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Heavy-Metal-Free Flexible Hybrid Polymer-Nanocrystal Photodetectors Sensitive to 1.5- μ m-wavelength

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ABSTRACT. Photodetection in the short-wave infrared (SWIR) wavelength window represents one of the core technologies allowing for many applications. Most current photodetectors suffer from high cost due to the epitaxial growth requirements and the ecological issue due to the use of highly toxic heavy-metal elements. Toward an alternative SWIR photodetection strategies, in this work, high-performance heavy-metal-free flexible photodetectors sensitive to $\lambda = 1.5 \mu\text{m}$ photons are presented based on the formation of a solution-processed hybrid composing of a conjugated diketopyrrolopyrrole-base polymer/PC₇₀BM bulk heterojunction organic host together with inorganic guest NaYF₄:15%Er³⁺ upconversion nanoparticles (UCNPs). Under the illumination of $\lambda = 1.5 \mu\text{m}$ SWIR photons, optimized hybrid BHJ/UCNP photodetectors exhibit a photoresponsivity of 0.73 mA/W and 0.44 mA/W respectively for devices built on rigid ITO/glass and flexible ITO/polyethylene terephthalate (PET) substrates. These hybrid photodetectors are capable of performing SWIR photodetection with a fast operation speed, characterized by a short photocurrent rise time down to 80 μs , together with an excellent mechanical robustness for flexible applications. Exhibiting simultaneously multiple advantages including solution-processability, flexibility, and the absence of toxic heavy metal elements together with a fast operation speed and good photoresponsivity, these hybrid BHJ(DPPTT-T/PC₇₀BM)/UCNP photodetectors are promising candidates for next-generation low-cost and high-performance SWIR photodetectors.

1. Introduction

In recent years, there has been an increasing demand for photodetection in the short-wave infrared (SWIR) spectrum for applications such as optical communication, environmental gas sensing, medical diagnostics, night vision, and light detection and ranging (LIDAR).^{1,2} In particular, at the wavelength of 1.5 μm , two advantages are offered: the optical loss of a typical silica fiber at this wavelength reaches its minimal value³ and lasers ($< 1 \text{ J/cm}^2$) operating at this wavelength are eye-safe.⁴ 1.5 μm is therefore considered as the “magic” wavelength widely applied in optical communications. Current photodetector technologies capable to detect 1.5 μm photons are mainly based on low-bandgap semiconductors such as InGaAs, InSb, PbS, Ge, and HgCdTe. While providing excellent performance, most of these current photodetectors suffer from the cost issue due to the epitaxial growth requirements and the ecological issue due to the use of highly toxic heavy-metal elements. Alternative photodetection strategies sensitive to 1.5 μm are therefore an important current topic of research.

For example, two-dimensional (2D) materials, such as graphene,^{5–8} MoS₂,⁹ and black phosphorus,^{10–12} as well as plasmonic hot carrier devices¹³ are rising stars demonstrating high promise in SWIR photodetection in terms of responsivity and operation at high modulation frequency. However, rigorous and non-solution-processed fabrication is required for these devices. By comparison, solution-processed colloidal nanocrystals^{14–16} are also excellent material candidates. They show advantages in terms of tunable absorption (from synthesis), high flexibility, and adaptability in low-cost and large-scale fabrication.^{17–19} In particular, photodiodes, photoconductors and phototransistors based on colloidal PbS quantum dots have been fabricated in different studies showing excellent responsivity in the SWIR spectral region.¹⁸ Nevertheless, the use of lead, a heavy metal element of high toxicity, is not desirable for low-

cost and large-scale fabrication due to environmental concerns.²⁰ Recently, the synthesis of lead-free perovskite nanocrystals and their application in photodetection have attracted much attention.^{21,22} Yet, these perovskite nanocrystals are only sensitive to the visible and the near-IR photons. Having similar advantages as colloidal materials, conjugated semiconducting polymers are heavy-metal-free and have aroused much interest for their application in low-cost photodetection.¹⁷ While there is continuous progress towards the synthesis of low-bandgap polymers, it is still difficult to have SWIR photodetectors entirely based on semiconducting polymers exhibiting responsivity beyond $\lambda = 1.2 \mu\text{m}$.^{23–27}

