments, Büchele *et al.*<sup>6</sup>  
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33  
34 demonstrated that the incorporation of gadolinium oxysulfide micro-particles into an  
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38 organic bulk heterojunction matrix consisting of poly(3-hexyothiophene) (P3HT) and [6,6]  
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41 - Phenyl-C71-butyric acid methyl ester (PCBM) can result in X-ray detector that enable  
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45 higher resolution imaging capabilities for medical applications extending beyond the  
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49 current market offerings based on amorphous silicon photodiodes coupled with a cesium  
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52 iodide scintillator. The importance of the hybrid inorganic-organic semiconductor systems  
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56 have also been exemplified in the recent work of Civatti *et al.*<sup>9</sup> where the X-ray sensitivity  
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3 of a previously demonstrated 6,13-bis(triisopropylsilylethynyl)pentacene system<sup>10</sup> was  
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7 enhanced by substitution of the silicon atom in organic semiconductor with germanium.  
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10 In addition to the above, there has also been significant interest in the utilization of  
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13 perovskite semiconductors as direct conversion ionization radiation detectors<sup>11-13</sup> due to  
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17 their high X-ray attenuation (as a result of their high average atomic numbers) and high  
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20 carrier mobilities that enable efficient charge extraction from thick devices (several  
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24 hundred of microns to millimeters) that is a pre-requisite to enable a fraction of the incident  
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28 X-rays to be attenuated.  
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31 Based on the insights from above developments, we reported a direct conversion X-ray  
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34 detector concept based on a ternary system comprising of P3HT, PCBM and Bi<sub>2</sub>O<sub>3</sub> NPs.<sup>5</sup>  
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38 Unlike conventional hybrid device concepts where organic semiconductors are utilized  
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41 for detection of visible – near infrared photons, this device architecture utilized P3HT and  
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45 PCBM as carrier selective charge transport pathways for free carriers generated due to  
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48 the interaction between the X-rays and the Bi<sub>2</sub>O<sub>3</sub> NPs. This enabled a number of benefits  
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52 including high X-ray sensitivities of  $\sim 1.7 \text{ mCmGy}^{-1}\text{cm}^{-3}$  when irradiated using “soft” X-  
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56 rays and  $\sim 30 \text{ } \mu\text{C mGy}^{-1}\text{cm}^{-3}$  under 6 MV “hard” X-rays. However, the thickness of the  
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3 devices were limited to  $< 30 \mu\text{m}$  due to the limitations in the fabrication process used as  
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7 well as due to the prevailing state of knowledge (during the period over which the work  
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10 was carried out) on the inability for organic semiconductors to transport charge over  
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13 several hundreds of microns. The high sensitivity obtained with such thin films has critical  
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17 implications including: a much lower dose detectability which is of importance in dosimetry  
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21 (*e.g.*: assessing damage to regions surrounding the area of interest in radiotherapy).  
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24 However, the thin nature and the resulting low attenuation of X-rays has significant  
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28 negative impact for X-ray imaging where a high X-ray attenuation is required for improving  
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31 image quality.  
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35 Recently, Gélinas *et al.* has shown that photo-generated electrons and holes in organic  
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38 semiconductors are efficiently separated through delocalized states on the femtosecond  
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41 time scale<sup>14</sup> which results in the performances typically observed for organic  
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44 photovoltaics. Furthermore, Burlingame *et al.* demonstrated that the resulting free carriers  
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48 generated can be transported over centimeter length scales,<sup>15</sup> challenging previously  
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51 held views of short charge transport lengths in these systems. Such long transport lengths  
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55 are particularly attractive, especially in terms of the development of ionizing radiation  
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3 detectors where thick absorbers are preferred for maximum radiation attenuation.<sup>5,6</sup>  
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7 Here, a highly sensitive X-ray photoconductor based on the integration of inorganic  
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10 nanoparticles in an organic bulk heterojunction matrix with hole drift lengths approaching  
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13 1 mm is demonstrated. These drift lengths which exceed those of organic single  
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16 crystals,<sup>16</sup> enables photoconductor thicknesses approaching a millimeter and X-ray  
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18 sensitivities of  $\sim 160 \mu\text{CmGy}^{-1}\text{cm}^{-3}$ .  
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## 28 RESULTS & DISCUSSION

### 31 Dose rate and thickness dependency of X-ray photocurrent response

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36 The X-ray photoconductor developed in this work is based on P3HT as a *p*-type  
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38 semiconductor, PCBM as an electron trap and Bi<sub>2</sub>O<sub>3</sub> NPs as the X-ray attenuator and a  
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40 route for free carrier generation (Figure 1a). The use of PCBM as an electron transporter,  
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43 as detailed in our previous work<sup>5</sup> was avoided due to the lower electron mobilities  
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46 generally observed in fullerene systems.<sup>17</sup> The photoconductor device was completed by  
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51 deposition of hole-selective gold contacts<sup>18</sup> (Figure 1b,c) resulting in the formation of a  
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3 strong Schottky barrier for electrons. Our preliminary investigations focused on a P3HT:  
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7 PCBM: Bi<sub>2</sub>O<sub>3</sub> weight ratio of 1:1:1 which within a photodiode architecture demonstrated  
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10 a sensitivity of ~1 mCmGy<sup>-1</sup>cm<sup>-3</sup>. Initially, a photoconductor with a thickness of ~180 μm  
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13 was fabricated and the X-ray photocurrent response was tested under a 70 kVp X-ray  
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16 source (Figure S1) with varying X-ray dose rate ( $D$ ) from 20 μGys<sup>-1</sup> to ~ 1 mGys<sup>-1</sup> over an  
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19 X-ray exposure duration of 7 s (Figure 1d) resulting in cumulative exposure doses of 0.14  
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22 - 7.5 mGy. The device demonstrated slow rise and decay behavior commensurate with  
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27 photo conducting characteristics. The X-ray sensitivity ( $S$ ) was evaluated based on<sup>5</sup>  
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$$S = \frac{1}{D \times T_{X-ray} \times V} \int_0^{T_{X-ray}} \Delta I_{X-ray} dt \quad (1)$$

