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Basudev Sahoo

Visible Light Photocatalyzed Redox-Neutral Organic Reactions and Synthesis of Novel Metal-Organic Frameworks

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Visible Light Photocatalyzed Redox-Neutral Organic Reactions and Synthesis of Novel Metal-Organic Frameworks

Doctoral Thesis accepted by
University of Münster, Germany

Springer

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To my beloved parents, brothers and sisters-in-law

Supervisor's Foreword

In Dr. Basudev Sahoo's thesis work, conceptually novel and synthetically valuable methods were developed using visible light photocatalysis. This emerging field has become an indispensable tool for organic synthesis and employs environmentally benign and abundant visible light in the presence of a photosensitizer as an attractive alternative to harmful UV light in photo-mediated reactions. During his doctoral studies, Dr. Sahoo merged the concept of gold catalysis with visible light photocatalysis in a dual catalytic fashion, demonstrating the compatibility of these two important and challenging catalytic modes for the first time. This novel dual catalytic system allowed for the development of mild protocols for the difunctionalization of non-activated alkenes and has since been expanded upon and employed in further reactions by us and other groups. Moreover, his knowledge and expertise in photocatalysis helped him to develop a novel trifluoromethylation method which combined radical addition chemistry with a polar rearrangement to synthesize valuable fluorinated compounds. The incorporation of fluorinated groups onto organic molecules is attracting increasing attention as these compounds feature heavily in pharmaceuticals, agrochemicals, and material research. Since nitrogen-based heterocycles make a large class of bioactive compounds, a mild method for the synthesis of indolizine heterocycles was also developed using a photochemical approach, which has been seldom explored for this class of compound. During this study, the product of the reaction was found to mediate its own formation under photochemical conditions. This rarely observed phenomenon obviated the need for an external photocatalyst and could inspire the future development of autocatalytic photochemical reactions. In addition to his work on photocatalysis, he has also been engaged in synthetic work focused on the preparation of highly porous metal-organic framework (MOF) materials. The scientific contributions made by Dr. Sahoo, presented in this thesis, have significantly accelerated the development of the fields he has worked on, and have inspired many new projects in my group.

Münster, Germany
April 2016

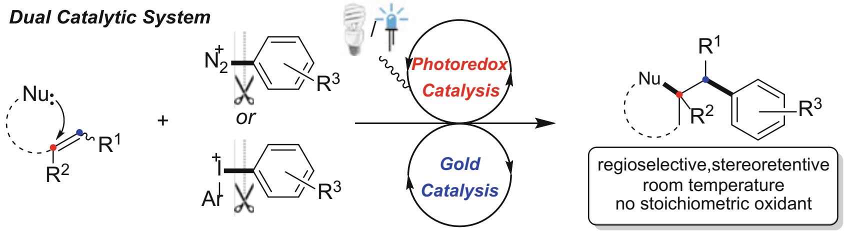
Prof. Frank Glorius

Abstract

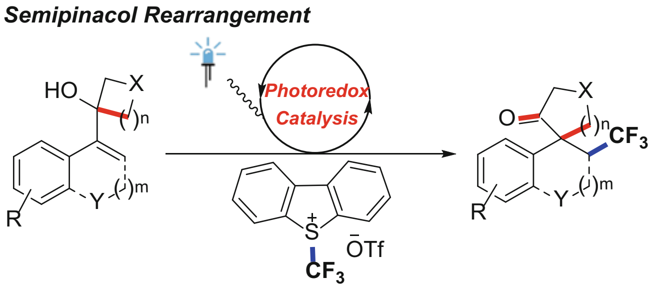
Visible light-mediated photocatalysis has emerged as an environmental friendly elegant approach for streamlined organic synthesis. Recently, many conceptually novel and challenging advancements have been accomplished in this growing research area. The content of this thesis is about the developments of novel methodologies for synthesis of valuable organic compounds using visible light photocatalysis as toolbox and also synthesis of novel metal-organic frameworks (MOFs) as characteristic porous materials.

In initial phase of my Ph.D. work, a novel dual catalytic system combining gold with visible light photoredox catalysis has been developed for selective intra- and intermolecular heteroarylation of non-activated alkenes under mild reaction conditions (Scheme 1.1). In this work, the compatibility of gold catalysis with photoredox catalysis was demonstrated for the first time. Furthermore, this methodology benefits from mild reaction conditions and readily available light sources and avoids the use of strong external oxidants in contrast to previous methods.

