Reductive Photoredox Catalysis

Anthraquinones as Photoredox Catalysts for the Reductive Activation of Aryl Halides

Javier I. Bardagi,[a] Indrajit Ghosh,[a] Matthias Schmalzbauer,[a] Tamal Ghosh,[a] and Burkhard König*[a]

Abstract: Quinones are ubiquitous in nature as structural motifs in natural products and redox mediators in biological electron-transfer processes. Although their oxidation properties have already been used widely in chemical and photochemical reactions, the applications of quinones in reductive photoredox catalysis are less explored. We report the visible-light photoreduction of aryl halides (Ar–X; X = Cl, Br, I) by 1,8-dihydroxyanthraquinone. The resulting aryl radical anions fragment into halide anions and aryl radicals, which react through hydrogen abstraction or C–C bond-forming reactions. The active photocatalyst is generated from 1,8-dihydroxyanthraquinone by photoinduced single-electron reduction to the radical anion or subsequent protonation and further reduction (or vice versa) to the semiquinone anion. Subsequent visible-light excitation of the anthraquinone radical anion or semiquinone anion converts them into very potent single-electron donors. A plausible mechanism for the reaction is proposed on the basis of control experiments and spectroscopic investigations.

Introduction

The use of visible light for the generation of reactive intermediates in organic transformations has many advantages, and the growing interest in visible-light-mediated photoredox catalytic synthetic transformations over the last decade demonstrates the feasibility of the approach.[1–9] Ru- and Ir-based coordination complexes have received enormous attention because of their excellent visible-light-harvesting properties, modest to extremely high oxidation and reduction potentials, relatively long excited-state lifetimes, and reasonably good chemical and photostabilities under synthetic oxidative and reductive conditions.[2] In addition, considerable efforts have been made to develop metal-free photoredox catalytic methods with organic dyes[8,10–14] such as eosin Y[10,11] or rhodamine derivatives[13,14] and organic heterogeneous photocatalysts[15] for synthetic transformations.

Quinones[8,16,17] occur in nature and are known for their excellent electron-accepting and hydrogen-abstracting abilities.[16,18] Not surprisingly, different quinone derivatives have been used for photo-oxidative transformations under visible light.[19–22] Fukuzumi reported the photoredox catalytic conversion of benzene to phenol with 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) under visible-light irradiation.[23] Itoh and subsequently Yuan reported the trifluoromethylations of arenes and heteroarenes with anthraquinone-2-carboxylic acid[24] and

DDQ,[25] respectively. Itoh reported the synthesis of carboxylic acids from their respective methyl aromatics with 2-chloro-anthraquinone.[26] Recently, Brasholz disclosed cascade dehydrogenation/6π-cyclization/oxidation reactions of 1-(nitromethyl)-2-aryltetrahydroisoquinolines in the presence of 1-aminoanthraquinone to obtain tetracyclic 12-nitroindolo-[2,1-a]isoquinoline products.[19] Similarly, the same group also reported an intermolecular version with 1,5-diaminoanthraquinone as a photocatalyst for the synthetic transformations of N-aryltetrahydroisoquinolines and nitromethane to prepare the same product.

Anthraquinone (Aq) and its derivatives (Figure 1A) form colored radical anions upon single-electron reduction [see Figure 1B for the absorption spectra of the electrochemically generated radical anion of 1,8-dihydroxyanthraquinone (Aq-OH)]. The radical anions of anthraquinones possess moderate reduction potentials in their ground states [e.g., E^0(Aq/Aq$^{•-}$) and E^0(Aq-OH/Aq-OH$^{•-}$) are –0.82 and –0.55 V vs. saturated calomel electrode (SCE), respectively][27] and can be accessed electrochemically, chemically, or through photoinduced single-electron transfer (SET) processes in the presence of a suitable electron donor under an inert atmosphere (see Figure 3A). Eggins[28] as well as Lund and Eriksen[29] showed that the excited states of the colored radical anions of Aq (or in general quinone derivatives, see ref.[28]) are powerful reductants and can transfer electrons to organic substrates with extremely negative reduction potentials (e.g., 1,2-dibromobenzene, an aryl halide substrate with a reduction potential of –1.88 V vs. SCE).[28] Although the radical anions of quinone derivatives are common intermediates in natural and synthetic photochemical energy storage,[16,30] they have not yet been applied in photoredox catalytic reductive transformations. As the excited states of radical anions act as powerful reductants,[12,13,28,29,31] we en-

[a] Institute of Organic Chemistry, University of Regensburg,
93040 Regensburg, Germany
E-mail: burkhard.koenig@ur.de
http://www-oc.chemie.uni-regensburg.de/koenig/index.html
Supporting information and ORCID(s) from the author(s) for this article are
available on the WWW under https://doi.org/10.1002/ejoc.201701461.

