Leveraging of Sulfur Anions in Photoinduced Molecular Transformations

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ABSTRACT: This perspective describes recent advances in the use of sulfur anions to promote molecular transformations under irradiation with visible light. The topics are classified by the following reaction modes performed by the key sulfur anions: (1) C–S coupling via electron donor–acceptor (EDA) interactions, (2) photoinduced molecular transformation via sulfur anion EDA catalysis, (3) sulfur anions as photoredox and hydrogen atom transfer (HAT) catalysts, and 4) dithiocarbamate and xanthate as nucleophilic catalysts for photoinduced radical cascade reactions.

KEYWORDS: Sulfur anions, Single-electron transfer, Hydrogen atom transfer, Electron donor–acceptor interaction, Photocatalysis

INTRODUCTION

Harnessing of readily available light energy in place of conventional thermal force would be a green and sustainable choice to drive molecular transformations for the production of functional small molecules. Photoinduced chemical processes are endowed with various chemical activation modes including single-electron transfer (SET), hydrogen atom transfer (HAT), and energy transfer as well as their combinations, which are generally induced by photoexcitation of light-absorbing substrates or complexes.1–10

Recently, readily available sulfur anions have been identified as versatile key reagents capable of mediating/catalyzing a wide range of photochemical transformations in unique reaction modes.11 In these photoinduced reactions, sulfur anions play various roles such as an electron donors to form an electron donor–acceptor (EDA) complex, a photoexcited single-electron reductant, and a precursor of visible-light-absorbing reactive intermediates through nucleophilic substitution reactions with organic electrophiles, thus efficiently promoting downstream radical cascade reactions under milder reaction conditions. This Perspective highlights and discusses the latest development of the use of sulfur anions for photochemical molecular transformations with particular emphasis on the roles of sulfur anions and their reaction mechanism. It should be noted that this Perspective does not include radical C–S coupling via oxidative generation of thyl radicals from thiolate anions or thiols under photoredox catalysis. Readers can find representative examples in ref 12.

C–S COUPLING VIA EDA COMPLEXES

Thiolate anions have been employed as an electron donors to induce unimolecular radical nucleophilic substitution (SRN1).13–16 For example, Bunnett previously discovered that thiophenolate anions promote their coupling with aryl halides in liquid ammonia under irradiation with Pyrex-filtered light, affording diaryl sulfides (Scheme 1).17 For example, the reaction of thiophenol (1) with iodobenzene (2) in liquid NH₃ under light irradiation afforded diphenyl sulfide (4) in 94% yield, whereas the reaction with bromobenzene (3) resulted in poorer conversion. The S₅N₅ radical chain could be initiated by photoinduced electron transfer from thiopholate ion 5 to iodobenzene (2) to form a phenyl radical via mesolysis of the C–I bond. The resulting phenyl radical 6 is coupled with thiophenolate ion 5 to generate the anion radical of diphenyl sulfide 7, which is assumed to be strongly reducing on the basis of the reduction potential of diphenyl sulfide (4) (E_{red} = -2.7 V vs saturated calomel electrode (SCE)).18 Thus, a subsequent single-electron reduction of iodobenzene (2) (E_{red} = -2.24 V vs SCE)19 liberates diphenyl sulfide as the product along with the regeneration of phenyl radical 6 to maintain the radical chain. The inefficient process with bromobenzene (3) (E_{red} = -2.44 V vs SCE)19 is probably due to a higher energy barrier...
for the photoinduced single-electron transfer to initiate the SRN1 radical chain. It should be noted that the second-order rates for the addition of a thiophenolate ion (PhS\(^-\)) to carbon-centered radicals were examined independently by Savéant,\(^{20}\) Beckwith,\(^{21}\) and Galli.\(^{18}\) The rates with nonactivated aryl radicals were estimated to be around 10\(^7\) M\(^{-1}\) s\(^{-1}\), whereas those with electron-deficient aryl radicals were at the diffusion limit. The rates with alkyl radicals were calculated to be around 10\(^8\) M\(^{-1}\) s\(^{-1}\).

There are other mechanistic possibilities for the C--S coupling events closely associated with the SRN1 mechanism (Scheme 2). One of the typical examples is the radical homolytic substitution (SH\(^2\)) mechanism of carbon-centered radicals with disulfides,\(^{22,23}\) which are known to be formed via dimerization of thyl radicals nearly at the diffusion limit.\(^{24}\) (Scheme 2A). In addition, radical cross-coupling of carbon-centered radicals and thyl radicals might be an alternative mechanistic scenario, especially when the reactions involve arene thyl radicals under photoradiation (Scheme 2B). Although both radicals could be considered transient in nature, a recent study by Nicewicz\(^{25}\) indicated that homolysis of diaryl disulfide is promoted under irradiation with visible light and thus arene thyl radicals could gain longer-lived lifetimes under a photocontrolled equilibrium with the corresponding diaryl disulfides.

