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Highly Chemoselective Catalytic Photooxidations Using Solvent as a Sacrificial Electron Acceptor

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Supporting information for this article is given via a link at the end of the document.

Abstract: Catalyst recovery is an integral part of photoredox catalysis. It is often solved by adding another component—a sacrificial agent—whose role is to convert the catalyst back into its original oxidation state. However, an additive may cause a side reaction thus decreasing the selectivity and overall efficiency. Herein, we present a novel approach towards chemoselective photooxidation reactions based on suitable solvent—acetonitrile acting simultaneously as an electron acceptor for catalyst recovery, in combination with anaerobic conditions. This is allowed by the unique properties of the catalyst, 7,8-dimethoxy-3-methyl-5-phenyl-5-deazaflavinium chloride existing in both strongly oxidizing and reducing forms, whose strength is increased by excitation with visible light. Usefulness of this system is demonstrated in chemoselective dehydrogenations of 4-methoxy- and 4-chlorobenzyl alcohols to aldehydes without over-oxidation to benzoic acids achieving yields up to 70%. 4-Substituted 1-phenylethanol were oxidized to ketones with yields 80–100% and, moreover, with yields 31–98% in the presence of benzylic methyl group, diphenylmethane or thioanisole which are readily oxidized in the presence of oxygen but these were untouched with our system. Mechanistic studies based on UV-VIS spectro-electrochemistry, EPR and time-resolved spectroscopy measurements showed the process involving an electron release from an excited deazaflavin radical to acetonitrile forming solvated electron is crucial for the catalyst recovery.

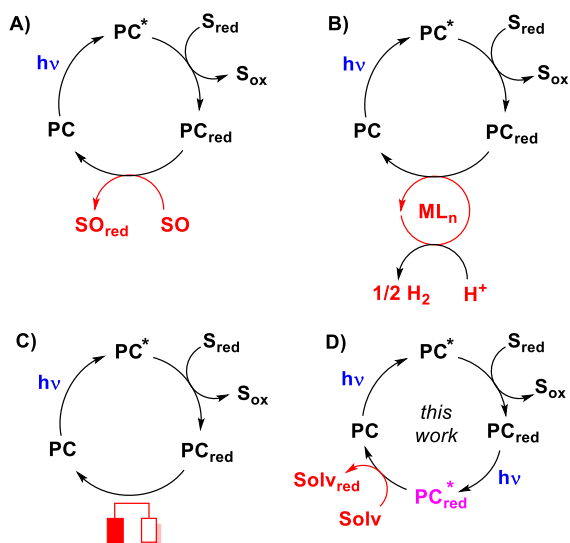
Introduction

Highly chemoselective procedures are at the forefront of modern organic chemistry.^[1] For oxidations, effective chemoselective systems based on stoichiometric agents, such as hypervalent iodine compounds,^[2] oxone^[3] and dioxirane^[4] or catalytic systems using transition metal complexes, nitroxyl radicals or neutral organic molecules have been described.^[5–7] Nevertheless, most

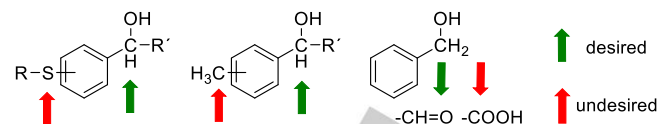
oxidants still lack selectivity allowing the undesired oxidation of an adjacent functional group or over-oxidation to occur. Photo-redox catalysis has been established as an alternative approach to oxidative transformations.^[8,9] However, the number of oxidation systems tolerating other sensitive functional groups is limited also in this research field.^[10]

Regeneration of a photocatalyst may cause chemoselectivity problems in photooxidation reactions. Oxygen is a favorable stoichiometric oxidizing agent from both an economic and environmental point of view.^[11] However, various reactive oxygen species (ROS) are formed when using oxygen, which can provide undesired side reactions.^[12] Several sacrificial oxidants other than oxygen have been studied in photooxidation reactions, including peroxosulfides, nitrobenzene or copper(II) salts, but these compounds also produce various redox-active by-products (Scheme 1A).^[13] The use of a transition metal co-catalyst providing (photo)catalyst regeneration at the expense of H₂ formation is an elegant way to perform acceptor-free dehydrogenation reactions (Scheme 1B).^[14] Analogous waste-free procedures use electrochemistry for either catalyst regeneration or the generation of reactive oxidative species (Scheme 1C).^[15] Nevertheless, both these systems are applicable in specific cases only. Herein, we present a novel approach towards chemoselective photooxidation reactions using a suitable solvent as an electron acceptor for catalyst recovery in combination with anaerobic conditions (Scheme 1D). This system does not need any additional agent and avoids the presence of ROS. In general, this approach may be applicable for catalysts with two photoactive redox states, one behaving as a strong oxidant (**PC***) and the other one as a strong reductant (**PC*_{red}**) upon photoexcitation (see ref.^[16] for examples of molecules with such properties).

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Scheme 1. Overview of photocatalyst (PC) regeneration in the oxidation of a substrate S_{red} to S_{ox} based on (A) a sacrificial oxidant - SO , (B) acceptorless dehydrogenation, (C) electrochemistry and (D) a solvent.



Scheme 2. Examples of chemoselectivity problems in oxidations of highly functionalized molecules.

Our attempt to convert neutral deazaflavin derivative **2**, the precursor of strongly reducing semiquinone, into a strongly oxidizing dye by the introduction of a positive charge has led to a novel deazaflavinium salt **3-Cl** (Figure 1A). This salt is readily available by bridging hydroxyethyl derivative **2b**. Compound **3-Cl** absorbs light at ~ 400 nm, providing blue fluorescence with $\Phi_F = 17\%$ (Figure 2). Particle 3^+ produces radical 3^{\cdot} ($E(3^+/3^{\cdot}) = -0.83$ V vs SCE) much more easily than neutral deazaflavins **2** ($E(2a/2a^{\cdot-}) = -1.41$ V^[20] vs SCE) and consecutive reduction leads to its reduced form 3_{red}^- (Figures 1B and 2). Protonated fully reduced $3_{red}H$ is bench stable in the dark and can be prepared from **3-Cl** via hydrogenation (see Experimental).

Results and Discussion

We demonstrate our chemoselective approach using a riboflavin (vitamin B2) derivative because flavins, in general, are recognized as versatile photoredox catalysts.^[8d,17,18] Among the flavin family (Figure 1), one can find very strong oxidizing agents such as salts **1-X** (Figure 1A), which are characterized by excited state reduction potentials higher than $+2.5$ V.^[19] On the other hand, the photoexcited radical of deazaflavin **2a** ($2a^{\cdot-}$) has been shown to be one of the strongest reducing agents reported to date, as demonstrated by its highly negative oxidation potential ($E_{ox}^* = -3.3$ V).^[20] Aerobic benzylic photooxidation is the main area of application of the flavins. However, although flavins have been shown to be selective in a few cases, the procedure for oxidizing the benzylic position in the presence of a heteroatom, such as sulfur in sulfides or nitrogen in an amino group, has not been described to date (Scheme 2).^[17b,21] Similar to other photocatalysts, the need for oxygen during flavin recovery causes chemoselectivity problems.

