Supplementary information

Highly efficient and stable tandem luminescent solar concentrators based on carbon dots and CuInSe$_{2-x}$S$_x$/ZnS quantum dots

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Experimental and Methods

Materials. Trans-aconitic acid (TAA, 98%), diethylenetriamine (DETA, 97%), indium acetate {In(Ac)$_3$, 99.99%} , 1-dodecanethiol (DDT, 98%), oleylamine (OLA, 80 ~ 90%), oleic acid (OA, 99.7%), 1-octadecene (ODE, ＞90.0%), Zn stearate (reagent grade), lauryl methacrylate (LMA, 96%) and Ethylene glycol dimethacrylate (EGDM, 97%) and Diphenyl (2,4,6-trimethylbenzoyl) phosphine oxide (IRGACURE 651, 97%) were purchased from Aladdin Reagent Co., Ltd, China. Sulfuric acid (H$_2$SO$_4$, 99.7%), copper iodide (CuI, 99.7%), methanol (CH$_3$OH, 99.7%) and polyvinylpyrrolidone K30 (PVP, 99.7%) were purchased from Chengdu Kelong Chemical Co., Ltd, China.

Synthesis of carbon dots. First, dissolve 0.52 g of trans-aconitic acid (TAA) and 2695 µl of diethylenetriamine (DETA) in 15 ml of distilled water (DW), and stir the solution well. Then, adjust the pH to 5 with 1 mol/L sulfuric acid. The solution was transferred to a Teflon-lined stain less steel autoclave, and a dark yellow solution was obtained after heating in an oven at 200 °C for 4 h. The dark yellow solution was dialyzed against distilled water for 12 h using a dialysis bag (MWCO = 1000 Da), and the solution in the dialysis bag was collected.

Synthesis of CuInSe$_{2-x}$S$_x$ quantum dots. Preparation of Se precursor: Dissolve 1 mmol Se powder in 0.75 mL OLA and 0.25 mL DDT solution in a 25 ml three-neck flask at room temperature under N$_2$ atmosphere. Core QDs preparation process: First, 1 mmol of cuprous iodide (CuI), 1 mmol of indium acetate {In (Ac)$_3$}, 5 mL of 1-dodecanethiol (DDT), and 1 mL of oleylamine (OLA) were added to a 50 mL three-neck flask. The flask was then heated to 90 °C and evacuated for 30 min (repeated three times), and then the temperature was raised to 140 °C and maintained for 25 min to wait for the complete dissolution of the precursors. The three-necked flask was heated to 180 °C and the prepared Se source was added dropwise. The temperature control was maintained for 10 min for quantum dot nucleation. The three-necked flask was then quickly heated to 235 °C and held for 40 min before the reaction was quenched and stopped with cold water. Finally, the prepared solution was stored in a 3 °C refrigerator.

Synthesis of CuInSe$_{2-x}$S$_x$/ZnS quantum dots. Preparation of ZnS precursors: 6.32

g of zinc stearate with 20 ml ODE, 10ml OA and 10 ml DDT was added to a 100 ml three-necked flask and degassed under vacuum at 90 °C for 30 min, and nitrogen was passed through the flask for 30 min (repeated 3 times). Then the temperature was elevated to 150 °C and kept for 10 min, and finally the temperature was kept at 50 °C for reserve. Core-shell QDs preparation process: First, the prepared $CuInSe_{2-x}S_x$ quantum dots were heated to 235 °C in a 100 ml three-necked flask, and then the prepared ZnS precursor was added into the three-necked flask in four additions, each at an interval of 2 h (each addition of ~ 11 ml, the temperature was kept at 235 °C). After the last addition of the ZnS precursor was kept at 235 °C for 4 h. At the end of the reaction, the temperature was quickly brought down to room temperature with cold water and then stored in a 3 °C refrigerator.

Fabrication of LSCs based on CDs. The CDs dispersed in methanol (4 mg/ml) were mixed well with a certain amount of PVP (PVP concentration of 200 mg/mL), and then the mixture was dropped onto a glass substrate for spin-coating (spin-coating parameter: 100 r.p.m./s at low speed, 300 r.p.m./s at high speed, and the size of the glass was $10 \times 10 \times 2$ cm^3).

