Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic Supporting Information

Large Area Quantum Dot Luminescent Solar Concentrators for Use With Dye-Sensitised Solar Cells

Lorcan J. Brennan[a], Finn Purcell-Milton[a⊥], Barry McKenna[a⊥], Trystan M. Watson[c], Yurii K. Gun'ko[a,b], and Rachel C. Evans[a,d]*

[a]*School of Chemistry and CRANN, Trinity College, The University of Dublin, Dublin 2, Ireland*

[b]*ITMO University, 197101 St. Petersburg, Russia*

[c]*SPECIFIC – College of Engineering, Swansea University, Bay Campus, Swansea, SA1 8EN, UK*

[d] *Department of Materials Science & Metallurgy, University of Cambridge, U.K.*

**E-mail: rce26@cam.ac.uk*

[⊥] These authors contributed equally to this work.

Table of Contents

1. Fabrication of Large Area LSCs

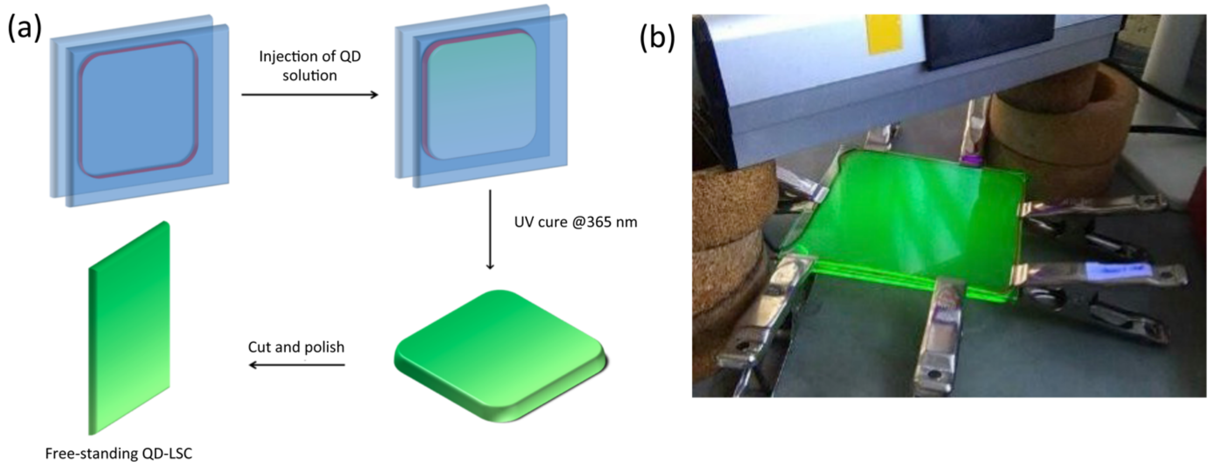

Figure S1. (a) Schematic representation of the fabrication procedure for a large-area quantum dot (QD)-doped luminescent solar concentrator (LSC). (b) Photographic image of the pre-polymerised solution encapsulated within the mould.

2. Fabrication and Characterisation of Thin Strip DSSCs

Electrode fabrication: TiO_2 electrodes were prepared on FTO-coated glass substrates. Glass substrates were cleaned in a detergent solution with ultra-sonication for 15 min followed by sonication in ethanol (10 min) and acetone (10 min). A bulk TiO_2 layer was applied by submerging the FTO-glass substrates in a hydrolysed $TiCl_4$ solution (40 mM) at 70 °C for 30 min. The substrates were removed and washed with water and alcohol. In order to form the mesoporous electrode, TiO_2 paste was applied to FTO-coated substrates using the doctor blade method. In short, a mask was fabricated using commercially available scotch tape. The mask was placed on top of the FTO-coated glass substrate and allowed to adhere to the surface. TiO_2 paste was placed at the mask edge and carefully cast along the mask using a glass rod. This procedure allowed the TiO_2 paste to fill the void created by the mask. Electrodes were produced with two coatings of light-absorbing TiO_2 paste (20 nm) (GCell 18OB). Following this, one layer of light-scattering TiO_2 (150–200 nm particle size) (Dyesol WERO-2) was deposited. The deposited electrodes were air dried for approximately 30 min to allow for excess solvent evaporation. The TiO_2 working electrodes were finally treated to a sintering profile which consisted of a drying period at 125 °C for 6 min, ramping to 350 °C and holding for 15 min, ramping to 450 °C and holding for 15 min and finally sintering at 500 °C for 15 min. Once cooled, the electrodes were re-immersed in an aqueous $TiCl_4$ solution (40 mM) and heated to 70 °C for 30 min. Upon removal from the bath, electrodes were cleaned with water and alcohol and treated to a second sintering step at 500 °C for 30 min.