One possible strategy to get around these issues is to apply photon upconversion, a phenomenon to convert low energy photons into high energy ones. Various upconversion systems in the form of solution-processed nanoparticles (NPs) have been synthesized,^{28–31} mostly based on the doping of trivalent lanthanide cations in a low phonon energy hosts and performing upconversion through a two- or multi-photon mechanism.³² Since then, they have been applied into many applications including biomedical engineering,^{33–35} thermal sensing,^{36,37} solar energy harvesting,^{38–40} and photodetection.^{41–45} Indeed, most of these photon upconversion applications are based on Yb^{3+} and Er^{3+} co-doped systems capable to upconvert near-infrared light with a wavelength maximum no larger than $1.0 \mu\text{m}$ (e.g. upconversion from 808 nm or 975 nm to visible photons). Material systems able to upconvert SWIR photons remain rare. Recently, Zhang et al. fabricated novel erbium silicate nanosheets to upconvert $\lambda = 1.5 \mu\text{m}$ photons to visible ones.⁴⁶ By combining these nanosheets with organo-lead halide perovskites, they achieved photoconductors sensitive to $\lambda = 1.5 \mu\text{m}$ with a modest photoresponsivity of 0.1 mA/W (at 1 V driving voltage) and a promising response speed (rise time $\approx 900 \mu\text{s}$). While these perovskite-erbium silicate photodetectors are important demonstrations, they can be assembled

only on rigid substrates (not suitable for flexible applications) and they involve the use of lead. In addition, the photodetector response speed is still to be improved as it is a major figure-of-merit directly determining the application range of the devices. Equally by a photoconductor device structure, Zhao *et al.* demonstrated flexible photodetectors based on a conjugated polymer/ Er^{3+} -doped nanoparticle hybrid sensitive to the wavelength of $1.5\ \mu\text{m}$.⁴³ While these polymer/ Er^{3+} -doped nanoparticle hybrid photoconductors are highly interesting, their response speed was not characterized and they suffered from high dark currents ($> \text{mA}/\text{cm}^2$ level) likely related to the photoconductor device architecture applied. There is therefore still room to improve towards high-performance flexible photodetectors sensitive to SWIR photons without the use of highly toxic heavy metal elements.

In this work, by a photodiode device architecture, we demonstrate high-performance heavy-metal-free flexible photodetectors sensitive to $\lambda = 1.5\ \mu\text{m}$ photons based on the formation of a solution-processed organic/inorganic hybrid composing of conjugated polymer/small molecule bulk-heterojunctions (BHJs, host) together with Er^{3+} -doped upconversion nanoparticles (UCNPs, guest). A series of monodisperse colloidal inorganic $\text{NaYF}_4:\text{Er}^{3+}$ UCNPs of various dimensions were synthesized by hydrothermal routes, providing effective upconversion of $\lambda = 1.5\ \mu\text{m}$ photons to visible photons. An organic host was applied containing a donor-accepter BHJ blend of diketopyrrolopyrrole (DPP)-based copolymer and [6,6]-phenyl- C_{71} -butyric acid methyl ester (PC_{70}BM). This organic host polymer/small molecule blend exhibits strong optical absorption covering the visible and near-infrared spectrum up to $\lambda \approx 1\ \mu\text{m}$ and thus capable to efficiently harvest most visible photons upconverted by the guest nanoparticles. Under the illumination of $\lambda = 1.5\ \mu\text{m}$ SWIR photons, optimized hybrid BHJ/UCNP photodetectors exhibit a clear photoresponsivity of $0.73\ \text{mA}/\text{W}$ and $0.44\ \text{mA}/\text{W}$ for devices built on rigid glass substrates and

flexible polyethylene terephthalate (PET) substrates, respectively. Remarkably, a fast operation speed characterized by a short photocurrent rise time down to 80 μ s was observed under the illumination of $\lambda \approx 1.5$ μ m photons, which is faster by more than one order of magnitude than previous photodetector studies applying Er^{3+} -doped upconversion systems,^{43,46} and by two to four orders than most other non-avalanche semiconductor photodetectors at SWIR wavelengths.^{47–51} Exhibiting advantages such as adaptability to flexible substrates, processability in solution, absence of highly toxic heavy-metals, and superior performance, the hybrid organic/inorganic photodetectors developed in this work can be a promising contender for next-generation low-cost and high-performance SWIR photodetectors.

