



A tan for molecules: photocatalyzed synthesis with direct sunlight

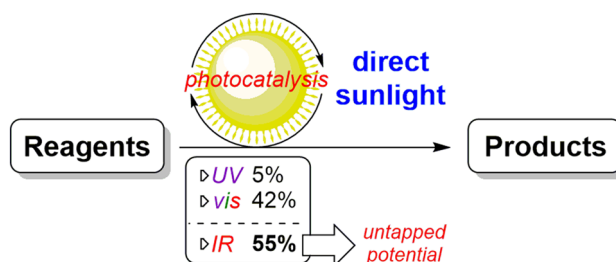
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Abstract

Photocatalytic processes applied to organic synthesis have known an impressive development over the last decade. The reactions are now routinely carried out upon irradiation with artificial light sources. However, several research groups have profited of direct sunlight to trigger such processes, in turn boosting the sustainability character of the devised synthetic protocols. This contribution gathers recent examples in the area, showcasing the possibility to fully exploit the different wavelength ranges of solar light, with particular regards to both ultraviolet and visible regions. On the other hand, near-infrared light, the main component of solar light, has not been exploited so far, albeit a handful of examples exploiting artificial near-infrared irradiation have been recently reported and development in this direction is expected soon.

Graphic abstract



Keywords Sunlight · Organic synthesis · Sustainable chemistry · Photocatalysis · Solar spectrum

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1 Introduction

The aim of synthetic photochemists is to transform molecules by shining light on them. The typical procedure of a photochemical synthesis requires the preparation of a solution and, after having identified the ideal conditions, to turn on the light coming from a dedicated source (Albini and Fagnoni 2009; Mattay and Griesbeck 2004). While electric discharge lamps (e.g., Hg-vapor lamps) have been the election choice until roughly 10 years ago, the area of illumination devices has recently known an impressive development, as demonstrated by the advent of light emitting diodes (LEDs). Notably, LEDs convert electricity into light with a higher efficiency compared to traditional lamps, and this brought a refreshing new tone into the photochemical approach. Remarkably, even more efficient solutions are

expected to be available in the near future (McAtee et al. 2019; Pattison et al. 2018).

Nevertheless, independently from the adopted light source, all these devices require electricity to work, thus causing an intrinsic economic and environmental cost. In view of this, since at present our energetic portfolio is mostly based on non-renewable sources (combustion of coal, petroleum and natural gas), running a photochemical reaction contributes to the release of carbon dioxide into the atmosphere, in turn concurring to the climate change we are currently experiencing (Armaroli and Balzani 2010). If we think that these fossil fuels are the result of an ancient sunlight-promoted photosynthetic process, we may indeed consider to avoid the use of artificial light sources and exploit directly the light coming from the Sun today, thus skipping all the intermediate conversions from one form of energy to another (Armaroli and Balzani 2010).

The possibility to run photochemical reactions with sunlight has been first demonstrated by the father of modern organic photochemistry, Giacomo Ciamician, that foresaw the possibility for mankind to master “the guarded secret of plants” (Ciamician 1912) in other words the opportunity to trigger at will chemical processes by simply shining (sun) light on the reaction mixtures (Protti and Fagnoni 2009; Ravelli et al. 2016; Schultz and Yoon 2014; Yoon et al. 2010). This idea is strictly connected with the belief that photochemistry is an intrinsically “sustainable” discipline, thanks to the use of the photon, the “traceless reagent” per excellence, that conveys a huge amount of energy in the reaction mixture, while leaving no traces behind (Albini and Fagnoni 2004). Indeed, it has been demonstrated that there may be a direct relationship between green chemistry and photochemistry, albeit this connection is not valid a priori and the actual advantages of photochemistry over traditional (thermal) methods depend from case to case (Ravelli et al. 2011).

Although the concepts of green chemistry and photochemistry do not always point towards the same direction, the replacement of an artificial light source with natural sunlight is intrinsically an eco-sustainable turning point. Of course, this may bring about some drawbacks, due to the discontinuous nature of the light source (day–night alternance), the dependence on climatic conditions (summer–winter alternance; possibility of cloudy weather, etc.) and the geographical position. Nevertheless, as recently reviewed, dedicated solar photoreactors have been developed and it has been demonstrated that exploiting natural sunlight in these apparatuses is a viable choice, affording the desired products in good to excellent yields (Oelgemöller 2016).

However, some reports have appeared in the literature where solar light was used in place of artificial light by simply exposing the reaction vessel to ambient sunlight, in

turn obtaining comparable (sometimes even better) results. In fact, the main focus of the present paper is to showcase recent examples in the area, demonstrating that everybody can perform a sunlight-promoted photochemical reaction with no need of sophisticated equipments, but simply adapting routine photochemical techniques to the use of this inexpensive and inexhaustible light source. Most of the reported examples involve photocatalytic processes, a family of photochemical reactions where light and a catalyst able to absorb the employed radiation are required (see below) (Fagnoni et al. 2019; Koenig 2013; Stephenson et al. 2018; Sideri et al. 2018).

1.1 The properties of solar light

The life on Earth is intimately associated with the Sun. The energy coming from our star promotes, either directly or indirectly, the occurrence of a myriad of processes, the photosynthesis of plants being perhaps the most noble example. When planning to exploit sunlight to promote chemical processes, two parameters must be primarily considered: radiation intensity and its spectral distribution.