Fabrication of LSCs based on $CuInSe_{2-x}S_x$/ZnS QDs. Firstly, lauryl methacrylate (LMA) and ethylene glycol dimethacrylate (EGDM) were mixed in a 4:1 mass. The solution is mixed with diphenyl (2,4,6-trimethylbenzoyl) phosphine oxide (mass fraction:1 wt%) and sonicated until a clear solution is obtained. Then, the solution was then injected into a flask containing dry QDs, and the mixture was homogeneously dispersed by sonication. The mixture was injected into a mould consisting of two glass plates separated by a flexible rubber spacer of $\approx$3 mm thickness. Finally, the mixtures were irradiated under a UV lamp (wavelength of 395 nm) for 5 min and darkened for 30 min.

Characterizations. Absorption spectra of the CDs and $CuInSe_{2-x}S_x$/ZnS QDs were acquired with a visible, near-infrared spectrophotometer (UV-3600i, Shimadzu Corp, Japan). The PL spectra of CDs and $CuInSe_{2-x}S_x$/ZnS QDs were measured with a time-resolved fluorescence spectrometer (FL3-22, Jobin-Yvon, USA). The FT-IR spectra of

CDs were recorded by an FT-IR spectrometer (Nicolet 6700, Thermo Electron, USA). Chemical elemental analysis of CDs and $CuInSe_{2-x}S_x/ZnS$ QDs was performed by X-ray photoelectron spectroscopy (XPS) AXIS Supra (Kratos, UK). The XRD detection of CDs and $CuInSe_{2-x}S_x/ZnS$ QDs was performed using X-ray diffraction (Empyrean, Panalytical, Netherlands). The size and morphology of CDs and $CuInSe_{2-x}S_x/ZnS$ QDs were characterized by TEM (Tecnai G2-F20-S-TWIN, Ectronoptics, Netherlands). The optoelectronic performance characterization of LSCs was obtained by a solar simulator (SS-X100R, Enlitech, China) at an intensity of AM 1.5G (100 mW/cm^2) and calibrated with a calibrated silicon solar cell.