2. Results and Discussion

A series of monodisperse colloidal $\text{NaYF}_4:15\%\text{Er}^{3+}$ UCNPs were first synthesized by an improved hydrothermal route.³⁰ To adjust the size of the upconversion nanoparticles, different molar amounts of sodium citrate tribasic dihydrate were used to react with a fixed amount of Ln^{3+} (containing 85 mol% Y^{3+} and 15 mol% Er^{3+}) and NaF. Detailed preparation process is described in the experimental section. With the rest of the synthetic parameters being identical, the amount of sodium citrate tribasic dehydrate allowed tuning the UCNP particle dimension from 150 nm to 1000 nm. The morphology and dimension of the as-synthesized UCNPs were characterized by scanning electron microscope (SEM, **Figure 1a-d** and Figure S1 of the supporting information). Powder X-ray diffraction (XRD) confirmed that the crystal structure of all batches of UCNPs of different dimensions to be the hexagonal β phase (Figure 1e), which is generally considered as the phase allowing strong fluorescence in contrast to the cubic α phase.⁵² The synthesis parameters and characteristics of the samples are summarized in Table S1.

Different Er^{3+} doping amounts (10 mol%, 15 mol%, and 20 mol%) were experimented in the synthesis of 300-nm diameter UCNPs. Energy Dispersive X-ray (EDX)/SEM elemental mapping analysis were performed on these samples (Figure S2, S3, and S4). The percentages of Er^{3+} measured by EDX were in excellent agreement with the values assumed from the synthesis (with ≤ 0.2 mol% of error).

Figure 1. (a-d) SEM images of $\text{NaYF}_4:15\%\text{Er}^{3+}$ UCNPs of different dimensions and $\text{NaF/citrate/Ln}^{3+}$ molar ratios applied in the synthesis. Scale bar = 1 μm . (a-d) correspond respectively to the sample 1, 3, 4, and 6 listed in the Table S1 of the supporting information. (e) XRD patterns of the UCNPs synthesized with different $\text{NaF/citrate/Ln}^{3+}$ molar ratios plotted together with the reference pattern JCPDS no. 00-016-0334.

The obtained $\text{NaYF}_4:15\%\text{Er}^{3+}$ UCNPs exhibited strong room-temperature fluorescence under the excitation of a $\lambda = 1.5$ μm laser. At this excitation, multiple fluorescence peaks were observed in the fluorescence spectrum, with their maximum intensity falling at the wavelength of 980 nm (infra-red), 810 nm (infra-red), 650 nm (red), 545 nm (green), and 520 nm (green)

(**Figure 2**). Mechanisms have been proposed to explain such photon upconversion properties in similar rare-earth-doped fluoride crystals.^{53,54} For instance, by a simplified picture, the red and the two green emission lines originate from a three-photon upconversion mechanism following by the de-excitations respectively from the $^4F_{9/2}$, $^4S_{3/2}$, and $^2H_{11/2}$ state to the $^4I_{15/2}$ state (Figure 2a). The two infrared emission lines originate from a two-photon upconversion mechanism by the de-excitations respectively from $^4I_{9/2}$ and $^4I_{11/2}$ states. UCNPs of other Er^{3+} doping amounts were also investigated. From single-particle fluorescence experiments, a $NaYF_4:Er^{3+}$ UCNP with 15% Er^{3+} doping appeared to exhibit the strongest upconversion fluorescence compared to a $NaYF_4:Er^{3+}$ UCNP with 10% or 20% of Er^{3+} doping (Figure S5). 15% of Er^{3+} doping was therefore chosen for the photodetector experiments described below. For a typical batch of $NaYF_4:15\%Er^{3+}$ UCNPs with a particle dimension of 300 nm, the upconversion fluorescence quantum yield (under a $\lambda = 1.5 \mu m$ laser excitation at 45 mW) was determined to be about 2% using an integrating sphere by a method established previously⁵⁵ (Table S2). Due to the nonlinear optical processes, lower quantum yield was found previously when very weak laser excitation was used.⁵⁶ The time-resolved upconversion fluorescence decay curves of these $NaYF_4:15\%Er^{3+}$ UCNPs were shown in Figure S6.

Figure 2. (a) Schematic illustrating the energy transitions corresponding to the upconversion fluorescence observed under the excitation of a $\lambda = 1.5 \mu\text{m}$ laser. ETU = energy-transfer upconversion, GSA = ground-state absorption, CR = cross-relaxation, ESA = excited-state absorption. (b) UV-vis absorbance spectra of a BHJ blend of DPPTT-T:PC₇₀BM in solution (grey) and in the form of a thin film (red). The upconversion fluorescence spectrum of the NaYF₄:15%Er³⁺ UCNPs with a dimension of 300 nm is exhibited by the blue curve with open squares (laser excitation $\lambda = 1.5 \mu\text{m}$, power = 25 mW). The molecular structure of DPPTT-T and PC₇₀BM is shown in (c) and (d), respectively.

