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Excited State Anions in Organic Transformations

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Dedicated to Prof. Ilhyong Ryu on the occasion of his 70th birthday
Abstract: Utilizing light is a smart way to fuel chemical transformations as it allows to selectively focus the energy on certain molecules. Many reactions involving electronically excited species proceed via open-shell intermediates enabling novel and unique routes to expand the hitherto used synthetic toolbox in organic chemistry. The direct conversion of non-prefunctionalized, less activated compounds is a highly desirable goal to pave the way towards a more sustainable and atom-economic chemistry. Photoexcited closed-shell anions have been shown to reach extreme potentials in single electron transfer reactions and reveal unusual excited state reactivity. It is therefore surprising, that their use as reagent or as photocatalyst is limited to a few examples. In this review, we briefly discuss the characteristics of anionic photochemistry, highlight pioneering work and show recent progress which has been made by utilizing photoexcited anionic species in organic synthesis.

1. Introduction

Initial attention to the versatile reaction modes of photoexcited organic anions and their special spectroscopic behaviour was drawn by the early reviews of Fox[1] and Tolbert[2]. Since then, other excellent publications followed, summarizing the photochemistry of excited organic anions with focus on their photoreductive properties and underlining the peculiarities of anionic organic molecules in photochemistry.[3,4] Compared to the neutral species, the absorption of an organic anion is usually red-shifted, which facilitates the selective excitation in complex mixtures and often allows to use visible light. Along with the enhanced electron-electron repulsion found in anionic molecules, negatively charged species are expected to act as particularly potent electron donors from their photoexcited states. In addition, a single electron transfer from an anionic donor to a neutral acceptor gives rise to a neutral radical and a radical anion. These species are free of attracting forces and are able to diffuse freely, which suppresses back electron transfer (BET) reactions resulting in higher reaction efficiencies. Organic anions can be easily formed in presence of base and their rather long excited state lifetimes distinguish them from radical anions.

Excited anionic species are also utilized in key photochemical steps in biology. For instance, in an ATP-driven process, the excited oxy Luciferin anion causes the bioluminescence of fireflies.[5] Moreover, phototrophic organisms show locomotory movement upon stimulus of light. The photoactive yellow protein (PYP) encloses the anionic trans-para-coumaric acid as blue-light photoreceptor. Subsequent trans-cis isomerization of the excited chromophore induces a conformational change of the protein leading to a biological signal transduction.[6] The enzyme-mediated repair of photodamaged DNA is another well-known example dealing with excited anions in living cells. A crucial step is the photoinduced electron transfer from the excited cofactor flavin adenine dinucleotide (FADH) which provides an electron for the light-driven repair catalyzed by photolyases.[7,8]

Literally, the last decade has been a very exciting time in terms of photochemistry and many novel chemical transformations have been developed which complement the available synthetic toolbox. We are sure that, inspired by nature and the herein presented examples, the photochemistry of closed-shell anions will be further developed towards the generation of ever stronger light-activated reductants and novel reaction modes. In this review, we briefly summarize key spectroscopic and electrochemical properties of organic anions and provide an overview of the versatile photochemistry of anionic species with a special focus on recent examples of organic anions used as photocatalysts or as light-activated reagents.

1.1. Spectroscopic Properties of Organic Anions

The chemistry of molecules excited by light is initiated by the absorption of a photon and thus, we will start with discussing the peculiarities of the absorption spectra for closed-shell anions. Compared to their neutral precursors, organic anions usually experience a significant bathochromic shift in their absorption spectra and pronounced absorption bands can be attributed to $\pi\rightarrow\pi^*$ transitions. The narrowed gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO, see Figure 1) causing the red-shift can be primarily explained by the increased shielding of the core due to an imbalance of charges. The strength of the electric field is reduced and electrons in the HOMO sense much weaker attracting forces. As a result, the spatial distribution of electrons becomes more diffuse as if the conjugation length is extended.[9] The absorption of organic anions is also affected by size and nature of the countercation, solvent polarity and ion pairing effects in solution. In non-polar or weakly polar solvents, contact ion pairs are formed and the properties of the anionic species are strongly influenced by the character of the countercation.

![Figure 1: Energetic destabilization of the ground state of a free ion pair in polar solvent compared to the contact ion pair in non-polar solvent and influence on the absorption spectrum.](image)

In contrast, the increased solubility of ions in polar solvents, induced by aligning molecular dipoles, causes solvent-separated...
in polar organic solvents the electrostatic work term usually contributes little to the free enthalpy change and is frequently omitted.\[17\]

PET from a neutral excited-state donor (D) to a neutral ground-state acceptor (A) causes a charge separation, resulting in a pair of radical ions. In contrast, the PET from an anionic excited-state donor to a neutral acceptor can be considered as a charge shift, generating products that are free of electrostatic attraction and expected to diffuse freely (Scheme 2). Hence, the lost channel of a back electron transfer, which would regenerate the initial non-excited status quo, is less competitive in a charge-shift process.\[16\]

![Scheme 2](image)

**Scheme 2.** Charge separation with neutral donor (left) and charge shift with anionic donor (right).

An anionic molecule is considered as a superior electron donor compared to its neutral parent. Both repulsion between electrons and the shielding from the nucleus are increased. As a consequence, the excess negative charge facilitates the removal of an electron. Experimentally, this becomes apparent when solvated electrons are expelled from organic anions in a biphotonic process using energy-rich UV light\[19\] in glassy matrices (77 K) or pulsed high-energy lasers\[20,21\] in alkaline aqueous solution. Working with visible-light LEDs and in common organic solvents however, renders the photo-ejection of an electron unlikely to occur and hence under these conditions electron transfer reactions are prevailing. We recently demonstrated that 9-anthracene and its derivatives are easily deprotonated in presence of carbonate base to form colored anions (e.g. AN\(^-\), Figure 2), which upon visible-light excitation turn into remarkably strong reducers.\[22\] Cyclic voltammetry measurements in alkaline DMSO revealed that the anionic ground state is already a good reductant, as the excess charge is removed easily due to resonance stabilization of the resulting radical. In sharp contrast, the dianions of fluorescein FL\(^2^-\) or eosin Y (EY\(^{2^-}\)) show a significantly decreased tendency towards electrochemical oxidation in alkaline MeOH and hence, the resulting excited state oxidation potentials are only moderate (cf., Table 1, Entry 5-7).\[23\]

![Scheme 3](image)

**Scheme 3.** Formation of the eosin Y radical trianion upon PET in presence of triethanolamine (top). Intramolecular PET from the amino group causing self-quenching of the fluorescence.
Furthermore, it was reported that FL$^{2−}$ and EY$^{2−}$, although being present as ground state dianions, are easily reduced upon photoexcitation in basic solutions containing triethanolamine or phenol to form radical trianions (Scheme 3, top). [24–28]Walt and co-workers attached an amino group on the benzoate scaffold of fluorescein NH$_2$-FL$^{2−}$ and found that the fluorescence quantum yield dropped by almost a factor of 60. They explained this observation by an intramolecular PET from the nitrogen lone pair to the fluorescein scaffold (Scheme 3, bottom). A similar fluorescence quantum yield with respect to non-modified FL$^{2−}$ was however recorded when adjusting the pH of the solution to a value around the pK$_a$ of the aromatic amine. Due to protonation of the amine, the nitrogen lone pair is no longer available for intermolecular PET resulting in increased fluorescence. [29]In 1991, Soumilion et al. showed that the fluorescence of the excited anion of the xanthene dye resorufin is quenched in presence of 2-naphtholate and the formation of a radical dianion of resorufin was proposed. [18] The moderate reducing abilities of negatively charged xanthene dyes (e.g. EY$^{2−}$, FL$^{2−}$) can be explained by an overwhelming contribution of the electron-deficient conjugated system to the overall electronic properties. Thus, to obtain strongly reducing excited anions, a facile single electron oxidation is crucial (cf., Table 1, Entry 5–6 show similar values for $E_{0,0}$ but differ significantly in their ground state and excited state oxidation potentials).