Electron donor–acceptor (EDA) complexes, which are typically endowed with red-shifted charge-transfer transition bands, induce inner-sphere electron transfer within the complexes upon their photoexcitation.\(^{26,27}\) Thus, photoinduced electron-transfer events in the EDA complexes often occur beyond the electrochemical potential limits of the individual electron donors and acceptors. This photoinduced single-electron transfer of the EDA complexes has been utilized to advance the state of the art of thiolate-anion-mediated cross-coupling chemistry. Miyake observed the EDA interaction between aryl halides and thiolate anions, which could promote radical aryl–S cross-coupling upon irradiation with visible light (Scheme 3A for the couplings between 4-methylbenzenethiol (8) and 4′-haloacetophenones 9 or 10 to form 11).\(^{28}\) In these processes, photoexcitation of the EDA complex 12 triggers an SET event to form an pair of thyl radical 13 and aryl halide anion radical 14. While unproductive back electron transfer (BET) causes them to return to their original ground states, mesolysis of the C--halogen bond of aryl halide anion radical 14\(^{29}\) allows the cage escape of aryl radical 15, which could be formally coupled with thyl radical 13 to form 11. This protocol could engage a wide range of aryl halides, including reductively inert haloarenes such as 2-bromonaphthalene (16) (E\(_{\text{red}}\) = −2.21 V vs SCE)\(^{30}\) and 2-chlorobenzonitrile (18), with excellent functional group compatibility (Scheme 3B). It should also be noted that benzyl mercaptan (20) can be utilized as a coupling partner.
Recently, Akiyama employed the EDA complex between thiophenol (1) and \( p \)-bromoacetophenone (10) in the presence of excess amounts of tetrahydrofuran (THF) (22) for photoinduced C(sp\(^3\))−H thiolation to afford 23 (Scheme 4).\(^3^1\) Upon photoexcitation of the EDA complex 24, the cage-escaped aryl radical 15 undergoes hydrogen atom transfer (HAT) with THF (22) to form \( \alpha \)-oxy alkyl radical 25, which could be coupled formally with thiyl radical 6 to afford 23. In addition to THF (22), this method could engage not only aliphatic heterocycles such as 1,4-dioxane (for 26), tetrahydrothiophene (for 27), and N-methylpyrrolidone (for 28) but also cycloalkanes (for 29) for the C−H thiolation with good to moderate efficiency.

Dithiocarbamate anions, generated in situ via addition of secondary amines 30 to carbon disulfide (CS\(_2\)) (31) in the presence of Cs\(_2\)CO\(_3\), were found to undergo photoinduced cross-coupling with 4′-iodoacetophenone to provide the S-aryl dithiocarbamate 32 under irradiation with compact fluorescent light (CFL) in DMSO (Scheme 5).\(^3^2\) The EDA interaction of 33 between 4′-iodoacetophenone and in situ formed dithiocarbamate was observed. In this protocol, aryl iodides bearing electron-withdrawing groups generally displayed higher reactivity, whereas the reaction efficiency was dramatically diminished when aryl bromides were used and no cross-coupling was observed with aryl chlorides.

The Katritzky salts\(^3^3\) prepared from 2,4,6-triphenylpyrylium salt and primary amines were also found to form EDA complexes with thiolate anions to initiate SET-driven radical reactions upon irradiation with visible light. For example, Liao demonstrated photoinduced deaminative thiolation of the Katritzky salts derived from \( \alpha \)-amino esters for the synthesis of \( \alpha \)-mercaptop acid derivatives (Scheme 6 for coupling of thiol 34 and the Katritzky salt 35 to form 36).\(^3^4\) This method could engage a wide range of thiolate anions derived from not only alkane- and arenesulfonilthioethanols but also thiobenzoic acid. The photoinduced SET event within the EDA complex 37 between a thiolate anion derived from 34 and the Katritzky salt 35 results in the formation of the thyl radical 38 and 1,4-dihydropyridine radical 39. Rapid radical fragmentation of 39 forms the \( \alpha \)-carbonyl radical 40 with exclusion of 1,3,5-triphenylpyridine (41). Finally, the alkyl radical 40 is engaged in the C−S bond forming event to afford 36.

