Solution-processed efficient organic upconversion device for direct NIR imaging

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Abstract

Infrared upconversion devices (UCDs) enable NIR imaging without array and readout circuits, making them desirable for portable sensor, imaging and monitoring. However, the exorbitant cost and high operating voltages associated with vacuum-deposited materials, which are usually employed in high-performance UCDs, restrict their application in flexible systems. Here, we report a solution-processed upconversion device (s-UCD), which is composed of detector and emitter, with high conversion efficiency (11.9%) and low turn-on voltage (1.2 V) achieved by rigorous device structure design and interlayer engineering. We investigated the role of the electron blocking layer in s-UCDs, and a peak luminance of 5500 cd m\(^{-2}\) and a luminance on-off ratio of 95,000 were achieved. Our s-UCDs exhibit high resolution, microsecond response time and are compatible with flexible substrates. With the high-performance large-area s-UCDs, we further performed direct non-invasive transmission-based bioimaging applications with high quality of bioimaging. Owing to the solution-processed fabrication, it is believed that our s-UCD imaging system offers potential applications for portable low-cost non-invasive tissue analysis, disease diagnosis, and virtual reality.

Introduction

Near-infrared (NIR) imaging is an increasingly important tool in biomedical research, materials science, and environmental monitoring. One popular choice for NIR imaging is direct imaging, which is non-invasive and sample-friendly\(^1\)\(^-\)\(^4\). However, traditional NIR imaging devices that use NIR-sensitive charged-coupled devices (CCDs) or complementary metal-oxide-semiconductor (CMOS) sensors have limitations such as limited spatial resolution, high manufacturing costs, and non-portability\(^5\),\(^6\). Organic upconversion devices (UCDs) are a promising alternative because they are low-cost, flexible, and portable\(^7\)\(^-\)\(^9\). UCDs are typically comprised of an NIR detection unit (IDU) and a visible light emission unit (VEU) in a back-to-back mode. The two units usually share the same carrier transport layer\(^10\),\(^11\). Unlike the traditional up-conversion of two or more low-energy photons into one high-energy photon (anti-Stokes conversion), the working mechanism of UCDs can be simplified as the up-conversion of a low-energy photon into a high-energy photon through electrical assistance\(^9\),\(^12\). In this method, a theoretically high photon-photon conversion efficiency can be achieved due to external circuit gain, which enables UCDs strong candidates for efficient NIR imaging devices.

Organic semiconductors are widely used in the fabrication of large-area devices due to their readily structural design, adjustable energy bands, and excellent solubility\(^13\)\(^-\)\(^15\). In addition, device properties, including absorption spectrum, extinction coefficient, and electrical conductivity of organic semiconductors can be easily adjusted by simple physical mixing, changing solvents, and annealing\(^16\),\(^17\). Moreover, the short carrier moving distance in organic semiconductors limits the lateral current of the device, enabling theoretical ultra-high spatial resolution for UCDs. Solution processing plays a role in semiconductor device processing, offering low cost, easy scalability, compatibility with flexible
substrates, and versatility\textsuperscript{13–15}. Therefore, organic UCDs prepared by solution processing are considered as one of the most promising ways for low-cost and easy-to-fabricate NIR imaging.

However, solution processing is currently limited to the preparation of IDUs of UCDs\textsuperscript{18}. Meanwhile, VEUs are usually fabricated in vacuum processing, posing a challenge for UCD devices, especially when it comes to large-area fabrication and adapting to flexible substrates\textsuperscript{19,20}. Some researchers have attempted to prepare solution-processed upconversion devices using curated materials, but their low photon-to-photon efficiency and limited brightness restrict their practical application\textsuperscript{8,21,22}. Additionally, the complexity of UCDs’ structure makes solution processing susceptible to problems such as interlayer dissolution and intrusion\textsuperscript{23}. Thus, a versatile preparation strategy for solution-processed UCD fabrication is still challenging, and deserves to be desired and investigated.

