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Mechanistic insights on two-photon driven photocatalysis in organic synthesis

Marianna Marchini, Andrea Gualandi, Luca Mengozzi, Paola Franchi, Marco Lucarini, Pier Giorgio Cozzi,* Vincenzo Balzani, Paola Ceroni*

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Abstract

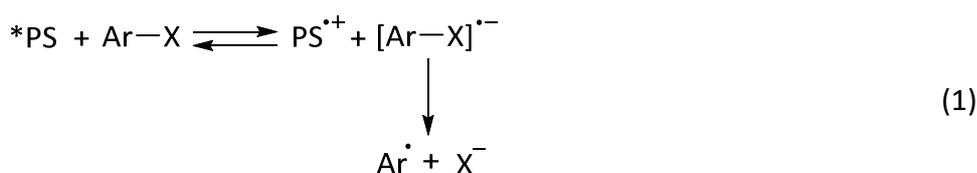
A mechanism based on the sequential absorption of two photons by the components of a redox couple was recently proposed for catalysis of the energetically demanding reduction of aryl halides. Here, we analyze the suggested photochemical mechanism of this reaction, which employs perylenediimide (PDI) as a photocatalyst, on the basis of spectroscopic, electrochemical and electron paramagnetic resonance data. Our results indicate that the photoexcited PDI radical anion ($^*PDI^{\bullet-}$) cannot play the role of a photosensitizer in the aforementioned process. Instead, the reduction of 4'-bromoacetophenone likely involves $^*PDI^{\bullet-}$ decomposition products. The extremely short lifetime of photoexcited transient species, as $^*PDI^{\bullet-}$, is a major general limitation for photocatalytic schemes based on sequential two-photon excitation. In order to better understand the potential of such schemes we discuss them in the context of the Z-scheme in natural photosynthesis.

Keywords: perylenediimide (PDI), Z-scheme, photochemistry, electron transfer, radical anion

Introduction

The use of light to speed up chemical reactions or to drive chemical transformations that are endoergonic in the dark is known since the origin of photochemistry. Until not so many years ago, organic photochemistry was mainly based on direct excitation of one of the reactants by UV light,^{1,2} since most of the organic molecules absorb in this spectral region. Irradiation by visible light, however, is much more convenient practically. Indeed, instead of expensive quartz apparatus, conventional glassware or even polymeric vessels in photochemical flow reactors, as well as much less expensive light sources (e.g. LEDs) or sunlight can be used in visible light driven processes. Early efforts in this direction were based on the use of a Ru(II) photocatalyst, namely [Ru(bpy)₃]²⁺ (bpy=2,2'-bipyridine), for example in debromination reactions³ and in Pschorr cyclizations.⁴

The last decade has evidenced an impressive growth in the number of studies using visible light to promote organic reactions.⁵⁻¹¹ In most cases, photocatalysts are involved in electron transfer processes, since electronically excited states are both better oxidants and better reductants.^{12,13} However, some reactions are still challenging upon visible light photocatalysis. For example, the lowest excited state of *fac*-[Ir(ppy)₃] (ppy=2-phenylpyridine) can drive the reduction of unactivated aryl iodides,¹⁴ but not of the corresponding bromides and chlorides. Only recently, reduction of aryl bromides was obtained by combining visible-light-mediated photoredox catalysis of another cyclometalated Ir(III) complex and silane mediated atom transfer via an intricate mechanism.¹⁵ As extensively studied by Savéant,^{16,17} the reduction of aryl iodides is usually concerted with C-I bond cleavage, while for aryl bromides and chlorides, reduction leads to the formation of a radical anion, which then undergoes a rate-determining C-X^{•-} bond cleavage. In the case of a reduction by a photosensitizer (PS), we can schematize the reaction as follows:



Back electron transfer between PS^{*+} and [Ar-X]^{•-} competes with aryl radical formation when X = Br or Cl. Only for aryl iodide the back electron transfer is highly disfavored since reduction and bond cleavage are concerted processes and the radical anion [Ar-X]^{•-} is eliminated from the electron transfer equilibrium.

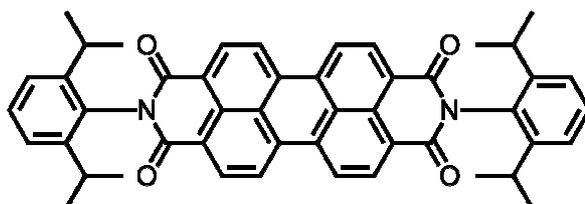
In search for more powerful reducing species activated by visible light to drive the reduction of aryl halides, König et al.¹⁸⁻²¹ have recently proposed an approach based on the sequential absorption of two photons by the two components of a redox couple. This approach conceptually mimics the so-called Z-scheme in the natural photosynthesis, where the two photoreaction centers work in conjunction to perform water splitting. Specifically, it was proposed¹⁸ that a

transiently formed excited singlet state of perylene-3,4,9,10-tetracarboxylic diimide (*PDI) participates in an electron transfer reaction, generating a PDI radical-anion (PDI^{•-}), whose reduction potential is yet too low to carry out reduction of arylhalides (Ar-X). However, upon the second excitation it is transformed into the excited radical (*PDI^{•-}), which was proposed to be ultimately responsible for the catalytic activity.

