



Light as a Tool in Organic Photocatalysis: Multi-Photon Excitation and Chromoselective Reactions

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Over the past decades, photoredox catalysis has developed to the big mature field of chemistry. Especially in the field of organic synthesis, more and more sustainable alternatives to conventional synthesis are being developed. Nonetheless, most research activities are focused on the development of new synthetic pathways, utilizing photons as a source of energy for breaking and building of new chemical bonds. We discuss here cases, where selection of the irradiation mode, light intensity (one-, two- photons) or wavelength (UV, blue, green) has a

crucial role on the outcome of the photocatalytic event. Thus, control over irradiation conditions influence the reaction mechanism and offers an access to highly reactive species that are otherwise hardly available. This allows for the unique chemical events to happen, such as deep reduction reactions. The principles of these concepts and their applications are reviewed for both homogeneous and heterogeneous photocatalysts.

1. Introduction

The principal goal of a synthetic organic chemist is to design a reaction system and optimize its conditions in order to maximize the yield and selectivity of the target product. One of the most efficient ways to achieve this goal is catalysis. It ensures highly efficient assembly of structures of different complexity. Not surprisingly, catalysis is extensively exploited in nature, as for example, enzymatic catalysis of bioprocesses.^[1] Furthermore, catalysis is one of the most sustainable approaches to run chemistry as it allows for the atom efficient synthesis. The atom economy principle, in turn, is one of the main metrics for the “greenness” of synthesis. All these benefits made catalysis ubiquitous in chemical industry of all kinds and around 90% of all commercially produced chemicals involve a catalytic process at some stage of their manufacture.^[2] Logically, one of the appealing approaches to pursue the development of chemistry is to design new catalytic platforms that would enable a wide range of chemical transformations in an efficient manner. One of these platforms is photocatalysis, namely catalytic processes triggered by photons. The photocatalyst is a compound or material that upon absorption of a photon produces pairs of electrons and holes that can react with starting materials present in the mixture. Many efforts are put into the design of new photocatalytic materials and systems. Commonly investigated homogeneous photocatalysts are transition metals complexes, especially based on ruthenium or

iridium metals, and otherwise organic dyes, e.g. acridinium salts, riboflavins.^[3] Among heterogeneous photocatalysts, apart from metal based inorganic compounds, an important role is taken by carbon nitrides, polymeric materials made of mainly C and N atoms.^[4] Photocatalysis has been extensively studied for the environmental purposes, including H₂ production from water splitting,^[5] CO₂ conversion to value-added chemicals and hydrocarbon fuels,^[6] pollutants degradation in the waste water treatment etc.^[7] In the past decades, photocatalysts have been also widely investigated for organic reactions.^[8] Analysis of available literature reveals that the main efforts of researches have been put into the development of materials with particular properties, such as high stability, high activity, and defined redox properties, as well as into their applications, that is the development of new reactions.

Albeit large number of publications in this field, we are still in its infancy as the properties of main components of the photocatalytic system, that is, photons are rarely investigated and are typically overlooked.^[9]

However, light is more than an energy source, more than just a driving force – it is a sustainable reagent, which through the variation of energy and intensity of photons can influence the photocatalytic processes, change reactivity and selectivity of the photocatalytic reaction, tune the properties of the catalyst, and alter the reaction mechanism. In this review, we aim to explore the effect of photons properties, e.g. intensity and energy, on the photocatalytic reaction.

2. Light as a tool in photocatalytic reactions

Photochemistry and photocatalysis have developed to the remarkable level of complexity and utility through adopting affordable tunable lasers and light-emitting diodes (LEDs) for running light-dependent reactions. This progress encourages us to consider light not only as a driving force for photochemical transformations, but rather as a powerful traceless reagent that

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plays an essential role as any other chemical reagent in organic reaction. Logically, this became possible as a result of detailed studies on the mechanisms of photochemical and photocatalytic reactions and the factors that affect them.

First of all, every photocatalytic reaction is wavelength-dependent. The chosen wavelength depends on the absorption spectra of the photocatalyst. This results from the principle of photochemical activation, known as Grotthus-Draper law:^[9a,10] only the light absorbed by a system can bring about the chemical change (Figure 1a).

Shifting from the polychromatic light sources (mercury vapors lamps) to monochromatic/near monochromatic LEDs allowed for the deeper understanding of this behavior. This correlation is true for all photochemical as well as photocatalytic transformations. As we will present later, broader absorption spectra of the photocatalyst also allows for the control over the reaction selectivity by varying the excitation between different wavelengths (Figure 1d).

Another point of light-dependence arises from one more basic principle of photochemistry, the Bunsen-Roscoe law,^[9a,10] which refers to the dependence of photochemical reaction on the intensity and duration of light exposure (Figure 1b). Thus, the quantum yield of the reaction depends on the power of used LED, transmittance of the reaction vessel and the time of irradiation. However, in photocatalysis, this correlation is not always simple and the incident light can influence the reaction mechanism and accordingly the quantum yield of reaction.^[11] In the next section, we will discuss how the intensity of light can be used to change reactivity of the photocatalyst. More precisely, how absorption of several photons sequentially offers new reactive states of the excited photocatalyst and how they can be used to run chemical reaction (Figure 1c).

Based on the stated, the photocatalytic systems that would be active at the entire visible light spectrum are one of the key points in developing sustainable photochemical processes that would run under direct solar light instead of artificial light sources. Moving extra to the near-infrared (NIR) light might also be useful for the biological and medical applications as this would allow photosensitizers activation through biological tissues, e.g. skin.^[12] However, broadening the absorption spectrum is not a trivial task and most available photocatalysts absorb below 500 nm. In addition, narrowing the optical gap of a photocatalyst decreases the driving force of the photoinduced electron transfer. There are several strategies that allow for the use of long waves for productive photocatalysis. Many organic dyes absorb at the longer wavelength of visible spectrum and

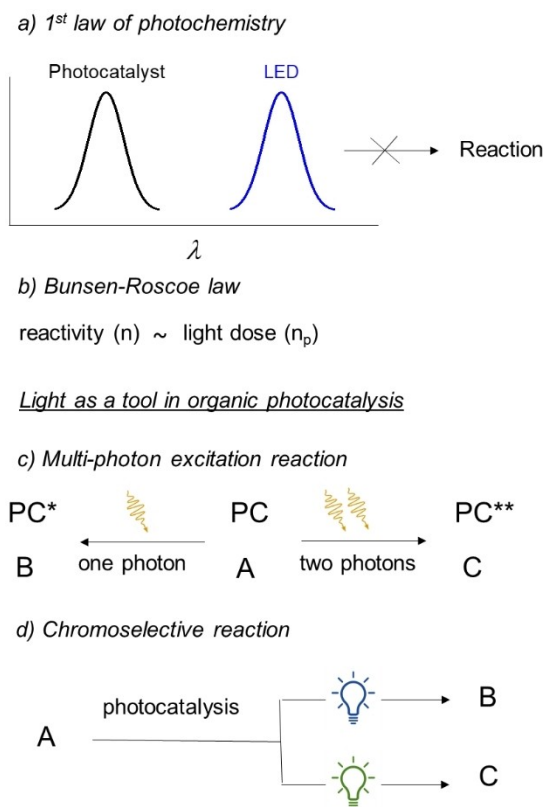


Figure 1. a) 1st law of photochemistry; b) Bunsen-Roscoe law; c) Schematic representation of a multi-photon excitation photocatalytic reaction; d) Schematic representation of a chromoselective reaction. PC – photocatalyst and its excited states PC* and PC** resulted from one-photon or two-photon excitation respectively. A – starting compound; B, C – possible products.

