This is the peer reviewed version of the following minireview: •Rosso, C; Filippini, G; Prato, M Use of Perylene Diimides in Synthetic Photochemistry. Eur. J. Org. Chem. 2021, 2021, 1193-1200, which has been published in final form at 10.1002/ejoc.202001616

This minireview may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Use of Self-Archived Versions.

Use of Perylene Diimides in Synthetic Photochemistry

Cristian Rosso,[a] Giacomo Filippini[a] and Maurizio Prato*[a,b,c]

Dedicated to Professor Franco Cozzi on the occasion of his 70th birthday

[a] C. Rosso, Dr G. Filippini, Prof. M. Prato
CENMAT, Center of Excellence for Nanostructured Materials,
Department of Chemical and Pharmaceutical Sciences, INSTM UdR
University of Trieste
Via Licio Giorgieri 1, Trieste 34127 (Italy)
prato@units.it
[b] Prof. M. Prato
Carbon Nanobiotechnology Laboratory
CIC BiomaGUNE, Paseo de Miramón 182
20009 Donostia-San Sebastian (Spain)
[c] Prof. M. Prato
Basque Fdn Sci, Ikerbasque, Bilbao 48013 (Spain)

Abstract: Perylene diimides (PDIs) are valuable organic chromophores that stand out for their outstanding optical and redox properties. Owing to these features, PDIs have emerged as prominent dyes capable of acting as photocatalysts for numerous relevant organic transformations. This Minireview highlights the recent advances in the application of PDIs in organic photocatalysis. The various mechanistic pathways of the photo-reduction reaction of aryl halides, recently proposed in independent studies, are discussed with an eye to unsolved challenges and forward-looking opportunities regarding the use of PDIs within this field.

1. Introduction

Perylene-3,4:9,10-bis(dicarboximide)s, commonly known as perylene diimides (PDIs), have become one of the most relevant organic dyes in the family of polycyclic aromatic compounds.[1,2] They consist of a rigid perylene scaffold (aromatic core) substituted with two dicarboxylic acid imide groups at the 3,4- and 9,10-peri-positions (Figure 1a).[2] Over the years, PDIs have attracted the attention of chemists, physicists and material scientists because of their incomparable physicochemical peculiarities. Among their distinctive features, it is worth to be mentioned the chemical and thermal stability along with the photochemical properties of PDIs, such as strong visible light absorption, excellent fluorescence and high electron acceptor ability.[1–4] Another peculiarity of PDIs is their tendency to aggregate mainly through π-stacking interactions, thus forming supramolecular fibers with tailorable solubility.[2]

In the past, PDIs were merely employed as pigments for automotive and textile industry due to the successful combination of their insolubility, photothermal inertness and weather resistance.[5–7] Specifically, since the early 10s of the last century, PDI derivatives have been prepared by simple modification of the *N*,*N' imide* substituents to manipulate their solubility and aggregation in the solid state.[1,5,8] Successively, a finer control of the chemical properties of PDIs has been achieved though the asymmetric substitution of the two imide positions by exploiting multistep synthesis.[2,9] During the following decades, the functionalization of the aromatic core at the *bay* region (positions 1,6,7 and 12) was tackled, providing a precise control of fluorescence and electronic features.[1,7] Nowadays, the development of a variety of synthetic methodologies that allow for the chemical transformation of the whole PDI structure, including the less reactive *ortho* positions (namely 2, 5, 8 and 11), has paved the way to the exploration of novel fields of application. These applications include optoelectronics, sensors, energy production and synthetic photocatalysis.

1.1. Synthesis, Properties and Application of PDIs

Unlike the pigment industry, the general poor solubility of PDIs in most common solvents and their strong tendency to aggregate remains a major obstacle in practical applications.[6] To solve this issue, organic chemistry offers formidable help, through the exploitation of tailored approaches. Indeed, PDIs with sufficient solubility have been traditionally produced through the suitable functionalization of the *imide* or *bay* positions. The first and easier approach consists of introducing swallow-tail chains or bulky *ortho*-substituted aryl groups at the PDI *imide* positions.[10] These substituents disrupt the face-to-face π-π stacking between the PDI molecules, therefore increasing their solubility.[1,7,10,11] To this aim, *N*-substituted PDIs are commonly synthesized from perylene-3,4,9,10-tetracarboxylic dianhydride (PDA) by imidization with the appropriate aliphatic or aromatic primary amines at high temperatures (above 160°C).[7] Such conditions can be reached using molten imidazole or quinoline as solvent leading, usually, to the production of the desired PDIs in high overall yields.[6,7] Fast and efficient preparation of PDIs was recently achieved with the assistance of microwave heating.[12]

Conversely, the *bay* functionalization approach consists of introducing substituents in those positions through electrophilic aromatic substitution (e.g. halogenation), potentially followed by nucleophilic aromatic reactions (e.g. alkylation or amination) or, alternatively, by metal-catalyzed cross-coupling transformations (e.g. Suzuki or Sonogashira coupling reactions).[1] As a consequence, the steric congestion at the *bay* positions conducts to the distortion of the flat PDI core, thus partially interrupting π-stacking and increasing the solubility of the dye.[1,2,7] In addition, these core derivatization can substantially affect the optical and electronic features of PDIs.[7] Lastly, an important modification of the PDI scaffold has involved the *ortho* functionalization. This

route has been uncovered in recent times by exploiting substitution reactions or transition metal catalyzed C–H activations (using Rh, Ru or Ir).[1,13,14] The so-obtained *ortho*-substituted PDI derivatives may show enhanced photochemical properties and solubility without significant deformation of the planar core.[1,7] This is of practical importance, since it allows the straightforward preparation of relevant optoelectronic devices.[4,7,15] Altogether, the described methodologies can afford PDIs with tailorable solubility and optoelectronic features, which arise both from the position and the nature of the substituents installed.