![Diagram of ground and excited state potentials of a photocatalyst (PC, top). Representatives of cationic, neutral and anionic organic photocatalyst (bottom).](Image)

**Figure 2.**

**Table 1.** Ground state ($E_{1/2}$) and excited state ($E_{0,0}$) redox potentials of selected cationic, neutral and anionic organic photocatalysts (PC) and the corresponding transition energies ($E_{0,0}$).

| Entry | PC$^a$ | $E_{1/2}(PC^n/PC^{n−1})$ | $E_{red}(PC^+/PC^{2+})$ | $E_{1/2}(PC^{n+1}/PC^n)$ | $E_{ox}(PC^{n+1}/PC^n)$ | $E_{0,0} [eV]$ |
|-------|--------|--------------------------|--------------------------|--------------------------|--------------------------|-----------------|
| 1$^{[7]}$ | TPT$^+$ | −0.50$^a$ | +1.84 | - | - | 2.34$^a$ |
| 2$^{[30]}$ | ACR$^+$ | −0.59$^b$ | +2.08 | - | - | 2.67 |
| 3$^{[21]}$ | 4CzIPN | −1.24$^d$ | +1.43 | +1.49$^d$ | −1.18 | 2.67 |
| 4$^{[22]}$ | PTH | - | - | +0.57$^h$ | −2.5 | 3.1 |
| 5$^{[22]}$ | ANT$^+$ | - | - | −0.34$^d,e$ | −2.65 | 2.31 |
| 6$^{[28]}$ | FL$^{2−}$ | - | - | +0.87$^d$ | −1.55 | 2.42 |
| 7$^{[17]}$ | EY$^{2−}$ | −1.06 | +1.23$^{b,h}$ | +0.76 | −1.58$^{b,h}$ | 2.31$^h$ |
| 8$^{[17]}$ | PhPH$^+$ | - | - | +0.83$^{b,h}$ | +0.67 | 1.91$^h$ |
| 9$^{[38]}$ | BIA-H$^+$ | - | - | 0.10$^d$ | −3.16 | 3.06 |
| 10$^{[33]}$ | TMA$^+$ | - | - | +0.06$^d$ | −2.71 | 2.77$^h$ |

Potentials are reported vs. saturated calomel electrode (SCE). Transition energy $E_{0,0}$ was determined from the intersection of normalized absorption and emission spectra. $^a$Potential recorded vs. normal hydrogen electrode (NHE) and converted to SCE by subtracting 0.141 V. $^b$Determined from the highest energy emission maximum. $^c$Potential recorded vs. Ag/AgCl and converted to SCE by subtracting 0.03 V. $^d$Potential recorded vs. the ferrocene redox couple (Fc/Fc$^+$) and converted to SCE by adding 0.38 V. $^e$Potential was measured in dry degassed DMSO with excess of Ca$_3$CO$_3$. $^f$Potential was measured in MeCN containing NaOH (0.1 mol) against Ag/AgCl and referenced to SCE by conversion; $^g$Values for singlet excited state; $^h$Potential recorded vs. Ag/AgCl and converted to SCE by subtracting 0.039 V; $^i$Values for triplet excited state; $^j$Potential was measured in MeCN with excess $t$BuOK. $^k$Estimated by the end absorption wavelength possessing 0.02 absorbance at 4.0 × 10$^{−5}$ M.
2. Anionic Compounds as Photocatalysts

2.1 Photoredox Catalysis

During the last decade, impressive progress has been made in the field of synthetic photoredox catalysis and many novel transformations, which were previously inaccessible, have been developed. Photoexciting a molecule changes the electron distribution in the molecular orbitals resulting in both increased oxidizing- and reducing abilities of the excited species compared to the ground state (see Figure 2). These redox properties can be fine-tuned by attaching electron donating or withdrawing substituents. [30-32] Up to now, a variety of photocatalysts have been reported which are often classified regarding their composition into polypryridyl transition metal complexes, [33] organic dyes [34] or polyoxometalates [35] (POMs). In addition, heterogenous organic semiconductors were successfully employed as photocatalysts. [36] Their intrinsic photophysical properties like excited state redox potential, absorption of light or the excited state lifetime define the scope and limitations of chemical reactions. Selected examples of organic photocatalysts are depicted in Figure 2. The photochemistry of the non-charged donor-acceptor dyad 4CzIPN covers a broad electrochemical range (see Table 1, Entry 3). Bearing a versatile excited-state reduction and oxidation potential, it is often used to replace precious and toxic Ru- or Ir-polypryridyl complexes. [37,38] However, to convert less activated substrates via photoinduced single electron transfer, the frontiers need to be pushed towards higher excited state potentials. Recently, it was shown that photoexcited, electron-rich N-arylphenothiazines (e.g. PTH) act as very strong reductants but these compounds do not absorb in the visible range and hence UV-light is necessary which might interfere with other reaction components. Large Stokes shifts were found for the substituted N-arylphenothiazines which result in high transition energy values (cf., Table 1, Entry 4). [39]

Apart from commonly used neutral organic dyes, molecules with a charged or an open-shell ground state or both were found to significantly increase achievable excited state potentials and allowed to widen the substrate scope for photoinduced electron transfer reactions (Scheme 4). Several organic dyes form stable and coloured radical anions in presence of suitable sacrificial donors via PET and hence, enable a subsequent second excitation (see Scheme 4, A). [37-40] The versatile photochemistry of excited radical anions allowed to convert various (hetero)aryl halides in coupling reactions and has been subject of several reviews. [41-44] Very recently, this strategy was reported to promote Birch-type reductions of benzene derivatives upon visible-light irradiation. [45] In contrast, the formation of super-oxidants has been reported upon photoexcitation of stable, chemically generated phenothiazine radical cations (see Scheme 4, B). [46] Furthermore, electron transfer from photoexcited doublet states of neutral radicals has been studied. [47-51] The acridine radical ACR+ was recently found to act as an extremely powerful photo-reductant upon excitation with blacklight (see Scheme 4, C). [52] Although, enabling high redox potentials, the photochemistry of excited open-shell species suffers from short lifetimes which are usually in the picosecond range. [52-54] As the photochemistry of open-shell molecules is beyond the scope of this review, the interested reader is referred to cited literature.

Photoreactions using catalytic amounts of closed-shell cations were found to be synthetically very useful (Scheme 4, D). The pioneering work of Fukuzumi and co-workers [55] paved the way for plenty of publications using acridinium-based donor-acceptor dyads as strongly oxidizing photocatalysts [17,56-58]. Moreover, a new benchmark regarding the excited state potential was set by using pyrylium-, quinolinium- or diazapyrenium salts as extremely powerful photooxidants. [17] Among other cationic dyes, the photoexcited pyrylium- or acridinium salts (e.g. TPT+ and ACR+) Figure 2) are strong oxidants in their excited states and found widespread synthetic applications. [17,59-67] Surprisingly, in contrast to the wealth of reports dealing with photoexcited cations, the photochemistry of closed-shell anions received far less attention although it constitutes the logical equivalent (Scheme 4, E).

![Scheme 4](image)

Scheme 4. Approaches leading to reactive excited state photocatalysts with extreme redox potentials (red) allowing to convert non-activated substrates (S). The initial activation by protonation/deprotonation (see D, E) is not required when the salt of the catalyst is directly used.

Hence, in the following section the ability of anionic photocatalysts to drive challenging transformations is underlined based on selected examples. Due to their moderate redox-potentials and the wealth of available reviews, reactions of anionic xanthene dyes like eosin Y, rose bengal or fluorescein are not discussed herein. [17,59-72] Furthermore, examples where anionic groups are mainly installed to increase the solubility of the sensitizer (e.g. 9,10-anthroquionone sulfonate salts) in polar media without changing its reactivity in a significant manner are excluded.

2.2 Phenolate Catalyzed Oxyarylation of Olefins with Aryl Halides

The low pKa value of phenol, caused by the charge-stabilizing effect of the benzene ring, allows facile deprotonation in presence of base to afford the phenolate, which is able to undergo photochemical reactions under visible-light irradiation. Xia and co-workers examined several 4-phenylphenol derivatives as potential photocatalysts for the visible-light oxyarylation of olefins upon photoirradiation of aryl halides (Scheme 5). [73] 4-Phenylphenol PhPH bearing bulky tert-butyl groups adjacent to the phenolic alcohol (see Scheme 6) showed the highest catalytic efficiency and the corresponding oxyarylated products formed in presence of aryl halides 3, olefins 4 and TEMPOH could be isolated in moderate to good yields. Remarkably, the estimated...
The reaction scope of tolerated olefins comprises various styrenes, aliphatic olefins, allylic sulfonamide and alcohol derivatives, enol ethers as well as 1,1- and 1,2-substituted olefins. In addition, the method allowed for intramolecular cyclization reactions using aryl iodides and for the late-stage modification of pharmaceuticals. Noteworthy, the use of TEMPOH as H-atom donor and radical trap seems to be crucial due to the weak nature of the O−H bond and the high stability of the aminoxyl radical formed. The proposed reaction mechanism involves the deprotonation of the phenol PhPH by base and a PET from the photoexcited *PhPH* to the aryl halide 3.1. Upon cleavage of the halide anion, the resulting aryl radical is trapped by the olefin 4.1 causing a carbon centered radical 3.1b. Hydrogen atom transfer between the oxidized species of the catalyst and TEMPOH recovers PhPH and causes the stable radical TEMPO•. The oxyarylation product 5.1 is formed upon radical-radical coupling (Scheme 6). The formation of a ground-state electron donor acceptor complex (EDA) between phenolate anion and aryl halide was excluded by UV-vis measurements. Fluorescence quenching experiments and isolated TEMPO-trapping adducts of the aryl radical intermediate support the mechanistic hypothesis. Moreover, a radical clock experiment suggests the formation of a benzylic radical, whereas intramolecular trapping experiments disprove the involvement of a benzylic carbocation formed upon oxidation of the radical 3.1b.

