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Visually attractive and efficient photovoltaics through luminescent downshifting

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Table S1: A few literature based comparisons of solar cell performance with and without LDS layers for different PV technologies

Solar cell	Device configuration	PCE (%)		
Si[1]	Organic lumogen dyes doped with PMMA were used as the LDS layer. The doped/ undoped PMMA based LDS layer was coupled to Si solar cells with silicone (Wacker Silgel 612) and prior to encapsulation, a metal tab was soldered to the busbar to permit electrical contact to the cell.	Modules using cells with 30Ω/sq emitters	Without LDS-undoped PMMA	14.6
			LDS-Lumogen570	13.8
			LDS-Lumogen083	14.5
			LDS-Lumogen300	14.7
		Modules using cells with 70Ω/sq emitters	Without LDS-undoped PMMA	13.9
			LDS-Lumogen570	14.5
			LDS-Lumogen083	13.8
			LDS-Lumogen300	14.4
Si[2]	Different Eu(III) complexes (**1**-**5**) on polyvinyl acetate (PVA) matrix were used as LDS materials. Film casting method was used for film depositions. Polymeric LDS films of 100- 200 µM thickness were deposited on c-Si PV module (Trina solar Co., Ltd)	Without LDS		16.05
		undoped PVA		16.04
		PVA-LDS film1		15.86
		PVA-LDS film2		16.12
		PVA-LDS film3		16.04
		PVA-LDS film4		16.26
		PVA-LDS film5		16.37
Si[3]	Large area luminescent films of lanthanide (EuIII)/Tb(III) doped ionic liquid (IL) solution with PMMA prepared by drop-casting to a glass substrate. These LDS layers were applied as coating on Si-based heterojunction solar cells	undoped PMMA		16.67
		With $Eu(pybox)_3IL$		16.76
		With $Tb(pybox)_3IL$		16.77
		With $Eu(tta)_3IL$		16.47
Si[4]	Lumogen violet 570 doped in PMMA was used as the LDS layer and, deposited on the top of monocrystalline-Si solar cells (2*2 cm, sunrydz Germany)	Without LDS		7.20
		undoped PMMA		6.35
		With LDS		8.54
Si[5]	Commercially available pc-Si solar cells without the Si_3N_4-antireflection layer were used. PVP doped $Gd_2O_2S:Eu^{2+}$ nanophosphors with different particle sizes (GS125, GS290 and GS419 having particle sizes 125±9 nm, 290±20 nm and 419±29nm, respectively) were used as the LDS materials and spin coated on the pc-Si solar cells	Without LDS		10.44
		undoped PVP		11.85
		With PVP/GS125		12.35
		With PVP/GS290		12.97
		With PVP/GS419		12.73
Si[6]	Ce^{3+}-doped yttrium aluminium garnet nanophosphor ($YAG:Ce^{3+}$) based LDS material was spin coated on the top of commercially available monocrystalline Si solar cells	Without LDS		15.30
		With LDS		15.46
Si[7]	Single crystalline Si (c-Si, T1S2-GC061) and multi-crystalline Si (mc-Si, T1M2-V0761) solar cells were purchased from Tainergy Tech. co., Ltd., Taiwan. An insitu fabricated $CH_3NH_3PbBr_3$ perovskite quantum dot/ polyacrylonitrile composite film was used as the LDS layer, which was spincoated on the surface of solar cell	c-Si without LDS		14.05
		c-Si with LDS		14.99
		mc-Si without LDS		10.44
		mc-Si with LDS		11.32
Si[8]	2D-BNCO (boron carbon oxynitride) silica gel was used as the LDS layer. BNCO was spin-coated on	Si solar cell		13.6