In this work, we showcase that a solution-processed quickly responsive UCD (s-UCD) created by ingenious organic structure design and device interface engineering, and it exhibited a high p-p efficiency of 11.9\%, a low turn-on voltage of 1.2 V@ 1 cd m\textsuperscript{−2}, and a high brightness of 5500 cd m\textsuperscript{−2}. Our s-UCD’s efficiency is comparable to the devices by vacuum processing and shows a two-fold increase relative to that of the highest solution-processed upconverter reported to date. The s-UCD has a lower turn-on voltage compared to previous UCDs, representing a 25\% reduction. The highest specific responsivity, detectivity, and linear dynamic range (LDR) of IDU under bias are 0.53 A W\textsuperscript{−1}@ 900 nm, 1.2 \times 10^{12} Jones@ 925 nm, and 110 dB@ 808 nm, respectively, ensuring the high sensitivity of our s-UCD. To realize compatibility with flexible substrates, polymers were mainly used in functional layers. Additionally, we have investigated the potential application of our s-UCD in direct non-invasive transmission-based NIR imaging. This technology allows for high-resolution non-destructive observation of biological internal tissue structures through using our s-UCD with a luminance linear dynamic range (L-LDR) of 53 dB.

**Results and discussion**

**Device design and material selection of s-UCD**

The s-UCD in this work is composed of a NIR active layer and a visible light emission layer in a back-to-back mode, and the two units share the same hole transport layer (PEDOT: PSS). Notably, the whole fabrication of s-UCDs’ functional layers was performed by solution spin coating (Fig. 1a). The utilization of specific polymers in the main functional layers ensured excellent bendability, and flexible s-UCDs were readily fabricated in Fig. 1b. For high exciton separation efficiency, the NIR active layer employing a narrowband donor polymer 66-PTB and a matched acceptor IEICO-4F, was fabricated in BHJ method\textsuperscript{24}. For highly efficient yellow-green light emission, the F8BT polymer with a peak emission spectrum at approximately 535 nm was chosen as the emission layer\textsuperscript{25,26}. Additional buffer layers were introduced to balance carrier injection and transportation, aiming to improve upconversion luminance and photon-photon conversion efficiency. Carrier-blocking layers of ZnO and TFB, with a low HOMO and a high LUMO energy level, respectively, were employed to seek low dark current and high sensitivity of s-UCDs.
Chemical structure and energy levels of the functional materials are shown in Fig. 1c - 1d. It is essential that no significant erosion occurs between functional layers to ensure their integrity in solution-processed multilayer devices. Typically, the use of orthogonal solvent is considered as an important means of resisting solution erosion. The supplementary information provides a detailed description of our solution processing and solvent system schemes. Furthermore, the high-resolution cross-sectional TEM and EDS mapping images in Fig. 1e clearly distinguish all functional layers, indicating that there was no significant erosion of the functional layers in the solution-processed devices. Furthermore, absorption spectrum of IDU and EL spectrum of VEU (Fig. 1f) show that the absorption of 66-PTB: IEICO-4F is mainly located in the near-infrared region, from 700 nm to 1000 nm. Moreover, there is almost no absorption in the green light (520–550 nm) region, which ensures that the emitting light of the s-UCD can overflow the device as much as possible, offering higher luminous efficiency and potential semi-transparent s-UCD fabrication. Based on our delicate structure design, flexible s-UCDs were fabricated and emitted green light with a spectral peak of 535 nm when illuminating it under 808 nm laser excitation. Figure 1g illustrates a photograph of the bent flexible device illuminated under an 808 nm laser through a grid mask to display a light-emitting pattern, which verified the adaptability of our solution processing for flexible UCDs.

**Interface engineering for structural optimization of NIR detection unit**

The NIR detection unit (IDU) plays a crucial role in UCDs, as it determines the device's sensitivity, responsiveness, quantum efficiency, and spectral response range. The phase-separated structure of the organic active layer and the interfacial layer of the device largely affect exciton dissociation and transportation of UCDs, in addition to the spectral response range determined by the donor and acceptor. In this work, we synthesized a narrowband donor polymer 66-PTB and a matching acceptor IEICO-4F, with peaks absorption spectrum of 784 nm and 880 nm (Fig. 2b), as the active layer. This photosensitive system has an absorption range that extends beyond 1000 nm, which makes it perfect for NIR response. Inverted device structure, ITO/ZnO/66-PTB: IEICO-4F/PEDOT: PSS/Ag, was employed as an optimization model (Fig. 2a). In order to regulate the phase separation and crystallization of the active layer, 1% v/v of 1-chloronaphthalene was added as an additive to the blend solution prior to spin-coating. The uneven distribution of the components in blend film indicates the presence of phase separations in the system (Fig. 2c). In addition, 66-PTB exhibits a distinct nanofiber phase distribution, demonstrating that the polymer can self-assemble into a fibrous intermolecular packing due to its planar skeleton and could facilitate carrier transport.