### 2.3 Naphtholate-Catalyzed Dehalogenation and Detosylation

The first studies of the photochemical behavior of 2-naphtholate anion NA* date back to 1989, when the countercation, temperature and solvent were systematically evaluated regarding effects on the luminescence lifetime and the absorption and emission maxima.[10] In the same year, Soumillion and co-workers demonstrated the application of the naphtholate anion in the photocatalyzed defunctionalization of 2-chloronaphthalene and 4-chlorobiphenyl (6.2-3) in degassed, alkaline MeOH (Scheme 7, left).[22] This concept was further extended in a heterogenous approach where 2-hydroxynaphthoic acid was covalently anchored to a silica surface via amidation reaction. The efficiency of the dechlorination however was significantly decreased.[23] The substrate scope was later broadened to mono- and dichloronitrobenezences.[24] In addition, NA* was shown to catalyze the detosylation of sulfonamides in presence of excess NaBH₄ as terminal reductant (Scheme 7, right).[25] Following this procedure, 2-phenylethylamine (9.2) and N-methylbenzylamine (9.5) were obtained in quantitative yield starting from the respective sulfonamides. Although a stoichiometric amount of 2-naphthol (NA) was utilized, the catalyst could be efficiently regenerated. The proposed reaction mechanism suggests the deprotonation of NA to form the naphtholate NA*. Upon excitation with blacklight the photoexcited state of NA* is oxidatively quenched by either aryl chloride or sulfonamide, which causes the formation of NA• and an arene radical anion. After cleavage of the respective anionic leaving group ([Cl* or 4-Me(C₆H₅)SO₄*]), an aryl- or nitrogen centered radical is formed respectively. Abstraction of a hydrogen atom from the solvent affords the defunctionalized...
arenes. The N-centered radical converts to the amine via H-atom abstraction from either the solvent or NaBH₄. To close the catalytic cycle, NA⁺ is transformed to NA via hydrogen atom abstraction from the solvent or NaBH₄, followed by subsequent deprotonation (Scheme 8).

Scheme 8. Proposed photocatalytic cycle for the naphtholate anion.

Recently, a zwitterionic visible-light-absorbing benzimidazolium naphtholate BINA was successfully employed in photocatalytic deiodination and desulfonylation reactions in the presence of a combined electron and hydrogen atom donor 10 (see Scheme 10).[76] The cationic benzimidazolium moiety can be considered as separated from the naphtholate, due to the tilted structure that prevents σ-conjugation. The photocatalytic activity was studied using different solvents with attributed Lewis-basic or Lewis-acidic character estimated by donor and acceptor numbers. The authors concluded that Lewis-basic solvents cause tight interactions with the Lewis-acidic benzimidazolium moiety, whereas the electronic properties of the Lewis-basic naphtholate anion are less governed, resulting in an increased electron donating ability. The best results (Scheme 9) were found using DMF as solvent. Utilizing 10 mol% of catalyst BINA and 1.2 eq. of 10 enabled the formation of cyclized 12 in 82% yield. A lower catalyst loading of only 1 mol% resulted in full conversion of the iodoarene 11, however the product yield was lowered (69%). In addition to the cyclization of iodoarene, the photocatalytic reactivity was demonstrated based on the reductive desulfonylation of tertiary sulfonamides 13 and β-ketosulfones 15. The respective secondary amines and desulfonylated ketones were obtained in good yields. The proposed photocatalytic cycle is depicted in Scheme 10.

Scheme 9. Cyclization of iodoarene and scope of desulfonylation. *NMR yields; †DMF, 6 h.

Upon photoexcitation (λ > 390 nm), the zwitterionic excited state catalyst BINA⁺ (Eπ – Δ 0.28 vs. SCE) reduces 11 via PET. Subsequent cleavage of iodide followed by fast 5-exo-trig cyclization affords the primary radical 11b·. The oxidized photocatalyst BINA⁺ is regenerated in presence of a sacrificial reductant 10 (E1/2 = +0.34 V vs. SCE) via single electron transfer to give the radical cation 10⁺* which acts as hydrogen atom donor to form 12 and in turn is converted to the cation 10⁺. In presence of other terminal reductants e.g. Hantzsch ester (E1/2 = +0.93 V vs. SCE) no product was formed as the higher ground state oxidation potential renders an electron transfer towards BINA⁺ endergonic.

Scheme 10. Proposed catalytic cycle for the radical cyclization of iodoarene in presence of photoexcited benzimidazolium naphtholate.

In previously published work, photoexcited 1,3-dimethyl-2-hydroxybenzylbenzimidazoline (BIA-H,1) was found to convert N-sulfonamides and N-sulfonylamines into the respective desulfonylated products.[77] Based on these results, Hasegawa et al. further developed the catalytic system depicted in Scheme 10 by utilizing the in situ reduction of benzimidazolium arylxides (BIA) in presence of readily available boron hydride donors to generate the anionic species BIA-H⁻.[78]

Scheme 11. Proposed photocatalytic cycle for the desulfonylation reported by Hasegawa et al.

In addition to the reported electron donor and hydrogen atom donor abilities of the benzimidazoline scaffold (cf., Scheme 10), the resulting benzimidazolium arylxides BIA-H⁻ are equipped with a photoredox active unit, the arylxide moiety. Reductant, H-atom donor and photocatalyst are thus combined in one molecule. Various benzimidazoline arylxides BIA-H,1-5 (Scheme 11) were synthesized and characterized regarding their spectroscopic and electronic properties.[78] The calculated excited state oxidation potential for BIA-H,1-5 (E1/2 = −2.71 V vs. SCE) was found to be significantly enhanced compared to the zwitterionic species BINA, allowing the conversion of less activated substrates. The elaborated protocol was used for the reductive desulfonylation of N-sulfonilylides, -amides, -amines, and α-sulfonyl ketones, affording the unprotected secondary amines as well as the α-defunctionalized ketones in good to excellent yield (Scheme 12).
For the desulfonylation of α-carbonyls, a less reactive hydride donor PicBH₃ was used to avoid the direct reduction of the carbonyl group. Remarkably, utilizing the developed photocatalytic protocol allowed to convert diphenylosulfonamide (17,4) and dibenzylsulfonamide (17,5) almost quantitatively in 24 and 48 hours, respectively. Note that both substrates exhibit a challenging reduction potential \(E_{1/2} < -2\) V vs. SCE. All synthesized catalysts BIA.1-5 were successfully tested in the desulfonylation reaction of N-tosylindole 17.1 but BIA.1 (or BINA, cf. Scheme 10) showed superior catalytic activity. Changing the light-source from a xenon lamp (500 W, \(\lambda > 390\) nm) to a white LED (7.3 W) afforded comparable product yields, but the reaction time increased. No product was formed in the absence of photocatalyst and only traces were found in absence of hydride donor or light. Regarding the mechanism, the authors propose the in situ formation of BIA-H⁺ via nucleophilic attack of a hydride on the benzimidazolium moiety of BIA. Excitation with either Xe lamp or white LED renders the catalyst a strong photo-reductant and allows PET onto the substrate. The open-shell fragment formed upon N-S or C-S bond-rupture abstracts a hydrogen atom from the photocatalyst BIA-H⁺ which is turned into a biradical BIA: and, upon intramolecular single electron transfer, the benzimidazolium BIA is regenerated. Eventually, a hydride transfer activates the catalyst for another catalytic cycle (Scheme 11). The acidic hydroxy group on the aryl oxide is easily deprotonated and enables to directly employ the benzimidazolium BIA-H⁺ instead of the betaine BIA as catalyst. In that case, the addition of base (sodium carbonate or butoxide) increased the reaction efficiency significantly, indicating a facile deprotonation of BIA-H⁺.