	the glass substrate and placed on the commercially available Si solar cells in two ways, LDS layer/Glass/Si solar cell and Glass/LDS layer/Glass/ Si solar cell.	LDS layer/Glass/Si solar cell		14.1
		Glass/LDS layer/Glass/ Si solar cell		14.6
DSSC[9]	Cells were assembled with D205-sensitized TiO_2, a iodide/triiodide electrolyte, pt-sputtered counter electrode, LDS (EuD_4TEA) was coated on the external side of photo anode	Without LDS		2.68
		With LDS		4.50
DSSC[10]	Eu^{2+}-doped red phosphors $CaAlSiN_3:Eu^{2+}$ (LDS1), $Ca_2Si_5N_8:Eu^{2+}$ (LDS2) and $CaZnOS:Eu^{2+}$ (LDS3) were used as the reflective LDS (R-LDS) material. The free-standing R-LDS layer was made by pressing the phosphor powder at pressure 2 MPa; the layer was placed on top of the DSSC on either the counter electrode (CE) side or working electrode (WE) side	Front illumination	Without LDS	3.6
			LDS1 -CE	5.0
			LDS2 -CE	4.8
			LDS3 -CE	4.5
		Back illumination	Without LDS	3.3
			LDS1 -WE	4.8
			LDS2 -WE	4.5
			LDS3 -WE	4.1
Organic solar cells[11]	After fabricating the standard P3HT: PCBM heterojunction device, the fluorescent LDS layer was evaporated at the back side. The device structure is LDS layer/glass/ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al	Without LDS		2.50
		With LDS		2.68
Polymer solar cells[12]	The PSCs were fabricated with an inverted structure, ITO/C545T:Alq_3/P3HT:PCBM/MoO3/Al. The LDS film was prepared by spin coating the formic acid solution of C545T:Alq_3 LDS sensitizer on ITO glass substrate in a glove box, then the active layer P3HT:PCBM were spin coated on top of the LDS substrate. Then finally MoO_3 hole collection layer and Al were thermal evaporated in a vacuum chamber through shadow masks.	Without LDS		3.28
		With LDS (3 wt% of C545T in C545T:Alq_3)		3.53
		With LDS (7 wt% of C545T in C545T:Alq_3)		3.82
		With LDS (10 wt% of C545T in C545T:Alq_3)		2.82
Organic solar cells[13]	The inverted cells were prepared by standard methods. The LDS layer AgPOP in $CHCl_3$ was deposited on the light incident surface of the OPV by doctor blading and allowing $CHCl_3$ to evaporate at room temperature. The final device structure is LDS layer/ITO/ZnO/PTB7:PCBM/MoO_3/Ag	Without LDS		3.66
		With LDS		3.76
Perovskite solar cells[14]	The perovskite solar cells with configuration ITO/PEDOT:PSS/$CH_3NH_3PbI_{3(1-x)}Cl_{3x}$/PCBM/Ag. Kremer fluorescent blue (KB) was used as the LDS material, 8 wt% solution of KB with PMMA in anisole was spin-coated onto the top facing side of the fused silica substrate and annealed at 60 °C for 15 min. A commercial UV filter (Solaronix, Switzerland) that cuts off light with a wavelength of less than 390 nm was used. The use of LDS layers showed a significant increase in lifetime of the PSC devices.	Bare cell		9.1
		With UV filter		7.6
		With LDS		7.9
Perovskite solar cells [15]	The perovskite solar cells were prepared with configuration FTO/LDS/FTO/TiO_2/ $CH_3NH_3PbI_3$/Spiro-OMeTAD/Au electrode. Au nanoparticle coated on the surface of $Y_2O_3:Eu^{2+}$ phosphor was used as the LDS material.	Without LDS		15.2
		With LDS		16.1
Perovskite solar cells[16]	Nanophosphor $Sr_2CeO_4:Eu^{3+}$ (SCOE) was used as the LDS material. Perovskite solar cells (PSC) were prepared with device configuration FTO/compact TiO_2/ SCOE LDS layer/ CsFAMA $PbBrI_2$ perovskite layer/ Spiro-OMeTAD/Ag. The	Without LDS	Reverse scan	16.6
			Forward scan	15.47
		With LDS	Reverse scan	18.95

	PSC also fabricated without LDS layer		Forward scan	18.40
Perovskite solar cells[17]	The PSC device configuration was FTO/Compact-TiO_2/ Mesoporous-TiO_2/Mixed Perovskite/Spiro-OMeTAD/Au. LDS coating composed of chloro-trifluoro-ethylene vinyl ether fluoropolymer binder, dimethacrylic oligomer with different weight ratios of Lumogen F violet 570 was used. LDS coating was spin coated on the front side of the device.	Without LDS		15.48
		With undoped fluoropolymer		14.47
		With LDS (0.5 wt% V570)		15.02
		With LDS (1 wt% V570)		15.66
		With LDS (1.5 wt% V570)		16.23
		With LDS (2 wt% V570)		16.93
		With LDS (2.5 wt% V570)		16.54
		With LDS (3 wt% V570)		16.65
CdTe -thin film solar cell[18]	CdTe mini module was purchased from Advanced solar power INC, China. Lumogen yellow dye doped with PMMA was drop-casted on glass substrate and left in oven for curing. The dried LDS layers were removed from glass and used. Further a plasmonic coupling between lumogen yellow dye and Ag nanoparticles have been studied for LDS. The plasomic LDS material (pLDS) was prepared by mixing dye and Ag nanoparticle in PMMA. The LDS/pLDS layers were directly deposited on the CdTe- mini module using PMMA solution to glue the layers.	Without LDS		5.3
		With LDS		5.8
		With pLDS		6.6

