Advanced Functional Materials

Efficient Broadband Triplet-Triplet Annihilation Assisted Photon Up-conversion at Sub-solar Irradiance in Full Organic Systems.

--Manuscript Draft--

Manuscript Number:	adfm.201502507R1
Full Title:	Efficient Broadband Triplet-Triplet Annihilation Assisted Photon Up-conversion at Sub-solar Irradiance in Full Organic Systems.
Article Type:	Full Paper
Section/Category:	
Keywords:	photon managing, triplet-triplet annihilation, broadband up-conversion, photovoltaics, asymmetric porphyrins
Corresponding Author:	Angelo Monguzzi, Ph.D. Universita degli Studi di Milano-Bicocca Milano, ITALY
Additional Information:	
Question	**Response**
Please submit a plain text version of your cover letter here. **If you are submitting a revision of your manuscript, please do not overwrite your original cover letter. There is an opportunity for you to provide your responses to the reviewers later; please do not add them here**.	Dear Editor: We would like to submit the manuscript entitled “Efficient Broadband Triplet-Triplet Annihilation Assisted Photon Up-conversion at Sub-solar Irradiance in Full Organic Systems” for your consideration as full paper in Advanced Functional Materials. Because all thesolar cells cannot exploit photons in the long-wavelength-tail of the solar spectrum, many strategies have been pursued to recapture this energy. The most promising approach is the up-conversion based on sensitized triplet-triplet annihilation processes (sTTA-UC), which already demonstrated its ability to blue-shift low-energy photons with good efficiency at excitation power not too far from the solar irradiance. Unfortunately, this approach suffers from two severe problems: it requires light intensities that are above the working range of conventional solar cells, and/or it relies on materials with narrow absorption bands that cannot harvest a large fraction of the solar spectrum. For these reasons the up-conversion is not yet used in real solar-energy devices. In this paper we demonstrate a reliable solution to these problems. In particular we accomplish for the first time the difficult task to synthesized a family of dyes with complementary absorption properties, which are able to simultaneously operate as sensitizer for the same up-converter. In such a way, we extended the overall absorption ability of our sTTA-UC system up to about 100 nm instead of the typical 10-20 nm. Using this strategy, we show two key advances. First, we doubled the number of the output up-converted photons. Second, and more important, with this full organic system we obtain an outstanding up-conversion yield of 10%in AM 1.5 broadband non-coherent illumination condition. This allows us to operate a dye-sensitized solar cell by exploiting exclusively sub-bandgap photons at an irradiance of one sun. We believe that our findings are especially sound not so much for the record performances, but because they show the way to move the sTTA-UC from the lab proof of principle to its application to real devices in real operating condition. For these reasons, we believe that this manuscript may be suitable for the general-interest readership of Advanced Functional Materials. If you need any further information, please do not hesitate to contact us. Sincerely, Angelo Monguzzi

	Franco Meinardi
Corresponding Author Secondary Information:	
Corresponding Author's Institution:	Universita degli Studi di Milano-Bicocca
Corresponding Author's Secondary Institution:	
First Author:	Angelo Monguzzi, Ph.D.
First Author Secondary Information:	
Order of Authors:	Angelo Monguzzi, Ph.D.
	Sergey Borisov
	Jacopo Pedrini
	Ingo Klimant
	Mario Salvalaggio
	Paolo Biagini
	Fabio Melchiorre
	Camilla Lelii
	Francesco Meinardi
Order of Authors Secondary Information:	
Abstract:	The last trend in solar cells technology is to develop photon managing processes in order to adapt the solar emission to the spectral range at which the devices show the largest intrinsic efficiency. Triplet-triplet annihilation assisted photon up-conversion (sTTA-UC) is currently the most promising process to blue shift sub-bandgap photons at the solar irradiance, even if the narrow absorption band of employed chromophores limits its application. In this work, we demonstrate how to obtain broadband sTTA-UC at sub-solar irradiance, by enhancing the system light-harvesting ability thanks to an ad-hoc synthesized family of chromophores with complementary absorption properties. The overall absorptance is boosted, thus doubling the number of up-converted photons and significantly reducing the irradiance required to achieve the maximum up-conversion yield. An outstanding yield of 10% is obtained in broadband AM 1.5 condition, which allows a DSSC device to operate by exploiting exclusively sub-bandgap photons.

WILEY-VCH

DOI: 10.1002/ ((please add manuscript number))
Article type: Full Paper

Efficient Broadband Triplet-Triplet Annihilation Assisted Photon Up-conversion at Sub-solar Irradiance in Full Organic Systems.

A. Monguzzi, S. Borisov, J. Pedrini, I. Klimant, M. Salvalaggio, P. Biagini, F. Melchiorre, C. Lelii and F. Meinardi**

Dr. A. Monguzzi, J. Pedrini, Prof. F. Meinardi
Dipartimento di Scienza dei Materiali, Università degli Studi Milano Bicocca, via R. Cozzi 55, 20125 Milano, Italy.
E-mail: angelo.monguzzi@mater.unimib.it; meinardi@mater.unimib.it

Dr. S. Borisov, Prof. I. Klimant
Institut für Analytische Chemie und Lebensmittelchemie, 8010 Graz, Stremayrgasse 9/II Austria.

Dr. M. Salvalaggio, Dr. P. Biagini, F. Melchiorre
Eni S.p.A. - Renewable Energy & Environmental R&D Center, Istituto Eni Donegani, via G. Fauser 4, 28100 Novara, Italy.

Dr.ssa C. Lelii
Department of Physical and Chemical Sciences, University of L'Aquila, via Vetoio (Coppito 1) – 67100, L'Aquila, Italy; actual address: Morgan Carbon Italia srl, process engineering department, via Roma 338, 64014 Martinsicuro – Teramo, Italy

Keywords: photon managing, triplet-triplet annihilation, broadband up-conversion, photovoltaics, asymmetric porphyrins, DSSC

The last trend in solar cells technology is to develop photon managing processes in order to adapt the solar emission to the spectral range at which the devices show the largest intrinsic efficiency. Triplet-triplet annihilation assisted photon up-conversion (sTTA-UC) is currently the most promising process to blue shift sub-bandgap photons at the solar irradiance, even if the narrow absorption band of employed chromophores limits its application. In this work, we demonstrate how to obtain broadband sTTA-UC at sub-solar irradiance, by enhancing the system light-harvesting ability thanks to an *ad-hoc* synthesized family of chromophores with complementary absorption properties. The overall absorptance is boosted, thus doubling the number of up-converted photons and significantly reducing the irradiance required to achieve the maximum up-conversion yield. An outstanding yield of ~10% is obtained in broadband AM 1.5 condition, which allows a DSSC device to operate by exploiting exclusively sub-bandgap photons.