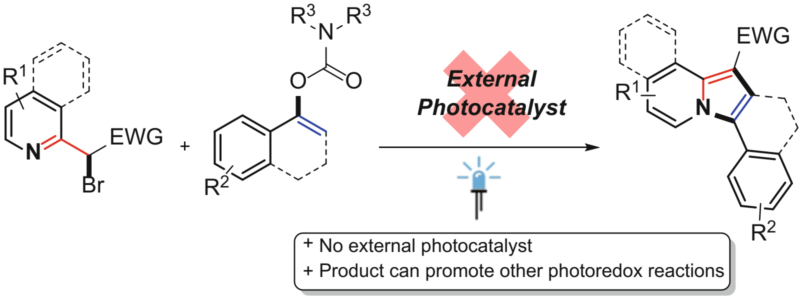
The second part of my Ph.D. work was concentrated on the visible light photoredox-catalyzed semipinacol rearrangement for trifluoromethylation of cycloalkanols (Scheme 1.2). This protocol gives access to a novel class of densely



Scheme 1.1 Dual gold and visible light photoredox-catalyzed heteroarylation of non-activated alkenes



Scheme 1.2 Visible light photoredox-catalyzed trifluoromethylation via semipinacol rearrangement

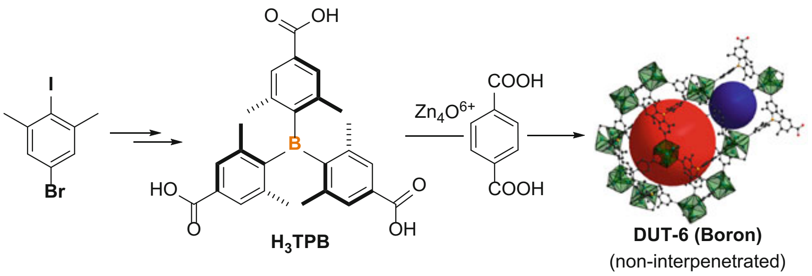


Scheme 1.3 Visible light photocatalytic synthesis of polycyclic indolizines

functionalized trifluoromethylated cycloalkanones with all carbon quaternary centers. Interestingly, these reactions proceed via radical–polar crossover followed by 1,2-alkyl migration. To the best of our knowledge, this methodology represents the first report of 1,2-alkyl migration in visible light-mediated photoredox catalysis.

In third part of my Ph.D. work, we have developed a novel methodology for the synthesis of valuable polycyclic indolizines under visible light-mediated reaction conditions (Scheme 1.3). To our delight, these reactions do not need any external photosensitizing agents in contrast to conventional photocatalysis, but do need visible light irradiation. Various analytical and laboratory experiments indicate that indolizine products are responsible in some way for their own formation, although further insightful investigations required for complete elucidation of mechanism. Furthermore, gratifyingly, this indolizine product can promote other photocatalyzed reactions in lieu of standard photocatalyst.

In final phase of my Ph.D. work, a triarylborane linker with three carboxylic acid anchoring groups, (4,4′,4″-boranetriyltris(3,5-dimethylbenzoic acid) (H_3TPB)), has been successfully developed and incorporated into the metal-organic frameworks along with a linear BDC co-linker to give mixed MOFs, DUT-6 (Boron) (Scheme 1.4). This new DUT-6 (Boron) showed fluorescent activity and exhibited



Scheme 1.4 Synthesis of triarylborane linker (H_3TPB) and incorporation into DUT-6

higher isosteric heat of adsorption for CO_2 in contrast to the DUT-6. However, this microporous DUT-6 (Boron) represents the first example of a highly porous non-interpenetrated MOF containing a triarylborane linker.