ChemPubSoc
Europe

EurJOC
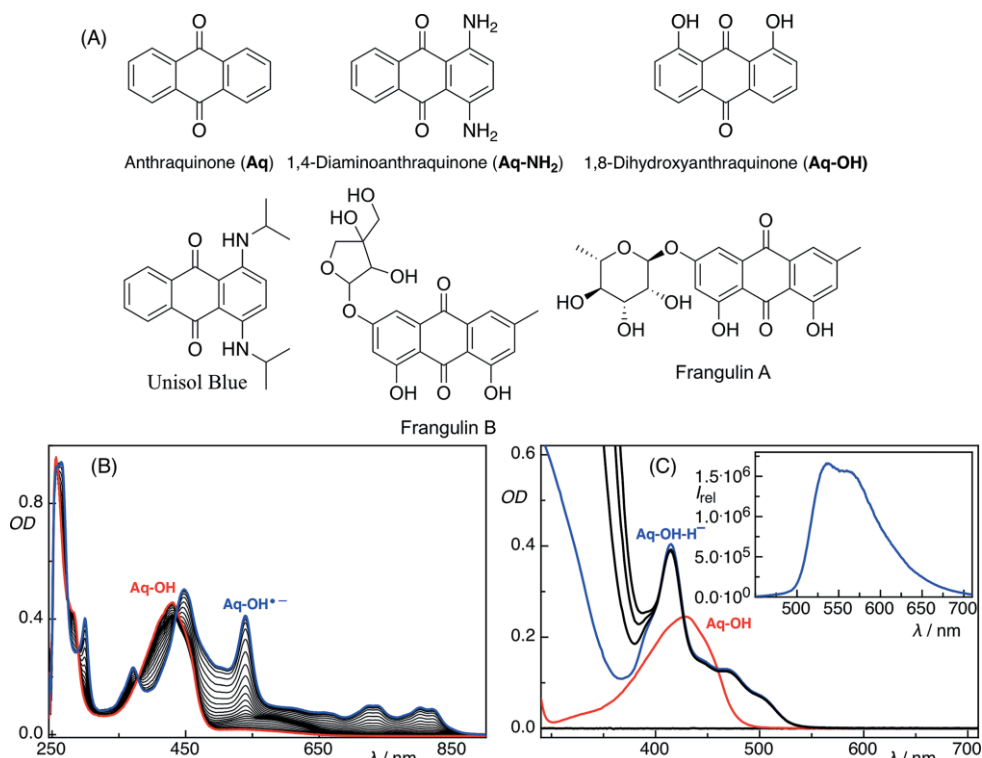European Journal
of Organic Chemistry

Full Paper

Figure 1. (A) Chemical structures of anthraquinone derivatives investigated herein. (B) Spectroelectrochemistry of Aq-OH in deaerated DMF. (C) Formation of 1,8-dihydroxyanthraquinone semiquinone anion (Aq-OH-H−) in the presence of Na2S2O4.[40] In the inset, the luminescence spectrum (λ_{Ex} = 427 nm) of Aq-OH-H− is shown. For the formation of the radical anion and the semiquinone anion of Aq-OH upon photoirradiation in the presence of Et3N, see Figure 3.

visioned that anthraquinone derivatives could be employed for the photoredox catalytic reduction of aryl halide substrates, including aryl chlorides, to obtain aryl radicals either for metal-free dehalogenation reactions[12,32–35] or for synthetically important carbon–carbon[12,32,36–38] bond-formation reactions. Such photoredox catalytic methods[12,13,32–39] are valuable alternatives to well-established transition-metal-based activation methods. Herein, we report the use of 1,8-dihydroxyanthraquinone as a photocatalyst for synthetically important C–C bond-formation reactions with aryl halides as bench-stable starting materials and visible-light irradiation.

Results and Discussion

We began our investigations with methyl 2-bromobenzoate (1a) as a test substrate and 1,8-dihydroxyanthraquinone as a photoredox catalyst. A mixture of 1a, Aq-OH (10 mol-%), and Et3N (1.0 equiv., as a sacrificial electron donor and hydrogen-atom donor, see below) was irradiated in N,N-dimethylformamide (DMF) with a blue light-emitting diode (LED, λ_{Ex} = 455 ± 15 nm) for 24 h. Methyl benzoate (2a) was obtained in 61 % yield (Table 1, Entry 1).[41] Continuous irradiation of the same reaction mixture for 48 h gave 2a in 74 % yield for ca. 90 % substrate conversion. Control experiments with the omission of each of the individual catalytic components confirmed that the photocatalyst, electron donor, and most importantly light irradiation are necessary for the photoredox catalytic dehalogenation reactions to occur (Table 1, Entries 1–6). Among the other derivatives of anthraquinone, including Unisol Blue,

Table 1. Control reactions and optimization of the photoredox catalytic reduction conditions with methyl 2-bromobenzoate (1a) as a test substrate under visible-light irradiation.[a]

Entry	Donor [equiv.]	Catalyst [mol-%]	Conditions	Yield [%] (conversion,%)[b]
Control reactions				
1	Et3N (1.0)	Aq-OH (10)	455 nm, 24 h	61 (80)
2	**Et3N (1.0)**	**Aq-OH (10)**	**455 nm, 48 h**	**74 (90)**
3	–	–	455 nm, 48 h	0 (1)[c]
4	Et3N (1.0)	–	455 nm, 48 h	≥1 (2)[c]
5	–	Aq-OH (10)	455 nm, 48 h	13 (24)
6	Et3N (1.0)	Aq-OH (10)	dark, 48 h	0 (0)[c]
7	Et3N (1.0)	Aq-OH (10)	455 nm, 48 h	9 (11)[d]
Optimization of the reaction conditions				
8	Et3N (1.0)	Aq-OH (2)	455 nm, 24 h	47 (58)
9	Et3N (1.0)	Aq-OH (5)	455 nm, 24 h	44 (54)
10	Et3N (0.7)	Aq-OH (10)	455 nm, 24 h	47 (64)
Different anthraquinone derivatives (see Figure 1A for chemical structures)				
11	Et3N (1.0)	Aq (10)	455 nm, 24 h	35 (62)
12	Et3N (1.0)	2-EtAq (10)	455 nm, 24 h	34 (62)
13	Et3N (1.0)	2-NH2-Aq (10)	455 nm, 24 h	48 (76)
14	Et3N (1.0)	Aq-NH2 (10)	455 nm, 24 h	6 (18)
15	Et3N (1.0)	unisol blue (10)	455 nm, 24 h	3 (16)
16	Et3N (1.0)	frangulin (10)	455 nm, 24 h	58 (74)

[a] Reactions were performed under nitrogen with 1a in DMF (1.0 mL) with a blue LED (λ_{Ex} = 455 ± 15 nm. See the Supporting Information for the reaction setup). [b] Calculated from GC analysis (error ca. ± 5 %) by the internal-standard method (see the Supporting Information for details). The substrate conversion is shown in parentheses. [c] The yield was below the GC quantification limit. [d] The reaction was performed with 4-bromoanisole as the substrate.

