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Organic photoredox catalysts for wastewater remediation: Beyond the established advanced oxidation processes

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ABSTRACT

Contaminants of emerging concern (CECs) constitute a wide class of organic molecules, which are found dissolved in wastewaters. Chemical properties of CECs are as wide as their chemical structures; nevertheless, most of the CECs can be removed from wastewaters using Advanced Oxidation Processes (AOPs). However, there are examples of CECs that have proven recalcitrant to AOPs. In such cases, Advanced Reduction Processes (ARPs) include those techniques able to achieve degradation of contaminants by producing highly reactive reducing radicals.

Organic photocatalysts have demonstrated to be an efficient alternative to other types of photocatalysts in AOPs. Moreover, several organic photocatalysts, according to their redox properties, could also act as reductants under appropriate scenarios, a process that has been much less explored than oxidation. As an example, Riboflavin (RF) is a natural water-soluble molecule, well-known as vitamin B2. The photophysical and redox properties of RF have been extensively applied for the oxidative photodegradation of contaminants in water. More recently, the potential of RF has been expanded to the photoreduction of more recalcitrant pollutants. For instance, benzotriazoles UV-stabilizers (BUVSs) constitute a vast family of recalcitrant contaminants, which have been successfully degraded in the presence of a commercially available derivative of RF (2′,3′,4′,5′-tetraacetylated riboflavin, RFTA) and visible light, assisted by an amine, which acts as electron donor to the excited states of RFTA, generating the $RFTA^{\cdot -}$. This species ultimately produces the reduction of the selected BUVSs. Photophysical experiments demonstrated the key role of the radical anion $RFTA^{\cdot -}$, and allowed determining the rate constants that were correlated to the observed photodegradations.

1. Introduction

Organic photocatalysts have demonstrated to be an efficient alternative to other types of photocatalysts based on semiconductors or those including non-abundant metals such as Ru or Ir. Among the advantages they offer, they absorb visible light, thus, they could use the free light coming from the Sun, they are usually cheap and they do not release metals in the natural environment. Even if in general, they do not produce directly hydroxyl radicals ($OH^{\bullet}$), electron transfer reactions from their excited states could be successfully applied in the field of wastewater treatment. In fact, besides being powerful oxidants/reductants from their excited states, in some cases, they also generate singlet oxygen giving rise to a broader chemistry. Different examples of organic photocatalysts, mainly used as oxidants from their excited states, are reported in literature for the oxidative abatement of pollutants in water or for synthetic purposes[1–3]. However, not all the contaminants could be removed from wastewaters upon oxidation. In such cases, several organic photocatalysts, according to their redox properties, could also act as reductants under appropriate scenarios, a process that has been much less explored than oxidation. Therefore, it looks appropriate to reconsider the properties of selected organic photocatalysts and to explore an alternative way of working to produce the reductive degradation of contaminants. For such purpose, a deep knowledge of the photoredox properties of the employed organic photocatalysts and of all the involved species will be crucial to understand the mechanism underlying the photoreduction processes.

This perspective presents a brief summary of the current situation for the advanced oxidation processes (AOPs), and why advanced reduction processes (ARPs) could be an alternative for recalcitrant pollutants. To illustrate the potential of organic photocatalysts in such developing area, we have selected Riboflavin as an example of a well-known visible-light dye that still could offer further possibilities beyond its oxidative

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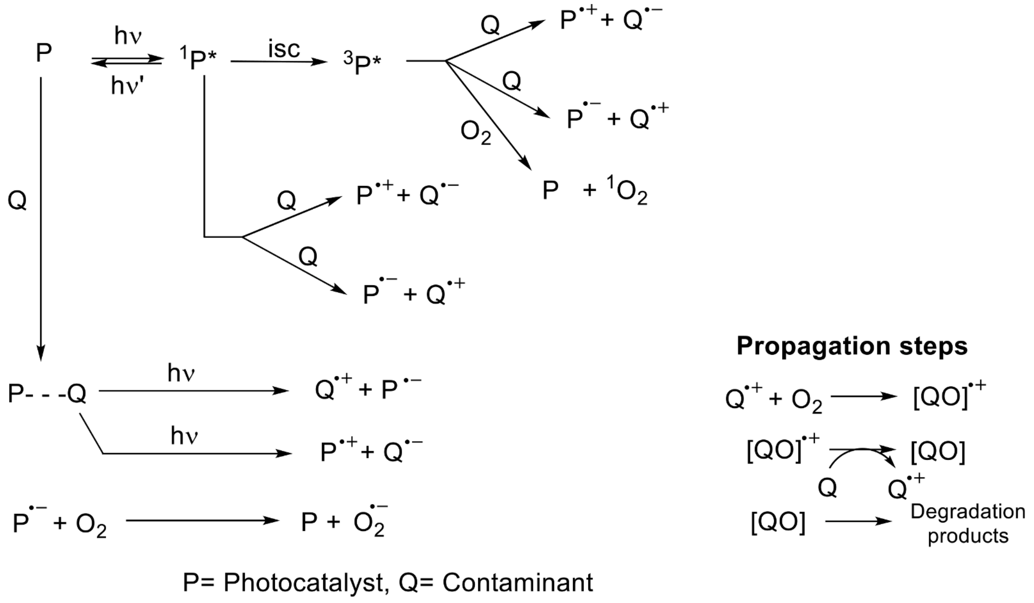


Scheme 1. Alternative mechanistic pathways in the AOPs of contaminants mediated by organic photocatalysts.

character. Recent examples of its potential as an oxidative photocatalyst acting through Type I and Type II mechanisms, and as a reductive photocatalyst will be presented.

