

## Electronic Supplementary Information (ESI)

### Anthracene/tetracene cocrystals as novel fluorophores in thin-film luminescent solar concentrators

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#### 1. LSC device fabrication

All LSC devices fabricated and tested in this work were fabricated on glass substrates (25 mm x 25 mm x 1.8 mm). For the preparation of the LSC thin film devices, solid PMMA (Perspex XT, Lucite) was dissolved under magnetic stirring at a concentration of 10 wt.% in hot chloroform (Sigma Aldrich), toluene (Sigma Aldrich), chlorobenzene or 1,2-dichlorobenzene (50 °C for chloroform, 100 °C for toluene and chlorobenzene, 150 °C for 1,2-dichlorobenzene solutions). After complete dissolution was achieved (approximately 2 h), the desired amount of anthracene (Ac, Sigma Aldrich) was added to the hot solution followed by the addition of tetracene (Tc, Sigma Aldrich). The hot solutions were maintained under magnetic stirring overnight to achieve complete dissolution. Different PMMA:Ac:Tc ratios (1000:250:1 and 750:250:1) and different Ac:Tc proportions (250:1, 250:5, 250:10) were investigated to explore the effect of these process parameters in LSC device performance. Before deposition of the LSC thin film, another chloroform solution of PMMA and TiO<sub>2</sub> (Ti-Pure R-706, DuPont) (chloroform:PMMA=85:15 by weight, 10 wt.% TiO<sub>2</sub>) was prepared under magnetic stirring (2 h) followed by ultrasonic bath treatment (1 h) to be used as diffuse back-reflector. The back reflector solution was deposited onto the glass substrates *via* spin-coating (1200 RPM, 40 s) and the deposited film was allowed to dry out in air. After deposition of the back-reflector, the solutions of Ac/Tc-doped PMMA were spin-cast onto the glass substrates (600 RPM or 1200 RPM, 40 s) and allowed to dry out in air before further processing. In addition, Ac-only (PMMA:Ac:Tc=1000:250:0) and Tc-only (PMMA:Ac:Tc=1000:0:1) LSC films were also prepared from toluene solutions (600 RPM, 40 s) for comparison. The so-formed LSCs were then coupled to four serially-connected mc-Si PV cells (SLSD-71N400 - active area 45 mm<sup>2</sup>, average power conversion efficiency of 10.5%, by Silonex Inc.) so that each edge of the glass substrate was connected to the photoactive area of the PV cell. Bonding was performed by means of a hotmelt thermosoftening polyurethane adhesive (Krystalflex PE399, Huntsman Polyurethanes) 0.5 mm thick that was placed hot (140 °C) on the active face of each PV cell onto which each edge of the LSC glass substrate was pressed for about 1 min, thus ensuring good optical contact with the PV cell. The LSC system was then allowed to cool down to room temperature so that hardening of the polyurethane could be achieved. This ensured firm bonding between the PV cell and the thin-film LSC and good handling resistance.

## 2. LSC characterization

The LSC film thickness was measured by optical profilometry (Microfocus, UBM). Surface roughness measurements were also carried out by optical profilometry. The results are presented in Table S1:

**Table S1.** Thickness and root-mean-square surface roughness measurements for the systems considered in this work. Processing conditions for each device have also been reported.

| LSC device <sup>a</sup> | PMMA:Ac:Tc | Solvent    | Spin coating speed rpm | Thickness $\mu\text{m}$ | R <sub>RMS</sub> $\mu\text{m}$ |
|-------------------------|------------|------------|------------------------|-------------------------|--------------------------------|
| A-CHCl <sub>3</sub>     | 1000:250:1 | chloroform | 1200                   | 7.21 $\pm$ 0.80         | 1.72 $\pm$ 0.11                |
| B-CHCl <sub>3</sub>     | 1000:250:1 | chloroform | 600                    | 9.21 $\pm$ 0.81         | 1.98 $\pm$ 0.19                |
| C-CHCl <sub>3</sub>     | 750:250:1  | chloroform | 600                    | 8.49 $\pm$ 0.81         | 2.56 $\pm$ 0.45                |
| A-TOL                   | 1000:250:1 | toluene    | 1200                   | 2.49 $\pm$ 0.12         | 0.33 $\pm$ 0.07                |
| B-TOL                   | 1000:250:1 | toluene    | 600                    | 2.45 $\pm$ 0.16         | 0.43 $\pm$ 0.05                |
| C-TOL                   | 750:250:1  | toluene    | 600                    | 2.77 $\pm$ 0.24         | 0.85 $\pm$ 0.17                |
| Ac-only                 | 1000:250:0 | toluene    | 600                    | 1.69 $\pm$ 0.06         | 0.48 $\pm$ 0.16                |