Parts of this thesis have been published in the following journal articles:

6. “External Photocatalyst-Free Visible Light-Mediated Synthesis of Indolizines” Basudev Sahoo,† Matthew N. Hopkinson,† Frank Glorius,* *Angew. Chem. Int. Ed.* **2015**, *54*, 15545-15549. (†These authors contributed equally to this work).
5. “Visible-Light Photoredox-Catalyzed Semipinacol-Type Rearrangement: Trifluoro-methylation/Ring Expansion via a Radical-Polar Mechanism” Basudev Sahoo, Jun-Long Li, Frank Glorius,* *Angew. Chem. Int. Ed.* **2015**, *54*, 11577–11580.
4. “Copolymerisation at work: the first example of a highly porous MOF comprising a triarylborane-based linker” Stella Helten,† Basudev Sahoo,† Volodymyr Bon, Irena Senkovska, Stefan Kaskel,* Frank Glorius,* *CrystEngComm.* **2015**, *17*, 307–312. (†These authors contributed equally).
3. “Dual Photoredox and Gold Catalysis: Intermolecular Multicomponent Oxyarylation of Alkenes” Matthew N. Hopkinson, Basudev Sahoo, Frank Glorius,* *Adv. Synth. Catal.* **2014***, 356,* 2794–2800.
2. “Dual Catalysis sees the Light: Combining Photoredox with Organo-, Acid and Transition Metal Catalysis” Matthew N. Hopkinson,† Basudev Sahoo,† Jun-Long Li, Frank Glorius,* *Chem. Eur. J.* **2014**, *20*, 3874–3886. (†These authors contributed equally).
1. “Combining Gold and Photoredox Catalysis: Visible Light-Mediated Oxy- and Aminoarylation of Alkenes” Basudev Sahoo, Matthew N. Hopkinson, Frank Glorius,* *J. Am. Chem. Soc.* **2013***, 135,* 5505–5508.

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Contents

Abbreviations

Ac	Acetyl
$^{\mathrm{i}}$Am	*Iso*-amyl
^{n}Bu	*Normal*-butyl
^{n}BuLi	*Normal*-butyllithium
^{t}Bu	*Tertiary*-butyl
^{t}BuLi	*Tertiary*-butyllithium
Bn	Benzyl
Bz	Benzoyl
CCDC	Cambridge Crystallographic Data Centre
CFL	Compact fluorescent lamp
Cp	Cyclopentadienyl
Cy	Cyclohexyl
d	Doublet
dap	2,9-dianisyl-1,10-phenanthroline
DBU	1,8-diazabycyclo[5.4.0]-undec-7-ene
DCE	1,2-dichloroethane
DCM	Dichloromethane
DEF	*N,N*-diethylformamide
DFT	Density functional theory
DIPA	Diisopropylamine
DIPEA	diisopropylethylamine
DMA	*N,N*-dimethylacetamide
DMAP	*N*,*N*-dimethylaminopyridine
DMF	*N,N*-dimethylformamide
DMSO	Dimethylsulphoxide
D_2O	Deuterated water
d.r.	Diastereoisomeric ratio
EI	Electron impact mass spectrometry
ESI-MS	Electrospray ionization mass spectrometry
EWG	Electron-withdrawing group

EDG	Electron-donating group
Et	Ethyl
Et_2O	Diethyl ether
EtOAc	Ethylacetate
EtOH	Ethanol
ee	Enantiomeric excess
equiv.	Equivalent
GC	Gas chromatography
HRMS	High-resolution mass spectrometry
Hz	Hertz
h	Hour(s)
IR	Infrared spectroscopy
IRMOF	Isoreticular metal-organic framework
J	NMR: coupling constant
LA	Lewis acid
LiCl	Lithium chloride
LED	Light-emitting diode
M	Molar
m	Multiplet
Mg	Magnesium
mg	Milligram
min	Minute(s)
m	Meta
*m*CPBA	*Meta*-chloroperoxybenzoic acid
mL	Milliliter
μL	Microliter
MS	Molecular sieves
MsOH	Methanesulphonic acid
MTBE	Methyl-*tert*-butyl ether
Me	Methyl
MeOH	Methanol
NBS	*N*-bromosuccinimide
NMR	Nuclear magnetic resonance
NTf_2	Ditrifluoromethanesulfonyl amine
o	Ortho
OTf	Trifluomethanesulfonate
OTs	*p*-toluenesulfonate
p	Para
PG	Protective group
Ph	Phenyl
Piv	Pivlolyl
$P(^tBu)_3$	tri-*tert*-butylphosphine
PEt_3	Triethylphosphine
PPh_3	Triphenylphosphine
PMe_3	Trimethylphosphine