In this paper, we discuss the proposed mechanism and present a variety of spectroscopic and electrochemical evidences, showing that *PDI^{•-} is not a viable catalytic intermediate due to its extremely efficient deactivation. We also compare the Z-scheme approach in organic synthesis with that of natural and artificial photosynthesis, in order to outline the potential and limitation of schemes utilizing sequential absorption of two photons.

The Z-scheme in organic synthesis and natural photosynthesis

PDI (Scheme 1) and its radical anion PDI^{•-} are the two photocatalysts involved in the proposed Z-scheme.¹⁸ Figure 1 reports their Jablonski diagram, according to literature data.²²



Scheme 1. Chemical structure of PDI derivative.

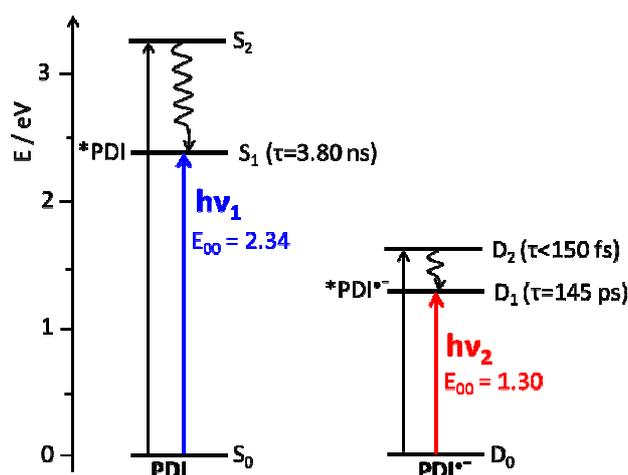


Figure 1. Jablonski diagram showing the relevant electronic states of PDI and PDI^{•-}. PDI has a closed-shell ground state electronic configuration, so that the excited electronic states are singlets (S) or triplets (not shown). PDI^{•-} has a ground electronic state configuration with an unpaired electron, so that both its ground-state and the first excited state are doublets (D). For more details, see ref. ²².

The reaction mechanism proposed in ref. ¹⁸ can be summarized as follows:



↓
products



The same reaction steps are reported in Figure 2a in terms of electronic states (photochemical point of view) and in Figure 2b in terms of redox potentials (electrochemical point of view).

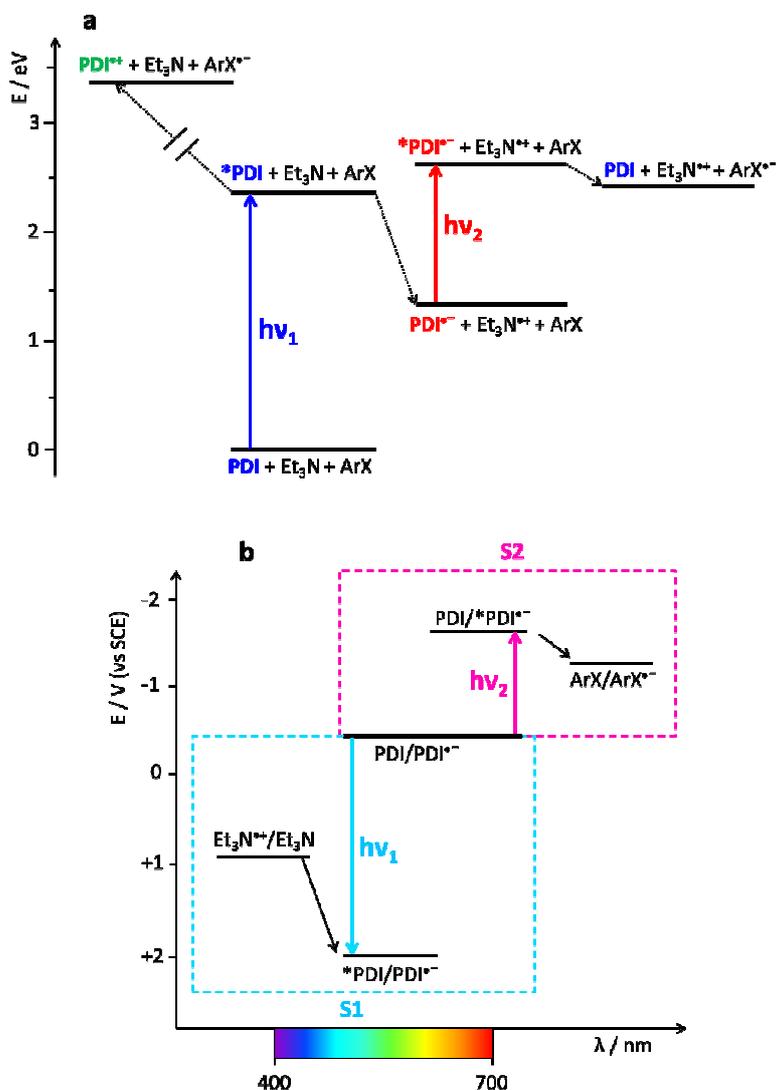


Figure 2. Reaction steps of the Z-scheme based on PDI/PDI^{•-} presented in terms of: (a) electronic states (photochemical point of view) and (b) redox potentials (electrochemical point of view). In