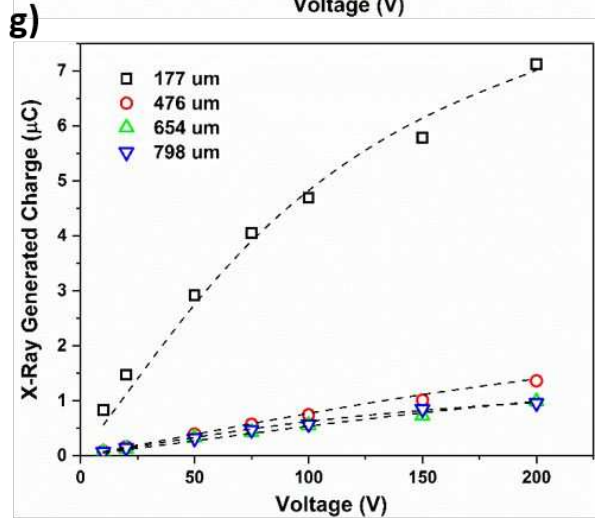
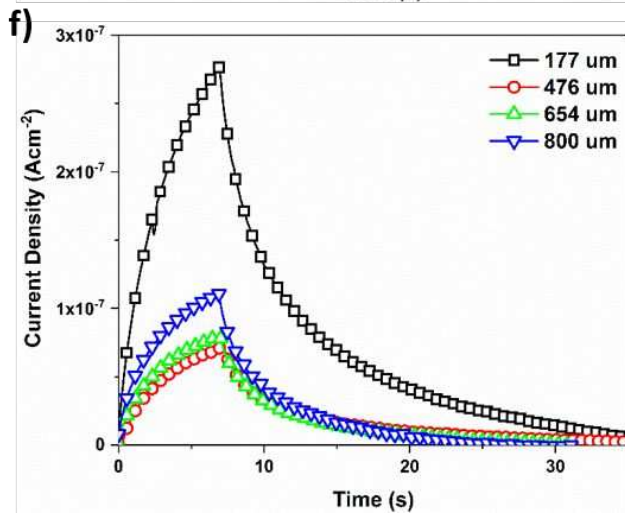
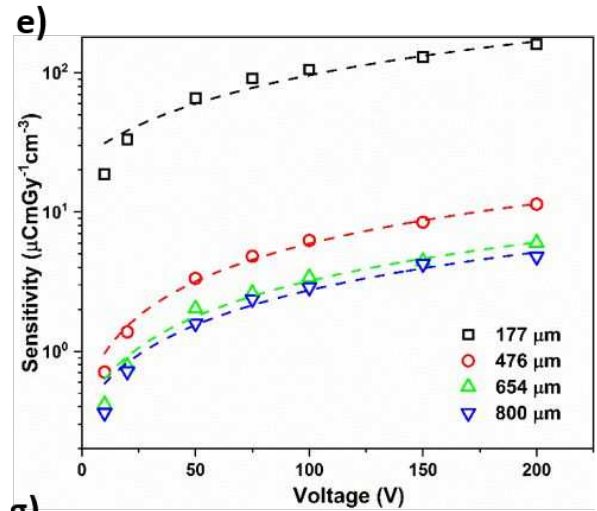
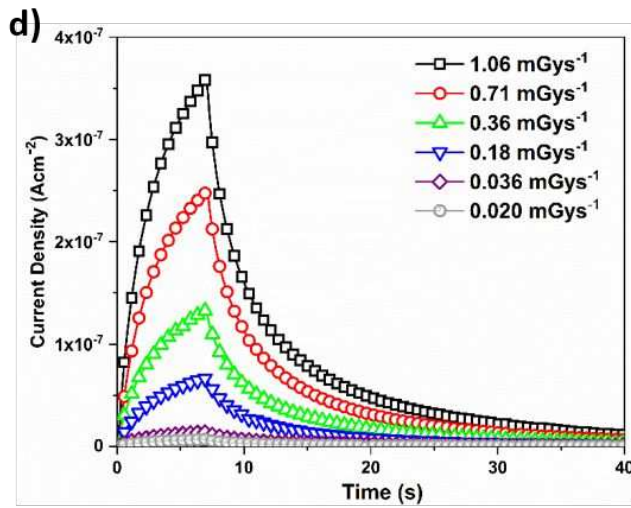
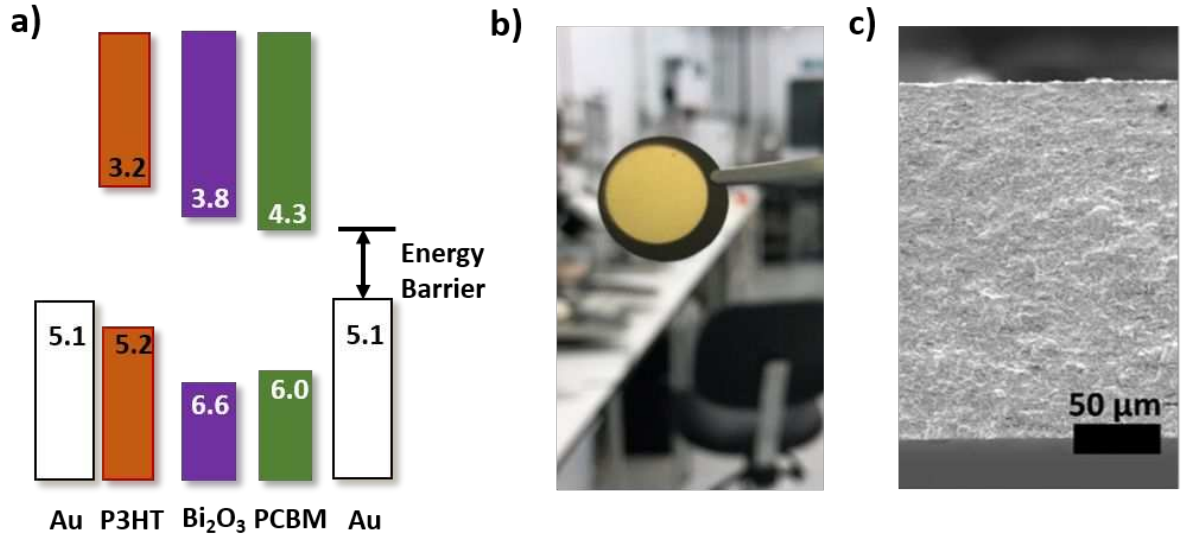
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35 where  $\Delta I_{X-ray}$  is the X-ray generated photocurrent over a duration of  $T_{X-ray}$  over which the  
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38 X-ray exposure was carried out and  $V$  is the detector volume. A high sensitivity of ~160  
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41 μCmGy<sup>-1</sup>cm<sup>-3</sup> under an applied bias of 200 V was achieved, corresponding to an electric  
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44 field ( $E$ ) of ~1.2 Vμm<sup>-1</sup>. These values are a significant improvement over those observed  
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48 for single crystal organic X-ray detectors<sup>19</sup> and compete with recent reports on single  
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3 crystal organic and perovskite X-ray detectors (Figure S2). The mobility-time constant  
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7 ( $\mu\tau$ ) for the above photoconductors were evaluated using the Hecht equation<sup>11</sup>  
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$$Q = \frac{Q_0\mu\tau V}{d^2} \left[ 1 - \exp\left(-\frac{d^2}{\mu\tau V}\right) \right] \quad (2)$$

