Electronic Supplementary Information (ESI) for

Green-to-UV photon upconversion enabled by new perovskite nanocrystal-transmitter-emitter combination

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Materials

All reagents and solvents were used as received otherwise noted. Cesium bromide (> 99.0%), 2,5-diphenyloxazole (PPO, > 99.0%), and oleic acid (> 99.0%) were purchased from TCI. Lead bromide (99.999%) and oleylamine (70%) were purchased from Sigma-Aldrich. Ethyl acetate (super dehydrated), toluene (deoxidized) and *N*,*N*-dimethylformamide (DMF, deoxidized) were purchased from Wako. P_{66614}PPOS and TIPS-Nph were synthesized and fully characterized in our previous reports, respectively.[1,2]

Synthesis of $CsPbBr_3$ perovskite nanocrystals[3]

All the sample preparations were conducted in an Ar-filled glove box (oxygen concentration < 0.1 ppm). As a precursor solution, CsBr (0.10 mmol, 21.3 mg) and $PbBr_2$ (0.10 mmol, 36.7 mg) were dissolved in 5 mL of DMF. 125 μL of oleylamine and 250 μL of oleic acid were added to the solution at 40 °C. 200 μL of this precursor solution was quickly added into 5 mL of toluene under vigorous stirring at room temperature. Within 2 minutes, 5 ml of ethyl acetate was added, and the solution was centrifuged using CHIBITAN-II (Millipore). The obtained PNCs were redispersed in toluene and centrifuged again to obtain the supernatant liquid.

Sample preparation for TTA-UC measurements

The surface PNCs was modified with P_{66614}PPOS by stirring overnight in the presence of P_{66614}PPOS, to which TIPS-Nph was further added to prepare TTA-UC solutions (PNCs/P_{66614}PPOS/TIPS-Nph). The final concentrations of P_{66614}PPOS and TIPS-Nph in toluene were 1 mM and 10 mM, respectively. The obtained solutions were sealed in quartz cells of 1 mm thickness in the glove box. For the preparation of PNCs/P_{66614}PPOS/PPO, PPO was used as an emitter with a concentration of 10 mM. In a PNCs/PPO/TIPS-Nph solution, 1 mM PPO and 10 mM TIPS-Nph were added as the transmitter and emitter, respectively. In a PNCs/PPO solution, 11 mM PPO was added as the transmitter/emitter.

Characterization

UV-vis absorption spectra were recorded on a JASCO V-780 spectrophotometer. Photoluminescence spectra were measured by using JASCO FP-8300 and FP-8700 spectrofluorometers. Transmission electron microscope (TEM) images were taken by a JEOL JEM-2010. The absolute photoluminescence quantum yield (PLQY) was measured in an integrating sphere using a HAMAMATSU multichannel analyzer C10027-01. Time-resolved photoluminescence lifetime measurements were carried out by using a time-correlated single-photon counting lifetime spectroscopy system, HAMAMATSU Quantaurus-Tau C11367-21, C11567-02, and M12977-01.

For TTA-UC emission measurements, a diode laser (515 nm, RGB Photonics) was used as the excitation source, and a 450 nm long-pass filter was used to remove shorter-wavelength light. The laser power was controlled by combining a software (Ltune) and a variable neutral density filter, and it was measured using a PD300-UV photodiode sensor (OPHIR Photonics). The laser beam was focused on a sample using a lens. The diameter of the laser beam ($1/e^2$) was measured at the sample position using a CCD beam profiler SP620 (OPHIR Photonics). The emitted light was

collimated by an achromatic lens, and the emitted light was again focused by an achromatic lens to an optical fiber connected to a multichannel detector MCPD-9800 (Otsuka Electronics). The excitation light was removed using a 450 nm short-pass filter, and obtained PL spectra above 350 nm were calibrated by using a standard lamp Ocean Optics HL-3 plus-CAL.

TTA-UC efficiency (η_{UC}) by the relative method

The TTA-UC efficiency η_{UC} (the theoretical maximum is 100%) was determined relative to a Rhodamine 101 in deaerated ethanol as a standard according to the following equation,[4]

$$\eta_{UC} = 2\Phi_{std}\left(\frac{1-10^{-A_{std}}}{1-10^{-A_{UC}}}\right)\left(\frac{E_{UC}}{E_{std}}\right)\left(\frac{I_{std}}{I_{UC}}\right)\left(\frac{n_{UC}}{n_{std}}\right)^2$$

where Φ, A, E, I, and n represent quantum yield, absorbance at the excitation wavelength (515 nm), integrated photoluminescence spectral profile, excitation intensity, and the refractive index of solvent, respectively. The subscripts UC and std denote the parameters of the PNCs/P_{66614}PPOS/TIPS-Nph mixed toluene solution and Rhodamine 101 solution.

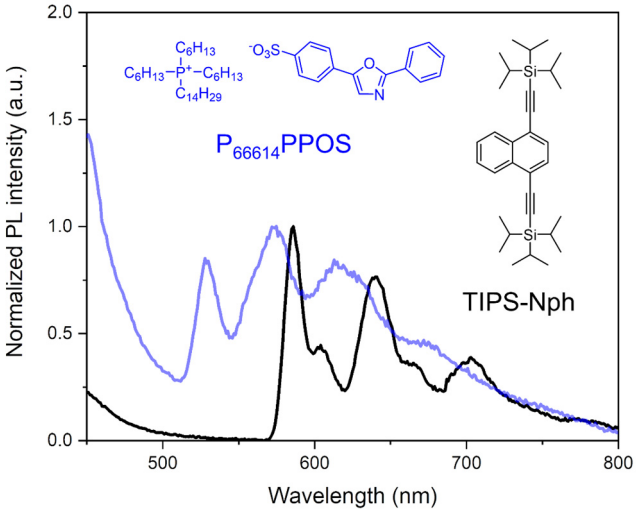

Figure S1. Normalized phosphorescence spectra of TIPS-Nph (black) and P_{66614}PPOS (blue) in toluene at 77 K ([TIPS-Nph] = 10 mM, [P_{66614}PPOS] = 10 mM, λ_{ex} = 320 nm).

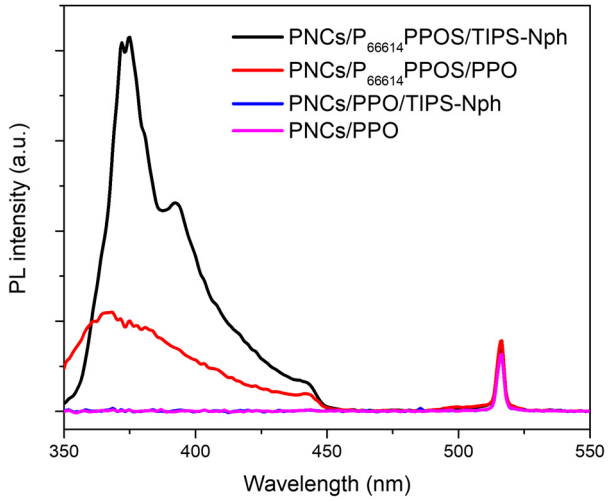

Figure S2. UC emission spectra of PNCs/P_{66614}PPOS/TIPS-Nph (black), PNCs/P_{66614}PPOS/PPO (red), PNCs/PPO/TIPS-Nph (blue) and PNCs/PPO (pink) in deaerated toluene (λ_{ex} = 515 nm, 450 nm short-pass filter, I_{ex} = 83.2 W cm^{-2}).

References

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