ChemPubSoc
Europe

EurJOC
European Journal
of Organic Chemistry

Full Paper

which is used for microscopy, Aq-OH was selected for further experiments because of the better chemical yield of the product (cf., Table 1, Entries 1 and 11–15). Naturally occurring Frangulin A/B, which are derivatives of 1,8-dihydroxyanthraquinone, perform as well as Aq-OH (Table 1, Entry 16); therefore, this core structure has superior catalytic performance.

After the optimization of the reaction conditions (see Table 1, Entries 1–2 and 8–10), which required the simple mixing of aryl halides, commercially available inexpensive Aq-OH, Et$_3$N, and photoirradiation with blue LEDs under nitrogen, the scope of the method was explored with different aryl halide substrates. Good-to-excellent photoreduction yields (up to 87 %) were obtained with aryl bromide substrates possessing different substituents, for example, –CN, –CO$_2$Me (–o, –m, and –p), –CHO, –COMe, and –CONH$_2$ (see Figure 2); therefore, the photoredox catalytic reactions proceed under mild conditions. Bromobenzene gave a poor product yield owing to its very high

reduction potential. The yield increased with iodobenzene as the substrate (25 %); the reduction of 4-iodotoluene proceeded in 27 % yield, and the reduction of 4′-iodoacetophenone proceeded in 60 % yield. Aryl chloride substrates with suitable reduction potentials (e.g., 2-chlorobenzonitrile, see Figure 2 for reductive C–H arylation reactions with 2-chlorobenzonitrile) could also be activated by this catalytic method. However, aryl halide substrates with very high reduction potentials (e.g., 4-bromoanisole) could not be activated effectively for synthetically useful transformations and demonstrate the limit of the substrate scope of the reaction.

The photoredox catalytic SET reduction reactions proceed by a radical mechanism, as strongly supported by the experimental results and recent reports.[32,42] Additionally, reaction mixtures containing 4′-bromoacetophenone and 2-bromobenzonitrile were irradiated in the presence of 1,1-diphenylethylene, which is a radical scavenger,[43,44] and the coupling products **3n**
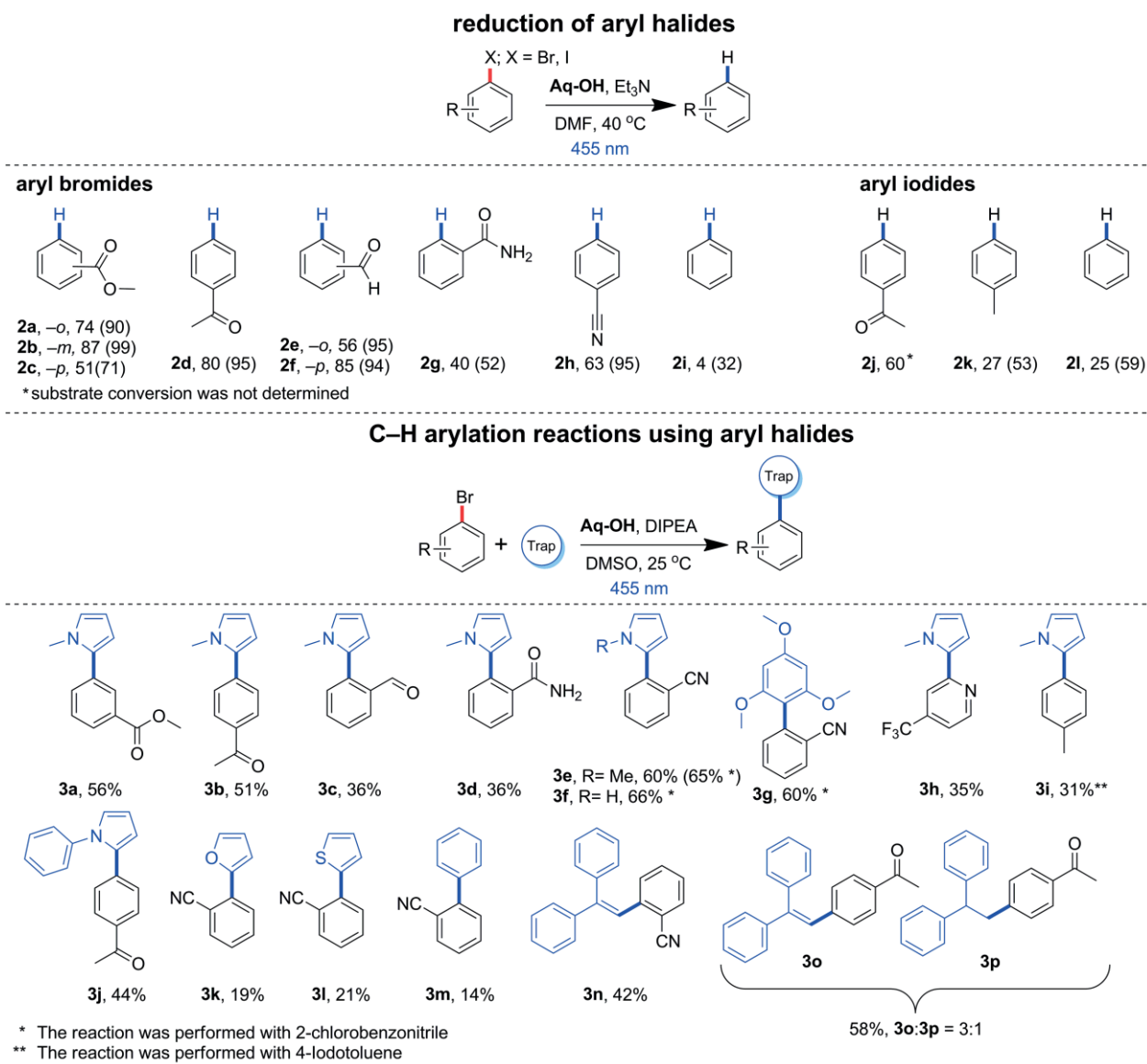