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14 where  $Q$  is the collected charge,  $Q_0$  is the generated charge and  $d$  is the detector  
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17 thickness. Fitting the above relationship to the  $Q\sim V$  characteristics, a  $\mu\tau$  constant of  $\sim$   
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21  $1.7\times 10^{-6} \text{ cm}^2\text{V}^{-1}$  was obtained. This is within two orders of magnitude of the values  
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24 reported for printable perovskite X-ray detectors ( $\mu\tau = 1 \times 10^{-4} \text{ cm}^2\text{V}^{-1}$ )<sup>13</sup> and chlorine  
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26  
27 doped cadmium telluride single crystals ( $\mu\tau = 7 \times 10^{-5} \text{ cm}^2\text{V}^{-1}$ ).<sup>20</sup> Based on the above  $\mu\tau$   
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30 values, we estimate a hole drift length ( $L$ ) of 170  $\mu\text{m}$ . based on  $L = \mu\tau E$  (for  $E = 1 \text{ V}\mu\text{m}^{-1}$ )  
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described photoconductor. This consolidates our understanding of the improved detector  
performance and rationale for their sensitivity.



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3 **Figure 1. a) The flat band diagram for the different semiconductor materials. All energy**  
4 **values are given in eV. b) Photograph of a fabricated X-ray detector and c) cross sectional**  
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7 **scanning electron micrograph of a detector. d) X-ray photocurrent transients under an**  
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10 **applied bias of 20 V and different dose rates over a 7 s exposure window. e) Variation in**  
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12  
13 **the detector sensitivity under a range of applied voltages for different photoconductor**  
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15  
16 **thicknesses, f) example transients under an electric field of 0.2 – 0.3 V $\mu\text{m}^{-1}$  for different**  
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18 **photoconductor thicknesses and g) the Hecht fits for different photoconductor**  
19  
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21 **thicknesses.**  
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32 The fraction of X-rays stopped within the active volume of the detector ( $F$ ) is given  
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36 by<sup>21</sup>

