Manifestation of peripheral group effects in photoredox reactions of complexes

Jozef Šima

Department of Inorganic Chemistry, Slovak Technical University, SK-812 37 Bratislava, Slovak Republic

Contents

Abstract

This review deals with the state of the art in the field of correlations between photoredox reactivity parameters (quenching constant k_q, threshold energy E_{th}, quantum yield ϕ) and ground-state parameters of complexes, their ligands and the peripheral groups of the ligands (redox potential $E_{1/2}$, ionization energy I, electronegativity x, Hammett parameter σ, etc.). Practical aspects of the possibilities to tune and optimize photoredox reactivity complexes are evaluated. © 1997 Elsevier Science S.A.

Keywords: Peripheral group effects; Photoredox reactions of complexes; Photoredox parameters; Ground state parameters

1. Introduction

One of the main missions of chemical theory and research is to provide tools enabling industrial chemists to design and create chemical compounds and materials exhibiting desired properties. To approach such a state of the art, relationships between various factors governing the structure and reactivity of chemical compounds are being gradually unveiled and rationalized, and the knowledge reached exploited for practical purposes. Almost all of such structure–properties–utilization

relationships concern ground-state chemistry of molecules and compounds. Notwithstanding that the ground state is the most common state, it is only one of the set of existing states, the others being electronically excited states.

Many of the photoredox processes play important, and some of them even key roles, for mankind and in nature (e.g. photosynthesis, ozone–dioxygen cycle, conversion and storage of solar energy including photocatalysed water decomposition, photopolymerization and polymer photodestruction [1,2]).

Unlike ground-state chemistry, knowledge and methods allowing prediction and optimization of the course and efficiency of photoredox reactions are still in their infancy. In particular, the field of the possibilities to tune photoreactivity, offered by peripheral groups effects, seems to be a vast blank area. In this article the current state in this field is reviewed and some prospectives are sketched.

2. Peripheral groups and their ground-state characteristics

The term 'peripheral group effect' denotes an influence of the electronic properties of the atoms or polyatomic moieties bonded on the periphery of ligands on chemical processes involving the central atom of complexes. The electronic properties of the peripheral groups are usually characterized by relevant substituent (Hammett or Taft) constants [3].

The observed trends in chemical behaviour can be attributed as being a consequence of the variation in the peripheral group properties only for homologous series of compounds having similar size and ligand skeleton, the same chromophore and charge.

There have been a number of attempts to quantify the peripheral group effects or, more generally, the influence of ligands on the properties of complexes (see e.g. the Lever group's [4–6] and our [7] approaches to electrochemical properties of complexes of various central atoms). It would be worth mentioning that, especially for electron transfer processes, the extent of the peripheral group effects may strongly depend on the nature of the central atom involved, particularly on the symmetry of its redox orbital [6,8,9]. This phenomenon can be illustrated on the electrochemical behaviour of Cu(II), Co(II), and Fe(III) complexes containing structurally similar nearly planar tetradentate open-chain Schiff base $N_2O_2R_2^{2-}$ ligands (Fig. 1) possessing different peripheral groups R. The results obtained (Table 1) can be summarized as follows [8,9].
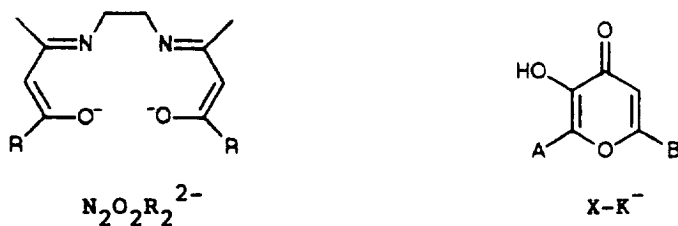

Fig. 1. Structure of ligands $N_2O_2R_2^{2-}$ and X–K$^-$.