As for the first point, this is known as “solar constant” and it is a measure of the amount of electromagnetic radiation coming from the sun per unit area incident on a plane perpendicular to the rays, at a distance of one astronomical unit (the mean Earth–Sun distance). Recent reports indicate a value of 1361 W m^{-2} , slightly lower than that previously accepted (Kopp and Lean 2011), but surely enough to carry out a typical photocatalyzed process (for more information about the light intensities commonly adopted, see e.g., the Supporting Information of Le et al. 2017).

As for the solar spectrum, the total radiation output is equivalent to that originating from a black body at 5776 K. Accordingly, it encompasses different regions, namely the ultraviolet (UV; $< 400 \text{ nm}$), visible (VIS; $400\text{--}700 \text{ nm}$, albeit according to some definitions the VIS range extends up to 800 nm) and infrared (IR; $> 700 \text{ nm}$) ranges, with a share of approximately 10, 40, and 50% of the total radiant energy emitted from the Sun, respectively (Fu 2003). However, these values refer to the situation at the top of the atmosphere and completely neglect its contribution. When passing through the atmosphere, solar radiation can be absorbed and/or scattered by gases, aerosols and clouds present in it; furthermore, the Earth’s surface has a role as well in reflecting the incident photons. This is known as “albedo” and accounts for ca. 30% of the incoming solar radiation (Fu 2003). However, the effect of these processes is not homogeneous over the entire solar spectrum, thus affecting each wavelength range to a different extent. As a result, sunlight at Earth’s surface consists of UV, VIS and IR light in 3–5,

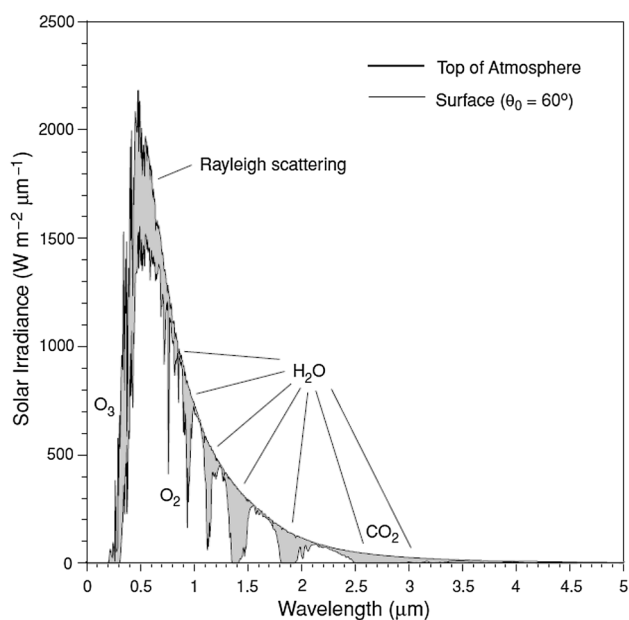


Fig. 1 Solar spectrum at the top of the atmosphere and on the surface of the Earth. Reproduced with permission from (Liou 2002)

42–43 and 52–55% amounts, respectively¹ (Oelgemöller 2016). Figure 1 gathers the different solar spectra at the top of the atmosphere and on the surface of the Earth (a solar zenith angle of 60° has been considered; no contributions from aerosols or clouds), also highlighting the reasons for the observed differences between the two plots (Fu 2003).

1.2 Direct irradiation and photocatalysis

When a molecule absorbs a photon, it is promoted to an excited state through the displacement of one electron from an occupied to an unoccupied orbital. This state shows extremely interesting features in terms of reactivity and typically leads to the formation of open-shell reactive intermediates (e.g., radicals and radical ions) that are characteristic of photochemical activation (Scheme 1, top). In turn, these intermediates participate in bond-forming reactions through pathways that are often complementary to those observed in ground state counterparts. Within the realm of small organic molecules, the population of an excited state is usually achieved upon irradiation with highly energetic UV-light sources ($280 < \lambda < 315$ nm, UV-B range, or $100 < \lambda < 280$ nm, UV-C range) (Esser et al. 1994). However, such high-energy photons can cause the occurrence of uncontrolled parasite processes, such as decomposition