2. Contaminants of emerging concern (CECs)

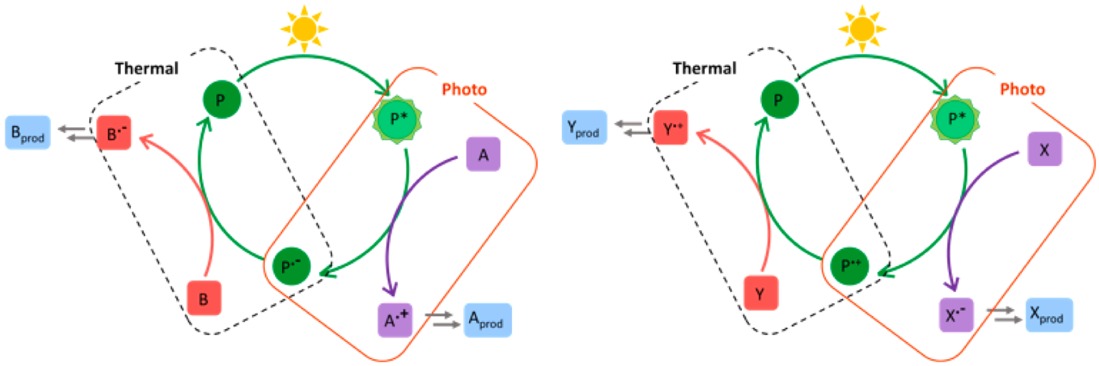
Freshwater constitutes an important resource for the survival of human beings, but unfortunately, its availability is limited. Most of the natural water is polluted due to urbanization, industrialization, agriculture, and the increase of the human population, which consequentially implies an increase of the clean water's demand. Therefore, pollution of water has emerged as one of the most relevant environmental problems of the last decades. According to the definition written by Goel, a pollutant is a physical, chemical, or biological factor causing esthetic or detrimental effects on aquatic life and on those who consume the water[4]. Among all the types of pollutants, contaminants of emerging concern (CECs) constitute a wide class of organic molecules found dissolved in wastewaters. The definition of CECs is a bit tricky; on one hand, the qualification of "emerging" is relative because what was emerging as an important environmental contamination issue a decade or two ago, might no longer be qualified as an emerging contaminant. On the other hand, this class also includes traditional contaminants, from which a deep chemical information is available[5]. To sum up, this term is currently used to cover not only newly developed compounds but also compounds newly rediscovered in the environment often due to analytical developments, and also compounds that have only recently been categorised as contaminants. More specifically, CECs include pharmaceuticals and personal care products (PPCPs), pesticides, veterinary products, industrial compounds/by-products, food additives, per- and poly-fluoroalkyl substances (PFASs), as well as metabolites and transformation products (Fig. 1)[6]. More than 40,000 organic chemicals have been identified and assigned as CECs[7]. Given the vast number of identified chemicals with different chemical properties, a big effort is needed to investigate how they pose risks to humans and to the natural environment and update their regulation accordingly[5].

Chemical properties of CECs are as wide as their chemical structures; nevertheless, most of the CECs can be removed from wastewaters using oxidative degradation processes. However, there are examples of CECs that resist bio-degradation and even more, have proven recalcitrant to AOPs[8]. For example, PFASs are a huge class of CECs that are well-known as persistent, bio-accumulative and toxic. As a matter of fact, they have been detected in different environmental matrices, in wildlife and even in humans, with drinking water being considered as the main exposure route[9]. Currently, there are not *in situ* groundwater treatment technologies that can efficiently address the removal of the full range of PFAS. In fact, a next generation of viable PFAS water treatment technologies based on different treatments, such as adsorption, separation, and destruction is being developed[10].

As illustrated with PFAS, unfortunately not all the contaminants can be abated upon traditional or the newer AOPs water treatments. Moreover, many of the currently new water treatment techniques applied to contaminated water, such as ion exchange, reverse osmosis, and nanofiltration/ultrafiltration, only concentrate the contaminants without degrading or eliminating them[11]. Therefore, alternative approaches are still needed to produce the abatement of recalcitrant CECs.

3. Organic photocatalysts for oxidative degradation of CECs

In the recent decades, different methods have been developed for the degradation of CECs in water, being those classified as AOPs, and among them those mediated by light, the most employed ones. These techniques are mainly based on the generation of reactive oxygen species (ROS) which subsequently react in a non-selective way towards organic molecules. Hydroxyl radical ($OH^{\bullet}$) is the main oxidative radical formed during AOPs, and because of its high oxidation potential ($E^{\circ} = 2.8$ V *vs* SCE), it is the most powerful species. Other oxidative species, such as hydroperoxyl radical ($HO_2^{\bullet}$) or hydrogen peroxide (H_2O_2) could also participate in the oxidation[12,13]. Semiconductors coupled with UV-light are commonly the first choice in the generation of oxidative radicals for water treatments. In such cases, photocatalysis takes place upon the activation of a semiconductor with electromagnetic radiation from solar or artificial light, followed by the population of the conduction band (CB) from the valence band (VB) and the subsequent generation of electron/hole pairs (e^-/h^+)[14,15]. In particular, TiO_2 is the most used semiconductor because of its high photochemical stability, its high oxidative strength, its nontoxic properties and because it is a cheap material. Moreover, playing with the dimension and the shape of the particles of TiO_2 it is possible to change the photochemical properties of the material. For example, the small dimensions of TiO_2 nanoparticles imply a high surface to volume ratio, which ensures a high amount of surface-active sites[16]. Besides, the well-known Fenton-based AOPs for water treatment have been mostly developed on iron-based catalysts.



Scheme 2. Overall photoredox cycles with the photocatalyst acting as an oxidant (left) or as a reductant (right) from their excited states. **P**: photocatalyst; **P***: photocatalyst in either singlet or triplet excited state; **A**: contaminants susceptible to suffer oxidation; **B**: O_2 or recalcitrant contaminants susceptible to suffer reduction; **X**: recalcitrant contaminants susceptible to suffer reduction and **Y**: sacrificial electron donor.

However, the restricted solubility of iron species, has inspired research efforts on the establishment of iron-free Fenton systems for the activation of H_2O_2. In this sense, metal complexes with multiple oxidation states and redox stability decompose H_2O_2 to efficiently generate $HO^{\bullet}$ even in neutral/alkaline conditions in both homogeneous and heterogeneous reaction conditions. For instance, highly stable ruthenium-based complexes have proven useful to decompose H_2O_2; nevertheless, as expensive and rare element, the practical use of the Ru-based Fenton systems may be limited in the photodegradation of aqueous pollutants[17].

Nevertheless, in this mini-review we are considering only AOPS in which visible-light is absorbed by organic molecules acting as photocatalysts.

An exhaustive list of organic photocatalysts applied to the oxidation of CECs was reported in literature a decade ago[1]. They were presented together with their relevant photophysical features, which included their absorption spectra, their singlet excited-state properties (emission wavelength (λ_{em}), singlet state energy (E_S), fluorescence quantum yield (Φ_F), and lifetime of the singlet excited state (τ_S)), as well as the most characteristic triplet excited state properties such as, intersystem crossing quantum yield (Φ_{ISC}), triplet-triplet absorption wavelength ($\lambda_{T\text{-}T}$), triplet state energy (E_T), lifetime of the triplet excited state (τ_T) and singlet oxygen quantum yield (Φ_{Δ}). The selected examples illustrate the importance of time-resolved techniques (emission and transient absorption spectroscopy, etc.) to provide relevant information, such as detection of short-lived excited states and evaluation of their kinetics, to determine reaction rate constants, which are key parameters to postulate the main mechanistic photodegradation routes (Scheme 1). In summary, that piece of work highlighted the importance of the mechanistic aspects involved in the oxidative abatement of pollutants, as the crucial understanding needed to push the development of the AOPs based on organic photocatalysts.