Results
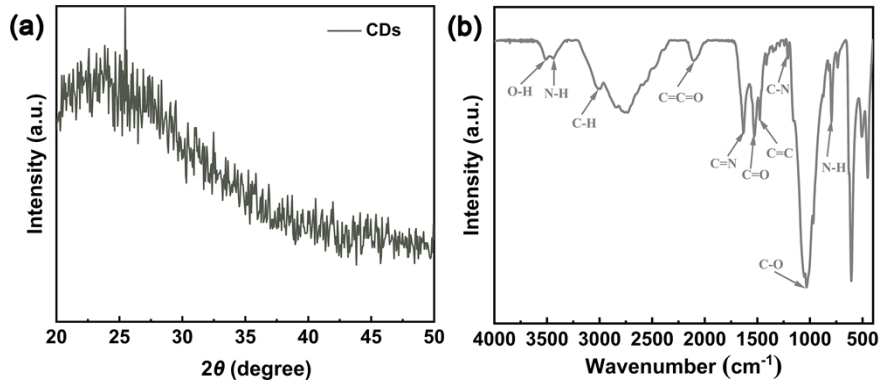
Fig. S1 (a) XRD and (b) FTIR patterns of CDs.
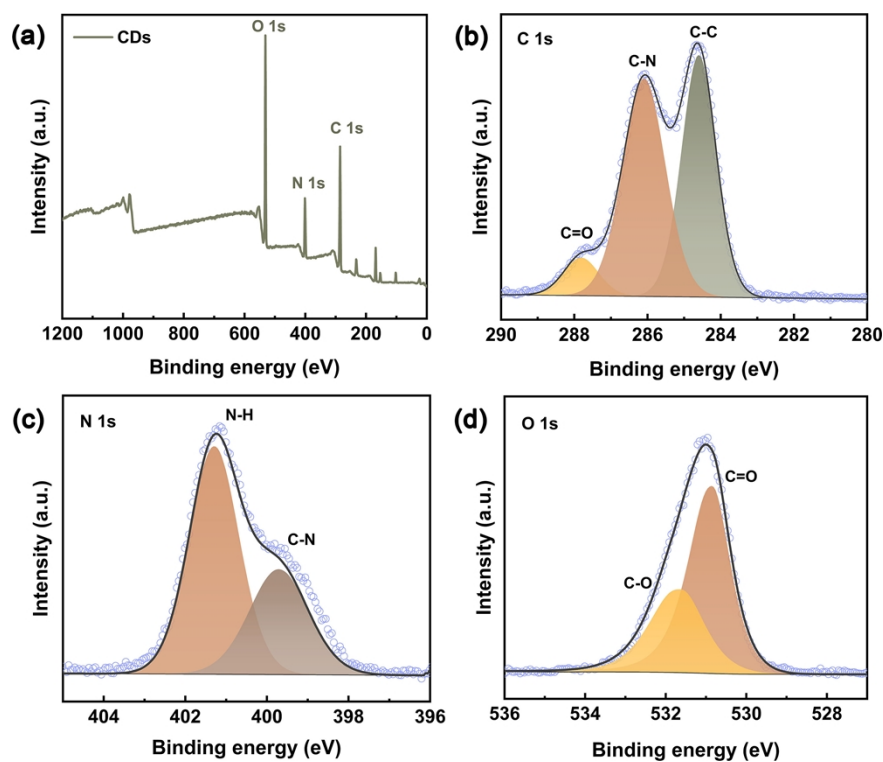
Fig. S2 (a) XPS analysis of the CDs. High-resolution XPS spectra of the C 1s (b), N 1s (c), O 1s (d).
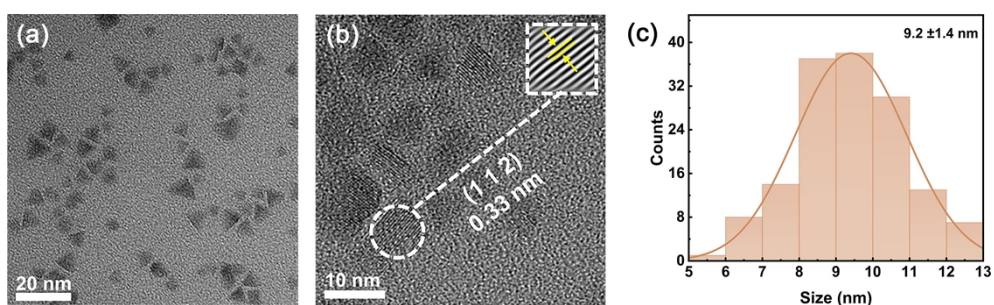
Fig. S3 Typical TEM and HRTEM images of CuInSeS QDs (a, b). (c) Size distributions of CuInSeS QDs.
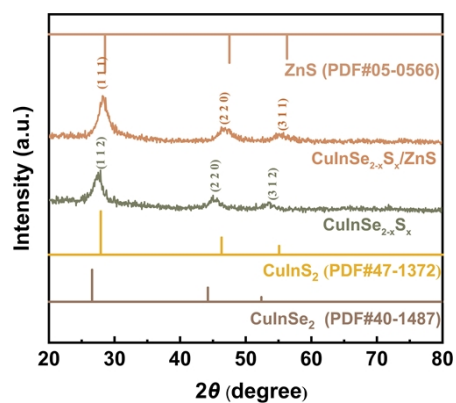