1. Introduction

The photovoltaic effect has been turned into a technology to produce electricity from 1954, when a silicon-based *p-n* junction device showed a solar power conversion efficiency of 6%.[1] Since then solar cells (SC) gained in efficiency, found many applications in the consumer market, and actually represent the main clean and sustainable source of energy meeting the global energy challenge.[2, 3] However, the SC efficiency is still limited by the spectral mismatch between the solar emission and the absorption spectrum of the employed semiconductors.[4] As instance, silicon based devices are unable to exploit infrared photons at wavelengths longer than 1 µm, and this problem is even more relevant for organic SCs. Polymeric, single molecule, and dye-sensitized solar cells (DSSC) have been developed in the last years as a potential alternative to inorganic SCs because of their low production cost and great flexibility of use. However, the absorption of commercially available organic SCs has not been yet extended to the red/near-infrared portion of the solar spectrum below 700 nm,[5] wasting a number of photons equal to that available in the UV-Vis range.[6] Same considerations apply to photocatalytic water splitting cells (PCWS) for hydrogen production. This technology converts light into chemical energy and, thanks to its simplicity, is considered as an attractive and challenging theme in green technological solutions for future global energy and environmental issues. However, sun-powered PCWS devices exploit only deep-blue/UV photons, while more than 95% of the solar radiation is lost.[7] In order to harvest low energy photons, solar devices can be upgraded in different ways (multiple junctions cells, new chromophores, new photo-anodes etc.), but all of them suffer for high fabrication costs or do not give rise to a significant enhancement of the efficiency. Therefore, the last trend in the field is to develop photon-energy managing processes to adapt the solar spectrum to the spectral range where the selected device is intrinsically highly efficient.[8] As sketched in **Figure 1**, this could be done by coupling SCs with optically active materials able to blue shift the unexploited photons through few different processes of light up-conversion

(UC).[9] It has been estimated that the recovering of sub-bandgap photons could allow an improvement of organic SC performances up to 50%,[3, 10] and even larger increments, up to 100%, are expected for PCWS.

Traditional UC methods rely on multi-photon processes (e.g., second-harmonic generation in non-linear crystals, or two-photon absorption in rare-earth doped materials)[11, 12] which require high light intensities (up to MW cm^{-2}) that are well above the solar irradiance (~1 kW m^{-2}).[2] To achieve efficient conversion at low power, photon up-conversion based on sensitized triplet-triplet annihilation (TTA) in organic bi-component systems (sTTA-UC) is investigated since it has been demonstrated under solar illumination in 2006. Briefly, a light-harvesting molecule, the sensitizer, absorbs low energy photons and transfers the harvested energy to metastable triplet states of another molecule, the emitter. Through TTA, two excited emitters combine their energy yielding one emitter in a high-lying fluorescent singlet state, thus generating high-energy photons (Fig. 1b and Supporting Information, **Figure S1**).[13, 14] The quick development of sTTA-UC materials led to conversion yields >30% with non-coherent excitation at irradiance comparable to several *suns* (1 *sun* = 100 mW cm^{-2} under Air Mass 1.5 condition),[15-18, 19-21] and sTTA-UC has been used to enhance the light-harvesting capability of photovoltaic and PCWS cells, simply by placing the up-converter on the backside of the device to recapture a fraction of the sub-band-gap transmitted photons.[21, 22] However, the improvements obtained with currently available sensitizers are so far rather limited. To date, the best proposed sensitizers are phosphorescent metalated porphyrins, which have the electronic properties suitable for i) efficient sensitization of the dark triplets of the highly fluorescent emitters used in sTTA-UC systems, and ii) prevention of re-absorption of up-converted light, thanks to their large transparency windows in the absorption spectrum (Fig. 1b).[24] On the other side, the low-energy absorption peak of these porphyrins, which is exploited in the sTTA-UC, shows a typical bandwidth of ~10-20 nm, allowing to harvest only a small fraction of the solar photons.[23] This is a crucial bottleneck, already faced

in rare-earth based up-converters, that prevents the employment of sTTA-UC in real world applications.[26] [12] [27]

The broadening of the sensitizer absorption band it is not only required to increase the number of collected photons, therefore boosting the total light output, but also to decrease the irradiance required for having the highest sTTA-UC yield. Indeed, in these systems the conversion efficiency (QY_{UC}), defined as the ratio between the number of converted photons and that of the absorbed ones, depends on the steady-state density of emitter triplets, which is determined by the light-harvesting ability of the system. In general, QY_{UC} is rather low at low excitation powers. Then, it increases linearly with the irradiance up to the so called excitation power density threshold I_{th}, above which rapidly saturates to its maximum value.[19] It is evident that, for applications in the SC technologies, I_{th} must be as low as possible and certainly below, or at least comparable, with the AM 1.5 solar irradiance. At the present, this goal has been accomplished only in hybrid devices, obtained by coupling to a sTTA-UC system a layer of cadmium selenide fluorescent nanocrystals working as booster for the sensitizer absorption. The drawback of this approach is to make the device architecture more complex, and, by introducing an additional photophysical step, intrinsically less efficient than a full organic sTTA-UC with a comparable absorption spectrum.[28]

A promising strategy to extend the absorption of a sTTA-UC system consists in the simultaneous use of more sensitizers. This concept was proposed for the first time in 2007 by Baluschev and co-workers, who achieved NIR-to-Vis conversion exploiting two different sensitizers simultaneously excited by two lasers or by concentrated solar light (1 W cm^{-2}), and only recently the same group developed a broadband absorbing system probably because of the lack of suitable dyes available on the market.[29, 30] Here, we taken to the extreme this approach by synthesizing a full set of sensitizers designed *ad hoc*, each one able to transfer the harvested energy to the same emitter. In such a way, we obtained an optimized sTTA-UC system with a continuous and broad absorption, which allowed achieving a QY_{UC} as large 10%

under 1 sun of broadband non-coherent excitation light. This system, coupled to a model DSSC, demonstrated the possibility to generate detectable electrical power at the solar irradiance by exploiting only sub-band gap photons.

2. Design and Fabrication of Broadband Absorption sTTA-UC systems.

As emitters, fluorescent polyacenes with emission matching the absorption of SCs are generally employed. For this experiment, we used the perylene (see Supporting Information, Figure S2), which is the ideal dye for this purpose thanks to its peculiar properties. First, its fluorescence quantum yield is close to one in diluted solution. Second, its triplet-to-ground state electronic transition is strictly forbidden, ensuring a triplet natural lifetime in the range of milliseconds even in organic solvents, which implies a large TTA probability.[31] Third, its electronic structure prevents the generation of high-energy triplets upon TTA, thus maximizing the efficiency of the annihilation step.[15, 16, 19]

As introduced above, phosphorescent metalated porphyrins are used for TTA sensitization.[32] Thanks to the central heavy-metal ion, they possess a fast intersystem crossing. Therefore, after photo-excitation, singlet states relax quickly into triplets, from which the energy is transferred to the optically dark triplets of emitters. The absorption spectrum of metalloporphyrins is usually composed of two main peaks, the so-called *B*- (high energy) and *Q*- (low energy) bands,[33] separated by a transparency window up to 200 nm wide, that can easily fit the up-converted emission. Of course, only the *Q*-band is exploited in sTTA-UC, while the *B*-band sets the maximum UC gain achievable in photon energy shift before incurring in the re-absorption of the converted emission. This outline of sTTA-UC chromophore properties gives the guidelines to prepare an ideal broadband up-converting multi-sensitizer system. The *Q*-bands of different light-harvesters must be shifted progressively to broaden the overall absorption band. The corresponding phosphorescence peak should not move significantly in order to maintain the resonance with emitter triplets. In

addition, the high energy *B*-bands should be unchanged to maintain a transparency window large enough to avoid the re-absorption. Unfortunately, the synthesis of this set of porphyrins is not an easy task. The Goutermann model states that the porphyrinic peculiar electronic structure is determined by the properties of the two top filled and two lowest empty π orbitals of the aromatic ring, whose combination results in the generation of the well-known absorption band profile.[32] Intensity changes and energy shifts of the absorption derive from changes of the conjugation length or of delocalized charge density on the ring. Accordingly, the electronic spectra depend on the peripheral substituent groups and axial ligands, the kind of central metal, the fusion of aromatic molecules and on the extent and deformation of the ring itself.[25, 33, 34] Among the others, the most efficient strategy to red-shift the porphyrin absorption is to condense phenyl groups on the central ring pyrroles, as demonstrated by the work of Yakutkin.[33] However, the standard symmetric condensation of four benzenes induces a large red-shift of all electronic energies, thus moving both *Q* and *B* absorption bands.[36] We overcome this problem by synthesizing a series of asymmetric naphthobenzoporphyrins. In this case, the perturbation of the central-ring is limited, allowing changing continuously the absorption peaks position. Most importantly, the asymmetric condensation plays an important role to determine the symmetry of the Goutermann orbitals. As suggested by Kobayashi and Konami calculations and demonstrated by Svagan *et al.*, this strategy allow tuning the *Q*-band position while keeping the *B*-band almost unchanged.[35] [30]