panel b the wavelength scale is related to the photons corresponding to the lowest-energy transitions of PDI ($h\nu_1$, $\lambda = 530$ nm, cyan light) and PDI * ($h\nu_2$, $\lambda = 955$ nm, NIR spectral region).

A similar two-photon mechanism was also proposed^{19,20} with a rhodamine photosensitizer for selective activation of aryl–halide bonds in order to carry out C-H arylation.

It is worth comparing the mechanism described in Figure 2b with the Z-scheme of natural photosynthesis reported in Figure 3. For splitting water into hydrogen and oxygen in the photosynthetic process that eventually leads to O₂ evolution and CO₂ reduction, Nature has solved the energy problem by light excitation of two photosystems, PS2 and PS1 that operate in series. The transport of an electron through the chain from H₂O to CO₂ requires absorption of two photons. The electron flow is as follows: in PS2 the chromophore P680 absorbs a photon and its excited state reduces pheophytin (Pheo) and, via a series of exergonic electron transfers, a plastoquinone (PC). The oxidized P680 $^{+}$ ultimately causes the oxidation of water. In PS1, the absorbed photon promotes P700 to its excited state, which is able to reduce the primary electron acceptor of PS1 (A₀) and finally generates the strong reducing nicotinamide adenine dinucleotide phosphate NADPH, which donates reducing equivalents to CO₂ to produce sugars and other organic molecules. The oxidized P700 $^{+}$ is reduced back to P700 by the reduced plastoquinone PQ $^{-}$ produced in PS1.

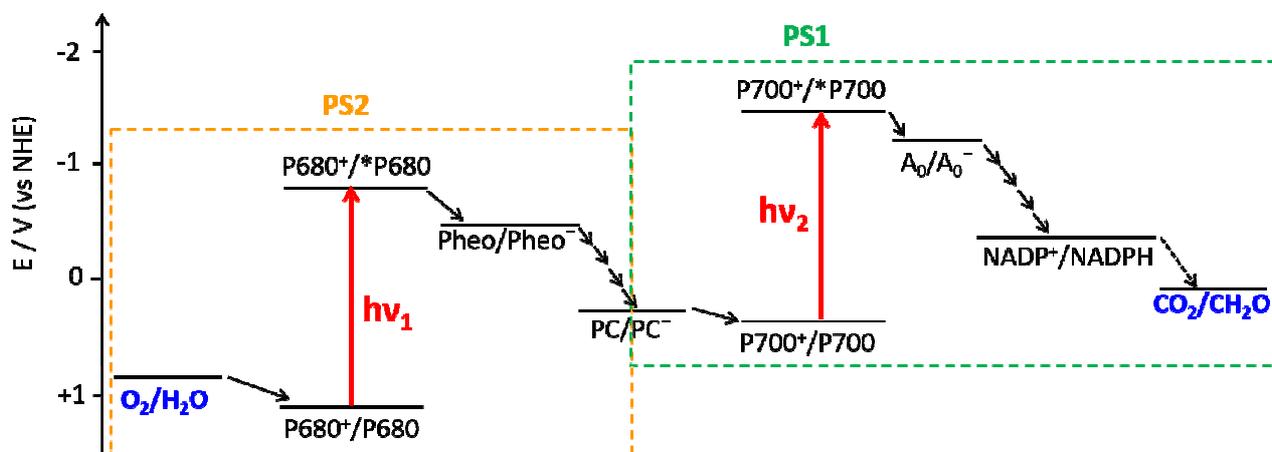


Figure 3. A simplified Z-scheme of the redox reactions occurring in the reaction centers of photosystems I and II (PS1 and PS2) in higher plants. The vertical axis reports the redox potentials in V (vs NHE) at pH=7 of some of the involved redox couples: pigments P680 and P700, pheophytin (Pheo), plastoquinone (PC), the primary electron acceptor of PS1 (A₀), nicotinamide adenine dinucleotide phosphate (NADPH). For the sake of simplicity, the radical nature of the cation and anion produced by electron transfer reactions is not specified in this scheme and multiple arrows indicate sequential electron transfer reactions among different redox couples in which only the initial and final ones are reported.