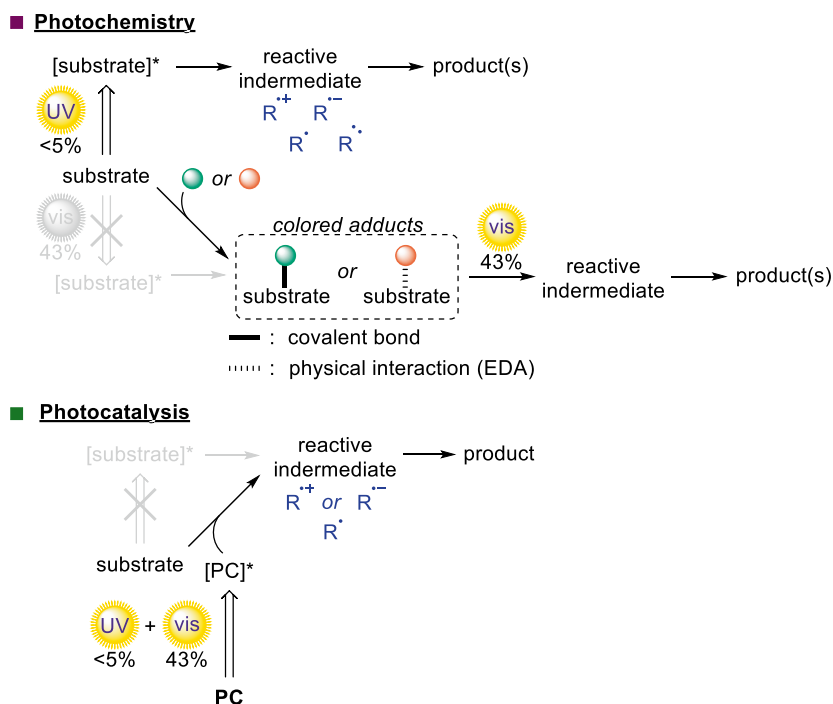
and/or polymerization, dramatically reducing the appeal of the photochemical approach. To make things worse, the application of sunlight irradiation for the direct excitation of small organic molecules is virtually impossible, due to the lack of UV-B and UV-C components in the solar radiation reaching the Earth's surface. Thus, the ozone layer in the atmosphere filtrates the most energetic and harmful part of the solar spectrum in the ultraviolet range, which cannot get to the reaction vessel (Fig. 1). A few exceptions exist, however, and these are based on the use of selected molecules, able to interact with the small UV-A fraction present in sunlight. These include, for example, derivatives of aromatic amines (Dichiarante et al. 2010) or aromatic carbonyls (Li et al. 2003).

One possibility to circumvent this limitation is to apply strategies for the modification of the absorption spectrum of the substrate (Scheme 1, top). This can be done in two main ways, either attaching a moiety able to convert the substrate into a colored derivative (Crespi et al. 2016), or through the addition of a compound (possibly, in catalytic amount) to the reaction mixture to generate in situ an electron donor–acceptor (EDA) complex (Silvi and Melchiorre 2018). Both strategies allowed for the convenient use of solar light in synthetic strategies, as in the case of the arylation of various (hetero) aromatics and isonitriles by arylazo sulfones (Opatz et al. 2018) and in the stereoselective catalytic α -alkylation of aldehydes (Arceo et al. 2013).

A much more popular and versatile approach makes use of a so-called photocatalyst (PC), a compound that is added to the reaction mixture to catch low-energy photons and to activate organic molecules (Scheme 1, bottom). In this case the absorption spectrum of the substrate is not influenced by the presence of PC, which is only active when in the excited state. Indeed, it is impossible to exaggerate the interest in sunlight as a cheap and unlimited source of energy to trigger photoreactions, that spread out in parallel with the recent studies in photocatalysis (Fagnoni et al. 2019; Koenig 2013; Stephenson et al. 2018; Sideri et al. 2018). This “natural” upgrade of photochemistry, mimicking the way plants exploit the energy coming from the Sun in photosynthesis, brings about two main advantages. First, since each catalyst shows a peculiar reactivity mechanism, depending on the properties of its excited state, different chemical transformations can be triggered, often with very high selectivity. Secondly, there is no need for the substrate to absorb directly the light, since the adopted PC takes care of that. Indeed, the routinely used PCs absorb low-energy light ($315 < \lambda < 400$ nm, UV-A or, more often, $400 < \lambda < 800$ nm, VIS light) and allow to generate indirectly the abovementioned open-shell intermediates. As a result, the photocatalytic approach can conveniently exploit a significant fraction of the Sun emission spectrum, around 45–50% of the total sunlight reaching the Earth's surface.

¹ Standardized solar spectra definitions are now available and they are routinely used for harmonization purposes (Gueymard et al. 2002). See also: <http://www.nrel.gov/grid/solar-resource/spectra.html>.

Scheme 1 Differences between the photochemical (top) and photocatalytic (bottom) approaches. The percentage below the image of the sun represents the amount of sunlight a chemist can rely upon to design a photoreaction. *UV* ultraviolet light, *VIS* visible light, *PC* photocatalyst, *EDA* electron donor–acceptor complex. The asterisks (*) mark the excited states



In the following, recent examples of photocatalyzed syntheses carried out under direct sunlight irradiation are reported. They have been classified according to the solar spectrum region suitable for excitation of the employed PC.

