Excited State Anions in Organic Transformations
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Dedicated to Prof. Ilhyong Ryu on the occasion of his 70th birthday
Utilizing light is a smart way to fuel chemical transformations as it allows the energy to be selectively focused on certain molecules. Many reactions involving electronically excited species proceed via open-shell intermediates, which offer novel and unique routes to expand the hitherto used synthetic toolbox in organic chemistry. The direct conversion of non-pre-functionalized, less activated compounds is a highly desirable goal to pave the way towards more sustainable and atom-economic chemical processes. 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 a reagent or 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 behavior was drawn by the early reviews of Fox[1] and Tolbert.2 Since then, other excellent publications followed that summarized the photochemistry of excited organic anions with a focus on their photoreductive properties and underlining the peculiarities of anionic molecules in photochemistry.3,4 Compared to the neutral species, the absorption of an organic anion is usually red-shifted, which facilitates selective excitation in complex mixtures and often allows visible light to be used. 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 and results in higher reaction efficiencies. Organic anions can be easily formed in the 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 example, in an ATP-driven process, the excited oxyluciferin anion causes the bioluminescence of fireflies.5 Moreover, phototrophic organisms show locomotory movement upon stimulus by light. The photoactive yellow protein (PYP) encloses the anionic trans-para-coumaric acid as a 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 photo-damaged DNA is another well-known example of 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.7–9

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 repertoire. 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 the use of organic anions 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 by discussing the peculiarities of the absorption spectra of closed-shell anions. Compared to their neutral precursors, organic anions usually experience a significant bathochromic shift of their absorption spectra, and pronounced absorption bands can be attributed to π,π* transitions. The narrowed gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO, Figure 1) causing the red-shift can be primarily explained by the increased shielding of the core because of 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

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diffuse as the conjugation length is extended.\textsuperscript{[1,9]} The absorption of organic anions is also affected by the size and nature of the countercation, solvent polarity, and ion-pairing effects in solution. In nonpolar 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.

In contrast, the increased solubility of ions in polar solvents, induced by aligning molecular dipoles, causes solvent-separated or free ion pairs and the mutual ionic interaction is diminished. In general, an increase in the solvent polarity and/or the ionic radius of the countercation results in a bathochromic shift of the absorption, which can be attributed to a destabilization of the ground-state ion pair. This destabilization effect is less pronounced in the excited state.\textsuperscript{[1,4]}

Similarly, the emission of excited organic anions is usually influenced by the solvent polarity and counterion. The fluorescence decay of sodium 2-naphtholate was studied in different solvents, for example.\textsuperscript{[10]} For polar protic and polar aprotic solvents, a monoeponential fluorescence decay was observed. However, the fluorescence lifetime in polar protic MeOH was remarkably decreased and the emission spectrum was blue-shifted compared to those in polar aprotic DMF or DMSO, which the authors attribute to a stabilization of the anion ground state caused by a strong hydrogen bonding of the solvent. In weakly polar THF, contact ion pairs and solvent-separated ion pairs of 2-naphtholate and Na\textsuperscript{+} coexist and cause a biexponential fluorescence decay because of their varying fluorescence lifetimes. The addition of crown ether to the system led to a monoexponential decay being recorded, which suggested that sodium cations are complexed and the ion pairs formed with naphtholate are solvent-separated in nature. Owing to the lack of ground-state stabilization in solvent-separated or free ion pairs, lifetimes similar to those obtained from experiments in polar aprotic solvents were found in the presence of a crown ether.

The nature of ion pairing might also affect the efficiency of bimolecular electron-transfer processes. Tamaoki et al. studied the quantum yield for the photodissociation of the benzene diazonium salt 1 in the presence of 9,10-dimethoxyanthracene-2-sulfonate (2) as the visible-light-absorbing counteranion (Scheme 1).\textsuperscript{[11]} The photodecomposition of the benzene diazonium cation 1 initiated by photoinduced electron transfer (PET) from the excited anion 2 was found to be six-times higher in CHCl\textsubscript{3} than in MeCN. The difference in the reactivity of the diazonium salt in the solvents was explained by the different nature of the ion pairs formed. The weakly polar solvent CHCl\textsubscript{3} promotes a fast reaction because of the proximity of 1 and 2 in a tight ion pair. Solvent-
separated loose ion pairs in polar MeCN allowed a distinct fluorescence lifetime to be measured. Upon excitation in polar media, the anionic donor needs to initially encounter a cationic acceptor to trigger the photodecomposition and, hence, increased lifetimes are recorded. For a more comprehensive discussion of ion-pairing and solvent effects, we refer to several excellent reports.[4,10,12–14]

1.2. Photoinduced Electron Transfer

Electron-transfer reactions from electronically excited states of molecules were among the earliest photochemical reactions reported.[15] Photoexcited molecules exhibit increased reduction and oxidation potentials compared to their ground states and the resulting excited-state potentials can be estimated, according to the free enthalpy change of a PET, by measuring the ground-state potentials $E_{1/2}$ and the transition energy $E_{0,0}$ (Figure 2).[16] 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, thereby resulting in a pair of radical ions. In contrast, 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 starting materials, is less competitive in a charge-shift process.[18]

An anionic molecule is considered to be a more superior electron donor than its neutral parent compound as both the 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-emitting diodes (LEDs) and common organic solvents, however, renders the photoejection of an electron unlikely to occur and, hence, electron-transfer reactions prevail under these conditions. We recently demonstrated that 9-anthracene and its derivatives are easily deprotonated in the presence of a carbonate base to form colored anions (e.g. $\text{ANT}^-$, Figure 2), which upon excitation with visible light turn into remarkably strong reductants.[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 because of resonance stabilization of the resulting radical. In sharp contrast, the dianions of fluorescein $\text{FL}^{2-}$ or eosin Y ($\text{EY}^{2-}$) show a significantly decreased tendency towards electrochemical oxidation in alkaline.

![Scheme 1. The rate of photoinduced electron transfer is influenced by the solvent polarity: fast in CHCl$_3$ (tight pair), slow in MeCN (loose pair).](image1)

![Scheme 2. Charge separation with a neutral donor (left) and charge shift with an anionic donor (right).](image2)

Figure 2. Diagram of the ground- and excited-state potentials of a photocatalyst (PC, top). Representatives of cationic, neutral, and anionic organic photocatalysts (bottom).
was, however, recorded when adjusting the pH of the solution to around the pKₐ value of the aromatic amine. As a consequence of protonation of the amine, the nitrogen lone pair is no longer available for intramolecular PET, thereby resulting in increased fluorescence. In 1991, Soumillon and co-workers showed that the fluorescence of the excited anion of the xanthene dye resorufin is quenched in the presence of 2-naphtholate, and the formation of a radical dianion of resorufin was proposed. 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 (Table 1, entries 5 and 6 show similar values for Eₒₓ, but differ significantly in their ground-state and excited-state oxidation potentials).

