Supplementary Materials for

Efficient solid-state infrared-to-visible photon upconversion on atomically thin monolayer semiconductors

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S1. Sample preparation

Fused silica substrates were cleaned by sequential sonication in detergent solution, deionized water, acetone, and isopropyl alcohol. Monolayers of MoSe₂ were mechanically exfoliated onto gel films (Gel-Pak) from bulk crystals (HQ graphene) and then transferred on substrates. The chemical vapor deposition-grown MoSe₂ samples (continuous film on sapphire and isolated triangles on sapphire) were purchased from Shanghai OnWay Technology Co., Ltd. Monolayers were identified with an optical microscope and confirmed by their PL spectra.

Rubrene (TCI, 99% GC) and DBP (Sigma-Aldrich, 98% HPLC) were purchased and used without further purification. The following procedure were performed in a nitrogen-filled glovebox to avoid oxygen. First, rubrene was dissolved in anhydrous toluene (Sigma-Aldrich) at 8 mg/mL and then mixed with DBP at a 0.25% molar ratio from a 0.12 mg/mL stock solution. Then the mixed solution was spin coated on MoSe₂ at 6000 rpm for 20 seconds. Afterward, the bilayer device was annealed at 80 °C for 10 minutes.

S2. Optical measurements

Steady-state micro-absorption and PL spectroscopy

In order to avoid the potential effect from oxygen, samples were sealed in a homemade nitrogen cell with thin transparent windows on both sides. Absorption and photoluminescence (PL) measurements were performed on a home-built microscope setup. The absorption spectra were measured using a white light supercontinuum laser (NKT Photonics, SuperK COMPACT) by comparing the transmitted light intensity from the sample on the substrate (I_s) to that from the bare substrate (I_0). The transmitted light was collected and analyzed by a spectrograph (Princeton Instruments, SP2300) coupled with an electron-multiplying charge-coupled device (EMCCD) (Princeton Instruments, ProEM1600). The absorption, in the unit of %, can be calculated by \( \frac{I_0 - I_s}{I_0} \). PL spectra were taken by the same spectrometer under continuous-wave laser excitation. The whole PL detection system was calibrated with both wavelength and intensity calibration (IntelliCal, Princeton Instruments). Specifically, the spectrometer wavelength was calibrated using the atomic emission lines from Hg and Ne/Ar lamps (Princeton Instruments, HGNE 2022) and the relative sensitivity versus wavelength was calibrated by a NIST intensity calibration lamp (Princeton Instruments, LSVN-0358). In such a way, system response is removed and the sample PL profile and intensity is recovered. PL spectra were taken under 772 nm continuous-wave laser excitation (with linewidth ~ 1 nm). The laser beam was focused on sample through a 50× objective with NA of 0.65. To take the full PL spectrum as shown in Fig. 2a main text, the linear excitation light was filtered by linear polarizer with high extinction ratio (~ 100000:1). To calculate incident power density, the photos of excitation laser beam on samples were taken with a camera and the beam size is determined by 1/e² definition (width between the two points where the intensity is 1/e² of the peak value), from which we can calculate power density. The power density for steady state PL measurement were controlled between 50 ~ 500 mW cm⁻².

Time-resolved PL

The TRPL of samples were recorded by time-correlated single-photon counting module (SPC-130) and a single-photon avalanche photodiode (SPAD). To measure the TRPL from MoSe₂, samples were excited at λ = 700 nm with a 10 MHz train pulses (YSL,
SC-OEM) and the near-infrared PL (750–850 nm) were collected by SPAD (MPD, PD-050-CTE-FC). The TRPL for UC emission was collected for 550–650 nm at 200 kHz. The excitation power was adjusted to obtain a ≤5% counting rate in each measurement to avoid pile-up artifacts in the detector. The instrument response function (IRF) of the TRPL setup was obtained by directly collecting the decay curve of laser pulse. The full-width-at-half-maximum (FWHM) of IRF is ~100 ps, which implies any process faster than ~20 ps (~IRF/5) can be indistinguishable and show identical curve as IRF. The power density for TCSPC were controlled to be 10 W/cm² for measuring UC PL and ~100 W/cm² for measuring MoSe₂ PL.