^{i}Pr	Isopropyl
^{n}Pr	*Normal*-propyl
ppb	Parts per billion
ppm	Parts per million
Py	Pyridyl
PC	Photocatalyst
q	Quartet
Q_{st}	Isosteric heat of adsorption
R_F	Retention factor in chromatography
R_t	Retention time
rt	Room temperature
s	Singlet
SET	Single electron transfer
SHE	Standard hydrogen electrode
SCE	Standard calomel electrode
S_N	Nucleophilic substitution
TBHP	*Tert*-Butyl hydroperoxide
THF	Tetrahydrofuran
TFA	Trifluoroacetic acid
TsOH	*p*-toluenesulfonic acid
TMS	Trimethylsilyl
TLC	Thin layer chromatography
TMEDA	Tetramethylethylenediamine
t	Triplet
UV	Ultraviolet
V	Volt
VIS	Visible
χ	Electronegativity

Chapter 1
Introduction to Photocatalysis

1.1 Historical Background

> On the arid lands there will spring up industrial colonies without smoke and without smokestacks; forests of glass tubes will extend over the plains and glass buildings will rise everywhere; inside of these will take place the photochemical processes that hitherto have been the guarded secret of the plants, but that will have been mastered by human industry which will know how to make them bear even more abundant fruit than nature, for nature is not in a hurry and mankind is. And if in a distinct future the supply of coal becomes completely exhausted, civilization will not be checked by that, for life and civilization will continue as long as the sun shines! [1]
>
> — G. Ciamician (1912)

The year 2012 was the centenary of the famous article “The photochemistry of the future” [1]. In this inspiring article, the Italian photochemist G. Ciamician presented his great vision of the future aspects of solar energy imagining a chemical industry where chemicals could be manufactured in a similar way to photosynthesis as used by plants in the presence of sunlight [1]. Although sunlight is considered to be a clean, safe, inexpensive and abundant natural energy source, the vast majority of organic compounds do not absorb photons in the visible region of the solar spectrum but rather absorb in the UV range [1–5]. This limitation has narrowed the scope of organic compounds able to be activated under visible light irradiation, restricting the progress of photochemical synthesis in industry until the recent development of energy-efficient UV photo-reactors. Photochemical synthesis (e.g. photo-induced pericyclic reactions) is considered to be much cleaner and sustainable in contrast to conventional synthetic routes. According to the principles of green chemistry, this is assumed as a green method since direct activation of the substrate by light reduces or eliminates the use of additional hazardous reagents for conventional activations [4, 6, 7]. However, since UV photons possess considerably high energy (in the order of the C–C bond cleavage energy) [8], reactions conducted under UV light irradiation often lead to decomposition when the molecules

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contain strained ring systems or relatively weak bonds. Although there are interesting reports on multistep syntheses of some complex molecules using photochemical key steps, interest in the photochemical synthesis of molecules has remained confined to a small part of the scientific community [9, 10].

In order to attenuate these limitations, photosensitizing compounds, which are capable of absorbing photons in the visible spectrum and subsequently passing on the energy to organic compounds, have exhibited great utility in visible light induced organic synthesis. Moreover, conducting reactions in the presence of catalytic photosensitizers under visible light irradiation from commercially available household light sources may obviate the expense inherent to the special set up of UV photo-reactors as well as avoiding the safety precautions needed for UV light mediated reactions. Over the last few decades, attention has been focused on the use of visible light photosensitizing compounds to convert solar energy into electricity in solar cells [11–16] and water splitting for the production of chemical fuels [17, 18]. However, visible light active photocatalysts did not receive the wide attention of synthetic organic chemists beyond few reports from Kellogg [19, 20] Pac [21] Deronzier [22, 23] Willner [24, 25] and Tanaka [26]. In 2008, MacMillan [27] Yoon [28] and Stephenson [29] disclosed elegant and groundbreaking reports on highly efficient visible light photoredox catalysis, reinventing this field in organic synthesis.