In order to harvest the multiple upconversion fluorescence peaks from NaYF₄:15%Er³⁺ UCNPs, a BHJ blend of poly-thieno[3,2-b]thiophene-diketopyrrolopyrrole-co-thiophene (DPPTT-T) and PC₇₀BM was employed as the organic host to incorporate the inorganic upconversion guest NPs in solution before the hybrid solution being spin-coated on a substrate for device fabrication. Such diketopyrrolopyrrole (DPP)-based copolymer DPPTT-T has been

shown as a high-mobility polymer leading to high-performance field-effect transistors and photovoltaic devices.^{57,58} As shown in Figure 2b, the BHJ blend of DPPTT-T/PC₇₀BM exhibited a broad optical absorption covering the whole visible and near-infrared spectrum up to the wavelength of about 1 μm . This organic blend should therefore be capable of absorbing the majority the upconversion fluorescence generated by the guest particles.

The schematic describing the hybrid BHJ(DPPTT-T/PC₇₀BM)/UCNP photodetector device architecture and the device operating principle are shown in **Figure 3a** and 3b. In these hybrid photodetectors, the inorganic guest UCNP are sensitive to $\lambda = 1.5 \mu\text{m}$ illumination on which the organic host has limited absorption capability. SWIR photons are upconverted by UCNP to visible ones followed by energy transfer to the organic BHJ host, where electron-hole pairs are generated, separated and transported toward respective electrodes. Due to the insulating nature of these wide band-gap fluoride UCNP,⁵⁹ in this work, the UCNP/organic bilayer device structure was not applied in order not to create charge transport barrier. In addition, inserting these guest UCNP inside the organic BHJ layer has advantage in terms of upconversion fluorescence harvesting by comparison to the bilayer device structure. Here we first optimized the device performance by comparing the incorporation of various batches of guest UCNP of different dimensions. Previous photovoltaic studies showed that the thickness of the active BHJ layer needs to be typically less than 400 nm for efficient charge transport and extraction.^{60–62} Here, the UCNP to be incorporated in the organic layer were thus chosen to have a dimension smaller than 400 nm in order not to drastically increasing the surface roughness of the hybrid layer, despite the observation that the fluorescence quantum efficiency increases along with the UCNP dimension (Table S2). Devices containing five different batches of UCNP of various particle dimensions ranging from 180 nm to 400 nm were compared (Figure S7). Among them, 300-nm

UCNPs enable the largest photocurrent in these hybrid photodetectors and they were then chosen for further studies described below. The observed peak device performance with the use of 300-nm UCNPs can be explained by a compromise between fluorescence quantum yield and the structural perturbation of the nanoparticles in the multi-layer BHJ device. Purely from the fluorescence point of view (Table S2), it is advantageous to apply large-size nanoparticles (e.g. the batch of 400 nm). However, large-size nanoparticles may create strong perturbation on the surface roughness of the hybrid layer. The 300-nm UCNPs thus represent the batch of nanoparticles allowing both optimized fluorescence and acceptable roughness of the hybrid device. Besides the UCNP dimension, the amounts of UCNPs to be incorporated into the hybrid devices are also optimized by changing the UCNP solution concentration during the device fabrication (Figure S8). The SEM characterizations of a hybrid BHJ(DPPTT-T/PC₇₀BM)/UCNP film fabricated by the optimized conditions are shown in Figure 3c, where a uniform dispersion of UCNPs in the organic layer is visible without the formation of either large aggregates or a compact NP layer.

