

Electronic Supplementary Information

Improving the light harvesting and colour range of methyl ammonium lead tri bromide (MAPbBr₃) perovskite solar cells through co-sensitisation with organic dyes

Tamara D. McFarlane,^a Catherine S. De Castro,^a Peter Holliman,^b and Matthew L. Davies^{a*}

^a Applied Photochemistry Group, Materials Research Centre, SPECIFIC IKC, Swansea University, Bay Campus, Fabian Way, Crymlyn Burrows, Swansea, SA1 8EN.

^b CEMEG-Swansea (Chemistry Engineering Materials Environment Group), Materials Research Centre, SPECIFIC IKC, Swansea University, Bay Campus, Fabian Way, Crymlyn Burrows, Swansea, SA1 8EN.

*Corresponding author. Tel.: (01792) 606955

Email address: M.L.Davies@swansea.ac.uk

This paper describes the successful co-sensitisation of methyl ammonium lead tri bromide (CH₃NH₃PbBr₃) perovskite solar cells (herein referred to as MAPbBr₃) using two separate dyes (D205 and SQ2). Co-sensitised MAPbBr₃ devices have shown increased spectral response and have generally shown improved performance in comparison to control non-sensitised devices. Improved short-circuit current is observed for 'hero' co-sensitised devices whereas an improvement in the fill factor was found to be an important factor in improving device efficiency. This ESI includes details of the materials and methods used to fabricate both control and co-sensitised MAPbBr₃ films and devices. Also detailed are the instrumental methods used to characterise the devices and the resultant testing data generated for each replicate.

Experimental

All chemicals were purchased from Sigma-Aldrich and used as supplied unless otherwise stated.

Thin film manufacture

A total of 13 devices were manufactured with 8 thermally evaporated pixels per device. Each pixel had an area of 0.1 cm². Devices were prepared on 2 mm thick fluorine doped tin oxide (FTO) glass (15 Ω sq⁻¹, R_a: 12 nm, NSG Pilkington). To prevent device shunting, the FTO was removed from the regions which would be under the anode contact during device measurement by etching with 2 M HCl and zinc powder. The etched FTO substrate was then cleaned and sonicated sequentially (10 minutes per solution) in 2% Hellmanex detergent, deionised water, acetone and isopropanol. A compact titania layer (Ti nanoxide BL/SC, Solaronix) was then deposited on each of the glass substrates through spin coating 100 μL of solution at 3000 rpm for 30 seconds followed by annealing on a pre-heated hotplate at 150 °C for 10 minutes. A mesoporous titania solution was prepared by diluting titania paste (30-NRD, Dyesol) in ethanol (2:7 by weight) and deposited *via* spin coating 100 μL at 4500 rpm for 30 seconds. The substrates were annealed at 150 °C for 10 minutes followed by sintering at 550 °C for 30 minutes.

Co-sensitising dyes

D205 dye (Sigma-Aldrich)

Systematic name: 5-[[4-[4-(2,2-Diphenylethenyl)phenyl]-1,2,3,3a,4,8b-hexahydrocyclopent[*b*]indol-7-yl]methylene]-2-(3-octyl-4-oxo-2-thioxo-5-thiazolidinylidene)-4-oxo-3-thiazolidineacetic acid.

Formula: C₄₈H₄₇N₃O₄S₃

Molecular Weight: 826.10 g/mol

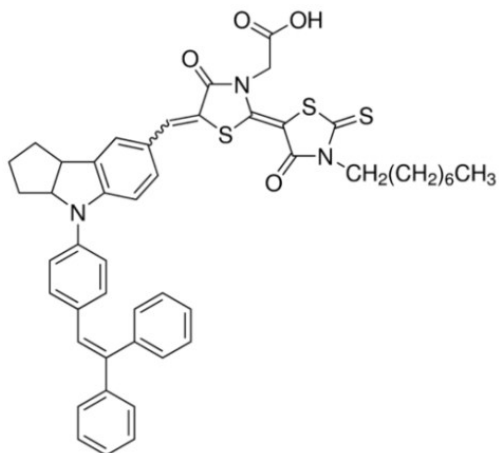
SQ2 dye (Solaronix)

Systematic name: 5-carboxy-2-[[3-[(2,3-dihydro-1,1-dimethyl-3-ethyl-1H-benzo[*e*]indol-2-ylidene)methyl]-2-hydroxy-4-oxo-2-cyclobuten-1-ylidene)methyl]-3,3-dimethyl-1-octyl-3H-indolium.