1.2 Classifications of Photocatalyst

Photocatalysts can be classified into two different major classes based on the catalytic nature of the materials: (a) homogeneous photocatalysts and (b) heterogeneous photocatalysts. Organometallic polypyridyl metal complexes (e.g. $[Ru(bpy)_3]Cl_2{\bullet}6H_2O$) [30, 31] and organic dyes (e.g. eosin Y) [32–35] belong to the homogeneous group of photocatalysts, while inorganic semiconductors comprising of metal oxides [36–43] or sulfides [39] (e.g. TiO_2 [36, 37, 39, 40], ZnO [40], $PbBiO_2Br$ [39], CeO_2 [38], and CdS [39]), polyoxometalates [44] and graphitic carbon nitride (g-C_3N_4) polymers, [45, 46] and photoactive metal-organic frameworks (MOFs) [47–50] make up the heterogeneous group. Organometallic polypyridyl transition metal complexes and organic dyes are the most common and most efficient photocatalysts and are nowadays widely applied in organic synthesis [4, 5, 31, 33–35, 51–65]. In some cases, polypyridyl metal complexes or organic dyes have been immobilized on photo-active solid supports (e.g. TiO_2) [39] or photo-inactive solid supports (e.g. silica particle) [66] or solvated in ionic liquids [67] for recyclability.

1.3 Characteristics of Homogeneous Photocatalysts

Due to their rich photophysical and electrochemical properties, organometallic polypyridyl transition metal complexes and organic dyes exhibit high photocatalytic activity under visible light irradiation [11, 30, 38–74]. The photo-activity of the photocatalysts (organometallic metal complexes or organic dyes) can be visualized in a Jablonski diagram (Fig. 1.1) [75, 76]. Absorbing a photon, the photocatalyst PC(S_0) in its singlet ground state is excited to one of the higher energy vibrational levels of the first singlet excited state *PC(S_1^n) which then relaxes to the lowest vibrational level of the first singlet excited state *PC(S_1^0) via internal conversion (vibrational relaxation). This singlet excited state *PC(S_1^0) can regenerate the singlet ground state PC(S_0) via a spin-allowed radiative pathway (fluorescence, k_f) or a non-radiative pathway (k_{nr}). Another deactivation pathway of *PC(S_1^0) involves its conversion to the lowest energy triplet excited state *PC(T_1^0) via successive fast intersystem crossing (ISC) (spin-orbital coupling) and internal conversion (vibrational relaxation). Since the transition of the triplet excited state to the singlet ground state is spin forbidden, the triplet excited state *PC(T_1^0) is reasonably long lived (e.g. $\tau = 1100$ ns for $\mathrm{Ru(bpy)_3}^{2+}$). This triplet excited state *PC(T_1^0) can undergo radiative deactivation (phosphorescence, k_p) or non-radiative deactivation (k_{nr}) to regenerate the singlet ground state PC(S_0), completing the cycle.

Photo-excited singlet states of organic dyes having heavy atoms (Br or I) and organometallic complexes of heavy metals (e.g. Cu, Ru, Ir, Au) undergo rapid intersystem crossing to the lower energy triplet excited states. In the presence of substrates possessing quenching ability, the triplet excited state *PC(T_1^0) can then be quenched to the singlet ground state PC(S_0), diminishing the phosphorescence intensity [76]. In photocatalysis, the photo-excited catalyst can be quenched by the substrates via outer-sphere single electron transfer (SET) or energy transfer (ET) processes leading to productive downstream reactivity (Fig. 1.2) [5].

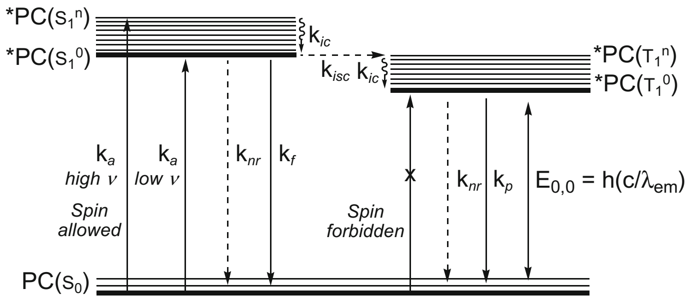


Fig. 1.1 Jablonski diagram. *PC* photocatalyst, k_a rate of absorption, k_{ic} rate of internal conversion, k_{isc} rate of intersystem crosssing, k_{nr} rate of non-radiative deactivation, k_f fluorescence, k_p phosphorescence, $E_{0,0}$ = energy of emission from the triplet state