Dye adsorption: TiO_2 electrodes were soaked in a solution of di-tetrabutylammonium cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II)) (N719) dye in a *t*-butanol/acetonitrile mixture (1:1 (v/v)) for 16 hr. The process enables adsorption of a monolayer of the light-harvesting dye onto the mesoporous TiO_2 electrode. Upon removal from the dye solution, the electrodes were washed with ethanol to remove unadsorbed dye molecules from the surface and dried under flowing nitrogen.

Cell construction: A surlyn sealant (25 μm) was placed around the active area of the dye-sensitized electrode and the counter electrode (CE) was placed on top. The CE was fabricated by depositing platisol adhesive paste (Dyesol) onto cleaned FTO-coated glass and thermally treating at 400 °C for 15 min. The device was sealed by clamping both electrodes together and heating to 130 °C. At this temperature the surlyn seal melts and once cooled acts as a sealant between both electrodes. The organic electrolyte was prepared from the following formulation: 1-butyl-3-methyl imidazolium iodide (0.6 M) iodine (0.03 M), guandinium thiocyanate (0.10 M) and 4-tert-butylpyridine (0.5 M) were dissolved in a solvent mixture of acetonitrile and valeronitrile (85:15 vol. ratio) as described by Ito *et al.*[1] The electrolyte (25 μl) was placed over a 1 mm^2 hole drilled into the back of the counter electrode and when placed under vacuum the electrolyte was driven into the chamber between the electrodes in the cell. The hole in the CE was then sealed using a small portion of surlyn and a piece of glass.

Characterisation: Current density-voltage *(J-V)* measurements were performed using a Keithley 2401 source meter and the data acquisition was recorded using the Tracer 2 software. The incident-photon-to-current-efficiency (IPCE) was measured using a home-built instrument, as shown in **Figure S2**.

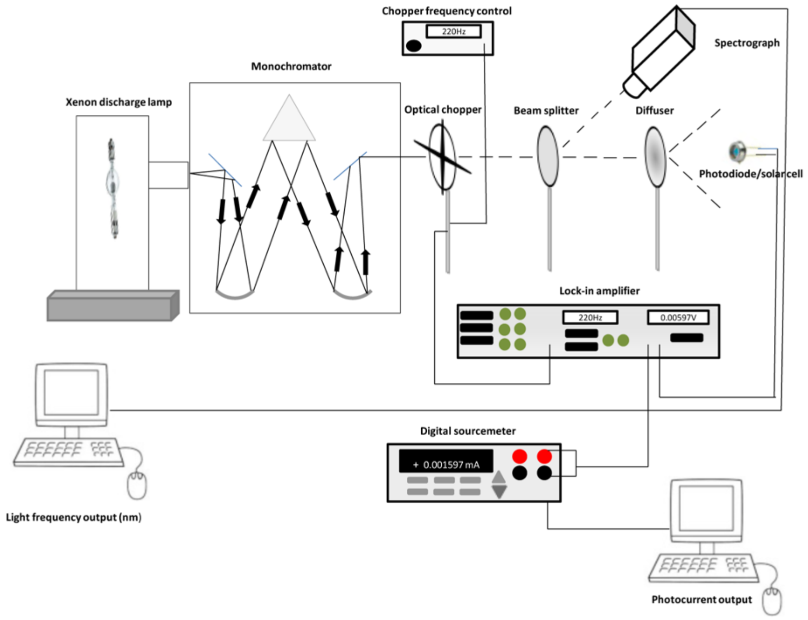

Figure S2. Experimental setup used to measure the IPCE (incident-photon-to-current) response of DSSCs (dye-sensitised solar cells).

3. Fabrication and Characterisation of QD-LSC-DSSCs

The thin strip DSSC was adhered to one edge of the LSC of choice using an optical grade sealant. Once the DSSC was sufficiently adhered to the surface of the LSC the performance of the integrated QD-LSC-DSSC device was evaluated as follows.

The power conversion efficiency (PCE) of the DSSC was first estimated using the optical power output (OP_{out}) of the single LSC edge to which the cell was adhered and the measured cell parameters according to:

$$PCE_{LSC} = \frac{I_{SC} V_{OC} FF}{OP_{in}} \tag{1}$$

where I_{SC} is the short-circuit current (0.76 mA), V_{OC} is the open-circuit voltage (0.56 V) and FF is the fill factor (0.55). The measured OP_{in} was 8.64 mW. NB: The areas of the LSC edge and the active surface of the DSSC are identical.