$$F = 1 - \exp(-\mu_m \rho d) \quad (3)$$

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41  
42 where  $\mu_m$  is the mass attenuation coefficient for a material of density  $\rho$  and thickness  $d$ .  
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46 Therefore, increasing the photoconductor thickness and/or its mass attenuation  
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49 coefficient enables a higher attenuation to be achieved. However, this can only be  
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53 effective if the entire detector active volume is depleted, with minimal additional  
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3 recombination centers which reduce the generated charge components. In view of the  
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7 exceptionally high carrier transport lengths observed, we first proceeded to investigate  
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10 the X-Ray photocurrent response of the P3HT:PCBM:Bi<sub>2</sub>O<sub>3</sub> (1:1:1) system by increasing  
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14 the photoconductor thickness up to ~1 mm. Even under such high thickness, not reported  
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16  
17 previously for P3HT and PCBM based organic semiconductor devices, sensitivities of ~  
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20 5  $\mu\text{CmGy}^{-1}\text{cm}^{-3}$  are obtained which are still competitive with the more recently reported  
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23  
24 perovskite based X-ray detectors.<sup>11</sup> In order to ascertain the charge extraction capabilities  
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26  
27 with increasing thickness, the  $\mu\tau$  product was evaluated based on Hecht fits (Figure 1g)  
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31 which leads to values of  $5 \times 10^{-6} \text{ cm}^2\text{V}^{-1}$  ( $d = 476 \mu\text{m}$ ),  $9 \times 10^{-6} \text{ cm}^2\text{V}^{-1}$  ( $d = 654 \mu\text{m}$ ) and  
32  
33  
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35  $2.5 \times 10^{-5} \text{ cm}^2\text{V}^{-1}$  ( $d = 798 \mu\text{m}$ ). The hole drift lengths, calculated based on the electric field  
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38 at  $E = 1.2 \text{ V}\mu\text{m}^{-1}$ , leads to an improvement in the carrier drift lengths with increasing  
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42 thickness resulting in values of ~1 mm. Such high drift lengths under low electric fields  
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45 are extremely beneficial in order to extract charges from detectors whose thicknesses lie  
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49 in the 100  $\mu\text{m}$  – 1 mm length scale (which enables device architectures allowing a higher  
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52 fraction of incident X-rays to be attenuated and subsequently to be collected).  
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4 The carrier transport length scales are significantly higher than those commonly  
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7 employed for organic photovoltaics, where the thickness is normally restricted to < 300  
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10 nm,<sup>22,23</sup> and for organic photodetectors,<sup>24,25</sup> where the thickness is constrained to be < 1  
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13  $\mu\text{m}$  to minimize recombination losses. On the other hand, the high drift lengths observed  
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16 here strongly support recent work by Gelinas *et al.*,<sup>14</sup> where the charge separation at the  
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19  $p$ -type organic semiconductor and  $n$ -type fullerene interface was driven through  
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22 delocalized states within the fullerene resulting in charge separation on a very short  
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25 timescale of 40 fs. While previous work has shown that photo generated electrons can be  
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28 transported over centimeter length scales, such large transport lengths have, so far, not  
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31 been utilized in an electronic device resulting in superior device performance. The ability  
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34 to achieve long charge transport lengths that approach millimeter length scales enables  
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37 the possibility to fabricate 100  $\mu\text{m}$  – 1 mm thick, high sensitivity X-ray sensors based on  
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40 a combination of low cost organic semiconductors and high Z nanoparticles with very little  
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43 or no dead volume within the detector.  
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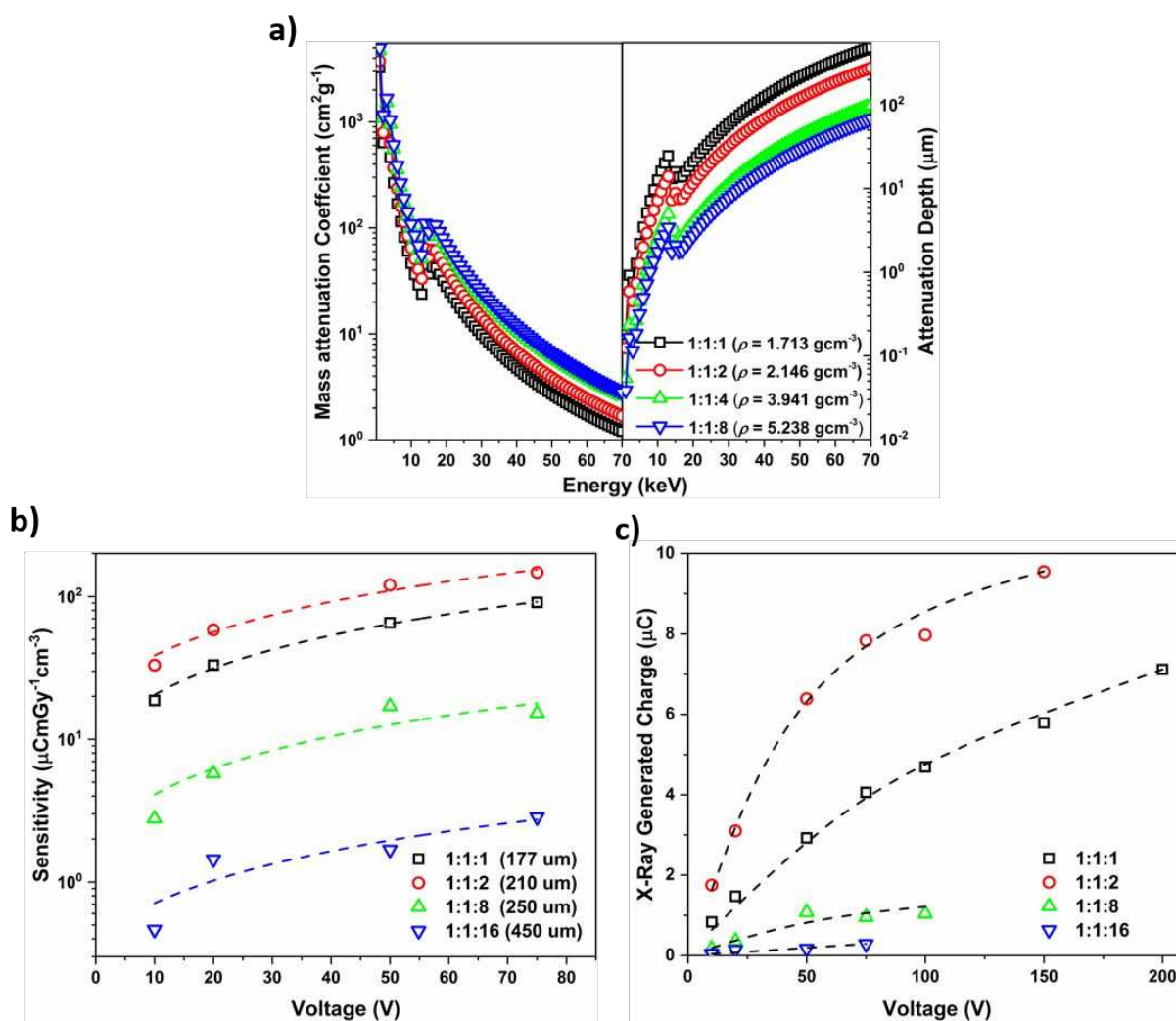
## 56 Impact of nanoparticle loading on X-ray photocurrent response

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4 Following the improvement in photoconductor thickness, we then proceeded to improve  
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7 the X-ray stopping power by further increasing the NP loading which in turn improves  $\mu_m$ .  
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10 This, in combination with increased detector thickness, could potentially allow for almost  
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14 100% attenuation of the incident X-ray photons thereby resulting in high sensitivities.  
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17 Simulation of the  $\mu_m$  using NIST XCOM<sup>26</sup> (Figure 2a) for P3HT:PCBM:Bi<sub>2</sub>O<sub>3</sub>, where the  
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20 Bi<sub>2</sub>O<sub>3</sub> NP loading is varied as 1:1:1, 1:1:2, 1:1:8 and 1:1:16, indicates an increase in  $\mu_m$   
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24 by  $\sim \times 10$ . This correspondingly reduces the X-ray attenuation length (*i.e.* the thickness  
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27 over which 63% of the incident X-rays are stopped) by an equivalent factor. (Figure 2a)  
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31 Under a bias voltage of – 20 V, increasing the NP loading results in a non-linear decrease  
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34 of the X-ray sensitivity from a high value of  $\sim 40 \mu\text{CmGy}^{-1}\text{cm}^{-3}$  for 1:1:1 loading, to  $< 40$   
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37  $\mu\text{CmGy}^{-1}\text{cm}^{-3}$  for higher NP loadings (Figure 2b). The reduced sensitivity despite the  
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40 increase in the NP loading points towards a disruption in the hole transport properties  
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44 within the photo conducting layer. This is indicative of a bottleneck in terms of the optimum  
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47 nanoparticle loading that enables sufficient attenuation of incident X-rays, together with  
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50 sufficient crystallinity within the charge transporting organic semiconductors to enable  
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54 high X-ray photocurrents to be realized. The above observations are further supported by  
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reduction in the  $\mu\tau$  product, based on Hecht fits (Figure 2c), which decrease from  $1.7 \times 10^{-6}$   $\text{cm}^2\text{V}^{-1}$  to  $2 \times 10^{-8}$   $\text{cm}^2\text{V}^{-1}$  when increasing the NP loading from 1:1:1 to 1:1:16. This is suggestive of a potential limit in NP loading when designing NP sensitized organic-inorganic hybrid detectors, especially at higher thickness ( $>50$   $\mu\text{m}$ ).