theoretically might be suitable for photocatalysis, however they can reach only short excited state lifetimes. This limitation does not allow them to act as photoredox catalysts, but they can be used for the sensitization of other materials, such as TiO₂. This strategy is used in dye-sensitized solar cells (DSSCs) and might be also applied in organic synthesis,^[13] however the latter is rare.^[14] The other strategies to reach photocatalytic activity at long wavelength up to the NIR and deep red are triplet fusion upconversion^[15] and forbidden S₀-T₁ transition at low-energy irradiation as recently shown for Os(II) terpyridine complexes.^[16] These strategies are either very specific or require expensive rare metals. Thus, the success in the development of sustainable



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photocatalytic system that would enable a broad scope of organic reactions under long wavelength irradiation was not yet obtained.

3. Multi-photon excitation photoredox catalysis

Another concern that must be considered while developing strategies for utilization of low-energetic light is thermodynamic limitations that photons of low energy would bring. This is not aligning with the constant movement towards performing more and more challenging transformations. Indeed, the energy of visible photons is limited to 300 kJ mol^{-1} (3.1 eV) and at least $\frac{1}{4}$ or even half of the photon energy is lost on the way to the substrate activation. The alternative approach to drive the thermodynamically challenging reactions in the broad range of visible light spectrum with already established photocatalysts might be multi-photon excitation photoredox catalysis (Figure 1d). This concept allows to combine the energy of two low-energetic photons in one catalytic turnover to satisfy high energetic requirements of the given reaction. This concept have been for long exclusively the tool of spectroscopists as it required expensive pulsed lasers.^[17] Amid the progress in LED technology, this concept is now exploitable also for preparative-scale reactions.

3.1. Consecutive photo-excitation

An approach based on the consecutive rather than simultaneous absorption of photons is apparently more feasible for the preparative-scale photocatalysis as it is accessible operating conventional LEDs and continuous wave (CW) lasers rather than expensive pulsed lases that are typically unavailable in chemistry laboratories. The excitation density is the key in such multi-photon excitation events and can be regulated by light intensity.

Kerzig and Wenger have used the collimated beam obtained by introducing the optical lens to the excitation-beam path of 1 W 447 nm CW laser to access two-electron excitation of the water-soluble iridium complex fac-tris[2-(50-sulfonatophenyl)pyridine]iridium(III) pentahydrate (Irsppy).^[18] It was shown that two completely different substrate activation mechanisms are initiated from one- or two-photon excitation (Figure 2a). One-photon excitation brings about excitation of one electron from the LUMO to the HOMO of the photocatalyst. This results in the formation of $^3\text{Irsppy}$ with a triplet excited state energy of 2.65 eV and a redox potential of -1.6 V vs. NHE, making it suitable for different triplet-triplet energy transfer reactions or one-electron substrate reductions. Two-electron excitation produces the super reductant hydrated electrons e_{aq}^- with its standard potential of -2.9 V vs. NHE, offering almost doubled energy for reduction reactions. Thus, in the reaction with *trans*-cinnamic acid, energy transfer mechanism

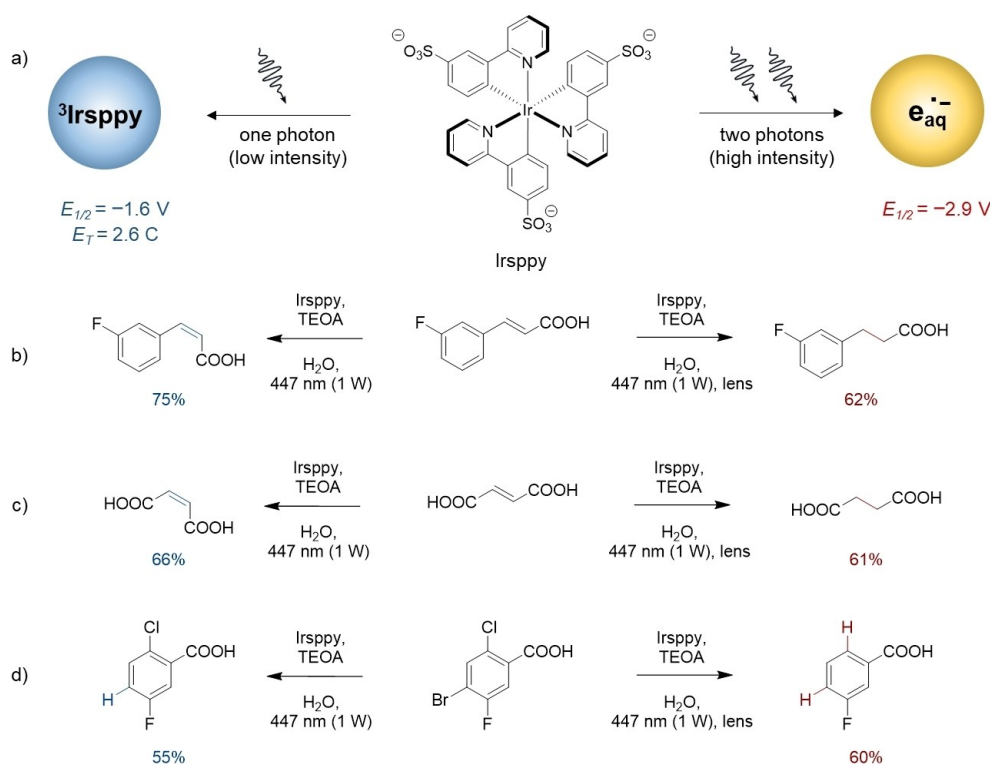


Figure 2. a) Reactivity control of Irsppy by changing the light intensity (left, one-photon mechanism; right, two-photon mechanism); *trans*-*cis* isomerization and hydrogenation with the olefinic substrates *trans*-3-fluorocinnamic acid (b) and fumaric acid (c); d) selective debromination and subsequent dechlorination carried out with 4-bromo-2-chloro-5-fluorobenzoic acid.

was activated upon one-electron excitation, which led to isomerization of the acid up to the *cis-trans*-ratio of 3:1 (Figure 2b). Under two-electron excitation, initiated by hydrated electrons reduction of the double bond was observed. By the analogue, the reaction was also successful with fumaric acid, however with less selectivity towards *cis*-isomer (Figure 2c). A clear difference between reducing power of $^3\text{Ir}^{\text{ppy}}$ and $\text{e}_{\text{aq}}^{\bullet-}$ was observed on the reaction of dehalogenation of benzoate. The first was able to induce only debromination, while the latter enabled additionally more demanding dechlorination of the benzoate (Figure 2d).