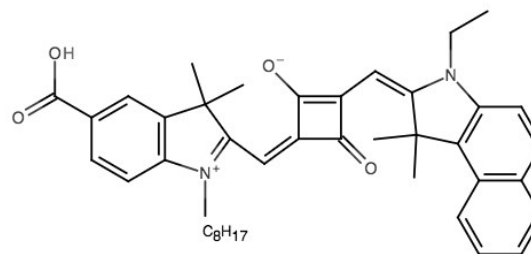
Formula: C₄₁H₄₆N₂O₄

Molecular Weight: 630.81 g/mol

(a)



(b)



ESI Fig 1. (a) Chemical structure of D205 dye and (b) chemical structure of SQ2 dye.

Dye solution preparation

Dye solutions of 1.0 mM SQ2 and 1.0 mM D205 were prepared in anhydrous toluene.

Solid state dyed thin film preparation

Solid state dyed thin films were prepared by submerging titania coated thin films (prepared as described above) in the appropriate dye solution for 10 minutes. The thin films were then dried with an air gun.

Perovskite precursor preparation

To synthesis a 1 mL MAPbBr₃ precursor solution, 0.140 g of methylammonium bromide (GreatCell Solar) was combined with 0.459 g of lead(II) bromide powder (99.9%, Sigma-Aldrich). A 1 mL 4:1 volume solution of N, N-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) was prepared by adding 0.8 mL of DMF to 0.2 mL of DMSO. The previously combined powders were then dissolved in the DMF: DMSO solution through stirring and heating at 60 °C on a pre-heated hot plate. Once fully dissolved, the perovskite precursor solution was removed from the hot plate and filtered through a 0.2 μm PTFE syringe filter (Minisart, Sartorius). 100 μL of this solution was then deposited onto the mesoporous titania layer *via* spin coating at 4000 rpm for 30 s. After spin coating, the MAPbBr₃ thin films were annealed on a pre-heated hot plate at 60 °C for 10 minutes.

Co-sensitisation of MAPbBr₃ thin films

Co-sensitisation/dyeing was carried out using one of two methods:

‘Dye before’ DB method

The mesoporous titania layer was dyed prior to deposition of the perovskite layer by submerging the titania coated thin film in the appropriate dye solution for 10 minutes. The thin films were then removed from the dye solution and dried with an air gun. Once dry, 100 μL of MAPbBr₃ precursor solution was deposited onto the mesoporous titania layer by spin coating at 4000 rpm for 30 s. After spin coating, the MAPbBr₃ thin films were annealed on a pre-heated hot plate at 60 °C for 10 minutes.

‘Dye after’ DA method

Co-sensitisation of the MAPbBr₃ layer was carried out following annealing of the perovskite. Once cooled to room temperature, the MAPbBr₃ thin films were submerged the appropriate dye solution for 10 minutes. The thin films were then dried with an air gun.

Toluene soak method

As a control measure and to assess the effect of the dye solvent, MAPbBr₃ thin films were submerged in anhydrous toluene for 10 minutes. The thin films were then dried with an air gun.

Full device manufacture

Following co-sensitisation, a hole-transport layer (HTL) solution was prepared which contained 0.085 g of 2, 20, 7, 70-tetrakis-(N, N-di-p-methoxyphenylamine)-9, 90-spirobifluorene (spiro-OMeTAD) (99%, Sigma-Aldrich) dissolved in 1 mL of chlorobenzene. 19 μL of lithium bis(trifluoromethanesulfonyl)- imide in acetonitrile (520 mg/mL) and 34 μL of 4-tert-butylpyridine was then added. 100 μL of the HTL solution was spin coated onto each thin film at 4000 rpm for 20 s. The thin films were left in air overnight to encourage oxidation of the spiro-MeOTAD layer. To complete as full devices, 80 nm gold contacts (pixels) were deposited on each film by the thermal evaporation of gold wire (Kurt J Lesker) through a shadow mask at 10⁻⁴ Torr. The shadow mask generated 8 pixels per device, each with an area of 0.1 cm².

Thin film characterisation

UV-Visible spectroscopy measurement

The UV-Visible spectra of both control MAPbBr₃ and co-sensitised MAPbBr₃ films were measured prior to the deposition of the HTL. A Perkin Elmer Lambda 9 UV-Visible-NIR spectrophotometer was used to measure the absorbance of the films over a wavelength range of 200-800 nm.