2.4 Anthrolate-catalyzed Generation of Hydrated Electrons

Goetz and co-workers thoroughly investigated the potential use of anionic 9-anthrolate (ANT⁻) as a sustainable source for hydrated electrons which are ejected upon laser irradiation.[20] Hydrated electrons are among the strongest reductants[79–81] and are capable to directly reduce dinitrogen[82,83] or carbon dioxide.[84] Approaches to liberate solvated electrons photochemically often rely on high-energetic and harmful UV-C light. Notably, pulsed 355 nm UV-A laser irradiation of ANT⁻ in alkaline aqueous media afforded hydrated electrons via a biphotonic photionization pathway. The first photon generates the excited anionic species (S₁ state) and the absorption of another photon within the excited state lifetime of *ANT* stimulates photo-ejection of a hydrated electron. The catalytic cycle is closed in presence of the ascorbate dianion, which acts as sacrificial reductant recovering the catalyst from its oxidized species ANT⁺ (Scheme 13). The sequence of photionization and regeneration of the catalyst could be repeated several times until the system was exhausted. At the same time, the initial concentration of the catalyst remained constant, indicating the robustness of anthrolate against an attack of the exceptionally reducing solvated electron. Despite its minute molar absorption coefficient at the wavelength used for exciting the system, the ascorbate dianion Asc⁻ was found to slightly contribute in generating hydrated electrons.

A follow-up work of the Goez group[21] focused on the direct photoionization of the ascorbate dianion in absence of catalyst by applying a 355 nm laser pulse. A possible application of solvated electrons generated in this way was demonstrated based on the efficient dechlorination of chloroacetate as a generic pollutant in waste water detoxification.

2.5. Activation of Aryl chlorides with 9-Anthrolate

Recently, the photochemical properties and synthetic applications of a series of 9-anthrene derivatives were studied by König and co-workers and the corresponding anions were found to reach remarkable excited-state oxidation potentials.[22] In solution, anthrone ANT is in equilibrium with its enolic form and is easily deprotonated to give the visible-light-absorbing anthrolate ANT⁻. The most efficient catalysts examined in that work are depicted in Figure 3.

In solution, anthrone ANT is in equilibrium with its enolic form and is easily deprotonated to give the visible-light-absorbing anthrolate ANT⁻. The most efficient catalysts examined in that work are depicted in Figure 3.
These photocatalysts were proved successful in catalyzing the C–H arylation reaction of several (hetero)aryl chlorides with electron-rich (hetero)arenes, isocyanides, phosphine and B$_2$pin$_2$ (Scheme 14). In presence of base, anion ANT is deprotonated, which causes a red-shift in the absorption spectrum with a new distinct absorption band arising in the visible range. Upon excitation with blue LED light, the strongly reducing excited anion "ANT" is formed (cf., Table 1, Entry 5 for ANT). Exceeding the reduction potential of the aryl chloride, oxidative quenching of the excited catalyst would form an arene radical anion 21.1° and the open-shell ANT. A subsequent mesolytic bond cleavage gives rise to a reactive aryl radical 21.1a, which is trapped by an electron rich arene 22. In alkaline media, the emerging bicyclic radical intermediate gets deprotonated to afford the radical anion 21.1b°. The catalytic cycle is closed via electron transfer from 21.1c° to ANT (Scheme 15). Time-resolved luminescence quenching experiments of the excited photocatalyst ANT with various tolerated aryl chlorides shortened the lifetime, whereas unsuccessful aryl chlorides caused no quenching.

![Scheme 15](image)

**Scheme 15.** Proposed mechanism of the photocatalyzed C–H arylation in presence of 9-anthracene.

TEMPO-trapping experiments confirmed the formation of aryl radical 21.1a° and bicyclic radical 21.1b°. Remarkably, in contrast to other photocatalyzed procedures for aryl halide activation[40,52,84] no sacrificial electron donor (e.g. DIPEA) was necessary and the scope of aryl chlorides as well as tolerated radical trapping reagents could be broadened. In the model reaction, the catalyst loading could be lowered to 5 mol% (92% yield) which indicates a turn-over number greater than 18. In accordance with recently reported photocatalyzed C–H arylation procedures[40,52,84] it was found that excess of the trapping reagent is crucial for reaction outcome, as a stoichiometric amount with reference to the aryl halide resulted in significantly decreased product yield. Anthrolates are converted in presence of oxygen yielding the corresponding anthraquinones, thus reactions were carried out under inert atmosphere. Noteworthy, acridone (ACO) afforded the desired arylation product 23.2 in good yield (83%) in non-degassed solvent and in presence of air, indicating an increased stability in presence of oxygen.

### 2.6. Anthrolate Catalyzed C–H Carboxylation of (Hetero)arenes and Styrenes with CO$_2$

Very recently, the visible-light-absorbing, strong photocatalytic tetramethoxanthrolate TMA° ($E_{\text{onset}} = -2.92$ V vs. SCE) was utilized to achieve the photocatalytic direct reduction of (hetero)arenes and styrenes to their respective radical anions.[85] The associated nucleophilic character of such electron rich species was exploited in C–H carboxylation reactions with gaseous CO$_2$ affording the aromatic carboxylic- and cinnamic acids in moderate to excellent yields. Among others, non-

The regioselectivity of the carboxylation reaction can be predicted by theoretical means. In contrast to the carboxylation mediated by organometallic reagents, the reported photocatalyzed, redox-neutral insertion of CO$_2$ into non-activated sp$^2$-hybridized C–H bonds benefits from increased regioselectivity, giving rise to only one regioisomer 26.18 and 26.25, respectively. In presence of base, TMA is in equilibrium with the anionic form, which in contrast to the neutral species shows distinct absorption in the visible range. Excitation with a blue LED generates the excited state of the anionic catalyst "TMA" which acts as a remarkably strong photo-reductant. Upon SET, benzophenone 24.20° is reduced to the resonance stabilized radical anion 24.20°. Subsequent nucleophilic attack affords the carboxylic acid 24.20a°. The closure of the catalytic cycle is proposed to occur via an electron-rich radical dianion intermediate 24.20b°, formed upon deprotonation of 24.20a°, which regenerates the active anionic catalyst by single electron transfer causing the carboxylation 24.20c°. Eventually, acidic work-up affords the carboxylic acid 26.20 (Scheme 17). An alternate pathway via direct H-atom abstraction from 24.20a° caused by the open-shell species TMA° is also conceivable. In both cases, the gain in energy upon re-aromatization of the compound is considered as the driving force to close the catalytic cycle.
The mechanistic hypothesis was supported by time-resolved luminescence quenching experiments of the catalyst *TMA* in presence of (hetero)arenes and styrenes. Tolerated substrates shortened the excited-state lifetime of the photocatalyst and linear Stern-Volmer plots could be developed. Although the direct reduction of CO₂ (*E*ₐₓ = −2.21 V vs. SCE)²⁹ by the excited catalyst is thermodynamically feasible, a DMSO solution saturated with carbon dioxide was found to scarcely affect the excited-state lifetime. Examined substrates that showed quenching of the photoexcited state of the catalyst however failed to give the respective carboxylic acids are considered to exhibit insufficient nucleophilicity when present as radical anions and thus do not react with carbon dioxide. In addition, deuterium-labelling experiments of 24.21 in presence of D₂O and 'BuOD respectively, caused the incorporation of deuterium into the reactive C-2 position, which supports the assumption of a basic radical anion intermediate.