Table 1
Redox potential data $E(M^{III}/M^{II})$ (V vs. NHE) for the complexes $[M(N_2O_2R_2)]$ (M = Cu, Ni, Fe and Co), Hammett constants $\sigma(R)$ of the peripheral groups R, reaction parameters ρ and regression coefficients R [9,10]

R	$\sigma(R)$	$E_{pa}(Cu)$	$E_{1/2}(Fe)$	$E_{1/2}(Co)$
$CH_3OC_6H_4$	−0.21	0.730	−0.285	0.088
$CH_3C_6H_4$	−0.15	0.775	−0.273	0.083
CH_3	−0.14	—	−0.290	—
C_6H_5	−0.13	0.798	−0.274	0.053
ClC_6H_4	−0.08	0.825	−0.273	0.099
BrC_6H_4	−0.06	0.842	−0.254	0.088
$NO_2C_6H_4$	0.00	0.925	—	—
ρ		0.442	0.087	0.027
R		0.984	0.745	0.186

(a) For Cu(II) complexes with an in-plane (xy) oriented redox orbital, their electrochemical behaviour, as expressed through the redox potential value E, is strongly sensitive to the electronic changes, expressed by the Hammett constants $\sigma(R)$ of the peripheral groups R, in this plane. The reaction parameter ρ:

$$\rho = dE / \sum d\sigma(R) \qquad (1)$$

has the value of 0.442. For these complexes the redox potential depends only slightly on the properties of axial ligands [10].

(b) For Co(II) and Fe(III) complexes with an out-of-plane oriented redox orbital (d_{yz}), changes in the equatorial plane xy (due to groups R) are reflected only to a small extent in redox potential values (the values of the reaction parameters ρ are small), whereas changes in axial positions have a stronger influence on those values [10].

3. Excited-state reactivity parameters of complexes

3.1. Rate constant k_q

The excited-state–ground-state dependences involving the rate constant k_q are evaluated mostly for outer-sphere electron-transfer processes occurring often in systems, the irradiation of which, due to a fast back electron transfer, does not lead to any net chemical change.

The rate constant k_q has been correlated with the Gibbs energy of the bimolecular redox reactions ΔG°, the redox potentials E°, and the ionization energies I, each of the quantities being a ground-state parameter of the reactants.

From the viewpoint of the peripheral group effect, systems with one excited complex and a series of structurally similar quenchers differing in peripheral groups,

and systems with one quencher and a homogeneous series of excited complexes possessing ligands differing in the peripheral groups, have been investigated.

The oxidative quenching of $_{MLCT}^3[Ru(bpy)_3]^{2+}$ by a series of Co(III) complexes [11,12]:

$$_{MLCT}^3[Ru(bpy)_3]^{2+} + Co(III) \rightarrow [Ru(bpy)_3]^{3+} + Co(II) \qquad (2)$$
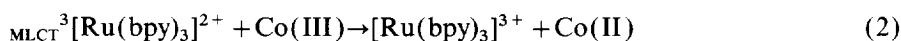
can be taken as an example of the former case. The quenching constant values k_q are correlated with $E_{1/2}(Co^{III/II})$ and ΔG° of the electron transfer process. It follows from the data in Table 2 that in the Arrhenius portion of the log $k_q - E_{1/2}$ plot there is a good agreement between theoretical expectations based on the Rehm–Weller approach and the experimental values.

An illustrative example of the peripheral group effect on the quenching rate constant k_q is the electron transfer from excited $*[Ru(NN)_3]^{2+}$ complexes to hydrated M^{n+} ions, where NN denotes bipyridine and phenanthroline derivatives, M^{n+} is Cu^{2+}, $HgCl_2$, Eu^{3+}, Cr^{3+} and Fe^{3+} (the data for Cu^{2+} are listed in Table 3

Table 2
Rate constants k_q of the oxidative quenching of the excited $[Ru(bpy)_3]^{2+}$ by a series of Co(III) quenchers, redox potentials $E_{1/2}(Co^{III/II})$ for quenchers, and the Gibbs energy ΔG° of the electron transfer processes [11,12]

Quencher	$E_{1/2}(Co^{III/II})$ (V)	k_q (M^{-1} s^{-1})	ΔG° (eV)
$[Co(sar)]^{3+}$	-0.42	3.0×10^6	-0.46
$[Co(NH_2mesar)]^{3+}$	-0.36	8.0×10^6	-0.50
$[Co(Clsar)]^{3+}$	-0.29	4.2×10^7	-0.57
$[Co(sep)]^{3+}$	-0.28	3.4×10^7	-0.58
$[Co(en)_3]^{3+}$	-0.18	6.1×10^7	-0.68
$[Co(NH_3)_6]^{3+}$	0.10	1.2×10^8	-0.96
$[Co(NH_3)_5(H_2O)]^{3+}$	0.37	3.9×10^8	-1.23
$[Co(bpy)_3]^{3+}$	0.34	1.3×10^9	-1.20
$[Co(phen)_3]^{3+}$	0.40	1.9×10^9	-1.26