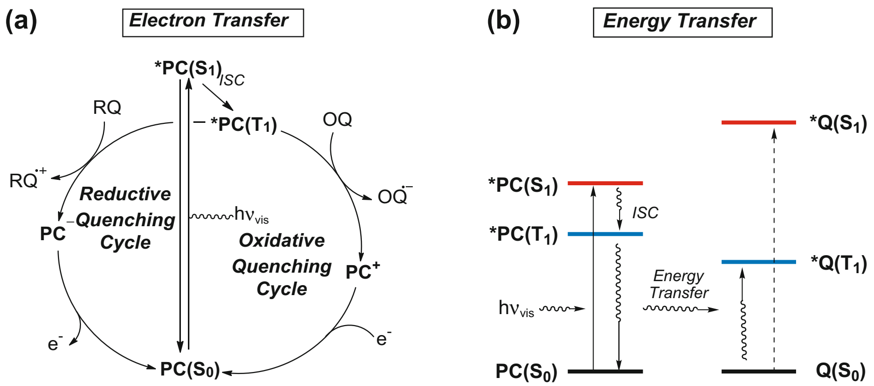


Fig. 1.2 Visible light photocatalysis: **a** photoredox catalytic cycle via single electron transfer (SET); **b** photocatalytic cycle via energy transfer (ET). *PC* photocatalyst, *Q* quencher (e.g. substrate), *RQ* reductive quencher, *OQ* oxidative quencher, *ISC* intersystem crossing. S_0 singlet ground state, S_1 first singlet excited state and T_1 first triplet excited state

In an outer sphere electron transfer process, the photo-excited triplet state *PC (T_1) can be quenched by two different mechanisms: reductive quenching and oxidative quenching (Fig. 1.2a) [5, 30, 31, 52, 60, 77]. In a reductive quenching process, the excited photocatalyst in the *PC(T_1) state accepts an electron from an electron-rich substrate (RQ), affording the reduced photocatalyst (PC^-) and a radical-cation ($RQ^{\bullet +}$). The reduced photocatalyst (PC^-) then donates electron to an electron-deficient species in a subsequent step to regenerate the ground state photocatalyst (PC). The radical-cation ($RQ^{\bullet +}$) releases radical or cationic intermediate, which can engage in a subsequent step. In a similar manner, in oxidative quenching, the photocatalyst in the *PC(T_1) state donates an electron to an electron-deficient substrate (OQ), delivering the oxidized photocatalyst (PC^+) and a radical-anion ($OQ^{\bullet -}$). The oxidized photocatalyst (PC^+) then accepts an electron from an electron-rich species present in the reaction mixture to regenerate the ground state photocatalyst (PC) and the radical-anion releases a radical upon mesolysis capable of reacting via a number of different pathways in subsequent steps. This process largely depends on the redox potentials of the species involved.

In an energy transfer process, the photo-excited triplet state *PC(T_1) interacts with the substrate, which has an accessible low energy triplet state (comparable to the photo-excited triplet state energy, Fig. 1.2b) [5]. In this interaction, triplet-triplet energy transfer results in a photo-excited triplet state of the substrate and regenerates the ground state of the photocatalyst. The photo-excited substrate can then engage in photochemical reactions. Stern-Volmer luminescence quenching experiments are generally performed to find out the actual quencher from a set of reagents present in the reaction mixture [31].

In visible light photocatalysis, coordinately saturated organometallic-based photocatalysts are chemically and conformationally stable under the reaction conditions and do not generally bind to the substrates. As a result, no other types of activations are generally observed except outer sphere electron transfer or energy transfer. Furthermore, the long-lived excited states of the photocatalysts provide sufficient time for effective interactions with the substrates in their proximity. In addition, an appropriate redox potential window of the photoredox catalyst is highly desirable for the reaction design.

In the photoredox catalyst toolbox, well investigated organometallic photocatalysts are either homoleptic (one type of ligand) or heteroleptic (two or more different types of ligands) polypyridyl metal complexes. The most common homoleptic photocatalysts are $[Ru(bpy)_3](PF_6)_2$ (bpy = 2,2′-bipyridine) and *fac*-Ir $(ppy)_3$ (ppy = 2-phenylpyridine) [31]. On the other hand, the most common heteroleptic photocatalysts are $[Ir(ppy)_2(dtbbpy)](PF_6)$ (dtbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine) and $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF_6)$ ($dF(CF_3)ppy$ = 2-(2,4-difluorophenyl)-5-trifluoromethylpyridine) [31]. For organometallic photocatalysts, various sets of redox potentials can be accessed by tuning the electronic properties of the ligands and metal ions and thus changing the HOMO-LUMO energy gap for metal to ligand charge transfer (MLCT) [30]. Electron-rich ligands (e.g. ppy) increases the reductive power of the ground state metal complex while electron-poor ligands (e.g. bpz, bpz = 2,2′-bipyrazine) increases the oxidative power of the metal complex in ground state [30]. The redox potential of the excited photoredox catalyst cannot be directly determined. These values are instead calculated with the help of cyclic voltammetry and spectroscopic data following the Rehm-Weller equation [78].