Device Testing

Efficiency measurement

Prior to testing, each device was masked using a sheet of black-painted steel (with an aperture of set dimensions) which was overlaid over the active area. The current-voltage (JV) curves of the masked devices were measured using a class AAA solar simulator (Newport Oriel Sol3A) which was calibrated against a KG5-filtered silicon reference cell (Newport Oriel 91150-KG5) to provide an irradiance of one sun (AM 1.5 and 100 mW cm⁻²). Voltage sweeps across the device were applied using a Keithley Instruments 2400 source meter from 1.2 V to -0.1 V at 0.015 Vs⁻¹ with a 100 ms dwell time between points. A 3 mA current limit was also used.

ESI Table. 1 Measured photovoltaic performance data for control MAPbBr₃ devices, MAPbBr₃ devices submerged in toluene (MAPbBr₃/Tol), MAPbBr₃ devices co-sensitised with SQ2 and D205 using the ‘dye before’(DB) method (MAPbBr₃/SQ2 DB and MAPbBr₃/D205 DB, respectively) and MAPbBr₃ devices co-sensitised with SQ2 and D205 using the ‘dye after’ (DA) method (MAPbBr₃/D205 DA and MAPbBr₃/D205 DA, respectively) when measured at 1 Sun (100 mW.cm⁻²). Tabulated values represent the measured values for the 8 pixels per device. The grey shaded rows represent the ‘hero’ pixel of the pixels measured per variable. Pixels marked with an asterisk (*) represent anomalous results believed to arise from device defects. These values (0.1% efficiency or below) were omitted from the final average device values listed in Table 2.

Device ID	Pixel ID	J_{sc} (mA/cm ²)	V_{oc} (V)	Fill Factor	PCE (%)
Control MAPbBr₃ (1)	1	4.2	0.81	50	1.7
	2	4.47	0.81	46	1.7
	3	4.49	0.81	45	1.6
	4	4.21	0.82	52	1.8
	5	3.96	0.84	51	1.7
	6	4.76	0.81	50	1.9
	7	4.89	0.79	51	2.0
	8	4.49	0.79	56	2.0
Control MAPbBr₃ (2)	1	3.9	0.8	58	1.8
	2	4.34	0.59	30	0.8
	3	4.3	0.78	43	1.4
	4	4.15	0.76	49	1.6
	5	4.55	0.31	36	0.5
	6	4.93	0.74	43	1.6
	7	4.89	0.74	51	1.9
	8	4.71	0.71	57	1.9
MAPbBr₃/Tol (1)	1	3.84	0.74	21	0.6
	2	3.53	0.26	23	0.2
	3	3.62	0.39	23	0.3
	4	4.08	0.91	51	1.9
	5	4.69	0.67	33	1.0
	6	4.75	0.91	30	1.3
	7	4.75	0.91	38	1.6
	8	4.68	0.89	70	2.9
MAPbBr₃/Tol (2)	1	4.3	0.86	68	2.5
	2	4.24	0.91	60	2.3
	3	4.4	0.96	60	2.5
	4*	4.09	0.08	28	0.1
	5	4.38	0.95	58	2.4
	6	4.38	0.92	61	2.5
	7	4.85	0.94	50	2.3
	8	4.6	0.84	46	1.8

MAPbBr₃/Tol (3)	1	4.51	0.76	57	2.0
	2	4.53	1.02	72	3.3
	3	4.57	1.00	69	3.2
	4	4.67	1.00	58	2.7
	5	4.42	0.93	53	2.2
	6	4.55	0.96	39	1.7
	7	4.93	0.91	30	1.4
	8	4.46	0.85	33	1.3
MAPbBr₃/SQ2 DB (1)	1*	2.75	0.15	26	0.1
	2	2.82	0.84	56	1.3
	3	2.82	0.88	57	1.4
	4	2.8	0.88	56	1.4
	5	3.18	0.85	56	1.5
	6	3.23	0.84	50	1.4
	7	3.11	0.84	50	1.3
	8	2.83	0.83	52	1.2
MAPbBr₃/SQ2 DB (2)	1	2.38	0.82	59	1.2
	2	2.63	0.85	58	1.3
	3	2.56	0.84	57	1.2
	4	2.56	0.84	55	1.2
	5	1.49	0.77	54	0.6
	6	3.26	0.81	45	1.2
	7	3.07	0.82	48	1.2
	8	3.06	0.82	53	1.3
MAPbBr₃/D205 DB (1)	1	2.42	0.96	54	1.3
	2	3.07	0.95	61	1.8
	3	3.08	0.98	67	2.0
	4	2.57	0.92	66	1.6
	5*	0.73	0.36	43	0.1
	6	2.42	0.86	57	1.2
	7	2.03	0.85	56	1.0
	8	3.06	0.96	61	1.8