To enable a consecutive photo-excitation mechanism, the catalyst must show very high stability after the absorption of the first photon to be able to absorb the second one. Thus, photostability and robustness of the photocatalyst are key points that must be considered developing other synthetic procedures following this pattern. Apart from the stable transition metal complexes, 9-anthrolate^[19] and 3-aminoperylene^[20] were also shown to produce hydrated electrons via two-photon excitation to enable photocatalytic reaction.

3.2. Consecutive photoinduced electron transfer (ConPET)

This type of multi-electron excitation photocatalysis is more common, as it does not require particular stability of the catalyst's excited state PC^* . In this case, the photoexcited catalyst undergoes reductive quenching with strong sacrificial electron

donors (SED) resulting in the formation of relatively stable radical anion $\text{PC}^{\bullet-}$ that can further absorb a photon to form $\text{PC}^{\bullet-*}$. This excited state is highly unstable, has shorter lifetime than previously discussed hydrated electrons, but has remarkably high reduction potential (Figure 3a). The first reported reaction following this mechanism was reduction of aryl halides with perylene diimide (PDI) as catalyst and triethylamine as SED (Figure 3b).^[21] Later mechanistic investigations confirmed the proposed mechanism for the substrates with reduction potentials more positive than -1.7 V vs. SCE.^[22] Thermodynamically challenging reduction of alkyl chlorides (-2.8 eV vs. SCE) under blue LED irradiation in the microstructured solution with $[\text{Ir}(\text{dtbbpy})^*(\text{ppy})_2]$ complex was recently presented (Figure 3c).^[23] L-ascorbic acid was used as the terminal reducing agent. Authors also exploited this approach to activate alkyl chlorides for intermolecular C–C coupling and intramolecular cyclization with alkenes.

Mesityl acridinium salt ($\text{Mes-Acr}^+\text{BF}_4^-$) typically considered as a photocatalyst for oxidation reactions,^[3a] was recently shown to form a neutral acridine radical with an excited-state redox potential of -3.36 V vs. SCE, which makes its reducing power similar to elemental lithium.^[24] Indeed, authors reported several reactions with $\text{Mes-Acr}^+\text{BF}_4^-$ photocatalyst that typically require alkali metal reductants. The investigation of excited-state dynamics of Mes-Acr^* revealed two main excited states formed: a lower-energy doublet (D_1) and a higher-energy twisted intramolecular charge-transfer (TICT) state. The excited-state redox potentials of these states were estimated to be -2.91 V and -3.36 V vs. SCE respectively, which are among the

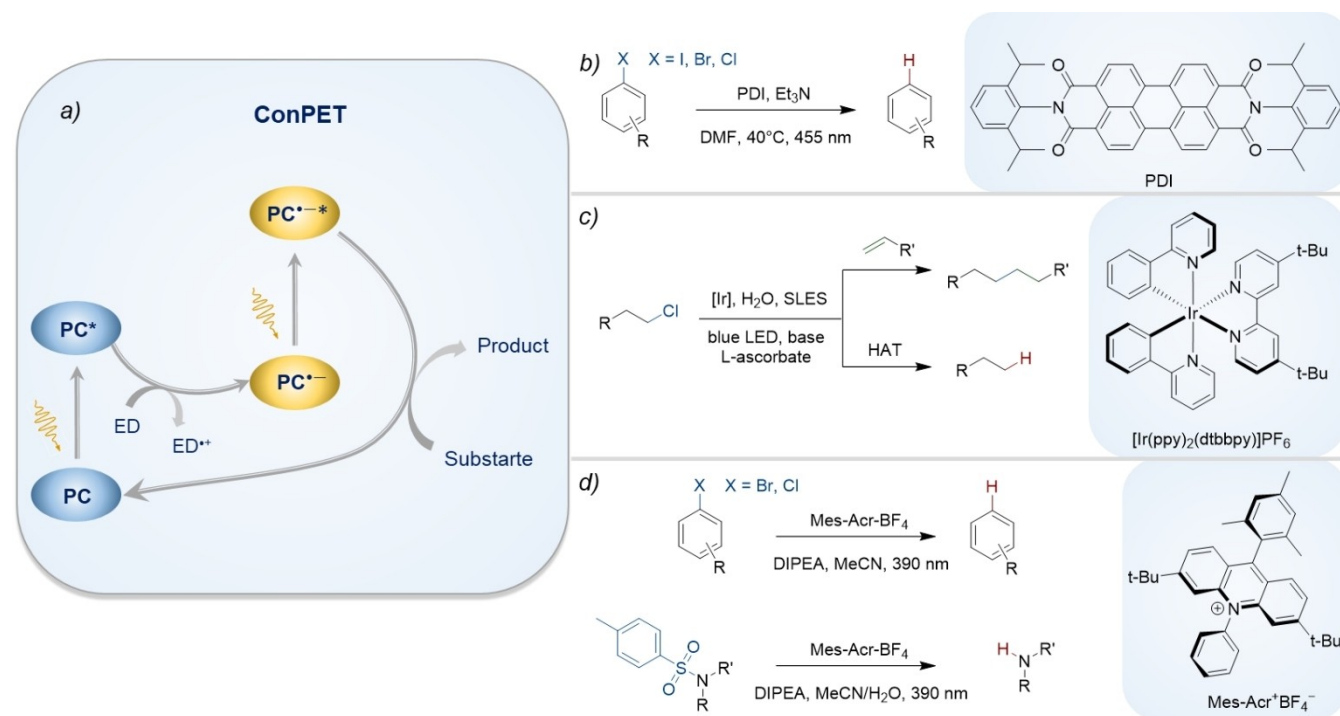


Figure 3. a) Schematic reaction via Consecutive Photoinduced Electron Transfer; b) Reduction of aryl halides with perylene diimide (PDI) photocatalyst; c) Reduction of alkyl chlorides and their C–C coupling with alkenes catalyzed by $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$; d) Dehalogenation of aryl halides and detosylation of amines with $\text{Mes-Acr}^+\text{BF}_4^-$ photocatalyst.

highest reported for an organic molecule. The developed system was applied for dehalogenation of aryl halides (bromides and chlorides) and desosylation of amines (Figure 3d).