Table 3
Quenching constants k_q, cage escape quantum yields ϕ_{ce}, redox potentials $E^\circ([Ru(NN)_3]^{3+/2+})$ and Gibbs energy ΔG° for oxidative quenching of $_{MLCT}^3[Ru(NN)_3]^{2+}$ by Cu^{2+} ions [13]

NN-ligand	E° (V)	ΔG° (eV)	k_q (M^{-1} s^{-1})	ϕ_{ce}
3,4,7,8-Me$_4$phen	1.02	-1.26	1.0×10^8	0.95
4,7-Me$_2$phen	1.09	-1.16	8.6×10^7	0.96
4,4'-Me$_2$bpy	1.10	-1.09	8.7×10^7	0.94
5,6-Me$_2$phen	1.20	-1.08	7.6×10^7	0.79
5-Mephen	1.23	-1.05	6.0×10^7	0.74
5-Phphen	1.26	-1.02	5.7×10^7	0.51
phen	1.26	-1.02	7.5×10^7	0.54
bpy	1.26	-0.99	6.2×10^7	0.56
5-Clphen	1.36	-0.92	4.0×10^7	0.31
5-Brphen	1.37	-0.91	4.2×10^7	0.30

[13]). The redox potential dependence of k_q is strong for Eu^{3+} and $HgCl_2$, moderate for Cu^{2+}, weak for Fe^{3+} and none for Cr^{3+} [13]. Only for Fe^{3+} and $HgCl_2$ quenchers does the quenching constant k_q approach the diffusion limited value in the strongly exoergonic region.

In spite of the fact that some questions are still open to discussion (e.g. the Marcus inverted region, adiabaticity of the electron transfer step) the following conclusions regarding the tuning and optimization of the redox quenching rate constant k_q can be drawn:

(1) correlations of the quenching constant k_q with the ground-state redox potential $E°$ for both excited complexes and their quenchers, and with the driving force $\Delta G°$, are for bimolecular outer-sphere electron transfer photoreactions both theoretically rationalizable and justifiable;

(2) knowledge of such correlations allows tuning and optimization of the quenching rate constant values that is meaningful, particularly for the highly exoergonic and Arrhenius part regions;

(3) the results obtained are, at present, of negligible practical importance.

3.2. Threshold energy E_{th}

In spite of its practical importance (it informs, e.g., which radiation wavelengths should be avoided to prevent undesirable reactions from occurring), the threshold energy still remains outside the photochemists' interests.

In his pioneering work [14,15], Endicott determined the E_{th} values for inner-sphere photoredox Co–ligand bond cleavage in some Co(III) complexes. For the complexes $[Co(NH_3)_5X]^{2+}$ he found a good correlation of the E_{th} values with the optical electronegativity $x(X^-)$ of acidoligands X^- (Table 4). Strictly speaking, however, such a correlation does not fall in the category of the peripheral group effects investigation.

The threshold energy for Co–CH$_3$ homolysis in the complexes $trans$-$[Co(N_4)(H_2O)(CH_3)]^{2+}$

$$*[Co^{III}(N_4)(H_2O)(CH_3)]^{2+} \rightarrow [Co^{II}(N_4)(H_2O)]^{2+} + {}^{\cdot}CH_3 \qquad (3)$$
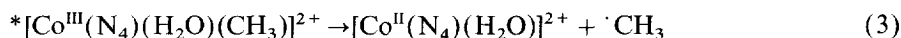
Table 4
Ground-state properties (ionization energy I; optical electronegativity x; redox potential $E°$) and threshold energies E_{th} for the central atom–ligand homolyses in some Co(III) and Fe(III) complexes [14,16]

Property of X^-	Cl^-	Br^-	I^-	SCN^-	N_3^-	NO_2^-
$x(X^-)$	2.83	2.74	2.21	2.53	2.77	2.60
$I(X^-)$ (eV)	3.61	3.36	3.06	2.13	2.70	2.38
$E°(X/X^-)$ (V)	2.41	1.92	1.33	1.63	1.33	1.04
Complex	E_{th} (eV)					
$[Co(NH_3)_5X]^{2+}$	3.21	2.69	2.05	2.45	2.68	2.57
$[Fe([15]pydieneN_5)X_2]^+$	3.82	3.21	—	2.34	2.86	—
$[Fe([15]pyaneN_5)X_2]^+$	4.85	4.27	—	—	3.77	—

exhibits a dependence on the saturation and peripheral groups of the macrocyclic tetraaza ligands coordinated in the equatorial plane of the complexes. Thus, for $N_4 = [14]aneN_4$, $E_{th} \leq 2.31$ eV; for $N_4 = Me_4[14]tetraeneN_4$, $E_{th} = 2.16$ eV, and for $N_4 = Me_6[14]4,11$-dieneN$_4$, $E_{th} < 1.87$ eV.