Figure 2 depicts the molecular structure and absorption spectra of the full set of synthesized light-harvesters (see Methods and Supporting Information). It includes a Pt(II)-*meso*-tetra(4-fluorophenyl)tetrabenzoporphyrin (PtTPTBPF) and three derivatives (Pt1N, Pt2N, Pt3N) obtained by progressive condensation of naphthalene on the macrocycle in order to continuously shift the absorption towards low energies. All these dyes show the typical absorption spectrum of the porphyrins (Fig. 2b-d), with two well separated absorption maxima in the blue (the *B*-band) and in the red (the *Q*-band).[25, 32] However, while the *B*-band

is nearly fixed around 440 nm, the *Q*-band peak moves from 630 nm (PtTPTBPF) to 670 nm (Pt3N). In order to complete the spanned absorption range, the set of sensitizers has been integrated with two additional dyes: the Pd(II)-*meso*-tetra(4-fluorophenyl)tetrabenzoporphyrin (Fig. 2c), where the *Q* band is bathochromically shifted in respect to Pt(II) analogous because of the different effects of the central ion, and a donor-acceptor Schiff base (palladium(II) 2,3-bis[(4-dibutylamino-2-hydroxybenzylidene)-amino]but-2-enedinitrile, PdDBA). This latter allows to harvest also the light at wavelength shorter than 600 nm (Fig. 2a) thanks to a complex absorption structure with a well defined maximum at 585 nm and only few very weak absorption peaks in the UV-blue region. It should be noted that the transparency window of all the sensitizers match the photoluminescence spectrum of perylene (see Fig. 1b).[36]

The effective ability of the prepared sensitizers to excite the perylene triplet state has been studied in tetrahydrofuran (THF) solution by continuous wave and time-resolved photoluminescence measurements (see Methods). In particular, we monitored the sensitizer photoluminescence spectra and yields, the intersystem crossing efficiency ϕ_{ISC} and, after addition of the emitter at suitable concentrations, the energy transfer yield ϕ_{ET} (see Supporting Information, Table T1). We found that all the sensitizers have a ϕ_{ISC} close to one and show phosphorescence in the near infrared, with emission peaked between 770 nm and 870 nm, i.e. resonant with the perylene triplet at ~800 nm.[31, 37] However, the observed ϕ_{ET} is not the same for all the light-harvesters. When levels are perfectly resonant, the occurrence of an unavoidable back-ET from emitters to sensitizers can be only partially controlled by changing the relative dye concentrations. This effect is even more evident when sensitizers triplet state lays slightly below the one of the emitter.[38, 39] Therefore, the ideal condition to maximize ϕ_{ET} is when the sensitizer triplet level is slightly above that one of the emitter. The time resolved phosphorescence measurement of the six sensitizers, discussed in the details in the Supporting Information (**Figure S4**), shows the occurrence of all the described behaviors.

With a perylene concentration as large as 10^{-3} M, we obtained an ET efficiency larger than 95% for PdDBA, PtTPTBPF, and PdTPTBPF. In the case of Pt1N ϕ_{ET} is still as large as 55%, while for the remaining dyes it settled at around 20-30%. By considering the spectral coverage offered by each compound, and in order to avoid unnecessary complication of the system, in the following we restricted our investigation to mixture of PtTPTBPF (8.6×10^{-5} M), PdDBA (7.9×10^{-5} M), Pt1N (8.5×10^{-5} M) and perylene (10^{-3} M), which offers an good ϕ_{ET} and ϕ_{ISC}, as well as a broad and uniform absorption in the full range from 550 to 650 nm. In the next section, the sTTA-UC performances of this multisensitizer system are discussed in details.

3. Efficiency of Broadband sTTA-UC.

For application in real devices, instead of considering the classic QY_{UC}, it is more convenient to introduce an effective up-conversion yield ϕ_{eff}, defined as the ratio between the number of converted photons and the number of the incident ones. It can be written as a function of the excitation intensity I_{exc} and of the system harvesting efficiency ϕ_{harv}, as

$$\phi_{eff}(I_{exc},\phi_{harv}) = QY_{UC}(I_{exc},\phi_{harv})\phi_{harv} = 0.5 f \phi_E \phi_{TTA}(I_{exc},\phi_{harv})\phi_{harv}, \text{ (Eq. 1)}$$

where the factor 0.5 takes in to account that two photons are needed to produce one photon at higher energy. f is the statistical probability to obtain an excited singlet state upon annihilation of two triplets, which is a fixed parameter characteristic of the emitter, ϕ_E is the emitter fluorescence efficiency, and ϕ_{TTA} is the TTA yield.[39] As outlined in Equation 1, ϕ_{TTA} is a function of both I_{exc} and ϕ_{harv} because it results from the competition between the triplet spontaneous decay and that due to their reciprocal annihilation, which is in turn determined by the excited states density. In the limit of high excitation intensity, i. e. when we can assume that all triplets decay by annihilation, ϕ_{TTA} becomes equal to one. In this

condition ϕ_{eff} is independent from I_{exc}, and it is limited only by the light-harvesting capability of the system:

$$\lim_{I_{exc}\to\infty} \phi_{eff}(I_{exc}, \phi_{harv}) = 0.5 f \phi_E \phi_{harv} = 0.5 f \phi_E \underbrace{\bar{\alpha}\phi_{ISC}\phi_{ET}}_{\phi_{harv}}. \qquad \text{(Eq. 2)}$$