2 Examples of sunlight-induced photocatalyzed syntheses

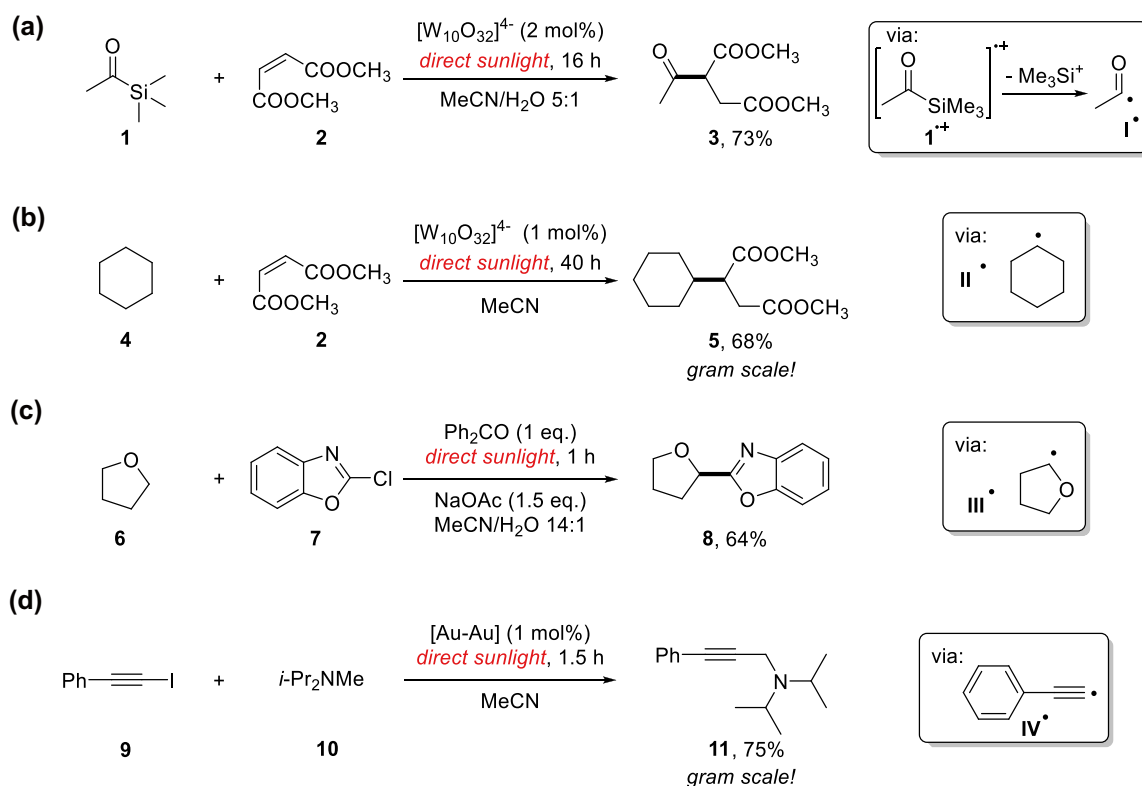
2.1 UV-A region

As mentioned, only the less energetic part of the ultraviolet light coming from the Sun reaches the Earth's surface, namely UV-A with $\lambda > 315$ nm. To take full advantage of such a modest amount of light and design reliable synthetic protocols, very efficient and robust photocatalysts are required. A notable example is represented by tetrabutylammonium decatungstate (TBADT, $(n\text{-Bu}_4\text{N})_4[\text{W}_{10}\text{O}_{32}]$) (Ravelli et al. 2016; Tzirakis et al. 2009), whose excited state owns a remarkably high redox potential ($E([\text{W}_{10}\text{O}_{32}]^{4-*}/[\text{W}_{10}\text{O}_{32}]^{5-}) \sim +2.4$ V vs SCE) (De Waele et al. 2016). This feature makes it an ideal PC for the activation of a huge variety of substrates via oxidative single-electron transfer (SET). Moreover, this state is endowed with a partial radical character on the oxygen atoms of the cluster, which renders its ability to cleave homolytically $\text{C}(sp^3)\text{-H}$ and $\text{C}(sp^2)\text{-H}$ bonds in a plethora of aliphatic derivatives via a hydrogen atom transfer (HAT) step (Ravelli et al. 2016; Tzirakis et al. 2009).

A representative example of the use of TBADT for SET under direct sunlight irradiation is offered by our recent work on the smooth generation of acyl radicals from acylsilanes, in turn applied to the synthesis of unsymmetrical ketones (Scheme 2a). We found that the excited state of TBADT can oxidize acylsilane **1** to the corresponding radical cation $\mathbf{1}^{*+}$ under sunlight irradiation, thus promoting a mesolytic fragmentation to afford acyl radical \mathbf{I}^{\bullet} . In turn, \mathbf{I}^{\bullet} was trapped by electrophilic dimethyl maleate **2** to afford the desired carbonyl compound **3** in high yields, without the need of other additives (Capaldo et al. 2018).

On the other hand, TBADT has been used as a photocatalyst for HAT under solar light irradiation in several instances (Ravelli et al. 2016). As an example, our group reported the use of this polyoxometalate for the solar light-driven photocatalyzed cleavage of C–H bonds in aldehydes, ethers, amides and even cycloalkanes to obtain the corresponding C-centered radicals. Remarkably, the activation of the inert C–H bond embedded in cyclohexane **4** was achieved on a gram-scale within a few days of irradiation (40 h over 5 days; Scheme 2b). The thus generated cyclohexyl radical intermediate (\mathbf{II}^{\bullet}) was efficiently trapped by **2** to afford the corresponding alkylated adduct **5** in 68% yield. Notably, this powerful transformation could be triggered by merely exposing the solution to the sun in a glass vessel on a window ledge (Fig. 2, left) (Protti et al. 2009).