The discussed cases are rather representative to the concept and presented to show versatility of the mechanism. There have also been other systems reported on the ConPET process. These include 9,10-dicyanoanthracene for aromatic substitutions of non-activated aryl halides;^[25] anthraquinones for reduction of aryl halides or C–C coupling reaction;^[26] Ru-complexes for hydrated electron production for hydrogenation of cinnamates and fumarates, dehalogenation of benzoates, cross-coupling reactions;^[27] benzo[ghi]perylene imides for Birch-type reductions of benzene derivatives.^[28] Similarly, several examples of ConPET reactions were reported with Rhodamine 6G photocatalyst, such as the case discussed later in Section 4.1 as a relevant example of chromoselective photocatalysis.^[29] Significant mechanistic studies were recently reported on ConPET mechanism with this photocatalyst that are recommended for detailed information.^[30] In this review, we don't aim to present detailed mechanistic investigations of ConPET and other multi-photon excitation reactions, but rather to overview different available approaches for utilization of photons as a tool to control photocatalytic reactions. Thus, the mechanism schemes in Figure 3 and Figure 4 are serving for simple visual interpretation and do not reflect the mechanism complexity.

Overall, multi-photon excitation processes is a powerful tool in photoredox catalysis that allow for conducting highly energy demanding reactions. However, it has only recently started to be applied on the preparative scale. Moreover, as shown on the presented examples, it is mainly applied for reduction reactions and only limited information is available on the possible multi-photon oxidations. Nevertheless, several examples as well as mechanistic insights of the latter approach were reported by Wagenknecht and coauthors.^[31] Authors proposed to use N-phenylphenothiazine as a photocatalyst for activation of sulfur hexafluoride SF₆ and different styrenes for pentafluorosulfanylation reaction (Figure 4). Mechanistic investigation revealed two consecutive electron transfer steps to activate both SF₆ and the substrate. The first excitation and electron transfer events produce catalyst radical cation PC^{•+} and SF₅ radical. Excitation of PC^{•+} with second photon to PC^{•++} allows for oxidation of alkene substrate that can be further trapped by presented in the reaction system nucleophile, e.g. formed SF₅ anion.

This approach could also be combined with an intramolecular radical-alkyne addition to form such heterocycles as oxepans, tetrahydropyrans and tetrahydrofurans (Figure 4d).^[31c] Thus, this approach offers an exclusive opportunity to use SF₆ as a direct pentafluorosulfanylation reagent for the synthesis of valuable building blocks with high structural complexity, that cannot be simply prepared by other synthetic methods.

In this review, we have discussed classical consecutive two-photon absorption processes, that have already found synthetic application in organic chemistry and are relatively good understood due to the present extensive spectroscopic investigations. Additionally, consecutive two-photon excitation reactions are useful to control the reaction outcome, using excitation wavelength or the irradiation power as control parameters, which

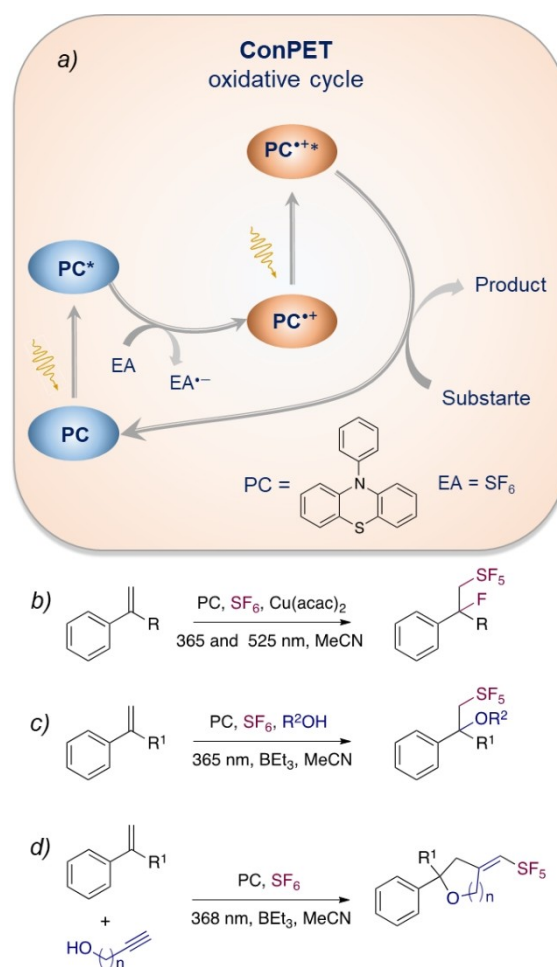


Figure 4. a) Schematic reaction via Consecutive Photoinduced Electron Transfer (oxidative cycle); b) Pentafluorosulfanylation of styrene derivatives with SF₆; c) α-Alkoxy pentafluorosulfanylation of styrene derivatives with SF₆; d) Pentafluorosulfanylation domino cyclization of α-substituted alkenes to oxaheterocycles by using SF₆.

match with the concept of this review. However, there are other multi-photon mechanisms reported in literature,^[32] such as bimolecular systems, that do not directly lay in the scope of our review, but might have significant synthetic potential. For more details on the multi-photon excitation redox reactions and overview of other systems a dedicated review by Wenger *et al.* is recommended.^[32]

The reported literature are prevailed by homogeneous systems, although the heterogeneous catalysts are not necessarily excluded.^[33] Finally, the multi-photon excitation approach is rather a way to control the reactivity of the photocatalyst, more precisely to reach highest excited state redox potentials, than to control selectivity of reaction. Thus, we will further focus on the recent developments on the selectivity control of organic reactions regulating the excitation light.

4. Chromoselective photocatalysis

Apart from controlling intensity of light flux discussed previously, one can choose to control energy of photons, e.g. wavelength. Indeed, photons are traceless reagents that bring certain energy to the photocatalytic system (Figure 5a).

This photoenergy by means of photocatalysts is transformed into chemical energy, that is, the energy of chemical bonds that are being broken and/or created. A photocatalytic reaction is possible, when the thermodynamic requirements for it are met. These are primarily defined by photoredox potential of the photocatalyst and the energy brought by photons. Photons of different energy (wavelength) are able to activate different excitation states of the photocatalyst or substrate and thus,^[9b] initiate different reaction pathways, what in conventional reaction is achieved by changing chemical reagents (Figure 5b). Thus, in the same reaction mixture, upon different irradiation light wavelength, different products might be achieved (Figure 5c). Summarizing, light wavelength can be

used for fine tuning of the reaction selectivity. Herein, we will refer to these reactions as chromoselective.

There are chromoselective reactions reported for both, homogeneous and heterogeneous photocatalysts, and we will discuss them in more details below.