Here, $\bar{\alpha}$ is the fraction of incident photons absorbed by the sensitizer, i.e. the wavelength-integrated absorptance (see Supporting Information for details). As previously introduced, in order to quantify the irradiance at which the high excitation limit starts, in the sTTA-UC we must look at the excitation intensity threshold I_{th} . It is the power density at which ϕ_{TTA} is 0.5, which can be written as [24]

$$I_{th} = \frac{Z}{(\bar{\alpha}/d)\phi_{ISC}\phi_{ET}}, \qquad \text{(Eq. 3)}$$

where d is the sample thickness, and Z is a parameter depending on the emitter triplet decay and annihilation cross sections and on the diffusion constant of the energy/molecules in the system. Equations 2-3 indicate the main road to achieve large conversion efficiencies at low excitation power, as requested by the solar technologies. Considering sensitizers with ϕ_{ISC} = 1, and once ϕ_{ET} has been maximized by a proper choose of the emitter concentration, further enhancements of ϕ_{eff} at low power can be obtained by incrementing $\bar{\alpha}$. However, it is worth pointing out that $\bar{\alpha}$ cannot be raised simply by increasing the sensitizer concentration (C_{sens}). Indeed, the molar absorption coefficient of common sensitizers is so large that for C_{sens} >10^{-4} M the incident light within their absorption band is completely harvested in an optical path of less than 0.1 cm.[25] Moreover, high C_{sens} could lead to chromophore aggregation and enhances back-ET from the emitter to the sensitizer (see Supporting Information, Fig. S1).[17] On the contrary, the simultaneous use of complementary sensitizers allows increasing

significantly $\bar{\alpha}$ by broadening the absorption band, without the issues deriving from high C_{sens}. As figure of merit of the multisensitizer sTTA-UC effectiveness, we define a light-harvesting gain factor η as the ratio between the multisensitizer harvesting ability $\bar{\phi}_{harv}$ and the single sensitizer one ϕ_{harv}. In the case of negligible overlap between sensitizer absorptions (see Supporting Information for details), it can be written as

$$\eta = \frac{\bar{\phi}_{harv}}{\phi_{harv}} = \frac{\sum_i \bar{\alpha}_i \phi_{ISC}^i \phi_{ET}^i}{\bar{\alpha}\phi_{ISC}\phi_{ET}} \quad , \qquad \text{(Eq. 4)}$$

where the sum index *i* runs over the full set of sensitizers. Equations 2-4 predict that ϕ_{eff} and I_{th} must be proportional and inversely proportional to η, respectively.

On this basis, we studied the multi-sensitizer system ϕ_{UC} as function of the excitation intensity I_{exc}. In particular, real word operating conditions have been reproduced by exciting the samples with a xenon lamp properly filtered to simulate irradiance and emission profile of the solar light after going through a SC device with an absorption edge at 540 nm.[7, 40] Figure 3 compares the excitation light spectrum with the transmittance of single/multi sensitizers. Calculating the respective wavelength-integrated absorptance (Fig. 3a), we obtain a light-harvesting gain of η ~3, which implies an expected enhancement (reduction) of ϕ_{eff} (I_{th}) of the same magnitude. Fig. 3b shows the photoluminescence spectra of the sample excited in the high excitation limit (irradiance = 20 suns). Perylene luminescence is clearly observable, with its maximum at 470 nm. The converted light intensity I_{UC} of the multisensitizer system is remarkably ~2.2 higher than that emitted by the single sensitizer, not far from the value predicted with the Equation 4, proving the enhanced $\bar{\phi}_{harv}$ ability granted by the co-presence of many absorbing species. The measurements of the I_{UC} dependency on the excitation irradiance are even more interesting (Fig. 3c). Here we show in a log-log scale for both samples the relative up-conversion efficiency ϕ_{eff}. For both samples, ϕ_{eff} follows linearly

the excitation intensity at low powers, and then saturates becoming independent from the excitation above the respective power thresholds.[24] In the case of the single sensitizer solution, the slope change occurs at I_{th}= 2.1×10^{17}ph cm^{-2} s^{-1}, while for the multi-sensitizer one we measure a three-fold reduction of the threshold, I_{th}= 6.5×10^{16}. By considering the solar power distribution at AM 1.5 global condition, the I_{th} value measured for the multi-sensitizer system corresponds to a sub-solar irradiance (0.9 *suns).* This is the lowest value observed for a full organic sTTA-UC system, definitively demonstrating the suitability of this photon managing process for the SC technologies.

It is interesting to note that, while the observed decrease of I_{th} exactly matches the value predicted by the theory, the experimental increase of ϕ_{eff} is smaller than the expected one. In Equations 2 and 3, the only parameter affecting ϕ_{eff}, and not I_{th}, is the emitter quantum yield, thus suggesting a reduction of the fluorescence/light-collection efficiency of perylene in the multi-component system despite the same concentration of emitter has been used in both cases. Indeed, in the high excitation regime, we measured for the multisensitizer system a conversion yield QY_{UC} = 21% instead of the 33% reported for the model single sensitizer solution (see Supporting Information, Figure S6).[19] This is due to a partial overlap between the low-energy tail of the multisensitizer *B*-bands and the up-converted perylene photoluminescence, which induces both self-absorption and resonant back ET from the emitters to the sensitizers. By comparing the shapes of the UC spectra reported in Fig. 3b, it is evident that the low energy tail of the multisensitizer system is strongly reduced in respect with that of the single sensitizer one. The missing emission, due to self-absorption of the UC photoluminescence, corresponds to about one third of the observed yield reduction while the remaining fraction of the yield loss must be ascribed to an emitter-to-sensitizers Förster back ET.

Finally, it is important to note that, thanks to the reduction of I_{th} at 0.9 suns thanks broadband absorption, the 21% of maximum sTTA-UC quantum efficiency corresponds to a QY_{UC} at one sun as large as 10% (Fig. S6), which is a value about three times larger than the one of the standard bi-component system (Fig. 3c).

4. Application of Broadband sTTA-UC to a DSSC cell.

In order to demonstrate that sTTA-UC is able to produce light suitable for SC, we coupled the system described in the previous session to a research-grade DSSC as reported in Figure 4. Fig. 4a shows the absorption spectrum of the employed cell, which begins to be transparent at wavelength longer than about 550 nm (blue solid line). Therefore, the use of the Xe lamp filtered at 540 nm as excitation source (orange shaded spectrum) ensures that only the up-converted photons can be exploited in the current generation. By using the experimental set-up sketched in Fig. 4b, we measured the current produced in the cell under a bias voltage of 0.8 V with (*on* condition in Fig. 4c) and without (*off* condition in Fig. 4c) the broadband up-converter. The data reported in Fig. 4c confirm that the DSSC does not work without the converter, but it supplies a short-circuit current density J_{uc}= 65 μA cm^{-2} under an irradiance of 7 suns when the sub-bandgap photons are up-converted into blue ones. Because of our DSSC illuminated with un-filtered white light produces a current density of J_0= 5.74 mA cm^{-2} (see Supporting Information, Figure S7), the gain $\xi = (J_{uc} + J_0)/J_0$ in the photocurrent generation corresponds to more than 1%, matching the performance of similar system obtained at much higher irradiances.[12, 22, 41] Under 1 sun of excitation, the photocurrent by UC drops down to ~ 30 μA cm^{-2}. As expected, the gain achievable by TTA-UC is lower, but still a measurable value. It is worth pointing out that ξ can be significantly enhanced by optimizing the optical coupling between the solar cells and the up-converting layer, which in our case is very poor, i. e. by using efficient solid-state TTA-UC materials mechanically coupled to the cell.

5. Conclusions.

In conclusion, we demonstrated how to obtain efficient, broadband sTTA-UC at sub-solar irradiance by enhancing the system light-harvesting ability thanks to an *ad-hoc* synthesized family of sensitizers with complementary absorption properties. The simultaneous use of many harvesters allowed extending significantly the system absorption spectral coverage. In such a way, the system absorptance has been effectively boosted achieving two important benefits. First, the number of solar-spectrum photons that are up-converted is doubled. Second, the irradiance required to obtain the maximum sTTA-UC yield is lowered by a factor of three. In such a way, we eliminated one of the main intrinsic limitations of sTTA-UC systems in which the use of classical sensitizers with narrow absorption bands implies the need of super-solar irradiance. The obtained photon up-conversion yield of 10% in AM 1.5 broadband condition strengthen the position of the sTTA-UC as the most promising photon managing strategy for applications to the solar-based devices.