A different class of compounds operating under UV-A irradiation is that of aromatic carbonyls (see above), the most representative example being benzophenone. While



Scheme 2 **a** Sunlight-driven generation of acetyl radical via TBADT-photocatalyzed mono-electronic oxidation of acylsilane **1**. **b** Sunlight-driven photocatalyzed alkylation via TBADT-mediated HAT on cyclohexane **4**. **c** Benzophenone as a sunlight-triggered photocatalyst

for the functionalization of benzoxazole **7**. **d** Dimeric complex $[\text{Au}_2(\mu\text{-dppm})_2]^{2+}$ as photocatalyst for the synthesis of propargylic amines under direct solar light irradiation



Fig. 2 (left) Reaction vessels employed for sunlight-promoted TBADT-photocatalyzed C–H alkylations. Adapted from (Protti et al. 2009) with permission from The Royal Society of Chemistry.



(right) The “sunflow” apparatus adopted for the benzophenone-promoted functionalization of benzoxazoles. Reproduced with permission from (Nauth et al. 2017)

one of the most widespread reactions of these compounds under sunlight is pinacolization (Li et al. 2003), it has been recently reported that benzophenone can utilize direct

sunlight to catalyze the reaction between tetrahydrofuran (THF, **6**) and 2-chlorobenzoxazole **7** to give the corresponding substitution product **8** in 64% yield (Scheme 2c).

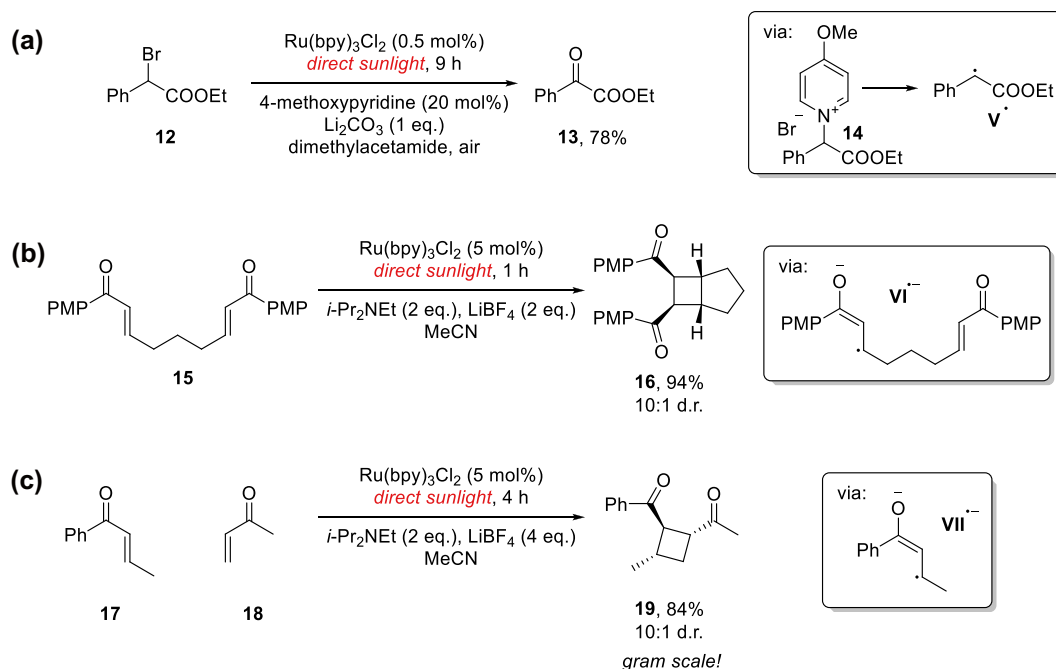
A stop-flow technique was adopted, whereby the reaction mixture was loaded in a very thin FEP (fluorinated ethylene-propylene polymer) tubing hanging on an aviary fence (“sunflow” approach; Fig. 2, right) and exposed to direct sunlight. The reduced optical path resulted into an optimal penetration of solar light and, hence, in short reaction times (1 h) (Nauth et al. 2017).

Quite recently, the gold complex $[\text{Au}_2(\mu\text{-dppm})_2]^{2+}$ [dppm = 1,1-bis(diphenylphosphino)methane] has been shown to possess an intriguing reductive attitude ($E^0(\text{Au}_2^{3+}/\text{Au}_2^{2+*}) = -1.5$ to -1.7 V vs SCE) under direct sunlight irradiation (Revol et al. 2013; Xie et al. 2015). In one example, this feature was exploited to synthesize propargylic amines from tertiary aliphatic amines and iodoalkynes. Thus, when a solution of (iodoethynyl)benzene **9** and diisopropylmethylamine **10** was irradiated in the presence of this dimeric gold complex, the desired product **11** was obtained on a gram-scale in 75% yield after only 90 min irradiation. Upon absorption of a photon, the highly reducing excited state of the gold complex was generated and readily interacted with **9** to afford alkynyl radical **IV***. Afterwards, **10** was involved in the regeneration of the photocatalyst, in turn leading to the formation of an α -aminoalkyl radical intermediate. Propargylic amines were then obtained via a radical–radical coupling between the photogenerated radical intermediates (Scheme 2d).