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4 **Figure 2. X-ray attenuation and response characteristics under different  $\text{Bi}_2\text{O}_3$  loadings.**

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7 **a) The variation of the mass attenuation coefficient (left) and attenuation depth (right) , b)**

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10 **X-ray sensitivity and c) X-ray generated charges under applied bias with Hecht fits for**

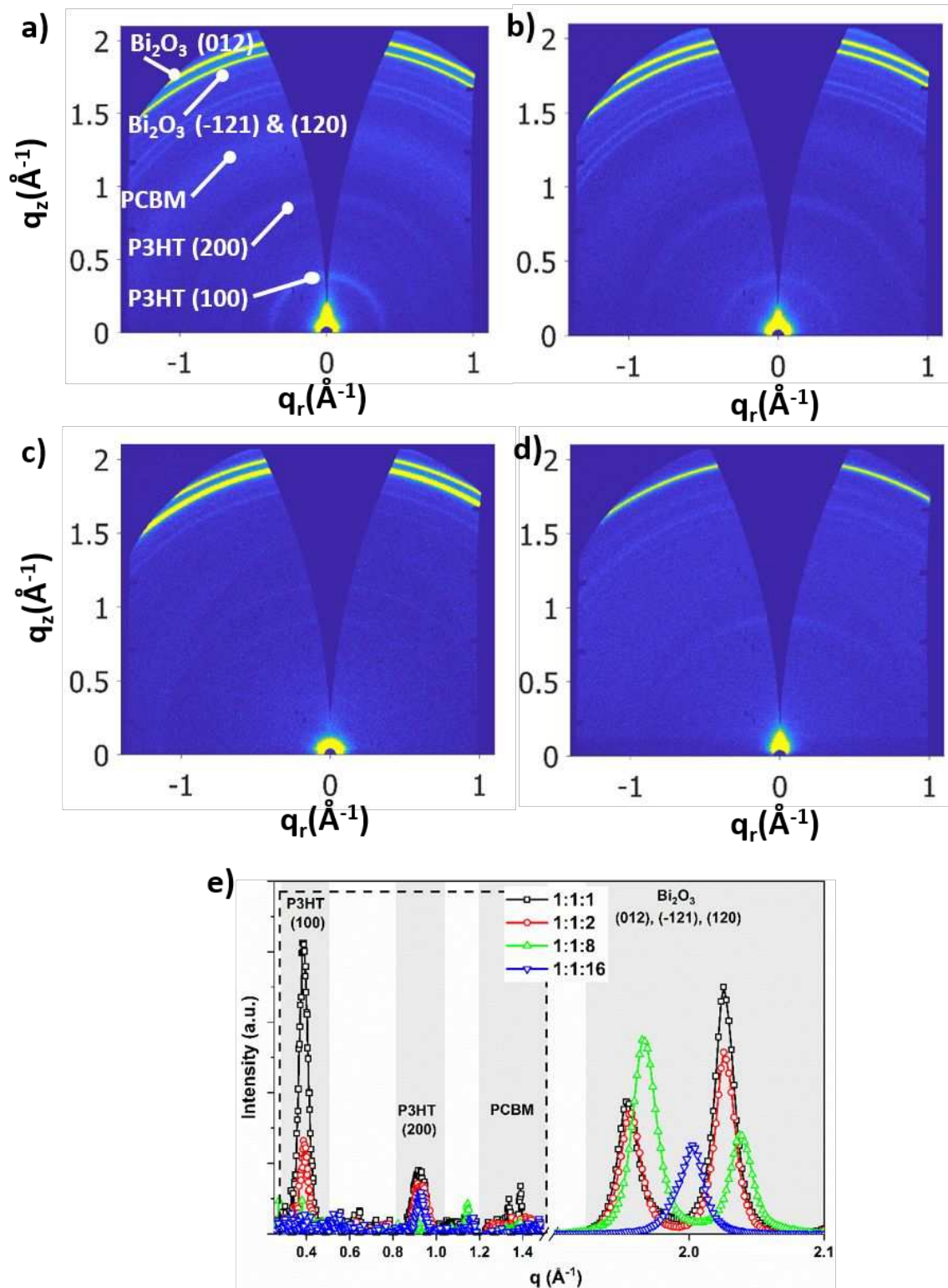
11  
12  
13 **P3HT:PCBM: $\text{Bi}_2\text{O}_3$  photoconductors for 1:1:1, 1:1:2, 1:1:8 and 1:1:16 ratios.**