6. Experimental Section

6.1. Sensitizers Synthesis. All the light-harvesting chormophores (PdDBA[42]; PtTPTBPF and PdTPTBPF[43]; Pt1N, Pt2N and Pt3N[44]) were prepared according to previously published procedures.

6.2 Photoluminescence studies.

Optical Absorption. Absorption spectra of chromophores solution in anhydrous tetrahydrofuran (THF, >99.9%, inhibitor free from Sigma-Aldrich) have been recorded with a Cary Varian 50 spectrophotometer at normal incidence in a quartz cuvette of thickness 0.1 cm.

Up-conversion continuous wave and time-resolved photoluminescence. We measured QY_{UC} by comparison with a standard sTTA-UC system. We used the perylene (10^{-3} M) and palladium(II) *meso*-tetra(4-fluorophenyl)tetrabenzoporphyrin (10^{-5} M) as the emitter and

sensitizer, respectively, in THF solution. This sTTA-UC system shifts photons from the red (~632 nm) to the blue (~475 nm) with an giving an effective up-conversion maximum QY_{UC} of ~33%.[19] All solutions have been prepared and sealed in glove box under nitrogen atmosphere in order to prevent the quenching of involved triplets states by molecular oxygen. Photoluminescence spectra were recorded by a nitrogen cooled CCD coupled with a spectrograph Triax-190 (Horiba Jobin-Yvon), with a spectral resolution of 0.5 nm. As excitation source a filtered high pressure xenon lamp has been used. The source irradiance has been measured by a Thorlabs S302C thermal power sensor. To proof the energy transfer towards emitter molecules, the sensitizer's photoluminescence has been studied by continuous wave and time-resolved techniques. As excitation source, we used a Roithner solid-state laser diode RLTMRL-635-100-5 at 1.95 eV (635 nm). For time-resolved studies, the source has been modulated by using a TTi TG550 wave function generator. The photoluminescence decay in time has been recorded in photon-counting mode using a Hamamatsu R943-02 photomultiplier connected to an Ortec 9353 multichannel scaler, with an overall time resolution better than 3 ns.

6.3 DSSC cell preparation and characterization.

Dye Synthesis. The synthesis of the organic dye employed as light harvester for our model DSSC, namely the (*E*)-2-cyano-3-(5-(4-(diphenylamino)phenyl)thiophen-2-yl)acrylic acid (TTCA) was carried out as already described in the literature, by palladium catalyzed Suzuki coupling or direct arylation of the suitable and commercially available reagents (see Supporting Information for details).[45] All reactions were performed using standard glass vessels under an inert nitrogen atmosphere. All the solvents were purchased from Sigma Aldrich and, unless otherwise specified, they have been used without further purification. ^{1}H NMR spectra were recorded on a 400 MHz Avance (Bruker) in CD_2Cl_2 as solvent, reference peak: δ(1H)= 5.30 ppm. DCI-MS analysis was carried out on a Finnigan Mat 95S magnetic

mass spectrometer, loading a drop of sample solution in CH_2Cl_2 on the metal emitter placed on the top of a direct insertion probe.

Device Fabrication. The fabrication of the devices was performed by conventional techniques.[46] TiO_2 electrodes were prepared by spreading (doctor blading) a colloidal TiO_2 paste (20 nm sized; ‘‘Dyesol’’ DSL 18NR-T) onto a conducting glass slide (FTO, Hartford glass company, TEC 8, having a thickness of 2.3 mm and a sheet resistance in the range 6–9 Ω/cm^2) that had been cleaned with water and EtOH, treated with a plasma cleaner at 100W for 10 min, dipped in a freshly prepared aqueous $TiCl_4$ solution ($4.5x10^{-2}$ M), at 70 °C, for 30 min, and finally washed with ethanol. After a first drying at 125 °C for 15 min, a reflecting scattering layer containing >100 nm sized TiO_2 (Solaronix Ti-Nanoxide R/SP) was bladed over the first TiO_2 coat and sintered till 500 °C for 30 min. Then the glass coated TiO_2 was dipped again into a freshly prepared aqueous $TiCl_4$ solution ($4.5x10^{-2}$ M), at 70 °C for 30 min, washed with ethanol and heated once more at 500 °C for 15 min. At the end of these operations the final thickness of the TiO_2 electrode was in the range 8–12 µm, as determined by SEM analysis. After the second sintering, the FTO glass coated TiO_2 was cooled at about 80 °C and immediately dipped into a dichloromethane solution ($5x10^{-3}$ M) of the selected dye at r.t. for 24 h. The dyed titania-glasses were washed with EtOH and dried at r.t. under a N_2 flux. Finally, the excess of TiO_2 was removed with a sharp Teflon penknife and the exact active area of the dyed TiO_0 was calculated by means of a microphotography. A 50 µm thick Surlyn spacer (TPS 065093-50 from Dyesol) was used to seal the photoanode and a platinized FTO counter electrode. Then the cell was filled up with the I^-/I_3^-electrolyte solution. Photocurrents has been measured by a Keithley 2400 Picoammeter/Voltage Source.

6.4 sTTA-UC enhanced DSSC.

The described DSSC cell was coupled to a broadband up-converting solution in order to demonstrate that the sTTA-UC produces photons suitable to enhance the PV performances.

To this aim quartz cuvette of thickness 0.1 cm was filled with a THF solution (Sigma Aldrich, anhydrous, ≥99.9%, inhibitor-free) of PtTPTBPF (8.6×10^{-5} M), PdDBA (7.9×10^{-5} M), Pt1N (8.5×10^{-5} M) and perylene (10^{-3} M). The cuvette was placed in close contact with the front side of the DSSC by using a Cargille refractive index matching liquid to remove the air/quartz interface and improve the optical coupling between the up-converter and the PV cell. As excitation source, we used a high pressure Xenon lamp filtered with a 540 nm long pass colored filter. In such a way, the only photons that can be exploited by the DSSC to generate photocurrent are the blue ones produced by the sTTA-UC.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was supported by funding from Eni Corporate - S.p.A, Divisione Energie Rinnovabili, Istituto Donegani (Novara). A.M. acknowledges support from Edison S.p.A. and Centro Volta for the Somaini Scholarship.

Received: ((will be filled in by the editorial staff))
Revised: ((will be filled in by the editorial staff))
Published online: ((will be filled in by the editorial staff))

References

[1] D. M. Chapin, C. S. Fuller, G. L. Pearson, *J. Appl. Phys.* **1954**, 25, 676.
[2] M. A. Green, *Third Generation Photovoltaics: Advanced Solar Energy Conversion*, Springer, Berlin 2006.
[3] D. Ginley, M. A. Green, R. Collins, *MRS Bull.* **2008**, 33, 355.
[4] G. F. Nemet, Energy Policy 2006, 34, 3218.
[5] B. Kippelen, J.-L. Bredas, *Ener. Environ. Sci.* **2009**, 2, 251.
[6] V. Jankus, E. W. Snedden, D. W. Bright, V. L. Whittle, J. A. G. Williams, A. Monkman, *Adv. Funct. Mater.* **2013**, 23, 384.
[7] A. Kudo, Y. Miseki, *Chem. Soc. Rev.* **2009**, 38, 253.
[8] F. Meinardi, A. Colombo, K. A. Velizhanin, R. Simonutti, M. Lorenzon, L. Beverina, R. Viswanatha, V. I. Klimov, S. Brovelli, *Nat. Photonics* **2014**, 8, 392; D. N. Congreve, J. Lee, N. J. Thompson, E. Hontz, S. R. Yost, P. D. Reusswig, M. E. Bahlke, S. Reineke, T. Van Voorhis, M. A. Baldo, *Science* **2013**, 340, 334.
[9] T. Trupke, M. A. Green, P. Würfel, *J. Appl. Phys.* **2002**, 92, 4117; J. de Wild, A. Meijerink, J. K. Rath, W. G. J. H. M. van Sark, R. E. I. Schropp, *Ener. Environ. Sci.* **2011**, 4, 4835; X. Huang, S. Han, W. Huang, X. Liu, *Chem. Soc. Rev.* **2013**, 42, 173; S. Ji, J. Ge, D.

