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Visible-Light Induced Fixation of SO$_2$ into Organic Molecules with Polypyridine Chromium(III) Complexes

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Incorporation of sulfur dioxide into organic compounds is achieved by a photocatalytic approach using sensitizers made from earth-abundant chromium(III) ions and visible light leading to sulfones and sulfonamides. We employed three different chromium(III) sensitizers **[Cr(ddpd)$_2$]$^{3+}$**, **[Cr(bpmp)$_2$]$^{3+}$** and **[Cr-(tpe)$_2$]$^{3+}$** with long excited state lifetimes and different ground and excited state redox potentials as well as varying stability under the reaction conditions (ddpd = N,N'-dimethyl-N,N'-dipyridin-2-yl-pyridine-2,6-diamine; bpmp = 2,6-bis(2-pyridylmethyl)pyridine; tpe = 1,1,1-tris(pyrid-2-yl)ethane). Key reaction steps of the catalytic cycles are identified by electrochemical, luminescence quenching, photolysis, laser flash photolysis and catalytic experiments delivering a detailed picture of the challenges in these transformations. The reactivity of the reduced chromium complex was identified as a key property to explain the reaction outcomes. Initial cage escape yield determinations with **[Cr(tpe)$_2$]$^{3+}$** revealed that desired photoreactions occur with unusually high quantum efficiencies, whereas side reactions are almost unproductive.

Introduction

Sulfur dioxide (SO$_2$) is an important chemical feedstock and produced in enormous amounts every year.[1,2] It is a widely used preservative (E220) in the food industry, e.g. for wine or dried fruits. SO$_2$ is used as reducing agent to bleach papers or clothes, corn processing, water and waste treatment, oil recovery, ore refining and the sulfonylation of aromatic compounds to give important drugs.[1–3] SO$_2$ is also a major air pollutant and has significant impact on public health and the environment.[4,5] In the last twenty years, there has been increasing interest in the direct incorporation of SO$_2$ into the sulfonyl functionality (–SO$_2$–) in small organic molecules.[3,6–13] This interest mainly stems from the broad application of sulfonyl containing molecules, such as sulfones or sulfonamides, in particular in drug discovery and development.[14,15] Compared to traditional methods,[16] these novel processes enable highly modular and inherently more sustainable synthesis of sulfones or sulfonamides utilizing SO$_2$ as key building block.[17] The introduction of easy-to-handle surrogates for the toxic and corrosive SO$_2$ gas, such as the 1,4-diazabicyclo[2.2.2]octane (DABCO)-sulfur dioxide adduct DABSO, has been a major driving force in this field.[18–20] Yet, the stoichiometric release of DABCO mitigates atom economy and may pose other concerns such as side reactions.

Among the different approaches, photochemical processes driven by visible-light are particularly attractive for the direct fixation of SO$_2$.[21,22] Although there have been some reports on the visible-light driven incorporation of SO$_2$ in the absence of any external photosensitizer,[23–25] the use of designated photoactive catalysts provides significant advantages in terms of reaction rates, scope and applicability. The emergence of visible-light photoredox catalysis has opened intriguing possibilities to directly activate otherwise unreactive substrates in single-electron transfer pathways.[26–28] Photoredox catalysis has led to the development of novel tools for the construction of carbon-sulfur bonds.[29–31] Visible-light driven fixation of SO$_2$ so far mainly relies on two types of photocatalysts, transition metal complexes of noble metals and organic chromophores.[21,22]

Transition metal complexes, such as [Ru(bpy)$_3$]$^{2+}$ or Ir(ppy)$_3$ (bpy = 2,2'-bipyridine, ppy = deprotonated 2-phenylpyridine)[32] possess long excited state lifetimes, which is an important prerequisite for efficient catalysis. Furthermore, their excited state and ground state redox potentials can be adjusted in a straightforward manner employing ligand modifications.[33,34] These properties make them preferable to organic chromophores in many cases. However, they fall short concerning

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sustainability, due to the low earth-abundance of precious metals like Ru or Ir.

Consequently, there has been a sustained interest in replacing precious metals in photoactive complexes with earth-abundant metals, such as chromium, manganese, iron or copper.[35–37] Copper complexes have already been successfully utilized in photocatalytic C–S bond forming reactions.[38–42] Chromium(III) complexes with polypyridine ligands have been identified as excellent photoluminescent materials with very high excited state lifetimes, even in the presence of oxygen.[43–47] Yet, their application in organic synthesis has so far been limited to cycloaddition reactions, singlet oxygen generation, triplet-triplet annihilation followed by cycloaddition reactions and a few photoredox catalytic cycles which mostly rely on oxygen as terminal oxidant, which can impart problems due to the formation of reactive oxygen species.[48–54]