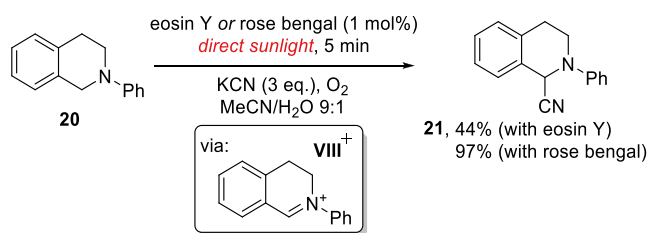
2.2 Visible region

Despite the efficiency of the catalysts presented in the previous paragraph, UV-light remains a minor fraction of the solar spectrum. Accordingly, a more convenient choice would be to select catalysts prone to activate organic molecules under visible light excitation, which consists of about 42% of the total sunlight radiation. Undoubtedly, the most investigated photocatalysts belonging to this group show a characteristic absorption in the violet–blue range of the spectrum ($400 < \lambda < 500$ nm). These include polypyridyl-based transition-metal complexes containing Ru^{II} or Ir^{III} centers and the mesityl acridinium cation or the 2,4,5,6-tetra(9H-carbazol-9-yl)isophthalonitrile (4CzIPN) derivative. On the other hand, some derivatives, including eosin Y and Rose bengal, show a typical absorption in the green–yellow region ($500 < \lambda < 590$ nm), while methylene blue is one of the few photocatalysts able to work under orange–red light irradiation ($590 < \lambda < 800$ nm) (Fagnoni et al. 2019; Prier et al. 2013).

In one instance (Su et al. 2011), $\text{Ru}(\text{bpy})_3\text{Cl}_2$ was used under ambient sunlight irradiation to catalyze the aerobic oxidation of the α -aryl halogen derivative **12** to the corresponding ketone **13** in the presence of 4-methoxypyridine as an activating agent (Scheme 3a). In particular, the reaction between the heterocycle and **12** generated in situ the easily reducible pyridinium salt **14**, which liberated a stabilized C-centered radical (**V***) after electron transfer and subsequent fragmentation. The so-obtained intermediate was in



Scheme 3 $\text{Ru}(\text{bpy})_3\text{Cl}_2$ photocatalyzed processes promoted by direct sunlight irradiation. PMP *p*-methoxyphenyl



Scheme 4 Oxidative α -cyanation of tetrahydroisoquinoline **20** in the presence of air as terminal oxidant

turn trapped by molecular oxygen to afford the oxygenated product **13**.

The same ruthenium photocatalyst was also used to promote a [2 + 2] cycloaddition between two olefinic reaction partners. The process occurred via a SET mechanism and it was demonstrated to work both in an intramolecular and intermolecular fashion. Initially, it was shown that the exposure to ambient sunlight of a solution containing aryl enone **15** resulted in an intramolecular [2 + 2] cycloaddition to obtain cyclobutane **16** in 94% yield after irradiation for just 1 h. The proposed mechanism involves the reduction of substrate **15** to intermediate $\text{VI}^{\bullet-}$ by the excited state of the photocatalyst; a stepwise cyclization finally afforded **16** (Scheme 3b) (Ischay et al. 2008). Later on, the same approach was successfully extended to crossed [2 + 2] intermolecular photocycloadditions, where two different enones could be used to achieve heterodimerization. For example, the easily reducible enone **17** was responsible for the oxidative quenching of the ruthenium-based photocatalyst to afford intermediate $\text{VII}^{\bullet-}$. The latter was readily intercepted by a non-reducible enone such as **18**, leading to product **19** via a stepwise radical cycloaddition (Scheme 3c) (Du and Yoon 2009).

Moving towards photocatalysts with an absorption maximum in the green region, it is worth mentioning one example focusing on the aerobic, oxidative α -cyanation of tetrahydroisoquinoline **20** to give the corresponding α -aminonitrile **21** catalyzed by either of the photoorganocatalysts eosin Y or rose bengal (Nauth et al. 2017). In particular, the “sunflow” approach was again exploited and, remarkably, the reaction took place in only 5-min irradiation, affording the desired product **21** in 44 and 97% yield in the presence of eosin Y or rose bengal, respectively, through the intermediacy of iminium ion VIII^+ (Scheme 4). Interestingly, when the blue-light-absorbing $\text{Ru}(\text{bpy})_3\text{Cl}_2$ complex was used in the role of photocatalyst, α -aminonitrile was obtained in 57% yield.

Turning to the red region of the solar spectrum, there are only a handful of examples dealing with the use of methylene blue as photosensitizer for the generation of singlet oxygen and ensuing trapping in cycloaddition processes. Rigorously speaking, these examples are outside the scope of the present review, since they have been carried out in dedicated solar reactors. Indeed, the first example deals with the synthesis of

Juglone under medium concentrated sunlight (Oelgemöller et al. 2006), while the second is a recent report describing a luminescent solar concentrator (LSC) for continuous-flow photochemical applications, where the described benchmark reaction was the preparation of the endoperoxide of 9,10-diphenylanthracene (Cambié et al. 2017).

