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Electronic Supplementary Information (ESI)

on

Near-infrared-to-visible upconversion from 980 nm excitation band by binary solid of PbS quantum dot with direct attaching emitter

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A. Materials, sample preparation, and ordinary measurements

Materials. Oleic-acid capped PbS QD dispersed in toluene (emission peak at 1000 nm, 10 used mg/ml) purchased from Sigma Aldrich and was received. 5,11as (TES-ADT, >99%) bis(triethylsilylethynyl)anthradithiophene from Luminescence Technology Corp. and IR-140 (5-chloro-2-[2-[3-[(5-chloro-3-ethyl-2(3H)-benzothiazolylidene)ethylidene]-2-(diphenylamino)-1-cyclopenten-1-yl]ethenyl]-3-ethyl benzothiazoleum perchlorate) from Exciton Inc. were used without further purification. Spectroscopic grade toluene was used for solution casting.

Fabrication of PbS QD:TES-ADT binary solid by solution casting. First, mixed mother solutions were prepared by adding 0.6 mL of the diluted dispersion solution of PbS QD (3.33 mg/ml) onto the different amounts of TES-ADT powder so as to result in the TES-ADT concentrations of 30 mM, 50 mM, 75 mM, 100 mM, 150 mM, and 200 mM. The concentration of PbS QD was 50 μ M for all, determined from absorption spectrum by the reported method. [I. Moreels et al., *ACS Nano* 2009, **3**, 10, 3023] The concentration ratios were 1:600, 1000, 1500, 2000, 3000, and 4000, respectively. 40 μ L of the prepared solution was drop-cast on to a pre-cleaved glass substrate. The solvent was quickly dried within 1-2 minutes forming a solid film of PbS QD/TES-ADT on to glass surface. Preparation of the solution and drop casting were performed in N₂ filled glove box with <1 ppm O₂ and very low humidity (due point <-78 °C). Solution cast samples were then taken out of the glove box for upconversion quantum yield measurement and time dependent decay time analysis.

Measurements. UV-visible absorption spectrum was recorded by a *Shimadzu UV-3150* spectrophotometer. Prompt fluorescence spectrum of each compound was recorded by a *JASCO FP-8300* spectrofluorometer. The thickness of the cast film was mechanically measured by a *KLA-Tencor P-15* stylus profilometers.

B. Upconversion emission and quantum yield measurement of individual micro crystals

Optical setup. The upconverted emission of individual microcrystal of the binary solid of PbS QD:TES-ADT were measured by using a homemade microspectroscopic setup (Fig. S2) based on an Olympus IX73 inverted microscope. This setup was the modification of the previously reported setup [A. Abulikemu, et al., ACS Appl. Mater. Interf. 2019, 11, 20812] so that the two colors beams (785 and 975 nm) were aligned coaxially and switched by the flip mirror. As the light source, cw-laser diode modules (Integrated Optics, MatchBox785L and MatchBox0975L were used for 785 and 975 nm. The excitation beam was expanded with a telescope in noncollimated manner and then lead to an objective lens (20×, NA 0.45) so as not to focus on the sample but to illuminate uniformly. The transverse profile of the excitation beams at sample position measured by an NIR-enhanced CMOS camera was circular for 785 nm bur elliptical for 975 nm. Elliptical two-dimensional Gaussian fit gave geometric means of e⁻² radius were 125 µm (785 nm) and 89 µm (975 nm). On the other hand, the detection area of emission was concentric circle area with the diameter of 25 µm. Thus, the variation of the excitation intensity within the detection area was less than 4%, calculated from the gaussian distribution of the intensity. The emission from the sample was collected by the same objective lens and detected by a fiber-coupled spectrometer (Ocean Optics USB200FLG).