MAPbBr₃/D205 DB (2)	1*	2.75	0.08	24	0.1
	2	2.43	0.98	66	1.6
	3	0.97	0.78	53	0.4
	4	1.64	0.97	56	0.9
	5	1.73	1.0	56	1.0
	6	1.54	0.96	55	0.8
	7	1.29	0.76	60	0.6
	8*	2.28	0.21	26	0.1
MAPbBr₃/SQ2 DA (1)	1	4.48	0.79	66	2.3
	2	4.09	0.76	68	2.1
	3	4.8	0.75	73	2.6
	4	3.95	0.76	72	2.2
	5	4.05	0.78	71	2.3
	6	4.1	0.75	72	2.2
	7	4.25	0.73	74	2.3
	8	4.12	0.75	73	2.2
MAPbBr₃/SQ2 DA (2)	1	4.11	0.33	30	0.4
	2	4.01	0.77	68	2.1
	3	3.87	0.77	68	2.0
	4	3.78	0.76	59	1.7
	5	3.79	0.75	63	1.8
	6	3.98	0.75	70	2.1
	7	3.87	0.74	65	1.9
	8	3.96	0.76	69	2.1

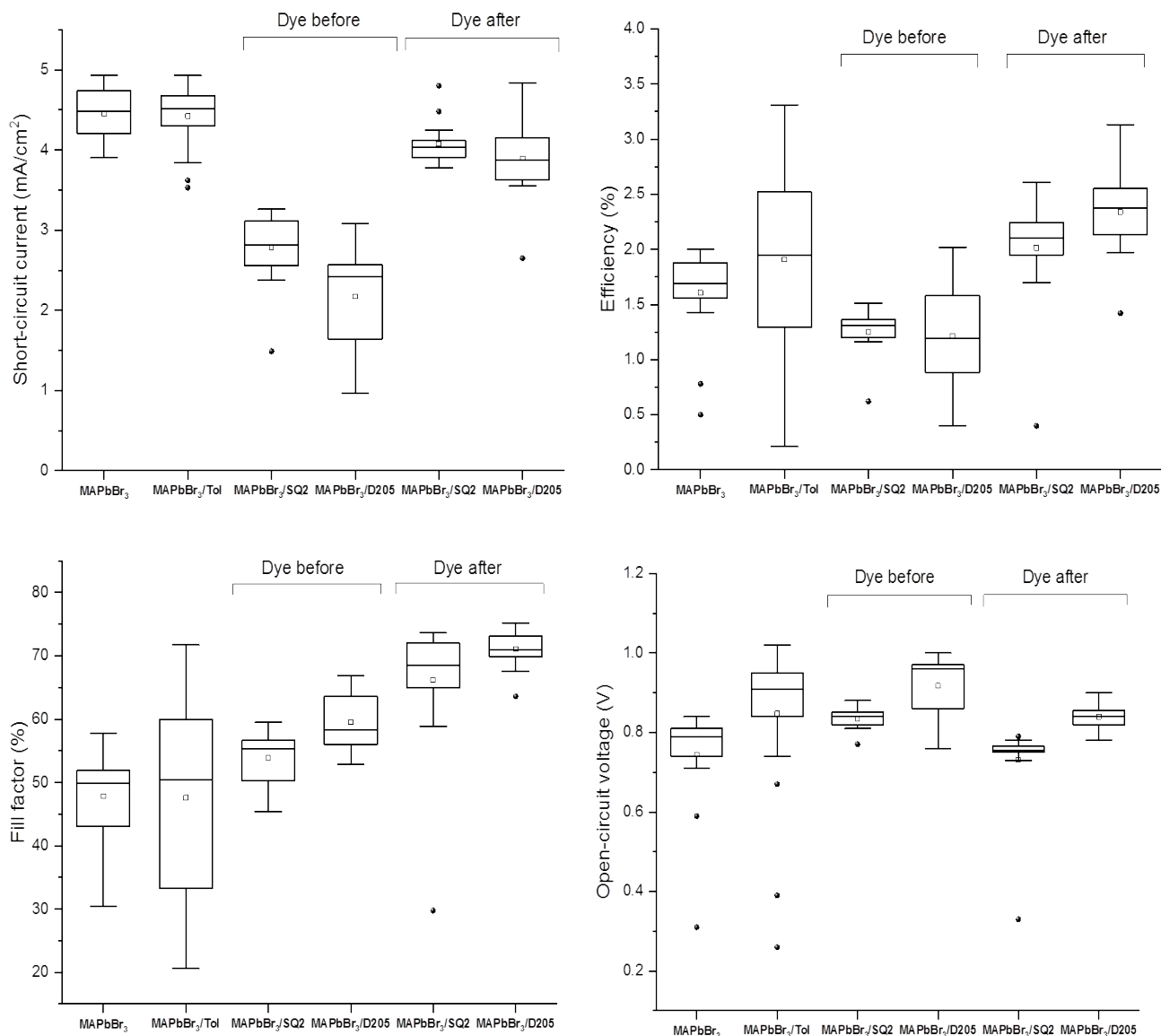
MAPbBr₃/D205 DA (1)	1	4.84	0.89	73	3.1
	2	4.21	0.85	73	2.6
	3	4.16	0.87	75	2.7
	4	3.74	0.9	75	2.5
	5	3.79	0.82	64	2.0
	6	3.63	0.82	72	2.2
	7	3.55	0.84	71	2.1
	8	3.89	0.83	74	2.4
MAPbBr₃/D205 DA (2)	1	4.11	0.85	70	2.5
	2	4.08	0.86	73	2.6
	3	3.85	0.84	70	2.3
	4	3.62	0.84	72	2.2
	5	2.65	0.78	69	1.4
	6	3.56	0.82	71	2.1
	7	4.15	0.84	68	2.4
	8	4.46	0.79	71	2.5

