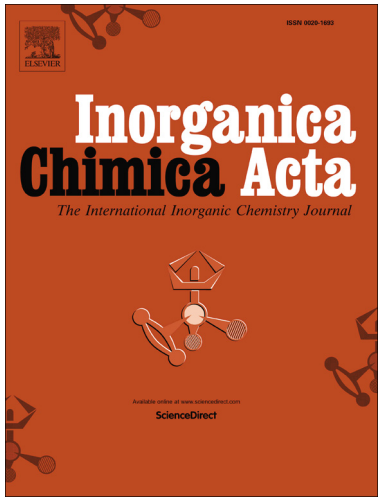

Research paper

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A new route to constructing rhenium(I)-based 8-hydroxyquinolate complexes: synthesis, structures and luminescent properties

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ABSTRACT: Three Re(I)-based complexes [*fac*-$Re(CO)_3$(hyq)(pim)] (**1**, Hhyq = 8-hydroxyquinoline; pim = 2-phenylimidazole), [*fac*-$Re(CO)_3$(hyq)(im)] (**2**, im = imidazole), [*fac*-$Re(CO)_3$(hyq)(hyp)] (**3**, hyp = 4-hydroxypyridine) were synthesized by reacting Re_2CO_{10} with 8-hydroxyquinoline, and three different monodentate N-donor species, respectively, under hydrothermal conditions. They were characterized by single-crystal X-ray diffraction and powder X-ray diffraction analyses, ^{1}H NMR, Mass, and infra-red spectra. The UV visible and solid-state photo-luminescent properties were investigated for complexes **1**–**3** and they showed modest emission intensities. We envisage that these compounds can be further developed for future opto-electronic applications.

1. Introduction

Luminescent materials based on metal–organic materials (MOMs) have been the subject of intense interest, not only because of their wide range of potential applications in many important areas of research, such as photocatalysts,[1,2] photoswitches,[3] light emitting devices,[4] and luminescence-based sensors,[5] but also for their properties can be altered by the combination of various multifunctional ligands.[6] Moreover, many biological systems, associated with life science are affected by pH change. As a result, monitoring small changes in pH is still an important issue.[7,8] Potentiometric methods are commonly in the measurement of pH, but the electrodes that have a high impedance, are mechanically fragile and often suffer from instability, and need frequent calibrations.[9] Searching for materials with pH-responsive optical properties are becoming more and more important, because they could be selective, sensitive and convenient for such measurements.[10] The rhenium organometallic complexes have been used as anion sensors, in biological imaging, and as light-induced anticancer drugs.[11,12] New opportunities for developing luminescent complexes by introducing chromophore-containing ligands would be highly desirable.[13] Although a few organometallic complexes have already been employed as sensors,[14] the Re(I)-based organometallic complexes were studied the photo-luminescent properties modulated by various pH vales is currently rare.[15]

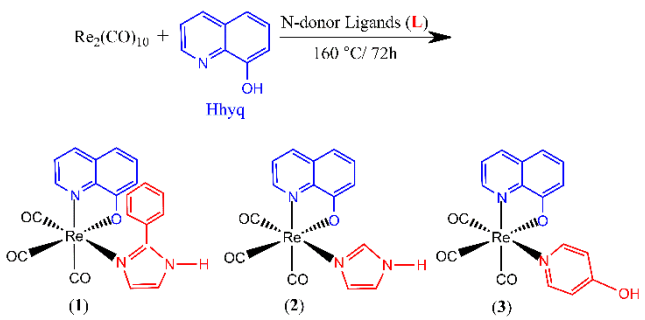
As part of our ongoing efforts in the design and synthesis of functional materials,[16] we report herein on three Re(I)-based organometallic complexes [*fac*-$Re(CO)_3$(hyq)(pim)] (**1**, Hhyq = 8-hydroxyquinoline; pim = 2-phenylimidazole), [*fac*-$Re(CO)_3$(hyq)(im)] (**2**, im = imidazole), [*fac*-$Re(CO)_3$(hyq)(hyp)] (**3**, hyp = 4-hydroxypyridine), that were synthesized by reacting 8-hydroxyquinoline and coligands with Re_2 $(CO)_{10}$ (Scheme 1). This work is noteworthy for several reasons: (i) the combination of Hhyq species and N-donor co-ligands was found to facilitate the assembly of Re(I) organometallic complexes in high yields; (ii) their UV visible absorptions in acetonitrile and solid-state photo-luminescent properties were studied and showed the modest emission intensities; (iii) suitable luminescent properties can be introduced to the target complexes by using Hhyq species and tuning with the ancillary N-donor co-ligands; (IV) their luminescent properties can be reproducible and reversibly performed modulated by different pH values. To the best of our knowledge, the use of such corresponding luminescent properties of simple Re(I)-based organometallic complexes could be modulated by various pH vales has never been reported.[17]

2. Experimental

2.1. Materials and methods

All reagents were purchased commercially and used as received without further purification. Thermogravimetric analyses (TGA) were performed under nitrogen with a Perkin-Elmer Pyris 6 analyzer. IR spectra were recorded in the 4000–400 cm^{-1} region using KBr pellets on a Perkin–Elmer Paragon 1000 spectrometer. Elemental analyses were determined using a Perkin-Elmer 2400 elemental analyzer. Powder X-ray diffraction (PXRD) patterns were recorded on a MPD Philips Analytical diffractometer at 40 kV, 30 mA for Cu K_α (λ = 1.5406 Å). The absorption spectra were measured on a Hewlett Packard UV-Vis spectrophotometer at room

Scheme 1. One step self-assembly of complexes **1**–**3**



Abbreviations: MOMs, metal–organic materials; PXRD, powder X-ray diffraction; LMCT, ligand-to-metal charge transfer.

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