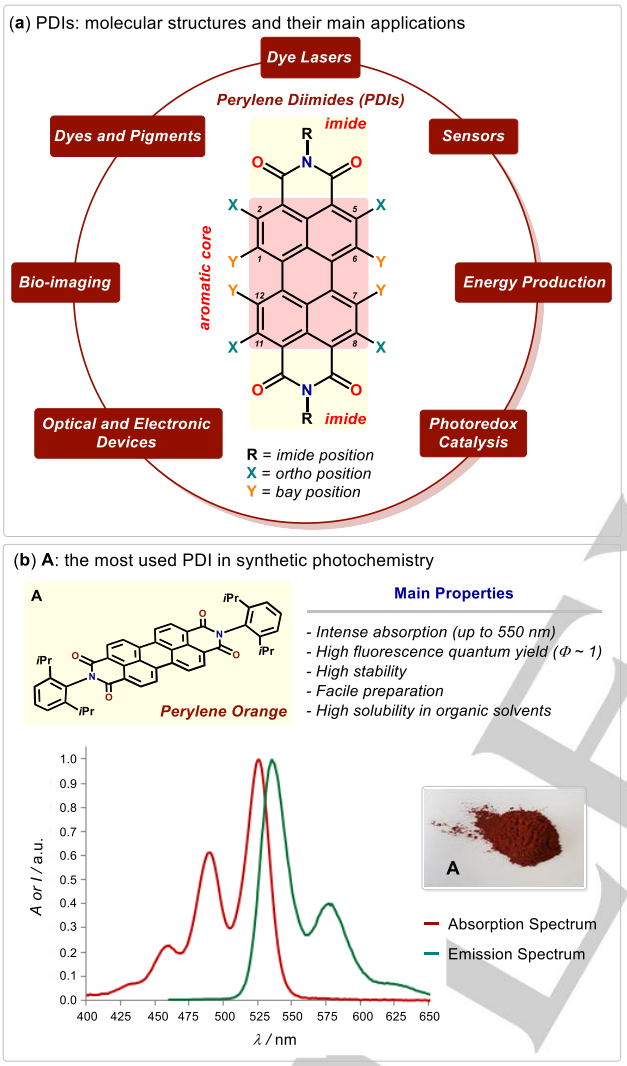


Figure 1. (**a**) Molecular structure and main applications of PDIs. (**b**) Main physicochemical properties of PDI **A**.

In general, the optical properties of PDIs are characterized by a strong absorption maximum centered at around 525 nm (absorptivity up to 10^5 M^{-1} cm^{-1}) and a bright emission with a small Stock shift, especially for core-unsubstituted PDIs.[2] Typically, the fluorescence quantum yields (Φ) are close to unity and the excited-state lifetimes are reasonably long, in the order of nanoseconds.[2,6,7] Moreover, due to the presence of nodes in both HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital), the aromatic core of PDIs is not electronically connected to the *imide* substituents. This means that the presence of different functionalities at such positions has a negligible effect on the absorption band.[2,7] On the contrary, the core substituents have a strong effect on the optical properties of PDIs. In fact, these groups highly affect the visual aspect of the PDI powders, and in turn the color of their resulting organic solutions, which can vary from red to blue.[2,4,16] In parallel, the redox features of PDIs follow the same trend in terms of functionalization. In particular, the electron-accepting character of PDIs can be modulated by installing electron-donating or withdrawing groups in their core. This results in a significant variation of both the oxidation and reduction potentials, despite similar overall bandgaps.[2,4,7]

In light of the above recalled properties, PDIs have found a wide range of applications in many fields of sciences. These applications span from optoelectronics (e.g., organic light-emitting diodes and solar cells), transistors, dye lasers, pigments, sensors, energy production to synthetic photochemistry (Figure 1a).[2,7,15,17–20] Although the synthesis and the utilization of PDIs in materials science have been summarized in recent reviews,[1,2] their application in organic photochemistry has not been covered. In this Minireview, we present the latest advances within this field, with particular attention to the still open discussion on the actual mechanism that drives the photochemical initiation of these valuable organic transformations.

2. PDIs as Organic Photocatalysts

Organic photocatalysis has become an established and broadly used branch of synthetic chemistry.[21] This approach relies on the ability of a photon-absorbing catalyst - namely a photocatalyst- to form, upon direct visible-light excitation, open-shell species from suitable precursors at ambient temperature. The possibility of forming reactive radicals under mild conditions allowed chemists to achieve unique bond constructions, while reducing energy consumption and waste production. Many of the most commonly employed visible-light photocatalysts are expensive and toxic polypyridyl complexes of ruthenium and iridium.[22] In addition, the production of these metal complexes requires, typically, multiple step synthetic routes.[23] For all these reasons, extensive efforts have been and are still devoted to developing new effective metal-free organic photocatalytic systems.[24]

In recent years, PDIs have attracted considerable attention within the scientific community as low price alternatives to metal-based photocatalysts for energy production.[2,20] PDIs may effectively form π-conjugated structures, and it was noted that this feature has a major impact on their photocatalytic activities.[25] Recently, PDIs have been also exploited in the field of organo-photocatalysis. In this regard, a simple symmetrical PDI, namely **A** (Figure 1b), turned out to be the dye of choice to drive most of the photochemical reactions reported so far.[26–29]

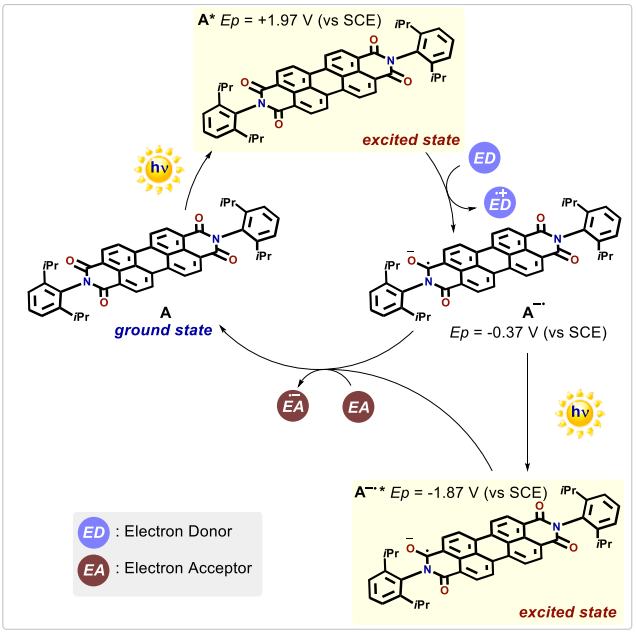


Figure 2. Mode of catalysis of the photoactive dye **A**.