Fluorescence cube in the microscope was switched depending on the measurement mode and excitation wavelength. For detection of upconversion (UC) emission, the fluorescent cube with a 700-nm short-pass dichroic beamsplitter (*Semrock FF700-SDi01*) and a 700-nm short-pass filter (*Thorlabs, FESH0700*) in detection side was used. For fluorescence (FL) detection of reference sample (*vide infra*) by 785 nm excitation, the fluorescent cube with a 785-nm notch beamsplitter (*Semrock NFD01-785*), and a 785-nm notch filter (OD 4, 25 nm, *Edmund, #67-121*) in detection side was used. These fluorescence cubes were designed to block the scattering of excitation beam and to pass the spectral region of interest. For absorption (transmission) measurements, the fluorescent cube with a chromium half mirror was used.

The spectral correction functions of all related optics were obtained and used to give a properly corrected emission spectrum, which is important for QY measurement. Excitation power at the sample position was measured by a calibrated microscope photodiode power sensor (*Thorlabs S170C*) and used to calculate the excitation intensity with the beam radii mentioned above.

Emission quantum yield measurements. Upconversion emission quantum yield (UC-QY) was measured by UC emission spectrum measurement and absorption (transition) measurement on the same sample position (see Fig. S3 for example) by using the microspectroscopic setup motioned above. The absorption measurement can be performed by using field illumination of microscope with W-lamp. With the same optical geometry for the reference sample (R) excited at λ_R and UC sample (X) excited at λ_X , the UC-QY for these samples is [Supporting information of N. Tripathi et al., *ACS Appl. Nano Mater.* 2021, **4**, 9680],

$$\Phi(X) = \Phi(R) \frac{F_X n_X^2 P_R (1 - 10^{-A_R}) \lambda_X^{-1}}{F_R n_R^2 P_X (1 - 10^{-A_X}) \lambda_R^{-1}} \quad \#(S1)$$

where $\Phi(R)$ is the photoluminescence QY of the reference sample under excitation 785 nm, which is known. As the reference sample, IR-140 solution in ethanol ($\Phi=0.17\pm0.01$ [K. Rurack et al., *Anal. Chem.*, 2011, **83**, 1232]) was used. Here, $\lambda_R=785$ nm for the reference and $\lambda_X=975$ nm for the sample. *F* is the integrated intensity of corrected emission spectrum, *n* is refractive index, *P* is the excitation intensity, *A* is absorbance at the excitation wavelength. On the integrated intensity, the blocked part of the UC emission spectrum (longer then 700 nm) was corrected by using the whole fluorescence spectrum of TES-ADT in solid measured separately. For solid samples, scattering can affect the measurement results. On this problem, we have tested the sample filled with high refractive index fluid (index matching oil) rather than Ar gas and the effect was smaller than the variation of the monitoring points in the sample [see K. Kamada, et al., *Mater. Horiz.* 2017, <u>4</u>, 83 and its ESI]. Method for the spectral correction for deformation by scattering can be found there. For each sample, more than 20 positions in the sample were measured to know the inhomogeneity of the cast film.

C. Time-resolved emission measurements

A Ti:sapphire laser operating at 1 k Hz with the pulse duration of 10 ns was used as light source for 800 nm excitation. The pulsed beam irradiates the sample tilted against the propagation direction and then the emission from the sample was collected by a high NA lens and led to a Si-APD (Thorlabs APD120A) through multimode optical fiber. A 700-nm short-pass filter (Thorlabs FESH0700) was used to collect the upconversion emission of the sample. The signal was recorded and accumulated by using a digital oscilloscope (500 MHz, 5G S/s). Instrument response function (IRF) can be found in Fig. S10. Influence of scattering of the excitation pulse was confirmed by inserting and removing the fundamental cut filter (HOYA E-CM500-S) and then the laser scattering around the time origin was removed from Fig. 5.



Fig. S1. Absorption (blue) and emission (red) spectra of (a) PbS QD dispersed in toluene and (b) TES-ADT in toluene and (c) TES-ADT in thin film with the microspectroscopic setup. The film was illuminated by a UV-LED (~ 360 nm) to obtain the emission spectrum.



