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Recent applications of biphotonic processes in organic synthesis

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Currently, evolution of chemical transformations by visible light irradiation is highly desirable from cost, safety, availability, and environmental friendliness points of view. Besides, activation of less reactive substrates under very mild conditions becomes one of the most challenging tasks in organic synthesis. However, the insufficient energy provided by one photon of visible light for their activation definitely makes necessary the development of new protocols together with the design of new photocatalytic systems to overcome this limitation. In this context, the implementation of biphotonic processes has been found to be a solution for these drawbacks. This new mechanistic paradigm which combines light upconversion processes with energy/electron transfers holds great potential for high energy demanding bond activations, expanding the accessible reactivity window. Here, we wish to highlight the recent applications of biphotonic processes in organic synthesis.

Sunlight strikes our planet every day with more energy than we consume in a whole year. The question arises why the chemistry community has not used sunlight as a synthetic tool for developing photochemical processes for almost one century.† The main reason lies in the inability of most organic compounds to absorb light in the visible range. Moreover, electronically excited states are often only available upon irradiation with shorter wavelengths of ultraviolet (UV) light. These high-energy photons can therefore cause uncontrolled photodecomposition processes, a factor that has limited the broad utilization of photochemical synthesis in the fabrication of complex organic molecules. For this purpose, many researchers have explored ways to efficiently employ visible light energy for the activation of organic molecules,[1] for example, the design, synthesis and development of photocatalysts that can absorb visible light and mediate the desired chemical transformations by different oxidative and reductive potentials. Activation of molecules with visible light offers the possibility of reaction pathways which are otherwise impossible to perform with classical nonphotochemical strategies.[2]

Another fascinating aspect of photochemistry boosted by visible light is the use of photons as "traceless and green reagents", rendering photochemical processes green and sustainable. In this context, the last decade has witnessed a fantastic growth in the field of organic photocatalysis using visible light as an energy source, emerging as a new and powerful tool for activating molecules.[3]

However, the scope of photocatalytic bond activations is limited not only by the energy of one visible photon but also by the energetic losses suffered by the photocatalysts such as intramolecular charge transfers or internal conversions.[3h] A plausible approach to expand the accessible reactivity window to less activated substrates is the use of photon upconversion (UC),[4] which converts low-energy radiation into higher-energy radiation by either the two-photon absorption (**TPA**) mechanism or the triplet–triplet annihilation (**TTA**) mechanism.[5] This technology has been successfully applied in diverse scientific fields ranging from energy to biology.[6] Although the utiliz-
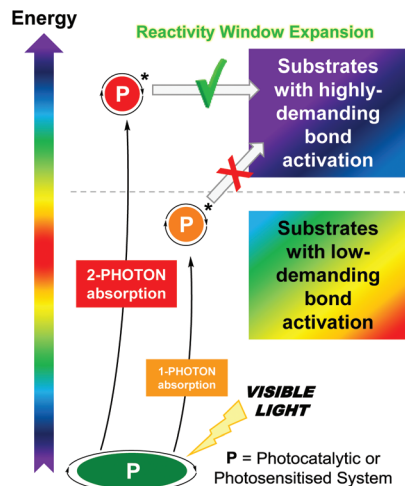
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†More than one century ago, the Italian chemist G. Ciamician published a *Science* article ("The Photochemistry of the Future") where he recognized that sunlight could be utilized as a promoter of organic reactions (see ref. 30). Inspired by the ability of plants to make use of solar energy, he was the first scientist to investigate photochemical reactions in a systematic way. His predictions on the advantages of utilizing solar energy to convert it into fuels have led to him being considered a pioneer of modern photochemistry (in 1998, this paper was cited for the first time in a JRC journal: see for instance ref. 31, source: SciFinder®).
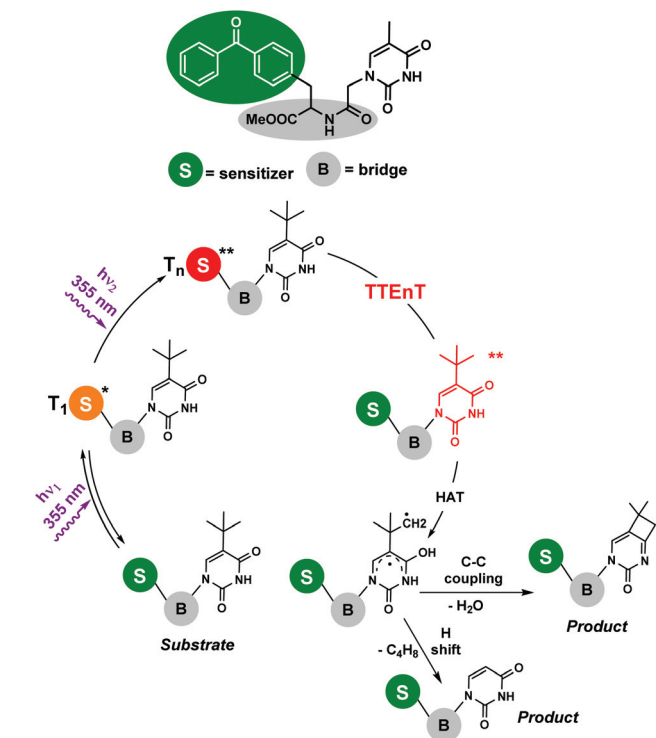
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Scheme 1 Conceptual scheme of this highlight article: the application of biphotonic processes expands the reactivity window for organic synthesis.