### 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, thereby resulting in the excited species having both increased oxidizing and reducing abilities compared to the ground state (see Figure 2). These redox properties can be fine-tuned by attaching electron-donating or withdrawing substituents. Up to now, a variety of photocatalysts have been reported and these are often classified in terms of their composition as polypyrrolyl transition metal complexes, organic dyes, or polyoxometalates (POMs). In addition, heterogeneous organic semiconductors have been successfully employed as photocatalysts. Their intrinsic photophysical properties such as the redox potential of the excited state, absorption of light, and the lifetime of the excited state define the scope of their applications.

#### Table 1: Ground-state (Eₒ, φₒ) and excited-state (Eₒₓ, φₒ) redox potentials of selected cationic, neutral, and anionic photocatalysts (PC) and the corresponding transition energies (Eₜₙ).

<table>
<thead>
<tr>
<th>Entry</th>
<th>PC⁺</th>
<th>Eₒ⁺(PC⁺/PC⁻) [eV]</th>
<th>Eₒ⁻(PC⁻/PC⁻) [eV]</th>
<th>Eₒ⁺(PC⁺+PC⁻) [eV]</th>
<th>Eₒ⁻(PC⁻+PC⁻) [eV]</th>
<th>Eₒ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1[7]</td>
<td>TTP⁺</td>
<td>-0.50[H]</td>
<td>+1.84</td>
<td>-</td>
<td>-</td>
<td>2.34[H]</td>
</tr>
<tr>
<td>2[20]</td>
<td>ACR⁺</td>
<td>-0.59[H]</td>
<td>+2.08</td>
<td>-</td>
<td>-</td>
<td>2.67</td>
</tr>
<tr>
<td>3[21]</td>
<td>4ClzIPN</td>
<td>-1.24[H]</td>
<td>+1.43</td>
<td>+1.49[H]</td>
<td>-1.18</td>
<td>2.67</td>
</tr>
<tr>
<td>4[22]</td>
<td>PTH</td>
<td>-</td>
<td>+0.52[H]</td>
<td>-2.5</td>
<td>-</td>
<td>3.1</td>
</tr>
<tr>
<td>5[22]</td>
<td>ANT</td>
<td>-</td>
<td>-</td>
<td>-0.34[H]</td>
<td>-2.65</td>
<td>2.31</td>
</tr>
<tr>
<td>6[21]</td>
<td>FL⁺</td>
<td>-</td>
<td>+0.87[H]</td>
<td>-1.55</td>
<td>-1.58[H]</td>
<td>2.42</td>
</tr>
<tr>
<td>7[7]</td>
<td>EY⁺</td>
<td>-1.06</td>
<td>+1.23[H]</td>
<td>+0.83[H]</td>
<td>+0.76</td>
<td>2.31[H]</td>
</tr>
<tr>
<td>8[22]</td>
<td>PhPh⁻</td>
<td>-</td>
<td>-</td>
<td>-0.10[H]</td>
<td>-3.16</td>
<td>3.06</td>
</tr>
<tr>
<td>9[29]</td>
<td>BIA-H.1</td>
<td>-</td>
<td>-</td>
<td>+0.06[H]</td>
<td>-2.71</td>
<td>2.77[H]</td>
</tr>
<tr>
<td>10[86]</td>
<td>TMA</td>
<td>-</td>
<td>-</td>
<td>-0.51[H]</td>
<td>-2.92</td>
<td>2.41</td>
</tr>
</tbody>
</table>

Potentials are reported vs. saturated calomel electrode (SCE). The transition energy Eₜₙ was determined from the intersection of the normalized absorption and emission spectra. [a] Potential recorded vs. normal hydrogen electrode (NHE) and converted into vs. the SCE by subtracting 0.141 V. [b] Determined from the lowest energy emission maximum. [c] Potential recorded vs. Ag/AgCl and converted into vs. SCE by subtracting 0.3 V. [d] Recorded vs. the ferrocene redox couple (Fc⁻'/Fc⁺) and converted into vs. SCE by adding 0.38 V. [e] Potential was measured in dry degassed DMSO with excess of Cs₂CO₃. [f] Measured in MeOH containing NaOH (0.1 mm) against Ag/AgCl and referenced to SCE by conversion. [g] Values for the singlet excited state. [h] Potential recorded vs. Ag/AgCl and converted to vs. SCE by subtracting 0.039 V. [i] Values for triplet excited state. [j] Potential measured in MeCN with excess BuOK. [k] Estimated by the end absorption wavelength with an absorbance of 0.02 at 4.0×10⁻³ m.

MeOH and, hence, the resulting excited-state oxidation potentials are only moderate (Table 1, entries 5–7). 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 to the benzoate scaffold of fluorescein NH₂-FLL⁻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 of FL⁻²⁻ to hereby resulting in increased fluorescence.
and limitations in chemical reactions. Selected examples of organic photocatalysts are depicted in Figure 2. The photochemistry of the uncharged donor–acceptor dyad 4CzIPN covers a broad electrochemical range (see Table 1, entry 3). As a result of the versatile chemistry arising from its excited state, it is often used to replace precious and toxic Ru- or Ir-polypyridyl complexes.[31,37] However, higher excited-state potentials need to be achieved to convert less activated substrates through photoinduced single-electron transfer. 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 values for the transition energy (see Table 1, entry 4).[32]

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 the substrate scope to be widened for photoinduced electron-transfer reactions (Scheme 4). Several organic dyes form stable and colored radical anions through PET in the presence of suitable sacrificial donors and, hence, enable a subsequent second excitation (see Scheme 4 A).[38–41] The versatile photochemistry of excited radical anions allowed various (hetero)aryl halides to be converted in coupling reactions and has been the subject of several reviews.[42–45] Very recently, this strategy was promoted by Birch-type reductions of benzene derivatives upon irradiation with visible light.[46] In contrast, the formation of super-oxidants has been reported upon photoexcitation of stable, chemically generated phenothiazine radical cations (Scheme 4B).[47] Furthermore, electron transfer from the photoexcited doublet states of neutral radicals has been studied.[48–52] The acridine radical ACR* was recently found to act as an extremely potent photoreductant upon excitation with black light (Scheme 4C).[53] Although excited open-shell species offer high redox potentials, their photochemistry suffers from short lifetimes, which are usually in the picosecond range.[54–56] 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 4D). The pioneering work of Fukuzumi et al.[57] paved the way for many publications based on the use of acridinium-based donor–acceptor dyads as strongly oxidizing photocatalysts.[17,57–60] Moreover, a new benchmark regarding the excited-state potential was set by using pyrylium, quinolium, 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 have found widespread synthetic applications.[17,61–68] Surprisingly, in contrast to the wealth of reports dealing with photoexcited cations, the photochemistry of closed-shell anions has received far less attention, although it constitutes the logical counterpart (Scheme 4E).