Figure 3. (a) Schematic describing the hybrid BHJ(DPPTT-T/PC₇₀BM)/UCNP photodetector device architecture. (b) Schematic of the operating principle of such hybrid photodetector by upconversion. (c) SEM image of a typical hybrid film containing the DPPTT-T/PC₇₀BM BHJ host with the upconversion guest NPs incorporated inside. Insert shows a zoom-in SEM image of this film. (d) Time-dependent short-circuit current (bias voltage = 0 V) of an optimized BHJ/UCNP photodetector under the illumination of a $\lambda = 1.5 \mu\text{m}$ laser at different laser powers. (e) Photocurrent and photoresponsivity as a function of incident laser power of the hybrid photodetector built on a glass substrate and a flexible PET film presented together with the characteristics obtained from a device without any guest NPs incorporated. (f) Time-dependent photoresponse under the illumination of a $\lambda = 1.5 \mu\text{m}$ laser at 9.6 μW modulated at 7 Hz and 1.177 kHz. (g) Response time study on a single representative light/dark cycle (τ_R = rise time,

and τ_D = decay time). (h) External quantum efficiency (EQE) of the hybrid photodetector built on a glass substrate and a flexible PET film. Inset exhibits the optical image of a flexible hybrid photodetector.

By the above-mentioned optimized conditions, hybrid photodetectors were fabricated both on rigid ITO/glass and flexible ITO/PET substrates. These hybrid photodetectors exhibit a clear rectifying behavior (Figure S9). Despite the wide band-gap and insulating nature of these UCNPs,⁵⁹ with an optimized NP concentration, their existence did not impede significantly the functioning of the BHJ photodiode. Importantly, under the illumination by a $\lambda = 1.5 \mu\text{m}$ laser at different laser powers, these photodetectors offered a fast rise of photocurrent without the need of any driving voltage and a low dark current on the order of 10^{-10} A (Figure 3d). At $\lambda = 1.5 \mu\text{m}$ illumination, the photoresponsivity of these hybrid photodetectors reaches 0.73 mA/W and 0.44 mA/W for rigid devices built on ITO/glass and flexible devices on ITO/PET, respectively (Figure 3e). By comparison to rigid devices, the slight reduction of photoresponsivity in flexible devices may originate from the differences in sheet resistance, surface roughness, optical transmission, and solvent wetting properties. In particular, lower optical transmission was found in the flexible ITO/PET substrate by comparison to the rigid ITO/glass substrate (Figure S10). In the organic BHJ device without any guest UCNPs, there was a weak photoresponse at $\lambda = 1.5 \mu\text{m}$ illumination possibly originates from the near-infrared absorption of the charge-transfer complex generated in the BHJ host (Figure 3e). Nevertheless, the photoresponse from such charge-transfer complex remains small by comparison to the hybrid devices, which exhibit a significantly higher photocurrent by nearly 2 orders of magnitudes. When comparing the light-intensity dependent photocurrent behaviors plotted in a log-log scale, the hybrid device exhibited a smaller slope (0.43) by comparison to that from the device without UCNPs (0.63) (red and

black symbols in Figure 3e). This is related to the above-mentioned upconversion fluorescence mechanisms of UCNPs (Figure 2a) leading to the necessity of two or three photons to generate one exciton in the hybrid device. As indicated in a previous study on similar fluoride upconversion nanoparticles,⁶³ two-photon upconversion emissions will progressively dominate the upconversion emission spectrum as the excitation power decreases. Here, as the illumination power decreases, the two-photon upconversion emissions (*i.e.* at 810 nm and 980 nm) will become more important by comparison to the three-photon upconversion emission (*i.e.* at 520 nm, 545 nm, and 650 nm). As the organic BHJ layer has limited optical absorption at 980 nm (Figure 2b), as the illumination power decreases, one expects that the upconversion fluorescence harvest by the organic BHJ in the present hybrid devices is not as favorable as at higher illumination power. Nevertheless, at low laser power ($< 10^{-4}$ W) illumination, the hybrid devices can still generate clear photocurrent whereas devices without any guest UCNPs are no longer capable to perform photodetection (Figure 3e).

The time-dependent photoresponse of the hybrid device under the illumination of a $\lambda = 1.5 \mu\text{m}$ laser at 9.6 μW modulated at 7 Hz and 1.177 kHz is shown in Figure 3f. The time-dependent photoresponse of the hybrid device under visible illumination is shown in Figure S11. From a single representative light/dark cycle at $\lambda = 1.5 \mu\text{m}$ illumination (Figure 3g), one can analyze the response time of a typical hybrid device. Defined as the time used by the photocurrent to increase from null to 80% of the saturation level or the time used by the photocurrent to decrease from the saturation level to 20% of it, the rise (τ_R) and decay time (τ_D) of the hybrid device were measured as 80 μs and 120 μs , respectively. Being an important figure-of-merit for photodetectors, the response speed of these hybrid devices characterized by a short rise time is faster by more than one order of magnitude than previous photodetector studies applying Er^{3+} -