**PL imaging**
The photon up-conversion imaging of the sample was performed on a home-built laser-scanning microscope. The samples were placed in an upright microscope frame (Olympus, BX51WI), equipped with a two-dimensional laser scanning galvanometer (Thorlabs, GVS002). The 2-ps, 785-nm laser with repetition rate of 80 MHz (Applied Physics & Electronics, picoEmerald) was used with a power of ~300 µW at the sample. The microscope objective was a high numerical aperture water-immersion lens (Olympus, 60×, NA = 1.2). The forward-going signal photons were collected by a high numerical aperture oil-immersion condenser (Olympus, NA = 1.4). A short-pass dichroic mirror (Thorlabs, DMSP 650) and two optical bandpass filters (Thorlabs, FELH 550, FESH 750) were used to clean up the signal photons, which were then detected by a photomultiplier tube (Hamamatsu, H7422-40). The extracted signal was then sent to a data acquisition unit. The final images were assembled in a home-built LabVIEW program during laser scanning. The image pixel dwell time was 10 µs per pixel. The power density for PL imaging were controlled to be ~1000 W/cm².

**S3. Calculation on solar irradiation and excitation density**
The AM1.5 (Global) solar spectra plotted in units of spectral irradiance and spectral photon flux were presented in Fig. S10, from which we integrate over a selected spectral range to obtain available intensity as well as solar photon flux. Integrating 600-800 nm range where MoSe₂ can absorb but rubrene cannot yields an available solar irradiance of 25.2 mW/cm² and a photon flux of 8.8×10¹⁶ photons cm⁻² s⁻¹. As shown in the main text, the UC threshold of rubrene/MoSe₂ is about 260 mW/cm² and corresponding 1×10¹⁸ photons cm⁻² s⁻¹ in units of flux (λₑₓ = 772 nm), which equals to ~10 suns. Considering about 4% absorptance at excitation wavelength, we could calculate the excitation density (excitation density = photon flux × absorptance at λₑₓ) to be 4×10¹⁶ ex cm⁻² s⁻¹.

**S4. Determining upconversion efficiency**
For such small bilayer heterojunction samples, the standard PL quantum yield setup using integrating sphere cannot be applied. Instead, we measured the UC emission efficiency from Rub/MoSe₂ sample following previous method of determining the PL quantum yield of exfoliated MoS₂ monolayer by micro-PL measurement, which has been feasible and accuracy enough. The measurement setup was same as described in Steady-state Micro-PL spectroscopy section. The system was both wavelength- and intensity-calibrated prior to measurements. The laser power was adjusted using various neutral density filters, and measured with a calibrated power meter (OPHIR, PD300 and 3A-FS).
As shown in Fig. S11, we used a 772 nm CW laser as excitation light and first collected the PL spectrum (with integrated counts of $N_{\text{sample}}$) from Rub/MoSe$_2$ sample. Then we replaced the sample by a calibrated diffuse reflector (Spectralon with > 99% Lambertian reflectance) and measured the spectrum (with integrated counts of $N_{\text{laser}}$) of excitation light from diffuse reflector which can be regarded as reasonable simulation of PL source. Compared to Spectralon diffuse reflector from which all photons can escape, because of underneath silica substrate with higher refractive index of $n$ (than air), only $1/4n^2$ generated photons could escape from the emitting layer. Together with sample absorbance at excitation wavelength ($A$), the UC EMISSION quantum yield ($\Phi_{\text{UC}}$)$^8$, which is the number of photons observed divided by the number of photons absorbed, can be calculated by

$$\Phi_{\text{UC}} = \frac{N_{\text{sample}}}{N_{\text{laser}}} \times \frac{4n^2}{A}$$

to be 1.1%. We note $\Phi_{\text{UC}}$ has a theoretical maximum value of 50%.

We note the PL quantum yield determined in this way should be considered as a lower limit, as this did not count the small fraction of photons that is trapped within the emitting layer by total internal reflection at emitting layer/air interface. To justify this, we compared the PL quantum yield $\Phi_{\text{PL}}$ from a CdSe/CdZnSe/ZnS quantum dots (QDs) film (30 nm thick) and a pristine rubrene/DBP film (15 nm, same as that used in UC study) by this Micro-PL method and by standard PL quantum yield setup using integrating sphere. The $\Phi_{\text{PL}}$ by latter method can be considered as a true value. The $\Phi_{\text{PL}}$ of QDs film and rubrene/DBP film under 532 nm excitation determined by Micro-PL method is 58% and 46%, respectively. These values are close, but both are smaller compared to values determined by integrating sphere, 74% and 52%, respectively. Comparing the $\Phi_{\text{PL}}$ of rubrene/DBP film measured by two methods, the reported value should be ~ 88% of the true value determined by integrating sphere. Therefore, the $\Phi_{\text{UC}}$ we reported in this study for rubrene/MoSe$_2$ is a conservative value.