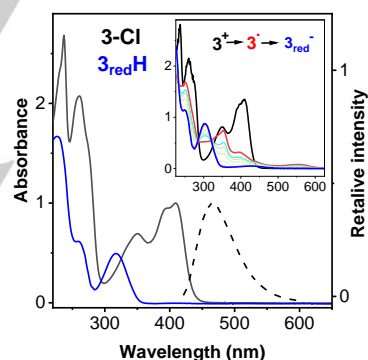


Figure 2 Absorption and emission spectra of synthesized **3-Cl** and $3_{red}H$, $c = 5 \times 10^{-5}$ mol L⁻¹, and absorption spectra of 3^+ and 3_{red}^- generated by electrochemistry (inset, see the Supporting Information S14 for details). Solvent: acetonitrile.

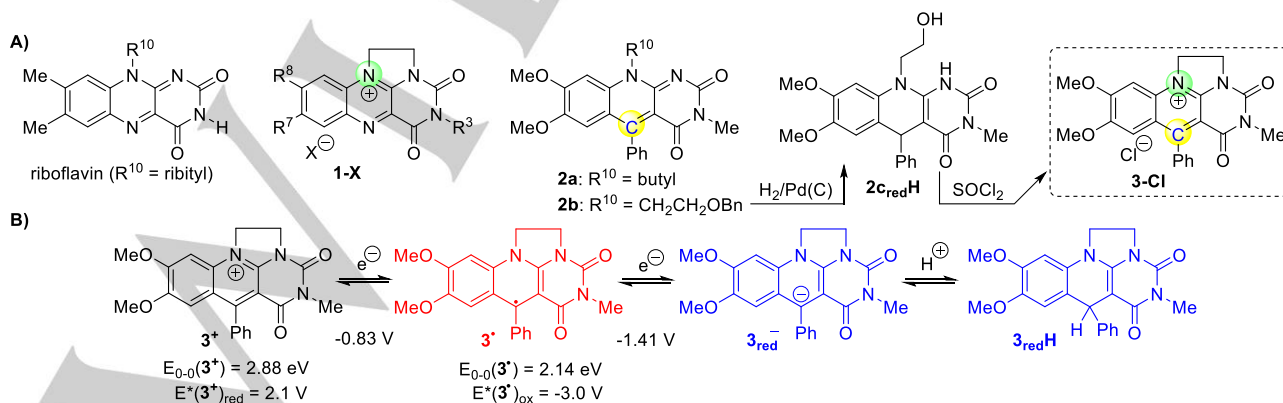
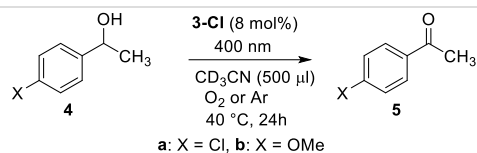


Figure 1 (A) Design of riboflavin derivatives for photocatalysis, synthesis of **3-Cl**, (B) redox forms of deazaflavinium species 3^+ with measured and calculated redox potentials in the ground and excited (\cdot) states (see Supporting Information S6-S9 for details). Solvent: acetonitrile, redox potentials relative to SCE.

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Table 1. Photooxidations of **4** mediated by **3-Cl** and other flavins under aerobic/anaerobic conditions.^[a]

Entry	Atm.	X	Conditions alternation	Yield of 5 [%] ^[b]
1	O ₂	Cl	-	quant.
2	Ar	Cl	-	80
3	Ar	Cl	in acetone-d ₆	20
4	Ar	Cl	in DMSO-d ₆	27
5	Ar	Cl	in DMF-d ₇	4
6	Ar	Cl	in benzonitrile	56
7	Ar	Cl	in nitrobenzene	35
8	O ₂	MeO	2b	50
9	Ar	MeO	2b	12
10	O ₂	MeO	RFTA	quant.
11	Ar	MeO	RFTA	7
12	O ₂	MeO	-	quant.
13	Ar	MeO	-	quant.

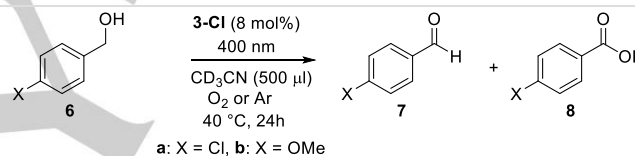
[a] Conditions: **3-Cl** (3 μmol), **4** (37.5 mmol), solvent (500 μL), 400 nm, 40 °C, oxygen (balloon) or Ar, 24 h (O₂/Ar), see Experimental for details. [b] Determined by ¹H NMR.

As expected, **3-Cl** is an efficient oxidative photocatalyst as proven using a model substrate, 1-(4-chlorophenyl)ethan-1-ol (**4a**), under aerobic conditions typically used for flavin-based oxidations (Table 1, Entry 1). Surprisingly, we observed similar reactivity using **3-Cl** under an argon atmosphere. Only 8 mol% of catalyst **3-Cl** was sufficient to convert 80% of alcohol **4a** into ketone **5a** upon irradiation with light at 400 nm in degassed acetonitrile in the absence of an additive (Table 1, Entry 2). Consequently, a question appeared how the catalyst was regenerated to reach such high conversions with a turnover number (TON) of ~10.

We hypothesized that acetonitrile served as an electron acceptor. Experiments in other potentially reducible solvents provided the desired product in relatively low yield (Entries 3–7) with the exception of benzonitrile. The reason is significantly lower photostability of **3-Cl** in DMF and acetone as compared with acetonitrile (see the Supporting Information S4). Also relatively low oxidation potential of DMF ($E_{ox} = 2.1$ V vs SCE^[22]) should be taken in account allowing its oxidation by **3*** in an excited state. In nitrobenzene and DMSO, several unidentified by-products were formed within anaerobic oxidation of **4a**, most likely as a result of radical intermediates interaction with products of nitrobenzene/DMSO reduction.

The unique catalytic properties of **3-Cl** were demonstrated by comparison with neutral deazaflavin **2b** and riboflavin tetracetate (RFTA), which is a prominent flavin derivative used in photooxidation reactions.^[17b-d] As expected, with **2b** and RFTA, the photooxidation of **4b** occurred in good to excellent yield under

an oxygen atmosphere. However, the reactions occurred in poor yields under an argon atmosphere, approximately corresponding to the catalyst amount (Entries 8–11). On the other hand, the reactions conducted using **3-Cl** provided **5b** in quantitative yield in both oxygenated and degassed solutions giving unequivocal evidence in regard to the catalyst regeneration process under inert conditions (Entries 12 and 13). It should be noted that the oxidation reaction did not proceed in the absence of light and a catalyst (for blank experiments, see Supporting Information S3). Using anaerobic conditions in the photocatalytic oxidation reactions with **3-Cl** prevents the occurrence of oxygenation processes. Therefore, we proved our novel methodology in a series of chemoselective dehydrogenation reactions. Initially, we performed the photooxidation of *p*-substituted benzyl alcohols **6**, which are known to be over-oxidized into their corresponding benzoic acid derivatives in various catalytic systems,^[23] including some with flavins.^[24] Indeed, we observed the exclusive formation of aldehyde **7** using **3-Cl** under anaerobic conditions (Table 2, Entries 3 and 4). On the other hand, comparative experiments conducted under an oxygen atmosphere provided quantitative yields of the benzoic acid **8** (Entries 1 and 2).