Scheme 2 Photoreaction of the benzophenone-modified nucleobase dyad. Involvement of a **TPA** process upon laser flash photolysis (λ_{exc} = 355 nm).

ation of biphotonic processes‡ as a potential synthetic tool is still in its infancy, it has gained great momentum over the past five years and has triggered renewed interest in photochemistry in general. Development of the biphotonic technology for addressing critical bond activations or electron transfers in organic synthesis has been found to be advantageous while retaining the benefit of mild reaction conditions using lower-energy visible light (Scheme 1).

In this highlight article, we therefore focus our attention on the existing examples of this emerging concept where several biphotonic processes such as **TPA**, **TTA** and consecutive photo-induced electron transfer (**ConPET**) have been successfully applied to chemical transformations.

Photosensitized two-photon absorption (TPA) reactions: The **TPA** mechanism involves an intramolecular simultaneous absorption of two photons *via* a virtual state,[7] and relaxation would lead to an emission with a greater frequency than those of the absorbed photons. Despite **TPA** requiring the use of high intensity excitation by laser beams with concentrated peaks, numerous potential applications in biophotonics, optics and nano-micro fabrication have been reported.[5] However, the involvement of **TPA** processes in organic transformations is quite rare, presumably because of difficulties in experimental designs. Nevertheless, some examples can be found in the literature focused mainly on photosensitized
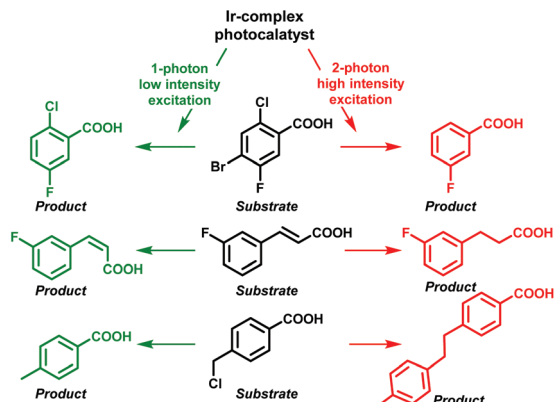
biphotonic irradiation for DNA damage. Miranda and co-workers[8] demonstrated the photochemistry of an upper thymine-like triplet state (nπ* triplet). The proposed mechanism involved the biphotonic excitation of benzophenone by high-energy laser pulses and a successful intramolecular sensitization. To avoid energetic losses, a dyad containing both the photosensitizer and the acceptor linked by an amide bridge was synthesized (Scheme 2). Thus, the benzophenone T_n formed by biphotonic excitation transferred its energy to thymine-like T_2 (nπ*), allowing the subsequent Norrish–Yang reaction to obtain the corresponding products. In this vein, the same research group has very recently published the inter-molecular version of this reaction,[9] using 2′-methoxyacetophe-none as a photosensitizer and *tert*-butyluracil as a modified pyrimidine base; however, the strategy was now different. After the first UVA (355 nm) photon was absorbed by the sensitizer, triplet–triplet energy transfer (TTEnT) occurred, giving rise to the nucleobase triplet which was able to absorb the second photon (355 nm) reaching a T_n state. The viability of this strategy was supported by two model reactions: (i) the Norrish–Yang photocyclization of *tert*-butyluracil and (ii) the photo-hydration of its uracil analogue, lacking the *tert*-butyl substituent.

