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Sensitization-Initiated Electron Transfer for Photoredox Catalysis

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Abstract: Photosynthetic organisms exploit antenna chromophores to absorb light and transfer excitation energy to the reaction center where redox reactions occur. In contrast, in visible-light chemical photoredox catalysis, a single species (i.e., the photoredox catalyst) absorbs light and performs the redox chemistry. Mimicking the energy flow of the biological model, we report a two-center photoredox catalytic approach in which the tasks of light energy collection and electron transfer (i.e., redox reactions) are assigned to two different molecules. $Ru(bpy)_3Cl_2$ absorbs the visible light and transfers the energy to polycyclic aromatic hydrocarbons that enable the redox reactions. This operationally simple sensitization-initiated electron transfer enables the use of arenes that do not absorb visible light, such as anthracene or pyrene, for photoredox applications. We demonstrate the merits of this approach by the reductive activation of chemical bonds with high reduction potentials for carbon-carbon and carbon-heteroatom bond formations.

Photosynthetic organisms transform light energy into chemical free energy through a series of energy-transducing reactions. Visible light is harvested by antenna pigments, such as chlorophyll b and β -carotene, and transferred to the reaction center pigment, chlorophyll a, to drive photosynthetic reactions.^[1-2] This strategy of using strongly absorbing antenna molecules for visible-light collection and weakly absorbing redox centers to drive chemical reactions enables the efficient conversion of light energy into redox energy for the simultaneous oxidation of water to molecular oxygen and the reduction of NADP⁺ to NADPH. In contrast, visiblelight-mediated photoredox catalysis,^[3-7] an emerging field in synthetic organic chemistry, uses visible light to drive chemical reactions, but relies on the use of the same molecule (i.e., a photoredox catalyst) for both visible-light absorption and the conversion of the light energy into redox energy to initiate redox reactions. This excludes the application of many chromophores that have extremely high redox potentials, but do not absorb visible light (e.g., polycyclic aromatic hydrocarbons for reduction reactions; c.f., sodium naphthalenide) in photoredox catalysis, and leads to a strong dependence on the inherent redox potentials of typical photoredox catalysts for the conversion of visible light into the maximum available redox energy.^[8] Aside from the typically very long reaction

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times and relatively poor photochemical quantum yields, the restricted redox energy gain upon visible-light photoexcitation limits the overall performance of a photoredox catalyst with respect to the substrate scope. Furthermore, in accordance with the common notion that the more reductive a catalyst, the less oxidative it is, synthetically demanding chemical modifications enhance the redox equivalence gain in one direction at the expense of the other (oxidative/reductive or vice versa).^[9]

Inspired by the natural photosynthetic systems, we envisioned using strongly absorbing molecules for light energy harvesting and funneling the excitation energy to a highly reducing molecule that does not absorb visible light. The redox potential of the latter species may be utilized to drive challenging redox reactions that are not feasible or less efficient with a single photocatalyst. The effective conversion of visible-light energy into redox equivalents in different photoredox catalytic systems is compared in Scheme 1. The energies of blue (455 nm) and green photons (530 nm) of 262 kJ mol⁻¹ or 2.72 eV and 226 KJ mol⁻¹ or 2.34 eV, respectively, are insufficient for the activation of many chemical bonds via direct photoexcitation. However, converting the same energy into redox equivalents enables the activation of such bonds through single-electron-transfer redox processes.

The many applications of visible-light photoredox catalysis for the activation of chemical bonds that have been reported over the last decade document the practicality of such energy transduction processes.^[3-7,10] However, as the electronic rearrangements of the photoredox catalysts upon light absorption commence the energy transduction processes, the intrinsic properties, in particular, the absorption and ground-state redox potentials of the photoredox catalysts, define how much light energy can be converted into redox energy (Rehm-Weller equation).^[11] As depicted in Scheme 1, the maximum reduction potential available in a typical $Ru(bpy)_{3}^{2+}$ -based photoredox catalytic system never exceeds a value of -1.33 V (the inherent ground-state reduction potential of $Ru(bpy)_{3}^{+}$).^[3] In contrast, the photoredox catalytic approach based on sensitization-initiated electron transfer (SenI-ET) uses the intrinsic properties (absorption and redox potentials) of two different molecules for the conversion of light energy into redox energy through a bimolecular energy-transfer process. Here, although the energy of visible light is insufficient to access the excited states of the redox-active species (the ΔE for photoexcitation), the relative energy of its excited state with respect to the visible-lightabsorbing sensitizer allows its excitation via a simple photoinduced energy-transfer process. As depicted in Scheme 1, such an energy transduction allows accessing the reduction potentials of polycyclic aromatic hydrocarbons, such as pyrene or anthracene. Even more interestingly, the reduction potentials of the radical anions of the polycyclic aromatic