Hence, in the following section the ability of anionic photocatalysts to drive challenging transformations is underlined through selected examples. As a consequence of their moderate redox potentials and the wealth of available reviews, reactions of anionic xanthene dyes such as eosin Y, rose Bengal, or fluorescein are not discussed herein.[17,69–71] Furthermore, examples where anionic groups are mainly installed to increase the solubility of the sensitizer (e.g. 9,10-anthraquinone 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 the presence of base to afford the phenolate, which is able to undergo photochemical reactions under irradiation with visible light. Xia and co-workers examined several 4-phenylphenol derivatives as potential photocatalysts for the oxyarylation of olefins upon the photoreduction of aryl halides initiated by visible light (Scheme 5).[72] 4-Phenylphenol bearing bulky tert-butyl groups adjacent to the phenolic alcohol (Scheme 6) showed the highest catalytic efficiency, and the corresponding oxyarylated products 5 formed in the presence of aryl halides 3, olefins 4, and TEMPOH could be isolated in moderate to good yields. Remarkably, the estimated excited-state oxidation potential of *PhPH (E_{ox}^{*} = −3.16 V vs. SCE) also allowed more inert and electron-rich aryl bromides and chlorides to be converted in the presence of 4-methoxystyrene. The developed procedure showed a broad scope, tolerating (hetero)aryl bromides and iodides including polyaromatic hydrocarbons, pyridines, indoles, quinolines, thiophen, thianaphthene, and benzofuran.
Various styrenes, aliphatic olefins, allicylic sulfonamide and alcohol derivatives, enol ethers, as well as 1,1- and 1,2-disubstituted olefins were tolerated in the reaction. In addition, the method enabled intramolecular cyclization reactions using aryl iodides and the late-stage modification of pharmaceuticals. Noteworthy, the use of TEMPOH as a H-atom donor and radical trap seems to be crucial because of 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 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 olein 4.1, thereby resulting in a carbon-centered radical 3.1b. Hydrogen atom transfer between the oxidized species of the catalyst and TEMPOH recovers PhPH and leads to 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 the 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 on the photochemical behavior of 2-naphtholate anion **NA**- date back to 1989, when the counteration, temperature, and solvent were systematically evaluated for their effects on the luminescence lifetime and the absorption and emission maxima.[10] In the same year, Soumillon et al. demonstrated the application of the naphtholate anion in the photocatalyzed defunctionalization of 2-chloronaphthalene and 4-chlorobiphenyl (6.2, 6.3) in degassed, alkaline MeOH (Scheme 7, left).[73] This concept was further extended in a heterogeneous approach where 2-hydroxynaphthoic acid was covalently anchored to a silica surface through an amidation reaction. The efficiency of the dichlorination, however, was significantly decreased.[74] This substrate scope was later broadened to mono- and dichloronitrobenzenes.[75] In addition, **NA**- was shown to catalyze the detosylation of sulfonamides in the presence of excess NaBH₄ as the terminal reductant (Scheme 7, right).[76] 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 black light, 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-
(C6H4)SO2−), either an aryl- or nitrogen-centered radical is
formed. Abstraction of a hydrogen atom from the solvent
affords the defunctionalized arene. The N-centered radical
converts into the amine through H-atom abstraction from
either the solvent or NaBH4. To close the catalytic cycle, NA− is transformed into NA through hydrogen atom abstraction
from the solvent or NaBH4, followed by subsequent depro-
tonation (Scheme 8).

Recently, a zwitterionic visible-light-absorbing benzimi-
dazolium 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).[77] The cationic benzimidazolium
moiety can be considered as separated from the naphtholate,
since the tilted structure prevents π-conjugation. The photo-
catalytic activity was studied using different solvents with
attributed Lewis-basic or Lewis-acidic characters, as esti-
mated by donor and acceptor numbers. The authors con-
cluded that Lewis-basic solvents cause tight interactions with
the Lewis-basic benzimidazolium moiety, whereas the elec-
tronic properties of the Lewis-basic naphtholate anion are
less governed, thereby 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 equiv 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
through the reductive desulfonylation of tertiary sulfona-
mides 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.

Upon photoexcitation (λ > 390 nm), the zwitterionic
excited-state catalyst *BINA (Eox* = −2.08 vs. SCE) reduces
11 through PET. Subsequent cleavage of iodide followed by
fast 5-exo-trig cyclization affords the primary radical 11b. The
oxidized photocatalyst BINA+ is regenerated in the presence
of a sacrificial reductant 10 (E1/2 = +0.34 V vs. SCE) by single-
electron transfer to give the radical cation 10+*, which acts as
the hydrogen atom donor to form 12 and in turn is converted
into the cation 10+. In the presence of other terminal
reductants, for example, the Hantzsch ester (E1/2 = +0.93 V
vs. SCE), no product was formed as the higher oxidation
potential of the ground state renders an electron transfer
towards BINA+ endergonic.

In previously published work, photoexcited 1,3-dimethyl-
2-hydroxynaphthylbenzimidazoline (BIA-H.1) was found to
convert N-sulfonamides and N-sulfonylamines into the
respective desulfonylated products.[78] Based on these results,
Hasegawa et al. further developed the catalytic system
derpicted in Scheme 10 by utilizing the in situ reduction of
benzimidazolium aryloxides (BIA) in the presence of readily
available boron hydride donors to generate the anionic
species BIA-H (Scheme 11).[79]
In addition to the reported electron-donor and hydrogen atom donor abilities of the benzimidazoline scaffold (see Scheme 10, 10), the resulting benzimidazoline aryloxides BIA-H are equipped with a photoredox active unit, the aryloxide moiety. Reductant, H-atom donor, and photocatalyst are thus combined in one molecule. Various benzimidazoline aryloxides BIA-H.1–5 (Scheme 11) were synthesized and characterized in terms of their spectroscopic and electronic properties.[79] The calculated excited-state oxidation potential for BIA-H.1 (E_{ox} = −2.71 V vs. SCE) was found to be significantly enhanced compared to the zwitterionic species BINA, thus allowing the conversion of less activated substrates. The elaborated procedure was used for the reductive desulfonylation of N-sulfonylindoles, -amides, -amines, and α-sulfonyl ketones to afford the unprotected secondary amines as well as the α-defunctionalized ketones in good to excellent yield (Scheme 12).

For the desulfonylation of α-carbonyl compounds, the less reactive hydride donor PicBH3, was used to avoid the direct reduction of the carbonyl group. Remarkably, utilizing the developed photocatalytic procedure allowed diphenylsulfonylamine (17.4) and dibenzylsulfonamide (17.5) to be converted almost quantitatively in 24 and 48 hours, respectively. Note that both substrates exhibit a challenging reduction potential (E_{red} < −2 V vs. SCE). All synthesized catalysts BIA.1–5 were successfully tested in the desulfonylation reaction of N-tosylinol 17.1, but BIA.1 (or BINA, see Scheme 10) showed superior catalytic activity. Changing the light source from a xenon lamp (500 W, λ > 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 the absence of a hydride donor or light. In terms of the mechanism, the authors propose the in situ formation of BIA-H through nulceophilic attack of a hydride on the benzimidazolium moiety of BIA. Excitation with either a Xe lamp or a white LED renders the catalyst a strong photoreductant and allows PET to the substrate. The open-shell fragment formed upon rupture of a N–S or C–S bond abstracts a hydrogen atom from the photocatalyst BIA-H, which is turned into a biradical BIA. The benzimidazolium BIA is regenerated upon intramolecular single-electron transfer. Eventually, a hydride transfer activates the catalyst for another catalytic cycle (Scheme 11).

The acidic hydroxy group on the aryloxide is easily deprotonated and enables the benzimidazolium BIA-H to be employed directly instead of the betaine BIA as the catalyst. In that case, the addition of base (sodium carbonate or butoxide) increased the reaction efficiency significantly, thus indicating a facile deprotonation of BIA-H.

