Polyhedron 123 (2017) 259–264

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Probing the use of long lived intra-ligand π–π^* excited states for photocatalytic systems: A study of the photophysics and photochemistry of $[ReCl(CO)_3(dppz\text{-}(CH_3)_2)]$

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ARTICLE INFO

Article history:
Received 15 August 2016
Accepted 2 November 2016
Available online 12 November 2016

Keywords:
Rhenium
Time-resolved IR
Photophysics
Intra-ligand excited state
Reductive quenching

ABSTRACT

We report the excited state photophysics and photochemistry of $[ReCl(CO)_3(dppz\text{-}(CH_3)_2)]$ (dppz-$(CH_3)_2$ = 11,12-dimethyl-dipyrido[3,2-a:2′,3′-c]phenazine) in CH_3CN using time-resolved infrared (TRIR) and Fourier transform infrared (FTIR) spectroscopy. Excitation of the ^{1}MLCT (metal-to-ligand charge transfer) band of $[ReCl(CO)_3(dppz\text{-}(CH_3)_2)]$ populates a ^{3}MLCT excited state which rapidly interconverts on a timescale <1 ns to a long lived IL (intra-ligand) $\pi\pi^*$ excited state with a lifetime of 190 (± 5) ns. In the presence of an electron donor (NEt_3), the IL excited state of $[ReCl(CO)_3(dppz\text{-}(CH_3)_2)]$ can be reductively quenched to $[ReCl(CO)_3(dppz\text{-}(CH_3)_2)]^-$ with the radical in the latter localised on the distal phenazine (phz) portion of the dppz ligand. The phz based electron in $[ReCl(CO)_3(dppz\text{-}(CH_3)_2)]^-$ has minimal interaction with the rhenium metal centre which increases the stability of the photosensitiser in its reduced form. In non-dried, non-degassed CH_3CN (1 M NEt_3), $[ReCl(CO)_3(dppz\text{-}(CH_3)_2)]^-$ shows no significant change in the carbonyl region of the IR spectrum for at least 2 h during continuous photolysis. In addition, we investigate the use of $[ReCl(CO)_3(dppz\text{-}(CH_3)_2)]^-$ to reduce the previously studied catalyst $[NiFe_2]$, with facile electron transfer from $[ReCl(CO)_3(dppz\text{-}(CH_3)_2)]^-$ to form $[NiFe_2]^-$.

1. Introduction

There is increased interest in the direct use of solar energy as an attractive and renewable alternative to fossil fuels. The use of light to drive the photochemistry required to split water to produce H_2, or the reduction of CO_2 to produce solar fuels, has attracted considerable interest and there are many approaches to achieve this goal [1,2]. Generally however, homogeneous systems have utilised a photosensitiser that mediates electron transfer to or from a multi-electron catalyst. A key parameter for such catalytic systems is the reductive/oxidative quenching of a short-lived photo-excited state that is typically MLCT-based (metal-to-ligand charge transfer) for metal diimine photosensitisers used in such cycles. We focus herein on photosensitisers that undergo reductive quenching to generate radical anions. For these processes, the absorption of a photon by the photosensitiser needs to generate a long-lived excited state, which is reductively quenched by an electron donor to generate the reduced photosensitiser, which can either reduce a catalyst [Scheme 1 (a)] or act as a catalyst itself. For MLCT excited states the lifetime can directly affect the efficiency of such cycles.

Abbreviations: MLCT, metal-to-ligand charge transfer; FTIR, Fourier transform infrared; TRIR, time-resolved infrared; IL, intra-ligand; LUMO, lowest unoccupied molecular orbital; DNA, deoxyribonucleic acid; bpy, 2,2′-bipyridine; dppz, dipyrido[3,2-a:2′,3′-c]phenazine; dppz-$(CH_3)_2$, 11,12-dimethyl-dipyrido[3,2-a:2′,3′-c]phenazine; $[NiFe_2]$, $[Ni`S_4'Fe_2(CO)_6]$ cluster (`$S_4$' = $(CH_3C_6H_3S_2)_2(CH_2)_3$); *i*-Pr-PyCa, pyridine-2-carbaldehyde N-isopropylimine; dapa, 2,6-diacetylpyridine bis(anil); dpp, 2,3-di(2-pyridylpyrazine); abpy, azo-2,2′-bipyridine.