UV-vis and fluorescence spectroscopy were performed on solid state samples deposited onto glass/quartz substrates by spin-coating (WS-400B-NPP Spin-Processor, Laurell Technologies Corp.) at 600 RPM for 40 s in air. UV-vis absorption spectra were recorded in air at room temperature in transmission mode by means of an Evolution 600 UV-vis Spectrophotometer (Thermo Scientific). Fluorescence emission spectra were recorded in air at room temperature on a Jasco FP-6600 Spectrofluorometer. The excitation wavelength was  $\lambda_{\text{exc}}=400$  nm. The surface morphology of the LSC films was investigated by optical microscopy using an Olympus BX-60 reflected-light optical microscope in bright-field (BF) imaging mode, equipped with an Infinity 2 digital camera

The current-voltage (*I-V*) curves of the illuminated LSC/solar cell system (the LSC device) were collected by means of a Keithley 2612 source-measure unit under AM 1.5G solar illumination at 100 mW cm<sup>-2</sup> (1 sun) (Abet Technologies 150 W solar simulator), calibrated by means of a NREL certified reference cell (PV Measurements). I-V testing was carried-out in air by performing scans between -0.2 V and 2.2 V with 10 mV steps on the illuminated device and by recording the current response. The solar simulator power output was monitored by means of a powermeter with thermopile sensor (Ophir).

## 3. LSC device performance evaluation

The evaluation of the performance of the LSC devices studied in this work was carried out by testing under AM 1.5G solar irradiation at 100 mW cm<sup>-2</sup> and by considering the following figures of merit.<sup>1</sup>

1. The power conversion efficiency of the LSC device  $\eta_{\text{LSC}}$ , defined as:

$$\eta_{\text{LSC}} = \text{FF} \frac{(I_{\text{SC}}/A_{\text{LSC}})V_{\text{OC}}}{P_{\text{IN}}} \quad (\text{Equation S1})$$

where FF (-) is the fill factor,  $I_{\text{SC}}$  (mA) is the short circuit current and  $V_{\text{OC}}$  (V) is the open circuit voltage extracted from the PV cells attached to the LSC waveguide,  $A_{\text{LSC}}$  (cm<sup>2</sup>) is the area of the LSC top surface, and  $P_{\text{IN}}$  (mW cm<sup>-2</sup>) is the incident solar power density.

2. The optical efficiency of the LSC device  $\eta_{\text{opt}}$ , defined as:

$$\eta_{\text{opt}} = \frac{\eta_{\text{LSC}}}{\eta_{\text{PV}}} \quad (\text{Equation S2})$$

where  $\eta_{\text{PV}}$  is the power conversion efficiency of the PV cell under front face direct illumination.

3. The concentration factor  $C$ , defined as:

$$C = \eta_{\text{opt}} G \quad (\text{Equation S3})$$

where  $G$  is the geometric gain of the LSC device, defined as:

$$G = \frac{A_{\text{LSC}}}{A_{\text{edge}}} \quad (\text{Equation S4})$$

where  $A_{\text{edge}}$  is the LSC edge surface area.