Figure 2. Yields for photoredox catalytic reductions and C–C bond-forming reactions with aryl halide substrates (Ar–X; X = I, Br, Cl). For the photoreduction reactions, the substrate conversions after 48 h are shown in parentheses (also see the Supporting Information).

ChemPubSoc
Europe

EurJOC
European Journal
of Organic Chemistry

Full Paper

and **3o** + **3p** were obtained in 42 and 58 % isolated yields (see Figure 2 and the Supporting Information for further details), respectively; these results provide further evidence for the radical nature of the reaction.

We explored the photoredox catalytic generation of aryl radicals from their respective halides for C–C bond-forming reactions with arenes, heteroarenes, and unsaturated double bonds. The main challenge in this case is the competing hydrogen-atom abstraction by the reactive aryl radicals either from the radical cation of the amine or from the solvent to form the reduction product, as was also observed for other photoredox catalytic C–H arylation reactions of aryl halides.[12,13,32,36–38] However, when a reaction mixture containing 2-bromobenzonitrile, Aq-OH, *N,N*-diisopropylethylamine (DIPEA), and benzene was irradiated with blue LEDs, the desired product **3m** was obtained in 14 % yield.[45] Similarly, when furan and thiophene were introduced as the radical trapping reagents, the desired products **3k** and **3l** were obtained in useful yields. Note that

thiophene and furan efficiently trap aryl radicals under photoredox conditions in redox-neutral reactions in which the excited state of the photocatalyst transfers an electron to the aryl radical precursor and no sacrificial electron donor is necessary (e.g., the photoredox catalytic generation of aryl radicals from their respective diazonium salts).[11,32] However, they consistently fail to trap aryl radicals generated from the respective aryl halides under other reported photoredox catalytic conditions. For instance, it has recently been reported that thiophene and furan fail to trap 2-benzothiazole radicals generated through SET from the respective bromides under photoredox catalytic conditions in the presence of *fac*-Ir(ppy)$_3$ (ppy = 2-phenylpridine) and R$_3$N as an electron donor.[36] The reason for this is still unclear and needs further detailed investigations. The Aq-OH photoredox catalytic system allows the C–H arylations of thiophene and furan, albeit in low isolated yields of ca. 20 %. When 1,3,5-trimethoxybenzene, a substituted arene, was used as a trapping reagent for the 2-cyanophenyl radical, the expected product
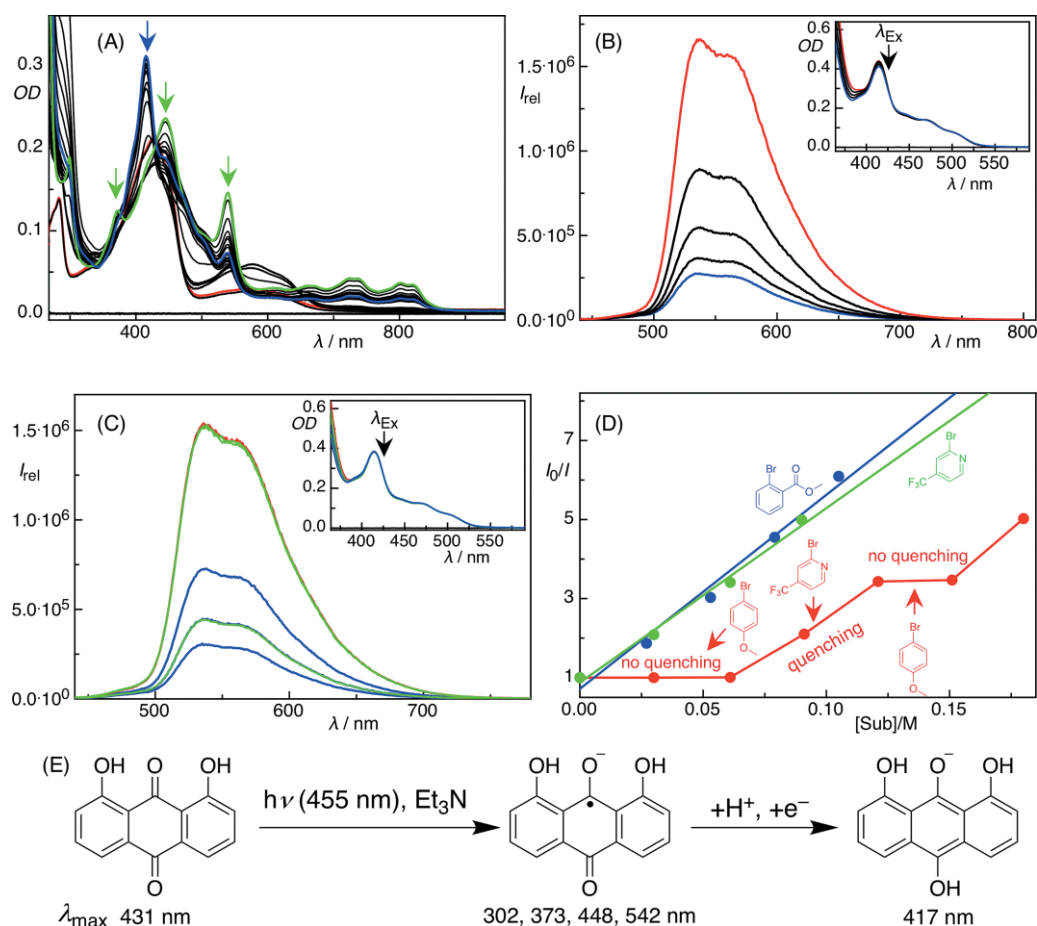

