Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels. This journal is © The Royal Society of Chemistry 2018

## SUPPLEMENTARY MATERIAL

The photon flux emitted by a blackbody of temperature T over the restricted energy range from  $E_i$  to  $E_j$  is

$$N(E_{i}, E_{j}, T, \mu, \theta) = \theta \frac{2\pi}{h^{3}c^{2}} \int_{E_{i}}^{E_{i}} \frac{E^{2}}{exp(\frac{E - \mu}{kT}) - 1} dE$$
(S1)

where h is Planck's constant, c is the speed of light, k is Boltzmann's constant,  $\theta$  is the projected solid angle subtended by the radiation source, and  $\mu$  is chemical potential. The maximum current (I) extractable from a PV cell is the difference between the current pumped to the conduction band by photon absorption, and the current associated with luminescent emission:

$$I/_{q} = \dot{N}_{S} - \dot{N}_{R} = aN(E_{g}, \infty, T_{S}, 0, \theta_{S}) - \varepsilon N(E_{g}, \infty, T_{c}, qV, \theta_{em})$$
(S2)

where q is the elementary charge,  $\dot{N}_S$  and  $\dot{N}_R$  are the current contributions associated with photon absorption and emission, a and  $\varepsilon$  are the absorptivity and emissivity of the cell,  $E_g$  is the bandgap energy,  $T_S$  and  $T_c$  are the respective temperatures of the sun and the cell, V is the applied voltage, and  $\theta_S$  and  $\theta_{em}$  are, respectively, the projected solid angles subtended by the sun and cell emission (with the contribution of the background blackbody radiation from the environment being neglected here).

In the radiative limit<sup>S1</sup>

$$\eta_{PV} = \frac{\left\{ qV \left[ N_S(\mu = 0) - N_R(\mu = qV) \right] \right\}_{max}}{P_{in}}$$
 (S3)

where  $P_{in}$  is the incident solar flux, and the radiative limit refers to

- 1. each absorbed photon generating one and only one electron-hole pair,
- 2. no absorption of sub-bandgap photons,
- 3. the only loss mechanism being radiative recombination,
- 4. negligible resistive losses, and
- 5. the cell being maintained at ambient temperature (taken here as 300K).
- S1 A. S. Brown and M. A. Green, *Prog. Photovolt: Res. Appl.*, 2002, **10**, 299-30.