4.1. Chromoselective photocatalytic homogeneous reactions

In 2016, the chromoselective one- or two-fold substitution reaction of 1,3,5-tribromobenzene by N-methylpyrrole with Rhodamine 6G (Rh-6G) photocatalyst was reported (Figure 6a).^[29] Different redox states of the excited Rh-6G could be achieved under different colors of excitation light, which led to the selective transformations of aryl-halide bonds in C–C bonds. Thus, upon excitation with green (530 nm) light, in presence of N,N-diisopropylethylamine (DIPEA), the stable radical anion Rh-6G^{•−} was formed. The latter possesses a reduction potential of −1.0 V vs. SCE and is able to activate polybromoarenes that after bromide loss generate an aryl radical, which can be further trapped with N-methylpyrrole. The reduction potential of Rh-6G^{•−} is not sufficient under these conditions (530 nm irradiation) for subsequent activation of the remaining carbon–bromine bonds. Upon excitation with blue (455 nm) light, in the presence of DIPEA, a higher excited state Rh-6G^{•−*} is formed upon excitation of Rh-6G^{•−}, which increases the reduction potential to −2.4 V vs. SCE. Under these conditions, the reaction proceeds to the two-fold-substituted products. Formation and photoreactions of the Rh-6G radical in ConPET process have recently been investigated by single molecule spectroscopy,^[30b] transient absorption spectroscopy in the time range from femtoseconds to minutes and supported with quantum chemical calculations.^[30a] Thus, dedicated literature is recommended for the detailed mechanistic insights.

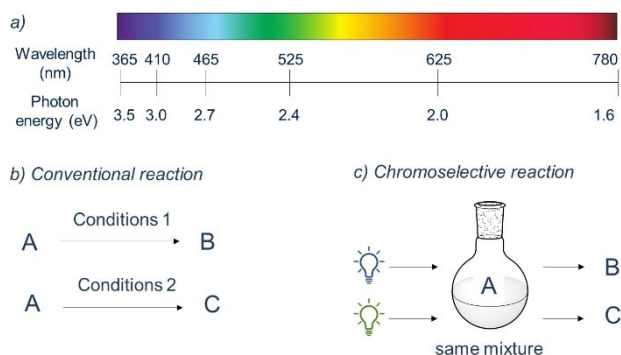


Figure 5. a) Correlation of light wavelength to photon energy; b) Schematic conventional reaction; c) Schematic chromoselective reaction.

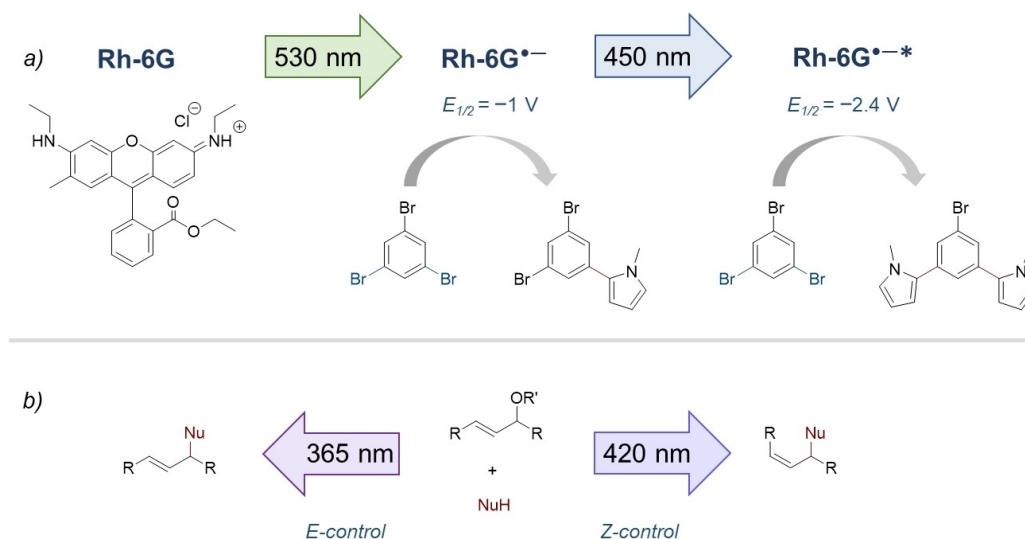


Figure 6. a) Chromoselective one- (under 530 nm) or two-fold (under 450 nm) substitution of 1,3,5-tribromobenzene by N-methylpyrrole catalyzed by Rhodamine 6G; b) Chromoselective control of the double bond (Z or E) isomerization in the allylation of indoles, pyrroles, amines, and alcohols reaction.

In 2019, a chromoselective photocatalytic approach for allylation of indoles, pyrroles, amines, and alcohols has been proposed (Figure 6b).^[34] An approach to control the isomerization process of the double bond (*Z* or *E*) was built up on the use of different light irradiation wavelength and photocatalyst with suitable redox potentials and absorption profile. Photocatalyst with high reduction potential (≥ 2.35 V vs. SCE) was needed for the activation of the allylic derivative. Thus, irradiation of the reaction system with 10-phenyl-10H-pheno-thiazine (PTH) photocatalyst at 365 nm led to the selective formation of *Z*-isomers (*Z*/*E* of 94:6). This was explained by the significant absorption at 365 nm of the *E*-isomer and consequently possible photosensitization and isomerization. Thus, for the selective formation of the corresponding *E*-isomer, irradiation with 420 nm LED was chosen and the photocatalyst was changed to the phenoxazine dye, which absorbs strongly at this wavelength (*Z*/*E* of 5:95). The fine optimization of reaction conditions allowed for the fast reaction time and smaller excess of the nucleophile (2 equivalents).

While such control over the reaction path is indeed rare, another point of view was recently presented on the example of debenzylolation reaction. In this case, the longer wavelength of 525 nm was used to control reactivity of the photocatalyst, namely to slow the reaction down. This was needed to achieve higher selectivity, whereas excitation with 440 nm instead, where the photocatalyst absorbs strongly, the oxidation at benzylic position was promoted.^[35]

4.2. Chromoselective photocatalytic heterogeneous reactions

Most of semiconductors that are being used as heterogeneous photocatalysts do not absorb beyond 500 nm. The narrow absorption spectrum significantly limits the use of these materials for chromoselective photocatalysis, as the use of more than one wavelength, preferably in the visible region, is necessary. Thus, the first step towards the chromoselective catalysis in the visible light is to investigate how one can influence/broaden the absorption spectrum of these materials. One of the most easily tunable heterogeneous materials used in photocatalysis is the group of carbon nitrides. These are polymer materials made from various nitrogen rich precursors that consist mostly of C and N atoms. The photocatalytic applications of carbon nitrides are being extensively explored in the past decades and numerous literature are published on their synthesis, environmental applications, and fine organic synthesis.^[4,36] As was concluded in our previous review, the performance of carbon nitride-based materials is indeed similar to the commonly considered metal-based complexes.^[37] Tunable properties of these materials allow among other to refine their optical properties. The typical for carbon nitrides (CN) band gap of 2.7 eV, for example, can be reduced to 2.56 eV by co-condensation of urea and oxamide (CN-OA) followed by calcination. Such material can effectively use photons of more than 500 nm for hydrogen production by water splitting, reaching 10% AQY at 525 nm irradiation (Figure 7a, Figure 7b).^[38] Grafting of CN groups on the carbon