Interfacial layer strongly influences carrier transport, and further determine sensitivity and responsiveness of UCDs. PEDOT: PSS, due to the advantages of outstanding hole transport properties, high conductivity, excellent solution processability, and ductility, is widely used in organic optoelectronic devices. However, the typical commercial grade PEDOT: PSS Al 4083 is an aqueous solution, which is difficult to spread out over organic layers. Thus, PEDOT: PSS was rarely used in inverted devices. To address this
issue, a fluorinated nonionic surfactants FS-31 (Fig. 2d) were utilized to reduce its surface energy, meanwhile, isopropanol (IPA) was used to further enhance its wettability. Compared with pristine PEDOT: PSS, contact angle of modified PEDOT: PSS with 0.3 wt% FS-31 was reduced from 96.7° to 45.7° on 66-PTB: IEICO-4F blend film, indicating a significant improvement in wettability (Fig. 2e and Supplementary Fig. S1a). With the addition of an equal mass of IPA, the contact angle was further reduced to 40.6° (Fig. 2f), which was sufficient for spreading out during spin coating. The morphology and phase diagram changes of different modified PEDOT: PSS subsequently spread on 66-PTB: IEICO-4F blend layer, were characterized by AFM (Fig. 2g-2j and Supplementary Fig. S2-S3). Although the contact angle was significantly reduced by introducing a small amount of wetting agent, the quality of the film obtained by spin-coating is still very poor, and obvious holes can be observed (Fig. 2g and 2i). This problem can be alleviated by further addition of more wetting agent, but the roughness of the resultant film significantly increased from 1.48 nm for 0.3 wt% FS-31 to 1.61 nm for 1 wt% FS-31. More defects may be produced in devices and result in low conversion efficiency. In the control group where IPA was added, a similar phenomenon was observed (Supplementary Fig. S2-S3), where roughness increased (from 1.41 nm for 0.3 wt% to 2.19 nm for 1 wt%) with the higher addition of FS-31. Conversely, with the assistance of IPA, a minimal addition of FS-31 was enough for PEDOT: PSS to form a smooth film with a minimal roughness of 1.41 nm (Fig. 2h and 2j) on the active layer, with no significant defects were observed. Consequently, we chose this optimized formulation (PEDOT: PSS/IPA/0.3 wt% FS-31) for device fabrication and further verified the performance of the optimized interface by conducting a photovoltaic conversion efficiency test (Supplementary Table S2).

Moreover, we investigated the detection performance of IDU using an optimized interface. For the detection of weak light signals, small reverse biases under short-circuit conditions (e.g., -0.1 V) or photovoltaic mode (0 V) are also employed, and a low dark current ($J_{\text{dark}}$) is required to achieve potentially low noise levels and high sensitivity to weak light signals. Our detector exhibits an asymmetric current–voltage ($J$–$V$) character (Supplementary Fig. S4c) in the dark, and $J_{\text{dark}}$ can reach as low as $1.96 \times 10^{-9}$ A cm$^{-2}$@ 0V and $4.4 \times 10^{-7}$ A cm$^{-2}$@ -0.1V, respectively, suggesting the low noise level. With the rising input light power density, the increase of open-circuit voltage ($V_{\text{oc}}$) suggests strong photovoltaic photocurrents and reveal that the detector operates in photovoltaic mode. Moreover, photocurrents increase linearly at the rising light power density with a calculated linear dynamic range ($LDR$) of 110 dB (Fig. 2k and Supplementary Fig. S4d).