A, commonly known as *perylene orange*, is prepared from PDA by imidization with 2,6-diisopropylaniline at high temperature.[1] Structurally, the presence of bulky groups on the *imide* positions provides better solubility in organic solvents by preventing the aggregation in solution.[11] Furthermore, **A** exhibits excellent optical and redox properties, showing a strong absorption in the visible region ($\varepsilon_{A\ \lambda=450\ nm}$ = 11000 M^{-1} cm^{-1}, Figure 1b).[28] Moreover, upon light absorption, **A** becomes a strong oxidant in the excited state (**A***), with a reduction potential for the couple **A***/**A**$^{\bullet-}$ of +1.97 V (*versus* saturated calomel electrode, SCE), according to Rehm-Weller equation (Figure 2).[30,31] Therefore, **A*** can effectively drive photo-oxidation reactions with suitable electron donors (ED), generating its corresponding radical anion (**A**$^{\bullet-}$, E = –0.37 V *vs* SCE for the couple **A**/**A**$^{\bullet-}$).[19,21] In addition, the reduced species is still redox active and can further carry out reductive transformations in the presence of appropriate electron-acceptors (EA).[18] Alternatively, **A**$^{\bullet-}$, due to its color and persistency in deaerated solutions,[32] can absorb another visible photon reaching its highly energetic excited state (**A**$^{\bullet-*}$, E = –1.87 V *vs* SCE for the couple **A**$^{\bullet-*}$/**A**).[26,33] This species (**A**$^{\bullet-*}$) is thus able to drive the reduction of strongly unreactive acceptors. Which means that **A** is able to employ the energy of two photons before closing the overall photoredox catalytic cycle *via* two consecutive photoinduced electron transfer (PET) processes. This property makes PDIs unique with respect to classical organic photocatalysts.[24] However, it is worth mentioning that this mechanistic pathway is still debated. More details will be shown in the dedicated section (Section 3). Beside this, in the following paragraphs the most relevant organic reactions driven by the photochemical activity of **A** will be presented.

2.1. Reduction of Aryl Halides

Indubitably, a milestone in the use of PDIs in synthetic photochemistry is represented by the work of König and co-workers, published in 2014 (Figure 3).[26] The authors described an efficient route for the reduction of stable aryl halides **1** in the presence of **A** under blue light irradiation (455 nm). Remarkably, these metal-free catalyzed radical reactions are receiving growing attention as complementary methods to standard transition metal-catalyzed C-C bond forming transformations (Figure 3).[34] In addition, dehalogenation reactions might find application in wastewater treatment, since chlorinated and brominated aromatics are ubiquitous environmental contaminants.[35,36] The breakthrough of this method was the possibility of transforming even unreactive aryl chlorides (E < –1.7 V *vs* SCE) by means of a bioinspired approach.[21,37]

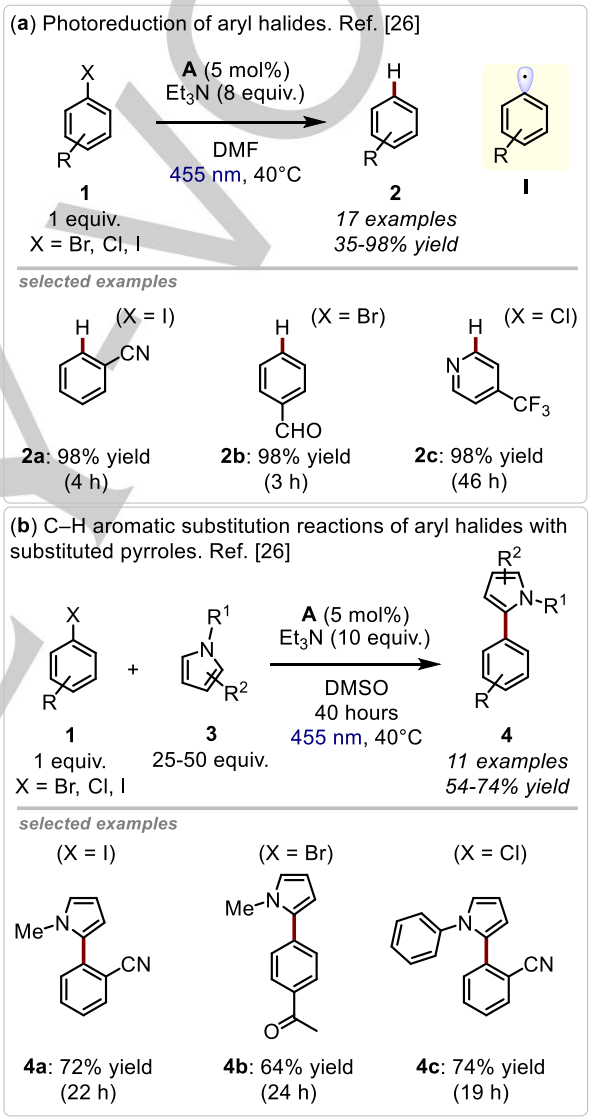


Figure 3. (**a**) Use of **A** as photocatalyst for the reduction of aryl halides. (**b**) Use of **A** to photocatalyze C–H aromatic substitution reactions.

In particular, the authors observed that **A** can imitate the Z scheme of biological photosystems that consists in accumulating the energy of two photons in one catalytic cycle. In Nature, this is possible by exciting two different systems which operate in series.[38] Practically, upon irradiation of **A** in the presence of an electron donor, namely triethylamine, the corresponding radical anion (**A**$^{\bullet-}$) is generated through a photoinduced electron transfer

(PET). This new chemical entity is deeply colored and stable in deaerated solutions. Therefore, it can absorb another photon providing a stronger reducing agent in the excited state (**A**•⁻*).[26,32] Thus, the highly energetic **A**•⁻* is able to reduce aryl halides **1**, leading to the formation of the carbon-centered radicals **I**. These meaningful open–shell intermediates (**I**) can be then trapped by hydrogen atom donors or used in C–C bond formation, hence affording valuable compounds **2**,**4**.

An analogous approach was proposed by Duan and co-workers.[39] They used PDI-based metal-organic polymers for the preparation of compounds of the type of **2**,**4**. Specifically, a unique channel structure, within the crystalline aggregates, was formed through the coordination of zinc ions with PDIs bearing terminal carboxylic groups at the imide positions. In particular, the authors demonstrated that working under heterogeneous conditions can be beneficial for the PDI photocatalyst in terms of recovery and reutilization, while maintaining similar catalytic activity compared to **A**. Furthermore, the reactivity of these highly porous PDI-based materials was expanded to other benchmark transformations, such as alcohol or amine oxidation. Similarly, Chen and co-workers reported the application of PDIs anchored to the surface of silica nanoparticles for the dehalogenation of a brominated environmental pollutant, namely decabromodiphenyl ether (BDE 209).[40]

Interestingly, the group of Lin illustrated how the structural modifications of **A** (HOMO = -5.98 eV; LUMO = -3.43 eV) at the *bay* position may affect the photocatalytic performances for the reduction of aryl halides **1** (Figure 4).[27] These authors found that the presence of two electron-donating phenoxyl groups (PDI **C**) improves the conversion of **1** in the direction of products **2**. On the contrary, when four phenoxyl groups are installed in the *bay* region (PDI **D**), the product yields dropped.