4. Characterisation of CdSe@ZnS/ZnS polymer composites

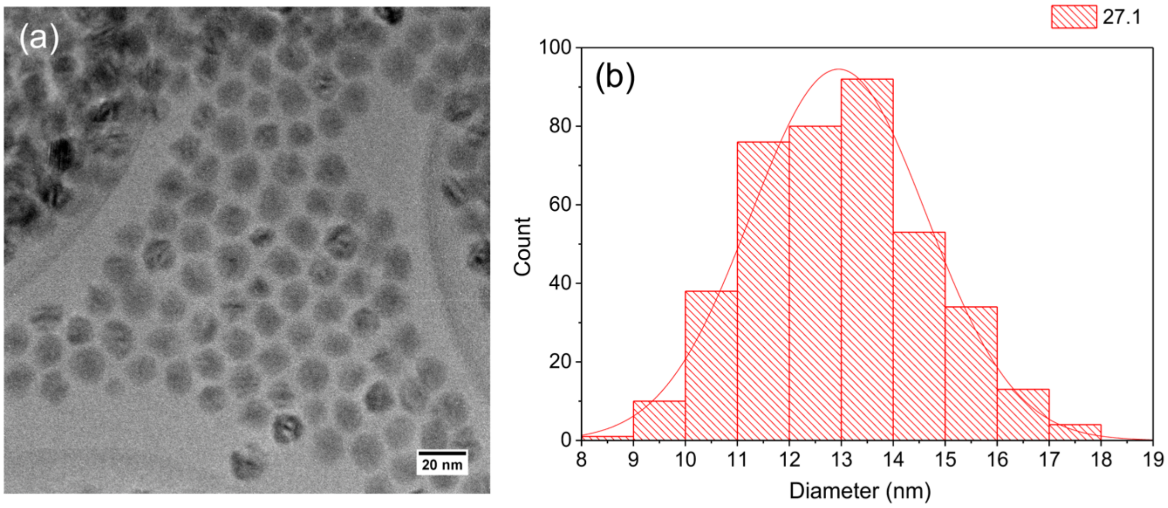

Figure S3. (a) Representative HRTEM image of CdSe@ZnS/ZnS nanoparticles and (b) histogram of the corresponding diameter of the nanoparticles as analysed by TEM using the ImageJ programme. The solid line represents a Schulz distribution fit to the data.

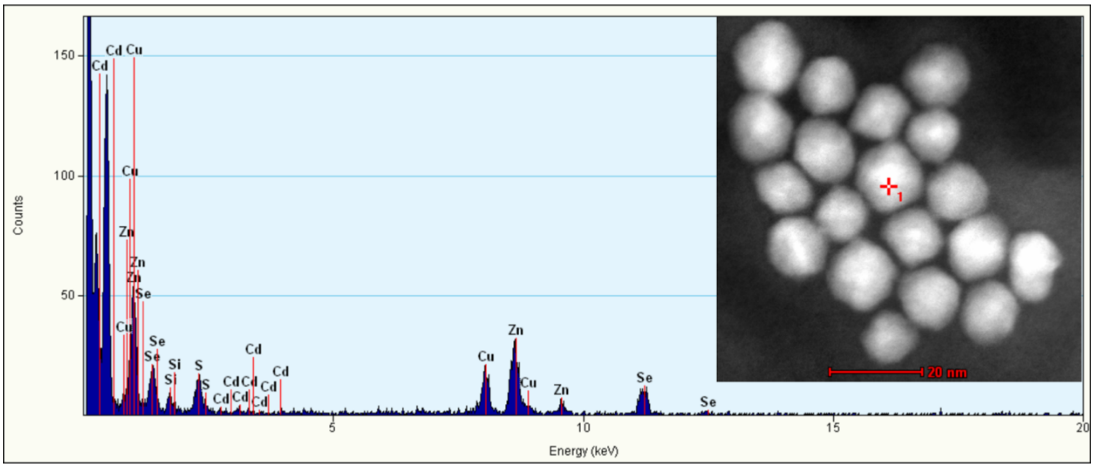

Figure S4. Energy dispersive x-ray (EDX) spectrum of CdSe@ZnS/ZnS QDs carried out using scanning tunneling spectroscopy conditions (inset: point of analysis).

