

Supplementary Materials: Transparent luminescent solar concentrators using Ln³⁺-based ionosilicas towards photovoltaic windows

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Table S1. Thickness of the active layer of the LSCs deposited on glass.

Sample	Thickness (μm)
PMMA-Tb	10.70±0.05
PMMA-Eu	5.10±0.09

Table S2. Quantification of parameters expressed in Equation (2) of the manuscript for η_{opt} calculation.

	I_{SC}^L (A)	V_0^L (V)	I_{SC} (A)	V_0 (V)	A_e (m ²)	A_s (m ²)	η_{solar}	η_{PV}
PMMA-Tb	4.1×10 ⁻⁶	1.69	4.0×10 ⁻⁵	3.5	2×10 ⁻⁵	7×10 ⁻⁴	57.6	30.2
PMMA-Eu	2.4×10 ⁻⁵	0.72	1.0×10 ⁻⁴	1.9				44.2

Table S3. Simulated optical conversion efficiency values considering all the photons reaching the edge (η_{opt} , %) and only the converted photons (η'_{opt} , %) for the LSCs based on PMMA-Ln.

LSC	η_{opt}	η'_{opt}
PMMA-Tb	0.16	0.02
PMMA-Eu	0.23	0.11

Table S4. Typical values for the electrical power interval available at a USB port and required to charge small electronic devices.

Power (W)	
devices	PC USB
	2.5
	Mobile phone
	5
	Tablets
	12
	LED lamps
	2.3–18
	Movement sensors
	0.32–0.45
	Wi-fi routers
	0.85–11

Table S5. Ellipsometric parameters from the Cauchy absorbent model, Equation (S1) in the Supplementary Information.

Sample	A	B (×10 ⁴ nm ²)	C (×10 ⁹ nm ⁴)
PMMA	1.48±0.02	(4.5±0.2) × 10 ³	−66±3
PMMA-Tb	1.484±0.003	(3.9±0.2) × 10 ³	(−1.6±0.3) × 10 ²
PMMA-Eu	1.48±0.01	(4.7±0.5) × 10 ³	(−4.7±0.7) × 10 ²

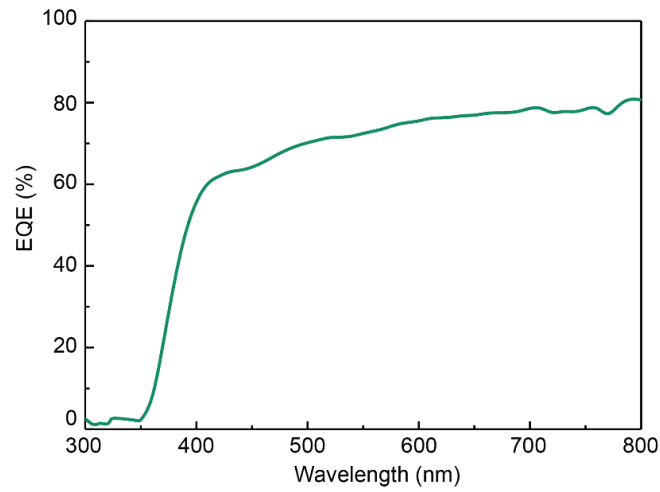


Figure S1. EQE curve of the c-Si PV cell used in this work.

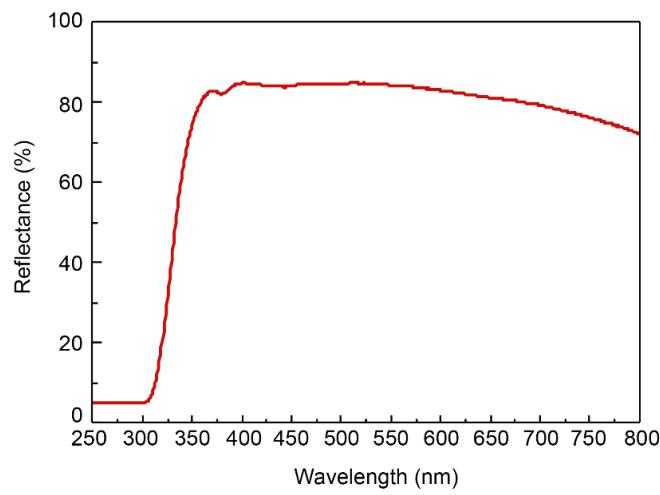


Figure S2. Reflectance curve of the reflective tape used in the LSCs.