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Scheme 1. Biological (left), typical photoinduced (PET, middle), and sensitization-initiated electron transfer (SenI-ET, right) photoredox processes. The relative redox potential gains upon photoexcitation using the same visible-light energy for PET and SenI-ET processes are also depicted. Upon photoexcitation using the same light energy (i.e., 2.0 eV), the SenI-ET catalytic method accumulates 0.8 V more redox energy than the typical photoredox PET cycle (see text).

hydrocarbons (PAHs; e.g., pyrene: -2.1 V vs. SCE, which is 0.8 V more negative than the reduction potential of Ru-(bpy)₃⁺) can be accessed by using 530 nm light in a process that requires approximately 120 KJ mol⁻¹ or 1.2 eV less energy than the energy required for direct excitation. Note that pyrene absorbs only up to about 350 nm (energy ca. 342 kJ mol⁻¹ or 3.5 eV).

Diffusion-controlled sequential energy- and electrontransfer processes, however, impose two challenges for the development of such two-center photoredox catalytic systems for synthetic applications (herein, we report photoredox catalytic reduction reactions): 1) The energy transfer from the energy-harvesting molecule to the redox-active (and visiblelight-inactive) molecule should be faster, ideally by one order of magnitude or higher, than single-electron transfer from the sacrificial electron donor that is present in the system (see Scheme 1). 2) Upon energy transfer, the triplet energy acceptor should be quickly transformed into its radical anion by electron transfer from the sacrificial electron donor. With these mechanistic challenges in mind, we began our investigations with $Ru(bpy)_3^{2+}$ as the light-harvesting complex (i.e., sensitizer) and various PAHs as triplet energy acceptors as they have exceptionally high reduction potentials.^[12] To our delight, the luminescence of Ru(bpy)₃²⁺ was quenched efficiently by a range of PAHs, such as anthracene (An), pyrene (Py), and 9,10-diphenylanthracene (DPA; see Figure 1 and the Supporting Information for luminescence quenching experiments). Furthermore, the luminescence quenching of $Ru(bpy)_3^{2+}$ via energy transfer by the investigated PAHs was faster by at least one order of magnitude than electron transfer from N,N-diisopropylethylamine (DIPEA).^[13,14] Triphenylene or naphthalene, however, were ineffective triplet acceptors owing to their high triplet-state energies (see Figure 1). Among the successful PAH quenchers, we selected Py for further investigations owing to its superior ground-state reduction potential (ca. -2.1 V, see Figure 1), and observed relatively fast C-H arylation reaction kinetics (see below and Table S1 in the Supporting Information).

The SenI-ET approach to photoredox catalysis is particularly suitable for the activation of carbon–(pseudo)halogen bonds in aryl chlorides, bromides,^[15–19] or pseudohalides for the following reasons: 1) Aryl halides and pseudohalides do not absorb visible light, and therefore cannot be activated by direct excitation with visible light. 2) Their high reduction potentials are beyond the reach of many typical photoredox catalysts including Ru(bpy)₃²⁺, but lower than the reduction potentials of the radical anions of polyaromatic hydrocarbons.^[10,20] 3) Owing to the strong carbon–halogen bonds and the two-step bond-dissociation kinetics,^[20] very long reaction times are required even with very good electron donors^[21] or highly reducing conPET photoredox catalytic systems^[22] for



Figure 1. Top: Chemical structures of Ru(bpy)₃Cl₂·H₂O and the PAHs investigated herein. Ground-state reduction potentials and triplet energies are also given.^[12] The depicted reduction potentials are against the saturated calomel electrode (SCE). Bottom: Spectroscopic investigations. A) Changes in the luminescence spectra (in this case, intensity; $\lambda_{ex} = 470$ nm) of Ru(bpy)₃²⁺ upon successive addition of pyrene in DMSO. In the insets, changes in the absorption spectra of Ru(bpy)₃²⁺, Py, and An (ii) are shown. B) Stern–Volmer plots for the quenching of Ru(bpy)₃²⁺ with different PAHs (An, Py, Naph, and Tpn), DIPEA, and 2-bromobenzonitrile.