### PHOTOINDUCED MOLECULAR TRANSFORMATION VIA SULFUR ANION EDA CATALYSIS

In addition to the utilization of sulfur anions for EDA-driven C−S couplings, a new catalysis concept that leverages the EDA interaction between sulfur anions and arenes has recently emerged. Xanthate and dithiocarbamate salts were successfully employed by Melchiorre as catalysts to promote various photoinduced radical cascade processes.\(^3^5\) For example, the treatment of vinyl sulfone 41 and N-acloyloxy phthalimide 42 with a catalytic amount of xanthate 43 in the presence of \( \gamma \)-terpinene (44) as a stoichiometric reductant under irradiation
alkylation of vinyl sulfone 41 is initiated by the radical fragmentation of N-acyloxy phthalimide 42 through the photoinduced SET of the EDA complex 46, providing alkyl radical 47 and thiyl radical 48. The resulting nucleophilic alkyl radical 47 adds onto vinyl sulfone 41 to afford the \( \alpha \)-sulfonyl radical 49, which undergoes HAT with \( \gamma \)-terpinene (44) to liberate the hydroalkylation product 45. The concomitantly formed thyl radical 48 could be reduced to xanthate 43 in the following two mechanistic scenarios to maintain the catalytic turnover. One is the SET reduction of thyl radical 48 by cyclohexadienyl radical 50. Similarly to the reactivity of diaryl disulfide and the ary thyl radical discussion in Scheme 2B, thyl radical 48 could also gain a longer lifetime through a photocontrolled equilibrium with the xanthate dimer 51. An alternative mechanism is a sequence of HAT of thyl radical 48 with \( \gamma \)-terpinene (44) and deprotonation of 54.

This EDA catalysis was extended to the use of a Katritzky salt such as 54 as the source of alkyl radicals, allowing for deaminative Giese-type hydroalkylation of electron-deficient alkenes such as 55 (Scheme 8). In this case, dithiocarbamate 56 having an S-bromoinole moiety, which was originally engineered by Melchiorre, was identified to be a superior catalyst to promote the formation of the EDA complex 58.

König disclosed the employment of thiolate anions as catalysts to promote the photoinduced radical borylation of reductively inert aryl (pseudo)halides (Scheme 9). For example, a reaction of fluorobenzene (PhF) (59) and bis(pinacolato)diborane \([\text{B}2(\text{pin})2]\) (60) with 30 mol % of sodium pyridine-2-thiolate (2-PySNa) (61) and tetramethylammonium fluoride (Me4NF) (62) under irradiation with violet light delivered a phenylboronic acid pinacol ester (63) in 81% yield. The observation of a red-shifted charge-transfer transition band in the mixture of substrates 59−62 indicated the presence of the EDA complex 64, comprised of a pyridine-2-thiolate \(-\text{B}2(\text{pin})2\) adduct as an electron-donor moiety and fluorobenzene likely having an interaction with boryl anion species \([\text{B}2(\text{pin})2\text{−F}]^-\) as an electron-acceptor part. Photo-excitation of the EDA complex 64 induces SET to generate of thiyl radical 65 (which is most likely under photocontrolled equilibrium with its disulfide, see Scheme 2B) and radical anion of fluorobenzene 66. The resulting radical anion 66 undergoes mesolysis of the C−F bond to form phenyl radical 6, which is subsequently trapped by borylanion species \([\text{B}2(\text{pin})2\text{−F}]^-\) to liberate the borylation product 63 along with the boryl radical anion \([\text{F}−\text{B}(\text{pin})]\)\(^•\)−. In turn, thyl radical 65 is reduced by the boryl radical anion \([\text{F}−\text{B}(\text{pin})]\)\(^•\)− to regenerate pyridine-2-thiolate 61, which maintains the catalytic turnover. This method was applicable for the borylation of a wide variety of aryl electrophiles, including electron-rich 4-fluoroanisole (67), chlorobenzene (68) \((E_{\text{red}} = −2.78 \text{ V vs SCE})\), 6-chloroindole (69), aryl carbonate 70, and aryl sulfone 71.
Sulfur Anions as Photoredox and Hydrogen Atom Transfer Catalysts

Recent studies revealed that several sulfur anions absorb visible light and the resulting photoexcited species function as potent and unique SET reductants. For example, Hamashima recently reported photoinduced C−H arylation of benzyl amine 72 with 1,4-dicyanobenzene 73 in the presence of commercially available thiobenzoic acid (74) as a catalyst to produce diarylmethylamine 75 (Scheme 10). In this process, the photoexcited benzothioate ion \( S^2^- \) undergoes SET reduction of 1,4-dicyanobenzene 73 \( (E_{\text{red}} = -1.64 \text{ V vs SCE}) \) to generate a persistent anion radical of 1,4-dicyanobenzene 77. The simultaneously formed thyl radical 78 induces HAT from benzyl amine 72 to form the transient benzylic radical 79, which could be coupled with the anion radical 77 to liberate the C−H arylated product 75. The resulting thiobenzoic acid 74 is continuously deprotonated to regenerate benzothioate ion 76, thus maintaining the turnover of the SET−HAT relay photocatalysis.