The strong effect of saturation of macrocyclic ligands on the E_{th} values (1 eV shift in the oxidation of a given X^-) was observed also in *trans*-$[Fe(N_4)X_2]^+$ undergoing an Fe(III)–X$^-$ homolysis from their LMCT states (Table 4). For complexes with both saturated and unsaturated macrocyclic ligand, a good correlation between the E_{th} and ionization energy $I(X^-)$ was found [16]. An interesting feature of the complexes is that the redox potentials $E°([Fe([15]pydieneN_4)X_2]^{+/0})$ do not depend on X^-, whereas their charge-transfer absorption spectra do.

There is not enough data in the chemical literature to permit formulations of more definite conclusions linking the peripheral group effects to the threshold energy of photoredox reactions. Obviously, the work initiated by Endicott calls for successors in order to build up a good theoretical background for understanding and optimizing the excited state parameter E_{th}, based on ground-state parameters of complexes or peripheral groups of their ligands.

3.3. Quantum yield ϕ

To photochemists, quantum yield is the most familiar photochemical parameter; and from the practical point of view, overall quantum yield is the most important one.

Published data regarding the tuning and optimizing of quantum yields can be divided into two parts. The first concerns the primary quantum yields and those based on the elementary steps of photoreactions; the second deals with overall quantum yields.

High cage-escape quantum yields ϕ_{ce} ($\phi_{ce} = k_{-d}/(k_{-d} + k_{bet})$, where k_{-d} and k_{bet} are the rate constant of diffusion of the redox changed molecules from the solvent cage and the rate constant of the back electron transfer within the solvent cage respectively) were measured for systems containing excited $[Ru(NN)_3]^{2+}$ with various peripherally modified bipyridine and phenanthroline NN-ligands and metal ions as quenchers (Table 3 [13]). The regression coefficient value R for the ϕ vs. $E°([Ru(NN)_3]^{3+/2+})$ plot, using the Cu^{2+} quencher:

$$_{MLCT}{}^3[Ru(NN)_3]^{2+} + Cu^{2+} \rightarrow [Ru(NN)_3]^{3+} + Cu^+ \tag{4}$$
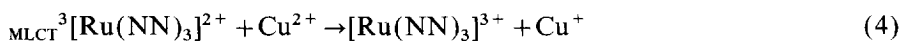
($R = 0.959$) is even higher than for the $\log k_q$ vs. $E°([Ru(NN)_3]^{3+/2+})$ plot ($R = 0.940$). Such a linear dependence on the redox potential is not, however, a general characteristic of the cage escape quantum yield. For Ru(II) complexes quenched with EDTA or TEOA, no dependence of ϕ_{ce} on $E°$ values was observed [17].

A study of the reductive quenching of the excited $[Ru(bpy)_3]^{2+}$ by seven Co(III) cage complexes [12] documented that the overall quantum yield of Co(II) formation increased with increasing oxidation power of the Co(III) complexes (Table 5).

In all the systems discussed above the quantum yields were related to simple

Table 5
Overall quantum yields of Co(II) formation $\phi_{Co(II)}$, redox potentials $E°(Co^{III/II})$, and Gibbs energy $\Delta G°$ for oxidative quenching of excited $[Ru(bpy)_3]^{2+}$ by Co(III) cage complexes [12]

Quencher	$E°(Co^{III/II})$ (V)	$\Delta G°$ (eV)	$\phi_{Co(II)}$
$[Co(\{Me\}OsarH)]^{2+}$	−0.59	−0.25	$< 10^{-4}$
$[Co(COOC_2H_5\{Me\}OsarH)]^{2+}$	−0.53	−0.31	$< 10^{-4}$
$[Co(sar)]^{3+}$	−0.42	−0.42	0.004
$[Co(NH_2\{Me\}sar)]^{3+}$	−0.36	−0.48	0.01
$[Co(Clsar)]^{3+}$	−0.29	−0.55	0.05
$[Co(sep)]^{3+}$	−0.28	−0.56	0.04
$[Co(azacapten)]^{3+}$	−0.05	−0.79	0.6

electron transfer processes which were not accompanied by further subsequent or consecutive reactions or other types of quenching. In the majority of such instances the quantum yields can be correlated with ground state parameters of complexes or their ligands, including the peripheral group parameters. Trends in such quantum yields can, therefore, be predicted and their values optimized within a homogeneous series of complexes.