To further quantify their spectral response, the external quantum efficiency ($\text{EQE}$) under different reverse bias was measured as a function of incident light wavelength. As shown in Supplementary Fig. S4a, the detector exhibited a strong response in NIR region, with an external quantum efficiency of 61% @ 820 nm at 0 V, indicating that the active layer has excellent photon-electron conversion in the NIR region. As the reverse bias increases, the external quantum efficiency improves slightly due to the photogenerated carriers are more easily separated and collected by the electrodes in the presence of an electric field. The responsivity ($R$) of a photodetector is an important figure-of-merit that characterizes the ratio of electrical output to optical input$^{33}$. The spectral profile of responsivity peak around 900 nm, reaches 0.44 A W$^{-1}$
As reverse bias increased, the responsivity of the IDU enhanced slightly, and the highest responsivity can reach to 0.53 A W$^{-1}$ at 900 nm under −1 V.

Furthermore, as shown in Fig. 2l, over a wide range of 770 nm-930 nm, detectors show a large $D^{*}_{sh} \approx 10^{12}$ Jones under −0.1 V bias, indicating the high sensitivity of detector to weak NIR. Moreover, $D^{*}_{sh}$ decreased with higher reverse bias due to the rising dark current. For the response time of IDU, transient photocurrent was measured to obtain the rise and fall time, as shown in Fig. 2m. IDUs were tested for several cycles under 808 nm LED irradiation, and a rise and fall time of 1.76 µs and 1.69 µs were obtained, respectively, ensuring high refresh rate NIR imaging.

**Effect of the Electron Blocking Layer on the UCDs**

By stacking visible emission unit (VEU) and optimized NIR detection unit (IDU), UCDs with a structure of Anode /Electron Transport Layer (ETL)/ Active layer/HTL (Hole Transport Layer)/ Electron Blocking Layer (EBL)/ Emission Layer (EML)/ Electron Transport Layer (ETL)/ Cathode were fabricated successfully by solution processing. Typically, Electron Blocking Layers (EBLs) are always employed to capture electrons in emission layer and increase electron density, which can enhance luminescence efficiently, due to their high LUMO. Several p-type polymers, such as TFB, PVK, and poly-TPD, have been widely used in LED optimization\[^8,26,34\]. In this work, considering energy level compatibility with the emitting polymer F8BT and the principle of orthogonal solvent, TFB with a high LUMO energy level of -1.9 eV was employed as the EBL. Figure 3a shows the current density–voltage characteristics of the UCDs with and without the EBL. For the UCD incorporating EBL, a low dark current can be observed, which is 1–2 orders of magnitude lower than the one of UCD without EBL. Benefiting from the lower dark current, on-off ratios of UCD differ by up to 2 orders of magnitude with/without EBL assistance (Fig. 3b).

Introducing EBL can improve the optical response of UCDs, specifically enhancing luminance and photon-photon efficiency. Figure 3c presents the luminance changes of UCDs with/without EBL under NIR illumination or in darkness. Obviously, luminance of UCDs after 808 nm illuminance increase four times and reach to about 2800 cd m$^{-2}$@7V with introduction of EBL. In contrast, the luminance decreased remarkably in darkness. Moreover, a reduction from 2.3 V to 1.8 V in turn-on voltage ($V_{on}$) can be observed. For p-p efficiency, the introduction of EBL enables it to improve from 0.6–2.6% at 7 V under a 42 mW cm$^{-2}$ 808 nm laser (Fig. 3d).