Polysulfide anions play the key redox roles in alkali-metal−sulfur batteries, and thus their electrochemical reactivities have been studied in detail. For example, electrochemical potentials of the ground-state redox couples \( S_3^{2-}/S_3^- \) and \( S_4^{2-}/S_4^- \) are estimated to be around −1.35 and −0.85 V, respectively, vs SCE in dimethylformamide (DMF). It is also known that these polysulfide anions possess distinctive absorbance in the UV−visible spectral region. For example, a degassed DMSO solution of potassium polysulfide (K\(_2\)S\(_x\)) includes a steady-state equilibrium mixture of persistent \( S_3^{2-} \) \( (\lambda_{\text{max}} \text{ at } 618 \text{ nm with a wide bandwidth ranging from 450 to 800 nm}) \), \( S_4^{2-} \) \( (\lambda_{\text{max}} \text{ at } 436 \text{ and } 333 \text{ nm}) \), and \( S_5^{2-} \) \( (\lambda_{\text{max}} \text{ at } 273 \text{ nm}) \). Chiba recently disclosed that these polysulfide anions could serve as visible-light photoredox catalysts to promote a series of aryl cross-coupling reactions. For example, a heterobiaryl cross-coupling reaction between \( 4^\prime\)-bromoacetophenone (10) and N-methylpyrrole (80) was promoted by a catalytic amount of K\(_2\)S\(_x\) in DMSO under irradiation with visible light (440 nm), affording biaryl 81 in good yield within 1.5 h (Scheme 11). The process is proposed to be initiated by SET reduction of aryl bromide 10 by photoexcited \( S_4^{2-} \) to form the radical anion of aryl bromide 82, which subsequently undergoes C−Br bond mesolysis to form aryl radical 83. The simultaneously formed \( S_4^{2-} \) \( (E_{\text{red}} = -0.85 \text{ V vs SCE}) \) undergoes charge transfer with \( S_3^{2-} \) \( (E_{\text{ox}} = -1.35 \text{ V vs SCE}) \), allowing for the regeneration of ground-state \( S_4^{2-} \) and \( S_5^{2-} \). At the same time, the resulting aryl radical 83 adds to the aryl bromide 84, which is most likely oxidized by the photoexcited state \( S_4^{2-} \) to generate the final product 81 through deprotonation of cationic intermediate 85. This photocatalytic catalytic system with polysulfide anions could engage a wide range of ary halides possessing reduction potentials \( (E_{\text{red}}) \) as low as −2.4 V (vs SCE).

Moreover, this catalytic protocol was found to be applicable to the borylation of aryl halides such as 86 with bis(pinacolato)diboron (B\(_2\)(pin)\(_2\)) (60) (Scheme 12A). Polysulfide anion photocatalysis could be further extended to an SET−HAT relay manifold for the \textit{anti}-Markovnikov hydroarylation of alkenes such as 88 using the Hantzsch ester 89 as the stoichiometric reductant, where hydrogen polysulfide anions might serve as hydrogen atom carriers (Scheme 12B).
DITHIOCARBAMATE AND XANTHATE AS NUCLEOPHILIC CATALYSTS FOR PHOTOINDUCED RADICAL CASCADE REACTIONS