In cases when the primary photoredox step is followed by other redox (dark) reactions, the situation is more complicated and the predictability of the quantum yields can disappear. Some of the data obtained in our laboratory [18–26], regarding the manifestation of the peripheral group effects in photoredox behaviour of Fe(III) complexes containing tetradentate Schiff base open-chain ligands denoted $N_2O_2R_2^{2-}$ and/or bidentate γ-pyranones denoted X–K$^-$ (Fig. 1), are gathered in Tables 6 and 7.

Of the complexes listed in Tables 6 and 7, for the sake of simplicity, only the

Table 6
Overall quantum yields of Fe(II) formation $\phi(\lambda_{irr})$ for *trans*-$[Fe(N_2O_2R_2)(NCS)_2]^-$ and *cis-β*-$[Fe(N_2O_2R_2)(OH–K)]$, Hammett constants $\sigma(R)$ of the peripheral groups R of the tetradentate ligands $(N_2O_2R_2)^{2-}$ [18,22,23]
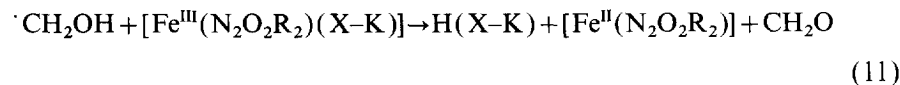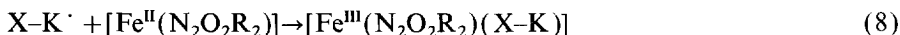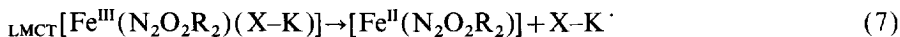
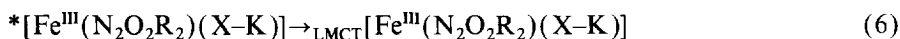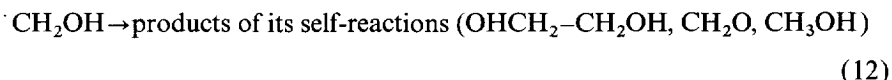| R	$\sigma(R)$	NCS$^-$/OH–K$^-$	$\phi(254\ nm)$	$\phi(313\ nm)$
$CH_3OC_6H_4$	−0.21	NCS$^-$	0.78	0.37
		OH–K$^-$	0.056	0.037
$CH_3C_6H_4$	−0.15	NCS$^-$	0.49	0.22
		OH–K$^-$	0.044	0.021
CH_3	−0.14	NCS$^-$	0.84	0.41
		OH–K$^-$	0.045	0.025
C_6H_5	−0.13	NCS$^-$	0.91	0.39
		OH–K$^-$	0.047	0.029
ClC_6H_4	−0.08	NCS$^-$	0.51	0.089
		OH–K$^-$	0.020	0.015
BrC_6H_4	−0.06	NCS$^-$	0.12	0.014
		OH–K$^-$	0.047	0.040

Table 7
Overall quantum yields of Fe(II) formation $\phi(\lambda_{irr})$ for the complexes [Fe(X–K)$_3$] irradiated in methanol, the sum of Hammett constants $\sum\sigma$ of the peripheral groups A and B of the kojic acid derivatives X–K$^-$ [25,26]

A	B	$\sum\sigma$	ϕ(254 nm)	ϕ(313 nm)	ϕ(365 nm)	ϕ(436 nm)
H	CH_2OH	−0.70	0.16	0.10	0.029	0.018
H	$CH_2ScycloC_6H_{11}$	−0.25	0.16	0.15	0.049	<0.0001
H	$CH_2SC_8H_{17}$	−0.23	0.30	0.086	0.047	<0.0001
H	CH_2Br	−0.22	0.13	0.11	0.043	0.026
H	CH_2Cl	−0.19	0.17	0.14	0.061	0.038
CH_3	H	−0.18	0.0030	0.0018	0.0016	0.0012