Carbazole-based compounds were also found to be effective biphotonic sensitizers for the DNA photodamage.[10] Experimentally, the DNA photocleavage was successfully achieved in the presence of photosensitizers upon irradiation with not only visible light but also with 800 nm NIR light *via* a

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Scheme 3 Control over the reactivity relying on the one- or two-photon mechanism.
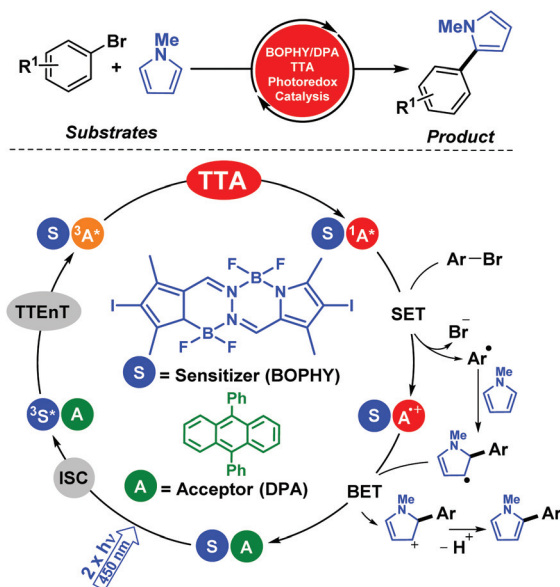

Scheme 4 Photon upconversion technology based on **TTA**. After the absorption of low-energy photons ($h\nu_1$), a sensitizer triplet is produced by intersystem crossing (ISC) from its singlet. Subsequently, TTEnT from sensitizer triplets to the acceptor (Dexter mechanism) occurs. When two acceptor molecules in their triplet states are capable of colliding during their lifetimes, a higher singlet energy level is formed by **TTA** and, consequently, generates delayed upconverted fluorescence ($h\nu_2$).

TPA process. The proposed reaction mechanism involved a hydrogen atom abstraction (HAT) by N-centred radicals (type I mechanism) under anaerobic conditions. Accordingly, subsequent computational studies on these findings evidenced the great efficiency of these compounds as sensitizers in the NIR region; however, the rationalization of the mechanism of action revealed the involvement of solvated electrons ($e^-_{(aq)}$) produced by a spontaneous photoionization that in turn were responsible for DNA strand cleavage.[11]

In this respect, Wenger and co-workers also observed that efficient two-photon excitation of a metal complex generated an $e^-_{(aq)}$ upon ionization.[12] This fact allowed them to control the reactivity over several photochemical reactions relying on the light intensity. Hence, the one-photon mechanism (low-powered intensity) permitted energy transfer from the photocatalyst to the substrates achieving debromination, *cis–trans* isomerization or HAT; in contrast, the use of high-powered light intensity (**TPA**) electron transfer from the $e^-_{(aq)}$ took place, affording in this case dechlorinated, hydrogenated and dimer products, respectively (Scheme 3).

Regarding the challenging dechlorination reactions, Yamaji and co-workers carried out two-colour two-laser photolysis on several chlorinated diketones.[13] The results revealed the formation of halogen-free diketones as the sole products by a Cl elimination mechanism in which the upper triplet T_n ($n \geq 2$) state was involved. Finally, chemical reactions involving quinoline-based photoremovable protecting groups using **TPA** processes have been recently proven as a powerful tool for physiological studies.[14] Thus, photolysis at longer wavelengths (740 nm light from a Ti:sapphire laser) allowed the efficient release of homopiperonylic acid in a high yield under simulated physiological conditions.