### 14 15 16 17 18 **Impact of nanoparticle loading on the organic semiconductor crystallinity**

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23 One of the dominant structural properties that affect the performance of such detectors  
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26 is the crystallinity of the organic semiconductor systems used. In the case of the detector  
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29 architecture utilized in this work, achieving a high crystallinity for the P3HT phase is  
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32 preferable as this would have direct impact on the charge transport properties.<sup>5</sup> In order  
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35 to observe the impact of the NP loading on the crystallinity of the P3HT, we carried out  
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38 grazing incidence wide angle x-ray scattering (GIWAXS) measurements on pressed  
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41 pellets (Figure 3a) and analyzed the evolution of the X-ray scattering peaks for the P3HT,  
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44 PCBM and  $\text{Bi}_2\text{O}_3$  NP phases (Figure 3a). Based on the X-ray scattering spectra, it is  
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46  
47 evident that increasing the P3HT:PCBM: $\text{Bi}_2\text{O}_3$  ratio from 1:1:1 to 1:1:2 results in a  
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50 decrease in intensity for the scattering peaks related to the P3HT phase ((100) and (200))  
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3 planes))<sup>5</sup> while these peaks are not observed for the higher NP loadings of 1:1:8 and  
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7 1:1:16. The higher intensities observed for the (100) plane of P3HT indicates that despite  
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10 the powder nature of the starting material, P3HT has a more preferential “edge on”  
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13 orientation where the P3HT lamellar align parallel to the planar surface of the pellet with  
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16 the side chains oriented perpendicular to the planar pellet surface. With regards to the  
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21 PCBM, we note that a noticeable scattering peak is unobservable. This is attributed to the  
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24 GIWAXS spectra being strongly dominated by the scatter peaks due to the Bi<sub>2</sub>O<sub>3</sub> NPs  
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26  
27 resulting in weakly scattering peaks (such as those due to the PCBM phase) to be  
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31 unobservable. The observation of sharp peaks in the GIWAXS spectra for the Bi<sub>2</sub>O<sub>3</sub> NPs  
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33  
34 are in agreement with the crystalline nature of this material whose characteristics based  
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37 on X-ray powder diffraction studies were reported previously.<sup>5</sup> In order to verify that the  
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41 loss of crystallinity is not due to the fabrication methodology utilized, we carried out  
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44  
45 differential scanning calorimetry (DSC) on the P3HT:PCBM:Bi<sub>2</sub>O<sub>3</sub> starting powders used  
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48  
49 for the fabrication of the pellets (Figure S3).<sup>20</sup> DSC analysis for the P3HT phase in  
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51  
52 P3HT:PCBM:Bi<sub>2</sub>O<sub>3</sub> samples at ratios of 1:1:1 and 1:1:2 shows crystallinity of around 5-  
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56 6%. On the other hand, the crystallinity of P3HT is well below the limits that can be  
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3 observed for the 1:1:8 and 1:1:16 systems which is in agreement with the observations  
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7 made from the GIWAXS analysis. The loss in crystallinity for the P3HT phase which in  
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9  
10 the detector architecture utilized here explains the poor sensitivity and  $\mu\tau$  constants for  
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14 the 1:1:8 and 1:1:16 samples where the charge extraction is inhibited due to the more  
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17 disordered nature of the hole transporting P3HT phase.  
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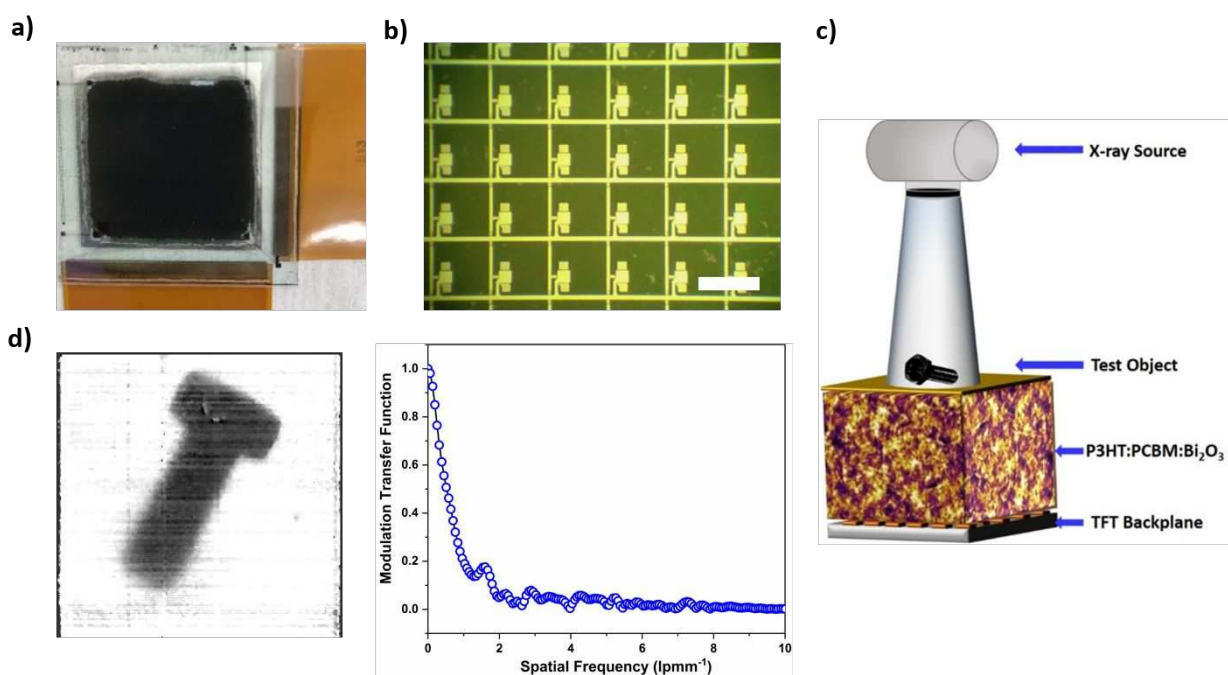
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4 Figure 3. 2D GIWAXS spectra for the hybrid pellets based on P3HT:PCBM:Bi<sub>2</sub>O<sub>3</sub> NP  
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7 ratios of a) 1:1:1, b) 1:1:2, c) 1:1:8 and d) 1:1:16. e) 1D spectra extracted from the 2D  
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9  
10 GIWAXS plots. A noticeable decrease in the peak intensities for the (100) and (200) P3HT  
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13 crystalline planes are observed for 1:1:8 and 1:1:16 samples indicating loss of P3HT  
14  
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16 crystallinity while scatter peaks for the PCBM phase are not observable due to the high  
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18  
19 scattering intensities of the Bi<sub>2</sub>O<sub>3</sub> NPs. The X-ray scattering intensities in the range of  $q$   
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21 = 0.2 – 1.5 Å<sup>-1</sup> (indicated by the dashed box) have been scaled by x30.  
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### 31 X-ray imaging characteristics