photoredox behaviour of [Fe(N$_2$O$_2$R$_2$)(X–K)] will be discussed in detail. An interesting feature of the photoredox reactions of these complexes is that the primary excitation localized on the ligands N$_2$O$_2$R$_2^{2-}$ (the absorption of a photon at 254 nm or 365 nm is connected with a change in the π-system of the peripheral phenyl groups R or the C=N double bond of the tetradentate ligands respectively) influences the efficiency of the photo-oxidation of another coordinated ligand (X–K$^-$ or monodentate acidoligand X$^-$). The wavelength dependence of quantum yields ϕ documents an effective communication of the excited states involved and reflects the different kinetic energy of the geminate redox pair and the different extent of their back reactions. Based on the spin-trapping EPR identification of the radicals X–K$^\cdot$ and $^\cdot$CH$_2$OH and determination of the final products Fe(II) and CH$_2$O, a mechanism of the photoreactions for the complexes [Fe(N$_2$O$_2$R$_2$)(X–K)] can be tentatively proposed as follows, where the asterisk denotes any of the primary populated sextet excited state, and the reaction in Eq. (6) represents all intersystem crossing and/or internal conversion processes leading to the redox reactive quartet or sextet LMCT states):

$$*[Fe^{III}(N_2O_2R_2)(X–K)] \rightarrow_{LMCT}[Fe^{III}(N_2O_2R_2)(X–K)] \tag{6}$$

$$_{LMCT}[Fe^{III}(N_2O_2R_2)(X–K)] \rightarrow [Fe^{II}(N_2O_2R_2)] + X–K^\cdot \tag{7}$$

$$X–K^\cdot + [Fe^{II}(N_2O_2R_2)] \rightarrow [Fe^{III}(N_2O_2R_2)(X–K)] \tag{8}$$

$$X–K^\cdot + CH_3OH \rightarrow H(X–K) + {}^\cdot CH_2OH \tag{9}$$

$$X–K^\cdot \rightarrow decomposition\ products \tag{10}$$

$$^\cdot CH_2OH + [Fe^{III}(N_2O_2R_2)(X–K)] \rightarrow H(X–K) + [Fe^{II}(N_2O_2R_2)] + CH_2O \tag{11}$$

$$\dot{}\text{CH}_2\text{OH} \rightarrow \text{products of its self-reactions (OHCH}_2\text{–CH}_2\text{OH, CH}_2\text{O, CH}_3\text{OH)}$$

$$(12)$$

Tetradentate $N_2O_2R_2^{2-}$ ligands do not undergo redox changes and remain attached to the iron central atom. The mechanisms of the other Fe(III) complexes investigated are similar.

The results gathered in Tables 6 and 7 (and other data listed in Refs. [18–26]) show some common features. The peripheral groups R of the tetradentate ligands $N_2O_2R_2^{2-}$ influence the ability of the other ligand to undergo photo-oxidation and the central atom to become reduced. There is, however, no correlation between the electronic properties of the anionic axial ligands X^-, the peripheral groups of the ligands $N_2O_2R_2^{2-}$ and X–K$^-$ and the efficiency ϕ of the overall photoredox processes. Among the reasons explaining this experimental observation (for a detailed discussion see Ref. [18]) the key one lies probably in different kinetic parameters of existing deactivation modes of excited complexes, and rates of the back, simultaneous and consecutive redox processes of ground-state products of the primary photoprocesses.

It should be pointed out that there are also homologous series of complexes for which the overall quantum yields are constant throughout the whole series, e.g. as observed in the case of excited Fe(III) porphyrins in ethanol [27].

The questions regarding the possibility of tuning and optimizing quantum yields and their connection with the ground-state properties of ligands and their peripheral groups, can be, based on current knowledge, answered as follows:

(1) for some homogeneous series of complexes a fair correlation between the relevant ground-state redox properties of the complexes, their ligands and the electronic properties of the peripheral groups of ligands, and the primary quantum yields is observed. The existence of such correlations enables us to predict the primary quantum yields for the members of such series and optimize their values. Such correlations should not, however, be transferred to another series of complexes without prior experimental testing;

(2) current knowledge does not, unfortunately, allow us easily to utilize available ground-state quantities of complexes for modelling their composition and structure, peripheral groups included, in order to obtain just the required efficiency of their photoredox properties;

(3) scientific rationalization of the observed experimental behaviour, and the practical needs to achieve the ability to purposefully modify the photoredox and photocatalytic processes of complexes should lead to the development of the questions concerning justification, possibilities and limitations of the predictability of both the primary and overall quantum yields, and their optimization for applicative purposes.

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