Based on these derived data, we propose a possible operation mechanism of our UCDs. In the dark, it is difficult for holes to be injected into the device through anode because of the deep HOMO level (-8.2 eV) of ZnO. However, the cathode's work function does not differ much (0.2 eV) from that of ETL, making electron injection easier. As a result, a high dark current was observed without the EBL due to electron transport from the cathode to the anode (Fig. 3e). Under NIR illuminance, photo-generated excitons dissociate into electrons and holes at the donor-acceptor interface. The electrons are collected by the anode through the ETL, and the holes pass through the HTL to recombine with electrons in the EML,
radiating visible light. This process results in realizing the NIR-visible upconversion (Fig. 3f). However, without the EBL, the injected electrons would transport to the active layer and recombine with photo-generated holes, resulting in a weak upconversion luminance of UCD since non-radiative recombination. Furthermore, electrons injected from the external circuit can directly transport into the active layer, which may be detrimental to the exciton separation in the active layer, affecting the performance of the UCD. Due to the high LUMO level, EBL can effectively block electrons from passing through the whole device and forming a leakage current (Fig. 3a) or a dark luminescence (Fig. 3c), which could significantly lower conversion efficiency and sensitivity. Under the combined contribution of high-LUMO energy level for EBL (-1.8 eV) and deep-HOMO energy level for ETL (-8.2 eV), fewer carriers can pass through the device (Fig. 3g), a very low dark current generated and resulting in dark luminance of UCD with EBL. As for the case of NIR irradiation, the operating mechanism of UCD with EBL is similar to that without EBL. The difference is that the electron blocking properties of EBL play a key role in reducing non-radiative recombination, and meanwhile, the injected electrons are confined to the emission layer when EBL is involved. Moreover, when a larger external voltage was applied, the electrons injected from the external circuit will form a pileup at the EBL/EML interface, leading to energy band bending at the EBL, which lowering the potential barrier for hole injection from the active layer to the EML, and further making photogenerated hole injection easier and faster (Fig. 3h). Ultimately, photogenerated electrons are transported relatively slowly through active layer, resulting in holes at the ETL being more readily injected into the UCD and participating in the radiative recombination in the EML. Based on this device structure, the radiative recombination of photogenerated holes and injected electrons in the emission layer is facilitated, resulting in improved device luminance and upconversion efficiency. Moreover, carriers are collected quickly with the increased electric field, resulting in less time for lateral diffusion, which would improve the spatial resolution.

Performance of solution-processed upconversion devices.

After the structure optimization, solution-processed UCDs, with a structure of ITO/ZnO/66-PTB: IEICO-4F/PEDOT: PSS/TFB/F8BT/PO-T2T/LiF/Al, were fabricated, and emerged outstanding performance. Upconversion luminance is a crucial parameter for UCDs and plays a key role in their imaging application. Even when the s-UCD operated under a bias of 7 V and without any NIR illuminance, no emission can be observed, which can be contributed to the extremely strong blocking ability of ZnO and TFB for holes and electrons, respectively (Fig. 4a). However, the s-UCD emitted green light when it was excited by weak infrared light (0.47 mW cm$^{-2}$). Luminance increases with rising input NIR power density due to more photogenerated excitons, and an operating maximum luminance of 5500 cd m$^{-2}$ @ 7 V under 183 mW cm$^{-2}$ 808 nm illuminance was achieved, six times higher than that of UCDs without EBL (Fig. 4a and Supplementary Fig. S5a). Moreover, a low turn-on voltage ($V_{on}$) of 1.2 V@ 1 cd m$^{-2}$ was achieved while applying higher input NIR power density via interface and processing optimization. Furthermore, for each constant input NIR power, the luminance shows an ultimate equilibrating whilst the bias exceeds the corresponding voltage. For most cases of lower input power, 3 V was selected as the device operating voltage because of the sufficiency for achieving brightness requirements of daily use. Photon-photon
efficiency is another significant parameter of UCDs. The p-p efficiency is mainly determined by photogenerated carriers and their transport, as well as their recombination and gain of external carriers. Thus, another essential factor for efficient UCD is a smooth carrier transfer path, which relies on stepped energy level arrangement (Fig. 1d) and high-quality interlayer interfaces. Based on organic photoelectric materials selection and interface optimization, we can estimate p-p efficiency by the equation S5. Thus, the p-p efficiency of our s-UCDs was varied with the rising bias voltages and different input NIR power (Fig. 4b and Supplementary Fig. S6a). For each constant NIR input power, p-p efficiency clearly increases with rising voltage until it reaches equilibrium; and for different NIR powers, the efficiency first rises and then falls with increasing power. Under the appropriate NIR irradiation with power density of 2.78 mW cm$^{-2}$, the maximum p–p efficiency rises up to 11.9% with 7 V voltage bias and then declines with higher bias voltage since the leakage current from exceeding voltage (above 8 V) will damage device and also reduce operating life of it. However, for higher incident NIR power densities, the p-p efficiency decreases because the photon-electron conversion tends to oversaturate, and the p-p efficiency still can reach close to 1% at high NIR incident power density (183 mW cm$^{-2}$). As for the ones without EBL, p-p efficiency shows obvious reduction compared with s-UCD with EBL (Supplementary Fig. S6a and Fig. S6c) due to the higher leakage current which does not participate in recombination for visible emission. In addition, power-power efficiency of s-UCDs takes the similar trends (Supplementary Fig. S6b and Fig. S6d). Figure 4c shows luminance on-off ratio of s-UCD, which stands for ratio of UCD luminance with or without NIR irradiation. With the assistance of extremely low dark luminance, the luminance on-off ratio can reach a really high level of 95000 @ 5.5 V, and decline tightly with higher bias voltage because of higher leakage current. In addition, current on-off ratio of s-UCDs with and without EBL are shown in Supplementary Fig. S7. The maximum current on-off ratio of s-UCD with EBL can reach to 6700 @ 4 V and is about 9 times higher than that of s-UCD without EBL.