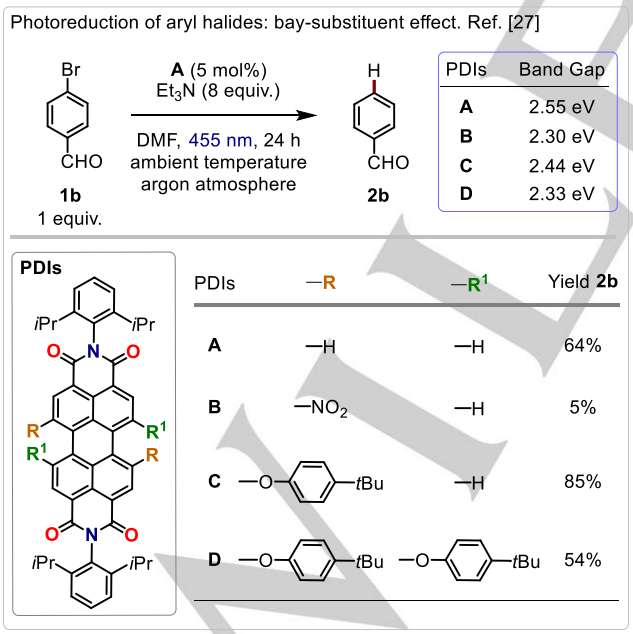


Figure 4. Use of PDIs **A-D** as photocatalyst for the reduction of aryl halide **1b**.

This was attributed to the lower photo-oxidative power of **D** (HOMO = -5.09 eV; LUMO = -2.76 eV) compared to **C** (HOMO = -5.42 eV; LUMO = -2.98 eV), which may hamper the formation of the corresponding PDI radical anions. This appreciably decreases the activity of photocatalyst **D** and highlights the need for a proper tuning of the redox properties of the PDIs. At the other extreme, a PDI bearing electron-withdrawing nitro groups at the *bay* positions (**B**, HOMO = -6.32 eV; LUMO = -4.02 eV) gave almost no reaction. This result was correlated with the lower electron transfer ability of **B**•⁻* towards substrates **1**. As anticipated in the previous sections, it is worth mentioning that PDIs bearing electron-donating groups in their core exhibit an increase of both HOMO and LUMO, whereas PDIs bearing electron-withdrawing groups show a decrease of both these molecular orbitals. These results can be attributed to the injection or the suction of electron density to the aromatic core by the different substituents. However, since both HOMO and LUMO are contemporary shifted, distinct core-functionalized PDIs have almost identical band gaps (blue box, Figure 4).[2]

2.2. Oxidation of Sulfides

As mentioned before, PDI **A** is a strong oxidant in the excited state and can therefore initiate photo-oxidation reactions or even photo-oxygenations in the presence of molecular oxygen. O_2 is probably the greenest oxidant available for organic synthesis, therefore its utilization is getting more and more significance for academia and industry.[41,42] To this regard, Zhang, Fan, and co-workers reported the aerobic oxidation of sulfides **5** to sulfoxides **6** by means of the photochemical activity of **A** under blue light irradiation (Figure 5).[43] This relevant transformation has practical application in the preparation of valuable biologically active sulfoxide derivatives.[44] Remarkably, the authors found that two different reaction mechanism could be operative. Indeed, both electron transfer and energy transfer pathways could in principle lead to the conversion of sulfides **5** to sulfoxides **6**.

In the first route, the light-excited photocatalyst **A*** can oxidize substrate **5**, giving its sulfur-centered radical cation. Subsequently, the so-obtained PDI radical anion (**A**•⁻) can reduce molecular oxygen to superoxide radical anion ($O_2^{\bullet-}$). Lastly, the reaction between the sulfide radical cation and $O_2^{\bullet-}$ affords product **6**. Alternatively, **A** can act as photosensitizer for the production of singlet oxygen ($^1O_2$) through an energy transfer process. $^1O_2$ can then react with substrate **5** ultimately producing sulfoxide **6**.

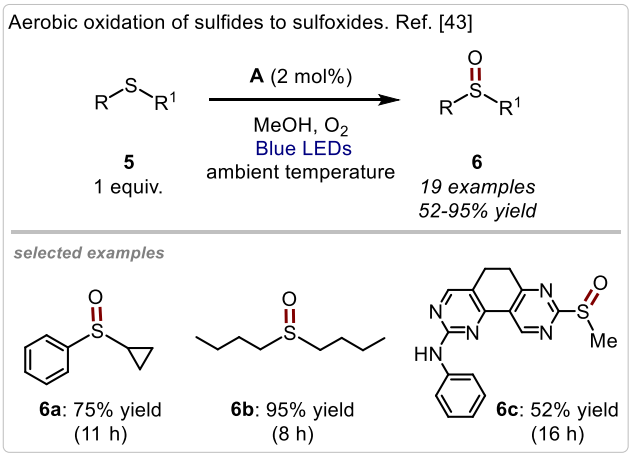


Figure 5. Use of **A** as photocatalyst for the oxidation of sulfides to sulfoxides.

2.3. Iodoperfluoroalkylation of Olefins

In 2019, we described an efficient procedure for the photochemical iodoperfluoroalkylation of alkenes catalyzed by PDI **A** (Figure 6).[28] This methodology is of practical importance because fluorinated compounds play a crucial role in medicinal chemistry, agrochemistry, and materials science.[45] Specifically, PDI **A** (0.05 mol%) is able to drive atom transfer radical addition (ATRA) reactions between terminal olefins **7** and perfluoroalkyl iodides **8** under blue light irradiation (450 nm). This photocatalytic process turned out to be extremely convenient since it proceeds with very high rates of production (about 700 mmol of product **9** g^{-1} photocatalyst **A** h^{-1}). Interestingly, such a high level of reactivity outperforms current available methods.[46] In this transformation, the use of sodium ascorbate (ED) was found to be pivotal for the reactivity, since it brings to the effective formation of the PDI radical anion (**A**$^{\bullet-}$). Moreover, due to the persistency in solution of **A**$^{\bullet-}$ and the high tendency of **8** to give ground–state associations with anions, we hypothesized that an electron donor–acceptor (EDA) complex between these species could be at play. This complex could photochemically generate fluorinated radicals, therefore initiating the ATRA process.[21,32,47–49] Although **A** turned out to be an efficient photoredox catalyst for this transformation, a bleaching of the organic dye was observed over time. This suggested that a degradative pathway, which decreased the lifespan of **A**, is operative under the experimental conditions. We found out that the presence of fluorinated open–shell species stimulated such collateral route.[50,51]

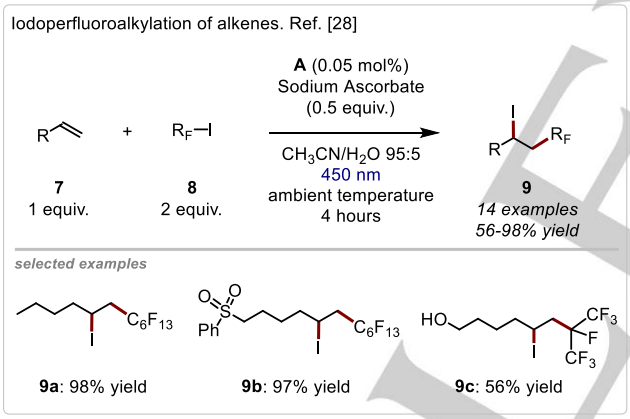


Figure 6. Use of **A** as photocatalyst for the iodoperfluoroalkylation of olefins.