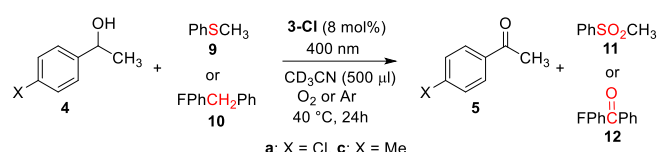
Table 2. Chemoselective photooxidation of **6** mediated with **3-Cl** under aerobic/anaerobic conditions.^[a]

Entry	Atm.	X	Additives	Yield [%] ^b	
				7	8
1	O ₂	MeO	-	0	quant.
2	O ₂	Cl	-	0	quant.
3	Ar	MeO	-	70	0
4	Ar	Cl	-	22	0

[a] Conditions: **3-Cl** (3 μmol), **6** (37.5 μmol), solvent (500 μL), 400 nm, 40 °C, oxygen (balloon) or Ar, 24 h (O₂/Ar), see Experimental for details. [b] Determined by ¹H NMR.

To demonstrate the chemoselectivity of the reaction in the presence of other centers sensitive to oxidation, we performed the competitive oxidation of a series of secondary benzylic alcohols in the presence of thioanisole (**9**) or substituted diphenylmethane **10** (Table 3). Thioanisole (**9**) easily undergoes aerobic electron transfer or singlet oxygen oxygenation reactions to form sulfoxide or sulfone.^[26] Diphenylmethanes **10** are converted into their corresponding benzophenones using several photocatalytic methods.^[18d,25a,27] In our photocatalytic system, alcohols **4a** and **4c** were selectively transformed into ketones **5a** and **5c** under an argon atmosphere with the other substrates remaining intact (Table 3, Entries 5–8). As expected, both substrates in the reaction mixture were always oxidized non-selectively under an oxygen atmosphere (Entries 1–4). It should be noted that the yields obtained in the presence of competitive substrates were lower, most probably as the catalyst was also involved in non-productive PET with **9** or **10**.

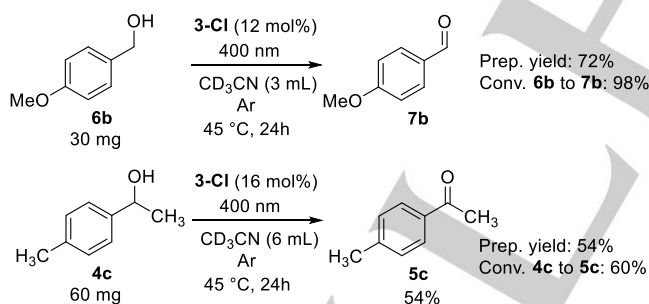
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Table 3. Competitive experiments on photooxidation of **4** mediated with **3-Cl** under aerobic/anaerobic conditions.^[a]


Entry	Atm.	X	Competitive substrate	Yield [%] ^[b]	
				5	11/12
1	O ₂	Cl	9	63	64/-
2	O ₂	Cl	10	86	-/58
3	O ₂	Me	9	80	quant./-
4	O ₂	Me	10	91	-/60
5	Ar	Cl	9	31	0/-
6	Ar	Cl	10	37	-/0
7	Ar	Me	9	66	0/-
8	Ar	Me	10	52	-/0

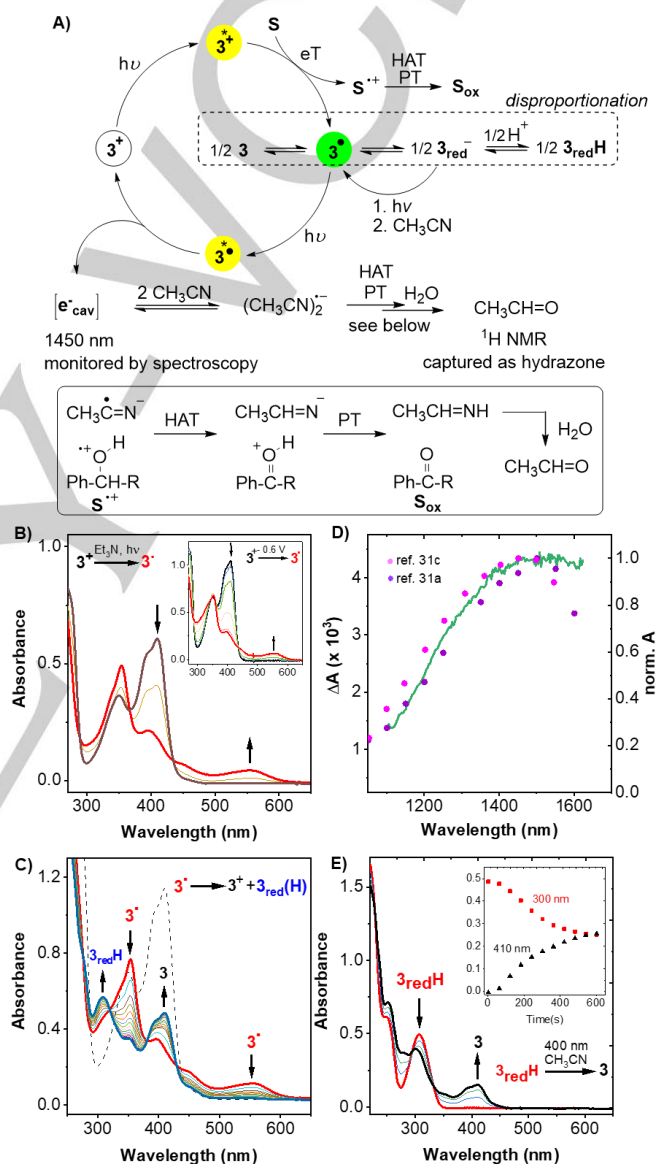
[a] Conditions: **3-Cl** (3 μmol), each substrate (37.5 μmol), solvent (500 μL), 400 nm, 40 °C, oxygen (balloon) or Ar, 24 h (O₂/Ar), see Experimental for details. [b] Determined by ¹H NMR and ¹⁹F NMR.

Semi-preparative experiments with product isolation were performed using benzylic alcohols **6b** and **4c** (Scheme 3). In both cases, the reaction proceeded chemoselectively to give the dehydrogenation product with good to high conversions achieving preparative yields of 72 and 54% for aldehyde **7b** and acetophenone **5c**, respectively.

**Scheme 3.** Semi-preparative anaerobic chemoselective oxidations mediated with **3-Cl** under optimized conditions (see Experimental for details).