doped upconversion systems.^{43,46} The external quantum efficiencies (EQEs) of these hybrid photodetectors over the visible-SWIR spectrum are shown in Figure 3h, revealing an EQE up to 10^{-2} % at $\lambda = 1.5 \mu\text{m}$. The photoresponse (A/W) of these hybrid photodetectors over the SWIR spectrum was shown in Figure S12. Similar SWIR photodetector studies capable to detect $\lambda = 1.5 \mu\text{m}$ illumination were summarized in **Table 1** together with the current results. These hybrid BHJ(DPPTT-T/PC₇₀BM)/UCNP photodetectors are one of the rare cases that exhibit simultaneously multiple advantages including solution-processability, flexibility, and the absence of toxic heavy metal elements together with a fast operation speed and competitive photoresponsivity.

Table 1. The performance of photodetectors based on different materials under $\lambda = 1.5 \mu\text{m}$ illumination of 1.5- μm -wavelength.

Materials	Driving voltage ^a (V)	Responsivity	Rise/Decay time	Absence of heavy metal elements	Solution-processed	Flexible	Ref.
Monolayer graphene	0.1	0.2 A/W	~ 50 s	Y	N	N	6
Chip-integrated graphene	0 to 1	0.1 A/W (@1 V) 15 mA/W (@0 V)	100-200 ns ^b	Y	N	N	7
Gold NP array + graphene	10	83 A/W	600 ns	Y	N	N	8
Graphene-PbS	5	5×10^5 A/W	10 ms/ 100 ms to 1 s	N (Pb)	N	N	⁶⁴
Black phosphorus	0.1/11	6 mA/W	0.1 ms/0.3 ms	Y	N	N	12
MoS2	10	~ 33 mA/W	-	Y	N	N	9
Gold grating-based hot carrier device	0 (Self-driven)	0.45 mA/W	-	Y	N	N	13

Cu ₂ SnS ₃ Quantum Dots		0.93 mA/W	4.1 s/3.8 s	Y	Y	N	16
PbS:P3HT:PCBM	-5	0.5 A/W	69 μ s/91 μ s	N (Pb)	Y	N	⁶⁵
PbS	0 to -1	$\sim$ 0.1 A/W	$\sim$ 50 μ s	N (Pb)	Y	N	14
Perovskite-Erbium Silicate	1	0.1 mA/W	0.9 ms	N (Pb)	N	N	⁴⁶
Graphene-Cu ₃ -xP NC film	0 (Self-driven)	19.16 mA/W	0.79 s/0.54 s	Y	N	Y	⁶⁶
DPPTT-T/PC70BM/ NaYF ₄ :Er ³⁺	0 (Self-driven)	0.73 mA/W (glass) 0.44 mA/W (PET)	80 μ s/120 μ s	Y	Y	Y	This work

^a For some studies based on field-effect transistor structures, two applied voltages are indicated: source-drain voltage V_{ds} / gate voltage V_g

^b Estimated from device bandwidth

Mechanical bending tests were carried out on the flexible hybrid BHJ(DPPTT-T/PC70BM)/UCNP devices built on ITO/PET substrates in order to test their robustness. Through an adjustable mechanical set-up^{67,68} (shown in the insert of **Figure 4a**), a more than 120° bending angle was observed on these devices and the photocurrent under $\lambda = 1.5 \mu\text{m}$ illumination was measured after a certain bending times (Figure 4). Minimal photocurrent roll off ($\approx 5\%$) was observable after five hundred bending times. As shown in Figure 4b, after two hundred bending times, the time-dependent photoresponse under $\lambda = 1.5 \mu\text{m}$ illumination of the flexible hybrid device is nearly identical as that before bending, suggesting a highly reproducible photodetector functionality for flexible applications.

Figure 4. Bending test of a flexible hybrid BHJ(DPPTT-T/PC₇₀BM)/UCNP photodetector built on a ITO/PET substrate. (a) Photocurrent of this device measured after a certain bending times under the illumination of a $\lambda = 1.5 \mu\text{m}$ laser at $96 \mu\text{W}$. Inset shows the schematic and the image of a bended BHJ/UCNP photodetector. (b) Time-dependent photoresponse of the same device after 1-time-bending and 200-time-bending.