In addition, upconversion luminance increase linearly with the rising NIR power density within a calculated luminance linear dynamic range (L-LDR) of 53 dB (Fig. 4g and Supplementary Fig. S5b and S5d). In order to examine the spectral responsiveness of s-UCD, upconversion luminance under three constant input NIR wavelength of 808 nm, 850 nm and 980 nm (same power density of 42 mW cm$^{-2}$) were investigated (Fig. 4e). Upconversion luminance under 850 nm show the similar tendency and is slightly higher than that of 808 nm, which is consistent with the higher responsiveness of the IDU at 850 nm. Because of the low responsiveness of IDU at 980 nm, however, s-UCD emerges a low luminance of about 150 cd m$^{-2}$ @ 7 V. Therefore, our s-UCDs are more suitable to operate in the near-infrared band of 800–850 nm. This is due to the main absorption peak of the active layer, which is located in this wavelength range. The emission response time of s-UCD reaches 2.25 µs and 77.25 µs for rise and fall time, respectively (Fig. 4f). Notably, fall time is much longer than rise time, which is mainly attributed to the longer exciton lifetime of the luminescent material F8BT$^{26}$. Furthermore, after applying NIR illuminance, an upward abrupt change can be observed in emission intensity-time curves, and then signal drops and remains steady state caused by the existence of defects in the device. Extremely short response time of 80 µs, whose equivalent refresh rate can reach to 12500 Hz, is precondition for our s-UCDs to realize high-speed NIR upconversion imaging. Moreover, our s-UCDs demonstrated the highest
maximum brightness and p-p conversion efficiency compared to all previously reported solution-processed UCDs (Fig. 4g purple region and Supplementary Table S3). In addition, a highest luminance on-off ration of 95000 is also validated on our s-UCDs. More comparable details are shown in Supplementary Table S3. Under the same operating conditions (diode-based operation), the peak brightness of our s-UCD can be close to the highest value previously reported (Fig. 4g gray region). Meanwhile, the solution-processed optimization method we derived is also applicable to more upconversion devices based on other operating methods (organic photomultiplier or organic field effect transistor).

Moreover, the s-UCD structure can be extended to fabricate large-area and flexible devices through solution processing (Fig. 1c). Based on the large-area s-UCDs, we verified their imaging ability under NIR irradiation through a schematic verification approach (Fig. 4h). When NIR laser beam pattern produced onto s-UCDs through photomasks, the corresponding dazzling visible green pattern can be observed. Figure 4i shows the operating (3 V bias) large-area s-UCD under an 850 nm NIR (42 mW cm\(^{-2}\)) laser irradiation through a hollowed-out butterfly-shaped metal mask, and the green pattern on the s-UCD moves rapidly as the mask moves, (Supplementary Video S1), indicating the high-speed response of our s-UCDs. In addition, flexible s-UCDs were also fabricated and their imaging presentation are shown in Fig. 1g and Supplementary Video S2. Under an 850 nm NIR (42 mW cm\(^{-2}\)) laser irradiation through a grid mask, the imaging quality did not change significantly as the flexible device was bent back and forth several times. In addition to fast responsiveness, high resolution also determines the upconversion imaging quality of the UCDs. The NIR signal propagating through the 50 µm wide mask is precisely upconverted by our s-UCD (Fig. 4j), as evidenced by the 10 clear line pairs. Because of the preparation process limitation of the photomask, we only detected that s-UCD is capable of high-resolution imaging at 50 um width, and have successfully achieved a minimum equivalent pixel density of 508 dpi. Based on the homemade measurement platforms (Fig. 4h), high-resolution NIR upconversion imaging quality has been precisely realized, validating the superiority of all organics-based upconversion devices, because organic-based VEUs are intentionally driven under electron-rich conditions in the UCDs as well as short carrier transverse migration distances in organic materials\(^{35-37}\). Furthermore, we demonstrated multiple NIR-Visible pattern displaying on our large-area UCDs using different masks (Fig. 4k). Different patterns with clear and glaring geometrical morphology appeared on our s-UCD, illustrating the outstanding upconversion performance of our s-UCDs.