#### 4. Absorption and emission spectra of anthracene and tetracene

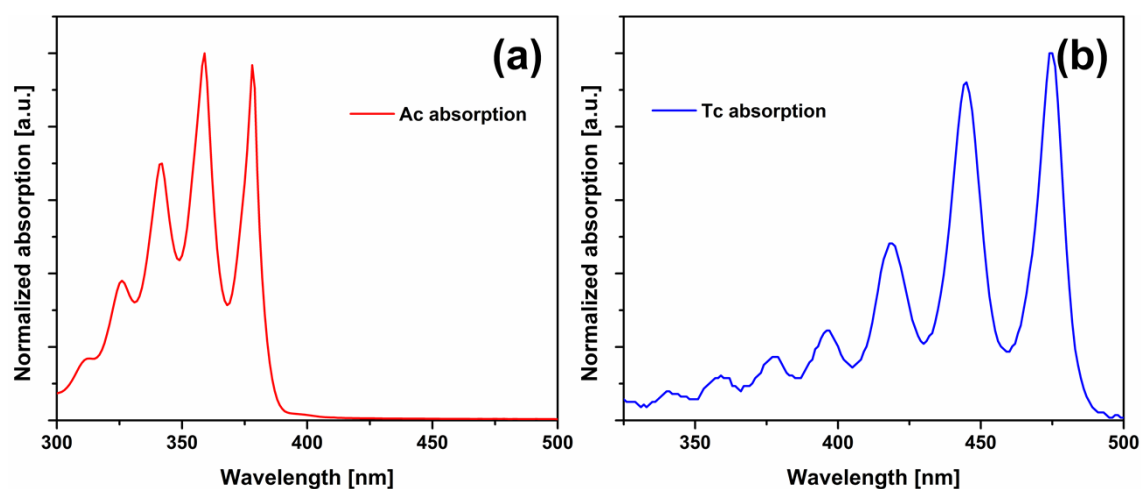


Fig. S1 Normalized UV-vis absorption spectra of (a) anthracene and (b) tetracene in chloroform solution.

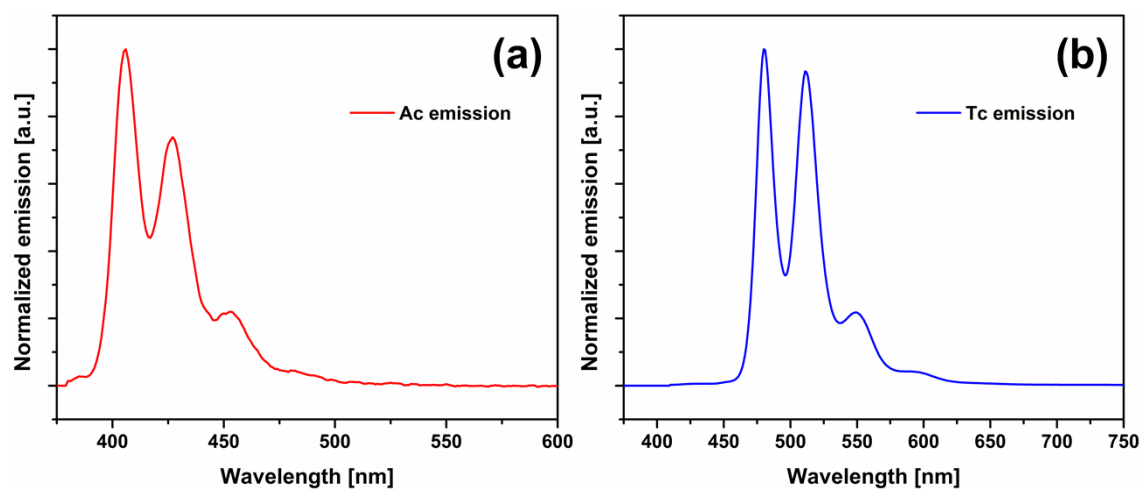
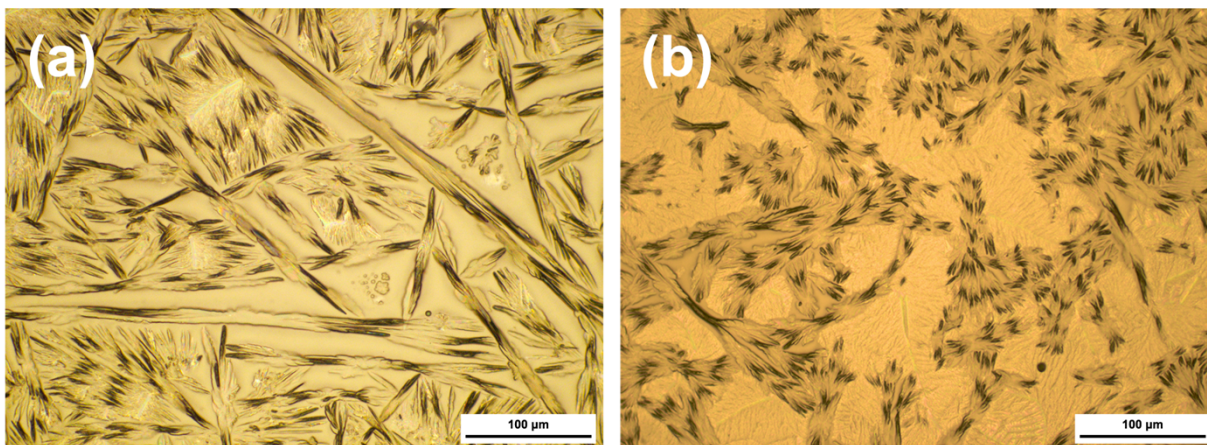