The proposed mechanism based on our investigations is given in Figure 3A. The catalytic cycle starts with PET between the substrate and **3***, analogous to other flavin-based photooxidations.^[18d,25b,28] Excited **3*** ($E_{red}^* = 2.1$ V vs SCE) is strong enough to oxidize **4b** ($E = 1.57$ V vs SCE^[19b]), **9** ($E = 1.34$ V vs SCE^[26a]) and other substrates, even chloro-substituted benzyl alcohols ($E_{ox} = 2.16$ V vs SCE^[19b] for **4a**) albeit with lower efficiency as the ΔG was close to 0 kJ mol⁻¹.^[29] The efficient PET was also confirmed by the effective fluorescence quenching of **3-Cl** in the presence of the substrates used in this work (see the Supporting Information S16). Interestingly, unlike other flavin derivatives, only a weak triplet state of **3-Cl**, which is not

quenched by the substrate, was observed by transient absorption spectroscopy (see Supporting Information S15). This may indicate that **3-Cl** participates in PET in its singlet excited state analogous to a similar ethylene-bridged dimethoxyflavinium salt **1a-Cl** (see Figure 1; R³ = Me, R⁷=R⁸= OMe).^[19a] Neutral radical **3*** is formed via PET as monitored using steady-state spectroscopy in the model reaction with trimethylamine. The UV-Vis spectrum of the species formed via PET corresponds to that generated electrochemically at ca. -0.6 V vs SCE (Figure 3B) with EPR corresponding to the theoretical spectrum of **3*** (see the Supporting Information S17).

**Figure 3.** (A) Proposed mechanism of anaerobic photooxidations with **3-Cl** including disproportionation of **3*** (dash-line box) and an example of hydrogen and proton exchange among reaction intermediates to illustrate acetonitrile transformation (full-line box), (B) radical **3*** formation from **3*** by PET and electrochemically (inset), (C) evidence of **3*** disproportionation by UV-VIS spectroscopy (**3*** was generated electrochemically; cf. Figure 3B), (D) difference absorption spectra of solvated electron in acetonitrile with 40 ± 20 ps lifetime after irradiation of **3-Cl** (in the presence of electron donor Et₃N) by 400 nm LED (20 s) and 350 nm laser pulse (0.8 μJ), i.e. at maxima of **3*** and **3*** absorption, respectively, (E) oxidative transformation of **3redH** to **3*** by irradiation of **3redH** solution in acetonitrile under argon. See Experimental and Supporting Information S11–14 for other details.

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Subsequently, excited 3^* ejects an electron into acetonitrile. Thus, the solvated electron is captured by acetonitrile producing an acetonitrile dimer radical anion with both species being in equilibrium.^[31] Finally acetonitrile reduction products are formed (see full-line box in Figure 3A), one of them, acetaldehyde, was detected in the ^1H NMR spectrum of the reaction mixture after the anaerobic dehydrogenation reaction (see Supporting Information S10). We performed other experiments supporting the occurrence of these processes: i) The solvated electron in acetonitrile was observed using sub-picosecond transient absorption spectroscopy of the irradiated mixture of **3-CI** in the presence of trimethylamine in acetonitrile (Figure 3D and the Supporting Information S11); ii) acetaldehyde in an amount corresponding to a TON = 12 was quantitatively determined via hydrazone formation in the gas phase above the irradiated reaction mixture (triphenylphosphine in the presence of a catalytic amount of **3-CI** in acetonitrile) when it was gently bubbled with argon (see Supporting Information S10). It is most likely that 3^* ejects an electron from its excited state. Species $(3^*)^*$ may be a very strong reducing agent with an E_{ox}^* ca. -3.0 V; It is able to carry out the reductive dehalogenation of 4-bromoanisole ($E = -2.75$ V vs SCE^[32]) similar to the excited radical anion prepared from **2a**, which has been shown to act via a consecutive electron transfer (conPET^[33]) mechanism (see the Supporting Information S5).^[20] Deazaflavin radicals are known to disproportionate into their oxidized and reduced forms.^[34] Similar behavior was observed for neutral radical 3^* undergoing disproportionation to 3^* and 3_{red}^- which can be protonated to 3_{red}H (see dashed-line box in Figure 3A and Figure 3C for spectroscopic evidence). Excited reduced deprotonated form 3_{red}^{-*} may be a strong reducing agent analogously to excited reduced deprotonated flavin cofactors acting in photolyases,^[35] engineered ene-reductases^[36a] or excited deprotonated reduced riboflavin recently used in artificial reducing systems.^[36b] Moreover, 3_{red}^- absorbs light in the visible region (Figure 1C and the Supporting Information S8) Therefore, the participation of 3_{red}^{-*} in the reduction of acetonitrile and consequently, the regeneration of 3^* during the anaerobic catalytic oxidation reactions cannot be excluded. This is supported by an observation of efficient oxidation of 3_{red}H to 3^* occurring by irradiation with 400 nm light in acetonitrile which was the only possible electron acceptor present in the reaction mixture (see Figure 3E and the Supporting Information S13).

Conclusion

In conclusion, we have observed the unprecedented anaerobic dehydrogenations of alcohols mediated by visible light and a novel deazaflavinium catalyst **3-CI** proceeding at an expense of acetonitrile reduction. This was allowed by the unique **3-CI** properties existing in both its strongly oxidizing and reducing forms, which could even be excited by light. We have demonstrated the practicality of this new system is highly chemoselective and mild photooxidation reactions with acetonitrile acting simultaneously as the solvent and sacrificial oxidant. This novel approach is expected to be expanded to other oxidative processes using other photoredox catalysts.

Experimental Section

General information and methods

Starting materials and reagents were obtained from commercial suppliers and used without further purification. The solvents were purified and dried using standard procedures. Riboflavin tetraacetate (RFTA) was prepared according to a described procedure.^[26a] For synthesis of deazaflavin **2b**, see the Supporting information S2. **NMR spectra** were recorded on a Varian Mercury Plus 300 (299.97 MHz for ^1H , 75.44 MHz for ^{13}C , and 282.23 MHz for ^{19}F) or Agilent 400-MR DDR2 (399.94 MHz for ^1H and 100.58 MHz for ^{13}C) at 298 K. Chemical shifts δ are given in ppm, using residual solvent or tetramethylsilane as an internal standard. Coupling constants J are reported in Hz. **High-resolution mass spectra** were obtained on Q-ToF Micro (Waters), equipped with a quadrupole and time-of-flight (TOF) analyzer and subsequent a multichannel plate (MCP) detector. Thin layer **chromatography** (TLC) analyses were carried out on a DC Alufolien Kieselgel 60 F254 (Merck). Preparative column chromatography separations were performed on a silica gel Kieselgel 60 0.040–0.063 mm (Merck). Flash chromatography was performed at Büchi Pure C-810 at Silica 40 μm irregular column. **Melting points** were measured on a Boetius melting point apparatus and are uncorrected.

Photocatalytic experiments were performed in vessels from borosilicate glass using commercial LED(s) as a light source: LED Engin, 1.35 W@700 mA, 400 nm (dominant wavelengths 385–410 nm). For geometry of the setup, see the Supporting Information S18.