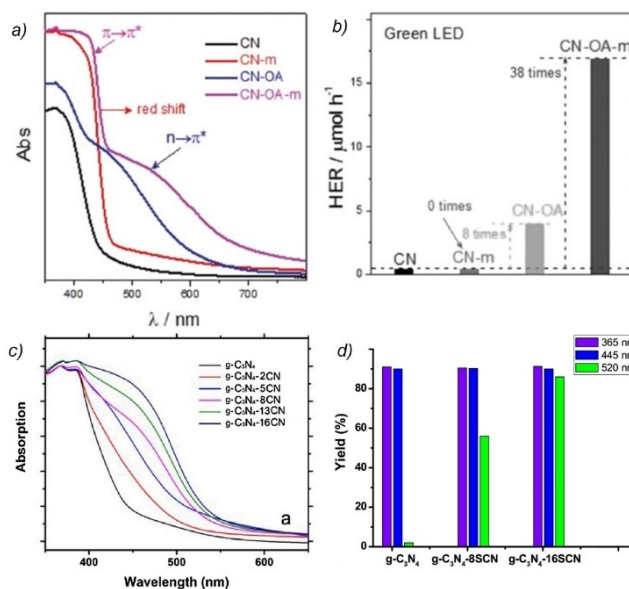


Figure 7. a) UV-Vis absorption spectra of CN and CN-OA materials; CN-m and CN-OA-m prepared in the molten salt (KCl/LiCl); b) Photocatalytic H₂ evolution activities of the samples under green light; c) UV-Vis absorption spectra of the g-C₃N₄-xCN samples; d) Photocatalytic performance of the materials in the coupling reaction between styrene and sodium benzenesulfinate. Figure 7a,b reproduced from ref. [38]. Figure 7c,d reprinted from ref. [39]. Copyright (2018), with permission from Elsevier.

nitride (g-C₃N₄-xCN) scaffold also results in the extended absorption up to 590 nm as was shown on the photocatalytic coupling reaction between styrene and sodium benzenesulfinate under 520 nm irradiation (Figure 7c, Figure 7d).^[39]

In 2018, the first example of chromoselective reaction catalyzed by carbon nitride was shown on the synthesis of azo- and azoxy-aromatics by reduction of nitroarenes (Figure 8a).^[40] As the absorption of g-CN is limited to blue region, only wavelength of lower than 460 nm could be used. In the proposed approach, the thermodynamic requirements of the

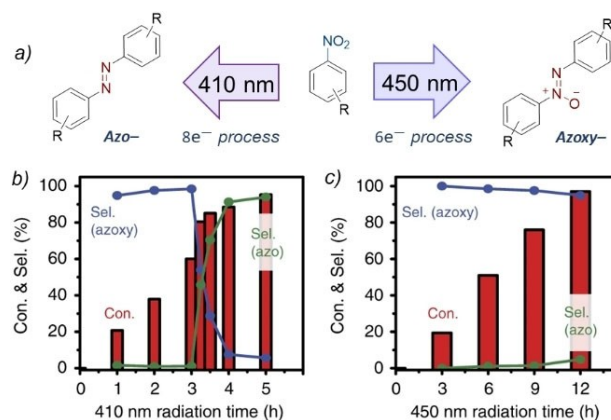


Figure 8. a) Chromoselective reduction of nitroaromatic compounds to azoxy- compounds (under 450 nm) and azo- compounds (under 410 nm); selectivity towards azo- and azoxy- compounds under 410 nm (b) and 450 nm (c) irradiation. Reproduced from ref. [40].

reduction reaction were used as the control point. Thus, reduction to the azoxy- compounds requires $6e^-$, while reduction to azo- compounds is $8e^-$ process. The first was achieved under 450 nm irradiation with selectivity of 99%, while the latter at 410 nm with 94% selectivity (Figure 8b, Figure 8c). As azoxy-aromatics are commercially more valuable, authors have optimized the reaction for their synthesis. Furthermore, this is also one of the few examples when the photocatalysis was performed on the big scale. The production of azoxy-aromatics was tested on the 800 mL and 80 L scale.

As was explained before, a broader absorption spectrum of the photocatalyst leads to extra versatility on the irradiation wavelength selection. Thus, previously described photocatalyst CN-OA-m, which absorbs broadly in the visible region (Figure 7a), was applied in several reactions where the longer wavelength were used to change activity and selectivity. First, it was used to overcome the substrate scope limitations and reproducibility issue due to deactivation of the nickel catalyst in the dual photoredox/nickel-catalyzed C–N cross-couplings of cyclic secondary amines with aryl halides (Figure 9a).^[41] The nickel salt catalyst suffers from the formation of nickel-black as a result of accumulation of lower valence Ni species under high rates of reductive elimination. This, consequently, leads to catalyst deactivation and low yields. The authors proposed to use CN-OA-m photocatalyst and irradiation with green light to

limit the rate of reductive elimination (RE) and to promote oxidative addition (OA). This significantly improved reproducibility and selectivity of C–N cross-couplings of electron-rich, -neutral and -poor aryl bromides with primary and cyclic secondary amines.

The same catalyst, CN-OA-m, more recently was shown to have different oxidation potentials under different irradiation wavelength. CN-OA-m has a strong absorption band up to 460 nm and a weaker band up to 700 nm (Figure 7a). These electron transitions were prescribed to $\pi-\pi^*$ and $n-\pi^*$ respectively. Excitation with 535 nm light, e.g. $n-\pi^*$ transition, leads to the formation of electron holes with lower oxidation potential than those formed from $\pi-\pi^*$ transition upon excitation with 440 nm (Figure 9b). This strategy was used to control the reaction pathway by changing irradiation between these two wavelengths. Activation of CN-OA-m photocatalyst with green light resulted in the formation of H_2O_2 in the presence of ethylbenzene and the *Aae*UPO, in turn, catalyze its asymmetric hydroxylation (Figure 9c).^[42] This way, (*R*)-1-phenylethanol with 99%*ee* was achieved. Under excitation with shorter wavelength, e.g. 440 nm, oxidation of ethylbenzene to acetophenone was preferred. The latter was subjected to reduction by enantioselective alcohol dehydrogenase from *Rhodococcus ruber* (ADH-A) to form (*S*)-1-phenylethanol with 93%*ee*. Thus, chromosomelective photo-chemo-enzymatic cascade reaction was