### 2.7. Catalytic Reactions of Anionic Metal Complexes

Transition-metal complexes like the Ru(II) polypyridine or the cyclometalated Ir(III) found widespread applications in photocatalysis, as they are photostable, show tuneable redox potentials and their excited states lifetimes are usually durable. In contrast to neutral complexes like fac-Ir(ppy)₃ or cationic metal-based sensitizers [e.g. Ru(bpy)₂⁺, Ir(ppy)₂(dtbbpy)²⁺], anionic transition-metal complexes are barely explored, which could be attributed to photo decomposition with monodentate anionic ligands and the shortage of more stable diatomic ancillary ligands available. Godbert and co-workers were able to synthesize and characterize the anionic iridium complex 28.1 with a diatomic orotate ligand (Scheme 18, top).²⁸ Later on, the complex was modified by exchanging the 2-phenylpyridine ligands with coumarin-derived ligands (28.2) to increase the visible-light absorption. The authors successfully demonstrated the use of 28.2 in visible-light-driven H₂ generation which resembled the first example of a photoinduced electron transfer using an anionic Ir(III) sensitizer.²⁷

Based on the well-established fac-Ir(ppy)₃, Weng and co-workers utilized a trisulfonated analogue 29⁺ (Scheme 18, top), which renders the sensitizer water-soluble and negatively charged, to generate hydrated electrons. A potential use of hydrated electrons in waste water treatment was demonstrated by the degradation of chloroacetate (Scheme 18, 31.1) and benzyltrimethylammonium salt (31.3). In addition, the defluorination of trifluoromethylbenzoate is possible in presence of such a strong reductant (31.2). The catalytic cycle is depicted in Scheme 18 (bottom right). The photocatalyst is excited with a 447 nm collimated diode laser. Remarkably, the absorption of a second photon stimulates the ejection of the electron within the lifetime (~1.6 µs) of the excited sensitizer. The photocatalyst is then regenerated by either sodium ascorbate or triethanolamine acting as sacrificial electron donors. Compared to the neutral fac-Ir(ppy)₃, the excited state oxidation potential of the anionic sensitizer 29⁺ (*E*ₐₓ = −1.89 V vs. SCE) was found to be slightly increased.

The trianionic, rare-earth-metal catalyst hexachlorocerate(III) [Ce₃Cl₆]²⁻ was found to be effective in the reductive dehalogenation of aryl halides 32.1 using UVA light (Scheme 19).²⁹ This complex is stable to air and moisture and can be generated in situ by mixing CeCl₃ and NELCl in acetonitrile. Blacklight irradiation causes a metal centered excited state with very negative potential (*E*ₐₓ = −3 V vs. SCE)²⁶ enabling a PET to the aryl halide 32.1 to afford a Ce⁶⁺ species. Interestingly, the reaction could also be performed with a catalytic amount of CeCl₃, owing to the complementary oxidative photochemistry of [Ce₃Cl₆]²⁻ (Scheme 19, right).²⁶ The addition of toluene (34) as the terminal reductant allowed to close the catalytic cycle in which it is converted to benzyl chloride 34b upon hydrogen atom abstraction and reaction with Cl⁻²⁻.

![Scheme 17](image1.png)

Scheme 17. Proposed reaction mechanism for the redox-neutral, photocatalyzed carboxylation of (hetero)arenes and styrenes utilizing TMA as strong photo-reductant. Calculated Mulliken spin populations for 24.20⁺ allow to predict the regioselectivity of the carboxylation.

![Scheme 18](image2.png)

Scheme 18. Negatively charged iridium complexes (top), Ir(ppy)₂⁺ catalyzed degradation of pollutants (center); Conversion was determined by crude NMR. Reaction conditions: Chloroacetate 61.1 (12.5 mM), NaHAsc (2.2 eq.) in D₂O (3 mL), 4 h; Reaction conditions: Trifluoromethyl arene 61.2 (15 mM), TEOA (5 eq.) in H₂O (16 mL), 4 h; Reaction conditions: Benzyltrimethylammonium salt 61.3 (10 mM), TEOA (5 eq.) in D₂O (3 mL), 3 h. Proposed catalytic cycle for the generation of hydrated electrons (bottom right).
In a follow-up work, the developed catalytic protocol was utilized for the photoinduced Miyaura borylation of aryl bromides and chlorides. Schelter and co-workers used diboron esters which functioned as both borylation reagent and terminal reductant to close the catalytic cycle.[99] Various aryloboronic ester could be obtained in moderate to good yields starting from substituted (hetero)aryl chloride derivatives (Scheme 20). Notably, Stern-Volmer quenching experiments revealed that both electron deficient and electron rich substrates do quench the luminescence of the cerium catalyst. The authors also demonstrated that a sequential borylation and subsequent Pdt-catalyzed cross-coupling reaction of the formed aryloboronic ester is possible. This procedure is beneficial as it avoids prior isolation of the boronate ester. Based on spectroscopic investigations and experimental findings, a reaction mechanism was proposed (cf. Scheme 19). The in situ formed $[\text{Ce}^{4+}\text{Cl}]^{−}$ gets photoexcited by blacklight. Upon PET towards 35.1 and loss of $\text{Cl}^{−}$, an aryl radical is formed which reacts with the diboron ester 36.1 to yield the aryl boronic ester 37.1 and a boryl radical $\text{B}^\cdot \text{(OR)}^\cdot$. The oxidized catalyst is regenerated in presence of excess $\text{Cl}^{−}$ via photoinduced ligand-to-metal charge transfer giving rise to the radical anion $\text{Cl}^{2−}$. A reaction quantum yield $\phi > 1$ was found by actinometry indicating a radical chain mechanism however, no product formation within the dark periods of an intermittent-light experiment was observed. The authors consider the boryl radical, which is stabilized in presence of $\text{Cl}^{−}$, to presumably propagate a chain mechanism via reaction with another substrate molecule.

(Relevant part of text continues here.)
Wu and co-workers disclosed the oxidant-free, site- and E-selective dehydrogenative alkenylation of alkanes or aldehydes with alkenes by combining decatungstate HAT photocatalysis and cobaloxime catalysis.[107] This dual-catalytic strategy enables efficient and direct alkenylation of C–H bonds with hydrogen gas being the sole by-product. A broad range of alkanes and aldehydes could be alkenylated. Notably, aryl halides (Cl, Br, I) alkyl bromides, alkenes and alkynes were tolerated which enables subsequent orthogonal functionalization via transition-metal catalysis. Moderate to good regioselectivity was observed for alkane substrates 42.13–14 and 42.19. In addition, the concept could be employed to the late-stage alkenylation of natural products (Scheme 23).

The excitation of the metal oxide cluster [W_{10}O_{28}]^{5–} (TBADT) enables the abstraction of a hydrogen atom from alkanes or aldehydes 42.1 and subsequent addition of the resulting carbon-centered radical 42.1a to an alkene 43.1 would furnish intermediate 42.1b. This species is expected to be reversibly captured by the Co(II)-complex 45.1 to form the alkyl-Co(III) intermediate 45.2.

Upon light-mediated formal β-H elimination the product 44.1 and Co(III)–H species 45.3 is formed, which reacts with a proton to release H₂ and the Co(III)-complex 45.4. Eventually the decatungstate and the cobalt catalyst are regenerated via SET (Scheme 24).

Wang et al. recently published the TBADT/Ni dual-catalytic asymmetric acyl-carbamoylation of tethered alkenes using a chiral nickel catalyst to form oxindole motifs bearing a quaternary stereogenic center 49.2–5 (Scheme 25).

The reaction starts with H–atom abstraction from the aldehyde by the excited decatungstate catalyst *[W_{10}O_{28}]^{5–}* and the resulting acyl radical 47.1a is captured by *in situ* formed Ni(0) to yield an acyl Ni(II) intermediate 50.2. Oxidative addition of the carboxamoyl chloride to 46.1 causes a Ni(III) species 50.3. In the enantioselective step, migratory insertion to the tethered double bond takes place (50.4) and subsequent reductive elimination affords the cyclized product 49.1 along with Ni(II) chloride 50.5. Both catalytic cycles are closed via SET presumably between the reduced decatungstate [W_{10}O_{28}]^{6–} and Ni(II)Cl 50.5 (Scheme 26).

Another example for a light-mediated asymmetric C–H functionalization was recently demonstrated by Pu-Sheng Wang and co-workers.[108] Upon hydrogen atom abstraction by TBADT, an alkyl, benzyl or allyl radical adds to an exocyclic enone and the resulting α-carbonyl radical regenerates the photocatalyst via hydrogen atom transfer. In the enantioselective step, the formed enol-intermediate is protonated by an aligned chiral spiror phosphoric acid generating a stereocenter in α-carbonyl position.