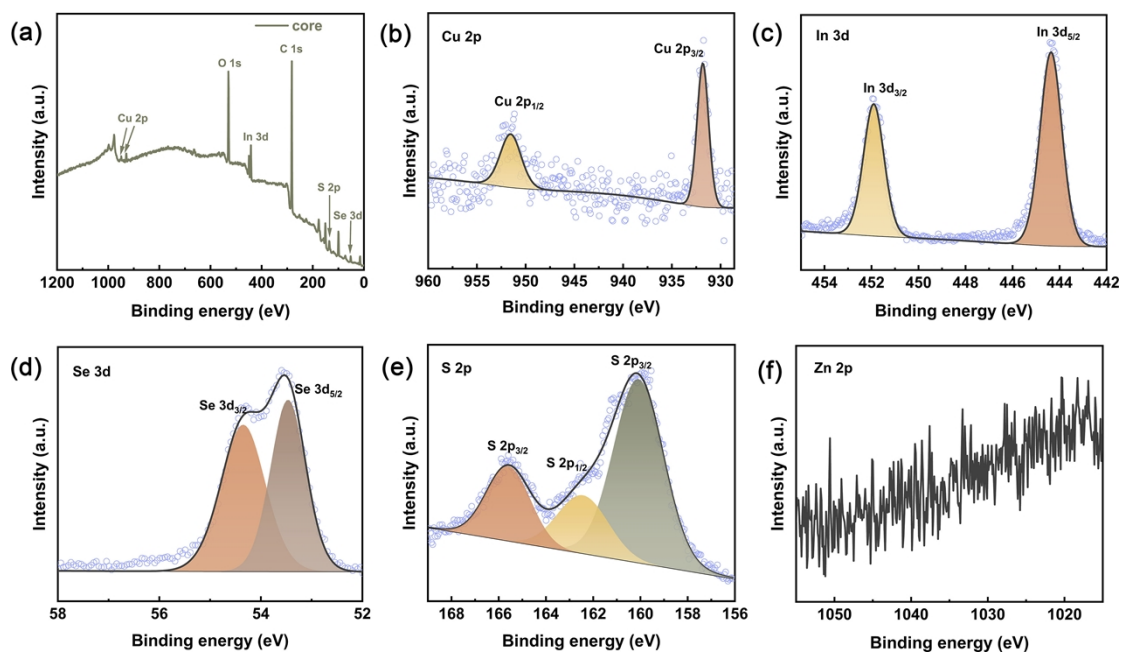**Fig. S4** XRD patterns of CuInSeS QDs and CuInSeS/ZnS QDs.

Fig. S5 (a) XPS survey spectra of CuInSeS QDs. High-resolution spectra of Cu 2p (b), In 3d (c), Se 3d (d), S 2p (e) and Zn 2p (f).
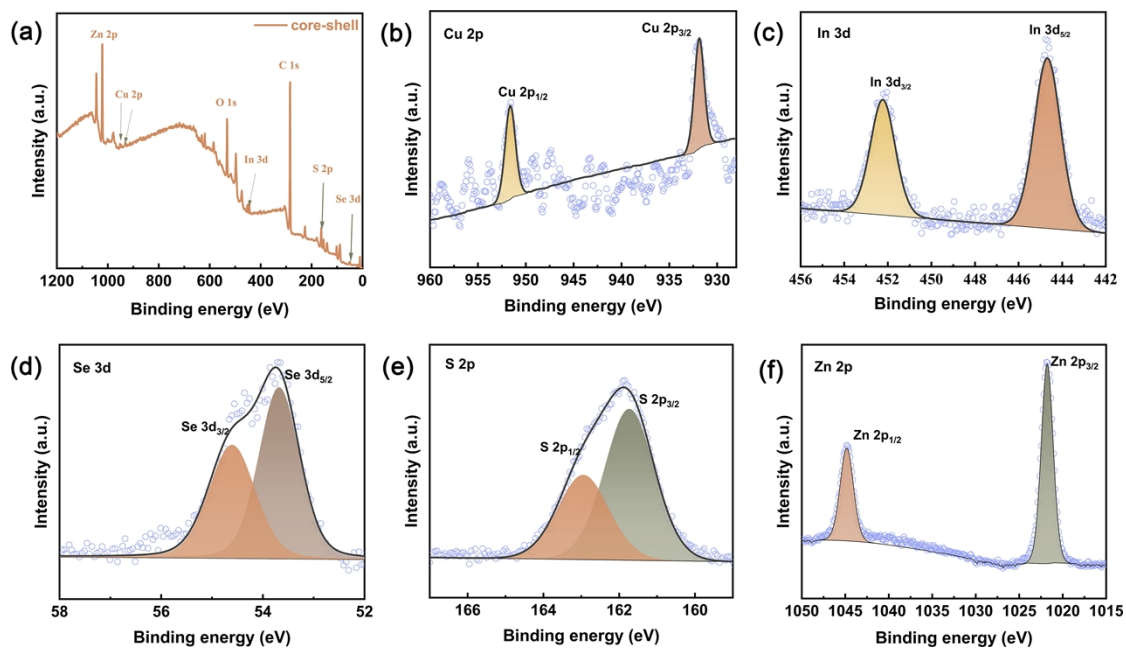

