Polyhedron 137 (2017) 231–237

Contents lists available at ScienceDirect

Polyhedron

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

Emission tuning in Re(I) complexes: Expanding heterocyclic ligands and/or introduction of perfluorinated ligands

Pavel A. Abramov [a,b,*], Konstantin A. Brylev [a,b], Aleksei Yu. Vorob'ev [b,c], Yuriy V. Gatilov [b,c], Gennadiy I. Borodkin [b,c], Noboru Kitamura [d], Maxim N. Sokolov [a,b,e]

[a] Nikolaev Institute of Inorganic Chemistry, 3 Akad. Lavrentiev Ave., 630090 Novosibirsk, Russia
[b] Novosibirsk State University, 2 Pirogova Str., 630090 Novosibirsk, Russia
[c] Vorozhtsov Novosibirsk Institute of Organic Chemistry SB RAS, 9 Akad. Lavrentiev Ave., 630090 Novosibirsk, Russia
[d] Department of Chemistry, Faculty of Science, Hokkaido University, 060-0810 Sapporo, Japan
[e] Kazan Federal University, Kremlyovskaya St., 18 Kazan 420008, Russia

ARTICLE INFO

Article history:
Received 3 June 2017
Accepted 29 August 2017
Available online 5 September 2017

Keywords:
Rhenium
Diimine
Luminescence
Perfluorinated ligands

ABSTRACT

Reactions of new heterocyclic ligands 2-(pyridin-2-yl)-[1,2,4]triazolo[1,5-*a*]quinolin-9-ol (**L-OH**), 2-(pyridin-2-yl)-[1,2,4]triazolo[1,5-*a*][1,10]phenanthroline (**L-Py**) and 2-methyl-[1,2,4]triazolo[1,5-*a*][1,10]phenanthroline (**L-Me**) with $[Re(CO)_5Br]$ in toluene afforded the complexes of the general formula $[(L)Re(CO)_3Br]$. Substitution of the Br^- ligand in $[(L)Re(CO)_3Br]$ by $C_3F_7COO^-$ leads to $[(L)Re(CO)_3(OOCC_3F_7)]$ and results in increased emission lifetime.

1. Introduction

During the past decade, there has been growing interest in the synthesis, properties and applications of organic photochromic materials [1]. They have been in the research focus owing to their potential applications in optically rewritable data storage systems, optical switching, and chemical sensing. Useful properties that can be photo-regulated include luminescence, refractive index, electrical conductance, magnetism, optical rotation, nonlinear optics, and redox chemistry. Photochromic transformations in these molecules are generally based on unimolecular processes involving interconversion between two isomers, such as *cis*/*trans* isomerization, ring opening/closing or intramolecular proton transfer. Various types of organic photochromic compounds such as azobenzenes, diarylethenes, fulgides, spirobenzopyranes, dimethyldihydropyrenes have been developed. Metal complexes featuring photoresponsive ligands are a viable alternative to purely organic photochromes. Combination of a photochromic moiety with an organometallic or coordination compound gives rise to new properties derived from the fusion of redox, optical and magnetic properties of the metal complexes with the photochromism, which opens almost a limitless scope for tuning desirable properties by simple changes in the coordination sphere [2]. In particular, photophysics, photochemistry and photocatalytic activities of tricarbonyl rhenium(I) diimine complexes *fac*-$[Re^{I}(LL)(CO)_3(L)]^{n+}$ [3] and *cis*,*trans*-$[Re^{I}(LL)(CO)_2(L)_2]^{n+}$ [4] (LL = bidentate diimine ligand, L = monodentate ligand) have been extensively investigated. Among these complexes, there are unique photocatalysts that do not require the presence of a photosensitizer or co-catalyst [5]. Initially the studies were focused upon *fac*-$[Re^{I}(LL)(CO)_3X]$ complexes (X = halide). The first complexes with X other than halide were *fac*-$[Re(bpy)(CO)_3(OOCH)]$ and *fac*-$[Re(bpy)(CO)_3\{BH_3(CN)\}]$ (bpy = 2,2′-bipyridine) reported in 1989 [6]. Many such complexes are known nowadays, e.g., $[Re(OTf)(CO)_3(Me_2\text{-bipy})]$ [14], $[(2,4,6\text{-}Me_3\text{-}G)Re(CO)_3(OOCCF_3)]$ (2,4,6-Me_3-G = [N,N-bis(2,4,6-trimethylbenzene)-1,4-diazabutadiene]) [7], *fac*-$[Re(CO)_3(bz_2en)OOCCF_3]$ (bz_2en = N,N-bis(benzophenone)-1,2-diiminoethane) [8], *fac*-$[Re(dmbpy)(CO)_3(COOH)]$ [9].

Excited state properties of a series of carboxylate complexes $[Re(CO)_3(2,2'\text{-bpy})(RCOO)]$ (RCOO = naphthalene-2-carboxylate, anthracene-9-carboxylate, pyrene-1-carboxylate and acetate) were investigated by steady-state and time-resolved spectroscopy. The presence of two emitting excited states play a major role in the photophysics of these complexes. The one emitting component showing a short emission lifetime is associated with the metal-to-ligand charge transfer (MLCT) excited state, Re^{I}-to-2,2′-bpy,

* Corresponding author at: Nikolaev Institute of Inorganic Chemistry, 3 Akad. Lavrentiev Ave., 630090 Novosibirsk, Russia.
E-mail address: abramov@niic.nsc.ru (P.A. Abramov).

http://dx.doi.org/10.1016/j.poly.2017.08.046
0277-5387/