Figure 3. (A) Changes to the absorption spectra of Aq-OH upon photoirradiation (λ_{Ex} = 455 ± 15 nm) in the presence of Et$_3$N under nitrogen in DMF. The green and blue arrows indicate the absorption maxima of Aq-OH$^{·-}$ and Aq-OH-H$^-$, respectively. For the photoirradiation experiment in DMSO, see Figure S2. (B) Changes to the fluorescence spectra of the 1,8-dihydroxyanthraquinone semiquinone anion (Aq-OH-H$^-$) upon the successive addition of **1a** (test substrate). In the inset, the changes to the absorption spectra of Aq-OH-H$^-$ upon the successive addition of **1a** are shown. (C) Alternative luminescence quenching titration plots of Aq-OH-H$^-$ with 4-bromoanisole (green curves) and 2-bromo-4-(trifluoromethyl)pyridine [blue curves, see the Stern–Volmer quenching plot in (D)]. In the inset, the changes to the absorption spectra of Aq-OH-H$^-$ upon the addition of 2-bromo-4-(trifluoromethyl)pyridine and 4-bromoanisole are shown. (D) Stern–Volmer quenching plots of Aq-OH-H$^-$ with methyl 2-bromobenzoate and 2-bromo-4-(trifluoromethyl)pyridine and the fluorescence response (in this case, intensity) of Aq-OH-H$^-$ upon the alternating addition of 2-bromo-4-(trifluoromethyl)pyridine and 4-bromoanisole (see the mechanism section and the Supporting Information for more details). (E) The chemical structures of the photo- and redox-active species of Aq-OH are depicted along with their reported absorption maxima.[27]

ChemPubSoc
Europe

EurJOC
European Journal
of Organic Chemistry

Full Paper

was obtained in 60 % isolated yield. For pyrrole derivatives as trapping reagents, the C–H arylated products were isolated in moderate-to-good yields. Notably, unprotected pyrrole reacts cleanly with the aryl radicals. All investigated heterocycles (i.e., furan, thiophene, and pyrrole derivatives) were selectively arylated at the 2-position (see Figure 2). The C–H functionalization reaction of 1,1-diphenylethylene with 2-bromobenzonitrile gave **3n** in 42 % yield. 4′-Bromoacetophenone gave a mixture of **3o** and **3p** in 58 % isolated yield, and this result confirmed that both the hydrogen-atom abstraction and the oxidation reaction occur after the aryl radical addition step (see Figure S3). The C–H arylation reactions were also effective for aryl chlorides as the precursors of the aryl radicals. The use of 2-chlorobenzonitrile as the substrate resulted in the formation of **3e**–**3g** in good isolated yields.

The presence of different photo- and redox-active species (including all intermediates in the reaction mixture) under the synthetic reaction conditions and the challenges of performing spectroscopic and electrochemical experiments under non-idealized reaction conditions do not allow us to report a complete mechanism. However, on the basis of previous reports[28,29,32,42] and spectroscopic investigations (see Figures 1 and 3 and the Supporting Information), a proposed mechanism is depicted in Figure 4. The reaction did not yield any photoreduction products (see Table 1, Entry 6) or C–H arylated products in the dark. The absence of effective luminescence quenching of Aq-OH in the presences of methyl 2-bromobenzoate demonstrates that the excited state of Aq-OH is not responsible for the initiation of the SET to the aryl halides (Figure S1). Upon visible-light photoexcitation, the excited state of Aq-OH is quenched by Et$_3$N to generate the radical anion Aq-OH$^{•-}$ (and the radical cation of Et$_3$N, i.e., Et$_3$N$^{•+}$), which forms the semi-