Method of preparation of LDS films in Figure 2a-f, from reference[19]

EVA (ethylene vinyl acetate) (PV 1650, DuPont) pellets were doped with different luminescent organic dyes to prepare coloured EVA sheets. Uniform thickness, coloured EVA sheets (each doped with a single dye) were obtained by means of extrusion and/or heat-assisted pressure molding. The pieces from differently coloured EVA sheets were cut using a CO_2 laser and manually assembled onto the mini-modules before lamination. The differently coloured EVA pieces were laminated directly on the top glass of the commercial solar cell mini-modules using a 50 μm-thick fluorocarbon film (FEP, DuPont) as cover. Vacuum laminator (EETS PVLAM 1.0) was used and an encapsulation cycle of 155°C for 4 min with no external pressure and 2 min under atmospheric pressure from the top was followed, resulting in bubble-free samples.

Method of preparation of LDS films in Figure 3, from reference[20]

A homogeneous DCM solution of PMMA pellets and dyes were poured onto a cleaned bare glass substrate, to get the LDS layer with 100 μm thick after the solvent evaporation. The sheets are first dried at room temperature inside a fume cupboard and covered with a cardboard box to prevent their surface drying too fast and rippling and then they are left overnight at 60ºC inside a vacuum oven. The layers are peeled from the glass substrate by placing them under water and pulling gently from their corners. LDS layers obtained by this method are very homogeneous, with a thickness dispersion of less than ±10% across the whole sample, excluding the edges that tend to be thicker. LDS sheets are cut to 10.5 cm × 10.5 cm excluding the thicker edges, and fixed on CdTe mini-modules (10 cm × 10 cm) using glycerine.
For CIGS and mc-Si solar cells non-formulated EVA PV1650 (Dupont) was used as the polymer host and appropriate dye was added before or during sheet extrusion. The LDS layer was attached to CIGS solar cells using glycerine. In case of mc-Si a vacuum laminator was used for attaching the LDS layer.

Method of preparation of LDS films in Figure 4, from reference[21]

The PMMA was dissolved in a mixture of 1,3-dimethoxybenzene and 5 vol% hexylbenzene and appropriate lumogen dye was added to it, to achieve PMMA films with different colours, to use as LDS layers. The printing conditions with 25 μm drop spacing and 5 nozzles in ambient conditions with a Dimatix DMP 2831 and a Fujifilm Dimatix 10 pl cartridge, resulted in the best layer formation. A custom designed waveform was applied and the maximum jetting frequency was set to 5 kHz. The print head temperature was set to 37 °C.

LDS-doped PMMA layers of varying thickness were printed on additional glass substrates. For the optoelectronic characterization of the coloured PSC prototypes, the LDS samples were simply stacked on top of the PSC, with the two glass substrates being optically coupled via a refractive index matching fluid.

Materials and methods used in our work

Ethylene tetrafluoroethylene (ETFE) films were purchased from Ossila Ltd, United Kingdom, and were activated by argon plasma treatment before printing, according to the reported literature.[22] Different solar cells were purchased from COLORADO INSTRUMENTS INC, USA. The various lumogen dyes used for printing, namely V570, Y083, R305, G170, O240 were procured from BASF, Germany and the red emissive europium complex, $Eu(tta)_3DPEPO$ was synthesized[23] and characterized in our lab. The EVA films used for lamination was purchased from the seller a1-cctv-electricals-solar through eBay. The host matrix PMMA polymer (mol. Wt. 15000) was purchased from Fisher scientific and used as received.

Method of preparation of LDS films used in our work (Figures 5-8 and S1-S8)

The inks used for printings were prepared according to a reported procedure,[21] for instance, 0.5 wt% solution of respective lumogen dye in PMMA was made with 1: 0.05 composition of dimethoxybenzene and hexylbenzene. Dimatix Materials Printer DMP-2831 was used for inkjet printing. The similar details and settings described by Richards et al was followed for printing,[21] which include, 5-16 nozzles; meniscus vacuum set point 5; cartridge temperature 46-50 °C; firing voltage from 16 to 25 V; platen temperature 60 °C; 1 to 4 layers of print; cleaning cycle: spit purge 0.5 s, but other works as well; waveform Pt_carbitol_2_5kHz-modified. ETFE film was then laminated on solar cell using standard EVA film as an adhesive. The thickness of the layer is approximately in the range of 25-50 μM. For lamination standard Amazon Basics A4 Thermal Laminator has been used.