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carbon-halogen bond activation. 4) The reduction potentials of both catalytic components are utilized for photoredox cascade reactions as the catalytic components are connected by diffusion-controlled energy transfer. Single-electron transfer to the (pseudo)halide substrates followed by (pseudo)halide anion extrusion generates (hetero)aryl radicals for the formation of new C-C or C-heteroatom bonds in the presence of suitable radical trapping reagents.

The reaction conditions were optimized by irradiating mixture of 2-bromobenzonitrile (model substrate), а $Ru(bpy)_{3}^{2+}$, Py, N-methylpyrrole (trapping reagent), and different sacrificial electron donors with blue light (λ_{ex} = 455 ± 15 nm; see Table S2). To our delight, when the reaction was conducted in the presence of $\text{Ru}(\text{bpy})_3^{2+}$ (1.0 mol%), Py (5.0 mol%), and a slight excess of DIPEA (1.4 equiv) in DMSO at room temperature (25°C), the C-H-arylated product 1a was obtained within about 2.5 h and isolated in 86% yield (GC yield: 92%; see Table S1). When the Ru- $(bpy)_3^{2+}$ and Py loadings were reduced, longer reaction times were required (see Table S2). With respect to the sacrificial electron donor, DIPEA was slightly more effective than triethylamine (Et₃N), and more effective than tributylamine (Bu₃N, probably owing to the lower solubility of Bu₃N in DMSO). A series of control experiments (i.e., omitting each individual component) confirmed that all components, that is, $Ru(bpy)_{3}^{2+}$, Py, the electron donor, and visible-light irradiation, are essential (Table S1, entries 1-8) for the photoredox catalytic C-H arylation reactions to take place. Interestingly, the reductive C-H arylation reactions were also effective and gave the products in similar yields when the reaction mixtures were irradiated with green LEDs ($\lambda_{ex} = 530 \pm 15 \text{ nm}$) as $Ru(bpy)_{3}^{2+}$ absorbs across a broad range of the visible spectrum. However, longer reaction times were necessary owing to the lower extinction coefficient of $Ru(bpy)_3^{2+}$ at 530 nm. Py could be recovered during the isolation of the C-H-arylated product **1a** (see the Supporting Information).

With the optimized reaction conditions in hand, which require only the mixing of substrates, $Ru(bpy)_3^{2+}$, Py, DIPEA, trapping reagent, and irradiation with visible light, we then explored the scope of this SenI-ET photoredox catalytic process with different (hetero)aryl bromides as (hetero)aryl radical precursors. A range of bromo(hetero)arenes reacted very efficiently under this reductive SenI-ET cross-coupling catalytic protocol (Figure 2). Aryl bromides with functional groups, for example, -CN, -COCH₃, -CHO, and -CO₂Et, were suitable arylating reagents (64-86% yield). Nitrogen-containing heteroaromatic substrates, such as bromo-substituted quinoline, pyridine, and pyrimidine, served as heteroarylating reagents (58-78% yield). Benzothiazole was functionalized at the C2 position in good yields. The C2 position of 2,4dibromothiazole could be activated selectively for C-H arylation, leaving the other C-Br bond intact for further synthetic modifications.

Interestingly, this redox-potential-dependent activation of carbon-halogen bonds in organohalides allows the use of halogenated (hetero)arenes as trapping reagents for the functionalization of carbon-halogen bonds, introducing another carbon-halogen bond for further synthetic modifications of the coupling product. For example, the reduction





Figure 2. The C-H arylation products obtained from (hetero)aryl halides with arenes and biologically important heterocycles. Yields of the isolated products are given.

potential of 5-bromo-3-methylindole is too high (see the Supporting Information for the cyclic voltammogram) for the activation of the carbon-halogen bond under these conditions. However, when it is used as a trapping partner for the aryl radicals, the C-H-arylated product **2 f** could be obtained in good yield (see Figure 2). When 2-bromo-1-methyl-1*H*-pyrrole was used as the trapping reagent, product **2 j** was isolated in 69 % yield.