In fact, the interest in the use of organic molecules as photocatalysts is still increasing; for example, 9-mesityl-10-methylacridinium (Mes-Acr-Me^+) has recently been reported as efficient photocatalyst for synthetic purposes. Interestingly, acridinium salts generally constitute powerful oxidants from their singlet excited states. In particular, Mes-Acr-Me^+ has become the most widely and efficiently used acridinium photoredox catalyst in recent years, due to the protective effect of the methyl substituents of the mesityl group, which prevent nucleophile and radical addition to the acridinium/acridinyl radical. Different examples, such as benzylic oxidations mediated by Mes-Acr-Me^+ and visible light have been reported (Fig. 2)[3].

Moreover, Mes-Acr-Me^+ has also proven to efficiently produce the photodegradation of different types of phenolic compounds in aqueous media under visible light irradiation. The mechanism of the photodegradation has been investigated based on time-resolved techniques. Thus, steady-state and time-resolved fluorescence quenching revealed that the studied phenolic pollutants were able to quench ^{1}(Mes-Acr-Me^+)*, with kinetic rate constants in the order of the diffusion limit. As a result, Type I photooxidation happening through the singlet excited state of the photocatalyst was postulated as the main operating process in the photodegradation of the studied pollutants (Fig. 3)[18].

It has been illustrated that AOPs are still useful methodologies to accomplish abatement of contaminants. In particular, the use of organic photocatalysts and photophysical techniques based on emission and absorption spectroscopy allow monitoring the photocatalyst-derived short-lived intermediates. As a result, the features that an ideal organic photocatalyst should exhibit are: (i) absorption in the visible region of the solar spectrum; (ii) appropriate redox potential from the excited states; (iii) high intersystem crossing quantum yield; and (iv) a long enough excited state lifetime[19,20].

4. Advanced reduction processes (ARPs)

Advanced Reduction Processes (ARPs) include those techniques able to achieve degradation of contaminants by producing highly reactive reducing radicals upon combining appropriate reagents and activation methods. The general idea is analogous to that of AOPs, but reducing species are generated instead of oxidizing ones[11]. For example, as $OH^{\bullet}$ is the main radical of AOPs, $SO_2^{\bullet}$ is the main radical in the ARPs, since its standard reduction potential of - 0.66 V, converts this species into a strong reductant. Other reducing radicals typically include sulfite radical anions ($SO_3^{\bullet -}$) and sulfur dioxide radical anions ($SO_2^{\bullet -}$), the hydrated electron (e_{aq}^-) and $H^{\bullet}$, depending on the employed activation methods and chemical solutes. The way to produce reduced radicals consists in the use of activation methods, ultraviolet light, electron beam (e-beam) treatment or ionizing radiation[11].

Hence, ARPs have already been applied to the treatment of different recalcitrant CECs. In particular, ARPs have been used to treat halogenated organic compounds, such as 1,2-dichloroethane[21], vinyl chloride[22,23], monochloroacetic acid[24], dichlorophenol[25], trichlorophenol [26] and PFAS[27,28]. They have also found to be very effective for treating organic compounds combined with bromate[29,30], perchlorate[31], nitrate[32], and other complex compounds, as drugs and pesticides[33–35]. More recently, a new dopped TiO_2 photocatalyst has been designed to reduce the potentially carcinogenic bromate (BrO_3^-). For this purpose, Bi nanoparticles were employed to trap the holes thus reducing the electron-hole recombination upon excitation; thus, allowing the photo-generated electrons to act as reductants of BrO_3^-[36].

The main advantage of ARPs is that they destroy the target contaminants directly by converting them into simple and biodegradable by-products, instead of generating intermediates with a higher toxicity [25]. Although the use of organic molecules and visible light could represent an innovative alternative to produce reduction of contaminants in wastewater treatment, the existing examples are very scarce.

5. Organic photocatalysts for reductive degradation of CECs?? Is it an option?

As it can be seen in Scheme 2 left, the typical photooxidation of a contaminant (A) mediated by an organic photocatalyst (P) starts with the absorption of light by P giving rise to P*. From there, A acts as a donor giving rise to $A^{\cdot+}$ and $P^{\cdot-}$; then, the photocatalytic cycle is closed in a subsequent thermal process governed by radical chemistry, which is mediated usually by O_2 (represented by B in this scheme), which accepts the electron with simultaneous recovery of P. Nevertheless, a further scenario could be envisaged in which A is a sacrificial electron donor, able to generate $P^{\cdot-}$ in a photoredox process, and B is a recalcitrant pollutant to be reduced by $P^{\cdot-}$, technically in a thermal redox process.

Still, there could be a different scenario, illustrated in the right part of Scheme 2, in which the first step is again the absorption of light by P giving rise to P*. From there, X represents a recalcitrant pollutant acting as an electron acceptor giving rise to $P^{\cdot+}$, thus becoming reduced to $X^{\cdot-}$. Then, the photocatalytic cycle is closed in a subsequent thermal process assisted by a sacrificial electron donor (represented by Y in this scheme), which gives an electron to $P^{\cdot+}$ to recover P.

Therefore, organic photocatalysts with appropriate features could in principle be found to produce the photodegradation of pollutants upon reduction. According to the scheme, two possibilities could result into the reduction of contaminants: i) organic photocatalysts able to generate reactive species, that could subsequently reduce recalcitrant contaminants (providing a sacrificial electron donor be used), and ii) organic photocatalysts able to produce reduction of the recalcitrant contaminants from their excited states.

Even more, an ideal situation would be that one in which either A or Y are not sacrificial electron donors but contaminants able to be oxidized. Thus, degradation of two pollutants could be achieved in one shot, one through oxidation and the other through reduction, minimizing the costs and the efforts of the process and being an example of circular economy.

Eosin Y (EY), a low cost xanthene synthetic dye with a characteristic band at 530 nm, responsible for its red-pink color, constitutes an example of organic photocatalyst able to produce reduction of the recalcitrant contaminants from its triplet excited state[37,38]. Its UV–visible absorption spectrum together with its well-known photophysical properties are shown in Fig. 4.[39]

Examples of the participation of EY as a photoreductant and photooxidant catalyst, are shown Figs. 5 and 6, respectively[39,40].