Successively, in order to achieve the synthesis of relevant fluorinated products **9** in preparative scale, we translated the described PDI-photocatalyzed reaction into continuous flow.[29] In this way, taking advantage from the intrinsic benefits of flow photochemistry,[52–54] iodoperfluoroalkyl compounds **9** have been prepared with high productivity in the order of minutes of irradiation (up to 7.6 g h^{-1}). The batch procedure has been readily adapted to operate in flow, by simply changing the sacrificial reducing agent (ED) from sodium ascorbate to triethylamine (Method a, Figure 7). It is worth noting that following a screening of irradiation wavelengths, reactivity was observed even in the absence of photocatalyst **A** by shining purple light at 405 nm. This result can be attributed to the photoactivation of perfluoroalkyl iodides **8** by triethylamine, through the formation of a halogen-bonded EDA complex. Moreover, in following studies, we demonstrated that even nitrogen–doped carbon–based nanomaterials can serve as photocatalysts for the iodoperfluoroalkylation of organic compounds.[55–57] The mentioned purple light strategy was employed for the construction of a key intermediate in the synthesis of the breast cancer drug, namely Fulvestrant, in gram-scale (Method b, Figure 7).

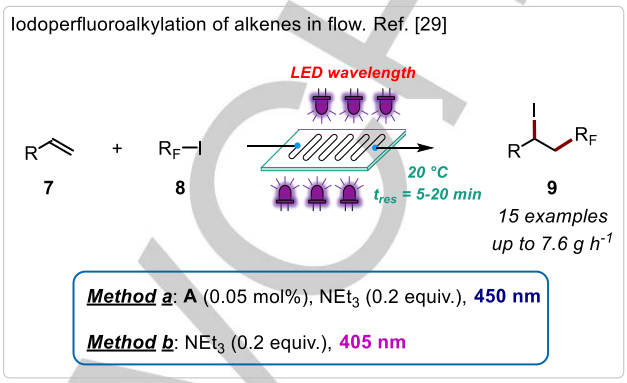


Figure 7. Iodoperfluoroalkylation of olefins in continuous flow.

3. Mechanistic Discussion: Reduction of Aryl Halides

The synthetic relevance and the fascinating photocatalytic properties of **A** have attracted the interest of numerous research groups. In fact, the mode of catalysis of **A** has been deeply investigated from different points of view, with particular attention to the aryl reduction reaction. These studies came to different conclusions, thus opening a recent discussion on the real photocatalytic mechanism of **A**. In this section, the diverse hypotheses are presented. König's group first proposed the sequential absorption of two photons by the photocatalyst **A** and its corresponding radical anion **A**$^{\bullet-}$.[26] The so-obtained excited species **A**$^{\bullet-*}$ was intended to be ultimately responsible for the reduction of aryl halides **1** (Figure 8a). This double photon mechanism was suggested since the ground-state PDI radical anion (**A**$^{\bullet-}$) is not able to carry out the direct reduction of **1**, according to their redox potentials (E = –0.37 V *vs* SCE for the couple **A**/**A**$^{\bullet-}$, while E < –1 V *vs* SCE for the radical sources).[21,26] On the other hand, the reduction potential of **A**$^{\bullet-*}$ was estimated to reach or surpass this threshold. The authors corroborated these hypotheses performing a series of control experiments. Specifically, chemically or photochemically generated **A**$^{\bullet-}$ did not drive any reactivity in the dark. Intriguingly, the formation of PDI degradation products was observed over the course of the dehalogenation reactions. However, the authors claimed that these side-products may also contribute to the conversion of **1**. Indeed, PDIs bearing different *imide* substituents showed similar photocatalytic activity towards the reduction of **1**.

In 2018, Cozzi, Ceroni and co-workers confirmed that **A**$^{\bullet-*}$ is not stable under the reaction conditions used for the dehalogenation of aryl halides.[30] Through a deep spectroscopic and electrochemical study, the authors highlighted that **A**$^{\bullet-*}$ does not seem to be a catalytic intermediate since, apparently, the reactivity was driven by its decomposition products (Figure 8b). These conclusions were supported by the very short lifetime of **A**$^{\bullet-*}$ (145 ps) that does not allow for an effective PET.[32] Indeed,

only 15% of the **A**•−* is quenched by **1** under the experimental conditions, by assuming that the reaction is diffusion controlled.[58] Furthermore, at the selected irradiation wavelength (455 nm), **A**•− absorbs around 9 times less than **A**.[32] Lastly, high conversion of aryl halides **1** were obtained when **A**•− was almost completely decomposed. Based on these pieces of evidence, the authors claimed that **A**•−* degradation species are the real radical initiators of this transformation. Nevertheless, the exact structure of these species has never been identified.

Another possible explanation for the mode of catalysis of **A** was suggested by Nicewicz and co-workers in 2016.[21] The authors reasoned that a preassociation between **A**•− and aryl halide **1** could be at play. This ground-state aggregation, namely EDA complex, could be held together by non–covalent interactions between the electron rich donor **A**•− and the electron poor acceptor **1**.[59] The EDA complex would be a new chemical entity that could absorb visible light.[60] Therefore, a PET from the donor to the acceptor might occur, leading to the formation of reactive open–shell intermediates (**I**, Figure 8c).[59] In this way, the issue of the redox potential matching between the reaction partners can be overcome, thus explaining the unpredicted reactivity of some case studies. Likewise, inspired by this possibility, our group hypothesized the formation of a similar EDA complex between **A**•− and perfluoroalkyl iodides **8** to afford the fluorinated compounds **9**.[28] Notwithstanding, there is no spectroscopic evidence that demonstrates the formation of such complexes due to the intrinsic difficulties in carrying out photochemical studies on **A**•−.[30]

Later on, Gschwind and co-workers implemented an in situ combination of Nuclear Magnetic Resonance (NMR) and Ultraviolet/Visible (UV/Vis) spectroscopy under light irradiation, to allow the simultaneous and time-resolved detection of paramagnetic and diamagnetic species.[61] Using this setup, the authors attempted to confirm the consecutive PET mechanism asserted by König for the dehalogenation of aryl halides **1**. Thereby, they easily observed the formation of **A**•− and the production of **2** over the time by shining blue light. However, no direct evidence for the involvement of **A**•−* in the reaction pathway has been provided.