Based on the synergy of decatungstate HAT catalysis and nickel catalysis, Wang and co-workers demonstrated the acylation of aryl halides and α-bromo acetates with aromatic and aliphatic aldehydes and the resulting aromatic ketones could be obtained in moderate to good yield.[109] In a similar fashion, the group of Zheng disclosed very recently the direct C–H arylation of
aldehydes enabled by merging decatungstate HAT photocatalysis and palladium cross-coupling catalysis. Applying this methodology allowed for the efficient linkage of various (hetero)aryl bromides, iodides and triflates with aliphatic aldehydes. Moreover, TBADT was shown to promote H/D exchange reactions of formyl C–H and a wide range of hydridic C(sp³)–H bonds in a synergistic system comprised of HAT photocatalyst and thiol catalyst. In presence of D₂O, this protocol allowed for the regioselective incorporation of deuterium into pharmaceutical relevant molecules and drug precursors. Furthermore, a few examples are known where polyoxometalates equipped with binding sites on the cluster shell or in presence of co-catalysts participate in reductive CO₂ activation or H₂ generation.

3. Excited Anionic Compounds as Reagents

Besides using a light-harvesting anionic catalyst as demonstrated in Section 2, chemical reactions can also be promoted via a direct photoexcitation of anionic reagents which will be discussed in the following part.

3.1 Excited State Phenolate as Photoreductant

Recently, Xia and co-workers made use of the remarkable excited-state potential of the phenolate 52.2 (E₁/₂ = −2.48 V vs. SCE) in a Heck-type arylation reaction promoted by blue LED light. Using a [112] excited state potential of the phenolate −63.2 V/2, the formed arylation products are high for most of the isolated compounds. The mild reaction conditions allowed to convert complex, biologically active substrates like chlorogenic acid, esculin and scutellarin. Upon deprotonation of the phenolic OH group, the absorption spectrum of 52.2 in DMSO is shifted towards longer wavelength enabling direct excitation of the phenolate 52.2⁻ with blue light. From the photoexcited state *52.2⁻* (Scheme 28) an electron transfer to the aryl halide 51.1 is feasible and subsequent cleavage of bromide forms the reactive aryl radical 51.2⁻, which preferentially couples to electron rich species like the vinylphenolate 52.2⁻:

The resulting radical anion 51.2⁻ is assumed to either initiate a radical chain mechanism by reducing another equivalent of 51.2 which affords the desired Heck-type arylation product 53.2 (Path b), or is converted to the latter in presence of the phenoxy radical 52.2 via direct hydrogen atom transfer or electron transfer followed by a proton shift (Path a).

Melchiorre and co-workers have recently demonstrated how phenolate can elicit the generation of perfluoroalkyl radicals via single electron transfer. The developed method allows for the direct perfluoroalkylation and trifluoromethylation of phenols bearing electron withdrawing substituents 57.2-15 (Scheme 29). In presence of the non-nucleophilic base 1,1,3,3-tetramethyldiguandine (TMG) the absorption spectrum of salicylaldehyde (55.2) is red-shifted and no change was observed upon addition of the perfluoroalkyl iodide 56.1, excluding the formation of a ground state EDA complex. The base-induced bathochromic shift allowed for the use of a CFL bulb as light source. Using a 300 W Xe lamp with cut-off filter (λ > 385 nm) still allowed to form the product however in slightly decreased yield. The proposed mechanism of this transformation (Scheme 30) starts with a SET from the photoexcited phenolate *55.1⁻* to 56.1. Subsequent reductive cleavage of iodine gives rise to a perfluoroalkyl radical 56.1⁻.

The synthetic utility was demonstrated based on the arylation of methyl 4-hydroxycinnamate 52.2 with various (hetero)aryl halides 51.1 (Scheme 27). In addition, other derivatives of cinnamic acid (52.2-13, 52.19), and flavonoids (52.16-18, 52.20) were shown to react smoothly via the generated aryl radical to afford the respective arylation products (53.1 & 54.1) in moderate to good yields. Remarkably, as the proposed mechanistic cycle is redox-neutral, no sacrificial electron donor is necessary. Besides electron deficient aryl iodides, the scope includes electron rich as well as electron neutral derivatives. In contrast, arylation products formed with less activated aryl bromides and chlorides are only shown with activated, electron deficient arynes. The E/Z ratios of the formed arylation products are high for most of the isolated compounds. The mild reaction conditions allowed to convert complex, biologically active substrates like chlorogenic acid, esculin and scutellarin. Upon deprotonation of the phenolic OH group, the absorption spectrum of 52.2 in DMSO is shifted towards longer wavelength enabling direct excitation of the phenolate 52.2⁻ with blue light. From the photoexcited state *52.2⁻* (Scheme 28) an electron transfer to the aryl halide 51.1 is feasible and subsequent cleavage of bromide forms the reactive aryl radical 51.2⁻, which preferentially couples to electron rich species like the vinylphenolate 52.2⁻:

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In the bond-forming step, the radical is trapped by the ground-state phenolate yielding a cyclohexadienyl radical \( \text{56.1b}^* \) which propagates the reaction by reducing another equivalent of \( \text{56.1} \) via SET. Subsequent proton shift affords the alkylated phenol \( \text{57.1} \). Stern-Volmer quenching studies of the phenolate in presence of alkyl iodide support the mechanistic proposal. For \( \alpha \)-substituted phenols the perfluoroalkylation proceeds with moderate regioselectivity giving rise to \( \alpha \)-, \( \beta \)-monoalkylated and \( \alpha,\beta \)-dialkylated products, whereas \( \beta \)-substituted phenols caused the formation of \( \alpha,\alpha',\beta \)-dialkylated products.

Monitoring the product distribution over the reaction time revealed that \( \alpha \)- and \( \beta \)-alkylated products are formed as intermediates and are further converted to bifunctionalized \( \text{ortho, para-} \)adducts. Non-substituted or methoxy-substituted phenols as well as nitrophenols failed to convert. Employing phenol \( \text{55.12} \) bearing electron withdrawing groups in \( \text{ortho} \) and \( \text{para} \) position afforded the mono-alkylated product as sole isomer. The demonstrated scope of perfluoroalkyl iodides comprises \( C_8, C_6, C_4 \) and \( C_1 \) chains (57.12-15).

### 3.2. Visible-light-promoted Arylation of Azaallyl Anions

Chruma and co-workers demonstrated how irradiation of the colored azaallyl anion \( \text{58.1}^* \) with visible light notably increases its excited state oxidation potential.\(^{[14]}\) In presence of strong bases (\( pK_a \) conjugated acid > 32), the formed 2-azaallyl anion acts as super-electron-donor in the dark\(^{[16]}\) and had been successfully employed in the functionalization of non-activated aryl iodides and tertiary alkyl halides.

The accessible substrate scope could be extended by employing visible light causing enhanced reduction potentials and allowed for the conversion of non-activated bromo- and chloro- (hetero)arenes \( \text{59.1} \), which are present in large excess with reference to \( \text{58.1} \). The regioselectivity of the arylation reaction is moderate and product mixtures of \( \text{60.1} \) and \( \text{61.1} \) are usually obtained (Scheme 31).

The authors propose an electron transfer from the excited state azaallyl anion \( \text{58.1}^* \) to the aryl halide \( \text{59.1} \). After cleavage of the carbon-halogen bond, a reactive transient aryl radical \( \text{59.1a}^* \) is formed which reacts with the stabilized azaallyl radical \( \text{58.1}^* \) to form the arylation products (Scheme 32).

### 3.3. Synthesis of Pyrazoles via Irradiation of \( N \)-centered Hydrazide Anions

Zhu and co-workers reported a series of substituted hydrazides \( \text{62.1} \) which are able to undergo cyclization in presence of base, affording pyrazole derivatives \( \text{63.1} \) mediated by sunlight.\(^{[16]}\) The UV-vis spectrum of the anionic hydrazide exhibits a significant red-shift compared to the neutral parent, enabling the use of visible light to accomplish the cyclization reaction. Selected examples of formed pyrazoles are depicted in Scheme 33.

The authors propose two possible mechanistic pathways (Scheme 34): Deprotonated \( \text{62.1}^* \) gets photoexcited and undergoes either direct anionic cyclization to \( \text{62.1a} \) (Path a) or is oxidized by \( O_2 \) to afford the \( N \)-centered radical \( \text{62.1}^* \) (Path b) which, upon intramolecular radical cyclization (\( \text{62.1a}^* \)) followed by...
cleavage of a tosyl radical, yields the pyrazole 63.1. Decreased yield is obtained when conducting the reaction under N₂ atmosphere or in presence of the radical trap TEMPO, indicative for the latter mechanistic proposal. Notably, the reactions were also shown to operate in water, however resulted in decreased yields.

Scheme 34. Proposed photoinduced reaction mechanism towards pyrazole formation.