Cost analysis for developing coloured/ graphically designed solar modules

According to the method described by Richards and co-workers, a 1 m^2 active area of PV module can be encapsulated with a lumogen dye doped EVA sheet at an additional cost of less than US$1¢.[24]

Our findings: We use 0.5% wt of the dye in PMMA (15 000 Da- from Fisher scientific costs 153$ per 100 g). Printed graphic has between 50-200 mg (like UoE logo) on 12.5 cm x 12.5 cm solar cell. This gives dye usage around 1 mg costing 1.5 ¢ and PMMA usage of 200 mg costing 30 ¢. The cost of PMMA will be negligible if the bulk supplier will be used. ETFE foil costs only 80 $ per 10 m, will be cheaper if orders are in bulk. Cost of printing will include also solvents but their usage is very low since viscous ink formulation need to be applied for high quality printing. Therefore, final cost of materials would rather in the range of few to ten cents per 1 m^2. Presented approach allows easy implementation with currently existing solar cell technologies with small cost up to maximum of 1 USD/m^2 (when fully covered with dye), while the cost of manufacturing the silicon solar cells was 250-300 \$/m^2 in 2009,[24] this has dropped dramatically to 50 \$/m^2 in 2017.[25, 26]The cost of LDS materials did not change over this time, therefore the cost of implementation of LDS in solar panels increased from about 0.4% to 2.0 %, which is still low enough to justify its use.