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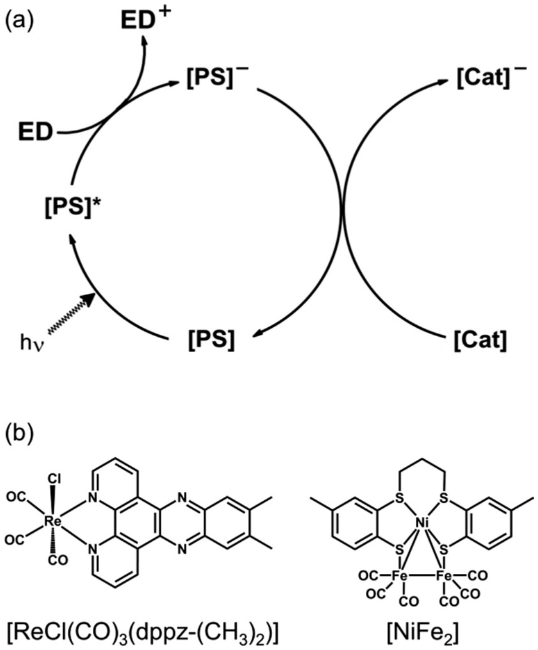
http://dx.doi.org/10.1016/j.poly.2016.11.005
0277-5387/



Scheme 1. (a) Simplified schematic of the one-electron reduction of a catalyst ([Cat]) by a photosensitiser ([PS]) proceeding *via* the reductive quenching of $[PS]^*$ by an electron donor ([ED]). (b) Structures of $[ReCl(CO)_3(dppz\text{-}(CH_3)_2)]$ and [NiFe2].

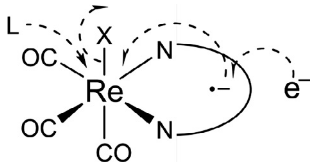


Fig. 1. Substitution mechanism of the axial ligand X in $[ReCl(CO)_3X(diimine)]$, promoted by the delocalised electron on the diimine ligand. Adapted from Ref. [19].

Example systems of this type are extensive; their applications for the reduction of CO_2, [3,4] and/or H^+ [5–8] have been reviewed recently.

For the successful implementation of a photocatalytic cycle, such as that in Scheme 1(a), it is essential that all components remain robust under the catalytic conditions employed, and as a result there is interest in developing photo-stable components with high turn-over numbers (TON). In recent studies, heterogeneous photosensitisers have shown remarkable stabilities under continuous photolysis. Thus, CdSe quantum dots have maintained activity for weeks, with TONs of 60,0000 or more [8,9]. Homogeneous systems generally do not show such long-lived stability, and often require rigorous purification and degassing of solvents. However, homogeneous systems still attract attention since their properties may be tuned, and they may be easier to study and are atom efficient in their design when compared to heterogeneous catalysts. In such homogeneous systems, the reduced form of the photosensitiser may undergo competing side-reactions rather than those associated with the intended catalytic cycle [5,8,10,11]. For example, rhodamine dyes have been studied as a photosensitiser in the reduction of a Co^{III} H_2-evolving catalyst [12]. Concentration dependent studies reveal that as the concentration of the Co^{III} catalyst decreases, the rate of decomposition of the reduced photosensitiser increased. Fast time-resolved IR (TRIR) has proven to be extremely useful for examining complex catalytic systems, [13] and we have recently used IR spectroscopy to probe catalytic systems for the photochemical production of H_2. These systems employ $[ReCl(CO)_3(bpy)]$ (bpy = 2,2′-bipyridine) based photosensitisers and a synthetic catalyst $[NiFe_2]$ [Fig. 1(b)] with a structure inspired by the nature of the active site of [NiFe] hydrogenases [14,15]. In our previous studies we noted that the catalytic efficacy of these systems is compromised by the decomposition of the photosensitiser during turnover and the catalyst decomposition on photolysis, complicating the mechanistic study of $[NiFe_2]$. Indeed, the rapid dissociation of Cl^- from $[ReCl(CO)_3(bpy)]^-$ in solution has been well documented [16–18]. The chemistry of a range complexes of type $[ReX(CO)_3(diimine)]^{0/+}$ (diimine = bpy, *i*-Pr-PyCa, dapa, dpp, abpy; X = Cl^-, Br^-, I^-, OTf^-, donor solvent, *n*-PrCN, PR_3, $P(OMe)_3$; *i*-Pr-PyCa = pyridine-2-carbaldehyde N-isopropylimine; dapa = 2,6-diacetylpyridine bis(anil); dpp = 2,3-di(2-pyridylpyrazine); abpy = azo-2,2′-bipyridine) have been studied following their one-electron reduction [16]. The stability of the Re–X bond appears to be related to the ability of the complex to accommodate the radical electron in the π^*-LUMO (lowest unoccupied molecular orbital) localised on the diimine unit; the stability of the Re–X bond follows the order bpy < *i*-Pr-PyCa < dapa < dpp < abpy. Studies on similar systems have concluded that there is orbital contribution between the π^*-LUMO in the diimine ligand and the σ(Re–X) antibonding orbital [19]. Thus, population of the π^*-LUMO weakens the Re–X bond, which can result in the reversible dissociation of the axial ligand [Fig. 1]. Consequently, for the development of an effective photosensitiser based on a $[ReCl(CO)_3(diimine)]$ unit the design elements of the diimine ligand are crucial, with a key consideration being to localise the π^*-LUMO away from the metal centre.