Conversely, Zhang, Schanze and co-workers have recently reported the use of picosecond time-resolved transient absorption spectroscopy to monitor the formation of **A**•−* and its bimolecular quenching by aryl halides **1** through Stern–Volmer studies.[33] The authors found that **A**•−* underwent efficient PET with electron poor halides **1** having reduction potential > –1.7 V *vs* SCE. Besides, they calculated the potential for the couple **A**•−*/**A** as −1.87 V *vs* SCE. However, a variety of unreactive halides (E < –1.8 V *vs* SCE) that are still effectively converted into the corresponding dehalogenated compounds **2**, did not show any quenching of **A**•−*. This can be attributed to a too slow electron transfer compared to the rapid decay of **A**•−*. In this case, the authors suggested that a thermally activated reaction between ground-state **A**•− and **1** (if [**1**] = 0.5 M) could take place, despite its endothermicity of more than 1 eV. According to them, this process might be feasible because the dehalogenation of **1**•− is very fast, thus making the slow electron transfer reaction irreversible.[62]

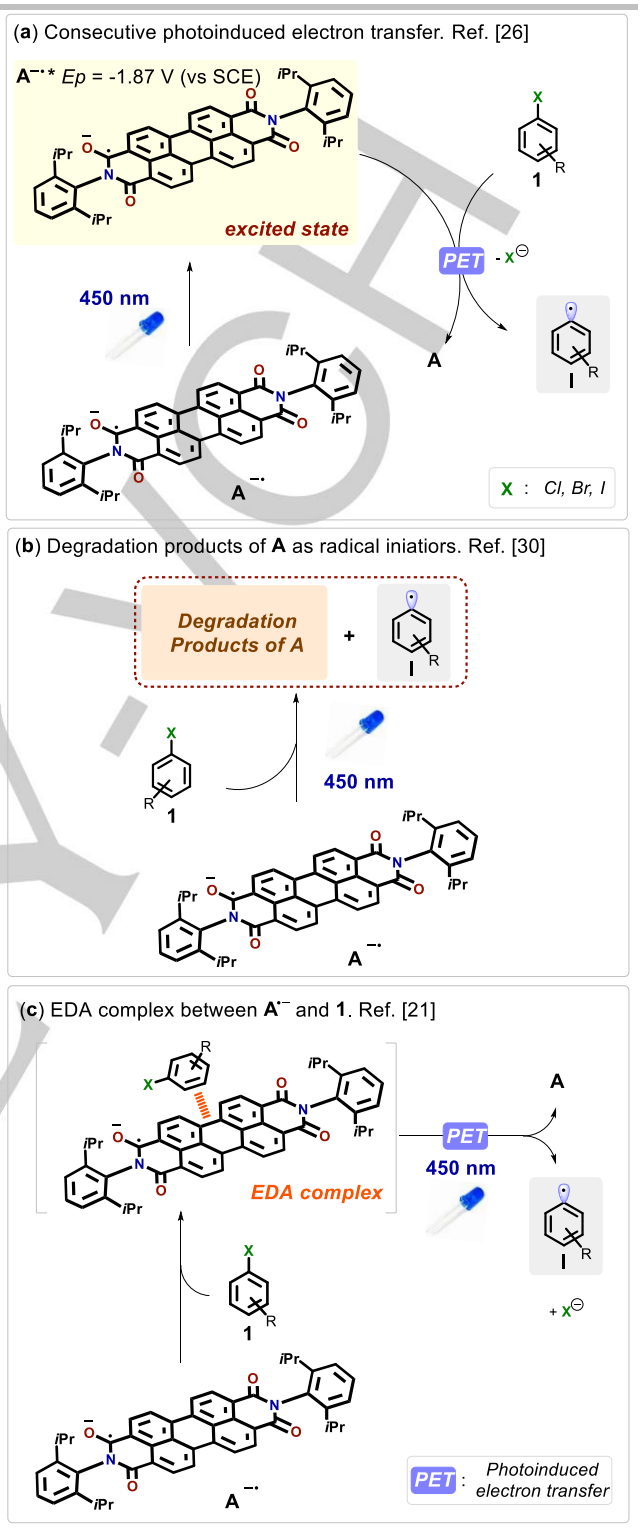
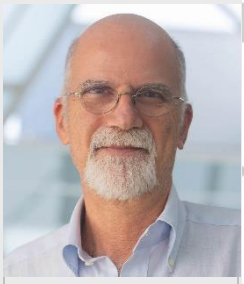


Figure 8. Suggested photochemical mechanisms for the production of aryl radicals **I**.

Cristian Rosso obtained his Master's degree in Chemistry from the University of Bologna (Italy) in 2016. In 2017, he started his doctoral studies in the group of Prof. Maurizio Prato at University of Trieste (Italy), focusing his research on the development of catalytic organic transformations. In 2019, he had the opportunity to join the group of Prof. Oliver Kappe at University of Graz (Austria) for a one-year stay, investigating continuous flow photochemical processes. Currently, he is studying carbon-based nanomaterials as organo-photocatalysts for synthetic purposes.

Giacomo Filippini obtained his Master's degree in Chemistry from the University of Bologna (Italy). In 2013 he joined the group of Prof. Paolo Melchiorre at ICIQ in Tarragona (Spain), where he undertook his doctoral studies. In 2017, he started a postdoctoral appointment in the group of Prof. Maurizio Prato at University of Trieste (Italy), where he is currently investigating the use of carbon-based nanomaterials to design novel organic transformations.



Maurizio Prato is Professor of Organic Chemistry at the University of Trieste and Ikerbasque Research Professor at CIC biomaGUNE, Spain. He was the recipient of two ERC Advanced Research Grant, European Research Council, in 2008 and 2020 and became a Member of the National Academy of Sciences (Accademia Nazionale dei Lincei) in 2010. His research focuses on the synthesis of innovative carbon-based functional materials, for applications in materials science, nanomedicine and catalysis.