**Direct transmission-based bioimaging application of s-UCDs**

With the outstanding performance s-UCDs, we pursued more application of s-UCD which directly converts NIR to visible light with high resolution and rapid response. Transmission-based bioimaging using NIR imaging devices offers unique advantages, including non-invasiveness and minimal damage to tissues. Moreover, the imagers can show penetration into the tissue demonstrating novel and remarkable information, apart from shapes and edges of biological tissues, which provides tremendous value for
future applications in the diagnosis of human pathology. However, photosensor array and readout circuits are often required in real-world imaging applications with significantly more complexity and difficulty. As for our s-UCDs, array and readout circuits are not required in high-resolution and high-refresh rate biological application due to the direct conversion emission of device composed of IDU and VEU. Moreover, distinction of weak transmitted NIR intensity difference offers high contrast image, making it more suitable for subtle and complex structure of biological tissue. In addition to non-invasive direct imaging of tissue specimens, bioimaging applications can use the approach shown in the schematic (Fig. 5a) to magnify the image of tissue by adjusting the angle of the incident NIR light, thereby observing more subtle features in the tissue. Furthermore, tissue images are performed on the device directly and can be observed by naked eyes. For clear documentation and observation of image details, camera and computer can be employed conveniently. Thus, our s-UCD was employed to carry out transmission-based bioimaging application by locating biological sample between NIR laser and s-UCD (Fig. 5a).

As a demonstration, several biological sections from commercial sources were observed using our s-UCD without any further treatment. As shown in Fig. 5b, regardless of the specimen, fewer details in biological tissues can be perceived through direct naked-eye observation. When observing biological samples with our s-UCD operating at 3 V, the internal details of them can be clearly observed, such as the internal texture of honeybee foot tissue, due to the stronger penetration of NIR and the high contrast and resolution of our s-UCD. In addition, when longer wavelengths of NIR were using (850 nm and 980 nm), more details can be observed on the imager, while the brightness of the imager appears to decrease significantly (especially 980 nm), because of the lower response of IDU. Apart from directly observation of internal texture of honeybee foot tissue, by taking advantage of the ability to magnify the image by adjusting the incidence angle, we were able to clearly observe the course of the muscle fibers in the thigh of little mouse and the state of the bones and muscle fibers. Moreover, for the fine tissue arrangement in sheep ovary sections which is usually difficult to observe with the naked eyes, the accumulation of which can be readily observed with our s-UCD. Furthermore, low operating voltages (3 V) and low incident optical power requirements guarantee the facile fabrication and portability of small NIR imagers. Thus, the imaging results show that a wide range of biological tissues can be successfully imaged, magnified, observed and differentiated using our device, suggesting that our s-UCD imaging system offers a potential application for portable non-invasive tissue analysis and disease diagnosis.

**Conclusion**

We fabricated flexible solution-processed upconversion devices (s-UCDs) based on organic photosensitive materials with a maximum response wavelength of up to 1100 nm through rigorous device structure design and interlayer engineering. The low turn-on voltage of 1.2 V and the high photon-photon efficiency of 11.9% are attributed to the efficient dissociation and transportation of excitons in the IDU, the introduction of blocking layers, and the compatibility between the multilayers. After systematically exploration of the role of EBL in s-UCDs, the brightness of device can be enhanced to 5500
cd m\(^{-2}\) and a remarkable luminance on-off ratio of 95,000 are achieved, to the best of our knowledge, these among the highest values in previous works. With the high-performance large-area s-UCDs, we pursued direct non-invasive transmission-based bioimaging application of s-UCDs that directly converts NIR to visible light with high resolution (508 dpi) and fast response (equivalent to 12500 Hz). The imaging results demonstrate that our s-UCD can successfully image and differentiate a wide range of biological tissues, suggesting that our s-UCD imaging system offers a potential application for portable non-invasive tissue analysis, disease diagnosis and virtual reality.