3.4. Utilizing Phthalimide Anions for H-Atom Abstraction

Already in 1988 the exceptionally high ability of the excited phthalimide anion 64* to abstract hydrogen atoms from alcoholic solutions was recognized 117. This procedure was further developed and could be extended to ethers, alkylbenzenes and amines, affording the reductive addition products with phthalimide (Scheme 35).118 The use of 4-methylanisole afforded a product mixture (66.8a-b) as H-atom abstraction is possible from the methoxy group or in benzylic position. In alkaline solution, phthalimide 64 is in equilibrium with its conjugate base 64*. The photoinduced electron transfer from 64* to ground-state phthalimide is a thermodynamically favourable process. Thus, the authors propose the phthalimidyld radical 64 as the hydrogen atom abstracting intermediate, which evolves from the excited anion 64* upon PET towards phthalimide 64.

Scheme 35. Light-triggered reductive alkylation of phthalimide. Yields are given on consumed phthalimide. Equivalents used of the hydr. are given in brackets. *Deviation from reaction conditions: 64 (13.6 mmol), NaOH (16 mL, 1x), BuOH (150 mL), mercury lamp (125 W), 5 h; *Deviation from reaction conditions: 64 (13.6 mmol), NaOH (10 mL, 1x), MeOH (160 mL), mercury lamp (125 W), 1 h.

Remarkably, the electrophilic radical 64* is able to activate C-H bonds possessing high bond dissociation energies (e.g. BuOH, E_{\text{Diss}} = 100 ± 2 kcal mol⁻¹) 119 and upon hydrogen abstraction, phthalimide 64 and the alkyl radical 65.9 are formed. Radical-radical coupling between the phthalimide radical anion 64* and the carbon-centered radical 65.9 affords the addition product 66.9 (Scheme 36).

3.5. Photocycloadditions of Phthalimide and Saccharin Anions

The formation of [2]benzazepine-1,5-dione derivatives 68.1 via [2+2] photocycloaddition using phthalimide 64 was previously limited to electron poor non-cyclic alkenes, due to competing excited-state electron transfer reactions. 120,121 Suau and co-workers thus mitigated the oxidizing strength by employing the anionic sodium phthalimide 64* and obtained efficient, regiocontrolled photocycloaddition with a broader range of alkenes being tolerated (Scheme 37). In contrast to the neutral species, 64* shows significant fluorescence emission, which was markedly quenched upon alkene addition indicating that the singlet excited state 64* is the reactive intermediate. The [2+2] cycloaddition of the photoexcited phthalimide anion to double bonds is a stereospecific process yielding the ring expanded cis-68.1 adduct. Epimerization caused by the alkaline media affords a mixture of cis- and trans-68.1 (Scheme 38).

Scheme 36. Light-mediated C-H abstraction and radical addition to phthalimide radical anion 64* initiated by the phthalimide radical 64*.

Scheme 37: [2+2] photocycloaddition of excited phthalimide anion with alkenes. *64 (6.8 mmol), NaOH (8 mL, 1M, 1.2 eq), MeCN/H₂O (160 mL, 7:1), 0.5 h, 125 W mercury lamp; *64 (6.8 mmol), NaOH (pH=10), MeCN/H₂O (7:1), 0.5 h, 125 W mercury lamp; *mixture of cis- and trans-68 was obtained; *64 (6.8 mmol), NaOH (10.2 mL, 1M, 1.5 eq), MeCN/H₂O (7:1), 2 h, 400 W mercury lamp.

Scheme 38. Proposed mechanism for the [2+2] photocycloaddition of phthalimide anion with cyclohexene.

The photoexcited saccharin anion 69* was recently found to show similar reactivity towards alkenes, which was utilized in regioselective ring expansion reactions giving benzosultams.
71.2-6 (Scheme 39) starting from the cheap and commercially available sweetener saccharin. \[122\]

![Scheme 39. Selected examples of isolated benzosultams upon ring expansion with alkenes. Reaction conditions: Photoflow reactor 0.75 mm internal diameter. *Phenylacetylene was used.](image)

Remarkably, common approaches to form benzo-fused seven-membered sultam derivatives are multistep reactions and rely on the use of toxic organotin hydrides \[123\] or expensive Pd catalysts \[124\]. A mechanism was proposed based on experimental and computational studies, suggesting the prevailing population of the $S_2$ state upon irradiation of the saccharin anion $69^{-}$. The computed data indicate a fast deactivation into the first singlet state. Presumably, the key step towards benzosultam formation is a nucleophilic attack of the nitrogen of the excited state. Regioselectivity is gained due to the formation between carbonyl group and alkene is expected to occur in the ground state. Regioselectivity is gained due to the kinetic preference of the nucleophile and computational studies, suggesting the prevailing population of the $S_1$ state upon irradiation of the saccharin anion $69^{-}$. A mechanism was proposed based on experimental and computational studies, suggesting the prevailing population of the $S_2$ state upon irradiation of the saccharin anion $69^{-}$.

For a more detailed study we refer to recent excellent reviews. \[125,126\]

Organic anions are also reported to form ground-state electron donor-acceptor (EDA) complexes with electron deficient species usually accompanied by the appearance of a new red-shifted charge-transfer absorption band. During the last years, EDA photochemistry has become increasingly popular. Among others, we highlight herein three examples to demonstrate the concept of organic anions participating in EDA complex formation. For a more detailed study we refer to recent excellent reviews. \[125,126\]
The aromatic perfluoroalkylation of $\alpha$-cyano arylacetates 72.1 developed by Melchiorre and co-workers \[127\] is mediated by visible light (CFL 23 W) although neither enolate 72.1 nor perfluoroalkyl iodide 56.1 or TMG show absorbance in that range of light. Mixing all the reagents together however results in a colored solution featured by a strong bathochromic shift in the absorption spectrum indicative for the formation of an EDA complex. Irradiation of $\beta$-substituted substrates allowed to perfluoroalkylate $\alpha$-cyano arylacetates selectively in ortho position.

![Scheme 40. Proposed reaction mechanism for the light-promoted formation of benzosultams.](image)

**3.6. Organic Anions involved in Donor-Acceptor Complexes**

Organic anions are also reported to form ground-state electron donor-acceptor (EDA) complexes with electron deficient species usually accompanied by the appearance of a new red-shifted charge-transfer absorption band. During the last years, EDA photochemistry has become increasingly popular. Among others, we highlight herein three examples to demonstrate the concept of organic anions participating in EDA complex formation. For a more detailed study we refer to recent excellent reviews. \[125,126\]

![Scheme 41. Selected examples for the perfluoroalkylation of (hetero)arenes. *Yield determined by $^{19}$F-NMR.](image)

A mixture of regioisomers was obtained when $\alpha$-substituted substrates were employed. In accordance with the proposed homolytic aromatic substitution (HAS) pathway lower yields were obtained with electron deficient arenes. Following the developed protocol, the substrate scope could be extended including heteroarenes and $\alpha$-cyano phenylketone (Scheme 41). Control experiments revealed that the formed product inhibits the reaction as the forming enolate 73.1 outperforms the absorbance of the EDA complex. This issue was addressed by utilizing a biphasic system consisting of tetradecfluorohexane and MeCN, which allowed for higher yields and a shorter reaction time.

![Scheme 42. Proposed reaction mechanism for the perfluoroalkylation of $\alpha$-cyano arylacetates involving the formation of a visible-light-absorbing EDA complex.](image)

The radical chain reaction is initiated by the base-promoted formation of the EDA complex 72.1$^−$-EDA, which absorbs visible light and releases a radical pair upon reductive cleavage of iodine consisting of the benzyl radical 72.1 and a perfluoroalkyl radical 56.1. The electron rich enolate 72.1 reacts with the alkyl radical $\alpha$ via HAS to afford the radical anion intermediate 72.1a$^−$. Chain propagation is assumed either by SET affording 72.1b or via atom-transfer radical addition (ATRA, 72.1c$^-$) followed by cleavage of HI. Reaction work-up yields the perfluoroalkylated product 73.1. Termination of the radical chain is possible upon direct radical-radical coupling of 72.1 and 56.1 (Scheme 42).

The Miyake group made use of the EDA complex formed between an electron rich thiolate anion 74.1 and aryl halides 75.1 to afford a broad scope of aromatic thioethers 76.1. \[128\] The
protocol allowed to convert both electron rich and poor thiophenols under visible-light irradiation and in presence of caesium carbonate (Scheme 43). Remarkably, tolerated aryl halides are not limited to activated, electron-deficient arenes, as thioethers were formed with iodobenzene and toluene; however, a prolonged reaction time was required (20-24 h).