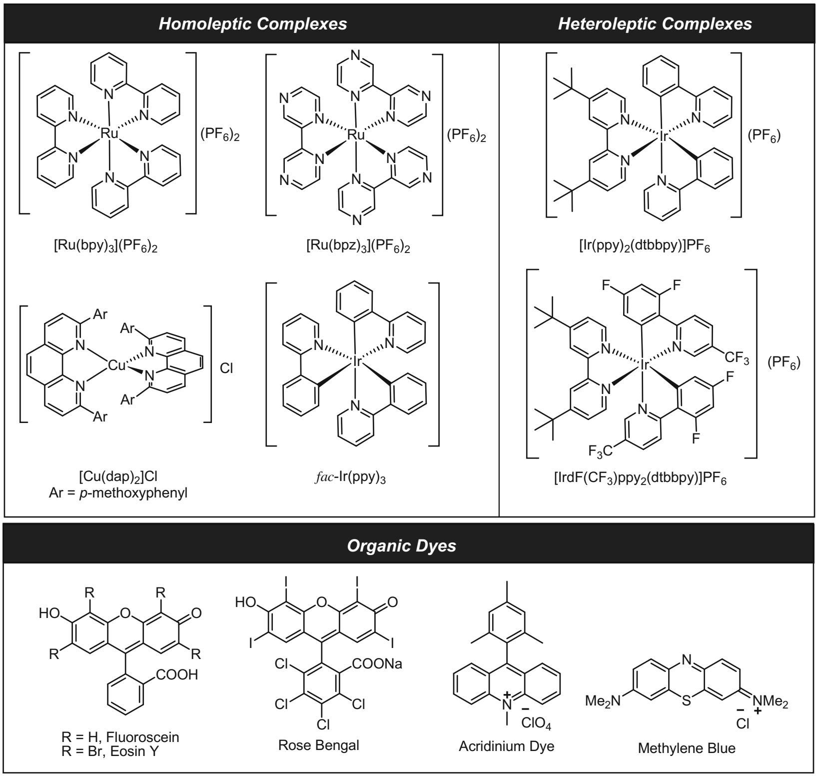
A list of organometallic photocatalysts and organic dyes is shown in Table 1.1. The photoelectronic properties of selected photoredox catalysts are outlined in Table 1.2. A list of selected reductive and oxidative quenchers is given in Table 1.3.

1.4 Visible Light Photocatalysis in Organic Synthesis

1.4.1 Photoredox Catalyzed Organic Transformations via Electron Transfer

Since photo-excited photoredox catalysts have higher oxidizing and reducing abilities compared to their ground states, giving access to two different sets of redox potentials with reasonably long life-times (Table 1.2), over the last three decades, and in particular over last seven years, there has been tremendous progress in the

Table 1.1 List of selected homoleptic and heteroleptic organometallic photocatalysts and organic dyes



field of photoredox catalysis in organic synthesis [4, 5, 31, 35, 51–59, 62, 64]. From a redox point of view, visible light photoredox-catalyzed reactions can be classified into three different categories: redox-neutral, net oxidative and net reductive reactions [31]. In redox-neutral processes, both the oxidation and reduction steps are involved in the same reaction mechanism maintaining overall redox neutrality. In net oxidative reactions, the products possess higher oxidation levels than the starting materials, while in net reductive processes the products are in lower oxidation levels compared to the starting materials. In this chapter, only redox-neutral visible light photo-redox-catalyzed processes are discussed in three sections, although many interesting organic transformations have been reported based on net redox processes over the last decades [31].