UV-Vis absorption spectra were performed on Agilent Cary 8454 spectrometer using quartz cells of 1 cm. The relative fluorescence intensities in quenching experiments were measured on a Varian Eclipse spectrometer. Stern-Volmer plots ($I_0/I = 1 + K_S[Q]$) were constructed, and constants K_S were evaluated as the slope of the dependence using Origin software. The pump-thaw degassed samples were illuminated in either 10×10 mm or 2×10 mm cells by 400 nm LEDs ($F(400) = 3.0 \times 10^{-7}$ Einstein s^{-1}) placed in a custom-made holder with perpendicular orientation in respect to the spectra recording beam.

UV-Vis emission spectra (Horiba Duetta spectrofluorometer) were recorded at room temperature. Fluorescence quantum yield was determined relatively to 9,10-diphenylanthracene in EtOH with a Horiba Duetta spectrofluorometer.

Spectro-electrochemistry measurements were performed in an OTTE Cell (Optically transparent thin-layer electro-chemical cell),^[37] pathlength = 0.02 cm, working electrode: Pt minigrd, counter electrode: Pt: minigrd, pseudo reference electrode: Ag wire. Samples were prepared by degassing a solution via argon bubbling for several minutes. UV-Vis spectra were recorded on Agilent Cary 8454 spectrometer. See the Supporting Information S19 for details.

Time-resolved spectroscopy. Transient absorption experiments were carried out using commercially available apparatus from Ultrafast Systems. Briefly, an Ytterbium femtosecond laser was used to generate 1030 nm with 400 μJ pulses at 1 kHz. The output was split into two parts, where 75% of the 1030-nm pulses were used to pump a collinear Optical Parametric Amplifier (OPA, APOLLO-Y) tuned to pump 330, 350 or 400-nm pulses (ca. 250 fs, 300–1000 nJ at the sample position) for sample excitation and 25% were used for generation of supercontinuum white light probe pulses by focusing into one of three different crystals giving a probe spectrum ranging from 350–500, 480–950 or 1100–1600 nm. Probe pulses were delayed via an optical motorized delay line with 8 ns time window. The pump and probe pulses were focused co-linearly into the sample to spot sizes of ca. 100 and 50 μm full width at half maximum, respectively. For longer delays reaching out from ns to μs time ranges, a similar spectrometer (EOS) was used in which the pump laser was electronically delayed relative to a sub-nanosecond pulsed probe light source (a

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photonic crystal fiber-based supercontinuum laser). The isotropic spectral signals were secured by use of an achromatic broadband depolarizer for the pump (ThorLabs, DPP-25-A). The data were corrected for chirp. Three to five individual scans with averaging 0.5 s per time point were typically recorded and the time axis—within total 300 points—was logarithmic from -0.4 ps to the maximum time delay and with the initial step 0.05 ps. The sample in pump-thaw degassing cuvette with 2 mm pathlength was randomly moved at 1 mm s^{-1} speed through the measurement. The stability of the sample was checked by recording steady-state absorption spectra before and after each measurement. No smoothing or filtering procedures were applied to the data. For measurements of solvated electron in MeCN samples were pre-irradiated 20s by 400 nm LEDs ($F(400) = 3.0 \times 10^{-7} \text{ Einstein s}^{-1}$).

Synthesis and characterization of **3-Cl** and **3_{red}H**

8,9-Dimethoxy-4-methyl-3,5-dioxo-6-phenyl-1,2,4,5-tetrahydro-3H-2a,4,10b-triazaaceanthrylen-10b-ium chloride (3-Cl). Deazaflavin **2b** (0.253 g; 0.51 mmol) and 10% Pd/C (13 mg) were dissolved/suspended in dichloromethane (25 mL) in an autoclave. After adding catalytic amount of acetic acid (2 drops), autoclave was filled with hydrogen (1.0 MPa) and the reaction mixture was stirred for 12 h. Reaction mixture was filtered through diatomaceous earth which was washed by chloroform (100 mL). Solvents were evaporated and thus obtained crystals of deprotected deazaflavin **2_{Cre}dH** (for characterization, see the Supporting Information S2) were dissolved in SOCl_2 (100 mL). Solution was stirred at room temperature for 6 h. Mixture was concentrated on evaporator and then acetonitrile (150 mL) was added. Solvents were evaporated to obtain yellow oil which was dissolved in chloroform (ca 10 mL) and poured into hexane (150 mL). Formed suspension was sonicated for 20 min and then it was filtrated. Target salt **3-Cl** (0.139 g; 64%) was obtained as yellow crystals. M.p.: 210–217 °C. $^1\text{H NMR}$ (401 MHz, CD_3CN) δ : 7.63 (m, 3 H_{Ar}), 7.35 (m, 3 H_{Ar}), 6.88 (s, 1 H_{Ar}), 5.22 (t, $J_{\text{HH}} = 9, 19 \text{ Hz}$, $\text{ArNCH}_2\text{CH}_2\text{N}$, 2 H), 4.67 (t, $J_{\text{HH}} = 9, 44 \text{ Hz}$, $\text{ArNCH}_2\text{CH}_2\text{N}$, 2 H), 4.21 (s, ArOCH_3 , 3 H), 3.68 (s, ArOCH_3 , 3 H), 3.25 (s, NCH_3 , 3 H) ppm. $^{13}\text{C NMR}$ (101 MHz, CD_3CN) δ : 160.8 (s, 1 C), 160.1 (s, 1 C), 159.2 (s, 1 C), 151.2 (s, 1 C), 148.6 (s, 1 C), 148.4 (s, 1 C), 136.2 (s, 1 C), 134.4 (s, 1 C), 130.5 (s, 1 C), 129.4 (s, 2 C), 129.0 (s, 2 C), 122.0 (s, 1 C), 109.1 (s, 1 C), 105.5 (s, 1 C), 99.0 (s, 1 C), 58.9 (s, 1 C), 56.7 (s, 1 C), 50.7 (s, 1 C), 45.5 (s, 1 C), 28.7 (s, 1 C) ppm. HRMS (ESI⁺) calculated for $\text{C}_{22}\text{H}_{20}\text{N}_3\text{O}_4^+$ ([M-Cl]⁺): 390.14483, found 390.14514.