Herein we report the, to the best of our knowledge, first application of chromium(III) photosensitizers in the visible-light mediated fixation of SO_2 into sulfones and sulfonamides complemented by mechanistic studies. In particular, we employ three chromium(III) photosensitizers **[Cr(ddpd)$_2$]$^{3+}$**,[55,56] **[Cr(bpmp)$_2$]$^{3+}$**[57] and **[Cr(tpe)$_2$]$^{3+}$**[58] (Scheme 1a, ddpd = N,N′-dimethyl-N,N′-dipyridin-2-yl-pyridine-2,6-diamine; bpmp = 2,6-bis(2-pyridylmethyl)pyridine; tpe = 1,1,1-tris(pyrid-2-yl)ethane) possessing extremely long excited state lifetimes of several hundreds of μs and different ground and excited state redox potentials in two three-component SO_2 fixation processes leading to sulfones and sulfonamides, respectively (Scheme 1b,c).[59,60] Mechanistic studies include electrochemistry of substrates, excited state quenching experiments, steady-state photolysis and quantitative laser flash photolysis (LFP) experiments providing deep insight into photocatalyst and substrate requirements for these visible light induced catalytic reactions.
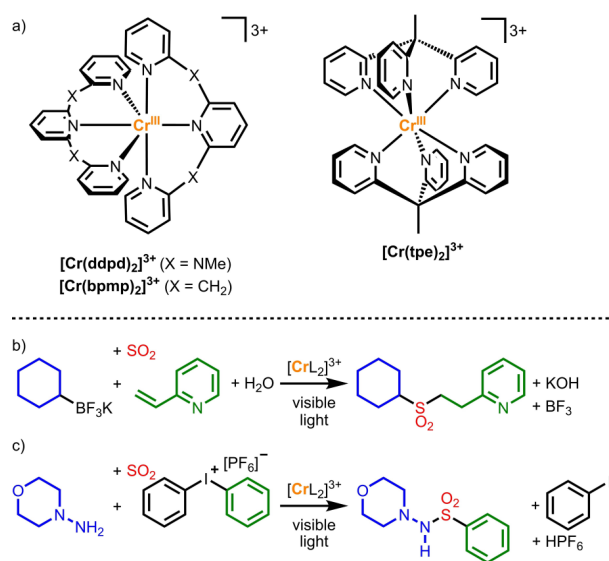
Results and Discussion

Considering the favorable photooxidative properties of poly-pyridine chromium(III) complexes, we hypothesized, that Cr^{III} complexes might be suited for reactions proceeding through a reductive quenching cycle. Therefore, we selected the photocatalytic three-component reaction between alkyltrifluoroborates, SO_2 and alkenes from the Wu group (Scheme 1b)[59] and the visible-light mediated aminosulfonylation of diaryliodonium salts developed by one of our labs (Scheme 1c),[60] as two representative model transformations. For both processes, an initial single-electron transfer from the starting material (cyclohexyltrifluoroborate CyBF$_3$K or 4-aminomorpholine 4-AM) to the photoexcited catalyst is the first chemical step of the photocatalytic cycle. From the excited state redox potentials of the photocatalysts[55,57,58] and ground state potentials of the two substrates (Figure 1) all three photocatalysts **[Cr(ddpd)$_2$]$^{3+}$**, **[Cr(bpmp)$_2$]$^{3+}$** and **[Cr(tpe)$_2$]$^{3+}$** are capable of oxidizing 4-AM in their excited states, while only **[Cr(bpmp)$_2$]$^{3+}$** and **[Cr(tpe)$_2$]$^{3+}$** should be able to photooxidize CyBF$_3$K (Supporting Information, Figures S1–S2).

However, the most oxidizing complex **[Cr(bpmp)$_2$]$^{3+}$** reacts with the two basic substrates already in the ground state by proton transfer, likely proceeding from the slightly acidic methylene bridges of the coordinated bpmp ligand[53] (Supporting Information, Figures S3–S4). Consequently, **[Cr(bpmp)$_2$]$^{3+}$** is not expected to engage efficiently in photoinduced electron transfer (PET) reactions with these basic substrates. The other two sensitizers **[Cr(ddpd)$_2$]$^{3+}$** and **[Cr(tpe)$_2$]$^{3+}$** are stable in the presence of the substrates.

4-AM quenches the emission of both sensitizers **[Cr(ddpd)$_2$]$^{3+}$** and **[Cr(tpe)$_2$]$^{3+}$** (Supporting Information, Figures S5–S6) as expected from the redox potentials. The emission of **[Cr(tpe)$_2$]$^{3+}$** is also quenched by CyBF$_3$K (Supporting Information, Figure S7). Although the excited state redox potential of **[Cr(ddpd)$_2$]$^{3+}$** and the oxidation peak potential of CyBF$_3$K are unfavorable for PET, we observe emission quenching (Supporting Information, Figure S8). This might be explicable by the lower onset potential of CyBF$_3$K and the irreversible oxidation process (Supporting Information, Figure S2). Upon

Scheme 1. a) Chromium(III) photosensitizers employed in this study. b) and c) Visible light induced SO_2 fixation reactions studied.
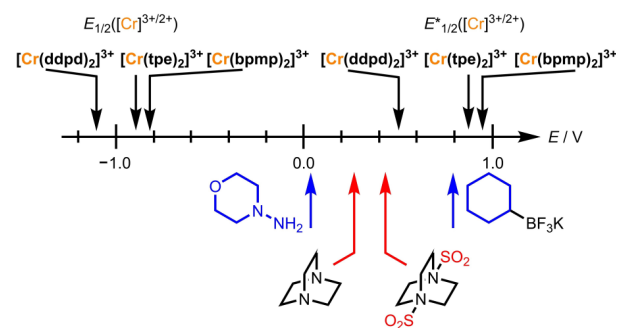
Figure 1. Pertinent ground and excited state redox potentials of the chromium(III) sensitizers[55,57,58] and peak potentials of the oxidation of substrates and by-products in CH$_3$CN in V vs. ferrocene/ferrocenium determined by cyclic voltammetry.