Photocatalytic reactions by triplet–triplet annihilation (TTA): Photon upconversion based on **TTA** between bimolecular organic systems has become one of the most attractive wavelength conversion technologies. Various combinations of compounds showing **TTA** properties can be found in the literature.[15] Scheme 4 shows the photochemical events associated with this synchronized biphotonic process which includes

intersystem crossing (ISC), TTEnT, **TTA** and upconverted fluorescence ($h\nu_2$).

This transformation of two low-energy photons ($2 \times h\nu_1$) into one higher-energy photon ($h\nu_2$) has been already productively applied in diverse scientific areas of research;[16] however, organic synthetic procedures using **TTA** processes have only recently been developed. For the first time, **TTA** was embedded in chemical reactions involving electron transfer activation of challenging organic molecules.[17] Thus, we pioneered this elegant concept investigating the photophysical and photochemical aspects of combining **TTA** events of two simple organic dyes (diketone and oxazole) with reductive activations of aryl bromides.[17a] This framework involved detailed spectroscopic, theoretical, and synthetic studies and ultimately led to the development of a new set of photocatalytic redox hydrodebrominations. Concomitantly with this work, we also contributed with the first intragel aerobic photoreduction of aryl halides catalysed by platinum(II) octaethyl-porphyrin (PtOEP) and 9,10-diphenylanthracene (DPA) as the **TTA** system in supramolecular gel networks.[17b] Thus, the gel network provided a stable microenvironment for the challenging multi-step process under aerobic conditions, at room temperature and without additional additives. These results demonstrated that low weight molecular (LWM) gelators could be used as confined reaction media or micro/nanoreactors, providing the background for more demanding photophysical processes.

We further developed this methodology for more complex processes such as C–C coupling reactions. In particular, photocatalytic aromatic functionalization of *N*-methyl pyrrole was achieved using a metal-free **TTA** system based on diiodoBOPHY-like derivative (BOPHY) and DPA.[18] The reaction reported good to high product yields and the mechanistic aspects of this procedure were elucidated by means of combining product analysis, spectroscopic data and computational studies (Scheme 5). It is worth mentioning that an economical blue laser pointer (λ_{exc} = 445 nm ± 10, 2 W) was employed that facilitated the management of the optimal conditions instead of using the laser flash photolysis technique.

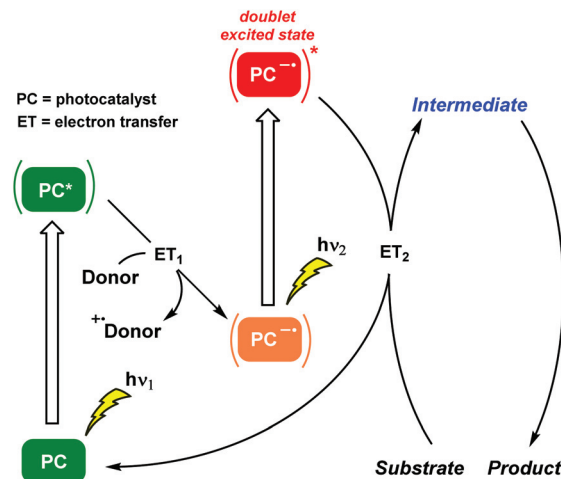This journal is © the Partner Organisations 2020

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Scheme 5 Aromatic functionalization of *N*-methyl pyrrole photocatalyzed by the **TTA** technology.

Scheme 6 The **ConPET** mechanism, which mimics the Z-scheme, adapted to organic transformations. Selective excitation of the PC led to its excited state which is quenched by an appropriate donor generating the PC radical anion. Then, excitation of the PC radical anion results in the formation of an excited PC radical anion (doublet excited state), a highly reducing agent.