Considering the ground-state reduction potential of Pv⁻, we anticipated that the redox power of this catalytic system exceeds the reduction potentials of substituted aryl chlorides. Consequently, we explored the SenI-ET method for C-H arylation reactions using (hetero)aryl chlorides as the (hetero)aryl radical precursors. Aside from aryl chlorides with functional groups such as -CN or -CO₂Me (see Figure 2), chlorinated N-heterocycles, such as pyridines, quinolines, and thiazoles, could be readily used as (hetero)aryl radical precursors (61-87% yield). The reaction times were slightly longer with the aryl chlorides than with the corresponding bromides (compare the reaction times of 1a and 3a) because of the stronger C-Cl bonds and the relatively slow C-Cl bond cleavage kinetics.^[20] Importantly, this method can also be used for the activation of carbon-chlorine bonds for C-H arylation reactions in the presence of brominated trapping reagents. A new carbon-carbon bond is formed by C-Cl bond activation, and simultaneously, a new C-Br bond is introduced for further functionalization (3d in Figure 2). Remarkably, the SenI-ET method also enables the conversion of aryl triflates^[23] into aryl radicals upon visible-light excitation,

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Figure 3. Photoredox catalytic cascade reactions, photo-Arbuzov reactions using aryl halides and trialkyl phosphites, and C–H arylation reactions using partially fluorinated aryl bromides.

extending the scope of aryl radical precursors that can be used in visible-light photoredox catalysis (**6a** and **6c** in Figure 3).

As the SenI-ET catalytic protocol operates via diffusioncontrolled interactions, we envisioned that the intrinsic redox potential of $\text{Ru}(\text{bpy})_3^+$ (ca. -1.33 V) and the redox potential of the catalytic system could be used sequentially to explore synthetically important photoredox cascade reactions with polychlorinated aromatic substrates. For example, when 2,4,6trichloropyrimidine was used as a substrate in the presence of $\text{Ru}(\text{bpy})_3^{2+}$ and DIPEA, the C–H-arylated product **4a** was obtained in good yield. However, when the same substrate was reacted under the SenI-ET photoredox catalytic conditions, the doubly arylated product **4b** was obtained. Moreover, two different coupling partners can be sequentially used to yield the disubstituted compounds **4c** and **4d**, but isolation of the intermediate is preferable to avoid the homocoupling product.

We then explored the SenI-ET method for carbonheteroatom bond formation using nucleophiles as the trapping partners for the aryl radicals (as in $S_{RN}1$ reactions)^[17] under visible-light irradiation. In this case, the challenges are competition with fast hydrogen atom abstraction of the aryl radical from the solvent and the radical cation of DIPEA, and the stability of the sensitizer in the presence of nucleophiles. We therefore selected (EtO)₃P as the coupling partner as its addition to aryl radicals is very fast. The expected phosphonylated products were obtained in excellent yields (products isolated in up to 89% yield; Figure 3) when aryl bromides and chlorides were irradiated in the presence of (EtO)₃P using the SenI-ET catalytic protocol. Aside from aryl halides, heteroaryl halides such as 5-bromopyrimidine and 3-bromoquinoline were phosphonylated (5d and 5e) in excellent yields. The use of other phosphites, such as $(MeO)_3P$, also gave the corresponding phosphonylated products in excellent yields (5g, 81% yield). The phosphonylated product 6b was isolated in 76% yield when the aryl triflate was used as the aryl radical precursor.

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Partially fluorinated aryl bromides were also used as the C–H arylating reagents using this photoredox catalytic method.^[24] For example, when 1,3-bis(trifluoromethyl)-5-bromobenzene or 3-bromo-5-fluorobenzotrifluoride were introduced as the precursors of the 1,3-bis(trifluoromethyl)-benzene and 5-fluorobenzotrifluoride radicals, respectively, in the presence of $\text{Ru}(\text{bpy})_3^{2+}$, only traces of the desired products were obtained. The SenI-ET method, however, provided products **7a**, **7b**, and **7c** in very good yields.

The experimental results along with recent literature reports^[10,18,22] strongly support our hypothesis that the C-H arylation reactions proceed via radical mechanisms. In addition, when 2-bromobenzonitrile was irradiated in the presence of 1,1-diphenylethylene, a radical scavenger,^[25] the coupling product 8a was isolated in 26% yield (see Figure 3 and the Supporting Information for further details), providing strong evidence for a radical reaction. The measured photochemical quantum yield of 0.12 ± 0.02 ($12 \pm 2\%$) of the photocatalytic reaction provides further support that discrete photoredox electron-transfer events take place.^[20,26] The C-H arylation reactions did not proceed in the dark, and the yields were very low when the reactions were performed without one of the catalytic components. In the presence of air (Table S1, entry 7 and Figure S18), the yield was very low. The luminescence of Ru(bpy)₃²⁺ was quenched efficiently in the presence of Py, and the quenching efficiency was at least one order of magnitude higher than the quenching efficiency of $Ru(bpy)_{3}^{2+}$ with DIPEA (see Figure 1 and Figure S2). The reactions did not proceed in the presence of PAHs (with even higher reduction potentials compared to Py) that possess higher triplet state energies than $Ru(bpy)_3^{2+}$ (see Figure 1) and do not quench the luminescence of $Ru(bpy)_3^{2+}$.