2.4. Anthrolate-Catalyzed Generation of Hydrated Electrons

Kerzig and Goez thoroughly investigated the potential use of anionic 9-anthrolate (ANT−) as a sustainable source for hydrated electrons, which are ejected upon irradiation with a laser.[30] Hydrated electrons are among the strongest reductants[80–82] and are capable of reducing dinitrogen[83] or carbon dioxide directly.[84] Approaches to liberate solvated electrons photochemically often rely on highly energetic and harmful UV-C light. Notably, irradiation of ANT− in alkaline aqueous media with a pulsed UV-A laser (355 nm) afforded hydrated electrons through a biphotonic photoionization 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 photoejection of a hydrated electron. The catalytic cycle is closed in the presence of the ascorbate dianion Asc2−, which acts as a sacrificial reductant to recover the catalyst from its oxidized species ANT+ (Scheme 13). The sequence of photoionization 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, Asc2− was found to slightly contribute to the generation of hydrated electrons.

A follow-up study by the Goez group[21] focused on the direct photoionization of Asc2− in the absence of a catalyst by applying a 355 nm laser pulse. A possible application of solvated electrons generated in this way was demonstrated through the efficient dechlorination of chloroacetate as a generic pollutant in wastewater.

2.5. Activation of Aryl Chlorides with 9-Anthrolate

Recently, the photochemical properties and synthetic applications of a series of 9-anthrone derivatives were studied by König and co-workers and the corresponding anions were...
TEMPO-trapping experiments confirmed the formation of aryl radical 21.1a and bicyclic radical 21.1b. Remarkably, in contrast to other photocatalyzed procedures for the activation of aryl halides,[38–41,85] no sacrificial electron donor (e.g., DIPEA) was necessary and the scope of aryl chlorides as the tolerated radical trapping reagents could also be broadened. In the model reaction, the catalyst loading could be lowered to 5 mol% (92% yield), which indicates a turnover number greater than 18. In accordance with recently reported photocatalyzed C–H arylation procedures,[38–41,85] it was found that an excess of the trapping reagent is crucial for the reaction outcome, as a stoichiometric amount with reference to the aryl halide resulted in a significantly decreased product yield. Anthrolates are converted in the presence of oxygen into the corresponding anthraquinones, thus reactions were carried out under an inert atmosphere. Noteworthy, acridone (ACO) afforded the desired arylation product 23.2 in good yield (83%) in non-degassed solvent and in the presence of air, thus indicating an increased stability in the presence of oxygen.

2.6. Anthrolate-Catalyzed C–H Carboxylation of (Hetero)arenes and Styrenes with CO₂

Very recently, the visible-light-absorbing, strong photo-reductant tetramethoxyanthrolate TMA⁻ (Eox⁺ = −2.92 V vs. SCE) was utilized to achieve the photocatalytic direct reduction of (hetero)arenes and styrenes to their respective radical anions.[86] The associated nucleophilic character of such electron-rich species was exploited in C–H carboxylation reactions with gaseous CO₂ to afford the aromatic carboxylic and cinnamic acids in moderate to excellent yields. Among others, naphthalenes, thiophenes, furans, indoles, pyrazoles, and styrenes that had not been prefunctionalized were converted into the corresponding carboxylic acids under exceptionally mild reaction conditions (Scheme 16). A gram-scale carboxylation of 2-cyanothiophene 26.9 illustrates the ease of scaling-up this reaction. Moreover, a late-stage C–H carboxylation of a Boc-protected thiophene analogue of propranolol 26.31 has been demonstrated following this procedure. Besides CO₂, ketones were found to convert into the corresponding tertiary alcohols (26.32, 26.33) by the same approach. Noteworthy, similar transformations usually require stoichiometric amounts of reactive organolithium reagents and are conducted under low temperature (−78°C).
Thus, a former protection of labile functional groups is often required, thereby leading to a multistep synthesis.\cite{87-89}

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 \textbf{26.18} and \textbf{26.25}, respectively. In the 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 \textbf{**TMA**}, which acts as a remarkably strong photoreductant. Upon SET, benzothiophene \textbf{24.20} is reduced to the resonance-stabilized radical anion \textbf{24.20$^-$}. Subsequent nucleophilic attack affords the carboxylate \textbf{24.20a$^-$}. The closure of the catalytic cycle is proposed to occur via an electron-rich radical dianion intermediate \textbf{24.20a$^2-$}, formed upon deprotonation of \textbf{24.20a$^-$}, which regenerates the active anionic catalyst by single-electron transfer to generate the carboxylate \textbf{24.20c$^-$}. Eventually, acidic work-up affords the carboxylic acid \textbf{26.20} (Scheme 17). An alternative pathway by direct H-atom abstraction from \textbf{24.20a$^-$} by the open-shell species \textbf{TMA$^+$} is also conceivable. In both cases, the gain in energy upon rearomatization 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 \textbf{**TMA**} in the presence of (hetero)arenes and styrenes. Tolerated substrates shortened the excited-state lifetime of CO$_2$ as a strong photoreductant. Calculated Mulliken spin populations for \textbf{24.20$^-$} allow the regioselectivity of the carboxylation to be predicted.

\textbf{2.7. Catalytic Reactions of Anionic Metal Complexes}

Transition-metal complexes such as Ru$^{1+}$-polypyridine or the cyclometalated Ir$^{III}$ analogue have found widespread applications in photocatalysis, as they are photostable, show tunable redox potentials, and their excited-state lifetimes are usually durable. In contrast to neutral complexes, such as \textit{fac}-Ir(ppy)$_3$, or cationic metal-based sensitizers [e.g. Ru(bpy)$_2$$^{2+}$, Ir(ppy)$_3$(dtbbpy)$_2^-$], anionic transition-metal complexes have been barely explored, which could be attributed to their photodecomposition with monodentate anionic ligands and the shortage of available more-stable dianionic ancillary ligands. Godbert and co-workers were able to synthesize and characterize the anionic iridium complex \textbf{28.1} with a dianionic orotate ligand (Scheme 18, top).\cite{90} Later on, the complex was modified by exchanging the 2-phenylpyridine ligands with coumarin-derived ligands (\textbf{28.2}) to increase the visible-light absorption. The authors successfully demonstrated the use of \textbf{28.2} in visible-light-driven H$_2$ generation, which was the first example of a photoinduced electron transfer using an anionic Ir$^{III}$ sensitizer.\cite{91}

Based on the well-established \textit{fac}-Ir(ppy)$_3$, Wenger and co-workers utilized a tris(2-pyridylmethyl)amine analogue \textbf{29} (Scheme 18, top), which renders the sensitizer water-soluble and negatively charged and generates hydrated electrons.\cite{92} A potential use of hydrated electrons in wastewater treatment was demonstrated by the degradation of chloroacetate \textbf{31.1} (Scheme 18) and the benzyltrimethylammonium salt \textbf{31.3}. In addition, the defluorination of trifluoromethylenzoxa is possible in the presence of such a strong reductant \textbf{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 (ca. 1.6 μs) of the excited sensitizer. The photocatalyst is then regenerated by either sodium ascorbate or triethanolamine, which act as sacrificial electron donors. Compared to the neutral fac-Ir(ppy)₃, the excited-state oxidation potential of the anionic sensitizer 29⁻ (E*ₘ₀ = −1.89 V vs. SCE) was found to be slightly increased.