From $\Phi_{\text{UC}}$, we can also calculate the UC STATES quantum yield ($\Phi_{\text{UCs}}$)$^8$, which is the number of upconverted states in the annihilator per the number of photons absorbed by sensitizer, $\Phi_{\text{UCs}} = \frac{\Phi_{\text{UC}}}{\Phi_{\text{PL}}(\text{org})(1-\Phi_{\text{BET}})}$. There, $\Phi_{\text{PL}}(\text{org})$ is the PL quantum yield of rubrene/DBP film and has been determined to be 52% by a calibrated standard PL quantum yield setup with integrating sphere. $\Phi_{\text{BET}}$ represents the optical loss due to the back energy transfer (BET) from emitter (rubrene/DBP) to sensitizer (MoSe$_2$). We estimate $\Phi_{\text{BET}}$ by comparing TRPL kinetics of rubrene/DBP with and without MoSe$_2$ monolayer underneath, $\Phi_{\text{BET}} = (k_{\text{Rub/MoSe2}} - k_{\text{Rub}})/k_{\text{Rub/MoSe2}}$, where $k_{\text{Rub/MoSe2}}$ and $k_{\text{Rub}}$ is the PL decay rate of rubrene/DBP on MoSe$_2$ and neat rubrene/DBP as shown in in Fig. S7. As singlets in rubener/DBP from TTA process by photoexciting MoSe$_2$ is more closer to interface than directly photoexcited singlets in rubener/DBP layer, BET under TTA condition should be more severe and $\Phi_{\text{BET}}$ estimated in this way should be considered as a lower limit. With estimated $\Phi_{\text{BET}}$ of 29% from TRPL results and $\Phi_{\text{PL}}(\text{org})$, $\Phi_{\text{UCs}}$ can be calculated to be 2.9%. Considering the underestimate of both $\Phi_{\text{UC}}$ and $\Phi_{\text{BET}}$, $\Phi_{\text{UCs}}$ should also be considered as a lower limit.

In addition to $\Phi_{\text{UC}}$ and $\Phi_{\text{UCs}}$, there are two other previously widely used but not standard UC quantum yields that should be mentioned. One is $\eta_{\text{UC}}$ which refers to the normalized UC EMISSION quantum yield and equals to twice $\Phi_{\text{UC}}$, namely, $\eta_{\text{UC}} = 2 \times \Phi_{\text{UC}}$. Another is “$\eta$”$_{\text{UCs}}$ which refers to the normalized UC STATES quantum yield
considering only emitter PL quantum yield $\Phi_{\text{PL(org)}}$ but no $\Phi_{\text{BET}}$, $\eta^{\prime}_{\text{UCs}} = \frac{2\times \Phi_{\text{UC}}}{\Phi_{\text{PL(org)}}}$. The $\eta_{\text{UC}}$ and $\eta^{\prime}_{\text{UCs}}$ for our Ruberene/MoSe$_2$ devices are also calculated and listed in Table S1 for reference.
| Sensitizer Emittor | Sensitizer Emittor | Sensitizer Emittor | Sensitizer Emittor | Sensitizer Emittor | Sensitizer Emittor | Sensitizer Emittor | Sensitizer Emittor |
|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| This work:        | Rubrene/DBP       | Rubrene/DBP       | Rubrene/DBP       | Rubrene/DBP       | Rubrene/DBP       | Rubrene/DBP       | Rubrene/DBP       |
| MoSe2 (~0.6 nm)   | 260               | 2.2               | 4.23              | 52                | 1.1               |
| PdPc              | Rubrene/DBP       | 2100              | --                | --                | --                | 0.07              |
|                  |                   | TBR/DBP           | --                | --                | --                | 0.3               |
| PdTPTAP           | Rubrene           | 116               | 0.5               | --                | --                | 0.25 Cal, a       |
| Y6                | Rubrene/DBP       | 19                | --                | --                | --                | 0.515             |
| ITIC-CI           | Rubrene/DBP       | --                | --                | --                | --                | 2.53              |
| PbS NC (OA ligand)| Rubrene/DBP       | 12000             | 0.57              | 1.2               | 46.3              | 0.085 Cal, a       |
| PbS NC (6C ligand)| Rubrene/DBP       | --                | --                | 7                 | 46.3              | 1.6 Cal (with IEU) |
| MA0.15FA0.85PbI3  | Rubrene/DBP       | 500               | --                | 3.1               | 9.3               | 0.15 Cal, b       |
| MA0.15FA0.85PbI3  | Rubrene/DBP       | 7.1               | --                | --                | --                | --                |
| MA0.15FA0.85PbI3  | Rubrene/DBP       | 61                | --                | 0.489             | 45.6              | 0.11 Cal, b       |

In this table, all non-standard quantum yields in references (i.e. $\eta_{UC}$ or $"\eta"_{UCs}$) are converted to standard quantum yield $\Phi_{UC}$ for comparison through their relationship. Values with line underneath and superscript Cal refers to the calculated values with follow details:

- $\Phi_{UC}$ is converted from $\eta_{UC}$ by $\Phi_{UC} = \frac{\eta_{UC}}{2}$.
- $\Phi_{UC}$ is converted from the expression $\Phi_{UC} = \frac{"\eta"_{UCs} \times \Phi_{PL(\text{org})}}{2}$.
- 7% published by Baldo and co-workers is the normalized TTA-UC states quantum yield $"\eta"_{UCs}$. The standard $\Phi_{UC}$ could be calculated to 1.6 % by $\Phi_{UC} = \frac{"\eta"_{UCs} \times \Phi_{PL(\text{org})}}{2}$ with $\Phi_{PL(\text{org})}$ of 46.3%. In addition, it should be noted that this UC QY was obtained using a specially designed Rub/PbS UC device structure where extra silver layer and AIQ3 layer were introduced to achieve interference-enhanced upconversion (IEU). They have also found that $\Phi_{UC}$ was enhanced by ~300% with this specially designed structure. Therefore, $\Phi_{UC}$ of the standard Rub/PbS bilayer device without IEU could be estimated to be 1.6%/3 = 0.53%.
**Fig. S1. AFM characterization of bilayer film.** (a) Representative optical and (b) AFM images of rubrene/MoSe$_2$ film on fused silica substrate. The region marked with blue line is the bilayer region with MoSe$_2$ underneath and the rest is rubrene only layer. (c) Two height profile extracted from corresponding two lines in Fig. b. The height profile shows a 15 nm rubrene thickness and same rubrene thickness on MoSe$_2$ monolayer and blank substrate. Atomic force microscopy (AFM) measurement was performed with an instrument (Oxford Cypher 5) in a nitrogen-filled glovebox, and topography images were collected in tapping mode.

**Fig. S2.** Scaled PL spectra of Rub/MoSe$_2$ bilayer at 772 nm which only excites MoSe$_2$ layer and 405 nm which directly excites rubrene layer largely. The close match between them at ~ 780 nm confirms negligible MoSe$_2$ emission in bilayer.
Fig. S3. TRPL decay curves of Rub/MoSe$_2$ bilayer and blank substrate at same experimental conditions, confirming negligible laser scattering contribution.

Fig. S4. TRPL kinetics of UC PL at different repetition rate and power. (a) UC PL dynamics of Rub/MoSe$_2$ device under irradiation with a 700 nm pulsed laser at different repetition rate of 200 and 500 kHz, showing faster rising and decay with increasing the repetition rate due to the bimolecular TTA-UC process and a build-up of the triplet population at higher rate. The energy of each excitation pulse at 200 kHz and 500 kHz are kept to be same thus the total power at 500 kHz is 2.5 times of it at 200 kHz. (b) UC PL dynamics of the Rub/MoSe$_2$ device at different excitation power ($\lambda_{\text{ex}}=700$ nm, 200 kHz). Obviously, the rising process becomes faster and the faster component becomes larger with increasing power, indicating the rapid TTA-UC at interface and slow diffusion-mediated TTA-UC$^{27}$. 
Fig. S5. TRPL decay curve for rubrene/DBP film excited by a 405-nm pulsed laser, showing a lifetime of $\sim 4.6$ ns.

Fig. S6. Absorption properties of mono- and few-layer MoSe$_2$. (a) Absorption (%) spectra of bilayer UC devices with different MoSe$_2$ layer number. (b) The relationship between MoSe$_2$ layer number and integrated NIR absorption (650-850 nm) as well as the linear fit ($R^2 = 0.996$).
**Fig. S7.** TRPL decay curves for rubrene/DBP film with and without MoSe₂ underneath. With increasing MoSe₂ thickness, TRPL decays faster due to increased back energy transfer from rubrene/DBP singlets to MoSe₂.

**Fig. S8.** The optical image of MoSe₂ continuous film grown by CVD method, showing clearly inhomogeneous surface.

**Fig. S9.** UC PL of Rub/WSe₂ bilayer device. (a) PL spectra of Rub/WSe₂ bilayer device and Rub itself under 730 nm photoexcitation; (b) Relative UC PL intensity of Rub/WSe₂ from different samples.
**Fig. S10 Solar spectrum.** (a) Spectral irradiance of the AM1.5 solar spectrum; (b) Photon flux of the AM1.5 solar spectrum.

**Fig. S11. Scheme of setup to measure emission quantum yield.** (Top panel) optical setup of measuring PL spectrum from sample. (Bottom panel) optical setup of measuring excitation light from Spectralon diffuse reflector (> 99%).