Among biological applications, near-infrared (NIR) radiation was also used for several organic transformations by utilizing the photophysical process of **TTA**.[19,20] Orange or blue light was accessed from low-energy NIR light (λ_{exc} = 730 nm) by pairwise combination of the **TTA** couple.[19] For instance, the delayed emission released from the NIR-to-orange upconversion system (Pd-complex/diketopyrrolopyrrole derivative as a sensitizer/annihilator) was absorbed by a photocatalyst (eosin Y or Rose Bengal) that subsequently photocatalyzed low energy demanding reactions such as dehalogenation of α-bromoacetophenone, amine oxidation or C–N bond activation. Besides, the combination of a NIR absorbing sensitizer Pt-complex with tetratertbutylperylene as a blue-emitter was adapted to the prototypical [Ru (bpy)₃]₂⁺-catalysed reaction, the intramolecular [2 + 2] cyclization of enones, obtaining moderate yields (48%). This **TTA** system was also employed directly for catalysing the cyclization of dienyl azides to pyrroles (80% yield) or the polymerization of methyl methacrylate. On the other hand, a photochromic reaction involving a C–N bond breaking was successfully achieved by **TTA**, where NIR light irradiation (λ_{exc} = 635 nm) was also implemented.[20]

Despite suitable **TTA** systems in aqueous media being barely known,[21] monodechlorination of trichloroacetate in air-saturated aqueous solution was successfully achieved by means of the **TTA** technology.[21d] This procedure constituted a promising green strategy for further photochemical transformations in homogeneous aqueous solution.

Consecutive photoinduced electron transfer (ConPET) reactions: Plants produce their own energy autotrophically from water, carbon dioxide and visible light. This combination, the renowned photosynthesis, follows a two-step photon excitation Z-scheme mechanism where accumulative photon absorption

is involved. Surprisingly, the application of the Z-scheme photosynthesis concept to activate substrates with high energy demanding bonds for organic synthesis is very recent (Scheme 6).
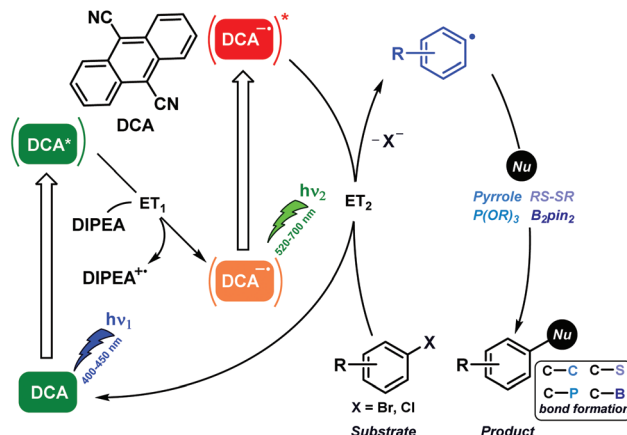
The kick-off work engaging these two terms is attributed to König and co-workers.[22] Photogeneration of radical anions of aryl halides (Br, Cl) was achieved by a **ConPET** process involving a doublet excited state. An organic perylene diimide (PDI)-based photocatalyst was capable of accumulating the energy of two visible light photons in order to reduce stable aryl halides, generating the corresponding aryl radicals which were trapped by hydrogen atom donors or by specific nucleophiles to form C–C bonds. Thus, this outstanding chemical model mimicked the Z scheme in biological photosynthesis and permitted the photocatalytic conversion of less reactive chemical bonds in organic synthesis. Subsequently, the same PDI-based photocatalyst was incorporated into the metal–organic polymer. This heterogeneous approach facilitated the **ConPET** process for the visible light-driven dehalogenation of aryl halides reducing markedly the irradiation times.[23] Regarding chromophore-diimide derivatives, a heterogeneous strategy based on the synergistic effects of **ConPET** and HAT processes was applied to aryl halide photoreduction. A new polyoxometalate-incorporated naphthalenediimide (NDI)-based metal–organic framework (MOF) was designed and, after visible light irradiation, the host–guest MOF could stably generate NDI·⁻ which was the critical intermediate for obtaining the photoreduced products.[24] Strategically, diimide-like photocatalysts required *a priori* tedious synthesis, in addition to low solubility in organic solvents and sometimes the use of elevated temperatures. Moreover, alternative investigations related to the PDI system might suggest other mechanistic interpretations.[25]