3 Recent trends in photocatalysis: moving to the IR range

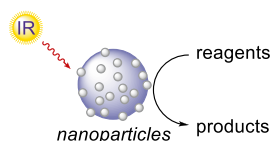
Electronic excitations typically requires the exploitation of photons in the UV or VIS range, since only such photons have the energy required to promote the desired electronic displacements among the relevant orbitals. In terms of sunlight utilization for photochemical/photocatalyzed syntheses, however, this is a severe limitation, since the near-infrared (NIR) spectral range represents the most abundant fraction, accounting for more than 50% of solar radiation hitting the Earth’s surface. So far, photochemical applications of NIR light are mainly found in biomedicine, due to its ability to penetrate deeply into biological tissues without causing damage. Notable examples involve photodynamic therapy, pro-drug activation or in vivo imaging (Barolet 2008). On the other hand, only sparse examples of NIR light induced photochemical syntheses have been reported in the literature so far and none of them exploits direct sunlight irradiation. Two approaches are possible: the exploitation of localized surface plasmon resonance (LSPR) or having recourse to photon upconversion (PU).

Localized surface plasmon resonance (LSPR, Scheme 5, top) consists in the collective oscillation of conduction electrons in metallic nanoparticles caused by incident light. For synthetic purposes, systems comprising of an anisotropic nanostructure with a LSPR absorption band in the NIR region and a catalytic component are commonly used (Gu et al. 2019). As an example, Au nanorods decorated with Pd nanoparticles have been developed for Suzuki reactions. The Au core is the plasmonic component for light harvesting and Pd nanoparticles act as catalyst. Indeed, it has been demonstrated that both plasmonic photocatalysis and photothermal heating contribute to improve the catalytic activity and the desired coupling products were obtained in yields from good to excellent (Jiang et al. 2013). Recently, semiconductor nanocrystals were employed as plasmonic component for cross-coupling C–C bond formation as well (Gu et al. 2019).

However, one of the main limitations in adopting NIR light for chemical transformations comes from the need for systems able to harvest such low-energy radiation and convert it into a more energetic one (typically in the UV–VIS range), prone to trigger the photochemical reaction. This approach is dubbed “photon upconversion”, namely a mechanism by which two or more low-energy photons

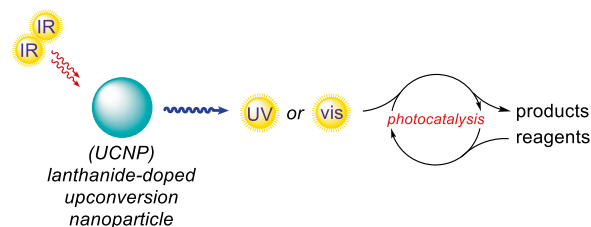
Scheme 5 Three pathways to exploit NIR radiation in organic synthesis: localized surface plasmon resonance (LSPR, top), upconversion nanoparticles (UCNPs, middle) and sensitized triplet–triplet annihilation (TTA, bottom)

■ **Localized surface plasmon resonance (LSPR)**

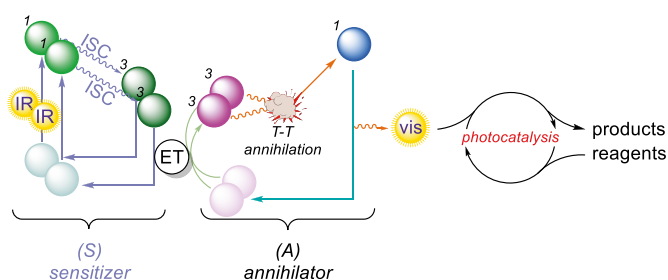


■ **Photon Upconversion (PU)**

- Upconversion nanoparticles (UCNPs)



- Sensitized triplet–triplet annihilation (TTA)



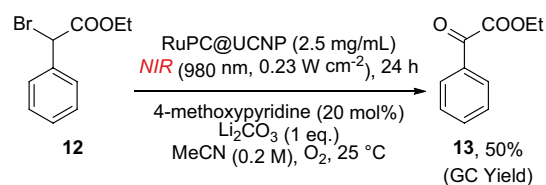
are converted into a single high-energy photon. Two main strategies can be exploited to trigger a photon upconversion, namely through the use of “upconversion nanoparticles” (UCNPs; Scheme 5, middle) (Wang and Liu 2009) or the so-called “triplet–triplet annihilation” (TTA) mechanism (Scheme 5, bottom) (Singh-Rachford and Castellano 2010).

As for the first option, lanthanide-doped UCNPs are mainly used. Indeed, lanthanide metal ions, thanks to the plethora of electronic transitions within the $4f$ electron shell, can absorb two near-infrared photons and convert them into one visible photon (Wang and Liu 2009). While this strategy has been known for a long time, only very recently preparative photochemical applications started to appear (Wu et al. 2017; Zhou et al. 2015).

An alternative option is represented by photon upconversion based on TTA (also known as triplet fusion). In these processes, the singlet excited state of an appropriately chosen sensitizer (S) undergoes intersystem crossing (ISC) to afford the corresponding triplet excited state ($^3S^*$). The latter transfers its energy to an annihilator (A), thus populating its triplet state ($^3A^*$). Finally, two molecules of $^3A^*$ interact resulting in one molecule returning to its ground state and the other one being promoted to a higher-energy singlet excited state ($^3A^* + ^3A^* \rightarrow A + ^1A^*$). This last species produces a high-energy photon upon decay to the ground state via fluorescence (Singh-Rachford and Castellano 2010).