Transition metal complexes containing ligands based on dppz (dppz = dipyrido[3,2-a:2′,3′-c]phenazine) have been used widely as intercalating probes for DNA (deoxyribonucleic acid) and the study of DNA-mediated electron transfer and DNA damage [20–22]. However, the photophysical properties of complexes containing dppz type ligands still remain ambiguous, partly due to the nature of the dppz ligand that can be described as a fusion of two moieties, phenanthroline (phen) and phenazine (phz), both of which contain localized π^* acceptor orbitals [23]. This leads to the possibility of four low-lying triplet excited states in dppz containing metal complexes, involving MLCT or IL (intra-ligand) $\pi\pi^*$ transitions to orbitals localised on either the phen or phz moieties of the ligand, where the LUMO lies on the phz moiety. The first reduction process for $[ReCl(CO)_3(bpy)]$ occurs at −1.74 V *vs.* Fc^+/Fc in DMF [19]. However, as the phz localised $[ReCl(CO)_3(dppz)]$ LUMO is lower in energy than the $[ReCl(CO)_3(bpy)]$ LUMO, the first reduction process for $[ReCl(CO)_3(dppz)]$ occurs at −1.42 V *vs.* Fc^+/Fc in CH_3CN [24]. Indeed, the one-electron reduction of $[ReCl(CO)_3(dppz)]$ results in a relatively small shift in ν(CO) band positions (*ca.* 7 cm^{-1} in CH_2Cl_2), evidence that the phz based electron does not interact significantly with the Re centre [24]. In this paper we investigate the photophysics and subsequent photochemistry of $[ReCl(CO)_3(dppz\text{-}(CH_3)_2)]$ ($dppz\text{-}(CH_3)_2$ = 11,12-dimethyl-dipyrido[3,2-a:2′,3′-c]phenazine) in CH_3CN. $[ReCl(CO)_3(dppz\text{-}(CH_3)_2)]$ has the potential to be used as a photosensitiser that is more robust under the reducing conditions of continuous photocatalysis than commonly used chromophores such as $[ReCl(CO)_3(bpy)]$. We chose to study $[ReCl(CO)_3(dppz\text{-}(CH_3)_2)]$ rather than $[ReCl(CO)_3(dppz)]$ because addition of methyl groups at the C11 and C12 positions of the dppz ligand simplifies the observed excited state photophysics in CH_3CN on the ns timescale (see below) and the reduced $[ReCl(CO)_3(dppz\text{-}(CH_3)_2)]$ photosensitiser (−1.48 V *vs.* Fc^+/Fc in CH_2Cl_2) possesses a more negative reduction potential than $[ReCl(CO)_3(dppz)]$ [24]. In addition, $[ReCl(CO)_3(dppz\text{-}(CH_3)_2)]$ has a long-lived $\pi\pi^*$ excited state and the use of such IL excited states have not been exploited extensively in photocatalytic applications [24].