ESI Table. 2 Averaged photovoltaic performance data for control and co-sensitised devices measured at 1 Sun (100 mW.cm⁻²). Tabulated values represent the average values generated for the pixels measured per variable listed in Table 1, also included are the standard deviation (SD) for the values.

Device ID	Average J_{sc} (mA/cm²)	J_{sc} SD	Average V_{oc} (V)	V_{oc} SD	Average Fill Factor	FF SD	Average PCE (%)	PCE SD
Control MAPbBr ₃	4.45	0.32	0.74	0.13	48	7.4	1.6	0.41
MAPbBr ₃ /Tol	4.42	0.36	0.85	0.19	48	16.4	1.9	0.85
MAPbBr ₃ /SQ2 DB	2.79	0.49	0.84	0.03	54	3.97	1.3	0.2
MAPbBr ₃ /D205 DB	2.17	0.7	0.91	0.08	59	4.82	1.1	0.6
MAPbBr ₃ /SQ2 DA	4.08	0.26	0.73	0.11	66	10.5	2.0	0.48
MAPbBr ₃ /D205 DA	3.89	0.48	0.84	0.03	71	2.91	2.3	0.38

External quantum efficiency measurement

External quantum efficiency (EQE) measurements were generated using a PV Measurements QEX10. Spectral response was measured in DC mode between 300-800 nm with a step size of 10 nm. A white light bias was not used. EQE measurements were made for the highest performing pixel out of the replicate devices (16 pixels in total) per variable.



ESI Fig. 2 Box plots displaying the spread of photovoltaic performance data generated for control MAPbBr₃ devices, MAPbBr₃ devices submerged in toluene (MAPbBr₃/Tol), MAPbBr₃ devices co-sensitised with SQ2 and D205 using the ‘dye before’ (DB) method (MAPbBr₃/SQ2 DB and MAPbBr₃/D205 DB, respectively) and MAPbBr₃ devices co-sensitised with SQ2 and D205 using the ‘dye after’ (DA) method (MAPbBr₃/SQ2 DA and MAPbBr₃/D205 DA, respectively) when measured at 1 Sun (100 mW.cm⁻²).

Acknowledgements

CSDC and MLD are grateful for the financial support from EPSRC (EP/R016666/1) and both EPSRC and Innovate UK for the SPECIFIC Innovation and Knowledge Centre and the European Regional Development Fund through the Welsh Government for support to the Sêr Solar program.