The trianionic, rare-earth-metal catalyst hexachlorocerate(III) [Ce⁶⁺Cl₆]⁻ was found to be effective in the reductive dehalogenation of aryl halides 32.1 using UVA light (Scheme 19). This complex is stable to air and moisture and can be generated in situ by mixing CeCl₃ and NET₃ in acetonitrile. Oxidation renders them attractive candidates as catalysts. The authors also demonstrated that a sequential borylation and subsequent Pd-catalyzed cross-coupling reaction of the formed arylboronic ester is possible. This procedure is beneficial, as it avoids prior isolation of the diboron ester 36.1 to yield the aryl boric ester 37.1 and a boryl radical B(OR)₃. The oxidized catalyst is regenerated in the presence of excess Cl⁻ through photoinduced ligand-to-metal charge transfer, thereby giving rise to the radical anion Cl⁻.

In a follow-up study, the developed catalytic procedure was utilized for the photoinduced Miyaura borylation of aryl bromides and chlorides. Schelter and co-workers used diboron esters which functioned as both the borylation reagent and terminal reductant to close the catalytic cycle. Various arylboronic esters 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 quench the luminescence of the cerium catalyst. The authors also demonstrated that a sequential borylation and subsequent Pd-catalyzed cross-coupling reaction of the formed arylboronic ester is possible. This procedure is beneficial, as it avoids prior isolation of the diboron ester 36.1 to yield the aryl boric ester 37.1 and a boryl radical B(OR)₃. The oxidized catalyst is regenerated in the presence of excess Cl⁻ through photoinduced ligand-to-metal charge transfer, thereby giving rise to the radical anion Cl⁻. A reaction quantum yield Φ > 1 was found by actinometry, thus 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 the presence of Cl⁻, to presumably propagate a chain mechanism through reaction with another substrate molecule.

Polyoxometalates (POMs) are a class of widely studied molecular metal oxide anions. Their robustness upon irradiation renders them attractive candidates as catalysts. The
discussion of POM photocatalysis will be limited herein to recent, selected examples of decatungstates, which are routinely employed as sodium (NaDT) or tetrabutylammonium salts (TBADT, see Scheme 22). Hence, for a comprehensive study of POM chemistry we refer the interested reader to excellent reviews.\cite{100–104} Despite being negatively charged, these decatungstate anions act as strong oxidants from their excited states. This rare feature might be explained analogously to what was discussed for eosin Y and fluorescein (see Section 2.1). Tungsten is present in its highest oxidation state (+ VI), while the negative charge is centered on the oxygen atoms of the cluster, thus rendering the metal center highly electron-poor and prone to reduction. Upon photocexcitation, a ligand to metal charge transfer (O→M) is proposed to generate a relaxed excited-state cluster [W_{10}O_{32}]^{4-} which is easily reduced (E_{red} = + 2.44 V vs. SCE).\cite{100} Besides electron-transfer reactions, excited decatungstate has found widespread interest for its ability to abstract hydrogen atoms from non-activated C(sp^3)–H bonds. Fagnoni, Ryu, and co-workers summarized the site-selective C–H functionalization of alkanes, alcohols, ethers, ketones, amides, esters, nitriles, and pyridylalkanes by decatungstate and explained the observed regioselectivities on the basis of polar and steric effects.\cite{105} In 2018, MacMillan and co-workers demonstrated the powerful merger of anionic decatungstate photocatalysis and transition-metal-catalyzed cross-coupling.\cite{106} Based on this concept, a copper/decatungstate dual catalytic approach was recently developed that allowed the C(sp^3)–H trifluoromethylation of various biorelevant compounds, including natural products and medicinal agents, in moderate to good yield (Scheme 21).\cite{107} The introduction of a CF₃ group into drug molecules often improves pharmacokinetic properties and is, therefore, of interest. In the case of pyrrolidine (40.2), selectivity for the CF₃ functionalization is achieved upon protonation of the amine, which results in stronger and less hydridic α–C–H bonds and thus enables reactivity at the distal position. Regioselective functionalization was found at the benzylic (40.5, 40.6, 40.9) or sterically most accessible, electron-rich C(sp^3)–H bond (40.3, 40.7). The reaction is initiated by 390 nm light, which causes an electrophilic oxometallate excited state. Upon hydrogen atom abstraction from the β-C(sp^3)–H bond of the protonated pyrrolidinium species 38.2⁺, the reduced decatungstate catalyst H⁺[W_{10}O_{32}]^{5-} and the aliphatic radical cation 38.2⁺ are formed. Subsequent single-electron transfer to the Togni reagent II 39 regenerates the active HAT catalyst and enables the formation of a copper(II)–CF₃ species 41.2. The pyrrolidinium radical 38.2⁺ is captured by the copper complex to form an alkyl-copper(III)–CF₃ intermediate 41.3, and eventually the product 40.2 is formed upon reductive elimination and regeneration of the Cu⁰ catalyst 41.1 (Scheme 22).

Scheme 22. Proposed dual-catalytic mechanism for direct C(sp^3)–H trifluoromethylation.

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.\cite{108} This dual-catalytic strategy enables the 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 through transition-metal catalysis. Moderate to good regioselectivity was observed for alkane substrates 42.13, 42.14, and 42.19. In addition, the concept could be employed to the late-stage alkenylation of natural products (Scheme 23).

Scheme 23. Selected examples of the dehydrogenative alkenylation of alkanes and aldehydes with styrene derivatives. [a] The selectivity is reported as the percentage of the major regioisomer over all the regioisomers formed.
The excitation of the metal oxide cluster $[\text{W}_{10}\text{O}_{32}]^{4-}$ (TBADT) enables the abstraction of a hydrogen atom from alkanes or aldehydes 42.1. Subsequent addition of the resulting carbon-centered radical 42.1'$a$ to an alkene 43.1 then furnishes intermediate 42.1'$b$. This species is expected to be reversibly captured by the Co$^{II}$ complex 45.1 to form the alkyl-Co$^{II}$ intermediate 45.2.

Light-mediated formal $\beta$-H elimination from 45.2 results in formation of the product 44.1 and Co$^{III}$-H species 45.3, which reacts with a proton to release H$_2$ and the Co$^{III}$ complex 45.4. Eventually the decatungstate and the cobalt(II) catalysts are regenerated by SET (Scheme 24).

Wang et al. recently published the TBADT/Ni dual-catalytic asymmetric acyl-carbamoylation of tethered alkenes by using a chiral nickel catalyst to form oxindole motifs bearing a quaternary stereogenic center 49.2—49.5 (Scheme 25).