Fig. S6 (a) XPS survey spectra of CuInSeS/ZnS QDs. High-resolution spectra of Cu 2p (b), In 3d (c), Se 3d (d), S 2p (e) and Zn 2p (f).
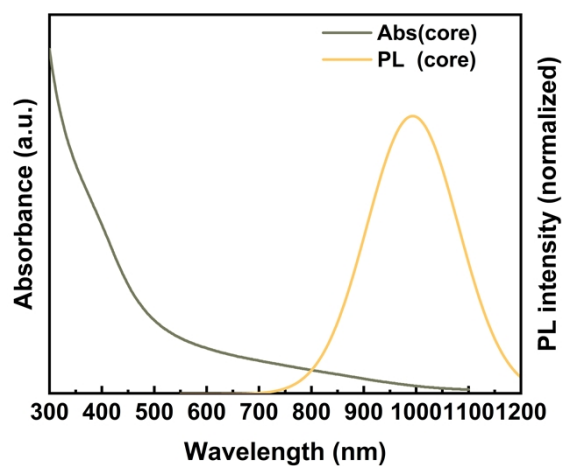
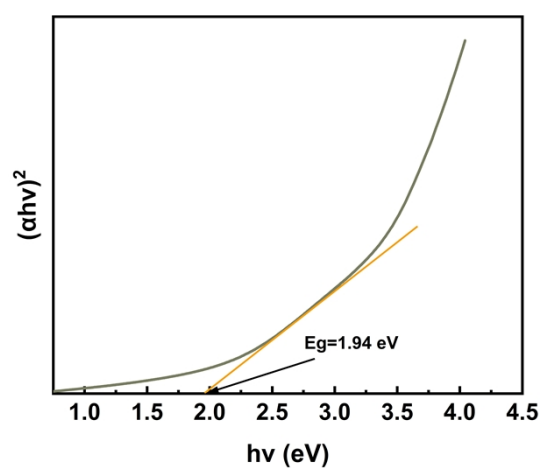**Fig. S7** Normalized absorption curves and PL spectrum of CuInSeS QDs in hexane.

Eg=1.94 eV
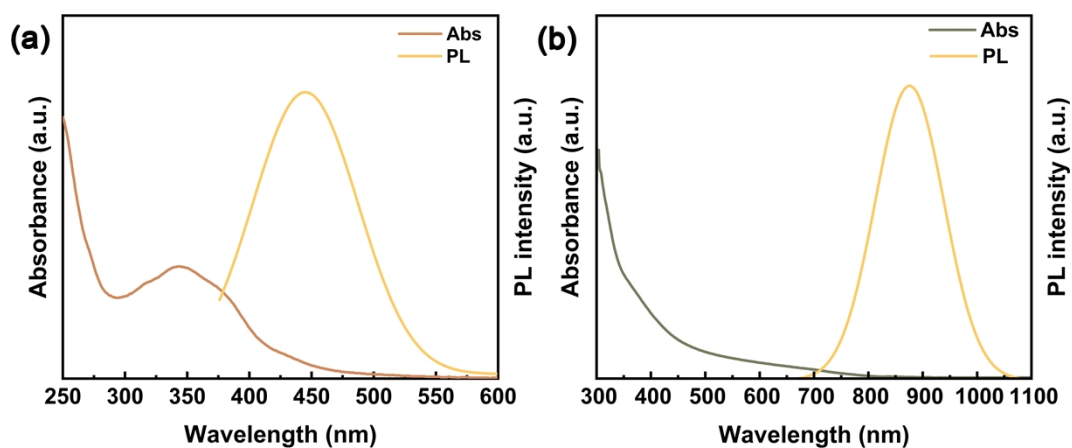
Fig. S8 Tauc plot of CuInSeS/ZnS QDs.

Fig. S9 Absorption and PL spectra of CDs in polymer (a) and CuInSeS/ZnS QDs in polymer (b).
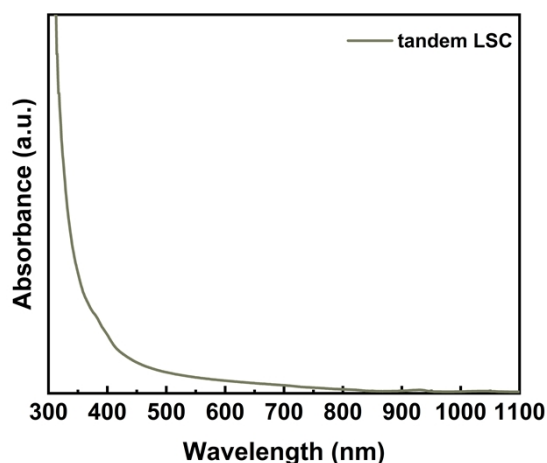
Fig. S10 Absorption spectrum of tandem LSCs based on CDs and CuInSeS/ZnS QDs.