The two-photon mechanism proposed to catalyse organic reactions has the following differences in comparison to the Z-scheme of natural photosynthesis: (i) the two photocatalysts of Figure 2b

belong to the same redox couple, so that the scheme is no longer Z-shaped, but the concept is similar;[‡] (ii) there is no need of a redox mediator to exchange electrons between the two photocatalytic systems since they are based on the same redox couple PDI/PDI^{•-}; (iii) half of the redox cycle involves an excess of a sacrificial reagent, namely triethylamine, which decomposes after oxidation (products in reaction 3), so that the bimolecular electron transfer reaction (3) is expected to be fast and irreversible; (iv) natural photosynthesis relies on a spatial organization of the different components, on the contrary of the diffusion-controlled processes reported in Figure 2; (v) the aim of natural and artificial photosynthesis is the conversion of light into chemical energy, which means that the overall chemical reaction must be endoergonic and no sacrificial reagent can be employed; in photocatalyzed organic synthesis the aim is to obtain a specific product, regardless of the free energy change of the overall chemical reaction, which includes the decomposition of the sacrificial reagent, and of the overall photocatalytic quantum yield since solar energy conversion and storage is not the target.

In order to understand the advantages and limitations of the so-called Z-scheme in organic synthesis, two fundamental spectroscopic and kinetic concepts need to be considered.

1. Molecules have usually several absorption bands, so that the amount of energy injected by photoexcitation can be tuned over a large range of energies. The upper lying electronically excited states, however, usually undergo very fast intramolecular decay (lifetime (τ) in the pico- or femto-second time scale). As a consequence, only the lowest excited state of each spin multiplicity generally exhibits a lifetime long enough to be involved in bimolecular diffusion controlled processes. In the case of PDI and its radical anion PDI^{•-}, it means that wherever we excite these species, the lowest S₁ and D₁ excited states are eventually populated (Figure 1). In other words, the redox potential of the *PDI/PDI^{•-} and PDI/*PDI^{•-} couples reported in Figure 2a can be estimated on the basis of the electronic energy E₀₀ of the S₁ (2.34 eV) and D₁ (1.30 eV) excited states of *PDI and *PDI^{•-}, so that we cannot expect any difference in the reducing power based on the excitation wavelength. The PDI^{•-} is not a highly reducing species (E(PDI/PDI^{•-}) = -0.37 V vs SCE,¹⁸ see Figure 2a), but its lowest-energy excited state (*PDI^{•-}) is expected to have E(PDI/*PDI^{•-}) = -1.67 V vs SCE, based on the E₀₀(PDI^{•-}/*PDI^{•-}) value of 1.30 eV, estimated by its lowest-energy absorption band.

2. Electron transfer in fluid solution can occur only if the two partners are pre-associated in the ground state (static quenching process), or if the excited state *A and the reaction partner B can encounter (dynamic quenching process), a process that cannot be faster than the diffusion rate constant (k_d) in the solvent used. Wasielesvski et al.²² reported that upon excitation of PDI^{•-} into higher lying D_n states, a rapid relaxation (within the 150 fs-resolution of the instrument) to the D₁

[‡] The same idea had been applied earlier in a supramolecular triad for photoinduced charge-separation.²⁹ Excitation of the donor yields the first intramolecular electron transfer and the successive excitation of the radical anion drives a further electron transfer, thermodynamically uphill in the dark.

state occurs without intersystem crossing to a long-lived quartet state. They have also found that the lowest excited state D_1 of $\text{PDI}^{\bullet-}$ has a lifetime of 145 ps. A dynamic quenching process was considered in the original paper since no ground-state interaction was observed between $\text{PDI}^{\bullet-}$ and the different substrates Ar-X. However, the radical anion $\text{PDI}^{\bullet-}$ is not the best candidate for a dynamic quenching process. For example, based on the Stern-Volmer equation,¹³ even in the best case, i.e. if the reaction is diffusion controlled (e.g., $k_q = k_d = 7.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in DMF),²³ only about 15% of the $\text{PDI}^{\bullet-}$ is quenched by the aryl halide under the experimental conditions used in the original paper ($[\text{Ar-X}] = 1.7 \times 10^{-1} \text{ M}$). On top of that, the excitation was performed at 455 nm,¹⁸ where the ratio of molar absorption coefficients of $\text{PDI}^{\bullet-}$ with respect to PDI is ca. 1:9. Under the conditions reported in the original paper (see e.g. Figure 1B of ref. ¹⁸), slightly less than 50% of PDI has been converted to $\text{PDI}^{\bullet-}$, so that the fraction of light absorbed by $\text{PDI}^{\bullet-}$ is very small.

Puzzled by these calculations, we decided to investigate the following reaction in a cuvette in order to monitor the presence of the different chromophores, namely PDI and its radical anion $\text{PDI}^{\bullet-}$, during the reduction of 4'-bromoacetophenone to acetophenone.