Escudero, Z. Wang, J. Zhao, D. Jacquemin, *J. Org. Chem.* **2015**, 80, 5958.; C. Zhang, J. Zhao, X. Cui, X. Wu, *J. Org. Chem.* **2015**, 80, 5674.
[10] T. Trupke, A. Shalav, B. S. Richards, P. Wurfel, M. A. Green, *Sol. Energy Mat. Sol. Cells* **2006**, 90, 3327.
[11] J. de Wild, J. K. Rath, A. Meijerink, W. G. J. H. M. van Sark, R. E. I. Schropp, *Sol. Energy Mat. Sol. Cells* **2010**, 94, 2395; G.-B. Shan, G. P. Demopoulos, Adv. Mater. 2010, 22, 4373.
[12] W. Zou, C. Visser, J. A. Maduro, M. S. Pshenichnikov, J. C. Hummelen, Nat Photon 2012, 6, 560.
[13] R. R. Islangulov, F. N. Castellano, Angew. Chem. Int. Ed. 2006, 45, 5957; S. Baluschev, T. Miteva, V. Yakutkin, G. Nelles, A. Yasuda, G. Wegner, Physical Review Letters 2006, 97; T. F. Schulze, T. W. Schmidt, *Ener. Environ. Sci.* **2015**, 8, 103.
[14] T. W. Schmidt, F. N. Castellano, The Journal of Physical Chemistry Letters 2014, 5, 4062.
[15] Y. Y. Cheng, B. Fuckel, T. Khoury, R. Clady, M. J. Y. Tayebjee, N. J. Ekins-Daukes, M. J. Crossley, T. W. Schmidt, *J. Phys. Chem. Lett.* **2010**, 1, 1795.
[16] Y. Y. Cheng, T. Khoury, R. Clady, M. J. Y. Tayebjee, N. J. Ekins-Daukes, M. J. Crossley, T. W. Schmidt, *Phys. Chem. Chem. Phys.* **2010**, 12, 66.
[17] A. Monguzzi, R. Tubino, S. Hoseinkhani, M. Campione, F. Meinardi, *Phys. Chem. Chem. Phys.* **2012**, 14, 4322.
[18] P. Duan, N. Yanai, N. Kimizuka, Chemical Communications 2014, 50, 13111; Y. C. Simon, C. Weder, *J. Mater. Chem.* **2012**, 22.
[19] S. Hoseinkhani, R. Tubino, F. Meinardi, A. Monguzzi, *Phys. Chem. Chem. Phys.* **2015**, 17, 4020.
[20] P. Duan , N. Yanai, N. Kimizuka, *J. Am. Chem. Soc.*, **2013**, 135, 19056.
[21] P. Duan, N. Yanai, H. Nagatomi, N. Kimizuka, *J. Am. Chem. Soc.*, **2015**, 137, 1887.
[22] Y. Y. Cheng, B. Fuckel, R. W. MacQueen, T. Khoury, R. G. C. R. Clady, T. F. Schulze, N. J. Ekins-Daukes, M. J. Crossley, B. Stannowski, K. Lips, T. W. Schmidt, *Ener. Environ. Sci.* **2012**, 5, 6953.
[23] T. F. Schulze, J. Czolk, Y.-Y. Cheng, B. Fückel, R. W. MacQueen, T. Khoury, M. J. Crossley, B. Stannowski, K. Lips, U. Lemmer, A. Colsmann, T. W. Schmidt, *J. Phys. Chem. C* **2012**, 116, 22794; A. Nattestad, Y. Y. Cheng, R. W. MacQueen, T. F. Schulze, F. W. Thompson, A. J. Mozer, B. Fückel, T. Khoury, M. J. Crossley, K. Lips, G. G. Wallace, T. W. Schmidt, *J. Phys. Chem. Lett.* **2013**, 2073; A. Monguzzi, F. Bianchi, A. Bianchi, M. Mauri, R. Simonutti, R. Ruffo, R. Tubino, F. Meinardi, *Adv. Energy Mater.* **2013**, 3, 680; R. S. Khnayzer, J. Blumhoff, J. A. Harrington, A. Haefele, F. Deng, F. N. Castellano, *Chem. Commun.* **2012**, 48, 209.
[24] A. Monguzzi, J. Mezyk, F. Scotognella, R. Tubino, F. Meinardi, *Phys. Rev. B* **2008**, 78, 195112.
[25] D. Papkovsky, T. O'Riordan, *J. Fluoresc.* **2005**, 15, 569.
[26] W. Shao, G. Chen, T. Y. Ohulchanskyy, A. Kuzmin, J. Damasco, H. Qiu, C. Yang, H. Ågren, P. N. Prasad, *Adv. Optical Mater.* **2015**, 3, 575.
[27] D. M. Wu, A. García-Etxarri, A. Salleo, J. A. Dionne, *J. Phys. Chem. Lett.* **2014**, 5, 4020.
[28] A. Monguzzi, D. Braga, M. Gandini, V. C. Holmberg, D. K. Kim, A. Sahu, D. J. Norris, F. Meinardi, *Nano Lett.* **2014**, 14, 6644.
[29] S. Baluschev, V. Yakutkin, G. Wegner, T. Miteva, G. Nelles, A. Yasuda, S. Chernov, S. Aleshchenkov, A. Cheprakov, *Appl. Phys. Lett.* **2007**, 90.
[30] A. J. Svagan, D. Busko, Y. Avlasevich, G. Glasser, S. Baluschev, K. Landfester, *ACS Nano* 2014, 8, 8198.