More recently, photoreduction of Cu(II) by ^{3}EY* was demonstrated based on steady-state, time-resolved emission, and laser flash photolysis experiments[41]. Overall, the good availability, strong absorption in the visible part of the spectrum and suitable redox potential values for a variety of organic transformations make EY an appealing and green photocatalyst for organic synthesis[42,43]. Although synthetic examples have demonstrated the potential of EY in photoreduction, to the best of our knowledge, there are no examples in which EY has been employed for the photocatalytic reduction of pollutants with environmental purposes.

6. Riboflavin (RF)

Riboflavin (7,8-dimethyl-10-ribityl-isoalloxazine) (RF) is a natural water-soluble molecule, well-known as vitamin B2. The chemical structure of RF is composed of a tricyclic system with a 7,8-dimethyl substitution and a ribityl chain at the N-10 position (Fig. 7).

RF is essential for our diet, and it is present in different types of food: milk and dairy products make the greatest contribution to riboflavin, but also cereals, meats, fatty fish, fruit and vegetable (especially the dark-green one) contain reasonably high concentrations of vitamin B2. The low intake of this vitamin could represent a problem, because it naturally participates into several redox metabolic reactions[44]. RF is also biosynthesized in plants and in many bacteria; it is also present in the retina of many mammals in high concentrations. As a result, it is naturally present in water systems, where under light irradiation it is partially responsible for the natural photodegradation of pollutants in aquatic systems[45].

Table 1
Reported photophysical data corresponding to RF and RFTA.

	Parameters	Data
RF	E_{red}	−0.29 vs NHE [60]
	E_s	2.48 eV [60]
	E_T	2.17 eV [60]
	E_{1RF*}	2.19 V [60]
	E_{3RF*}	1.88 V [60]
	Φ_{1O2}	0.49 [60]
RFTA	Φ_F	0.26 [61]
	Φ_{ISC}	0.74 [61]
	τ_S	5.0×10^{-9} s [49,62]
	τ_T	1.5×10^{-5} s [63]

As a matter of fact, the photochemical properties of riboflavin and the photochemical processes it is able to promote have been deeply investigated in the last century[46–49]. RF presents an absorption spectrum in aqueous solution with four structureless peaks centered at 446, 375, 265, and 220 nm. All four absorption maxima possess high molar absorption coefficients ($> 10^4$ M^{-1}cm^{-1}), indicative of π→π* type transitions. In particular, the absorption maximum at 373 nm corresponds to transitions to the second singlet excited state, which relaxes rapidly to the first singlet excited state followed by emission (Fig. 7 bottom)[50]. The fluorescence spectrum has a maximum at 525 nm, while the phosphorescence has a maximum at 615 nm[49]. Photophysical and electrochemical data of riboflavin and its tetraacetylated derivative (RFTA) are shown in the following table (Table 1):

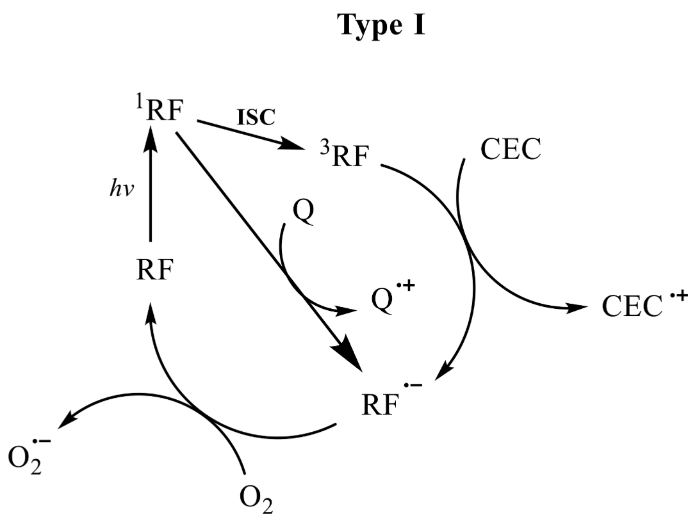
When irradiated in the presence of oxygen, riboflavin is irreversibly decomposed to give lumiflavin, lumichrome and fragments of the ribityl chain, due to the reaction with $^1O_2$ efficiently generated from its triplet excited state[51–53]. Riboflavin, also undergoes anaerobic photoreduction even in the absence of an added electron donor, due to the ability to donate H of its own photoproducts[54]. Nevertheless, in the natural environment, RF has demonstrated to be efficient for decontamination and bacterial inactivation; in most cases the formation of singlet oxygen has been claimed as the main species responsible for the observed effects[55–59].

7. Riboflavin in the photodegradation of contaminants: oxidation

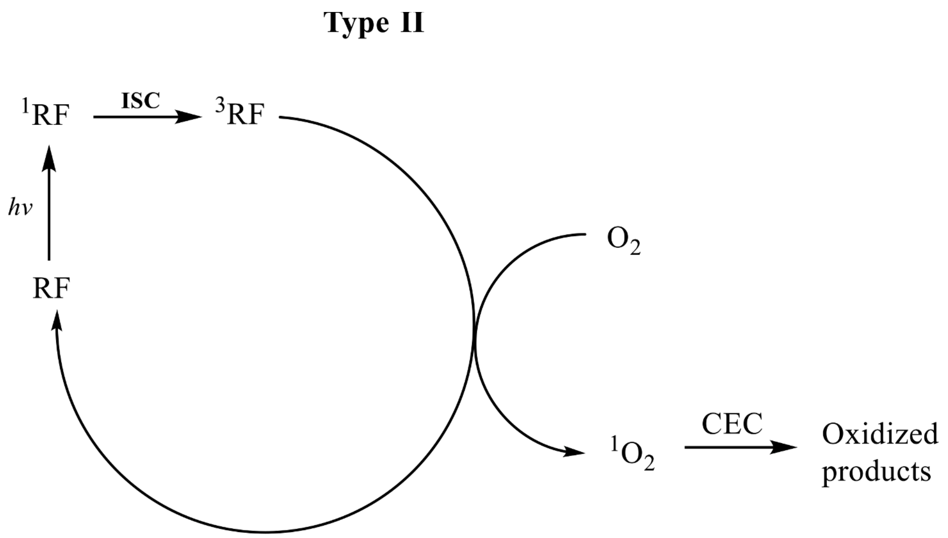
The photophysical and redox properties of RF have been extensively applied for the oxidative photodegradation of contaminants in water. The oxidation of contaminants photocatalyzed by RF could occur through two main pathways, called Type I (Scheme 3) and Type II (Scheme 4).