Photochemical measurements. We performed the experiments under the same conditions as those reported in the original paper,¹⁸ with regard to solvent, irradiation conditions, concentration of 4'-bromoacetophenone (0.017 M, 1 equiv) and Et_3N (0.13 M, 8 equiv). The only difference was the amount of PDI ($c = 5 \times 10^{-4} \text{ M}$, 0.03 equiv), which we decreased by a factor of 1.7 in order to register its absorption spectrum in a 0.1 cm path length cuvette.♦

Figure 4a reports the decrease of PDI absorption upon irradiation at 450 nm for 20 minutes in the presence of Et_3N (see SI for more details on irradiation conditions), and the resulting formation of the radical anion $\text{PDI}^{\bullet-}$, that exhibits absorption bands in the red and NIR spectral region, as previously reported:²² the solution turns from orange to blue (Figure S5). Figure 4b reports the spectral changes upon irradiation up to 390 minutes: the absorption features of $\text{PDI}^{\bullet-}$ disappears, non-structured absorption profile between 600 and 800 nm develops and the solution turns brown (Figure S5). By monitoring the product formation by HPLC and the presence of $\text{PDI}^{\bullet-}$ by absorption spectroscopy, we can correlate the disappearance of the radical anion $\text{PDI}^{\bullet-}$ with the formation of acetophenone as a function of time (Figure 5). It is clear that the formation of the product is not directly correlated to the concentration of $\text{PDI}^{\bullet-}$. Most of the production of acetophenone (from 10 to 60% conversion) occurs after 200 minutes of irradiation, when $\text{PDI}^{\bullet-}$ is almost completely decomposed (less than 5% left in solution).

♦ Similar results were obtained when the concentration of PDI was the same as that used in the original paper (see Supporting Information), showing that the concentration of PDI does not affect the reaction mechanism.

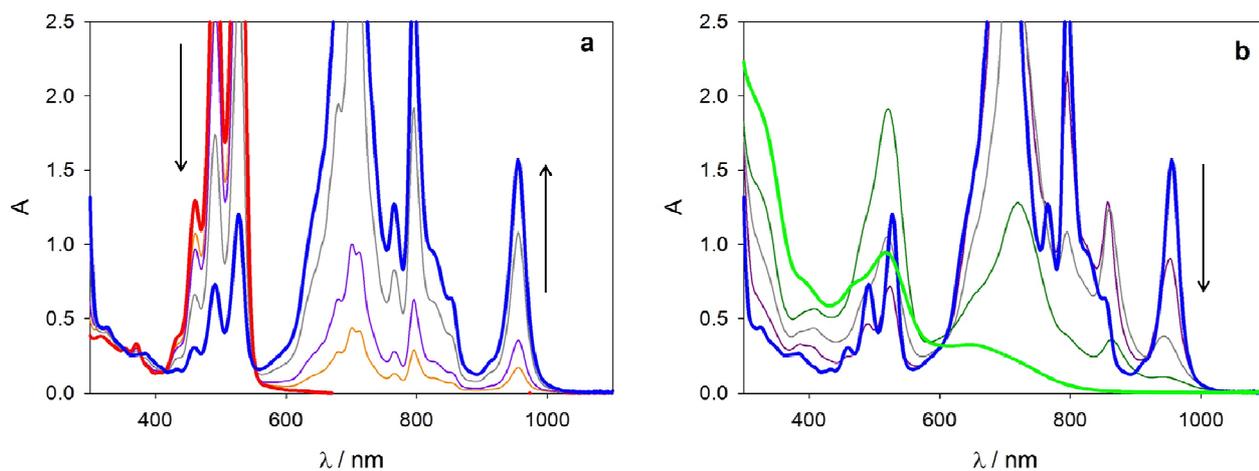


Figure 4. Absorption spectra of PDI 5×10^{-4} M in degassed DMF solution in the presence of Et_3N 0.13 M and 4'-bromoacetophenone 0.017 M upon irradiation at 450 nm by a LED source (for more details, see SI) in the time interval: (a) 0 - 20 minutes (red and blue thick lines, respectively) and (b) 20 - 390 minutes (blue and green thick lines, respectively).