8,9-Dimethoxy-4-methyl-6-phenyl-1,2-dihydro-3H,6H-2a,4,10b-triazaaceanthrylene-3,5(4H)-dione (3_{red}H). Salt **3-Cl** (0.14 g; 0.33 mmol), 10% Pd/C (0.02 g) and K_2CO_3 (0.045 g; 0.33 mmol) were dissolved/suspended in dichloromethane (25 mL) in an autoclave. Autoclave was filled with hydrogen (1.0 MPa) and the reaction mixture was stirred at room temperature for 24 h. Solids were filtered off through diatomaceous earth and it was washed by chloroform (150 mL) and solvents were evaporated. Reduced deazaflavin **3_{red}H** (0.052 g; 40%) was obtained as a white solid. M.p.: 250 °C with decomposition. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.24 (m, 4 H_{Ar}), 7.15 (m, 1 H_{Ar}), 6.66 (s, 1 H_{Ar}), 6.35 (s, 1 H_{Ar}), 5.22 (s, CHPh , 1 H), 4.39 (td, $J_{\text{HH}} = 9, 90 \text{ Hz}$, $J_{\text{HH}} = 2, 61 \text{ Hz}$, $\text{ArNCH}_2\text{H}_b\text{CH}_2\text{N}$, 1 H), 4.25 (m, $\text{ArNCH}_2\text{H}_b\text{CH}_2\text{N}$, 1 H), 4.19 (m, $\text{ArNCH}_2\text{CH}_a\text{H}_b\text{N}$, 1 H), 3.95 (m, $\text{ArNCH}_2\text{CH}_a\text{H}_b\text{N}$, 1 H), 3.91 (s, ArOCH_3 , 3 H), 3.75 (s, ArOCH_3 , 3 H), 3.25 (s, NCH_3 , 3 H) ppm. $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ : 162.7 (s, 1 C), 149.6 (s, 1 C), 148.7 (s, 1 C), 147.5 (s, 1 C), 146.5 (s, 1 C), 145.9 (s, 1 C), 130.3 (s, 1 C), 128.6 (s, 2 C), 127.8 (s, 2 C), 126.7 (s, 1 C), 117.9 (s, 1 C), 113.9 (s, 1 C), 97.7 (s, 1 C), 85.4 (s, 1 C), 77.4 (s, 1 C), 56.4 (s, 1 C), 45.3 (s, 1 C), 43.6 (s, 1 C), 41.3 (s, 1 C), 27.5 (s, 1 C) ppm. HRMS (ESI⁺) calculated for $\text{C}_{22}\text{H}_{21}\text{N}_3\text{O}_4$: 392.16384 ([M+H]⁺), found 392.16037; calculated 414.14243 ([M+Na]⁺), found 414.14236.

Photooxidations on analytical scale

General procedure for aerobic oxidations. A substrate (37.5 μmol) and the deazaflavinium catalyst **3-Cl** (8 mol%; 3 μmol) were placed in a vial tube and dissolved in CD_3CN (500 μL). Vial was closed with a septum and

balloon with oxygen was installed (see S18 for details on experimental setup). The reaction mixture was irradiated (LED, 400 nm) at 40 °C (tempered by a Peltier unit) for 24 h. The reaction mixture was analyzed by $^1\text{H NMR}$.

General procedure for anaerobic oxidations. A substrate (37.5 μmol) and the deazaflavinium catalyst **3-Cl** (8 mol%; 3 μmol) were placed in a 5 mL Schlenk tube and dissolved in CD_3CN (500 μL). Tube was capped and degassed using the freeze–pump–thaw technique and filled with argon. The reaction mixture was irradiated (LED, 400 nm) at 40 °C (tempered by a Peltier unit) for 24 h. The reaction mixture was analyzed by $^1\text{H NMR}$.

General procedure for competitive experiments. The substrates (both 37.5 μmol) and the deazaflavinium catalyst **3-Cl** (3 μmol) were placed in 5 mL Schlenk tube and dissolved in CD_3CN (500 μL). Tube was capped and degassed using the freeze–pump–thaw technique and filled with argon (for anaerobic experiment) or equipped with balloon with oxygen (for aerobic experiments). The reaction mixture was irradiated by LEDs (400 nm) at 40 °C for 24 h. The reaction mixture was analyzed by $^1\text{H NMR}$ and $^{19}\text{F NMR}$ spectroscopy.

Photooxidations on semi-preparative scale

Oxidation of 6b to 7b. Alcohol **6b** (30 mg; 217.1 μmol) and **3-Cl** (12 mol%; 27 μmol) were dissolved in CD_3CN (3 mL) and solution was divided to 3 Schlenk tubes (3 \times 1 mL). Tubes were degassed using the freeze–pump–thaw technique and filled with an argon. The reaction mixtures were irradiated by LEDs (400 nm) and heated to 45 °C for 24 h. Reaction mixtures were collected, and solvents were evaporated. Crude product which contained only 2% of starting material (monitored by $^1\text{H NMR}$) was purified by flash chromatography (ethyl acetate – hexane 1:4) to obtain **7b** (22 mg; 72%) as a colorless oil. $^1\text{H NMR}$ (400 MHz, CD_3CN) δ : 9.86 (s, CHO, 1H), 7.85 (m, H_{Ar} , 2H), 7.07 (m, H_{Ar} , 2H), 3.88 (s, ArOCH_3 , 3H) ppm. $^{13}\text{C NMR}$ (101 MHz, CD_3CN) δ : 191.5 (s, 1C), 165.6 (s, 1C), 132.7 (s, 2C), 131.1 (s, 1C), 116.0 (s, 2C), 56.8 (s, 1C) ppm. HRMS: calculated for $\text{C}_8\text{H}_8\text{O}_2$: 137.0524 ([M+H]⁺), found for $\text{C}_8\text{H}_8\text{O}_2$: 137.0537 ([M+H]⁺).

Oxidation of 4c to 5c. Alcohol **4c** (60.0 mg; 440.6 μmol) and **3-Cl** (16 mol%; 72 μmol) were dissolved in CD_3CN (6 mL) and solution was divided to 6 Schlenk tubes (6 \times 1 mL). Tubes were degassed using the freeze–pump–thaw technique and filled with an argon. The reaction mixture was irradiated by LEDs (400 nm) and heated to 45 °C for 24 h. Reaction mixtures were collected, and solvents were evaporated. Crude product contained only **4c** and **5c** in ratio 40/60 (and not product of methyl group oxidation) according $^1\text{H NMR}$. It was purified by column flash chromatography (ethyl acetate–hexane 1:4) to obtain **5c** (32 mg; 53%) as a colorless oil. $^1\text{H NMR}$ (400 MHz, CD_3CN) δ : 7.86 (m, H_{Ar} , 2H), 7.31 (m, H_{Ar} , 2H), 2.53 (s, COCH_3 , 3H), 2.39 (s, ArOCH_3 , 3H) ppm. $^{13}\text{C NMR}$ (101 MHz, CD_3CN) δ : 198.7 (s, 1C), 145.0 (s, 1C), 135.8 (s, 1C), 130.2 (s, 2C), 129.3 (s, 2C), 26.9 (s, 1C), 21.6 (s, 1C) ppm. HRMS: calculated for $\text{C}_9\text{H}_{10}\text{O}$: 134.0810 ([M+H]⁺), found for $\text{C}_9\text{H}_{10}\text{O}$: 135.0785 ([M+H]⁺).

Extended information are described in the **Supporting Information** including description of the precursor **2b** synthesis, NMR/MS characterisation, additional mechanistic and computational studies and copies of NMR spectra. XYZ coordinates are presented in a separate document.