4. Summary and Outlook

Thanks to the outstanding optical and redox properties of PDIs, these organic chromophores have received growing attention in many fields of application. In particular, a highly soluble diaryl PDI derivative, namely **A**, turned out to be an excellent candidate to drive synthetically useful photocatalytic transformations. This Minireview summarized the latest advances within this field, highlighting the versatility of **A** to carry out both photo-oxidation and photo-reduction processes of practical importance. Moreover, the mechanistic discussion focused on the relevant photo-reduction of aryl halides (**1**) was presented. Different pathways have been proposed, including (*i*) the formation of highly reducing $\mathbf{A}^{\bullet-*}$, (*ii*) the photodegradation of $\mathbf{A}^{\bullet-}$ which initiates the radical process or, alternatively, (*iii*) the formation of a ground-state EDA complex between $\mathbf{A}^{\bullet-}$ and the radical source. In addition, a recent study suggested a substrate-dependent mechanism, where even an energetically disfavored thermal reactivity should be taken into account.

Based on these considerations, there are still some aspects that could be tackled in the near future. For instance, the exploitation of computational studies, unprecedented for this reaction, might help discriminate between all possible photochemical mechanisms, thus evaluating the most likely catalytic intermediates and the actual role of **A**. In fact, similar investigations have been successfully carried out for analogous transformations.[48,63]

Besides, studies to clarify the degradation pathways of **A** should be undertaken in order to identify the real chemical structures of its by-products. By understanding these unsolved questions, more effective PDI–based photocatalytic systems could be designed, securing the possibility to expand the known reactivity towards other synthetically, industrially, or naturally relevant photochemical transformations.

Acknowledgements

M.P. is the AXA Chair for Bionanotechnology (2016-2023). This work was supported by the University of Trieste, INSTM, and the Italian Ministry of Education MIUR (cofin Prot. 2017PBXPN4). C.R. thanks the European Social Fund, Operational Program 2014/2020 - Friuli-Venezia Giulia (Regional Code FP1799043001) for a doctoral fellowship. Part of this work was performed under the Maria de Maeztu Units of Excellence Program from the Spanish State Research Agency Grant No. MDM-2017-0720.

Keywords: Perylene diimide • Photocatalysis • Reaction mechanisms • Redox chemistry • Synthetic methods

[1] A. Nowak-Król, F. Würthner, *Org. Chem. Front.* **2019**, *6*, 1272–1318.

[2] F. Würthner, C. R. Saha-Möller, B. Fimmel, S. Ogi, P. Leowanawat, D. Schmidt, *Chem. Rev.* **2016**, *116*, 962–1052.

[3] S. K. Lee, Y. Zu, A. Herrmann, Y. Geerts, K. Müllen, A. J. Bard, *J. Am. Chem. Soc.* **1999**, *121*, 3513–3520.

[4] N. Zink-Lorre, E. Font-Sanchis, Á. Sastre-Santos, F. Fernández-Lázaro, *Chem. Commun.* **2020**, *56*, 3824–3838.

[5] W. Herbst, K. Hunger, *Industrial Organic Pigments: Production, Properties, Applications*, Wiley-VCH, **1997**.

[6] F. Würthner, *Chem. Commun.* **2004**, 1564–1579.

[7] C. Huang, S. Barlow, S. R. Marder, *J. Org. Chem.* **2011**, *76*, 2386–2407.

[8] P. M. Kazmaier, R. Hoffmann, *J. Am. Chem. Soc.* **1994**, *116*, 9684–9691.

[9] V. Kunz, V. Stepanenko, F. Würthner, *Chem. Commun.* **2015**, *51*, 290–293.

WILEY-VCH

[10] L. D. Wescott, D. L. Mattern, *J. Org. Chem.* **2003**, *68*, 10058–10066.

[11] Z. Chen, B. Fimmel, F. Würthner, *Org. Biomol. Chem.* **2012**, *10*, 5845–5855.

[12] F. Rigodanza, E. Tenori, A. Bonasera, Z. Syrgiannis, M. Prato, *Eur. J. Org. Chem.* **2015**, *2015*, 5060–5063.

[13] G. Battagliarin, C. Li, V. Enkelmann, K. Müllen, *Org. Lett.* **2011**, *13*, 3012–3015.

[14] T. Teraoka, S. Hiroto, H. Shinokubo, *Org. Lett.* **2011**, *13*, 2532–2535.

[15] X. Zhan, A. Facchetti, S. Barlow, T. J. Marks, M. A. Ratner, M. R. Wasielewski, S. R. Marder, *Adv. Mater.* **2011**, *23*, 268–284.

[16] D. Gutiérrez-Moreno, Á. Sastre-Santos, F. Fernández-Lázaro, *Org. Chem. Front.* **2019**, *6*, 2488–2499.

[17] T. Weil, T. Vosch, J. Hofkens, K. Peneva, K. Müllen, *Angew. Chem. Int. Ed.* **2010**, *49*, 9068–9093.

[18] I. Ghosh, *Phys. Sci. Rev.* **2019**, 20170185.

[19] F. Glaser, C. Kerzig, O. S. Wenger, *Angew. Chem. Int. Ed.* **2020**, *59*, 10266–10284.

[20] M. Bonchio, Z. Syrgiannis, M. Burian, N. Marino, E. Pizzolato, K. Dirian, F. Rigodanza, G. A. Volpato, G. La Ganga, N. Demitri, S. Berardi, H. Amenitsch, D. M. Guldi, S. Caramori, C. A. Bignozzi, A. Sartorel, M. Prato, *Nat. Chem.* **2019**, *11*, 146–153.

[21] N. A. Romero, D. A. Nicewicz, *Chem. Rev.* **2016**, *116*, 10075–10166.

[22] C. K. Prier, D. A. Rankic, D. W. C. MacMillan, *Chem. Rev.* **2013**, *113*, 5322–5363.

[23] M. H. Shaw, J. Twilton, D. W. C. MacMillan, *J. Org. Chem.* **2016**, *81*, 6898–6926.

[24] M. Fagnoni, D. Dondi, D. Ravelli, A. Albini, *Chem. Rev.* **2007**, *107*, 2725–2756.

[25] W. Wei, S. Ouyang, *J. Semicond.* **2020**, *41*, 091708.

[26] I. Ghosh, T. Ghosh, J. I. Bardagi, B. Konig, *Science* **2014**, *346*, 725–728.

[27] H. Gong, Z. Cao, M. Li, S. Liao, M. Lin, *Org. Chem. Front.* **2018**, *5*, 2296–2302.

[28] C. Rosso, G. Filippini, P. G. Cozzi, A. Gualandi, M. Prato, *ChemPhotoChem* **2019**, *3*, 193–197.

[29] C. Rosso, J. D. Williams, G. Filippini, M. Prato, C. O. Kappe, *Org. Lett.* **2019**, *21*, 5341–5345.