3. Conclusion

In summary, high-performance heavy-metal-free flexible photodetectors sensitive to $\lambda = 1.5 \mu\text{m}$ photons were fabricated based on the formation of a solution-processed hybrid composing of a conjugated DPP-base polymer/PC₇₀BM BHJ organic host together with inorganic NaYF₄:15%Er³⁺ upconversion guest particles. In these hybrid photodetectors, the inorganic guest UCNPs are sensitive to $\lambda = 1.5 \mu\text{m}$ illumination on which the organic host has limited absorption. SWIR photons are upconverted by UCNPs to visible ones followed by energy transfer to the organic BHJ host, where photocurrents were generated. Under the illumination of $\lambda = 1.5 \mu\text{m}$ SWIR photons, optimized hybrid BHJ/UCNP photodetectors exhibit a photoresponsivity of 0.73 mA/W and 0.44 mA/W respectively for devices built on rigid

ITO/glass substrates and flexible ITO/PET substrates. In these devices, a fast operation speed characterized by a short photocurrent rise time down to 80 μ s was observed. Mechanical bending tests revealed a highly reproducible character in these hybrid photodetectors even after hundreds of bending times for flexible applications. Exhibiting simultaneously multiple advantages including solution-processability, flexibility, and the absence of toxic heavy metal elements together with a fast operation speed and good photoresponsivity, these hybrid BHJ(DPPTT-T/PC₇₀BM)/UCNP photodetectors open bright opportunities for next-generation low-cost and high-performance SWIR photodetectors.

4. Experimental Section

Synthesis of NaYF₄:Er³⁺ UCNPs: UCNPs were synthesized by an improved hydrothermal route.³⁰ To adjust the dimension of UCNPs, different concentrations of sodium citrate tribasic dihydrate (1 to 18 mmol) in 5 mL deionized (DI) water were used to react with 1 mmol of Ln³⁺ (e.g. 85% Y³⁺ and 15% Er³⁺) in 5 mL DI water and 12 mmol of NaF in 5 mL DI water. In a typical synthesis for 300-nm NaYF₄:15%Er³⁺ UCNPs 15 mol % Er³⁺ UCNPs: a 5 mL aqueous solution of Ln(NO₃)₃·6H₂O (0.2 mol/L, Y³⁺: Er³⁺ molar ratio = 85:15) was mixed with a 5 mL aqueous solution of sodium citrate tribasic dihydrate (1.2 mol/L) under vigorous stirring until the formation of a white precipitate of lanthanide citrate. A 5 mL aqueous solution of NaF (2.4 mol/L) was then added slowly into the above mixture. After being stirred for 1 h, the resulting precursor solution was transferred to a 75-mL-volume autoclave. The autoclave was sealed and then placed into an oven heated at 120 °C for 2 hours. After 2 hours, the autoclave was allowed to cool down to room temperature naturally. Subsequently, the NaYF₄:15%Er³⁺ UCNPs in the autoclave were separated from the reaction media by centrifugation (6000 rpm, 30 min) and then washed several times with deionized (DI) water. The obtained UCNPs were then dried in

vacuum at 60 °C for 24 h followed by a 300 °C annealing process for 2 hours. UCNPs of other dimensions or with other Er³⁺ concentrations were prepared by the same procedure.

Synthesis of ZnO nanoparticles: In two separated containers, we dissolved tetramethylammonium hydroxide (TMAH) in 30 mL of ethanol (0.55 M) and zinc acetate dihydrate into 90 mL of dimethyl sulfoxide (DMSO) (0.1 M). The TMAH solution was then added dropwise (about 2 mL/min) into the zinc acetate DMSO solution at room temperature under stirring. This solution was further stirred at room temperature for 1 hour and then storage in a refrigerator (4 °C) until use. At the moment of use, 4 mL of the above-mentioned mixture was taken into a centrifuge tube. Ethyl acetate was added into the centrifuge tube followed by centrifugation at 6000 rpm for 10 min. After centrifugation, the mother liquid was decanted and the precipitate was collected and dispersed into 2.5 mL of ethanol. Such centrifugation process repeated one more time. The ZnO NP solution dispersed in ethanol was then deposited onto the substrate by spin-coating at 2000 rpm for 60 s following by a mild annealing at 80 °C for 15 minutes.