quinone anion, Aq-OH-H$^-$, through protonation and successive reduction (or vice versa through consecutive or coupled steps). The presence of both Aq-OH$^{•-}$ and Aq-OH-H$^-$ species was confirmed by the irradiation of a mixture of Aq-OH and Et$_3$N under nitrogen in DMF and dimethyl sulfoxide (DMSO, see Figures 3A and S2). Notably, the electron transfer from the ground-state radical anion of anthraquinone or the semiquinone anion to the aryl halide substrates is thermodynamically unlikely owing to their intrinsic low ground-state reduction potentials [cf., E^0(Aq-OH/Aq-OH$^{•-}$) ≈ – 0.5 V vs. SCE and ref.[46]]. The semiquinone anion Aq-OH-H$^-$ could be generated in the presence of Na$_2$S$_2$O$_4$ under nitrogen (see Figure 1) and is luminescent.[40,47] The absorption spectrum of Aq-OH-H$^-$ did not change in the presence of methyl 2-bromobenzoate, but the Aq-OH-H$^-$ luminescence was significantly quenched (Figure 3). The luminescence of Aq-OH-H$^-$ was also quenched in the presence of 2-bromo-4-(trifluoromethyl)pyridine (another investigated substrate) but was not affected significantly by the presence of 4-bromoanisole (a substrate that is difficult to activate under the photoredox catalytic conditions, see Figure 3). The alternating quenching experiment (see Figure 3), in which 2-bromo-4-(trifluoromethyl)pyridine and 4-bromoanisole were added alternatively, gave the expected luminescence responses [i.e., when 4-bromoanisole was added the luminescence was unaltered, but the luminescence was quenched when 2-bromo-4-(trifluoromethyl)pyridine was added to the same solution]. Upon photoexcitation, the radical anion of Aq-OH can transfer an electron to the investigated aryl halide substrate. Previous work[28,29] on the luminescence quenching of the excited state of Aq$^{•-}$ by aryl halides supports this proposal.

Through SET to aryl halides (Ar–X, X = Cl, Br, and I), the generated Ar–X$^{•-}$ subsequently fragments to yield aryl radicals that
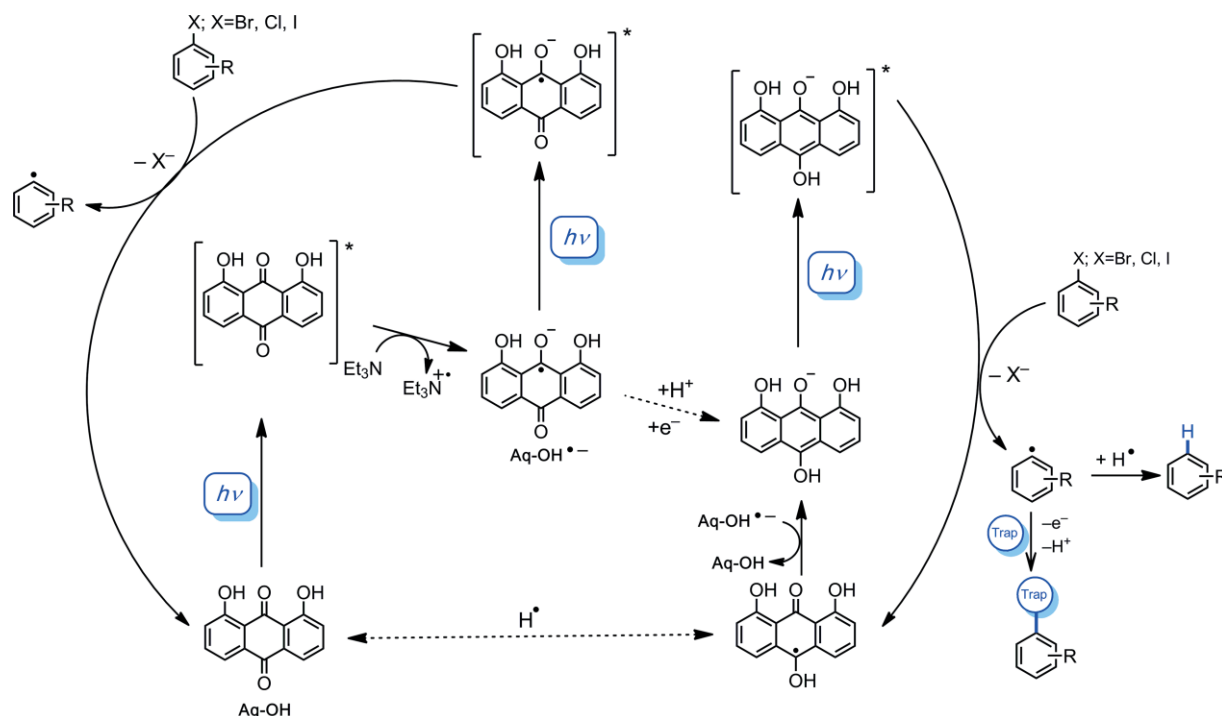

Figure 4. Proposed mechanism for the photoredox catalytic cycle for the photoreduction of aryl halides and C–C bond-formation reactions with suitable trapping reagents.

ChemPubSoc
Europe

EurJOC
European Journal
of Organic Chemistry

Full Paper

either (1) abstract a hydrogen atom from the radical cation of R$_3$N (i.e., Et$_3$N$^{\cdot+}$ or DIPEA$^{\cdot+}$) or from the solvent molecules (in this case, DMF or DMSO) to yield the reduction product or (2) react with (hetero)aryls or unsaturated double bonds to yield the corresponding C–C coupling products after oxidation and release of a proton (Figure 4). Gas chromatography–mass spectrometry (GC–MS) analysis of the crude product mixture confirmed the formation of diethylamine (see Figure S3). During the photoreaction, Aq-OH degrades. Such bleaching is often observed in photoredox catalytic reactions with organic dyes[44] or transition-metal photocatalysts.[48] In addition, the formation of substituted Aq-OH from a reaction with the aryl radicals was observed.[49] These photoproducts can continue to participate in the photoredox transformations.[50]

Conclusions

Radical anions and semiquinone anions of anthraquinones, a class of quinoid compounds, gain sufficient redox energy under visible-light irradiation to perform synthetically challenging reductive transformations. 1,8-Dihydroxyanthraquinone (Aq-OH) forms its colored radical anion and semiquinone anion upon visible-light irradiation in the presence of R$_3$N under nitrogen. The radical anion and the semiquinone anion are excited by visible light and transfer a single electron to aryl halides, which react in dehalogenation or C–C bond-forming reactions. We believe that the described results will pave the way to a broader use of commercially available and inexpensive anthraquinone derivatives in synthetic photoredox catalytic reductive transformations.