The reaction starts with H-atom abstraction from the aldehyde 47.1 by the excited decatungstate catalyst $[\text{W}_{10}\text{O}_{32}]^{4-}$, and the resulting acyl radical 47.1'$a$ is captured by the in situ formed Ni$^0$ to yield an acyl Ni$^{II}$ intermediate 50.2. Oxidative addition of the carbamoyl chloride 46.1 results in a Ni$^{III}$ species 50.3. In the enantioselective step, migratory insertion into the tethered double bond takes place 50.4, and subsequent reductive elimination affords the cyclized product 49.1 along with Ni$^0$ chloride 50.5. Both catalytic cycles are presumably closed through SET between the reduced decatungstate $[\text{W}_{10}\text{O}_{32}]^{4-}$ and Ni$^0$Cl 50.5 (Scheme 26).

Another example of a light-mediated asymmetric C–H functionalization was recently reported by Pu-Sheng Wang and co-workers. Upon hydrogen atom abstraction by TBADT, an alkyl, benzyl, or allyl radical adds to an exocyclic enone and the resulting $\alpha$-carbonyl radical regenerates the photocatalyst through hydrogen atom transfer. In the enantioselective step, the formed enol intermediate is protonated by an aligned chiral spiro phosphoric acid, thereby generating a stereocenter at the $\alpha$-position of the carbonyl moiety.

Based on the synergy of decatungstate HAT catalysis and nickel catalysis, Wang and co-workers demonstrated the acylation of aryl halides and $\alpha$-bromo acetates with aromatic and aliphatic aldehydes, whereby the resulting aromatic ketones and 1,3-dicarbonyls could be obtained in moderate to good yield. In a similar fashion, the group of Zheng disclosed very recently the direct C–H arylation of aldehydes by merging decatungstate HAT photocatalysis and palladium cross-coupling catalysis. Application of this method allowed the efficient linkage of various (hetero)aryl bromides, iodides, and triflates with aromatic and aliphatic aldehydes. Moreover, TBADT was shown to promote H/D exchange reactions of formyl C–H bonds and a wide range of hydridic C(sp$^3$)–H bonds in a synergistic system comprised of a HAT photocatalyst and a thiol catalyst. In the presence of D$_2$O, this procedure allowed the regioselective incorporation of deuterium into pharmaceutically relevant molecules and drug precursors. Furthermore, a few examples are known where polyoxometalates equipped with binding sites on the cluster shell or in the presence of co-catalysts participate in the reductive activation of CO$_2$ or generation of H$_2$.

3. Excited Anionic Compounds as Reagents

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

3.1 Excited-State Phenolate as a Photoelectroactive

Recently, Xia and co-workers made use of the remarkable excited-state potential of the phenolate 52.2 ($E_{\text{ex}}^\circ = -2.48$ V vs. SCE) in a Heck-type arylation reaction promoted by blue LED light.
The synthetic utility was demonstrated through the arylation of methyl 4-hydroxycinnamate (52.2) with various (hetero)aryl halides (52.1) (Scheme 27). In addition, other derivatives of cinnamic acid (52.2–52.13, 52.19), and flavonoids (52.16–52.18, 52.20) were shown to react smoothly via the generated aryl radical to afford the respective arylation products (53.1 and 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 arenes. The E/Z ratios of the formed arylation products are high for most of the isolated compounds. The mild reaction conditions allowed complex, biologically active substrates, such as chlorogenic acid, esculin, and scutellarin, to be converted. Upon deprotonation of the phenolic OH group, the absorption spectrum of 52.2 in DMSO is shifted towards longer wavelength, thereby 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 51.2 is feasible and subsequent cleavage of bromide forms the reactive aryl radical 51.2a, which preferentially couples to electron-rich species such as the vinylphenolate 52.2.

The resulting radical anion 51.2b− 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 into the latter by SET from the photoexcited phenolate *55.1 (Scheme 29). In the presence of the non-nucleophilic base 1,1,3,3-tetramethylguanidine (TMG), the absorption spectrum of salicylaldehyde (55.2) is red-shifted and no change was observed upon addition of the perfluoroalkyl iodide 56.1, thereby excluding the formation of a ground-state EDA complex. The base-induced bathochromic shift allowed the use of a compact fluorescent lamp (CFL) as the light source. The use of a 300 W Xe lamp with a cut-off filter (λ > 385 nm) still resulted in the formation of 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 56.1a.

In the bond-forming step, the radical is trapped by the ground-state phenolate to yield a cyclohexadienyl radical 56.1b*, which propagates the reaction by reducing another equivalent of 56.1 by SET. Subsequent proton shift affords the


Scheme 27. Substrate scope of the Heck-type arylation reaction reported by Xia and co-workers. [a] E/Z > 19:1.

Scheme 28. Proposed reaction mechanisms for the photochemical Heck-type arylation of vinylphenols.

Scheme 29. Scope of the perfluoroalkylation of substituted phenols. Minor positional isomers estimated by 19F NMR analysis of the crude product are marked with (*); 6 equiv of alkylating agent 56.1 were used for products 57.7–57.10.
alkylated phenol 57.1. Stern–Volmer quenching studies of the phenolate in the presence of alkyl iodide support the mechanistic proposal. The perfluoroalkylation proceeds with moderate regioselectivity with o-substituted phenols, giving rise to o- and p-monoalkylated as well as o,p-dialkylated products, whereas p-substituted phenols resulted in the formation of o,o'-dialkylated products.

Monitoring the product distribution over the course of the reaction revealed that o- and p-alkylated products are formed as intermediates and are further converted into bifunctionalized ortho- and para-adducts. Unsubstituted or methoxy-substituted phenols as well as nitrophenols failed to convert. Employing phenol 55.12 bearing electron-withdrawing groups in the ortho and para position afforded the monoalkylated product as the sole isomer. Perfluoroalkyl iodides with C₈, C₆, C₄, and C₁ chains can be used in the reaction (57.12–57.15).

3.2. Visible-Light-Promoted Arylation of Azaallyl Anions

Chruma and co-workers demonstrated how irradiation of the colored azaallyl anion 58.1 with visible light notably increases its excited-state oxidation potential. In the presence of strong bases (pKₐ(conjugated acid) > 32), the formed 2-azaallyl anion acts as a super electron donor in the dark and enables the functionalization of non-activated aryl iodides and tertiary alkyl halides.

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

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

3.3. Synthesis of Pyrazoles by Irradiation of α,β-Unsaturated Hydrazone Anions

Zhu and co-workers reported a series of substituted hydrazones 62.1 which are able to undergo cyclization mediated by sunlight in the presence of base to afford pyrazole derivatives 63.1.[118] The UV/Vis spectrum of the anionic hydrazone exhibits a significant red-shift compared to the neutral parent, thereby enabling the use of visible light to accomplish the cyclization reaction. Selected examples of pyrazoles formed are depicted in Scheme 33.

The authors propose two possible mechanistic pathways (Scheme 34): Deprotonated 62.1 gets photoexcited and undergoes either direct anionic cyclization to *62.1a (Path a) or is oxidized by O₂ to afford the N-centered radical 62.1 (Path b), which, upon intramolecular radical cyclization (62.1a) followed by cleavage of a tosyl radical, yields the pyrazole 63.1. A decreased yield is obtained when the reaction is conducted in a N₂ atmosphere or in the presence of the radical trap TEMPO, which is indicative of the latter mechanistic proposal (Path b). Notably, the reactions were

Scheme 30. Light-triggered perfluoroalkylation of phenolates bearing an electron-withdrawing substituent by Melchiorre and co-workers. For simplicity, only the ortho-alkylation pathway is shown.