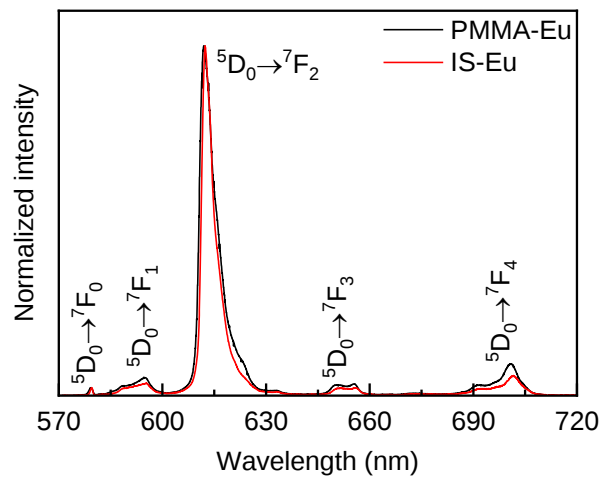


Figure S3. Room temperature emission spectra for PMMA-Eu and IS-Eu excited at 385 and 390 nm, respectively.

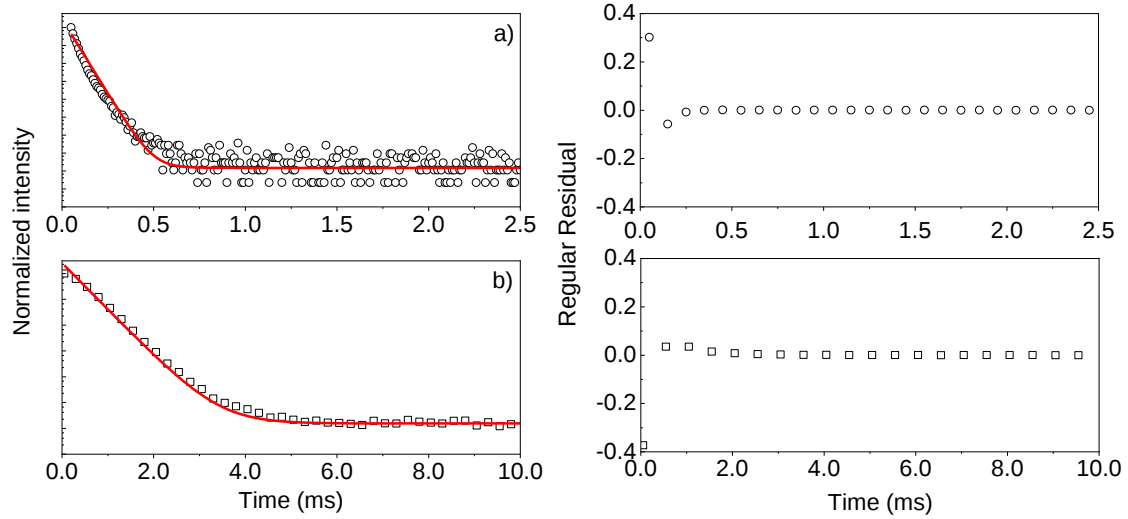


Figure S4. Room temperature emission decay curves for (a) PMMA-Tb and (b) PMMA-Eu excited at 380 nm and monitored at 544 and 612 nm, respectively. The solid lines represent the best fit to the data ($r^2 > 0.93$) using a single exponential function. The respective residual plots are shown on the right-hand side.