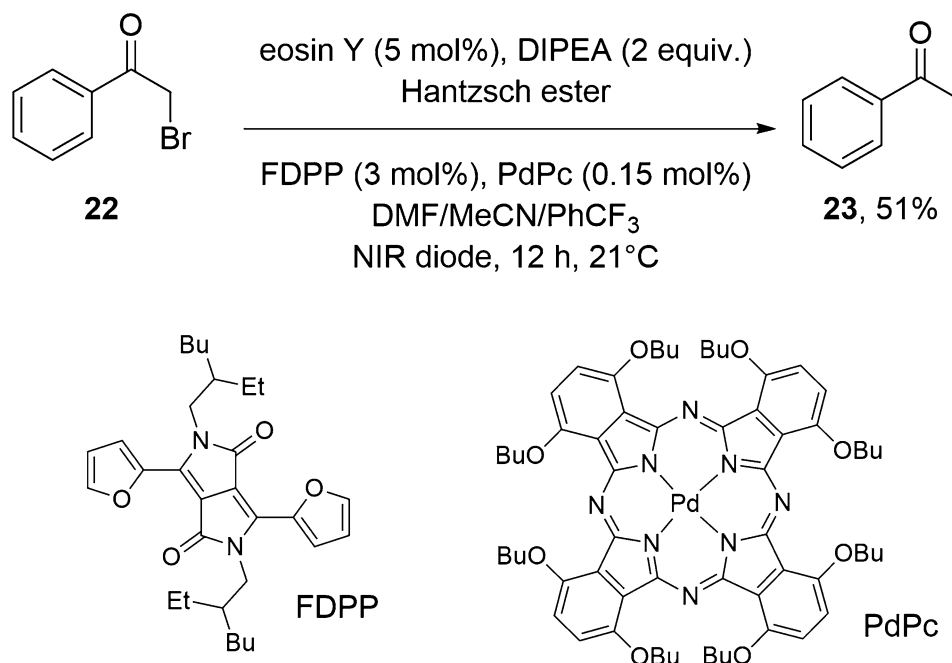
Very recently, photon upconversion strategies have been applied to perform syntheses upon NIR light irradiation. In one instance, an upconversion nanoparticle/photocatalyst system (tagged RuPC@UCNP) based on $\text{NaYF}_4:\text{Yb}, \text{Tm}$ nanoparticles, stabilized by a ligand containing a heteroleptic derivative of $[\text{Ru}(\text{bpy})_3]^{2+}$, was used. The role of NaYF_4 nanoparticles was to convert NIR radiation into VIS light which, through an energy transfer step, allowed the excitation of the ruthenium complex, in turn triggering the activation of the organic substrate. As for the chemistry, the RuPC@UCNP system has been successfully exploited for the NIR light-driven aerobic oxidation of ethyl 2-bromo-2-phenylacetate **12** to ethyl phenylglyoxylate **13** (Scheme 6; the same mechanism described for Scheme 3a operates here as well) (Freitag et al. 2018).

On the other hand, triplet fusion upconversion was applied to perform a wide range of photocatalyzed reactions



Scheme 6 NIR-light induced oxidation of ethyl 2-bromo-2-phenylacetate **12** by the RuPC@UCNP system

Scheme 7 Eosin Y photocatalyzed hydrodehalogenation of phenacyl bromide **22** promoted by NIR light



under NIR light irradiation (Ravetz et al. 2019). In particular, either orange or blue-light could be conveniently generated from NIR light by simply changing the nature of the sensitizer and the annihilator of the upconversion system. Among the several applications, the system based on furanyl diketopyrrolopyrrole (FDPP) as annihilator and palladium(II) octabutoxyphthalocyanine (PdPc) as sensitizer was used to promote the eosin Y photocatalyzed hydrodehalogenation of phenacyl bromide **22** to acetophenone **23**, occurring in the presence of DIPEA and Hantzsch ester (Scheme 7). Noteworthy was an example involving a [2+2] cyclization performed by irradiating the reaction system through a barrier consisting of a hemoglobin solution. The desired product was obtained with the same yield, both in the presence or absence of the barrier, demonstrating that NIR light was not affected. Moreover, the high penetration of NIR light renders these processes easily scaled-up. For example, the photoinduced polymerization of methyl methacrylate could be achieved also on a multi gram-scale in an opaque silicon mold and without the need of a NIR laser, but with a simple NIR lamp (Ravetz et al. 2019).

4 Conclusions and perspectives

According to the examples gathered in the present review, it is apparent that solar light is an intriguing opportunity to perform photochemical (and, more specifically photocatalyzed)

synthesis. The exploitation of solar light refers, however, only to specific wavelength ranges. Thus, even the small fraction of UV light present in the solar radiation can be conveniently exploited, albeit the number of reports encompassing the use of the VIS range is much higher. It is worth noting, however, that most of the examples exploit the most energetic radiations only, up to the green region. On the other hand, the number of reports describing the use of photocatalysts absorbing in the red range is very limited. Finally, the adoption of artificial NIR light in photocatalyzed synthesis is a very recent development and, to the best of our knowledge, no example dealing with natural sunlight has been reported yet. One limitation could be related to the required NIR light intensity (often lasers must be used), but the path is open and hopefully applications in this direction will appear soon.

Indeed, the goal in the future will be to exploit the whole solar spectrum, for example, by combining different systems that work in concert to reach a high overall efficiency, in turn allowing to fully exploit our source of energy per excellence and finally mastering “the guarded secret of plants”.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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