Scheme 31. Scope of the light-mediated azaallyl anion coupling with (hetero)aryl halides. Ratio (60/61) of the formed regioisomers is given. [a] Blue light. [b] The other regioisomer was not isolated.

Scheme 32. Arylation of 2-azaallyl anions with non-activated (hetero)-aryl halides.

Scheme 33. Selected examples of the pyrazoles formed by irradiation of N-centered hydrazone anions. [a] Scaled up to a 20 mmol reaction.
also shown to operate in water, but resulted in decreased yields.

### 3.4. Utilizing Phthalimide Anions for H-Atom Abstraction

The exceptionally high ability of the excited phthalimide anion $^{64}$ to abstract hydrogen atoms from alcoholic solutions was already recognized in 1988.$^{[110]}$ This procedure was further developed and could be extended to ethers, alkylbenzenes, and amines, thereby affording addition products with phthalimide (Scheme 35).$^{[120]}$ The use of 4-methyl-anisole afforded a product mixture (66,8a–b), as H-atom abstraction is possible from the methoxy group or the 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 favorable process. Thus, the authors propose the phthalimidyl radical 64 as the hydrogen atom abstracting intermediate, which evolves from the excited anion $^{64}$ upon PET to phthalimide 64.

Remarkably, the electrophilic radical 64 is able to activate C–H bonds possessing high bond dissociation energies (e.g. $^{\text{BuOH}}$, $^{\text{EtOH}}$, $^{\text{MeOH}}$) 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 by [2+2] photocycloaddition using phthalimide 64 was previously limited to electron-poor noncyclic alkenes, because of competing excited-state electron-transfer reactions.$^{[122,123]}$

Suau and co-workers$^{[122]}$ mitigated the oxidizing strength by employing the anionic sodium phthalimide 64$^{+}$ and obtained efficient, regiocontrolled photocycloaddition and 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, which indicates 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 that yields the ring-expanded cis-68.1 adduct. Epimerization caused by the alkaline media affords a mixture of cis- and trans-68.1 (Scheme 38).

The photoexcited saccharin anion $^{69+}$ was recently found to show similar reactivity towards alkenes, which was utilized in regioselective ring expansion reactions to give benzosultams 71.2 71.6 (Scheme 39) starting from the cheap and commercially available sweetener saccharin.$^{[124]}$

Remarkably, common approaches to form benzo-fused seven-membered sultam derivatives are multistep reactions and rely on the use of toxic organotin hydrides$^{[125]}$ or expensive Pd catalysts.$^{[126]}$ A mechanism was proposed based on experimental and computational studies that
suggests 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 atom of the excited state saccharin anion at the alkene. Moreover, no evidence for an azetidine intermediate (cf. 64.3a, Scheme 38) resulting from the $[2+2]$ cycloaddition of saccharin and alkene was found, neither in experiment nor in computational analysis. The $C\equiv C$ bond formation between the carbonyl group and the alkene is expected to occur in the ground state. Regioselectivity is gained due to the kinetic preference of the nucleophilic nitrogen atom to attack at the terminal, sterically less hindered side (Scheme 40).

Organic anions are also reported to form ground-state electron-donor–acceptor (EDA) complexes with electron-deficient species, and is usually accompanied by the appearance of a new red-shifted charge-transfer absorption band. During the last few years, the photochemistry of EDA complexes has become increasingly popular. Among others, we highlight herein three examples to demonstrate the concept of organic anions participating in the formation of an EDA complex. For a more detailed study we refer to recent excellent reviews.[127,128] The aromatic perfluoroalkylation of $\alpha$-cyano ary lacetates 72.1 developed by Melchiorre and co-workers[129] is meditated 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 with a strong bathochromic shift in the absorption spectrum indicative of the formation of an EDA complex. Irradiation of $p$-substituted $\alpha$-cyano ary lacetates in the presence of TMG and an alkyling agent allowed selective perfluoroalkylation at the ortho position.

A mixture of regioisomers and dialkylated products was, however, obtained when nonsubstituted or meta- or ortho-substituted $\alpha$-cyano ary lacetates were employed. In accordance with the proposed homolytic aromatic substitution (HAS) pathway, lower yields were obtained with electron-deficient arenes. Following the developed procedure, the substrate scope could be extended to include heteroarenes (73.11–73.13) and $\alpha$-cyano phenyl ketone 73.14 (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 tetradecafluorohexane and MeCN, which resulted in higher yields and a shorter reaction time.

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

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, and is usually accompanied by the appearance of a new red-shifted charge-transfer absorption band. During the last few years, the photochemistry of EDA complexes has become increasingly popular. Among others, we highlight herein three examples to demonstrate the concept of organic anions participating in the formation of an EDA complex. For a more detailed study we refer to recent excellent reviews[127,128]. The aromatic perfluoroalkylation of $\alpha$-cyano ary lacetates 72.1 developed by Melchiorre and co-workers[129] is meditated 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 with a strong bathochromic shift in the absorption spectrum indicative of the formation of an EDA complex. Irradiation of $p$-substituted $\alpha$-cyano ary lacetates in the presence of TMG and an alkyling agent allowed selective perfluoroalkylation at the ortho position.

A mixture of regioisomers and dialkylated products was, however, obtained when nonsubstituted or meta- or ortho-substituted $\alpha$-cyano ary lacetates were employed. In accordance with the proposed homolytic aromatic substitution (HAS) pathway, lower yields were obtained with electron-deficient arenes. Following the developed procedure, the substrate scope could be extended to include heteroarenes (73.11–73.13) and $\alpha$-cyano phenyl ketone 73.14 (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 tetradecafluorohexane and MeCN, which resulted in higher yields and a shorter reaction time.

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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 \(76.1\). \[130\] The procedure allowed both electron-rich and electron-poor thiophenols to be converted under visible light with visible light in the presence of caesium carbonate (Scheme 43). Remarkably, the tolerated aryl halides are not limited to activated, electron-deficient arenes, as thiophenols 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 were shown to convert in a similar manner. This procedure allowed the mild and efficient late-stage functionalization of pharmaceutically active compounds.

The formation of an EDA complex \(74.2\) -EDA between thiophenolate \(74.2\) and aryl halide \(75.2\) was confirmed by UV/Vis spectroscopy and TD-DFT calculations. The arising charge-transfer absorption band allows initiation of the reaction with visible light through 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 \(C\rightarrow S\) cross-coupled product \(76.2\) (Scheme 44).

Based on the perfluoroalkylation of thiophenols and aryl halides via the formation of a visible-light-absorbing EDA complex, the formation of the EDA complex can be utilized catalytically. \[133\] In the presence of base, 2-bromophenol (BrPhOH) was found to promote the visible-light-mediated 1,2-addition of fluoroalkyl iodides to alkene and alkynes. Noteworthily, although a significant amount of product was formed in the reaction of allylbenzene \(77.2\) and ethyl difluorooiodoacetate \(56.6\) in the absence of a phenol catalyst, the yield could be doubled by using a catalytic amount of BrPhOH. The use of a more polar solvent gave rise to Heck-type coupling products \(80.1\). Allylphenols, acting themselves as catalysts, could be converted into either the addition product \(79.1\) or the coupling product \(80.1\) without adding BrPhOH.