In both cases, reaction starts when RF absorbs light reaching its first singlet excited state, which is then converted into triplet excited state by intersystem crossing (ISC). Through a Type I mechanism, the triplet excited state is reduced by abstraction of electrons or hydrogen from a contaminant (Q) to form riboflavin radical anion ($RF^{\cdot-}$). The catalytic cycle is closed with the reaction between $RF^{\cdot-}$ and oxygen and the concomitant formation of ground state riboflavin and superoxide anion. In a Type II mechanism, ^{3}RF* reacts with molecular oxygen through an energy transfer mechanism giving rise to singlet oxygen. This species is ultimately responsible for the oxidation of the aqueous contaminants [64]. Table 2 shows a list of contaminants, whose photooxidation has been performed in the presence of riboflavin and visible light.

In order to increase the stability of RF acetylation has been reported



Scheme 3. Oxidative degradation of CECs in water photocatalyzed by RF through a Type I mechanism.



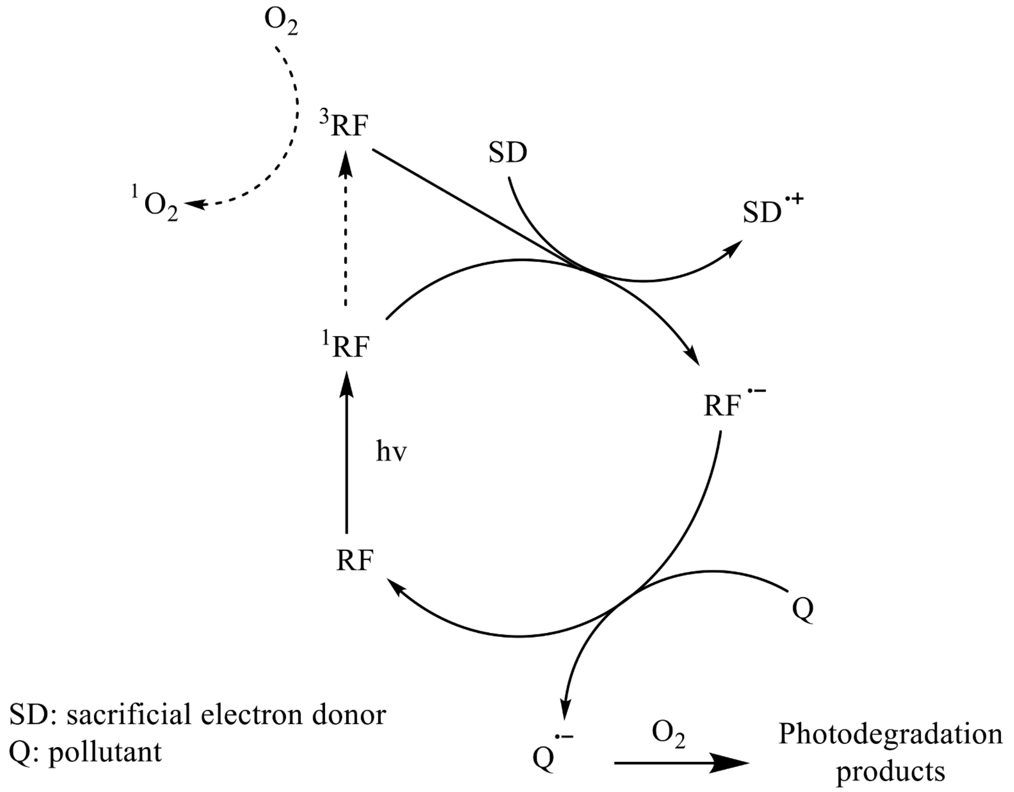
Scheme 4. Oxidative degradation of CECs in water photocatalyzed by RF through a Type II mechanism.

Table 2
List of aqueous contaminants photooxidized in the presence of Riboflavin.

Pharmaceuticals	Pesticides
Tetracycline and Tetracycline derivatives [68]	Atrazine [69]
Carbamazepine [67]	Monuron [70]
Atenolol [67]	Bromoxynil [71]
Ceftriaxone [72]	Dichlorophen [71]
Cefotaxime [72]	4-hydroxypyridine [73,74]
Niclosamide [75]	Norflurazon [76]
Imidazoline [77]	Maleic hydrazine [78]
5-Sulfaminouracil [79]	2,4,6-trichlorophenol [80]
Noscapine [81]	Triclosan [82]
Naturally occurring compounds	**Others**
Gallic acid [83]	2,4,6-Trinitrotoluene (TNT) [84]
Furaneol [85]	Phenolic derivatives [86]
Amino acids [87,88]	Bisphenol A [89]
Quercetin [90]	Benzidine [91]
Morin [90]	o-Tolidine [91]
Rutin [90]	Arsenic [92]
Evernyl [93]	Sulfides [94]
Propyl gallate [95]	
t-Butylhydroquinone [95]	

as a useful alternative. The 2′,3′,4′,5′-tetraacetylated riboflavin (RFTA) shows higher stability and analogous photophysical and redox properties, consequentially it exhibits a higher potential as photocatalyst for degradation of CECs[65,66].

Recent examples on the use of RFTA include the degradation of different pharmaceuticals in water, such as carbamazepine (CBZ), atenolol (ATN) and noscapine (NSC). The selected CECs were treated in the presence of RFTA and blue light under different experimental conditions, and the operating mechanism of degradation was investigated. Complete abatement of these pollutants was achieved when aerated aqueous solutions of drugs were irradiated in the presence of RFTA under visible light irradiation. For instance, up to 85% photodegradation of CBZ was accomplished in only 10 min; the photodegradation of ATN and NSC were slower; nevertheless, the complete abatement of CBZ, NSC and ATN occurred in 20 min, 60 min and 120 min, respectively. In detail, all the evaluated pharmaceuticals showed a direct interaction with the excited states of RFTA (in particular with the triplet excited state) and a subsequent electron-donor chain reactions which ended in the oxidation of the initial pollutants. Moreover, the ability of RFTA to generate $^1O_2$ was also promoting the photodegradation from a parallel (but not less important) pathway. The formation of oxidative photoproducts confirmed the postulated mechanism



Scheme 5. Reduction of contaminants (Q) in the presence of RF and sacrificial donor (SD) under visible light irradiation.