Time Resolved Spectroscopic Characterization

To explore the lifetime of QDs dispersed in liquids and solids, we performed time-correlated single photon counting (TCSPC) measurements. The lifetime decay of QDs dispersed in the solid and liquid are complex bi-exponential decay trend. The fitting equation is as follows:

$$I(t) = A_1 e^{(-\frac{t_1}{\tau_1})} + A_2 e^{(-\frac{t_2}{\tau_2})}$$

Where A_1 and A_2 are the coefficients of the fitting of PL decay, τ_1 and τ_2 are the related time constants. From these values, the average decay lifetime was calculated as follows:

$$\tau_{AVG} = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2}$$

Table S1 PL lifetimes of CuInSeS/ZnS QDs in hexane and polymer, and CDs in methanol and polymer.

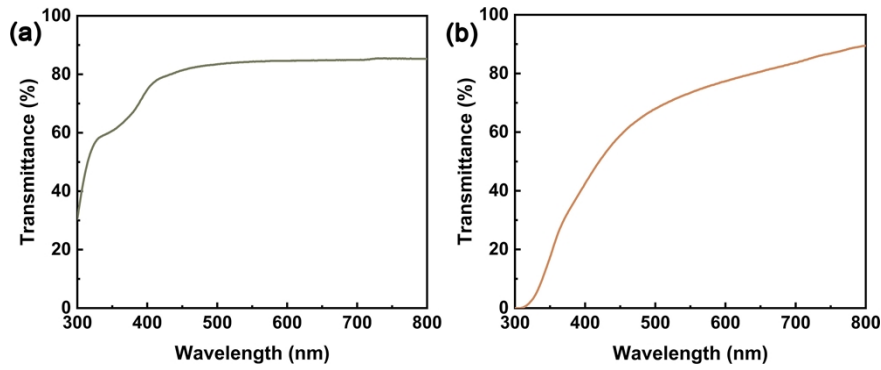| Samples	phase	A_1 (%)	τ_1 (ns)	A_2 (%)	τ_2 (ns)	τ_{AVG} (ns)
CuInSeS/ZnS QDs	liquid	37	263.54	63	925.79	831
	solid	38	114.22	62	559.23	510
CDs	liquid	88	9.55	12	22.7	12.8
	solid	56	1.94	44	8.68	7.2

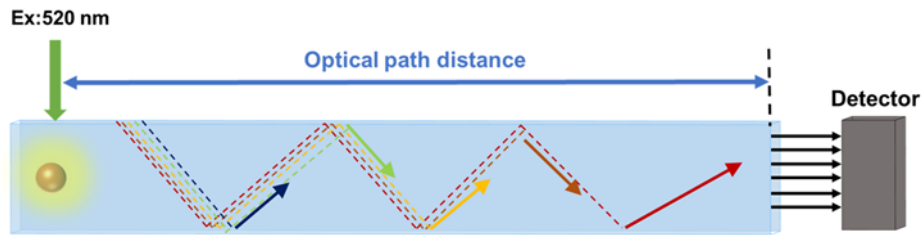**Fig. S11** Transmittances of LSCs based on CDs (a) and CuInSeS/ZnS QDs (b).