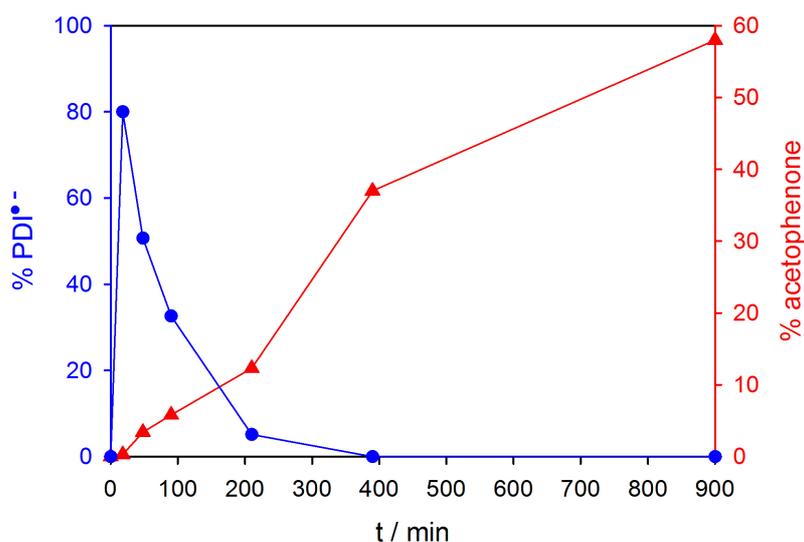


Figure 5. Irradiation at 450 nm of the reaction mixture: PDI 5×10^{-4} M, Et_3N 0.13 M and 4'-bromoacetophenone 0.017 M in degassed DMF solution. Percentage of $\text{PDI}^{\bullet-}$ (estimated from absorbance at 954 nm during the irradiation of the reaction mixture, blue circles), compared to the initial concentration of PDI, and percentage of acetophenone formation (estimated with HPLC analysis, red triangles), compared to the initial 4'-bromoacetophenone concentration, as a function of irradiation time.

From these experiments, we can conclude that: (i) $\text{PDI}^{\bullet-}$ is not the photocatalyst for aryl halide reduction, (ii) a photoreaction takes place upon irradiation of $\text{PDI}^{\bullet-}$ and its photoproduct is the photocatalyst of the 4'-bromoacetophenone reduction. The absorption spectrum of the radical

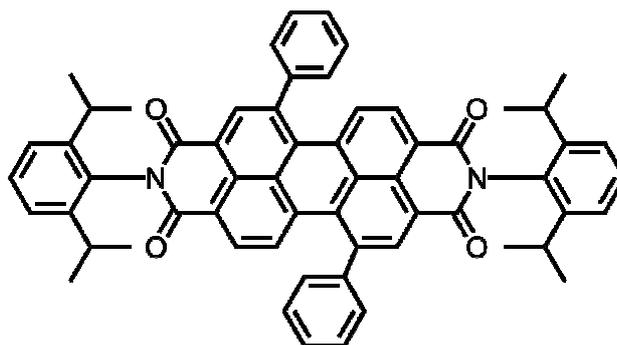
anion $\text{PDI}^{\bullet-}$ does not show significant changes upon addition of 4'-bromoacetophenone in the visible spectral region, but we cannot exclude a ground state interaction between $\text{PDI}^{\bullet-}$ and the aryl halide, as previously suggested by Nicewicz.²⁴

To get more insights into the mechanism, we performed experiments in different conditions. (i) If we irradiate for 20 minutes, as reported in Figure 4a, to form $\text{PDI}^{\bullet-}$ and stop irradiation at any time in the interval reported in Figure 5, the reaction stops: light is necessary for the formation of acetophenone. (ii) In the absence of 4'-bromoacetophenone, $\text{PDI}^{\bullet-}$ is formed upon irradiation of PDI in the presence of Et_3N , but it is photostable in solution (Figure S4), as previously observed by Wasielewski,²² due to the very short-lifetime of its lowest excited state: 4'-bromoacetophenone is directly involved in the photodegradation of $\text{PDI}^{\bullet-}$. (iii) Upon chemical reduction of PDI in the presence of sodium ascorbate 0.13 M and 4'-bromoacetophenone 0.017 M, the radical anion $\text{PDI}^{\bullet-}$ is quantitatively formed and upon irradiation at 450 nm, spectral changes very similar to those reported in Figure 4b are observed and acetophenone is formed (see SI for more details): Et_3N is not involved in the photoreaction of $\text{PDI}^{\bullet-}$. (iv) Upon repeating experiment (iii) and changing irradiation wavelength from 450 nm to $\lambda > 610$ nm, so that only $\text{PDI}^{\bullet-}$ is absorbing light, the same results are obtained: the photochemical reaction observed is not dependent on the irradiation wavelength, as expected from the experimental finding that high-lying excited D_n states of $\text{PDI}^{\bullet-}$ decay very rapidly by internal conversion to the lowest D_1 state that absorbs in the NIR spectral region.¹ (v) Similar results were obtained for the reduction of 4'-iodobenzaldehyde (Figure S8).

To isolate and characterize the $\text{PDI}^{\bullet-}$ degradation product(s), the reaction was performed on a larger scale, in the presence of 20 mol% of PDI (see SI for more details). The $^1\text{H-NMR}$ spectrum (Figure S11) of the crude reaction mixture presents broad signals, likely due to the presence of paramagnetic species derived from degradation of $\text{PDI}^{\bullet-}$ (see EPR measurements). Attempts to purify the reaction mixture was unsuccessful and analysis of the reaction mixture, before or after the work up, by NMR and ESI-MS did not enable identification of the degradation product(s) of $\text{PDI}^{\bullet-}$.