**Declarations**

**Conflict of Interest**

The authors declare no conflict of interest.

**Data availability**

Data supporting the findings of this study are available within the paper and its Supplementary Information files. All other relevant data that support the findings of this study are available from the corresponding author upon reasonable request.

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**References**


**Figures**
Figure 1

Device structure and materials of s-UCD (a) Schematic device structure. (b) Photograph of a flexible bent device. (c) Chemical structure and (d) energy levels of optoelectrical materials employed in s-UCD. (e) Cross-sectional high-resolution TEM image and EDS mapping of devices. (f) Absorption spectrum of IDU and EL spectrum of VEU. (g) Photograph of an operating flexible device through illuminating under an 808 nm NIR (42 mW cm$^{-2}$) with a mask.
Figure 2

Structural optimization and performance of NIR detection unit (IDU). (a) Schematic diagram of IDU structure. (b) Absorption spectrum and (c) AFM phase image of 66PTB: IEICO-4F Film. (d) Chemical structure of PEDOT: PSS and wetting agent FS-31. (e) Contact angles of modified PEDOT: PSS without IPA and (f) with IPA on 66-PTB: IEICO-4F film. (g) AFM height images of modified PEDOT: PSS without IPA and (h) with IPA spread out on 66-PTB: IEICO-4F film. (i) AFM phase images of modified PEDOT: PSS without IPA and (j) with IPA spread out on 66-PTB: IEICO-4F film. (k) Linear dynamic range (dashed line represents the linear fitting) of IDU under 808 nm. (l) The detectivity–wavelength relation of the IDU with different biases. (m) Transient rise and fall curves for multiple cycles when applying/removing 808 nm light.
**Figure 3**

**Effect of the electron blocking layer on electronic and optical outputs of UCDs, in the dark and under illumination.** (a) Current densities versus applied bias. (b) On-off ratio versus applied bias. (c) Luminance of UCDs versus applied bias. (d) Photon-photon efficiency of UCDs versus applied bias. The incident light source wavelength was 808 nm at an intensity of 42 mW cm\(^{-2}\). (e-f) Illustrations comparing charge transport and recombination processes for UCDs with and without the electron blocking layer.
Figure 4

**Performance of solution-processed UCDs.** (a) The luminance (b) photon-photon efficiency and (c) luminance on-off ration with the variation of bias and input power density at 808 nm. (d) Luminance liner dynamic range (line represents the linear fitting). (e) Luminance with the variation of bias and input NIR wavelength (power density: 42 mW cm\(^{-2}\)). (f) Luminance transient rise and fall curves when applying/removing 808 nm light (3V bias). (g) Comparison of reported UCDs with our work in regards to luminance and p-p efficiency. (h) Schema of NIR-Vis pattern display. (i) Operating large-area s-UCD under...
an 850 nm NIR (42 mW cm$^{-2}$) through a butterfly-shaped photomask. (j) Photographs of NIR light (850 nm; 42 mW cm$^{-2}$) propagating through a line-shaped photomask and the visible image upconverted by the device bias at 3 V with a deduced resolution of 508 dpi. Scale bar 1 mm. (k) Demonstration of multiple NIR-Visible pattern displays. Scale bar 2.5 mm.
NIR-bioimaging application of s-UCDs. (a) Schematic diagram of NIR imaging of biological sections. (b) The NIR-bioimaging under the illumination of 808, 850 and 980 nm, respectively. Pictures of the intrinsic biological section (including the third-pair feet of honeybee, thigh of light mouse, ovary of sheep) are shown on the left. Scale bar 2.5 mm. All the imaging application under 3 V bias. All the biological sections were purchased from commercial source and used without any further treatment.

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