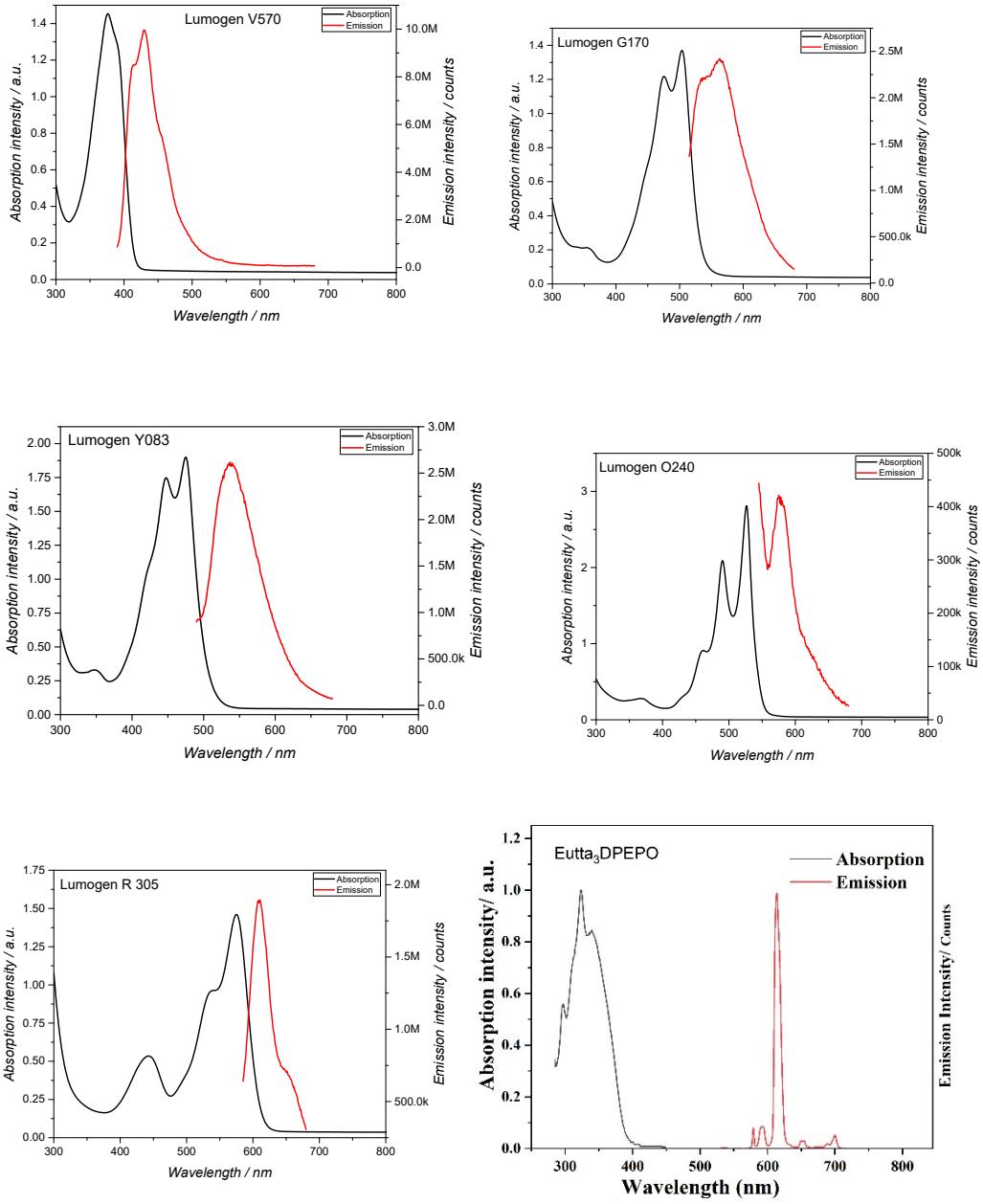

Figure S1: Absorption and emission spectra of different lumogen dyes used in Lumogen F Violet 570, Lumogen F Green 170, Lumogen F yellow Y083, Lumogen F Orange 240, Lumogen F Red 305 and Eutta$_3$DPEPO dyes used for developing coloured LDS layers in our work

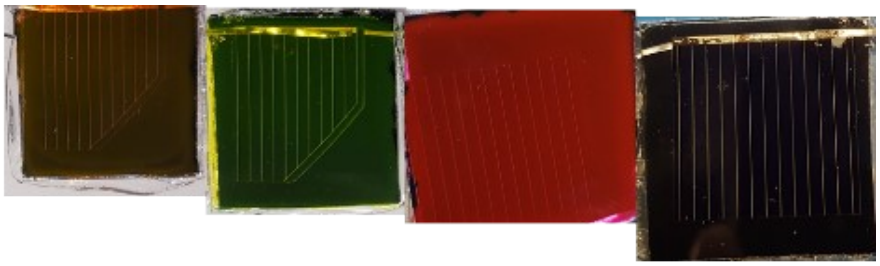

Figure S2. Prototypes employing single colour ETFE foil used for encapsulation of solar cells (2 cmx2 cm), under the sun (top) and UV-light illumination (bottom).