Remarkably fast coupling reactions (1 h) were observed between electron deficient aryl halides and electron rich thiophenols. In addition, benzylic halides revealed to convert similarly. Following the developed protocol allowed for the mild and efficient late-stage functionalization of pharmaceutically active compounds.

The formation of an EDA complex \(74.2^\text{•-EDA}\) between thiophenate \(74.2\) and aryl halide \(75.2\) was confirmed by UV-vis spectroscopy and TD-DFT calculations: The arising charge-transfer absorption band allows to initiate the reaction with visible light via an electron transfer from the thiolate anion to the aryl halide, followed by cleavage of the halide anion. The formed thyl- and aryl radical combine to afford the C=S cross-coupled product \(76.2\) (Scheme 44).

Based on the perfluoroalkylation of alkenes and alkynes, it was recently shown that the anionic counterpart involved in the EDA complex formation can be utilized catalytically.\(^{[129]}\) In presence of base, 2-bromophenyl (BrPhOH) was found to promote the visible-light-mediated 1,2-addition of fluoroalkyl iodides to alkenes and alkynes. Noteworthy, although a significant amount of product was formed in the reaction of allylbenzene \(77.2\) and ethyl iodo difluoroacetate \(56.8\) in absence of phenol catalyst, the yield could be doubled using a catalytic amount of BrPhOH. The use of a more polar solvent gave rise to Heck-type coupling products. Allylphenols, acting themselves as catalyst, could be converted to either the addition product \(79.1\) or the coupling product \(80.1\) without adding BrPhOH.

Initiation of the reaction is proposed to occur via EDA complex formation between phenolate BrPhO\(^{\text{•-}}\) and alkylating reagent \(56.6\). The photoexcited EDA complex causes the formation of radical \(56.6^\text{•-}\), which reacts with the olefin \(77.1\) to yield the radical intermediate \(77.1a^\text{•-}\). Depending on the reaction medium, either abstraction of an iodine atom from \(56.6\) affords the addition product \(79.1\) or SET with \(56.6\) gives rise to the cationic intermediate \(77.1a^\text{+}\), which forms the Heck-type product \(80.1\) upon deprotonation (Scheme 45).

**3.7. Organic Anions Promoting the Radical-Nucleophilic Substitution (S\(_\text{nn}\)1) Reaction**

In the course of S\(_\text{nn}\)1 reactions, radicals and radical anions are formed as intermediates and chain mechanisms are likely to occur. Proposed for the first time in the 1960s,\(^{[130,131]}\) the reaction affords nucleophilic substitution on aromatic and aliphatic compounds and tolerates a wide scope of nucleophiles and substrates.\(^{[132]}\) Initiation is commonly achieved by photoinduced electron transfer from an electron-rich anionic nucleophile to an electron-poor acceptor, leading to the open-shell nucleophile Nu\(^{\text{•-}}\) and a radical anion. EDA complex formations between nucleophile and substrate are reported and allow to initiate S\(_\text{nn}\)1 reactions by using less-energetic light.\(^{[123]}\) Upon mesolytic bond cleavage, the resulting radical R\(^{\text{•+}}\) is trapped by the nucleophile and forms a radical anion. A single electron transfer from the radical anion [R-Nu\(^{\text{•-}}\)] to the acceptor R-X affords the desired substitution product along with another radical anion [R-X\(^{\text{•+}}\)], which enables the propagation of a chain reaction (Scheme 46), provided that this SET is thermodynamically favourable.
Closely related to the concept of the light-induced S_{N}1 reaction is the photoinitiated base-promoted homolytic aromatic substitution reaction (photo-BHAS), affording C–H arylated products starting from aryl or alkyl halides in presence of a strong base (e.g. KO’Bu or NaH). The reactive intermediate R’ is proposed to add to the arene forming an aromatic radical, which is converted into the respective radical anion by deprotonation and eventually gives the arylated product upon SET to propagate the chain reaction. In absence of further additives, it has recently been shown that the dimsyl anion can be excited by visible light and plays a pivotal role for initiating the reaction (see Scheme 46).[133] The initiation of the BHAS reaction was also reported by other photo-activation modes e.g. through PET from an iridium sensitizer to R-X, or upon light-excitation of an in-situ formed photosensitive complex between KO’Bu and phenanthroline.[134,135] Non-nucleophilic bases are commonly employed to avoid the competing S_{N}1 reaction pathway. Light-mediated substitutions following the S_{N}1 reaction with organic anions as nucleophiles have been studied extensively and were subject of recent reviews[4,132,136–140] and thus will not be further discussed herein.

### 3.8. Direct Photodecarboxylation of Carboxylates

In presence of light, various organic carboxylates are known to undergo photodecarboxylation (PDC) affording CO₂ and either a carbonan intermediate (heterolytic cleavage) or an alkyl radical intermediate in combination with a solvated electron (homolytic cleavage). Meiggs et al.[141] performed flash photolysis of sodium phenyl acetate and could proof the formation of a benzyl radical intermediate by transient absorption spectroscopy. The formation of toluene, besides polyacids and dibenzyl, may suggest a competing heterolytic bond cleavage mechanism. Reaction pathways via high-energetic carbonan or radical intermediates are favoured in compounds’ binding stabilizing substituents. Hence, PDC is often observed upon irradiation of dissociated aryl acetic acids 81.1, causing intermediates which benefit from benzyl stabilization (Scheme 47). The light-mediated decomposition of carboxylates has been covered in detail in various reviews and thus is beyond the scope of this work.[142–144]

Photosis are important initiators of photopolymerization processes. Xanthone and thioxanthone acetic acids (81.7-8) form carbonan upon decarboxylation and have recently received interest as amine free alternatives to enable efficient thiol-epoxy polymerization.[145,146]

### 3.9. Sulfite Anions used in Photoreactions

The ability of cheap and available sulfite salt to generate hydrated electrons upon irradiation renders its use attractive (Scheme 48). The method was successfully applied for the photodegradation of hazardous halogenated pollutants like monochloroacetic acid[147] 83 and perfluorooctanesulfonate.[148] However, harmful high-energetic UV-light (254 nm) is necessary to photoexcite sulfite anions and the process efficiency suffers in more complex media due to light attenuation by scattering or competing absorption of other organic compounds including the solvent.

![Scheme 48. Dechlorination of monochloroacetic acid by solvated electrons produced upon UV-light excitation of sulfite anions.](image-url)

### 4. Summary and Outlook

Organic anions and light are a perfect combination to achieve challenging synthetic transformations as either reagents or photocatalysts. Compared to a corresponding neutral molecule, the absorption spectrum of the negatively charged anion usually exhibits a bathochromic shift and often fluorescence is exclusively observed for the anionic species. This allows photochemical conversions with less-energetic light, in many cases visible light. Fluorescence quenching studies enable the verification of interactions between substrates and the excited chromophore. The seminal work of Soumillion and co-workers in this field and their excellent review[132] demonstrated early the potential of organic anions as strong photoreductants in the dechlorination of arenes and the desulfonylation of sulfonamides using excited 2-naphtholate. The oxygen-centered radicals of photoexcited anionic decatungstates allow to break strong C(sp²)–H bonds of non-prefunctionalized alkanes to form new carbon bonds. Synergistic approaches of HAT and transition-metal-catalysis have recently found widespread interest and also enabled asymmetric reactions. In addition to the use of anions as photocatalysts, excited anions found applications as strong reductants to activate a reaction partner via PET followed by a subsequent conversion of both open-shell intermediates. Examples are the arylation of azaallylanions or the Heck-type reaction.
arylation of vinylphenols. Photoexcited organic anions allow cyclization reactions yielding pyrazoles or participate in ring-expanding reactions. Moreover, organic anions serve as potent electron-rich donor molecules for the formation of light-absorbing EDA complexes.

Overall, the use of photoexcited anions harbours enormous potential for applications in synthetic organic chemistry. We observe an increasing research interest in applying photoexcited anions as catalysts or reagents and hope that this review will stimulate more contributions to this yet underexplored but emerging field, which holds promise for many more exciting applications in organic synthesis.

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Conflict of Interest
The authors declare no conflict of interest.

Keywords: Excited anion • photoredox catalysis • photoreductant • synthetic photochemistry • single electron transfer

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I'm so excited! Anions act as powerful single electron reductants from their photoexcited state in catalytic or stochiometric transformations and are easily activated in the presence of a base. Their absorption is shifted bathochromically compared to the neutral molecules and visible light is often sufficient for their excitation.

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