Acknowledgements

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RESEARCH ARTICLE

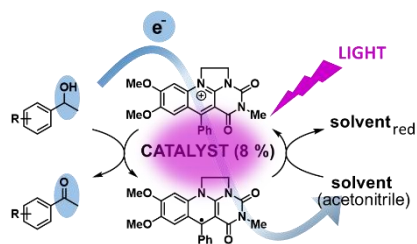
Keywords: chemoselectivity • flavin • oxidation • photocatalysis • solvated electron

- [1] a) I. P. Beletskaya, C. Nájera, M. Yus, *Chem. Soc. Rev.* **2020**, *49*, 7101-7166; b) R. A. Shenvi, D. P. O'Malley, P. S. Baran, *Acc. Chem. Res.* **2009**, *42*, 530-541.
- [2] a) A. Yoshimura, V. V. Zhdankin, *Chem. Rev.* **2016**, *116*, 3328-3435; b) M. Uyanik, K. Ishihara, *Chem. Commun.* **2009**, 2086-2099.
- [3] a) S. Alvi, V. Jayant, R. Ali, *ChemistrySelect* **2022**, *7*, e202200704; b) B. Yu, A.-H. Liu, L.-N. He, B. Li, Z.-F. Diao, Y.-N. Li, *Green Chem.* **2012**, *14*, 957-962
- [4] a) L. D'Accolti, C. Annese, C. Fusco, *Chem. Eur. J.* **2019**, *25*, 12003-12017; b) I. Triandafillidi, D. I. Tzaras, C. G. Kokotos, *ChemCatChem* **2018**, *10*, 2521-2535.
- [5] a) R. Yazaki, *Chem. Pharm. Bull.* **2021**, *69*, 516-525; b) H. Sterckx, B. Morel, B. U. W. Maes, *Angew. Chem. Int. Ed.* **2019**, *58*, 7946-7970; c) M. N. Kopylovich, A. P. C. Ribeiro, E. C. B. A. Alegria, N. M. R. Martins, L. M. D. R. S. Martins, A. J. L. Pombeiro, in *Adv. Organomet. Chem.*, Vol. 63 (Ed.: P. J. Pérez), Academic Press, **2015**, pp. 91-174.
- [6] a) L. Marais, A. J. Swarts, *Catalysts* **2019**, *9*, 395; b) in *Catalytic Oxidation in Organic Synthesis*, Georg Thieme Verlag, Stuttgart, **2018**; c) S. Hamada, T. Furuta, Y. Wada, T. Kawabata, *Angew. Chem. Int. Ed.* **2013**, *52*, 8093-8097; d) R. A. Sheldon, I. W. C. E. Arends, *Adv. Synth. Catal.* **2004**, *346*, 1051-1071.
- [7] a) J.-E. Bäckvall, Editor, *Modern Oxidation Methods, 2nd Completely Revised*, Wiley-VCH Verlag GmbH & Co. KGaA, **2010**; b) L. Melone, C. Punta, *Beilstein J. Org. Chem.* **2013**, *9*, 1296-1310; c) L. De Luca, G. Giacomelli, A. Porcheddu, *J. Org. Chem.* **2001**, *66*, 7907-7909.
- [8] a) N. Holmberg-Douglas, D. A. Nicewicz, *Chem. Rev.* **2022**, *122*, 1925-2016; b) Y. Lee, M. S. Kwon, *Eur. J. Org. Chem.* **2020**, 2020, 6028-6043; c) D. Petzold, M. Giedyk, A. Chatterjee, B. König, *Eur. J. Org. Chem.* **2020**, 2020, 1193-1244; d) I. K. Sideri, E. Voutyritsa, C. G. Kokotos, *Org. Biomol. Chem.* **2018**, *16*, 4596-4614.
- [9] a) W. Schilling, D. Riemer, Y. Zhang, N. Hatami, S. Das, *ACS Catalysis* **2018**, *8*, 5425-5430; b) H. Zhang, T. Guo, M. Wu, X. Huo, S. Tang, X. Wang, J. Liu, *Tetrahedron Lett.* **2021**, *67*, 152878; c) S. Fukuzumi, K. Ohkubo, *Chem. Sci.* **2013**, *4*, 561-574; d) F. Rusch, J.-C. Schober, M. Brasholz, *ChemCatChem* **2016**, *8*, 2881-2884; e) N. F. Nikitas, D. I. Tzaras, I. Triandafillidi, C. G. Kokotos, *Green Chem.* **2020**, *22*, 471-477.
- [10] X. Zhang, K. P. Rakesh, L. Ravindar, H.-L. Qin, *Green Chem.* **2018**, *20*, 4790-4833.
- [11] a) C. L. Hill, *Nature* **1999**, *401*, 436-437; b) A. B. Jones, J. Wang, A. T. Hamme II, W. Han, in *Encyclopedia of Reagents for Organic Synthesis*; c) R. A. Sheldon, *Chem. Commun.* **2008**, 3352-3365.
- [12] L. Xiong, J. Tang, *Adv. Energy Mat.* **2021**, *11*, 2003216.
- [13] L. Capaldo, D. Ravelli, *Eur. J. Org. Chem.* **2020**, 2020, 2783-2806.
- [14] a) C. Gunanathan, D. Milstein, *Science* **2013**, *341*, 1229712; b) Z. Chai, T.-T. Zeng, Q. Li, L.-Q. Lu, W.-J. Xiao, D. Xu, *J. Am. Chem. Soc.* **2016**, *138*, 10128-10131; c) H. Fuse, H. Mitsunuma, M. Kanai, *J. Am. Chem. Soc.* **2020**, *142*, 4493-4499; d) Z. Chai, *Chem. Asian. J.* **2021**, *16*, 460-473.
- [15] a) E. J. Horn, B. R. Rosen, Y. Chen, J. Tang, K. Chen, M. D. Eastgate, P. S. Baran, *Nature* **2016**, *533*, 77-81; b) J. Liu, L. Lu, D. Wood, S. Lin, *ACS Central Sci.* **2020**, *6*, 1317-1340; c) J. P. Barham, B. König, *Angew. Chem. Int. Ed.* **2020**, *59*, 11732-11747; d) L. Capaldo, L. L. Quadri, D. Ravelli, *Angew. Chem. Int. Ed.* **2019**, *58*, 17508-17510.
- [16] K. Targos, O. P. Williams, Z. K. Wickens, *J. Am. Chem. Soc.* **2021**, *143*, 4125-4132.
- [17] a) E. Svobodová, R. Cibulka, in *Flavin-Based Catalysis*, **2021**, pp. 265-291, <https://doi.org/10.1002/9783527830138.ch11>; b) A. Rehpenn, R. Walter, G. Storch, *Synthesis* **2021**, *53*, 2583-2593; c) J. B. Metternig, R. J. Mudd, G. R., in *Photocatalysis in Organic Synthesis*, 2019 ed. (Ed.: B. König), Georg Thieme Verlag, Stuttgart, **2019**, pp. 391-404; d) V. Srivastava, P. K. Singh, A. Srivastava, P. P. Singh, *RSC Adv.* **2021**, *11*, 14251-14259.