Device preparation and characterization: The synthetic procedure of the polymer DPPTT-T was described in a previous work.⁵⁷ To fabricate the hybrid photodetectors of this study, a layer of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS, Baytron P VP Al4083) was spin-coated onto a cleaned and pre-patterned indium tin oxide (ITO) glass substrates or an ITO-PET flexible substrates. The photoactive layer was deposited by spin coating on top. To formulate the photoactive solution, a certain concentration of UCNPs (2 to 8 mg/mL) were first dispersed in a solution containing a mixture of 80% of chloroform and 20% of 1,2-Dichlorobenzene (DCB). This UCNP solution was then used to dissolve a mixture of DPPTT-T (6 mg/mL) and PC₇₀BM (12 mg/mL). For devices without UCNPs, a solvent mixture

containing 80% of chloroform and 20% of DCB was used. The photoactive solution was then spin-casted at 3000 RPM onto the PEDOT:PSS-coated substrate followed by annealing at 130 °C for 30 minutes. The ZnO NP layer was then deposited by spin-coating the above-described ZnO NP solution dispersed in ethanol (2000 rpm, for 60s). Finally, 100 nm of gold (Au) top electrode was deposited by thermal evaporation with a vacuum level at 10^{-6} mbar. The active area of the cells was 4 mm². Photodiode J - V characteristics were measured inside an Ar-filled glovebox by a computer-controlled Keithley 2612B System SourceMeter® instrument. Devices were then encapsulated by an UV-curing resin and an encapsulation glass before being transferred outside the glovebox for EQE and photoresponse measurements (except for those devices undergoing bending tests). For EQE measurements, monochromatic light was obtained from a 50 W tungsten halogen lamp in combination with a monochromator (Oriel Cornerstone 130) and it was modulated by mechanical chopper. Under each monochromatic wavelength, the device short-circuit current I_{sc} was measured in air by a Stanford Research systems SR570 low-noise current preamplifier and a SR810 DSP lock-in amplifier. A NIST-calibrated Si and Ge cells were used as reference. For visible and SWIR device photoresponse, devices were under the illumination of a modulated laser either with a wavelength of 517 nm or 1.5 μ m. The photo-induced current was measured by a SR570 low-noise current preamplifier together with a digital phosphor oscilloscope (DPO2024B). Bending tests of the flexible devices were carried out by a home-built adjustable mechanical stretcher set-up.

Structural and optical characterizations. SEM characterizations were performed by a FEI Magellan 400 system with a standard field emission gun source equipped with a EDX detector. XRD spectrum were obtained by a PANalytical X'Pert X-ray diffractometer using Cu-K α radiation. UV-Visible absorption spectra were recorded in a transmission mode by an Ocean

Optics HL-2000 fiber-coupled tungsten halogen lamp and an Ocean Optics HR4000 spectrometer (200-1100 nm). Steady-state fluorescence measurements was recorded in a reflection mode by the same Ocean Optics spectrometer with the sample being excited by a $\lambda = 1.5\ \mu\text{m}$ single mode pigtailed laser diode. For fluorescence decay experiemnts, the sample was excited by a tunable Ekspla NT342B OPO laser with 7 ns pulsed duration at $\lambda = 1540\ \text{nm}$. The emission intensity was measured by placing a Jobin-Yvon HR250 monochromator between the sample and the RCA 8850 photomultiplier tube in order to filter out the targeted relaxation. Fluorescence quantum yield (under a $\lambda = 1.5\ \mu\text{m}$ laser excitation) was determined by a method established previously⁵⁵ using an integrating sphere and two Ocean Optics spectrometers (HR4000 and NIR-Quest 256). For single-particle fluorescence measurement, diluted UCNPs were first casted on a microscope glass slide. The microscope glass slide was then placed in an optical microscope with the $\lambda = 1.5\ \mu\text{m}$ laser excitation being focused on a single UCNP in a transmission mode. Single-particle upconversion fluorescence spectra were recorded by a CCD camera coupled with a monochromator (Jobin Yvon).

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge on the ACS Publications website.

Additional results on SEM images of $\text{NaYF}_4\text{:}15\%\text{Er}^{3+}$ UCNPs; Synthesis conditions and characteristics of the samples; EDX elemental analysis; Upconversion fluorescence spectrum obtained on a single $\text{NaYF}_4\text{:Er}^{3+}$ NP; Comparison of the hybrid photodetectors fabricated with UCNPs of different particle dimensions and different concentrations; Current-voltage

characteristic of a typical hybrid BHJ(DPPTT-T/PC₇₀BM)/UCNP photodetector; Optical transmission of ITO/glass and ITO/PET substrates; The photoresponse and response time study of an optimized hybrid device; (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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