Various organic, inexpensive, and soluble dyes such as 1,8-dihydroxyanthraquinone (Aq-OH), rhodamine 6G (Rh-6G) or 9,10-dicyanoanthracene (DCA) were found to be suitable photocatalysts for **ConPET** processes. For instance, Aq-OH transformed into its coloured radical anion or semiquinone anion in the presence of triethylamine upon the irradiation of one visible light photon. Then, excitation of these species by visible light led to an electron transfer process, activating aryl halides that reacted in dehalogenation or C–C bond-forming reactions.[26]

To date, the organic photocatalyst Rh-6G has been most widely used for organic synthesis.[27] The first work in this series described the selective aromatic functionalisation of arenes and heteroarenes by controlling the bond activation through light-controlled regulation of redox potentials.[27a] Subsequently, a series of synthetic applications photocatalyzed by Rh-6G through the **ConPET** process were reported. Thus, the synthesis of pyrrolo-[1,2-a]quinolines and ullazines was achieved in one pot in moderate to good yields (35–75%).[27b] Heteroaromatic biaryls were synthesized in moderate to excellent yields (41–91%) and, remarkably, this reaction worked for a broad range of brominated electron-rich heteroarenes and chlorinated heteroarenes bearing electron-withdrawing groups.[27c] A photo-Arbuzov reaction for the construction of aryl phosphonates with consistent yields was also achieved by this methodology through C–P bond formation.[27d] Moreover, this Rh-6G-**ConPET** protocol was found to be an alternative strategy of the C–H arylation procedures using halogenated nucleobases under UV-light irradiation.[27e] Combination of **ConPET** (Rh-6G) with metal catalysis (lanthanide ions) permitted the activation of even chlorobenzenes in order to form C–C and C–P bonds.[27f] Finally, it was demonstrated that gel networks could act as the reaction media for aerobic photocatalyzed C–C coupling reactions by Rh-6G through the **ConPET** mechanism, providing similar results to those obtained under inert atmosphere conditions.[27g]

Spectroscopic investigations obtained some insights into the mechanistic aspects of this **ConPET** process using Rh-6G. Hence, fluorescence spectroscopy showed that the Rh-6G radical anion could be generated from the singlet or triplet excited state of Rh-6G, relying on the sacrificial donor and varying its concentration.[27h] Very recently, the fate of the excited Rh-6G radical anion has been studied by femtosecond spectroscopy.[27i] The lifetime of the excited Rh-6G radical anion (350 fs) was found to be too short for diffusion-controlled electron transfer to the substrate. Therefore, the authors postulated that the excited Rh-6G radical anion generated $e^-_{(aq)}$ as an additional step in the photocatalytic cycle, which was now responsible for the aryl halide reductions.

In this context, the excited DCA radical anion lifetime previously ranged in the ns scale and it displayed an exceptionally high reducing potential of ca. −3 V.[28] Therefore, DCA possessed all prime qualifications for its use as a strongly reducing photocatalyst. Indeed, photocatalytic aromatic substitutions of poor reactive aryl halides by DCA were found to be operated via the **ConPET** mechanism.[29] Thus the resulting

Scheme 7 Aromatic substitutions of aryl halides photocatalyzed by DCA through the **ConPET** mechanism using cold white LEDs (410−700 nm). Fluorescence studies revealed the quantitative formation of the DCA radical anion that absorbs green light, giving rise to its doublet excited state; this species was capable of injecting one electron to the aryl halides.

excited DCA radical anion readily effected C–C, C–P, C–S, and C–B bond formations. The detailed information of the reaction mechanism of this biphotonic catalytic process was supported by product analysis, spectroscopic measurements, and computational studies (Scheme 7).

In summary, the biphotonic technology has emerged as a powerful tool for addressing important bond activations or electron transfer processes in organic synthesis under mild conditions and using lower-energy visible light. These biphotonic processes include **TPA**, **TTA** and **ConPET** reactions, which have been used to trigger, for instance, reductive activations of aryl bromides, C–C or C–heteroatom coupling reactions, dehalogenation of aryl halides and functionalisation of arenes and heteroarenes. The success of this approach lies on a judicious selection of the photocatalytic system to achieve the required photoregulation of the involved redox potentials. In the coming years, we foresee a significant increase in the use of this technology to assist modern organic synthesis.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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