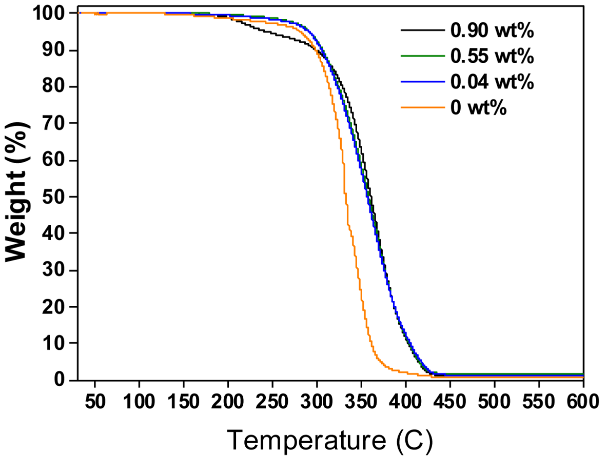

Figure S5. Thermogravimetric analysis of QD-doped LMA-*co*-EGDM polymer composite.

Table S1. Absolute photoluminescence quantum yields (Φ_{PL}) measured for CdSe@ZnS/ZnS quantum dots in hexane. Measurements were performed using an F-3018 integrating sphere 194 mounted into a FluoroMax-4 spectrophotometer (Horiba Jobin-Yvon). Samples were excited at 460 nm with a band pass of 1.1 nm.

Trial no.	**Φ_{PL} (%)**
1	63.1
2	62.3
3	68.4
Mean	**65±3**

5. Optical Efficiency of QD-LSCs

5.1 Experimental set-up for determination of the optical efficiency of LSCs

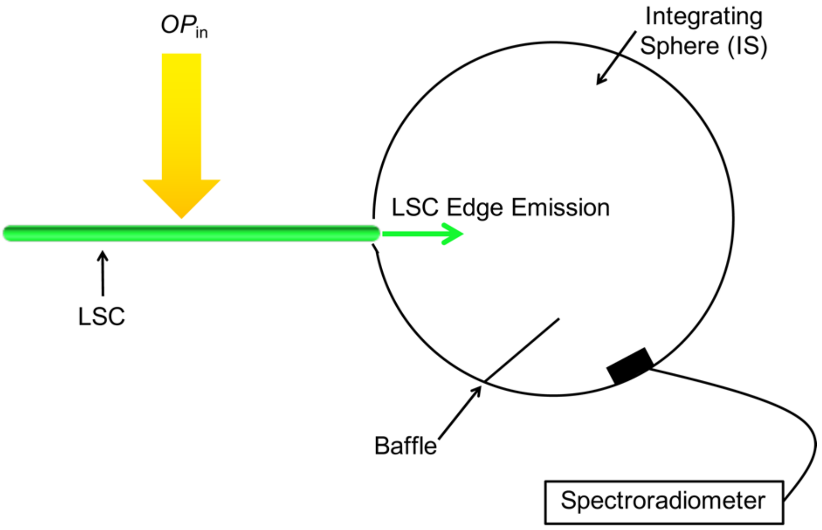

Figure S6. Experimental set-up used for measuring the optical efficiencies of fabricated LSCs. The top surface of the LSC is fully irradiated with solar simulated light. The edge emission from the LSC is directed towards the open port on an integrating sphere, which is connected via an optical fibre to a spectroradiometer.

5.2 Estimation of the Theoretical Efficiency of QD-LSCs

From the UV/Vis absorption spectrum of the CdSe@ZnS/ZnS QDs (Figure 2b, main manuscript), it can be estimated that photons are absorbed in the region from 350-500 nm. From the AM 1.5G solar spectrum[2], the number of photons between 350-500 nm is 3.80×10^{20} m^{-2} s^{-1}. The area of the top surface of the LSC is 0.009 m^2, and thus the total number of photons incident on the top surface of the LSC is (7.65×10^{20} m^{-2} $s^{-1} \times 0.009$ m^2) = 3.42×10^{18} s^{-1}. The photoluminescence quantum yield is 0.65 (Table S1). The theoretical loss of any LSC is approximately 30% (including the surface cone loss and the thermodynamic limit of the luminophore).[3] Therefore, accounting for these losses the maximum theoretical number of the photons that can be emitted from the edge of the QD-LSC is given by 3.42×10^{18} $s^{-1} \times 0.65 \times (1\text{-}30\%) = 1.56 \times 10^{18}$ s^{-1}. Assuming that all the edge emitted photons are centred at 513 nm (Figure 2b), the energy of the mitted photons is given by 1.56×10^{18} $s^{-1} \times h \times c/\lambda = 513$ nm = 0.6 W.