In order to check if the photoreaction of the radical anion $\text{PDI}^{\bullet-}$ involves an attack to the bay positions, we synthesized the PDI-Ph derivative (Scheme 2) and repeated the same experiments. We observed very similar results: the radical anion $\text{PDI-Ph}^{\bullet-}$ is formed and then a photodecomposition takes place (Figure S9). Also in this case, most of the acetophenone product is formed when $\text{PDI-Ph}^{\bullet-}$ is completely decomposed in the reaction mixture (see Figure S10).

¹ Wasielewski recently reported³⁰ that higher excited states (D_2 , D_3) of the $\text{PDI}^{\bullet-}$ radical anion are capable of electron transfer in a covalently linked dyad. Therefore, we irradiated the reaction mixture at first at 460 nm to generate the radical anion of PDI and then we irradiated the solution at $\lambda > 850$ nm, so that D_1 excited state of $\text{PDI}^{\bullet-}$ was selectively populated: the acetophenone product was formed also under this experimental conditions.



Scheme 2. Chemical structure of PDI-Ph derivative.

Taking advantage of a procedure reported by Tour,²⁵ PDI^{•-} was formed with a stoichiometric amount of KO₂ as chemical reductant: this procedure gives only O₂ as byproduct of the reduction. After the generation of PDI^{•-}, checked by UV analysis (see SI for details), 4'-bromoacetophenone was added and the mixture was irradiated for 20 hours. From HPLC analysis of the crude reaction mixture a 59% conversion was obtained. By MALDI-TOF analysis of the crude reaction mixture (Figures S16 and S17) it was not possible to identify the PDI^{•-} degradation product(s).

EPR measurements. Further confirmation of the picture outlined by photochemical experiments was provided by EPR spectroscopy. We initially characterized the paramagnetic species formed upon irradiation with visible light ($\lambda = 450$ nm) of a deoxygenated DMF solution containing PDI (5×10^{-4} M), Et₃N (0.13 M): a strong EPR signal consisting of a well resolved hyperfine structure is observed (Figure S19). On the basis of spectroscopic parameters ($a_{2N} = 0.62$ G, $a_{4H} = 1.75$ G, $a_{4H} = 0.66$ G, $a_{2H} = 0.63$ G, $a_{4H} = 0.55$ G, $g = 2.0028$) the spectrum was attributed to the radical anion PDI^{•-}.^{26,27} Further irradiation of the solution containing PDI^{•-} did not result in a change in the shape, nor in the disappearance of the EPR signal, thus confirming PDI^{•-} is photostable in solution.

Electrochemical reduction of a degassed DMF solution (0.1 M in Bu₄NPF₆ as supporting electrolyte) containing only PDI, afforded the same EPR signal observed under irradiation with visible light of PDI in the presence of Et₃N (Figure S20), this result confirms that the EPR signal is due to the radical anion PDI^{•-}.

The fate of PDI^{•-} was then monitored by mimicking the synthetic reaction conditions. Figure 6 reports the changes observed in the EPR spectra during irradiation of a solution containing PDI (8×10^{-4} M), Et₃N (0.13 M) and 4'-bromoacetophenone (0.017 M). Whereas the first spectra show well resolved hyperfine splitting assigned to the radical anion PDI^{•-}, the spectra recorded after 400 minutes of irradiation do not (Figure 6). Further irradiation of the reaction mixtures (up to 12 hours) does not produce significant changes in the shape of this new EPR signal. EPR spectroscopy reaffirms that under continuous irradiation of the reaction mixture containing 4'-bromoacetophenone, PDI^{•-} initially formed is quantitatively transformed into a new paramagnetic species.