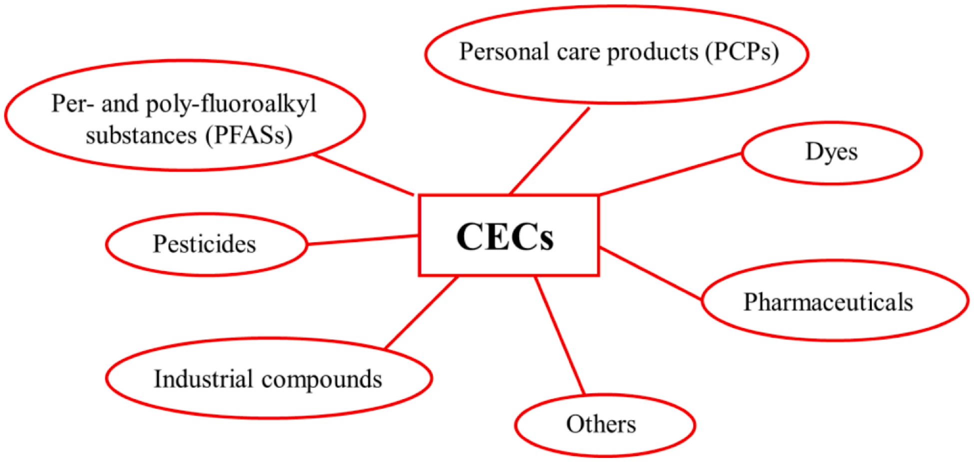


Fig. 1. Different sources of CECs.

and the strong role of RFTA* in the oxidation of CECs[67].

Recently, RF was supported on silica materials in order to improve the stability of the photocatalyst under visible light precluding the generation of $^1O_2$, and therefore, increasing the reusability of the material for consecutive runs. The new RF-based material (SiO_2-RF) was tested against different phenolic pollutants and results compared to the performance of RFTA under homogeneous conditions, both at 20 mol% under blue-LED irradiation. Complete heterogeneous photodegradation was achieved in all cases upon 12 h irradiation. On the contrary, in the presence of homogeneous RFTA, a fast pollutants' degradation was observed in the first 30 min; however, the photocatalytic activity stopped after the first one-two hours without achieving complete photodegradation. Even more, the novel SiO_2-RF organic heterogeneous photocatalyst kept 62% of its activity in the third consecutive run. Control experiments indicated that the pollutants exhibited a high affinity by the surface of SiO_2-RF, which facilitated a pseudo-intramolecular electron transfer to the short-lived first singlet excited state of RF. In summary, the heterogeneous SiO_2-RF photocatalyst demonstrated better performance than the homogeneous one, revealing that there are still opportunities to employ RF in the photocatalytic oxidation of contaminants[60].

8. Riboflavin in the degradation of contaminants: reduction

According to the well-known photophysical properties of RFTA, and the Scheme 2 left, RFTA could be used not only for the oxidation of contaminants but also for the reduction of recalcitrant ones, provided that suitable electron donors are present.

In an ideal scenario, the singlet excited state of RF should be efficiently reduced by a sacrificial electron donor (SD), preventing the

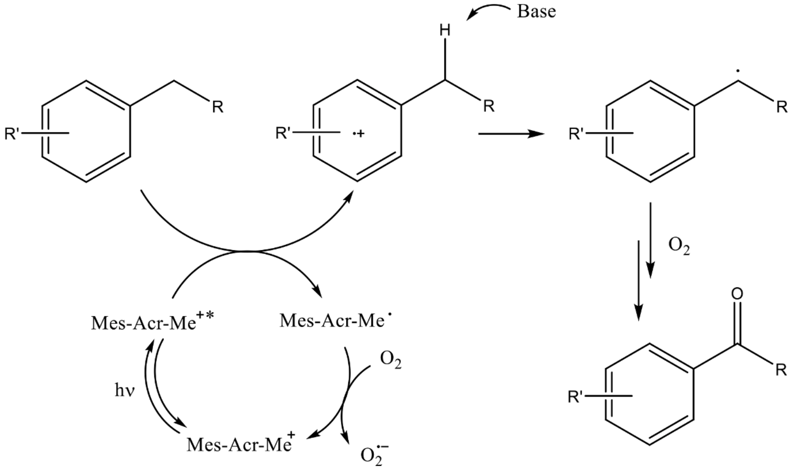


Fig. 2. Aerobic benzylic photooxidations catalyzed by Mes-Acr-Me$^+$ in the presence of visible light.

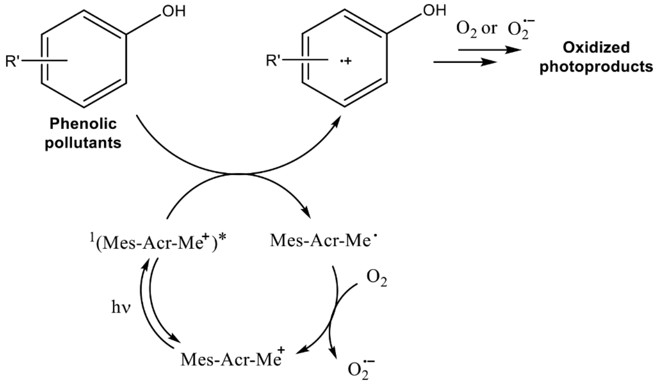


Fig. 3. Photoredox catalytic cycle of Mes-Acr-Me$^+$ involved in the photooxidation of phenolic pollutants.

intersystem crossing, and thus the undesired singlet oxygen species (Scheme 5). Nevertheless, sacrificial electron donors could be selected to also efficiently quench the triplet excited state, and their concentration could be tunned to compete with O_2.

Recent examples have been reported on the photoreduction of RFTA giving rise to $RFTA^{\cdot -}$, which ultimately was the species responsible for reduction of Cu(II) in a click reaction, or for the reduction of model halogenated compounds[41,61]. Specifically, synthetic amines such 1, 4-diazabicyclo[2.2.2]octane (DABCO), diisopropylamine (DIPA), *N, N*′-dimethylaniline (DMA) and triethylamine (TEA), as well as sodium azide were used as electron donors. Laser flash photolysis (LFP) experiments allowed determining the quenching rate constants for the photoreduction processes, and also proved the formation of $RFTA^{\cdot -}$. Moreover, the rate constant values for the reaction between $RFTA^{\cdot -}$ and Cu(II) or model bromides such as bromobenzene, benzyl bromide, and α-bromoacetophenone were determined. These pieces of work were the basis to try to explore the potential of RF to reduce those CECs that are recalcitrant to oxidation.