[31] M. Montalti, S. L. Murov, *Handbook of photochemistry*, CRC/Taylor & Francis, Boca Raton 2006.
[32] M. Gouterman, *J. Mol. Spectr.* **1961**, 6, 138.
[33] V. Yakutkin, S. Aleshchenkov, S. Chernov, T. Miteva, G. Nelles, A. Cheprakov, S. Baluschev, *Chem. Eur. J. -A* **2008**, 14, 9846.
[34] J. R. Sommer, A. H. Shelton, A. Parthasarathy, I. Ghiviriga, J. R. Reynolds, K. S. Schanze, *Chem. Mater.* **2011**, 23, 5296.
[35] N. Kobayashi, H. Konami, *J. Porph. Phthal.* **2001**, 05, 233.
[36] J.-H. Kim, F. Deng, F. N. Castellano, J.-H. Kim, *ACS Photonics* **2014**, 1, 382.
[37] R. H. Clarke, R. M. Hochstrasser, *J. Mol. Spectr.* **1969**, 32, 309.
[38] Y. Y. Cheng, B. Fuckel, T. Khoury, R. Clady, N. J. Ekins-Daukes, M. J. Crossley, T. W. Schmidt, *J. Phys. Chem. A* **2011**, 115, 1047.
[39] R. P. Groff, R. E. Merrifield, P. Avakian, *Chem. Phys. Lett.* **1970**, 5, 168.
[40] M. Grätzel, *Inorg. Chem.* **2005**, 44, 6841.
[41] T. F. Schulze, Y. Y. Cheng, B. Fückel, R. W. MacQueen, A. Danos, N. J. L. K. Davis, M. J. Y. Tayebjee, T. Khoury, R. G. C. R. Clady, N. J. Ekins-Daukes, M. J. Crossley, B. Stannowski, K. Lips, T. W. Schmidt, *Aus. J. Chem.* **2012**, 65, 480.
[42] S. M. Borisov, R. Saf, R. Fischer, I. Klimant, *Inorg. Chem.* **2013**, 52, 1206.
[43] S. M. Borisov, G. Nuss, W. Haas, R. Saf, M. Schmuck, I. Klimant, *J. Pohotochem. Photobiol. A: Chemistry* **2009**, 201, 128.
[44] F. Niedermair, S. M. Borisov, G. Zenkl, O. T. Hofmann, H. Weber, R. Saf, I. Klimant, *Inorg. Chem.* 2010, 49, 9333.
[45] M. Velusamy, K. R. Justin Thomas, J. T. Lin, Y.-C. Hsu, K.-C. Ho, *Org. Lett.* **2005**, 7, 1899; D. P. Hagberg, T. Marinado, K. M. Karlsson, K. Nonomura, P. Qin, G. Boschloo, T. Brinck, A. Hagfeldt, L. Sun, *J. Org. Chem.* **2007**, 72, 9550; W.-H. Liu, I. C. Wu, C.-H. Lai, C.-H. Lai, P.-T. Chou, Y.-T. Li, C.-L. Chen, Y.-Y. Hsu, Y. Chi, *Chem. Commun.* **2008**, 5152; D. J. Schipper, K. Fagnou, *Chem. Mater.* **2011**, 23, 1594; C. Lelii, M. G. Bawendi, P. Biagini, P.-Y. Chen, M. Crucianelli, J. M. D'Arcy, F. De Angelis, P. T. Hammond, R. Po, *J. Mater. Chem. A* **2014**, 2, 18375.
[46] S. Ito, T. N. Murakami, P. Comte, P. Liska, C. Grätzel, M. K. Nazeeruddin, M. Grätzel, *Thin Solid Films* **2008**, 516, 4613.
[47] S. M. Bachilo, R. B. Weisman, J. Phys. Chem. A 2000, 104, 7711; J. L. Charlton, R. Dabestani, J. Saltiel, *J. Am. Chem. Soc.* **1983**, 105, 3473.
[48] K. H. Grellmann, A. R. Watkins, *Chem. Phys. Lett.* **1971**, 9, 439.

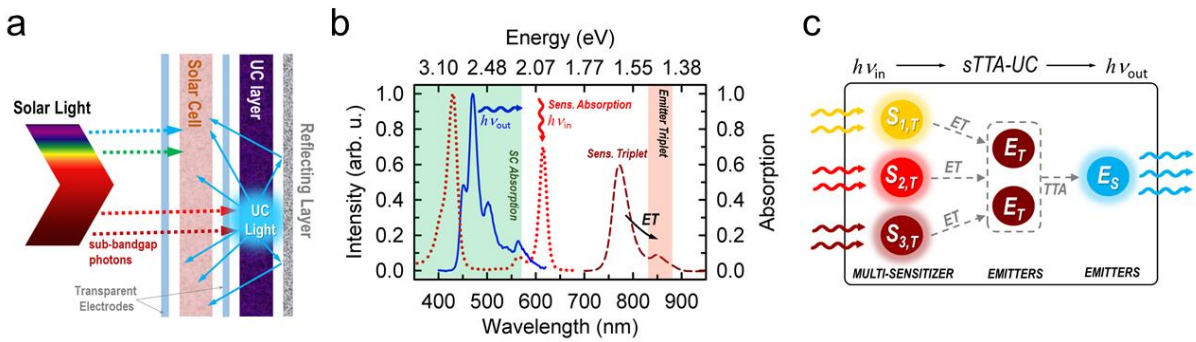

Figure 1. Operating principles of the photon up-conversion through sensitized TTA. (a) Sketch of a SC coupled to a sTTA-UC material for light harvesting enhancement. The transmitted sub-bandgap photons are blue shifted by the UC layer, in order to be exploited by the SC. (b) sTTA in a standard bi-component systems. A sensitizer absorbs the incoming photons with energy below the SC absorption edge (dotted line, $h\nu_{in}$) and excites the optically dark emitter triplets (red stripe) *via* Dexter energy transfer (ET) from its phosphorescent triplets (dashed line). Upon triplet-triplet annihilation (TTA), up-converted photoluminescence is generated (solid blue line, $h\nu_{out}$) and absorbed by the SC (light-blue stripe). (c) Outline of a multi-sensitizer TTA-UC system. Three sensitizers are excited simultaneously under white light illumination at different energies ($S_{i,T}$). All of them transfer the harvested energy to emitter triplets E_T, thus broadening the overall absorption of the system and increasing the number of emitter fluorescent singlets E_S generated upon TTA.

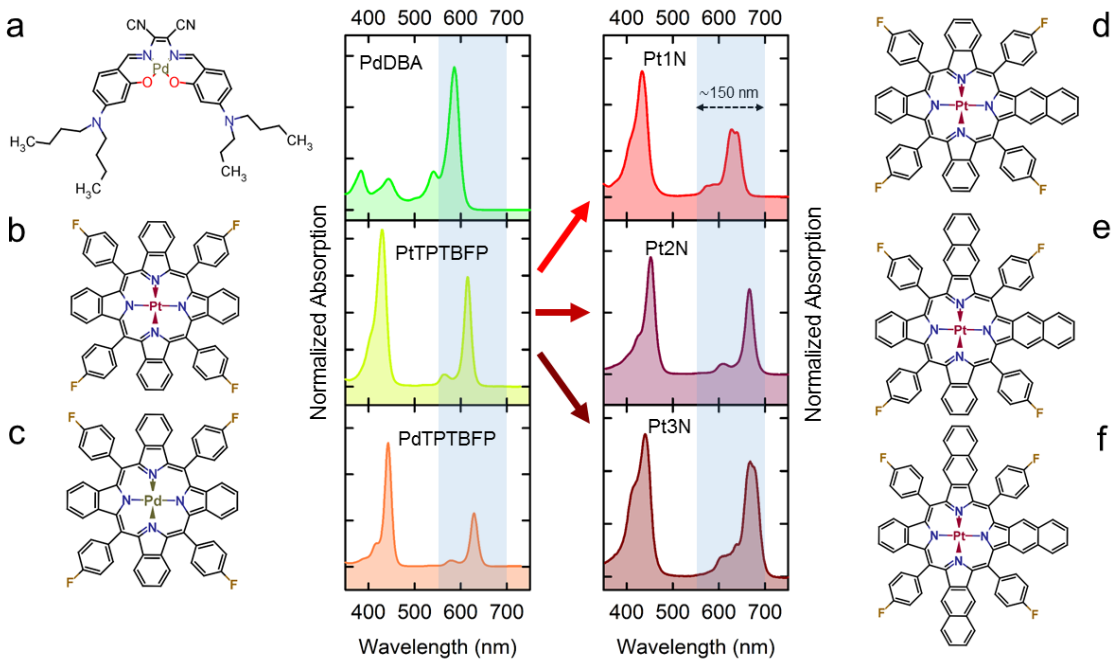

Figure 2. Molecular structures of the sensitizers used in the broadband-absorption sTTA-UC system. All the dyes are phosphorescent in the NIR, with emission wavelengths between 770 nm and 870 nm. The blue stripe shows the spectral range spanned by their long-wavelength absorption peaks. By several sensitizers, we can broaden the overall absorption band of the system up to 150 nm.