Fig. S12 Schematic diagram for measuring PL spectra as a function of excitation distance.
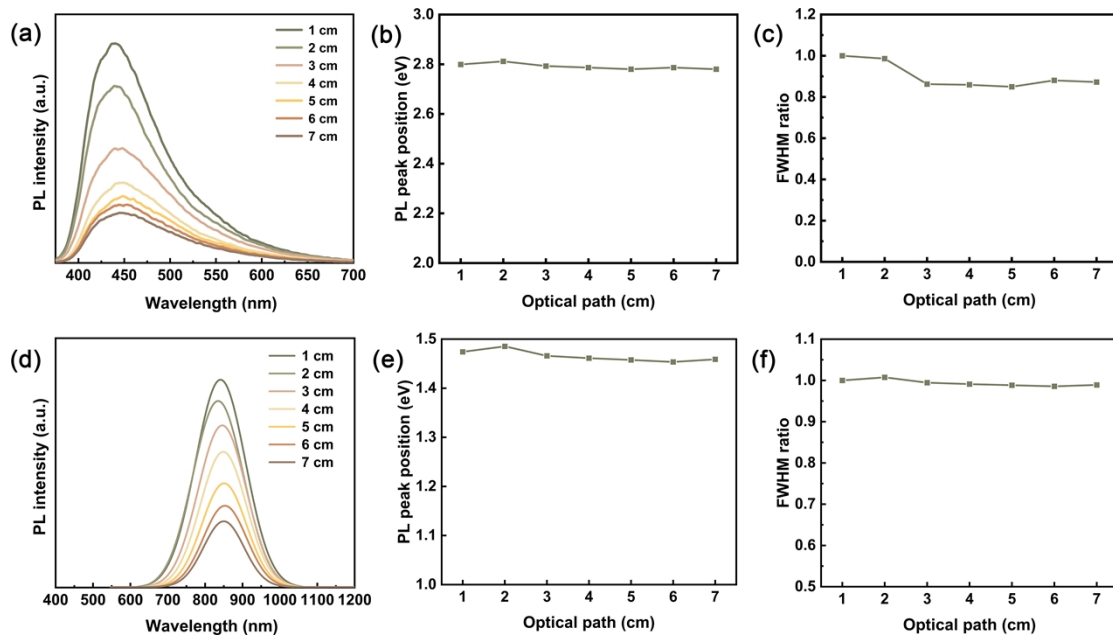

Fig. S13 PL attenuation spectra measured at different optical paths (L) for the CDs based LSCs (a) and the CuInSeS/ZnS QDs based LSCs (d). PL peak position of the CDs based LSCs (b) and the CuInSeS/ZnS QDs based LSCs (e) as a function of optical path. PL full width at half maximum (FWHM) ratio of the CDs based LSCs (c) and the CuInSeS/ZnS QDs based LSCs (f) as a function of optical path.
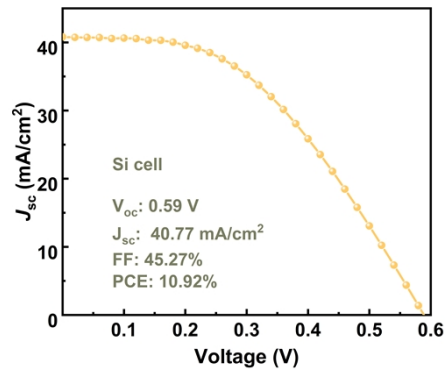
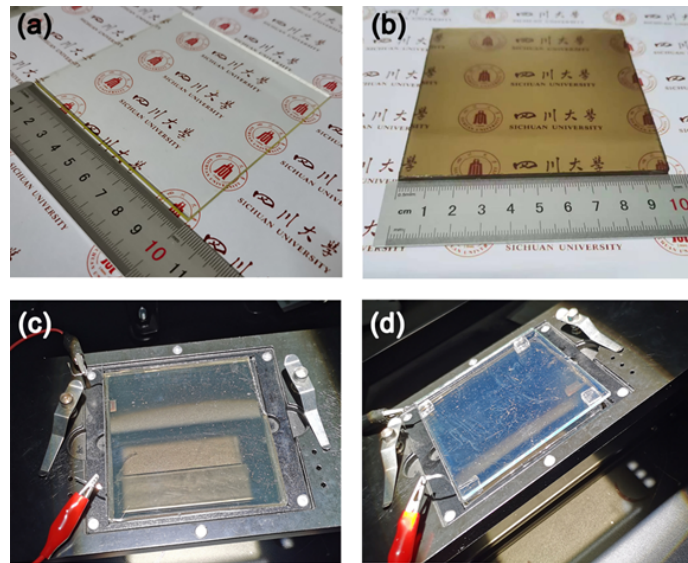**Fig. S14** J-V curve of a silicon solar cell under one sun illumination.