All experiments, spectroscopic investigations, and literature reports^[27] support the catalytic cycle proposed in Figure 4. Upon visible-light photoexcitation, $Ru(bpy)_3^{2+}$ transfers its energy to Py (as a representative PAH, see Figure 1). The excited Py is then reductively quenched by DIPEA to generate Py- and the radical cation of DIPEA (DIPEA⁺). Py⁻ in its ground state transfers one electron to the (hetero)aryl halide, yielding the (hetero)aryl radical precursor (Het)ArX⁻⁻ and regenerating neutral Py to complete the catalytic cycle. Fragmentation of (Het)ArX⁻⁻ yields the (hetero)aryl radical, which reacts with (hetero)arenes, alkenes, or nucleophiles ((EtO)₃P) to yield C-C and C-heteroatom coupling products. In a competing pathway, the aryl radical abstracts a hydrogen atom either from DIPEA⁺⁺ or from the solvent (in this case DMSO) to give undesired reduction products in minimal amounts and diisopropylamine (as confirmed by GC and GC-MS analysis of the crude reaction mixture). The inefficient photoredox reaction of excited-state $\text{Ru}(\text{bpy})_3^{2+}$ and DIPEA competes with the energy transfer from $Ru(bpy)_3^{2+}$ to Py but the rate constant is smaller by at least one order of magnitude.

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Figure 4. Proposed catalytic cycle for the SenI-ET catalytic C⁻⁻H arylation reactions using *N*-methylpyrrole as a representative trapping reagent. For the mechanism of the phosphonylation of aryl halides and pseudohalides, see Figure S29.

Notably, Py⁻ could also eject an electron upon photoexcitation.^[27] However, we excluded this possibility considering the observed substrate scope and the use of non-aqueous solvents.

In conclusion, sensitization-initiated photoredox electron transfer enhances the conversion of visible-light energy into redox energy for synthetic applications. The efficient funneling of the absorbed light energy enables the use of low-energy green light ($\lambda_{ex} = 530 \text{ nm}$, E = 2.3 eV) to access the redox potentials of highly reducing polycyclic aromatic hydrocarbons, such as pyrene or anthracene (ca. 0.8 V more negative than that of $Ru(bpy)_3^+$) that only absorb in the UV region $(\lambda_{abs}(Py) \le 350 \text{ nm}, E \ge 3.5 \text{ eV})$ for photoredox applications. Aryl halides (including aryl chlorides and heteroaryl chlorides) and pseudohalides are activated for carbon-carbon and carbon-heteroatom bond-forming reactions under extremely mild reaction conditions. The reaction times are short owing to a good photochemical quantum efficiency of 12%. The described SenI-ET method is a minimalistic chemical model of biological photosynthesis and extends the span of reaction methods in visible-light photoredox catalysis. Furthermore, it enables the use of extremely reducing molecules that do not absorb visible light for the activation of stable chemical bonds under visible-light irradiation.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: C–H arylation · electron transfer · energy transfer · photocatalysis · polycyclic aromatic hydrocarbons

