## Supplementary information for the manuscript

"Luminescent solar concentrators based on PMMA films obtained from a redemissive ATRP initiator" by Riccardo Mori, Giuseppe Iasilli, Marco Lessi, Ana Belén Muñoz-García, Michele Pavone, Fabio Bellina, and Andrea Pucci\*

## **Experimental part**

## **Optical Efficiency measurement**

The PV cell is masked with black tape to match the LSC edge (50x3 mm) so that limiting the stray light to negligible levels. The other three edges of the LSC were covered with a reflective aluminium tape. A led lamp (12V DC 5W, colour T = 5500K) was housed 10 cm above the sample and with the main body located outside the box to prevent its heating-up. The PV module is connected to a digital potentiometer (AD5242) controlled via 12C bv Arduino Uno an (https://www.arduino.cc) microcontroller using I2C master library. A digital multimeter (KEITHLEY 2010) is connected in series with the circuit, between the PV module and the potentiometer, to collect the current as a function of the external load (Figure S2). Conversely, the voltage is measured by connecting the multimeter in parallel to the digital potentiometer (Figure S3). Arduino Uno controls the multimeter via SCPI language over RS-232 bus using a TTL to RS-232 converter chip (MAX232). Arduino Uno is connected to pc via USB port and controlled by a Python script. A 12V DC voltage light source was selected so that the luminous flux is continuous and there is no need to compensate the PV module capacitance. The measurement cycle begins with a signal from PC to Arduino which sets the multimeter parameter to measure current. Then Arduino begins the measure loop: 1) set the potentiometer to a given value; 2) send trigger signal to the multimeter; 3) read the measured data; and 4) send the data back to PC. The loop is repeated 256 times for potentiometer values ranging 60  $\Omega$  – 1 M $\Omega$ . Arduino sets the multimeter to measure voltage and for each potentiometer value the system records 8 data samples which are subsequently processed by the Python script.



Figure S1. External quantum efficiency of the utilized Si-PV cell



Figure S2. Scheme of the apparatus utilized for the photocurrent measurement



Figure S3. Scheme of the apparatus utilized for the voltage measurement



**Figure S4.** a) UV-vis absorption spectra of TPE\_RED in DMSO solution as a function of fluorophore concentration (M) and b) absorbance maximum plotted as a function of the TPE\_RED content.



**Figure S5.** Size distribution of TPE\_RED aggregates in DMSO/water mixtures with 95% water fraction



**Figure S6.** a) Fluorescence spectra of TPE\_RED in DMSO/water mixture as a function of the water content (vol.%) and b) emission intensity variations plotted as a function of the water content. In the inset, pictures of the same solutions taken under illumination with a near-UV lamp at 366 nm



α (°)	$\Delta E_{S0}(eV)$	$\Delta E_{S1}(eV)$	$\lambda_{abs}$ (nm)	Stokes Shift (nm)
0	0	0	466	179
30	0.078	0.115	453	178
60	0.292	0.410	420	172
90	0.419	0.584	377	163
120	0.309	0.422	418	175
150	0.158	0.180	452	181
180	0.180	0.163	466	181
Opt.ª	-	-	466	183
150 180 Opt. <sup>a</sup>	0.158 0.180 -	0.180 0.163 -	452 466 466	181 181 183

<sup>a</sup> For optimized structures:  $\alpha_{\text{S0}}$  = 2° and  $\alpha_{\text{S1}}$  = 3°

**Figure S7.** Relative energies of the ground  $S_0$  ( $\Delta E_{S0}$ , blue dots) and excited  $S_1$  states ( $\Delta E_{S1}$ , red dots), plus absorption ( $\lambda_{abs}$ , blue arrows) and emission (red arrows) transitions of DA\_TPE with respect to the rotation across the dihedral angle  $\alpha$  (see Figure 2); the corresponding oscillator strengths (*f*) are indicated in blue and red for absorption and emission transitions, respectively. Data computed at the CAM-B3LYP/TZVP/PCM level of theory on  $S_0$  and  $S_1$  optimized geometries by varying only the angle  $\alpha$ .



Figure S8. <sup>1</sup>H NMR of PMMA\_TPE\_RED<sub>1.5</sub>



Figure S9. GPC analysis of the PMMA\_TPE\_RED polymers



Figure S10. DSC analysis (second heating) of the PMMA\_TPE\_RED<sub>0.75</sub>



**Figure S11.** Fluorescence of a PMMA\_TPE\_RED<sub>1.5</sub> film before and after continuous irradiation at 490 nm for 180 min