Therefore, the theoretical upper limit of the optical efficiency from this QD-LSC is 0.6 W / 1000 W $m^{-2} \times 0.009$ m^{-2} = 6.7%. The actual optical efficiency should be much less than this value as reabsorption losses, scattering losses and geometric effects are not included in the estimation.

5.3 Measurement of Edge Emission and Calculation of Optical Efficiency

Table S2. Measured edge emission, total optical power output (OP_{out}) and optical efficiencies (η_{opt}) of QD-LSCs. References

QD concentration (wt%)	Edge 1 (μW)[a]			Edge 2 (μW)[b]			Edge 3 (μW)[a]			Edge 4 (μW)[b]			Total OP_{out} (μW)	η_{opt}[d] (%)
	E1	E2	E3	E1	E2	E3	E1	E2	E3	E1	E2	E3		
0	3706	3778	4298	3996	4130	5475	5841	6284	5575	5545	4321	5143	46026	0.51
			Mean = 3977			**Mean = 4534**			**Mean = 5900**			**Mean = 5003**		
			Full Edge[c] = 9818			**Full Edge[c] = 10201**			**Full Edge[c] = 14750**			**Full Edge[c] = 11257**		
0.04	5835	4864	5641	4864	4235	4452	5185	4187	4232	6796	4636	5557	47858	0.53
			Mean = 5447			**Mean = 4517**			**Mean = 4534**			**Mean = 5663**		
			Full Edge[c] = 13617			**Full Edge[c] =10163**			**Full Edge[c] = 11337**			**Full Edge[c] =12742**		
0.15	4197	5466	4344	5030	4547	5251	4787	5546	5049	5924	4937	6119	48346	0.54
			Mean = 4669			**Mean = 4943**			**Mean = 5127**			**Mean = 5660**		
			Full Edge[c] = 11672			**Full Edge = 11121**			**Full Edge[c] = 12818**			**Full Edge[c] = 12735**		
0.30	4970	5791	4353	4795	5225	4636	6411	5532	5192	5222	6039	5996	50786	0.56
			Mean = 4669			**Mean = 4943**			**Mean** = 5127			**Mean = 5660**		
			Full Edge[c] = 11672			**Full Edge[c] = 11121**			**Full Edge[c] = 12818**			**Full Edge[c] = 12735**		
0.55	4749	5150	6308	6229	7438	7240	5646	6649	6260	5535	5079	5665	56858	0.63
			Mean = 5402			**Mean = 6969**			**Mean = 6185**			**Mean = 5426**		
			Full Edge[c] = 13506			**Full Edge[c] = 15680**			**Full Edge[c] = 15462**			**Full Edge[c] = 12209**		
0.70	10279	12303	9955	9538	7438	10219	11095	10858	11433	13554	11924	12606	106250	1.18
			Mean = 11033			**Mean= 9904**			**Mean = 11127**			**Mean = 12695**		
			Full Edge[c] = 27581			**Full Edge[c] = 22284**			**Full Edge[c] = 27822**			**Full Edge[c] = 28563**		
0.90	12210	10941	12325	10583	10932	10560	11744	9617	12844	11899	13033	11918	109761	1.22
			Mean = 11825			**Mean = 10692**			**Mean = 11402**			**Mean = 12283**		
			Full Edge[c] = 29563			**Full Edge[c] = 24056**			**Full Edge[c] = 28504**			**Full Edge[c] = 27638**		

[a] Edge length = 10 cm [b] Edge length = 9 cm. [c] Full edge = (mean/4)× edge length. [d] η_{opt} = Total OP_{out}/ OP_{in}. OP_{in} = 9000 mW.

The optical output at each edge of an LSC was determined by collecting the edge emission at three overlapping intervals (E_n) across the edge length using the 4 cm entry port to the integrating sphere, as illustrated in **Figure 4d** in the main manuscript. The optical power spectrum obtained at each interval was integrated between 250-1050 nm to obtain the optical power for a 4 cm slice. The mean integrated optical power for the three overlapping intervals was determined and this was extrapolated to obtain OP_{out} for the full edge length (9 or 10 cm). Total OP_{out} is the sum of the full edge optical output of all four edge

6. References

1. S. Ito, T. N. Murakami, P. Comte, P. Liska, C Grätzel, M. K. Nazeeruddin and M. Grätzel, *Thin Solid Films*, 2008, **516**, 4613.

2. http://rredc.nrel.gov/solar/spectra/am1.5/ Accessed 20th November 2017.

3. H. Hernandez-Noyola, D. H. Potterveld, R. J. Holt and S. B. Darling, *Energy Environ. Sci*, 2012, **5**, 5798.