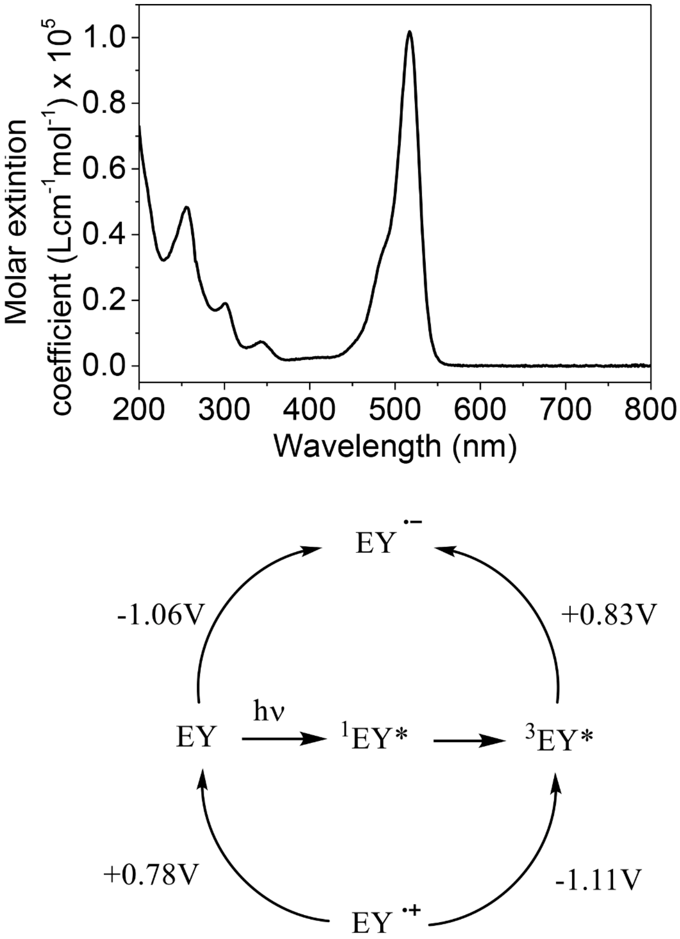


Fig. 4. Top: UV–Vis spectra of EY in aqueous solution; Bottom: Oxidative and reductive cycles of Eosin Y upon absorption of light.

In this regard, benzotriazole UV-stabilizers (BUVSs) constitute a vast family of additives widely used in industry as solar filters. Since their main purpose is to absorb light and prevent yellowing and light-induced degradation of the industrial products, they are very stable and resistant to natural photo/bio-degradation; therefore, they are considered recalcitrant contaminants. To the best of our knowledge, only one example of photodegradation of BUVSs has been reported, in which triplet excited states of chromophoric dissolved organic matter (CDOM) looked to play the dominant role in the photodegradation of UV-P[96]. Recently, we have demonstrated that aerobic aqueous solutions (10^{-5} M) of UV-326 (2-(2′-hydroxy-3′-*tert*-butyl-5′-methylphenyl)−5-chloro-2*H*-benzotriazole), UV-327 (2-(2′-hydroxy-3′,5′-di-*tert*-butylphenyl)−5-chloro-2*H*-benzotriazole) and UV-328 (2-(2′-hydroxy-3′, 5′-di-*tert*-amylphenyl)−2*H*-benzotriazole) could be degraded in the presence of RFTA (10% mol) and visible light (blue LED centered at 450 nm) assisted by DABCO[97]. Therein, the best experimental conditions involved the use of DABCO at a high concentration (10^{-2} M) to ensure the generation of $RFTA^{\cdot -}$, which eventually produced the reduction of

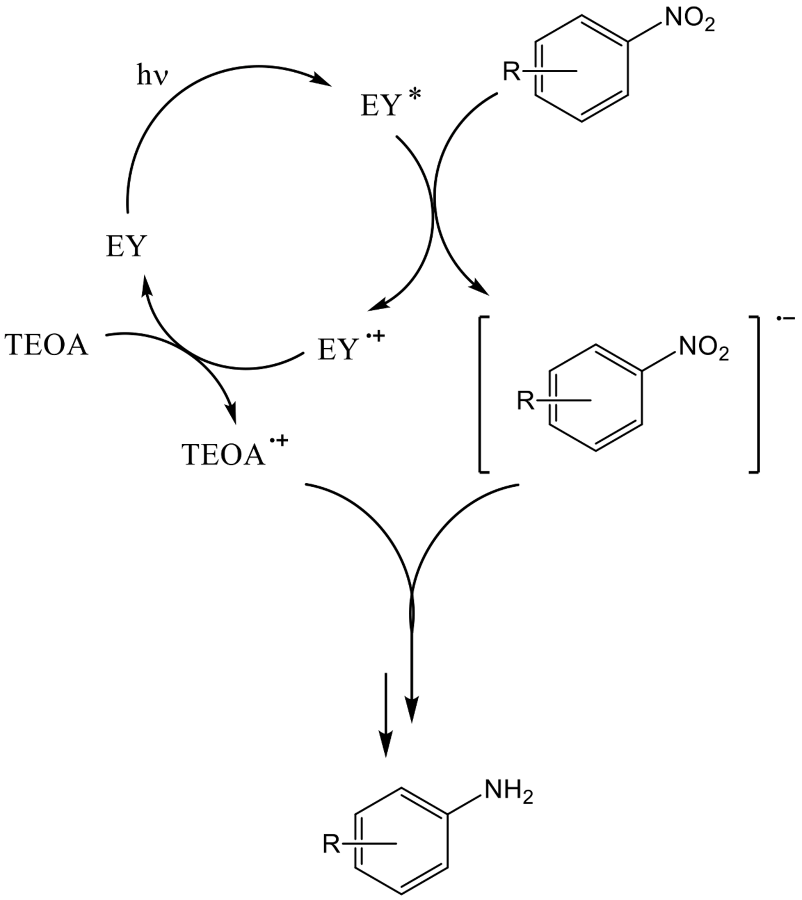


Fig. 5. Reduction of nitrobenzenes to anilines *via* visible light photocatalysis mediated by EY.