Experimental Section

General Procedure for the Photoreduction of Aryl Halides (Method A): In a 5 mL snap vial equipped with a magnetic stirring bar, the respective aryl halide (0.1 mmol, 1.0 equiv.) and catalyst (0.01 mmol, 0.10 equiv.) were dissolved in dry DMF (total volume of the solution 1.0 mL), and the resulting mixture was degassed (× 2) with a syringe needle. Triethylamine (0.10 mmol, 1.0 equiv.) was added under N$_2$, and the reaction mixture was irradiated through the plane bottom side of the snap vial at 40 °C with a LED (λ = 455 nm). The reaction progress was monitored by GC analysis. The yields of the reduction products were determined from GC measurements with appropriate internal standards.

General Procedure for C–H Arylation Reactions (Method B): In a 5 mL snap vial equipped with a magnetic stirring bar, the aryl halide (0.2 mmol, 1.0 equiv.) and Aq-OH (0.02 mmol, 0.1 equiv.) were dissolved in dry DMSO (total volume of the solution 1.0 mL), and the resulting mixture was degassed with a syringe needle. DIPEA (0.20–0.40 mmol, 1–2 equiv.) and the corresponding trapping reagent (4.0–6.0 mmol, 20–30 equiv.) were added under N$_2$, and the reaction mixture was irradiated through the plane bottom side of the snap vial at 25 °C with a LED (λ = 455 nm) for the time reported. The reaction progress was monitored by GC analysis until full conversion was obtained or the reaction slowed significantly. For workup, one of the two following procedures was used: (1) The reaction mixture was transferred into a separating funnel, and distilled water (10 mL) and brine (2 mL) were added. The resulting mixture was extracted with ethyl acetate (3 × 10 mL). The combined

organic layers were dried with MgSO$_4$, filtered, and concentrated in vacuo. Silica gel (ca. 1.0 g) was added to prepare the dry load for column chromatography. (2) The reaction mixture was transferred into a flask, and the DMSO was partially evaporated (ca. 0.5 mL) under reduced pressure. Ethyl acetate (10 mL) and silica gel (ca. 1.0 g) were added to prepare the dry load for column chromatography. In both methods, purification was achieved by silica gel flash column chromatography with petroleum ether/ethyl acetate as the eluent.

For the additional spectroscopic investigations and the characterization of the C–H arylated products, see the Supporting Information.

[1] D. A. Nicewicz, D. W. C. MacMillan, *Science* **2008**, *322*, 77–80.
[2] C. K. Prier, D. A. Rankic, D. W. C. MacMillan, *Chem. Rev.* **2013**, *113*, 5322–5363.
[3] C. Stephenson, T. Yoon, *Acc. Chem. Res.* **2016**, *49*, 2059–2060.
[4] B. König, *Eur. J. Org. Chem.* **2017**, 1979–1981.
[5] T. P. Yoon, M. A. Ischay, J. N. Du, *Nat. Chem.* **2010**, *2*, 527–532.
[6] M. H. Shaw, J. Twilton, D. W. C. MacMillan, *J. Org. Chem.* **2016**, *81*, 6898–6926.
[7] J. M. R. Narayanam, C. R. J. Stephenson, *Chem. Soc. Rev.* **2011**, *40*, 102–113.
[8] N. A. Romero, D. A. Nicewicz, *Chem. Rev.* **2016**, *116*, 10075–10166.
[9] For an example of the use of quantum dots in visible-light photoredox transformations, see A. Pal, I. Ghosh, S. Sapra, B. König, *Chem. Mater.* **2017**, *29*, 5225–5231.
[10] M. Neumann, S. Fuldner, B. König, K. Zeitler, *Angew. Chem. Int. Ed.* **2011**, *50*, 951–954; *Angew. Chem.* **2011**, *123*, 981.
[11] D. P. Hari, B. König, *Chem. Commun.* **2014**, *50*, 6688–6699.
[12] I. Ghosh, T. Ghosh, J. I. Bardagi, B. König, *Science* **2014**, *346*, 725–728.
[13] I. Ghosh, B. König, *Angew. Chem. Int. Ed.* **2016**, *55*, 7676–7679; *Angew. Chem.* **2016**, *128*, 7806–7810.
[14] A. Das, I. Ghosh, B. König, *Chem. Commun.* **2016**, *52*, 8695–8698.
[15] F. Z. Su, S. C. Mathew, L. Mohlmann, M. Antonietti, X. C. Wang, S. Blechert, *Angew. Chem. Int. Ed.* **2011**, *50*, 657–660; *Angew. Chem.* **2011**, *123*, 683.
[16] N. El-Najjar, H. Gali-Muhtasib, R. A. Ketola, P. Vuorela, A. Urtti, H. Vuorela, *Phytochem. Rev.* **2011**, *10*, 353–370.
[17] H. Nohl, W. Jordan, R. J. Youngman, *Adv. Free Radical Biol.* **1986**, *2*, 211–279.
[18] J. M. Lü, S. V. Rosokha, I. S. Neretin, J. K. Kochi, *J. Am. Chem. Soc.* **2006**, *128*, 16708–16719.
[19] F. Rusch, L. N. Unkel, D. Alpers, F. Hoffmann, M. Brasholz, *Chem. Eur. J.* **2015**, *21*, 8336–8340.
[20] S. Lerch, L. N. Unkel, M. Brasholz, *Angew. Chem. Int. Ed.* **2014**, *53*, 6558–6562; *Angew. Chem.* **2014**, *126*, 6676.
[21] N. Tada, Y. Ikebata, T. Nobuta, S. I. Hirashima, T. Miura, A. Itoh, *Photochem. Photobiol. Sci.* **2012**, *11*, 616–619.
[22] C. W. Kee, K. F. Chin, M. W. Wong, C. H. Tan, *Chem. Commun.* **2014**, *50*, 8211–8214.