Initiation of the reaction is proposed to occur through formation of an EDA complex between phenolate \(\text{BrPhO}^-\) and the alkylation reagent \(56.6\). The photoexcited EDA complex results in the formation of radical \(56.6\), which reacts with the olefin \(77.1\) to yield the radical intermediate \(77.1\). 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 \(77.1\), which forms the Heck-type product \(80.1\) upon deprotonation (Scheme 45).

3.7. Organic Anions Promoting the Radical-Nucleophilic Substitution (S<sub>n</sub>1) Reaction

In the course of \(S_n1\) reactions, radicals and radical anions are formed as intermediates, and chain mechanisms are likely to occur. Proposed for the first time in the 1960s, \[132,133\] the reaction results in nucleophilic substitution of aromatic and aliphatic compounds and tolerates a wide range of nucleophiles and substrates. \[134\] 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 \(\text{Nu}^+\) and a radical anion \([R-X]^-.\)

The formation of EDA complexes between the nucleophile and substrate are reported and allow the \(S_n1\) reactions to be initiated by using less-energetic light. \[125\] Upon mesolytic bond cleavage, the resulting radical \(R^+\) is trapped by the nucleophile and forms a radical anion. A single-electron transfer from the radical anion \([R-Nu]^+\) to the acceptor \(R-X\) affords the desired substitution product along with another radical anion \([R-X]^-.\), which enables the propagation of a chain reaction (Scheme 46), provided that this SET is thermodynamically favorable.

![Scheme 44. Proposed reaction mechanism for the C→S cross-coupling reaction of thiophenols and aryl halides via the formation of a visible-light-absorbing EDA complex.](image-url)
Closely related to the concept of the light-induced $S_{\text{RN1}}$ reaction is the photoinitiated base-promoted homolytic aromatic substitution reaction (photo-BHAS), which affords C–H arylated products starting from aryl or alkyl halides in the presence of a strong base (e.g., KOtBu or NaH). The reactive intermediate R$^\bullet$ is proposed to add to the arene to form a cyclohexadienyl-type radical, which is converted into the respective radical anion by deprotonation and eventually gives the arylated product upon SET to R-X to propagate the chain reaction. In the absence of further additives, it has recently been shown that the dimethyl anion can be excited by visible light and plays a pivotal role in initiating the reaction (see Scheme 46).$^{[135]}$ The initiation of the BHAS reaction was also reported by other photoactivation modes, for example, through PET from an iridium sensitizer to R-X, or upon excitation with light of an in situ formed photosensitive complex between KOtBu and phenanthroline.$^{[136,137]}$ Non-nucleophilic bases are commonly employed to avoid the competing $S_{\text{RN1}}$ reaction pathway. Light-mediated substitutions following the $S_{\text{RN1}}$ reaction with organic anions as nucleophiles have been studied extensively and were the subject of recent reviews$^{[4,134,138–142]}$ and thus will not be further discussed herein.

### 3.8. Direct Photodecarboxylation of Carboxylates

In the presence of light, various organic carboxylates are known to undergo photodecarboxylation (PDC) to afford CO$_2$ and either a carbanion intermediate (heterolytic cleavage) or an alkyl radical intermediate in combination with a solvated electron (homolytic cleavage). Meiggs et al.$^{[143]}$ performed flash photolysis of sodium phenyl acetate and could prove the formation of a benzyl radical intermediate by transient absorption spectroscopy. The formation of toluene, in addition to polyacids and bibenzyl, may suggest a competing heterolytic bond-cleavage mechanism. Reaction pathways via high-energetic carbanion or radical intermediates are favored with compounds bearing stabilizing substituents. Hence, PDC is often observed upon irradiation of dissociated aryl acetic acids 81.1, thereby generating intermediates that benefit from benzylic 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 Review.$^{[144–146]}$

![Scheme 45](image1.png)

**Scheme 45.** Selected examples of the fluoroalkylation of alkenes and alkynes to afford addition products or Heck-type coupling products (top). [a] Using KOAc (2 equiv) in DCE. [b] Without BrPhOH in dioxane. [c] Cs$_2$CO$_3$ instead of KOAc. [d] K$_2$CO$_3$ instead of KOAc. [e] Using K$_2$CO$_3$ (2 equiv) in DMSO. Proposed reaction mechanism for the visible-light-promoted fluoroalkylation using 2-bromophenol as an initiator (bottom).

![Scheme 46](image2.png)

**Scheme 46.** General reaction mechanism for the radical-nucleophilic substitution ($S_{\text{RN1}}$) reaction and for the photoinitiated base-promoted homolytic aromatic substitution reaction (photo-BHAS).

Photobases are important initiators of photopolymerization processes. Xanthone and thioxanthone acetic acids (81.7, 81.8) form carbamions upon decarboxylation and have recently received interest as amine-free alternatives for efficient thiol-epoxy polymerization.$^{[147,148]}$

![Scheme 47](image3.png)

**Scheme 47.** General scheme for the photodecarboxylation of dissociated aryl acetic acids and prominent examples.
3.9. Sulfite Anions Used in Photoreactions

The ability of cheap and available sulfite salts to generate hydrated electrons upon irradiation renders their use attractive (Scheme 48). The method was successfully applied for the photodegradation of hazardous halogenated pollutants such as monochloroacetic acid[149] and perfluorooctanesulfonate.[150] However, harmful high-energetic UV light (254 nm) is necessary to photoexcite sulfite anions, and the process efficiency suffers in more complex media because of light attenuation by scattering or competing absorption of other compounds, including the solvent.

Scheme 48. Dechlorination of monochloroacetic acid by solvated electrons produced upon excitation of sulfite anions with UV light.

4. Summary and Outlook

Organic anions and light are a perfect combination to achieve challenging synthetic transformations by acting as either reagents or photocatalysts. Compared to a corresponding neutral molecule, the absorption spectrum of its 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 Soumilion and co-workers in this field and their excellent review[21] demonstrated early on the potential of organic anions as strong photoreductants in the dechlorination of arenes and the desulfonfylation of sulfonamides using excited 2-naphtholate. The oxygen-centered radicals of photoexcited anionic decataungstates allow strong C(sp3)–H bonds of non-prefunctionalized alkanes to be broken to form new carbon bonds. Synergistic approaches of HAT and transition-metal catalysis have recently found widespread interest and have also enabled asymmetric reactions. In addition to the use of anions as photocatalysts, excited anions have found applications as strong reductants to activate a reaction partner by PET followed by a subsequent conversion of both open-shell intermediates. Examples are the arylation of azaallyl anions or the Heck-type arylation of vinylphenols. Photoexcited anions serve as potent electron-rich donor molecules for the formation of light-absorbing EDA complexes.

Overall, the use of photoexcited anions harbors enormous potential for applications in synthetic organic chemistry. We observe increasing research interest in applying photoexcited anions as catalysts or reagents and hope that this Review will stimulate more contributions to this yet underexplored 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.