[30] M. Marchini, A. Gualandi, M. Lucarini, P. G. Cozzi, L. Mengozzi, P. Franchi, V. Balzani, P. Ceroni, *Phys. Chem. Chem. Phys.* **2018**, *20*, 8071–8076.

[31] D. Rehm, A. Weller, *Isr. J. Chem.* **1970**, *8*, 259–271.

[32] D. Gosztola, M. P. Niemczyk, W. Svec, A. S. Lukas, M. R. Wasielewski, *J. Phys. Chem. A* **2000**, *104*, 6545–6551.

[33] C. J. Zeman, S. Kim, F. Zhang, K. S. Schanze, *J. Am. Chem. Soc.* **2020**, *142*, 2204–2207.

[34] C. S. Wang, P. H. Dixneuf, J. F. Soulé, *Chem. Rev.* **2018**, *118*, 7532–7585.

[35] C. Descorme, *Catal. Today* **2017**, *297*, 324–334.

[36] D. Sadowsky, K. McNeill, C. J. Cramer, *Environ. Sci. Technol.* **2014**, *48*, 10904–10911.

[37] M. Cybularczyk-Cecotka, J. Szczepanik, M. Giedyk, *Nat. Catal.* **2020**, *3*, 872–886.

[38] Govindjee, D. Shevela, L. O. Björn, *Photosynth. Res.* **2017**, *133*, 5–15.

[39] L. Zeng, T. Liu, C. He, D. Shi, F. Zhang, C. Duan, *J. Am. Chem. Soc.* **2016**, *138*, 3958–3961.

[40] J. Shang, H. Tang, H. Ji, W. Ma, C. Chen, J. Zhao, *Cuihua Xuebao/Chinese J. Catal.* **2017**, *38*, 2094–2101.

[41] F. Cavani, J. H. Teles, *ChemSusChem* **2009**, *2*, 508–534.

[42] C. A. Hone, C. O. Kappe, *Top. Curr. Chem.* **2019**, *377*, 2.

[43] Y. Gao, H. Xu, S. Zhang, Y. Zhang, C. Tang, W. Fan, *Org. Biomol. Chem.* **2019**, *17*, 7144–7149.

[44] J. Legros, J. R. Dehli, C. Bolm, *Adv. Synth. Catal.* **2005**, *347*, 19–31.

[45] S. Barata-Vallejo, M. V. Cooke, A. Postigo, *ACS Catal.* **2018**, *8*, 7287–7307.

[46] C. Wallentin, J. D. Nguyen, P. Finkbeiner, C. R. J. Stephenson, *J. Am. Chem. Soc.* **2012**, *134*, 8875–8884.

[47] M. Nappi, G. Bergonzini, P. Melchiorre, *Angew. Chem. Int. Ed.* **2014**, *53*, 4921–4925.

[48] V. M. Fernàndez-Alvarez, M. Nappi, P. Melchiorre, F. Maseras, *Org. Lett.* **2015**, *17*, 2676–2679.

[49] G. Filippini, M. Nappi, P. Melchiorre, *Tetrahedron* **2015**, *71*, 4535–4542.

[50] K. O. Johansson, M. P. Head-Gordon, P. E. Schrader, K. R. Wilson, H. A. Michelsen, *Science* **2018**, *361*, 997–1000.

[51] J. Lub, P. A. van Hal, R. Smits, L. Malassenet, J. Pikkemaat, R. A. M. Hikmet, *J. Lumin.* **2019**, *207*, 585–588.

[52] Y. Su, N. J. W. Straathof, V. Hessel, T. Noël, *Chem. Eur. J.* **2014**, *20*, 10562–10589.

[53] D. Cambié, C. Bottecchia, N. J. W. Straathof, V. Hessel, T. Noël, *Chem. Rev.* **2016**, *116*, 10276–10341.

[54] M. B. Plutschack, B. Pieber, K. Gilmore, P. H. Seeberger, *Chem. Rev.* **2017**, *117*, 11796–11893.

WILEY-VCH

[55] C. Rosso, G. Filippini, M. Prato, *Chem. Eur. J.* **2019**, *25*, 16032–16036.

[56] G. Filippini, F. Longobardo, L. Forster, A. Criado, G. Di Carmine, L. Nasi, C. D. Agostino, M. Melchionna, P. Fornasiero, M. Prato, *Sci. Adv.* **2020**, *6*, DOI: 10.1126/sciadv.abc9923.

[57] M. Garrido, L. Gualandi, S. Di Noja, G. Filippini, S. Bosi, M. Prato, *Chem. Commun.* **2020**, *56*, 12698–12716.

[58] M. Montalti, A. Credi, L. Prodi, M. T. Gandolfi, *Handbook of Photochemistry*, CRC Press, **2006**.

[59] Y. Yuan, S. Majumder, M. Yang, S. Guo, *Tetrahedron Lett.* **2020**, *61*, 151506.

[60] R. S. Mulliken, *J. Am. Chem. Soc.* **1950**, *72*, 600–608.

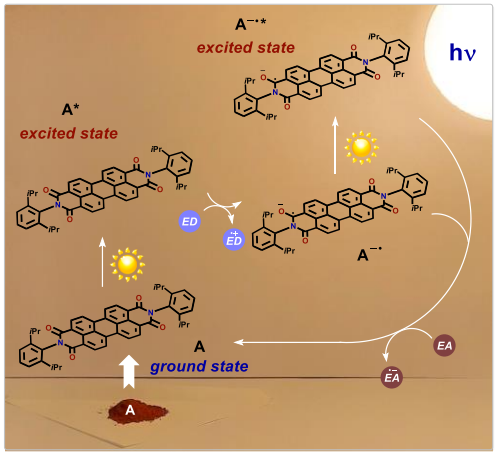
[61] A. Seegerer, P. Nitschke, R. M. Gschwind, *Angew. Chem. Int. Ed.* **2018**, *57*, 7493–7497.

[62] C. L. Perrin, *J. Phys. Chem.* **1984**, *88*, 3611–3615.

[63] C. Yang, W. Zhang, Y.-H. Li, X.-S. Xue, X. Li, J.-P. Cheng, *J. Org. Chem.* **2017**, *82*, 9321–9327.

WILEY-VCH

Table of Contents



Perylene diimides are a relevant class of organic dyes with excellent optoelectronic features. Therefore, they found application as photocatalysts for important organic transformations. This Minireview highlights the recent advances within this field, with a specific focus on the mechanism of these photochemical reactions. Finally, still unsolved challenges and forward-looking opportunities are mentioned here.

Institute and/or researcher Twitter usernames: @lab_carbon

WILEY-VCH