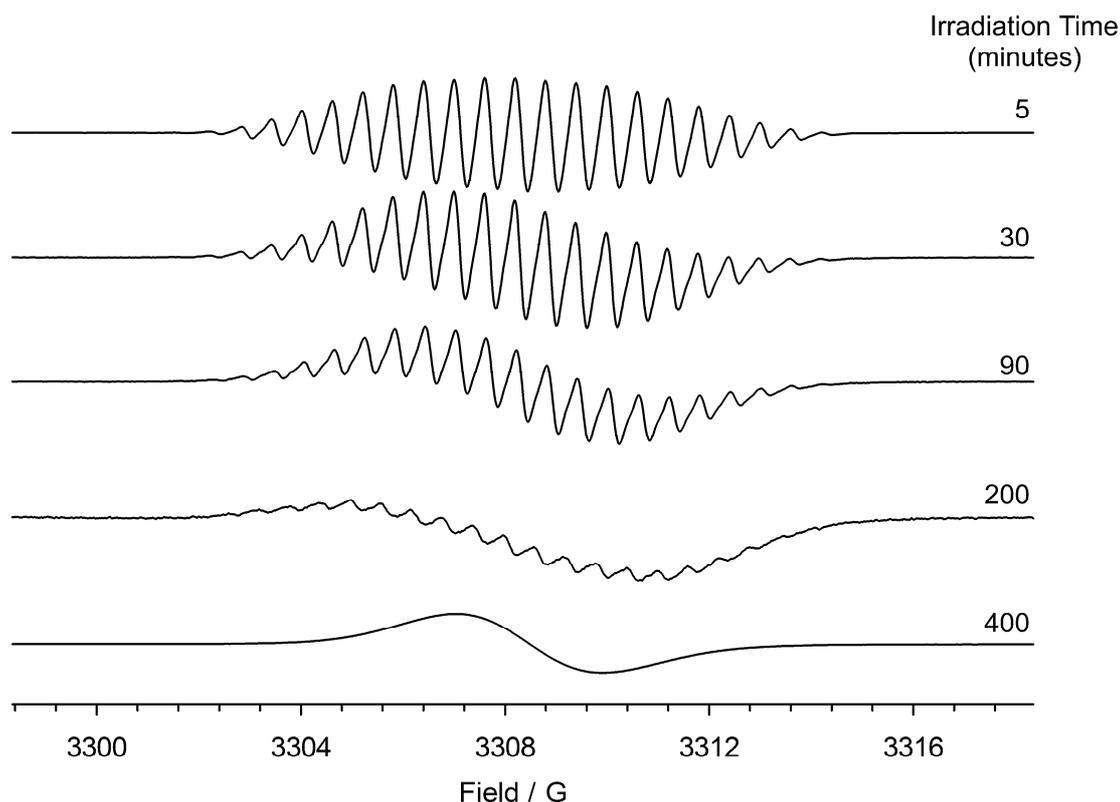


Figure 6. Time evolution of EPR spectra during irradiation at 450 nm of the reaction mixture containing PDI 8×10^{-4} M, Et_3N 0.13 M and 4'-bromoacetophenone 0.017 M in degassed DMF solution.

According to photochemical results, we attributed this new paramagnetic species to a decomposition product(s) of $\text{PDI}^{\bullet-}$. The absence of resolved hyperfine splitting prevented us to determine the nature of this new radical species. However, the measured g -factor ($g=2.0029$, very close to that of $\text{PDI}^{\bullet-}$) and the loss of spectral resolution suggest that the PDI symmetry has been broken and/or the radical electron is delocalized over a larger π -surface than that of PDI.²⁶ The presence of a paramagnetic species explained the broad and unclear signals obtained in the ^1H NMR of the crude reaction mixture (see Figure S11).

Conclusions

In search for highly reducing photocatalysts, the sequential absorption of two photons by the two components of a redox couple had been proposed in the literature.²⁸ This is reminiscent of the Z-scheme of natural and artificial photosynthesis and we thus compared the working principle of these Z-schemes with that used in organic synthesis. The first example of Z-scheme applied to the synthesis of organic molecules was the reduction of unactivated aryl bromide or chloride, a highly energy demanding reaction, in the presence of a perylenediimide photocatalysts (PDI).¹⁸ The

mechanism proposed in the original paper is the following: (i) the first photon is absorbed by PDI, which in the presence of the sacrificial electron donor triethylamine, forms the corresponding radical anion $\text{PDI}^{\bullet-}$ (reduction potential = -0.37 V vs SCE); (ii) the second photon is absorbed by the radical anion $\text{PDI}^{\bullet-}$ and the lowest-energy excited state $^*\text{PDI}^{\bullet-}$ has a sufficiently negative reduction potential (-1.67 V vs SCE) to drive the reduction of the desired aryl halides. Puzzled by the very short-lifetime of $^*\text{PDI}^{\bullet-}$, we performed photochemical, electrochemical and EPR investigations: the obtained results show that in the sequential two-photon processes the excited $^*\text{PDI}^{\bullet-}$ radical anion does not play the role of a photocatalyst and that reduction of 4'-bromoacetophenone takes place through $^*\text{PDI}^{\bullet-}$ decomposition product(s).

The sequential absorption of two photons by two components of a redox couple is very appealing, but it is difficult to realize: the short lifetime of the excited states and their photostability are key parameters that need to be carefully considered in the design of this kind of photocatalysis.

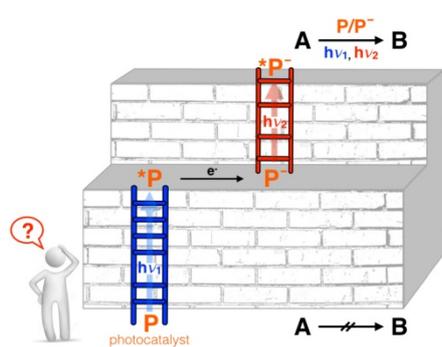
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Is two-photon catalysis better than one-photon? The sequential absorption of two photons by the components of a redox couple enables the production of highly reducing or oxidizing species, thus opening new photocatalysed reaction pathways. Short lifetime of the excited states and photostability of the photocatalyst pose significant limitations to this approach.