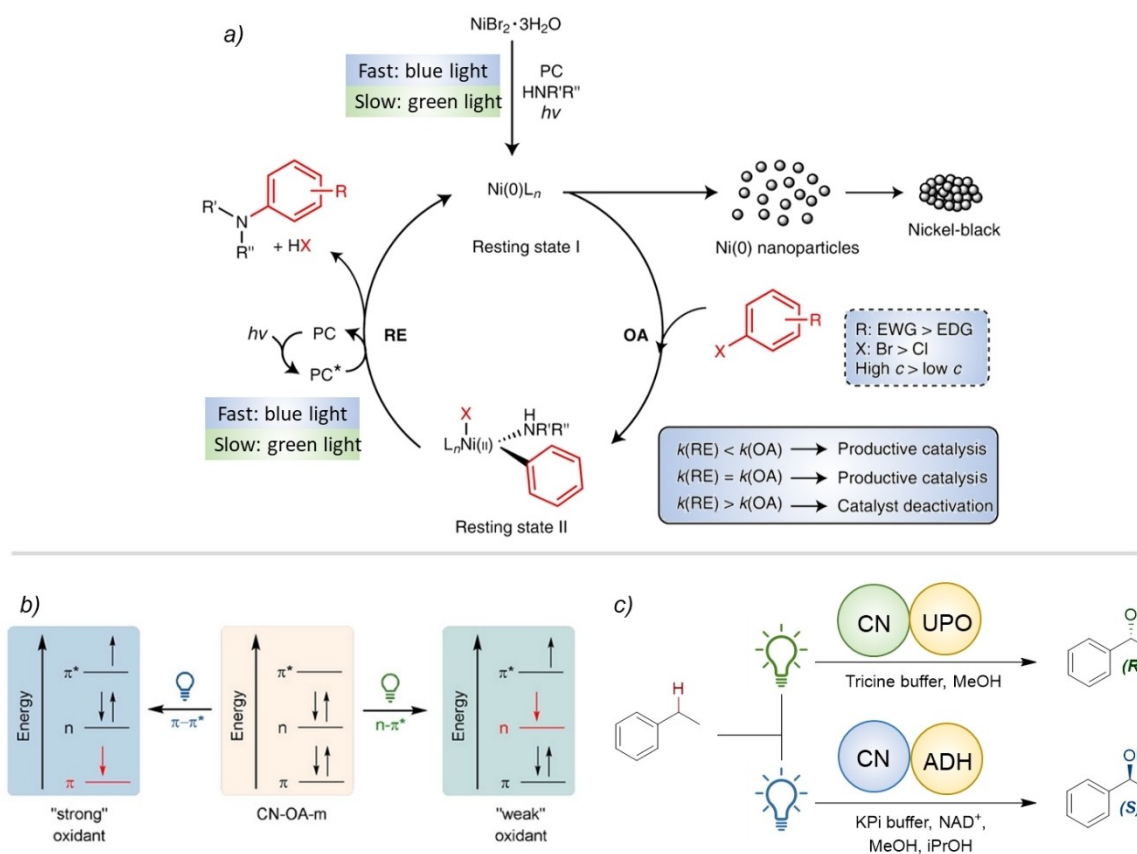


Figure 9. a) Overcoming limitations in dual photoredox/nickel-catalyzed C–N cross-coupling via optimizing light wavelength; b) Possible electron excitation in the CN-OA-m; c) Chromosomelective photo-chemo-biocatalytic cascades for synthesis of (*R*)- and (*S*)-1-phenylethanol by oxidation of ethylbenzene. Figure 9a reprinted from ref. [8c]. Copyright (2021), with permission from Elsevier. Figure 9b reproduced from ref. [42].

designed to obtain selectively (S)- or (R)-enantiomer of chiral benzylic alcohols.

Another well explored in organic photocatalysis member of the carbon nitride group, potassium poly(heptazine imide) (K-PHI) photocatalyst (Figure 10a), has an absorption spectrum with several bands that broaden up to the red region of the visible light (Figure 10b). This photocatalyst shows particular activity in oxidation reactions, such as oxidation of amines,^[43] alcohols,^[44] and even thermodynamically challenging oxidation of halide anions.^[45] On the other hand, due to the ability to accumulate significant amount of electrons upon excitation,^[46] it serves as a powerful tool in, for example, multi-electron reduction of nitroarenes.^[47]

Recently, the K-PHI photocatalyst was shown to activate the substrate even under red light in the deoxygenation reaction (Figure 10c).^[48] The irradiation with longer wavelength was used to improve selectivity for some substrates, such as aliphatic ketoximes. While the reaction was shown to be mostly photochemical under 465 nm irradiation, the photocatalytic mechanism was proved for 625 nm irradiation. The investigation of the reaction mechanism revealed the energy transfer to the oxygen to be the decisive point. Indeed, irradiation of K-PHI with red light is insufficient for the production of reactive electrons and holes. Thus, the [2 + 2] cycloaddition mechanism was proposed for the ¹O₂ and C=N bond of oxime.

The K-PHI photocatalyst shows at least two bands in the diffuse reflectance UV-vis (DRUV-Vis) spectrum that correspond to an intrinsic band gap (BG) typical for carbon nitrides of 2.64 eV and a band of ca. 1.86 eV related to intraband states

(IBS) (Figure 10b). Thus, different redox potentials are available upon excitation the catalyst with photons corresponding to these bands. In addition to the electron transfer mechanism, the energy transfer is also possible as was shown above in the deoxygenation reaction and in our previous studies.^[49]

These three possibilities were investigated in the reaction of thiophenol (or acetothiophenol) oxidation under different excitation lights (Figure 11).^[50] To study the chromoselectivity effect this reaction was carried out under the variety of wavelength: UV (365 nm), purple (410 nm), blue (465 nm), white (410–800 nm), green (525 nm), and red (625 nm) (Figure 11b). Three different products were obtained from the single reaction mixture depending on the light color. Thus, irradiation with 365 and 410 nm was necessary to yield arylchlorides. A 465 nm as well as white LED resulted in the formation of sulfonyl chlorides, and finally 525/625 nm light produced disulfides. The detailed mechanistic study of these phenomena revealed three different mechanisms of formation of these products, all being photocatalytic (Figure 11c). Irradiation with green or red light was only enough to promote energy transfer to oxygen and further thiol dimerization. Irradiation with blue LED induce electron transfer to thioacetate and oxygen. Excitation with UV light was sufficient for additional chlorine anion oxidation, which led to over-chlorination of the reaction intermediate and production of chlorobenzene.

This reaction represents a unique example of chromoselective reaction, where the control over reaction mechanism and selectivity towards one of the three possible products was achieved only by changing the color of irradiation light and otherwise identical conditions. Even though the mechanism is complex and several specific features of the photocatalyst, such as the presence of intraband states that allows for energy as well as electron transfer, high oxidation potential, ability for multi-electron transformations, and negatively charged polymeric structure, were involved in the process simultaneously, it reveals the principal opportunities that chromoselective reactions have to offer for organic synthesis.