- [18] a) J. Immel, M. Chilamari, S. Bloom *Chem. Sci.* **2021**, *12*, 10083-10091; b) A. H. Tolba, M. Krupička, J. Chudoba, R. Cibulka, *Org. Lett.* **2021**, *23*, 6825-6830; c) T. Hartman, M. Reiserová, J. Chudoba, E. Svobodová, N. Archipowa, R. J. Kutta, R. Cibulka, *ChemPlusChem* **2021**, *86*, 373-386; d) A. H. Tolba, F. Vávra, J. Chudoba, R. Cibulka, *Eur. J. Org. Chem.* **2020**, 2020, 1579-1585; e) J. Gurruchaga-Pereda, V. Martínez-Martínez, E. Rezabal, X. Lopez, C. Garino, F. Mancini, A. L. Cortajarena, L. Salassa, *ACS Catal.* **2020**, *10*, 187-196; f) H. Guo, H. Xia, X. Ma, K. Chen, C. Dang, J. Zhao, B. Dick, *ACS Omega* **2020**, *5*, 10586-10595; g) L. M. Bouchet, A. A. Heredia, J. E. Argüello, L. C. Schmidt, *Org. Lett.* **2020**, *22*, 610-614.
- [19] a) A. Pokluda, Z. Anwar, V. Boguschová, I. Anusiewicz, P. Skurski, M. Sikorski, R. Cibulka, *Adv. Synth. Catal.* **2021**, *363*, 4371-4379; b) J. Zelenka, R. Cibulka, J. Roithová, *Angew. Chem. Int. Ed.* **2019**, *58*, 15412-15420.
- [20] a) A. Graml, T. Neveselý, R. Jan Kutta, R. Cibulka, B. König, *Nat. Commun.* **2020**, *11*, 3174; b) T. Pavlovská, D. Král Lesný, E. Svobodová, I. Hoskovcová, N. Archipowa, R. J. Kutta, R. Cibulka, *Chem. Eur. J.* **2022**, e202200768.
- [21] B. Cheng, B. König, in *Flavin-Based Catalysis*, **2021** (Cibulka R. and Fraaije M., Eds) pp. 245-264, <https://doi.org/10.1002/9783527830138.ch10>.
- [22] D. S. Chung, S. H. Park, S.-G. Lee, H. Kim, *Chem. Sci.* **2021**, *12*, 5892-5897.
- [23] M. Uygur, J. H. Kuhlmann, M. C. Pérez-Aguilar, D. G. Piekarski, O. García Mancheño, *Green Chem.* **2021**, *23*, 3392-3399.
- [24] There are both flavin-based systems producing benzoic acids or their mixtures with aldehydes (ref. 17c,e) or selectively aldehydes (see ref.24).
- [25] a) B. Mühlendorf, R. Wolf, *Chem. Commun.* **2015**, *51*, 8425-8428; b) C. Feldmeier, H. Bartling, K. Magerl, R. M. Gschwind, *Angew. Chem. Int. Ed.* **2015**, *54*, 1347-1351.
- [26] a) T. Neveselý, E. Svobodová, J. Chudoba, M. Sikorski, R. Cibulka, *Adv. Synth. Catal.* **2016**, *358*, 1654-1663; b) S. M. Bonesi, I. Manet, M. Freccero, M. Fagnoni, A. Albini, *Chem. Eur. J.* **2006**, *12*, 4844-4857; c) E. Skolia, P. L. Gkizis, C. G. Kokotos, *ChemPlusChem* **2022**, *87*, e202200008; d) E. Skolia, P. L. Gkizis, N. F. Nikitas, C. G. Kokotos, *Green Chem.* **2022**, *24*, 4108-4118.
- [27] M. Oliva, G. A. Coppola, E. V. Van der Eycken, U. K. Sharma, *Adv. Synth. Catal.* **2021**, *363*, 1810-1834.
- [28] U. Megerle, M. Wenninger, R.-J. Kutta, R. Lechner, B. König, B. Dick, E. Riedle, *Phys. Chem. Chem. Phys.* **2011**, *13*, 8869-8880.
- [29] ΔG is calculated from Rehm-Weller equation $\Delta G = E_{ox}(\text{substrate}) - E_{red}(\text{oxidant}) - 0.06$; see ref.^[30] for details.
- [30] A. N. Romero, D. A. Nicewicz, *Chem. Rev.* **2016**, *116*, 10075-10166.
- [31] (a) D. C. Grills, S. V. Lyman, *Phys. Chem. B* **2022**, *126*, 262-269. (b) S. C. Doan, B. J. Schwartz, *J. Phys. Chem. B* **2013**, *117*, 4216-4221. (c) I. P. Bell, M. A. Rodgers, H. D. Burrows, *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 315-326.
- [32] M. Neumeier, D. Sampedro, M. Májek, V. A. d. I. P. O'Shea, A. J. v. Wangelin, R. Pérez- Ruiz, *Chem. Eur. J.* **2018**, *24*, 105-108.
- [33] (a) I. Ghosh, T. Ghosh, J. L. Bardagi, B. König, *B. Science* **2014**, *346*, 725-728. (b) I. A. MacKenzie, L. Wang, N. P. R. Onuska, O. F. Williams, K. Begam, A. M. Moran, B. D. Dunietz, D. A. Nicewicz, *Nature* **2020**, *580*, 76-80.
- [34] a) C. Greening, F. H. Ahmed, A. E. Mohamed, B. M. Lee, G. Pandey, A. C. Warden, C. Scott, J. G. Oakeshott, M. C. Taylor, C. J. Jackson, *Microbiol. Mol. Biol. Rev.* **2016**, *80*, 451-493; b) M. Goldberg, I. Pecht, H. E. A. Kramer, R. Traber, P. Hemmerich, *Biochim. Biophys. Acta - General Subjects* **1981**, *673*, 570-593.
- [35] a) Y.-T. Kao, C. Saxena, T.-F. He, L. Guo, L. Wang, A. Sancar, D. Zhong, *J. Am. Chem. Soc.* **2008**, *130*, 13132-13139; b) A. Sancar, *Chem. Rev.* **2003**, *103*, 2203-2238.
- [36] a) X. Gao, J. R. Turek-Herman, Y. J. Choi, R. D. Cohen, T. K. Hyster, *J. Am. Chem. Soc.* **2021**, *143*, 19643-19647; b) R. Foja, A. Walter, C. Jandl, E. Thyraug, J. Hauer, G. Storch, *J. Am. Chem. Soc.* **2022**, *144*, 4721-4726.
- [37] M. Krejčík, M. Daněk, F. Hartl, *J. Electroanal. Chem. Interfac. Electrochem.* **1991**, *317*, 179-187.

RESEARCH ARTICLE

Entry for the Table of Contents

NO OXYGEN + NO ADDITIVE = CHEMOSELECTIVITY



New way how to drive a catalytic cycle in photoredox catalysis. Highly chemoselective photooxidations of benzylic alcohols to carbonyl compounds in the presence of various easily-oxidizable groups are possible in a simple oxygen-free system consisting of a substrate, unique deazaflavinium catalyst and acetonitrile which acts simultaneously as a sacrificial electron acceptor and solvent.

Institute and/or researcher Twitter usernames: @VSCHT, @RadekCibulka1, @ChemistryKoenig