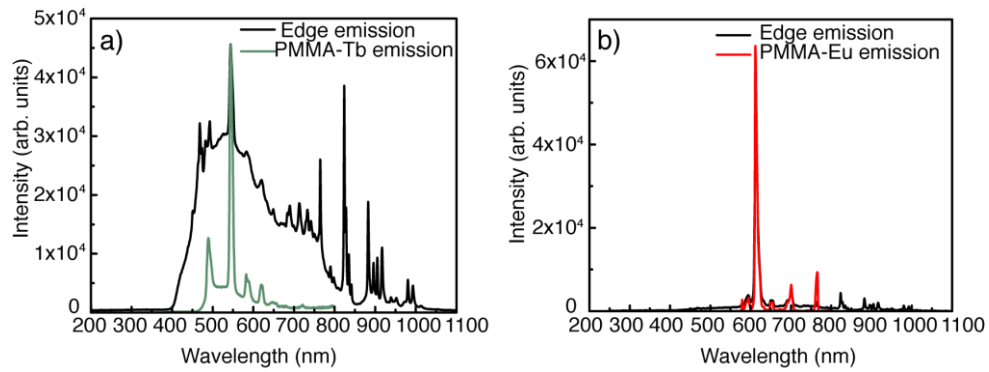


Figure S5. Emission of the LSCs collected at the edges of the LSCs based on (a) PMMA-Tb and (b) PMMA-Eu. The emission spectra at the edges of the LSCs spectra were acquired using a spectrometer OceanOptics Maya 2000 Pro coupled with an optical fibre under AM1.5G radiation.

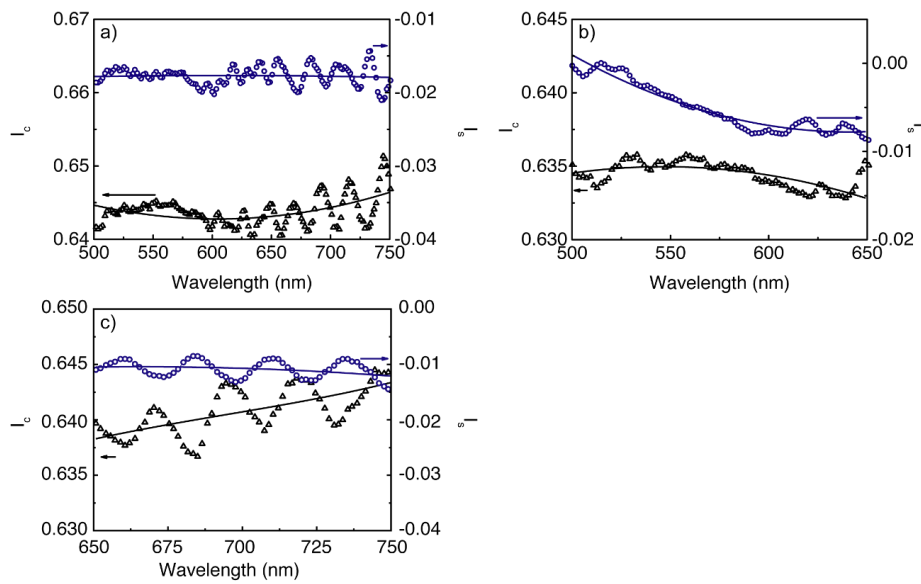


Figure S6. Ellipsometric parameters I_s (open circles) and I_c (open triangles) measured for (a) PMMA, (b) PMMA-Tb and (c) PMMA-Eu. The solid lines represent the data best fit.

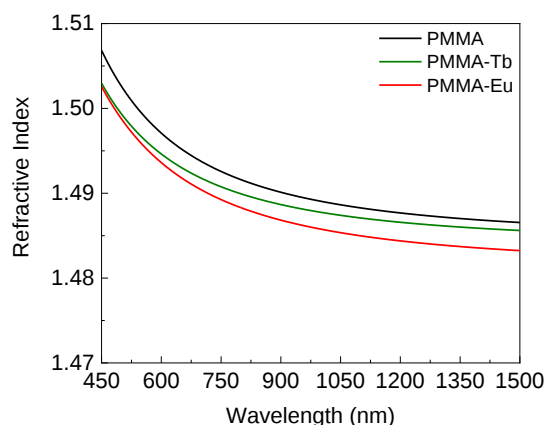


Figure S7. Dispersion curves measured for PMMA, PMMA-Tb and PMMA-Eu.