Table 1.2 Photoelectronic properties of selected photoredox catalysts [31, 34]

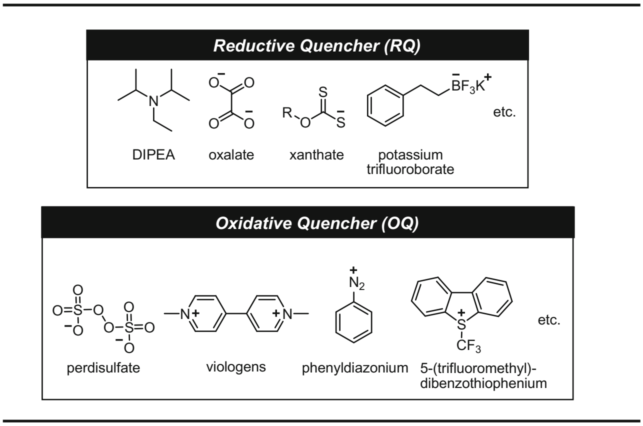
Photocatalyst	$E_{1/2}(M^+/M^*)$ (V)	$E_{1/2}(M^*/M^-)$ (V)	$E_{1/2}(M^+/M)^a$ (V)	$E_{1/2}(M/M^-)^a$ (V)	Absorption λ_{abs} (nm)	Emission λ_{em} (nm)	Excited-state life time (τ, ns)
$Ru(bpy)_3^{2+}$	−0.81	+0.77	+1.29	−1.33	452	615	1100
$Ru(bpz)_3^{2+}$	−0.26	+1.45	+1.86	−0.80	443	591	740
fac-Ir(ppy)$_3$	−1.73	+0.31	+0.77	−2.19	375	494^b	1900
$Ir(ppy)_2(dtbbpy)^+$	−0.96	+0.66	+1.21	−1.51	–	581	557
$Ir(dF(CF_3)ppy)_2(dtbbpy)^+$	−0.89	+1.21	+1.69	−1.37	380	470	2300
$Cu(dap)_2^+$	−1.43	–	+0.62	–	–	670^c	270
Eosin Y	−1.11	+0.83	+0.78	−1.06	539	–	24,000
Acridinium perchlorate	–	+2.06	–	−0.57	430	–	–

[a] Redox potential measured against SCE

[b] Measured in EtOH:MeOH (1:1)

[c] Measured in DCM

Table 1.3 List of selected reductive and oxidative quenchers [31, 34, 52, 73, 127, 128]



1.4.1.1 Redox-Neutral Photoredox Catalysis: Single Catalysis

Oxidative quenching cycle

Since photoredox catalysts are single electron transfer agents, most photoredox-catalyzed reactions involve radical or radical-ionic intermediates during the process and many of these reactions proceed via a key step: Radical-Polar Crossover.[1] In an oxidative quenching cycle, the photo-excited photocatalyst behaves as a strong reductant being itself oxidized. In 1984, Deronzier et al. [23] disclosed an overall redox-neutral visible light-mediated Pschorr synthesis of phenanthrene derivatives **1**, in the presence of $[Ru(bpy)_3](BF_4)_2$ (5 mol%). This method obviates the formation of the undesired byproduct **2** under direct photolysis (>360 nm) and benefits from milder reaction conditions compared to previously reported electrochemical processes [79] or thermal methods (Scheme 1.1) [23, 80, 81].

In a mechanistic hypothesis, single electron reduction of aryldiazonium substrates **3** by the photo-excited $^*[Ru(bpy)_3]^{2+}$ generates the higher-valent $[Ru(bpy)_3]^{3+}$ and an aryl radical **4**, which undergoes homoaromatic substitution (HAS) to deliver another cyclized radical intermediate **5**. In the next step, oxidation of this radical intermediate **5** to the cationic intermediate **6** by $[Ru(bpy)_3]^{3+}$, regenerating the photocatalyst $[Ru(bpy)_3]^{2+}$ via a radical-polar crossover, gives rise to the phenanthrene derivative **1** upon deprotonation (Scheme 1.2) [23].

After a long time in 2012, König et al. [82] reported an elegant method for the arylation of heteroarenes with aryldiazonium salts in the presence of the organic dye eosin Y and green light (Scheme 1.3). This reaction proceeds via oxidative quenching of photo-excited eosin Y with aryldiazonium salts **7** delivering aryl radicals **8** and oxidized eosin Y. Aryl radical addition to the electron-rich

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[1] Radical-Polar Crossover process will be described in brief in Chap. 3.