Melchiorre has developed a novel photocatalytic strategy to promote various radical cascade processes with alkyl (pseudo)halides as a radical precursor by employing dithiocarbamate 56 having a 5-bromoindole moiety as the catalyst.36 The process is initiated by nucleophilic substitution (SN2) reactions of alkyl (pseudo)halides with the dithiocarbamate catalyst 56 to form the corresponding S-alkyl dithiocarbamates. Due to the 5-bromoindole moiety, the resulting dithiocarbamates display absorbance in the visible spectral region. Thus, under irradiation with visible light (blue LEDs), the resulting S-alkyl dithiocarbamates undergo photoinduced homolysis of the weak C−S bond to form the corresponding alkyl radicals and thyl radical.46 While the resulting alkyl radicals take part in radical cascade events, the concomitant redox event via a SET reduction of the thyl radical or a HAT−deprotonation sequence can regenerate the dithiocarbamate, thus enabling the catalytic turnover for the formation of alkyl radicals. As one of the demonstrations of this photocatalysis concept, the Giese-type radical hydroalkylation of dimethyl fumarate (91) with benzyl chloride (92) is depicted in Scheme 13. Use of γ-terpinene (44) allowed for the smooth termination of the process via HAT to the alkyl radical intermediate 97, which is formed via the addition of benzyl radical 95 (derived from the photoinduced homolysis of 94) to 91. Regeneration of dithiocarbamate catalyst 56 from thyl radical intermediate 96 could operate in the same was as is shown in Scheme 7, either via SET with 50 or via HAT with 44 followed by deprotonation.

This photocatalytic manifold could function in a redox-neutral manner by using an electron-rich arene such as 98 (Scheme 14A) and a silyl enol ether such as 102 (Scheme 14B)47,48 as the radical acceptor, where the resulting radical intermediates 101 and 104 serve as the SET reductants to regenerate the dithiocarbamate catalyst along with the formation of the coupling products 100 and 103, respectively. Use of bis(catecholato)diboron (106) as the radical trapping reagent in DMF also enabled an efficient catalytic turnover for the radical borylation of benzyl bromide (107),49 where the DMF-boryl radical complex 111 formed via a radical borylation via transition state 109 working as the electron donor to regenerate the dithiocarbamate catalyst 56 (Scheme 14C).
Furthermore, Melchiorre extended this photocatalytic platform to the Giese-type hydroacylation of alkenes using carboxylic acid derivatives as the source of acyl radicals (Scheme 15A). For example, the reaction of benzoyl chloride (112) and acrylonitrile (113) was catalyzed by xanthate (43) in the presence of γ-terpinene (44) and Na₃PO₄ under irradiation with blue LED light, providing keto nitrile (114). The method takes advantage of nucleophilic acyl substitution of 112 with xanthate 43 for the formation of the visible-light-absorbing S-acyl xanthate 115. Irradiation with visible light induces the generation of acyl radical 116, which adds to acrylonitrile (113) to give the α-cyano radical 117. Subsequent HAT from 44 to radical 117 delivered the final product 114. Similarly, hydrocarbamoylation of acrylonitrile (113) with carbamoyl chloride 118 was catalyzed by diethyl dithiocarbamate 119 for the formation of amide 120 (Scheme 15B).

One of the keys to enabling the intermolecular traps of reactive alkyl and acyl radicals in an efficient manner (Schemes 13−15) is the unique reactivity of S-alkyl dithiocarbamates (e.g., 94) and S-acyl xanthates (e.g., 115) possessing highly radicophilic thiocarbonyl groups, which induce reversible addition of the radicals onto them (Scheme 16). The resulting adduct radicals 121 and 122 could serve as reservoirs of 95 and 116, respectively.

Scheme 14. Dithiocarbamate as a Nucleophilic Catalyst for Photoinduced Redox-Neutral Radical Cascade Reactions

Scheme 15. Dithiocarbamate and Xanthate as Nucleophilic Catalysts for Photoinduced Hydroacylation of Alkenes

Scheme 16. Reversible Addition of Reactive Radicals 95 and 116 to Thiocarbonylthio Derivatives 94 and 115
respectively, over the reaction courses. These systems allow the regulation of the concentration of the reactive radicals 95 and 116, thus making their subsequent radical traps smooth and efficient. Indeed, this fascinating chemical reactivity of the thiocarbonylthio derivatives has been applied in numerous types of radical molecular transformations by Zard. Further details can be found in the selected reviews cited in the references.57–61

CONCLUSION

We have shown in this Perspective that the combination of sulfur anions and visible light has enabled a wide repertoire of radical cascade reactions. These radical processes have traditionally required the use of precious transition-metal complexes, toxic reagents, and/or harsh reaction conditions (e.g., irradiation with energy-intensive UV light, strongly oxidative/reductive conditions, higher reaction temperature, etc.). On the other hand, the photochemical reactions with sulfur anions offer operationally simpler and greener protocols under transition-metal-free reaction settings. Given the versatile reactivities of sulfur anions to drive the photochemical processes, we anticipate that more unique and versatile sulfur anions will be devised and engaged in various opportunities of synthetic photochemistry.

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Notes

The authors declare no competing financial interest.

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