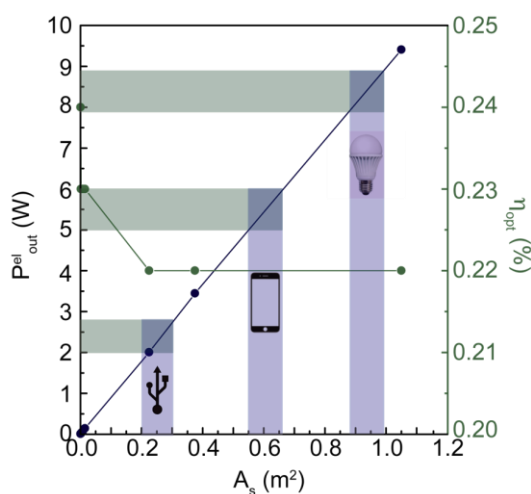


Figure S8. Monte Carlo ray-tracing optical conversion efficiency as function of the LSC surface area and predicted output electrical power. A constant thickness of 10^{-3} m (typical value for a glass window) was considered in all the simulations. The symbols refer to the A_s value needed to attain P_{out}^{el} comparable to the one delivered by an USB port and needed to charge the low-voltage devices indicated.

Materials Synthesis and Processing Details

Preparation of 1-butyl-3-[3-(trimethoxysilyl)propyl]imidazolium chloride ([B(TMSP)Im]Cl)

[B(TMSP)Im]Cl was synthesized by mixing BIm with CPTMS (molar ratio BIm:CPTMS = 1:1). The mixture was stirred at 70 °C for 5 days under nitrogen atmosphere. The resulting pale-yellow viscous product was washed thrice with anhydrous EtOAc (10 mL). It was then dried under vacuum to remove excess EtOAc and finally stored under vacuum conditions.

Preparation of the Na[Ln(TTA)₄] compounds with Ln = Tb, Eu.

TTA was dissolved in EtOH and then deprotonated with NaOH (molar ratio TTA:NaOH = 4:4) at 50–60 °C for 2 hours. To this solution $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$, dissolved in EtOH, was added dropwise (molar ratio TTA:NaOH: $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$ = 4:4:1) and the mixtures was maintained at 50–60 °C for 1 hour. The EtOH was evaporated under reduced pressure on a rotary evaporator and the as-produced salts were dried for 3 days at 50 °C.

Preparation of the 1-butyl-3-[3-(trimethoxysilyl)propyl]imidazolium tetra(2-thenoyltrifluoroacetate)terbate/europate (III) [B(TMSP)Im][Ln(TTA)₄] compounds and of the corresponding ionosilicas (IS-Ln)

Na[Ln(TTA)₄] was reacted with [B(TMSP)Im]Cl in THF under nitrogen atmosphere (molar ratio Na[Ln(TTA)₄]: [B(TMSP)Im]Cl = 1:1). The salts sodium chloride (NaCl) was removed by precipitation and centrifugation (thrice at 3000 rpm) of the solution. EtOH and water were then added to this solution (molar ratio [B(TMSP)Im][Ln(TTA)₄]: EtOH: H₂O = 1:4:1.5) to initiate the sol-gel process. The mixture was stirred in a sealed flask for approximately 30 minutes, cast into a Teflon mold, covered with Parafilm and left in a fume cupboard for 24 hours. The mold was subsequently transferred to an oven at 50 °C and the resulting IS-Ln sample, produced as a glassy monolith with a yellowish (Ln = Tb, Eu) hue, was aged for a period of 4 weeks.

Preparation of PMMA

A mass of 10 g of MM was mixed with 0.06 g of benzoyl peroxide in a glass vial. The mixture was heated at 80–90 °C for 30 minutes and then placed in an oven at 40 °C until complete polymerization.

Preparation of the IS-Ln-doped PMMA-based materials

A THF solution of [B(TMSP)Im][Ln(TTA)₄] was added to a PMMA solution in DCM. EtOH and water were then added to this solution (molar ratio B(TMSP)Im][Ln(TTA)₄]: EtOH: H₂O = 1:4:1.5). The mixture was then stirred in a sealed flask for approximately 30 minutes. PMMA solutions with a concentration of $X = 20\%$ wt. ($X = m_{IS-Ln}/m_{PMMA}$) of IS-Ln were produced. These samples will be hereafter designated as PMMA-Ln-X. The structural and optical characterization of such materials were performed in monoliths with $(104 \pm 2) \times 10^{-5}$ m thickness. The structural characterization results showed that the obtained materials are thermally stable and present an amorphous structure, as fully described elsewhere [1].