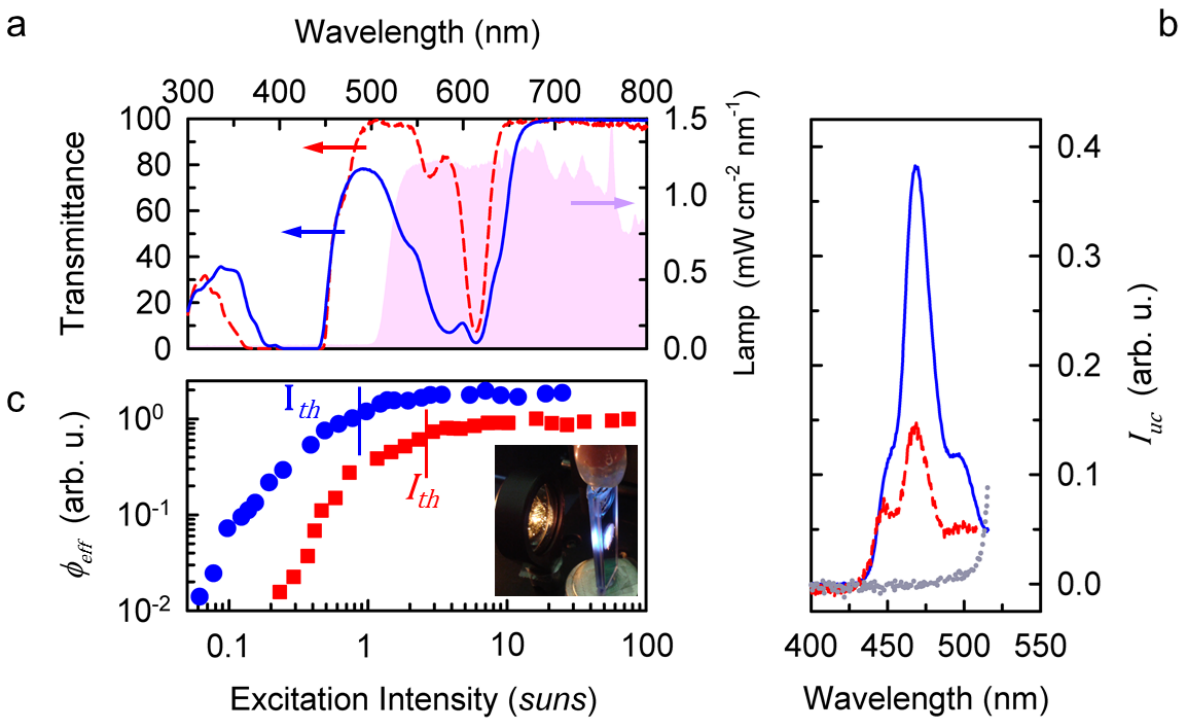

Figure 3. Optical properties of the described multisensitizer sTTA-UC. (a) Transmittance profile of a single- (PtTPTBPF:perylene, red dashed line) and of a multi- (PtTPTBPF:PdDBA:Pt1N:perylene, blue solid line) sensitizers TTA-UC solution in THF (optical path = 0.1 cm). The shaded pink spectrum it the emission spectrum of the filtered xenon lamp used as non-coherent source. (b) Photoluminescence spectra of the single- (red dashed line) and multi- (blue solid line) sensitizer sTTA-UC systems at an excitation power density of 20 suns. Without the emitter none up-converted light is detectable (dotted line). (c) Relative conversion yield ϕ_{eff} measured as a function of the excitation intensity for the single- (squares) and multi- (dots) sensitizer up-converters. The data are normalized to the high excitation limit value of the single sensitizer solution. The inset is a picture of the sample under 10 suns of broadband excitation.

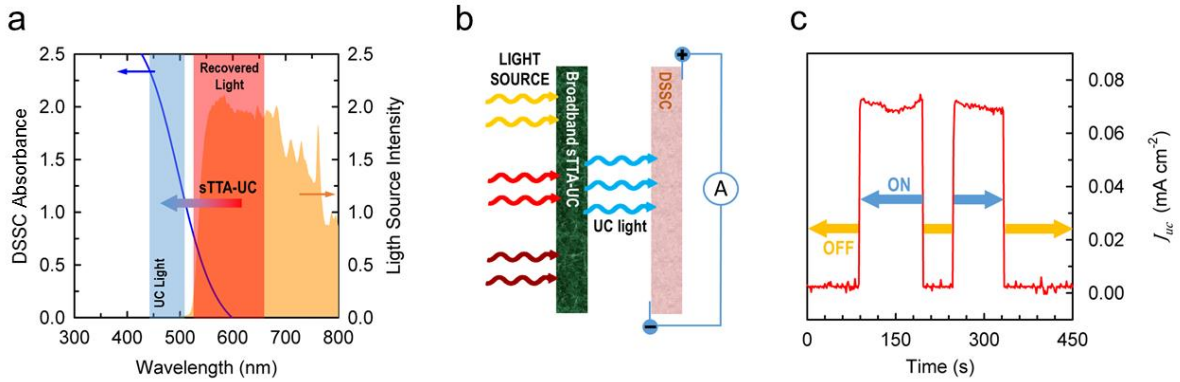

Figure 4. Test of the broadband sTTA-UC coupled to a research-grade DSSC. (a) Absorbance of the DSSC cell (solid line) and emission spectrum of the filtered white lamp employed as light source. Colored stripes outline the working range of the tested broadband sTTA-UC. The red one shows the spectral range of the recovered sub-bandgap photons, while the blue one shows the up-converted emission range matching the DSSC absorption. (b) Sketch of the experimental setup. (c) Photocurrent generated in DSSC devices with (*ON* condition) and without (*OFF* condition) the up-converter.

The table of contents entry

We demonstrate how to obtain broadband triplet-triplet annihilation assisted photon up-conversion at sub-solar irradiance with simultaneous use of several light harvesters. An unprecedented yield of 10% is obtained in AM 1.5 condition in a fully organic system, which allows a DSSC device to operate by exploiting exclusively sub-bandgap photons.

Keyword

photon managing, triplet-triplet annihilation, broadband up-conversion, photovoltaics, asymmetric porphyrins

A. Monguzzi, S. Borisov, J. Pedrini, I. Klimant, M. Salvalaggio, P. Biagini, F. Melchiorre, C. Lelii and F. Meinardi**

Efficient Broadband Triplet-Triplet Annihilation Assisted Photon Up-conversion at Sub-solar Irradiance in Full Organic Systems

Supporting Information

Production Data
Click here to download Production Data: TOC_file.docx