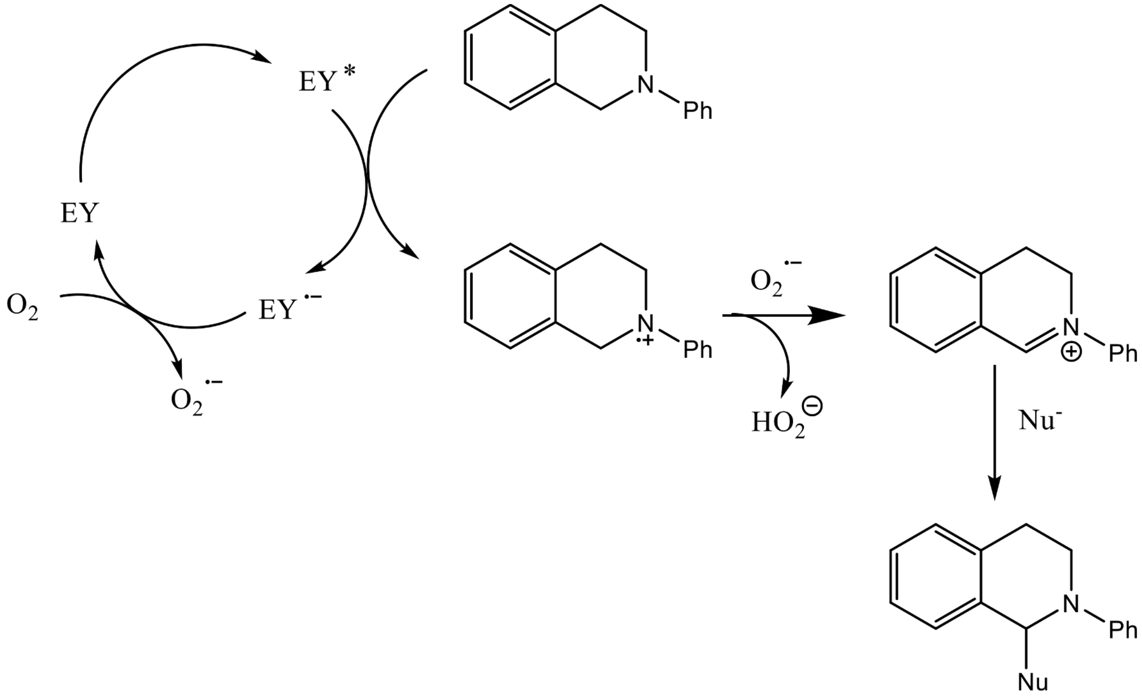


Fig. 6. Photocatalytic oxidative coupling reaction of tetrahydroisoquinolines mediated by EY and visible light.

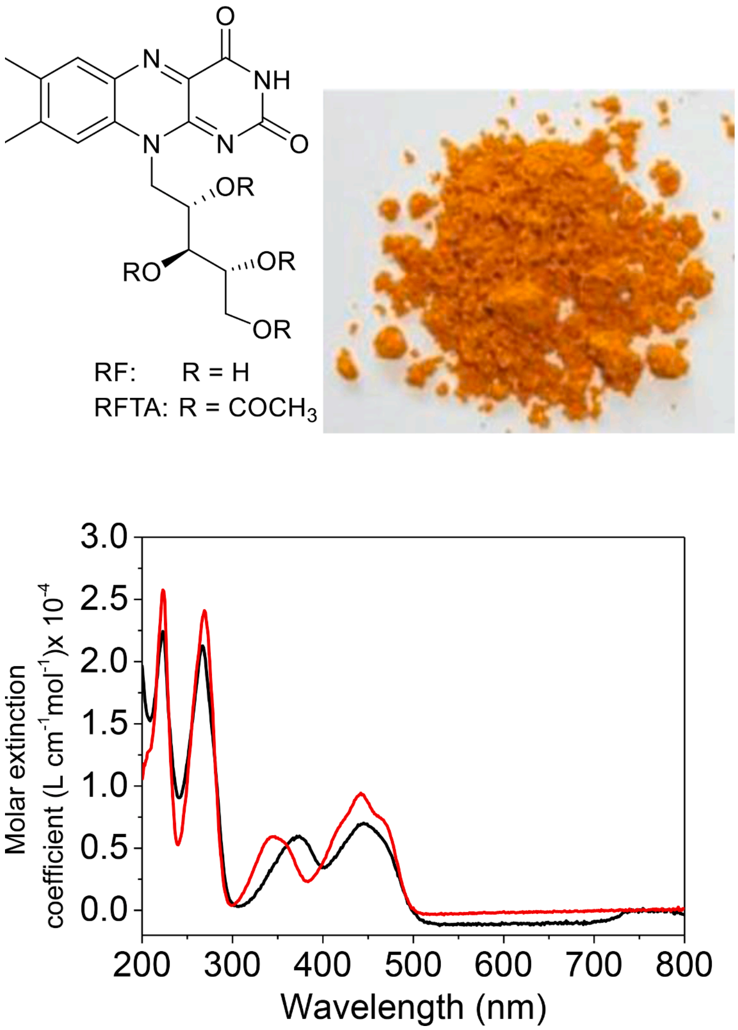


Fig. 7. Top: chemical structure of Riboflavin (RF) and the 2′,3′,4′,5′-tetraacetylated riboflavin derivative (RFTA); bottom: UV–Vis spectra of RF (black trace) and RFTA (red trace) in aqueous solutions.

the selected BUVSs. At that concentration of the electron donor, quenching of ^{3}RFTA* and thus formation of $^1O_2$ is precluded; nevertheless the presence of O_2 improved the efficiency of the photodegradations. In fact, under optimal experimental conditions, complete degradation of UV-326 and UV-327 and more than 70% of UV-328 was achieved in two hours.

Photophysical experiments demonstrated the efficient quenching of ^{1}RFTA* and ^{3}RFTA* by DABCO generating RFTA$^{\cdot -}$, and the subsequent key role of RFTA$^{\cdot -}$ in the reduction of BUVSs, and allowed determining the rate constants that were correlated to the observed photodegradations.

Thus, the well-known natural organic photocatalyst RFTA not only can produce oxidative degradation of pollutants, but its potential can be expanded to the photoreduction of more recalcitrant pollutants in the presence of appropriate electron donors. The role of electron donor can be played by naturally occurring substances, such as humic acids or dissolved organic matter.

9. Conclusions

Advanced oxidation processes (AOPs) include different techniques able to efficiently produce the oxidation of the vast majority of contaminants of emerging concern (CECs). However, the abatement of recalcitrant pollutants is still a matter of research. Visible-light absorbing organic molecules can be included into the AOPs since they have demonstrated to oxidize CECs, mainly through electron transfer and/or singlet oxygen production. Nevertheless, revisiting the redox potentials of organic photocatalysts, they could produce reduction of recalcitrant CECs under the appropriate scenario. Riboflavin, a natural water-soluble vitamin, with well-known photophysical and electrochemical properties has served as the example to demonstrate that organic photocatalysts can expand their potential and be included among the developing Advanced Reduction Processes (ARPs). Photophysical experiments are crucial to determine the species responsible for the reduction, and thus optimizing the experimental conditions accordingly.

Declaration of Interests

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