Optical characterization Details

Emission and excitation spectra and emission decay curves were recorded with a modular double-grating excitation spectrofluorimeter with a TRIAX 320 emission monochromator (Fluorolog-3, Horiba Scientific) coupled to a R928 Hamamatsu photomultiplier. The absolute emission quantum yield values (q) were measured at room temperature using a system (Quantaaurus-QY Plus C13534, Hamamatsu) composed by a 150 W xenon lamp coupled to a monochromator for wavelength discrimination, an integrating sphere as the sample chamber, and a multichannel analyzer for signal detection. The spectroscopic ellipsometry measurements were made using an AutoSE ellipsometer (HORIBA Scientific) with a total of 250 points in the wavelength interval 450–850 nm, an incidence angle (θ) of 69.8° and a signal quality of 30. A measurement spot area of $250 \times 250 \mu\text{m}^2$ was used. Three measurements were performed in each sample. The structural model consists of a three-layer structure incorporating the substrate layer, the PMMA-Ln layer and air as ambient medium with a refractive index value of 1.00. The data were minimized using the Simplex algorithm, and the dispersion curves were determined using Cauchy absorbent model, given by:

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}, \quad (S1)$$

where n is the refractive index, λ is the wavelength and A, B and C are constants, Table S5 in Supplementary Information.

Modelling details

As the thickness of the active layers (10^{-6} to 10^{-5} m) is much larger than that of the light coherent length ($\sim 10^{-7}$ m), thus, interference effects were neglected. The stochastic nature of the model is reflected in the fact that the propagated rays cannot split when reaching an interface but rather be

either transmitted or reflected, as predicted by Fresnel laws. We also note that incident light polarization is not taken into account. By modelling the path of each propagated ray, it is possible to know whether the photons are trapped inside the luminescent layer, absorbed by the luminescent species, lost due to escape cone or absorption and ultimately collected by the PV device.

This model does not include individual molecules or optically active centers, but applies statistical averaging of the absorption. First, the absorption probability is calculated ($p_{abs} = 1 - 10^{-\alpha d}$, where α is the attenuation coefficient in units cm^{-1} and d is the photon desired step size (step = $-\log_{10}(\xi)/\alpha$, where ξ is a random number between 0 and 1 in each iteration) as function of the wavelength and then compared with a random generated number between 0 and 1 for each launched photon. If p_{abs} proves to be higher than the random number, the photon is absorbed. Once a photon is absorbed, the subsequent fate of the excitation (i.e., emission or non-radiative relaxation) is again determined by the Monte Carlo sampling according to the emission quantum yield. The direction of the emission is obtained by a random uniform distribution, and the emission wavelength is sampled randomly from the normalized emission spectrum. The ultimate fate of each photon is, either loss due to non-radiative recombination or escape the luminescent layer from the front. When a photon hits the PV interface, it counts as a PV absorption and the wavelength of the photon and its position on the PV interface is recorded [2].

References

1. Frias, A. R.; Cardoso, M. A.; Gonçalves, H.; Correia, S. F. H.; Pereira, R. F. P.; Nunes, S. C.; André, P. S.; Carlos, L. D.; de Zea Bermudez, V.; Ferreira, R. A. S. Transparent luminescent down-shifting layers based on Ln^{3+} -based ionosilicas. *Unpublished work*, 2014.
2. Frias, A. R.; Pecoraro, E.; Correia, S. F. H.; Minas, L. M. G.; Bastos, A. R.; García-Revilla, S.; Balda, R.; Ribeiro, S. J. L.; André, P. S.; Carlos, L. D.; Ferreira, R. A. S. Sustainable luminescent solar concentrators based on organic-inorganic hybrids modified with chlorophyll. *J. Mater. Chem., A* **2018**, *6*, 8712–8723, doi:10.1039/C8TA01712C.