Fig. S2. Block diagram of two-color excitation microspectroscopic setup for upconversion quantum yield measurement. LD785, LD795: cw-laser diode (λ =785 nm and 975 nm respectively), M: mirror, FM: flip mirror, r-ND: rotational neutral density filter set, AP: iris aperture, L: lens, obj: objective lens (20×, NA 0.45), and FLC: fluorescence cube.



Fig. S3. Some examples of absorption spectrum of PbS QD:TES-ADT binary cast film measured at three different points on the sample by the microspectroscopic setup shown in <u>Fig. S2</u> and used to calculate the upconversion quantum yield with the emission spectrum measured at the same point of sample. Deformation of baseline due to scattering was subtracted so that shape of the obtained spectral matched to that of absorption spectrum of the excitonic peak of PbS QD in dispersion solution.



Fig. S4. Thickness profiles for the cast film of PbS QD:TES-ADT. The TES-ADT concentration of the mother solution is (a) 20 mM and (b) 100 mM.



Fig. S5. Plot of thickness of the solution cast film (surrounding rim) as a function of TES-ADT molar concentration of the mother solution.



Fig. S6. Crossed Nicol transmission images of rim part of the cast solid of PbS QD: TES-ADT. Sample was rotated by 0 and 45 degrees. The images are rotated so that the sample is oriented in the same direction on this sheet. The TES-ADT concentration of the mother solution was 100mM. Scale bar is 100 μ m.



Fig. S7. Microscopic transmission images (a-d) and corresponding upconverted emission images (e-h), respectively, of PbS QD:TES-ADT samples.



Fig. S8. Excitation intensity (I_{ex}) dependence of upconversion quantum yield (UC-QY) of the PbS QD:TES-ADT cast solid fabricated from the mixed solutions of [TES-ADT]= (a) 50 mM, (b) 75, (c) 150, and (d) 200 mM with theoretical fit based on eq. 1 in the main text. The obtained parameters by the fit are listed in Table S1.

Table S1. Preliminary results of upconversion quantum yield excited at 785 nm of PbSQD:TES-ADT cast solid. The excitation power used were 45 W cm⁻².

[TES-ADT] (mM)	$\Phi_{\scriptscriptstyle UC}$ (%)
100	0.14
150	0.09

Table S2. The obtained parameters by the curve fit to the data in Fig. S8 in ESI and Fig. 4 in the main text. Φ_{UC}^{∞} is upconversion quantum for the strong excitation limit and I_{th} is the threshold excitation intensity by eq. 1.

[TES-ADT] (mM)	$\Phi_{U\mathcal{C}}^{\infty}$ (%)	I _{th} (W cm ⁻²)
50	0.069 ± 0.008	2.0 ± 1.0
75	0.19 ± 0.02	4.7 ± 1.5
100	0.29 ± 0.02	2.5 ± 0.6
150	0.16 ± 0.01	2.8 ± 1.1
200	0.21 ± 0.02	5.8 ± 1.5



Fig. S9. Plot of Φ_{UC}^{∞} versus the concentration of TES-ADT in mother solution data from Table S1.



Fig. S10. Instantaneous response function (IRF) of the setup for nanosecond time-resolved emission measurement.

Table S3. Rise and decay time constants (τ_R and τ_D , respectively) obtained by the curve fitting by using eq. 3 to the time profiles upconversion emission of the cast solids of PbS QD:TES-ADT from the different concentrations of TES-ADT in the mother solution.

[TES-ADT] (mM)	$ au_R$ (ns)	$τ_D$ (μs)
20	100 ± 1	1.9 ± 0.1
30	100 ± 4	1.6 ± 0.1
50	173 ± 2	2.2 ± 0.1
75	174 ± 3	5.0 ± 0.1
100	180 ± 1	6.7 ± 0.1
150	131 ± 2	5.1 ± 0.1
200	151 ± 2	4.9 ± 0.1