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35 Finally, we proceeded to fabricate an X-ray imager (Figure 4a) based on the best  
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37 performing P3HT:PCBM:Bi<sub>2</sub>O<sub>3</sub> 1:1:1 loading condition at a detector thickness of ~250 μm.  
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40 For the fabrication of an array of detector pixels, for imaging purposes, the photo  
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42 conducting wafer was interfaced by contacting an array of thin film transistors (Figure 4b),  
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46 The spatial resolution of the detector was determined using the modulation transfer  
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49 function (MTF) (Figure 4e) *via* the slanted edge method. The MTF of the  
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3 P3HT:PCBM:Bi<sub>2</sub>O<sub>3</sub> based imager possesses a value of 0.2 at ~1 lpmm<sup>-1</sup> which is suitable  
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7 for applications where millimeter to submillimeter scale features require to be  
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10 discriminated as in for example, baggage scanning in border security. Therefore, we  
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13 envisage these photoconductors to be used for X-ray imaging in security applications  
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17 where the feature sizes of the objects observed are larger than several millimeters.  
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44 **Figure 4. X-ray imager characteristics. a) photograph of the 1<sup>st</sup> generation imager**  
45 **prepared using a ratio of 1:1:1 P3HT:PCBM:Bi<sub>2</sub>O<sub>3</sub>, and detector thickness of 250  $\mu$ m. b)**  
46 **photograph of pixelated array where each pixel is addressed by a transistor (scale bar =**  
47 **100  $\mu$ m). c) schematic of the imager architecture where the individual pixels are**  
48 **100  $\mu$ m). c) schematic of the imager architecture where the individual pixels are**  
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3 addressed using a matrix of transistors as shown in b). d) X-ray image of a screw obtained  
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7 using the imager and e) the MTF of the imager as obtained based on the slanted edge  
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10 method.

### 11 12 13 14 15 **Avenues for future developments**

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19 While the detector architecture developed in this work shows promise for dosimetry and  
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22 imaging applications, further developments of several key parameters are required in  
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26 order for this architecture to be truly competitive with existing commercial technologies.

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29 The rise and decay times of the devices presented here (as evident in the transient X-ray  
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32 photocurrent responses given in Figures 1d,f) proceeds over several seconds. This is in  
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36 contrast to commercial detector materials such as those based on the combination of  
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39 cesium iodide scintillators and amorphous silicon photodiodes which have been optimized  
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42 to obtain > 10 frames per second,<sup>27</sup> diamond single crystals<sup>28</sup> (rise and fall times of ~1.1  
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45 s and ~0.4 s, the latter limited by measurement apparatus used) as well as cadmium zinc  
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48 telluride single crystals (rise and fall times < 100 ns).<sup>29</sup> As the rise and decay times are  
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54 often a reflection of the charge trapping and de-trapping processes taking place within  
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3 the relatively disordered organic semiconductor matrix (in comparison to its inorganic  
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7 counterparts), we speculate that the replacement of the current organic semiconductors  
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10 or inclusion of a inorganic material possessing higher carrier mobilities are likely to lead  
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13 to significant improvement in the response times. Potential solution processible high  
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16 mobility semiconductors includes organic semiconductors developed for organic thin film  
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19 transistor applications such as 6,13-bis(triisopropylsilylethynyl)<sup>30</sup> or poly[4-(4,4-  
20  
21 dihexadecyl-4H-cyclopenta[1,2-b:5,4-b']dithiophen-2-yl)-alt-[1,2,5]-thiadiazolo[3,4-  
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23  
24 c]pyridine].<sup>31</sup>  
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31 The second key factor that affects the performance of the detector architecture  
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33 developed for both dosimetry and imaging is the high pixel dark currents observed (Figure  
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35 S4) which leads to a signal to noise ratio < 0.2. This in turn results in images that display  
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38 very low contrast (as visually evident from Figure 4d) as well as limit the dynamic range  
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41 of the detector. Among organic semiconductors used for organic photodiode applications  
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44 (including for indirect radiation detection), P3HT has been observed to result in high dark  
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46  
47 currents.<sup>6</sup> On the other hand, *p*-type organic semiconductors such as poly[N-9'-  
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49 heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] as well  
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3 as several other non-disclosed polymers have been reported to result in dark currents <  
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7  $1 \text{ nAcm}^{-2}$  <sup>32,33</sup> approaching the performance of amorphous silicon photodiodes.  
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10 Replacement of the current P3HT system with the above  $p$ -type semiconductors is more  
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14 than likely to enable the detector dark current to be reduced to an industry acceptable  
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17 level of  $0.1 \text{ nAcm}^{-2}$ .  
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## 20 21 CONCLUSION

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25 In conclusion, we have demonstrated hole drift lengths in P3HT:PCBM:Bi<sub>2</sub>O<sub>3</sub>  
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28 heterojunction architectures exceeding 100  $\mu\text{m}$ , where the PCBM phase acts as an  
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32 electron trap enabling hole only device behavior. The high hole transport lengths enable  
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35 thick P3HT:PCBM:Bi<sub>2</sub>O<sub>3</sub> device fabrication for high X-ray attenuation resulting in a best  
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38 X-ray sensitivity of  $\sim 160 \mu\text{CmGy}^{-1}\text{cm}^{-3}$ . Based on the above, the possibility of increasing  
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42 the X-ray attenuation through increased nanoparticle loading was investigated. However,  
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45 a noticeable decrease in the X-ray sensitivity was observed. Structural studies carried out  
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49 based on varying nanoparticle loading suggests that the increased nanoparticle length  
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53 leads to a loss in P3HT crystallinity which results in the degradation of the X-ray  
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3 photocurrent response, hence indicating the importance of an optimized nanoparticle  
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6 loading for such hybrid “inorganics-in-organics” materials. Based on the above  
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9 observations, a prototype imager was developed combining the P3HT:PCBM:Bi<sub>2</sub>O<sub>3</sub> X-ray  
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12 photoconductor with an a-Si backplane. The resulting imager demonstrates an MTF value  
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15 of ~ 1 lpmm<sup>-1</sup> which indicates the possibility of resolving features in the millimeter length  
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18 scales with potential applications such as in dose mapping for radiotherapy, scanning at  
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21 border control. However, there still exists several key characteristics features such as the  
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24 reduction of dark current, improving rise and decay times that would enable systems to  
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27 be utilized for dynamic X-ray imaging. Such developments are expected through  
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30 developments in organic semiconductors with high mobilities, which in combination with  
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33 the characteristics developed here are expected to enable a broad range of applications.  
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## 50 MATERIALS AND METHODS