- R. E. Blankenship, Molecular mechanisms of photosynthesis, 2nd ed., Wiley-Blackwell, Hoboken, 2014.
- [2] T. Mirkovic, E. E. Ostroumov, J. M. Anna, R. Van Grondelle, Govindjee, G. D. Scholes, *Chem. Rev.* 2017, 117, 249–293.
- [3] C. K. Prier, D. A. Rankic, D. W. C. MacMillan, *Chem. Rev.* 2013, 113, 5322-5363.
- [4] T. P. Yoon, M. A. Ischay, J. N. Du, Nat. Chem. 2010, 2, 527-532.
- [5] J. M. R. Narayanam, C. R. J. Stephenson, Chem. Soc. Rev. 2011, 40, 102–113.
- [6] N. A. Romero, D. A. Nicewicz, Chem. Rev. 2016, 116, 10075– 10166.
- J. Xuan, W. J. Xiao, Angew. Chem. Int. Ed. 2012, 51, 6828-6838; Angew. Chem. 2012, 124, 6934-6955.
- [8] For example, although both Ru(bpy)₃²⁺ and Ir(ppy)₃ are excited at similar visible-light wavelengths, depending on the solvent, the maximum available reduction potentials of the catalytic systems differ by the difference of their intrinsic ground-state reduction potentials of ca. 0.9 V.
- [9] Compare the reduction and oxidation potentials of Ru(bpy)₃²⁺ and Ru(bpz)₃²⁺ or *fac*-Ir(ppy)₃ and Ir[dF(CF₃)ppy]₂(dtbbpy)⁺ in acetonitrile. For the respective reduction and oxidation potentials, see Ref. [3].
- [10] I. Ghosh, T. Ghosh, J. I. Bardagi, B. Konig, Science 2014, 346, 725-728.
- [11] D. Rehm, A. Weller, Isr. J. Chem. 1970, 8, 259-271.
- [12] M. Montalti, A. Credi, L. Prodi, M. T. Gandolfi, *Handbook of photochemistry*, 3rd ed., CRC, Taylor & Francis, Boca Raton, 2006.
- [13] M. Wrighton, J. Markham, J. Phys. Chem. 1973, 77, 3042-3044.
- [14] S. P. Pitre, C. D. McTiernan, H. Ismaili, J. C. Scaiano, J. Am. Chem. Soc. 2013, 135, 13286–13289.
- [15] The generation of aryl radicals from aryl halides under photoredox catalysis is achieved by using strong bases, such as KOtBu,^[16] or nucleophiles under UV ($\lambda_{ex} \le 350$ nm) irradiation (S_{RN}1)^[17] and in the presence of an excess of highly reactive neutral organic reducing agents, such as N2,N2,N12,N12-tetramethyl-7,8-dihydro-6*H*-dipyrido[1,4]diazepine-2,12-diamine and UV-A (365 nm) irradiation as introduced by Murphy and co-workers.^[21] Highly reducing conPET catalytic systems^[10] and Ir complexes^[18,19] are also efficient in generating aryl radicals from aryl halides but typically require longer reaction times.
- [16] M. E. Budén, J. F. Guastavino, R. A. Rossi, Org. Lett. 2013, 15, 1174–1177.
- [17] R. A. Rossi, A. B. Pierini, A. B. Penenory, *Chem. Rev.* 2003, 103, 71–167.
- [18] J. D. Nguyen, E. M. D'Amato, J. M. R. Narayanam, C. R. J. Stephenson, *Nat. Chem.* 2012, *4*, 854–859.
- [19] H. Kim, C. Lee, Angew. Chem. Int. Ed. 2012, 51, 12303-12306.
- [20] L. Pause, M. Robert, J. M. Saveant, J. Am. Chem. Soc. 1999, 121, 7158–7159.
- [21] E. Cahard, F. Schoenebeck, J. Garnier, S. P. Y. Cutulic, S. Z. Zhou, J. A. Murphy, *Angew. Chem. Int. Ed.* **2012**, *51*, 3673–3676; *Angew. Chem.* **2012**, *124*, 3733–3736.
- [22] I. Ghosh, L. Marzo, A. Das, R. Shaikh, B. Konig, Acc. Chem. Res. 2016, 49, 1566–1577.
- [23] The reduction potentials of aryl triflates are very similar to those of aryl halides (see Figure S10).
- [24] Polyfluorinated aryl radicals (e.g., the pentafluorobenzene radical) can be generated from their bromide precursors owing to their extremely low reduction potentials, which are due to the electron-withdrawing effect of the fluorine atoms, using Ru- $(bpy)_3^{2+}$ or Eosin Y.

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- [25] 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.
- [26] Note that five consecutive events (light absorption, energy transfer, electron transfer from the sacrificial electron donor, electron transfer to the substrate, and stepwise cleavage of the carbon–halide bonds)^[20] are involved in the generation of the aryl radicals. Therefore, the quantum yield of 12 % demonstrates

an extremely efficient overall photoredox catalytic process combining several discrete energy- and photoredox electrontransfer events.

[27] C. Kerzig, M. Goez, Chem. Sci. 2016, 7, 3862-3868.

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Sensitization-Initiated Electron Transfer for Photoredox Catalysis



Inspired by nature: In the presented twocenter photoredox catalytic approach, $Ru(bpy)_3Cl_2$ absorbs visible light and transfers the energy to polycyclic aromatic hydrocarbons, which in turn enable an efficient redox process. This method was used for the activation of (hetero)aryl halides for the formation of carbon– carbon and carbon–heteroatom bonds.