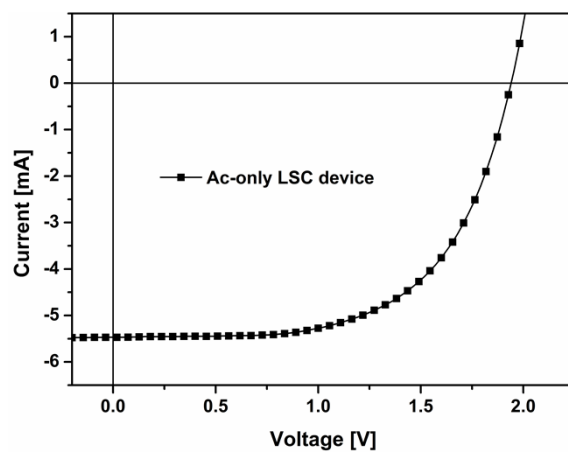
Fig. S2 Normalized fluorescence emission spectra of (a) anthracene and (b) tetracene in chloroform solution.

## 5. Optical microscopy



**Fig. S3** Optical microscope images (200x magnification) of PMMA:Ac:Tc (1000:250:1) LSC films deposited from toluene solution at 50 °C (a) and 100 °C (b).

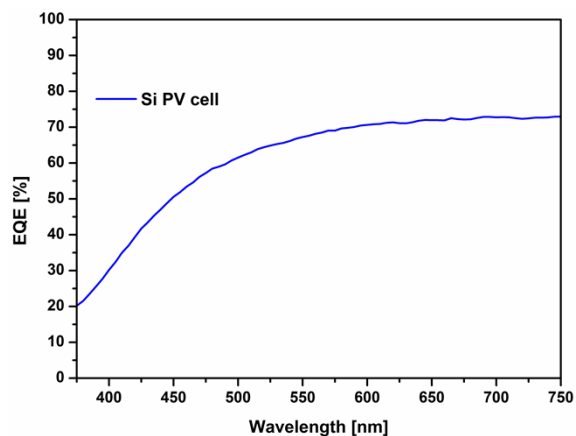
## 6. Ac-only LSC devices



**Fig. S4** Current-voltage (I-V) plot of an Ac-only LSC device (PMMA:Ac:Tc=1000:250:0).

### 7. Spectral response of the mc-Si PV cell

External quantum efficiency (EQE) measurements were performed on an Oriel QE-PV-SI apparatus equipped with a lock-in amplifier. The spectral response of the PV cells employed in this work is presented in Fig. S5.



**Fig. S5** External quantum efficiency of the mc-Si PV cells employed in this work.

### 8. References

- 1 L. Desmet, A. J. M. Ras, D. K. G. de Boer and M. G. Debije, *Opt. Lett.*, 2012, **37**, 3087-3089.