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4 **Powder preparation.** Regioregular P3HT (Rieke) and PCBM (Solenne) were added to  
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7 anhydrous chloroform at concentrations of  $80 \text{ mg ml}^{-1}$  each and left to stir overnight.  $\text{Bi}_2\text{O}_3$   
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10 nanopowder with an average particle size of 38 nm was added to form P3HT:PCBM: $\text{Bi}_2\text{O}_3$   
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13 mixtures with weight loadings as described. The mixture was left to stir overnight. Addition  
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16 of the organic semiconductors and the  $\text{Bi}_2\text{O}_3$  nanopowder was carried out in a  $\text{N}_2$  glove  
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19 box (MBraun) with  $\text{O}_2$  and  $\text{H}_2\text{O}$  content of  $< 1 \text{ ppm}$ . For precipitation of the powders, 1 ml  
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22 of ethanol was added to 1 ml of the starting solution and then rotary evaporated. The  
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25 dried powder was then further dried under vacuum overnight to remove any residual  
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28 solvent.  
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35 **Wafer and detector preparation.** A hydraulic press (Perkin Elmer FTIR pellet press) with  
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38 a 15 mm die was used for sintering. A polished stainless-steel cylinder was placed in the  
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41 bore of the cylinder body by an Al foil. 100–1000 mg of the P3HT:PCBM: $\text{Bi}_2\text{O}_3$  powder  
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44 was then loaded into the bore. Next, a second polished cylinder which is covered by an  
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47 Al foil and a plunger were inserted into the cylinder body. A 1000 kg load was applied to  
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50 form the pellet for 15 min with the pellet pressing being carried out at room temperature.  
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4 The use of the Al foils enables a visual identification of the smoothness of the pressed  
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7 pellets. For completion of the photoconductor devices, 100 nm of gold with an overlap  
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10 area of 1 cm<sup>2</sup> was sputtered through a shadow mask.

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14 **X-ray photocurrent response measurement.** The X-ray photo response was obtained  
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17 using a 70 kV X-ray source (Siemens MEGALIX Cat Plus 125/40/90, 124 GW) with a  
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19 tungsten anode. The X-ray spectrum was filtered with a 2.5-mm-thick Al plate. The dose  
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22 rate was varied by changing the X-ray tube current with calibrated with a PTW Diados  
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25 T11003-001896 dosimeter. Electrical readouts were carried out using a Keithley 2400  
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28 source measure unit at 100 ms. Image read-out and processing: A 256 × 256 amorphous  
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31 silicon thin film transistor panel was used for the imager in conjunction with a commercially  
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34 available read-out IC (ROIC) (ISC9717 from Flir). The pixel pitch is 98 μm. The input  
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37 signal was integrated, amplified and subjected to a low pass filter simultaneously and  
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40 converted from analog to digital using a 14-bit AD converter. The integrator feedback  
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43 capacitance used was 2 pF and the integration time was 10 ms. Dark images taken with  
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46 and without the sensor, were used in order to evaluate the noise of the system. Dark  
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4 image and flat field correction was carried out to obtain X-ray recordings. The modulation  
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7 transfer function (MTF) was determined using the slanted-edge method<sup>34</sup> *via* an ImageJ  
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10 plug-in.

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14 **GIWAXS.** GIWAXS measurements were performed using a Xeuss 2.0 (XENOCSS,  
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17 France) system equipped with a MetalJet (Excillum, Sweden) liquid gallium source which  
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20 provides a 9.24 keV X-ray beam. The beam was collimated to a spot of with a lateral  
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23 dimension of 400  $\mu\text{m}$  on the sample. Pilatus3R 1M 2D detector (Dectris, Switzerland)  
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26 placed at  $\sim 311$  mm from the sample was used to obtain the diffraction images. Calibration  
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29 of the sample=detector distance was carried out using a silver behenate calibrant in  
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32 transmission geometry while the GIWAXS measurements were carried out at an incident  
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35 angle of  $0.3^\circ$ . The diffraction images were then remapped from pixel to scattering vector  
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38 using the software Foxtrot (Soleil France).  
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## 46 47 **ASSOCIATED CONTENT**

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3 K.D.G.I.J., H.M.T., C.A.M. & S.R.P.S. have a filed patent (Direct Conversion Radiation  
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7 Detector, International Publication Number: WO 2018/078372 A1) which is assigned to a  
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10 startup company (SilverRay Ltd.).  
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### 18 **Supporting Information.**

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21 The Supporting Information is available free of charge on the ACS Publications website  
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23  
24 at [XXX](#)  
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29 The Supporting Information provided consists of additional details regarding the simulated  
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32 X-ray photon density spectrum, X-ray sensitivity comparison chart, DSC analysis and  
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36 dark current characteristics.  
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### 43 **AUTHOR INFORMATION**

#### 44 **Author Contributions**

45  
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50  
51 K.D.G.I.J. and H.M.T. conceived the idea and planned the project with additional input  
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53  
54 from S.F.T and C.A.M; prepared the powder for the fabrication of pellets. J.E.H. fabricated  
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3 the pellets and the imager while H.M.T. and S.F.T. carried out the X-ray detector and  
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5  
6 imager characterization. K.D.G.I.J. analyzed the X-ray photoconductor data while S.F.T.  
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9  
10 analyzed the measurements from the X-ray imager. A.J.P. carried out the GIWAXS  
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12  
13 measurements and analyzed the data with contribution from K.D.G.I.J. R.M.I.B. prepared  
14  
15  
16 samples for SEM measurements, and for DSC characterization and analyzed the results  
17  
18  
19 obtained. C.A.M and S.R.P.S. proposed the project and oversaw the delivery of the  
20  
21  
22 project objectives. K.D.G.I.J. drafted the manuscript and compiled the figures. All authors  
23  
24  
25  
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27 discussed the results and provided feedback on the manuscript.  
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47  
48  
49  
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51  
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54 Scholarship/University Research Scholarship. The GIWAXS measurements were  
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4  
5  
6  
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8  
9  
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14 results.  
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