Fig. S15 Photographs of LSCs based on CDs (a) and CuInSeS/ZnS QDs (b). Photographs of experimental setup for measuring opto-electronic performance of single LSCs (c) and tandem LSCs (d).
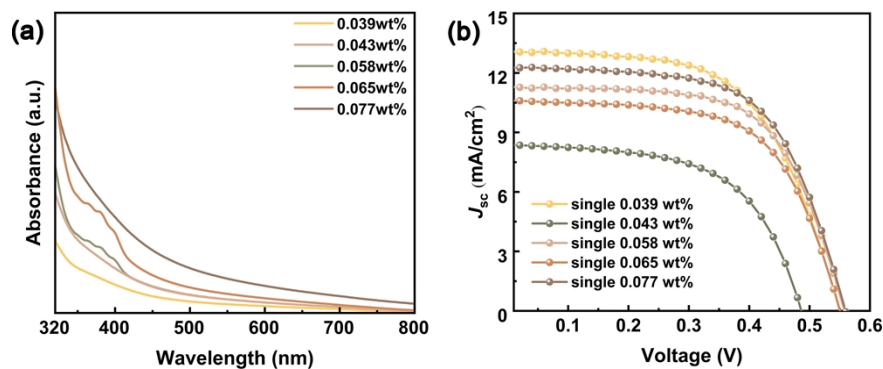

Fig. S16 (a) Absorption spectra of LSCs based on CuInSeS/ZnS QDs at different concentrations. (b) J-V curves of LSCs based on CuInSeS/ZnS QDs at different concentrations.
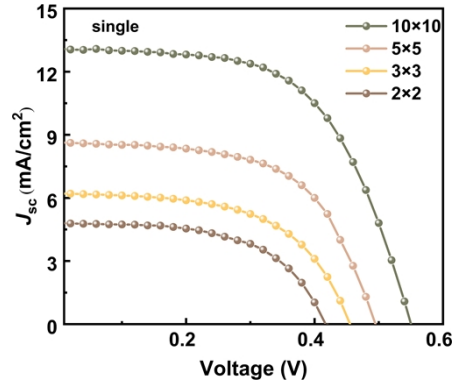
Fig. S17 J-V curves of the single LSC-PV system with different lateral areas.

Table S2 Power conversion efficiency, external optical efficiencies, internal optical efficiencies and absorptance for the single LSCs based on different types of fluorophores.

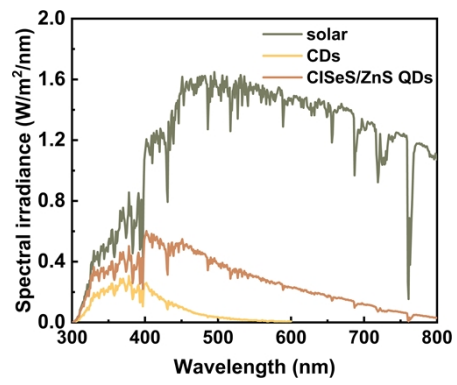| Types of QDs	PL peak position (nm)	PL QY (%)	Stokes Shift (meV)	LSC size (L × W × H) cm × cm × cm	PCE (%)	η_{ext} (%)	η_{int} (%)	η_{abs} (%)	Refs.
CuInSe$_{2-x}$S$_x$/ZnS	878	61	530	10 × 10 × 0.3	0.50	2.87	36.37	8	This work
				5 × 5 × 0.3	0.60	3.39	42.93		
				3 × 3 × 0.3	0.64	3.62	45.88		
				2 × 2 × 0.3	0.68	3.86	48.80		
CuInS$_2$/ZnS	862	91	>550	10 × 10	2.18	-	-	35.5	1
Yb^{3+}-doped CsPbCl$_3$ NCs	990	164	1847	5 × 5 × 0.2	-	3.70	120	3.1	2
CuInSe$_2$/ZnS	805	70	160	12 × 12 × 0.16	-	5.10	18.2	28	3

Fig. S18 Calculated absorption of the LSCs and solar spectrum (AM 1.5G, 100 mW/cm^2).

References

1. M. R. Bergren, N. S. Makarov, K. Ramasamy, A. Jackson, R. Guglielmetti and H. McDaniel, ACS Energy Letters, 2018, 3, 520-525.
2. X. Luo, T. Ding, X. Liu, Y. Liu and K. Wu, Nano Letters, 2019, 19, 338-341.
3. K. Wu, H. Li and V. I. Klimov, Nature Photonics, 2018, 12, 105-110.