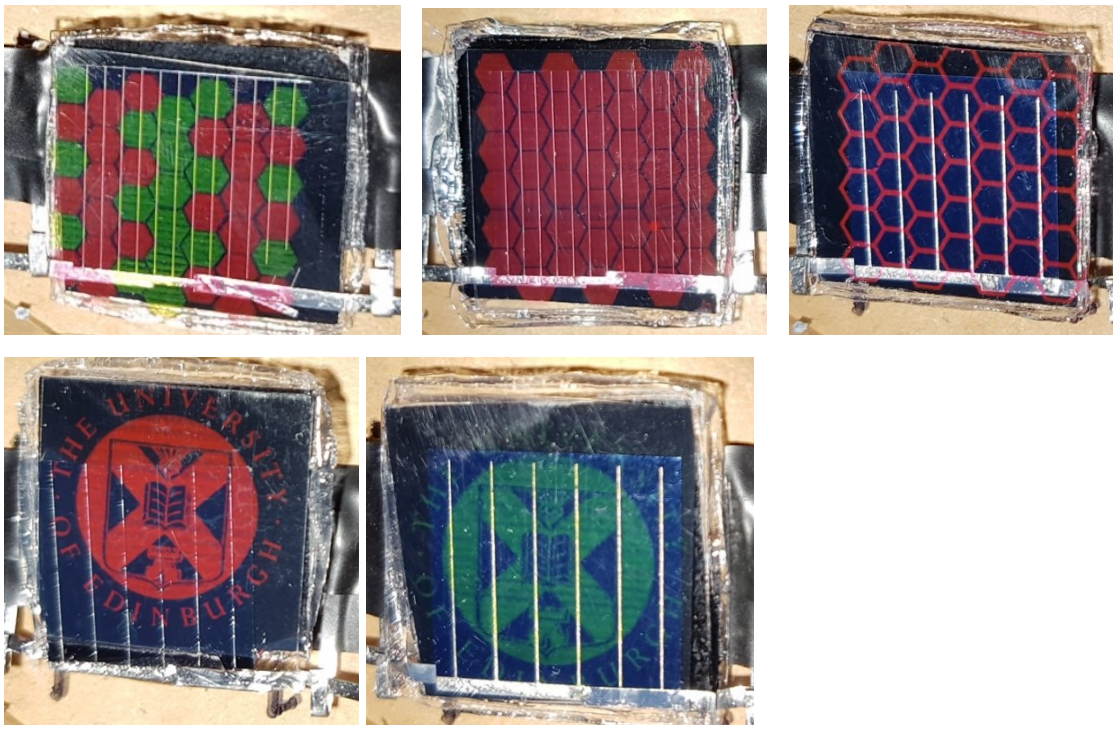

Figure S3. Prototypes demonstrating the versatile graphic design opportunities on solar cells with LDS materials (2 cm x 2 cm Si solar cells).

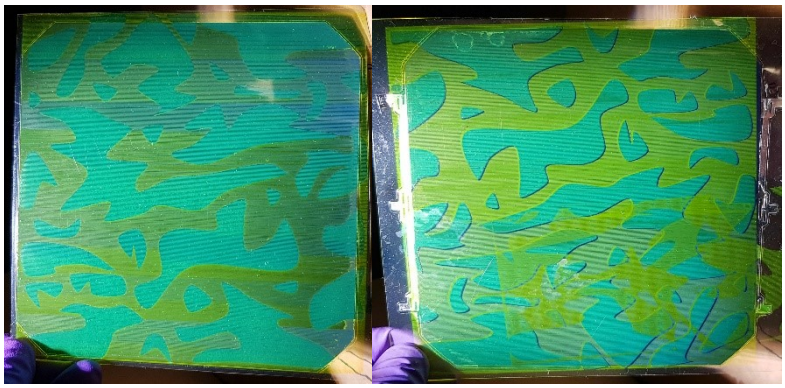

Figure S4. Prototypes demonstrating the versatile graphic design opportunities on solar cells with LDS materials (12.5 cm x 12.5 cm Sun power solar cells).

Cell	Voltage [V]	Current [mA]	Power [mW]
Bare	4.52	23.8	107
Printed	4.48	23.5	105

Figure S5. CIS solar cells laminated with graphically printed ETFE foil with LDS materials under the sun (top) and UV-light illumination (bottom) and comparison of the efficiency of the bare cell and after lamination with luminescent coating. The efficiency of the cell with the luminescent coating is only 2% lower than a bare cell.

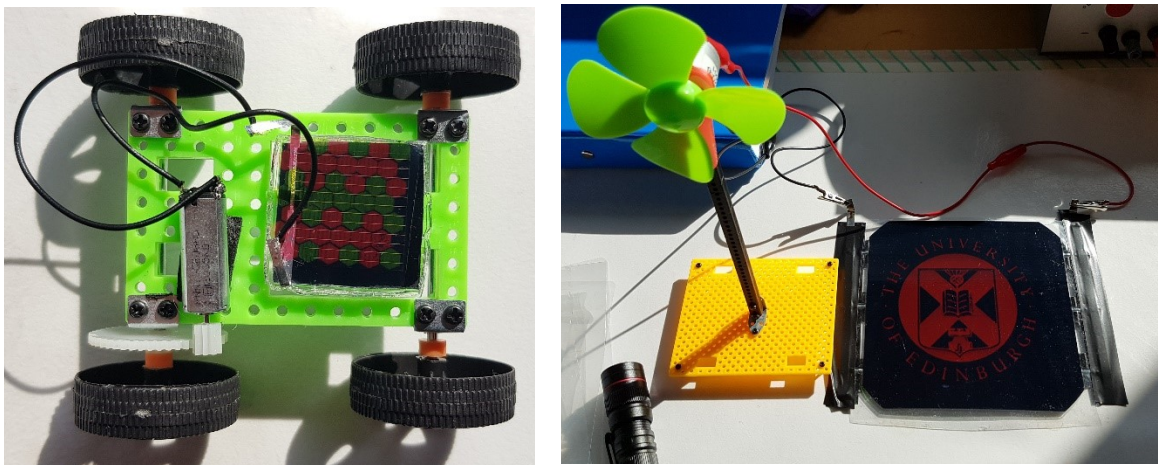

Figure S6. Examples of the prototypes used to power solar toys i.e. cars and turbines.

Figure S7 Photographs demonstrating the different artistic design opportunities with an inkjet printer on ETFE film using LDS materials

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