★ ChemPubSoc
  Europe

EurJOC
European Journal
of Organic Chemistry

Full Paper

[23] K. Ohkubo, A. Fujimoto, S. Fukuzumi, *J. Am. Chem. Soc.* **2013**, *135*, 5368–5371.

[24] L. Cui, Y. Matusaki, N. Tada, T. Miura, B. Uno, A. Itoh, *Adv. Synth. Catal.* **2013**, *355*, 2203–2207.

[25] B. Chang, H. G. Shao, P. Yan, W. Z. Qiu, Z. G. Weng, R. S. Yuan, *ACS Sustainable Chem. Eng.* **2017**, *5*, 334–341.

[26] N. Tada, K. Hattori, T. Nobuta, T. Miura, A. Itoh, *Green Chem.* **2011**, *13*, 1669–1671.

[27] R. M. Wightman, J. R. Cockrell, R. W. Murray, J. N. Burnett, S. B. Jones, *J. Am. Chem. Soc.* **1976**, *98*, 2562–2570.

[28] B. R. Eggins, P. K. J. Robertson, *J. Chem. Soc. Faraday Trans.* **1994**, *90*, 2249–2256.

[29] P. Nelleborg, H. Lund, J. Eriksen, *Tetrahedron Lett.* **1985**, *26*, 1773–1776.

[30] A. R. Cook, L. A. Curtiss, J. R. Miller, *J. Am. Chem. Soc.* **1997**, *119*, 5729–5734.

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

[32] I. Ghosh, L. Marzo, A. Das, R. Shaikh, B. König, *Acc. Chem. Res.* **2016**, *49*, 1566–1577.

[33] J. D. Nguyen, E. M. D'Amato, J. M. R. Narayanam, C. R. J. Stephenson, *Nat. Chem.* **2012**, *4*, 854–859.

[34] H. Kim, C. Lee, *Angew. Chem. Int. Ed.* **2012**, *51*, 12303–12306; *Angew. Chem.* **2012**, *124*, 12469.

[35] E. H. Discekici, N. J. Treat, S. O. Poelma, K. M. Mattson, Z. M. Hudson, Y. D. Luo, C. J. Hawker, J. R. de Alaniz, *Chem. Commun.* **2015**, *51*, 11705–11708.

[36] A. Arora, J. D. Weaver, *Org. Lett.* **2016**, *18*, 3996–3999.

[37] S. O. Poelma, G. L. Burnett, E. H. Discekici, K. M. Mattson, N. J. Treat, Y. D. Luo, Z. M. Hudson, S. L. Shankel, P. G. Clark, J. W. Kramer, C. J. Hawker, J. R. de Alaniz, *J. Org. Chem.* **2016**, *81*, 7155–7160.

[38] I. Ghosh, R. S. Shaikh, B. König, *Angew. Chem. Int. Ed.* **2017**, *56*, 8544–8549; *Angew. Chem.* **2017**, *129*, 8664–8669.

[39] M. Majek, U. Faltermeier, B. Dick, R. Perez-Ruiz, A. Jacobi von Wangelin, *Chem. Eur. J.* **2015**, *21*, 15496–15501.

[40] For the chemical generation of the semiquinone anion, we recommend that a fresh $Na_2S_2O_4$ solution is prepared under an inert atmosphere. See the Supporting Information for details.

[41] See the Supporting Information for the photochemical reaction setup and general procedures.

[42] C. Costentin, M. Robert, J. M. Saveant, *J. Am. Chem. Soc.* **2004**, *126*, 16051–16057.

[43] W. Liu, H. Cao, H. Zhang, H. Zhang, K. H. Chung, C. A. He, H. B. Wang, F. Y. Kwong, A. W. Lei, *J. Am. Chem. Soc.* **2010**, *132*, 16737–16740.

[44] A. Graml, I. Ghosh, B. König, *J. Org. Chem.* **2017**, *82*, 3552–3560.

[45] For the C–H arylation reactions, the use of DMSO as the solvent and DIPEA as the sacrificial electron donor provided better chemical yields.

[46] The electrochemical experiments reported in ref.[27] indicate that E^0(Aq-OH-H·/Aq-OH-H⁻) < –0.5 V vs. SCE.

[47] Note that the absorption maxima of Aq-OH-H⁻ generated in the presence of $Na_2S_2O_4$ are consistant with the reported values.[27]

[48] J. J. Devery III, J. J. Douglas, J. D. Nguyen, K. P. Cole, R. A. Flowers, C. R. J. Stephenson, *Chem. Sci.* **2015**, *6*, 537–541.

[49] Under the photoredox catalytic reaction conditions, the substitution products were identified by HPLC and HPLC/MS analysis.

[50] The role of such photoproducts in determining the kinetics or chemical yield is currently unclear.