5. Summary and outlook

Following the high interest to the topic of photocatalytic synthesis, most research activities are focused on the design of new materials and investigation of the trajectories for their application. Undoubtedly, light is an essential component of every photochemical and photocatalytic reaction, even though its properties are commonly overlooked. Apart from being a convenient source of energy, light offers a unique opportunity to effect the activity and selectivity of the photocatalytic reaction. This way, it might be considered as an equal to chemical reagent. Such properties, as energy or intensity of photons, are easy to tune and offer a convenient way to take control over the photocatalytic reaction. In photochemistry, light-dependent and photoselective reactions are quite common and well investigated, while in photocatalysis these are scarce. Nevertheless, in this review, we aimed to explore light as more than just a driving force but rather other possibilities that

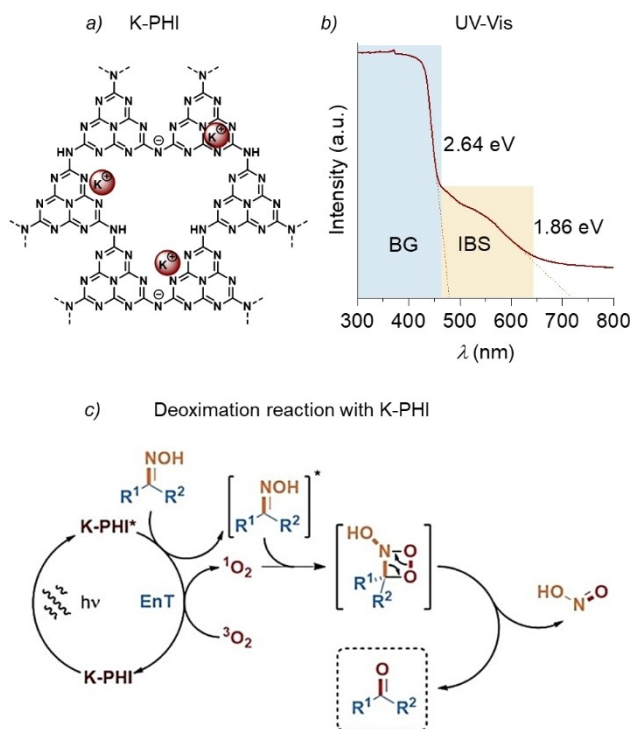
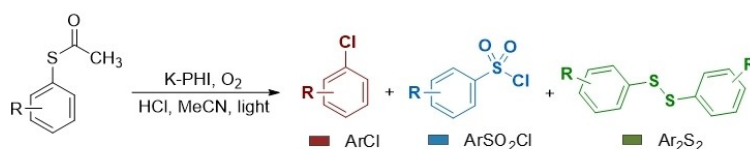
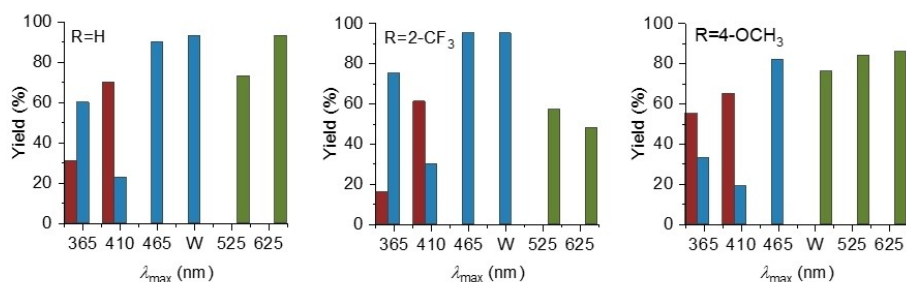


Figure 10. a) Structure of the K-PHI unit; b) UV-Vis absorption spectra of K-PHI; c) Mechanism of the deoxygenation reaction. Reproduced from ref. [48].

a) Possible products in the chromoselective oxidation of arylthioacetates



b) Results of the reaction at different wavelengths



c) Mechanism of chromoselective synthesis of sulfonyl chlorides, arylchlorides, and disulfides

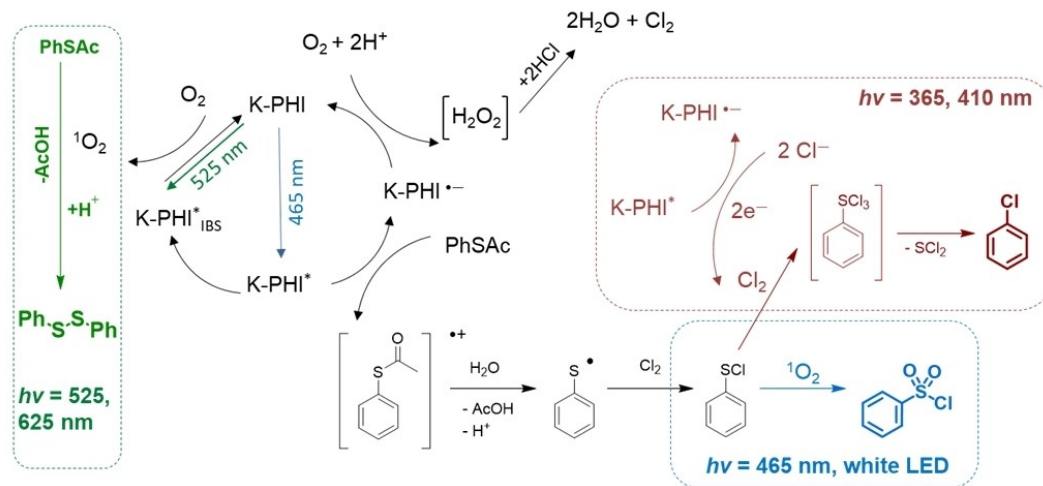


Figure 11. a) Possible products in the oxidation reaction of arylthioacetates with K-PHI; b) Results of the reaction under excitation with different wavelengths; c) Mechanism of the chromoselective conversion of thio-derivatives to sulfonyl chlorides, arylchlorides, and disulfides. Reproduced from ref. [50].

it has to offer for organic chemistry. We have discussed how intensity and energy of photons influence the reactivity of the catalyst and selectivity of the reaction.

The multi-photon excitations are applied to access the higher energy species, such as hydrated electrons, for demanding reduction reactions. Typically, low energy photons can be used. Multi-photon excitations are more common for homogeneous photocatalysts. Finally, this approach is explored for reduction reactions, and the information on the oxidation reactions is scarce.

Another concept relevant to the field of organic synthesis is chromoselective photocatalysis as control over selectivity is essential in organic reactions. Thus, selectivity and activity of the photocatalyst can be tuned by adjusting excitation light. Chromoselective reactions are used to control a reaction mechanism, where more than one product is possible. Carbon

nitride catalysts have shown good utility in this type of reactions, as they are robust materials that offer plenty of possibilities for adjusting optical and electronic properties.

Finally, the opportunity to take advantage of the properties of light sources for enhanced photocatalysis is also important for other fields of chemistry and should be further investigated.

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Conflict of Interest

The authors declare no conflict of interest.

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