



Sensitized near-infrared luminescence of lanthanide complexes by energy transfer from rhenium(I) complexes bridged by bis(benzimidazole) and phenanthroline-5,6:5',6'-pyrazine ligands



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ABSTRACT

A series of new rhenium-lanthanide heterobimetallic complexes bridged by bis(benzimidazole) (BibzImH₂) and 4,7-phenanthroline-5,6:5',6'-pyrazine (ppz) group were synthesized. The luminescent rhenium(I) complexes, [(CO)₃Re(L)] having vacant diimine site, were used as 'complex ligand' to prepare six new heterodinuclear d–f complexes by attaching a {Ln(dik)₃} fragment (Ln = Nd, Yb, or Er; dik = trifluoro theonyl acetone) at the vacant site. All prepared complexes were characterized by various spectral techniques. Upon excitation at the MLCT absorption band of Re, due to efficient energy transfer, sensitized emission occurs from lanthanide center in the near-infrared region. The lanthanide center has low-energy f–f excited states, which are capable of accepting energy from the ³MLCT excited state of the rhenium center, leading to the quenching of ³MLCT luminescence of the rhenium(I) and subsequent sensitized lanthanide(III)-based luminescence in the near-IR region. Because bis(benzimidazole) (BibzImH₂) is a short bridging ligand compared to phenanthroline-5,6:5',6'-pyrazine (ppz), it is able to assist in faster energy transfer from rhenium(I) to Ln(III). The Nd(III) species is found to be the most effective for quenching the ³MLCT luminescence of the rhenium component because of the high density of the f–f excited states of the appropriate energy, which makes it as a more effective energy-acceptor compared to Er(III) and Yb(III) ions.

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1. Introduction

The energy transfer processes leading to the population of 4fⁿ excited states in which broad excited states from the ligands interact with narrow, long-lived metal-ion states render the design of suitable molecular systems very experimental [1]. A more controlled approach is to take advantage of intermetallic communication between two (or more) metal ions inserted into polymetallic edifices so that directional energy transfer becomes feasible [2].

The use of d-block chromophores (e.g. Ru^{II}, Re^I, Os^{II}, Au^I, Pt^{II}, Ir^{III}) as antenna groups to generate sensitized luminescence from Ln^{III} centers (Ln = Nd, Yb and Er), following d → f energy transfer, is an area that has attracted much attention in the last few years [1–14]. Many types of transition metal units have been employed in d–f hybrid complexes in this way, because of their numerous

desirable characteristics [7–14]. These include strong absorbance of light in the visible region, a long-lived (usually ³MLCT (MLCT = metal-to-ligand charge transfer)) excited state which can act as energy donor, and a relatively low ³MLCT energy (compared to organic chromophores) which is a good match for the f–f levels of Ln^{III} ions such as Pr^{III}, Nd^{III}, Er^{III} and Yb^{III} which generate near-infrared luminescence [5–7].

The low-energy excited states responsible for near-IR emission are easily quenched by nearby O–H, N–H and C–H oscillators [7–13]. It is therefore desirable to minimize the number of these functional groups close to the metal center by using C–D or C–F bonds instead of C–H. Synthesis of these complexes is based on the well-known formation of eight-coordinate adducts between {Ln(dik)₃} units (Ln = lanthanide; dik = β-diketonate) and N,N-bidentate chelates such as 2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen) [8–10].

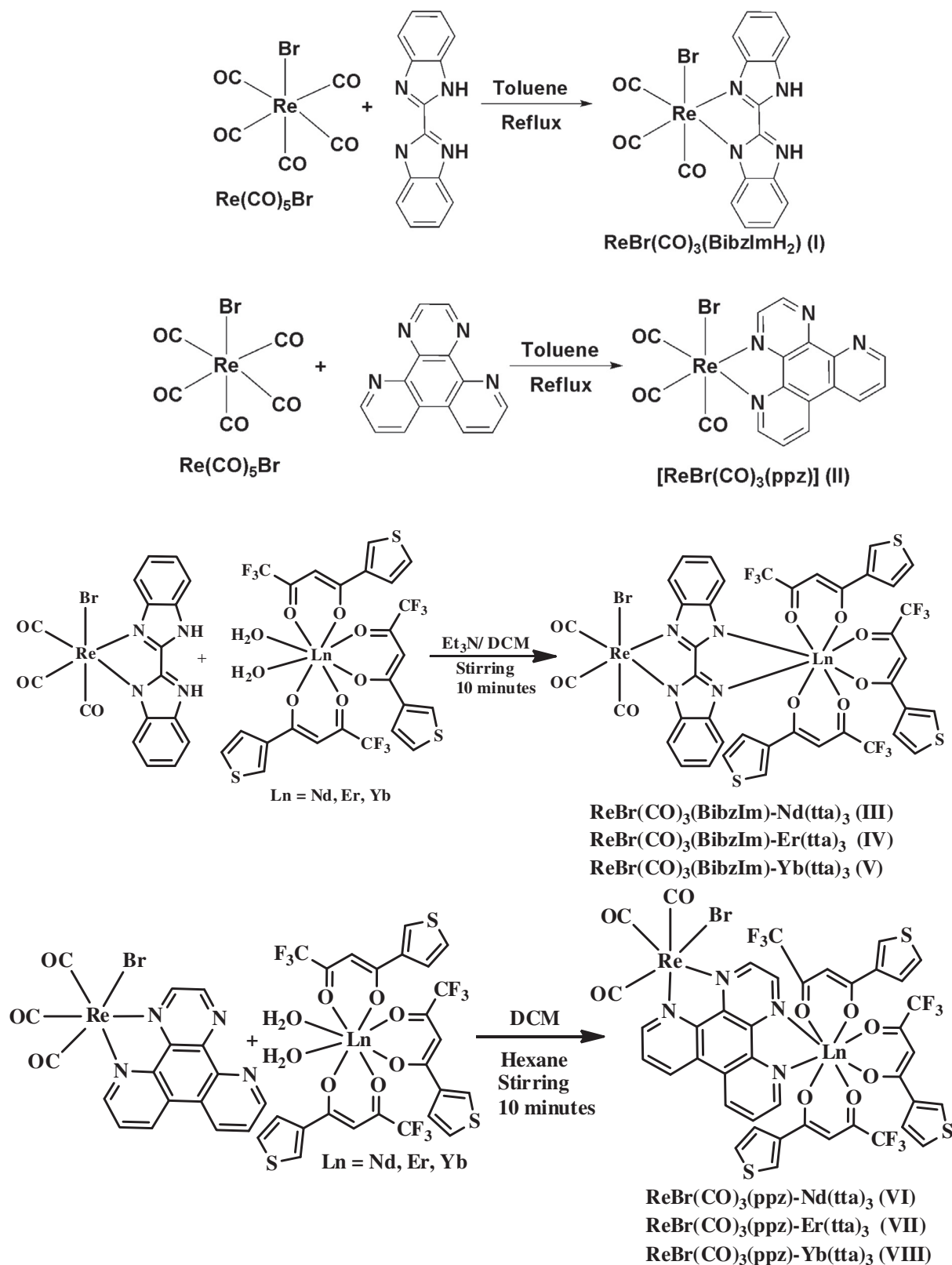
Herein we report on the synthesis of six new d–f dyads, in which the d-block donor unit and the f-block acceptor unit are bridged by a bis(benzimidazole) (BibzImH₂) and 4,7-phenanthroline-5,6:5',6'-pyrazine (ppz) ligands. The complex [(CO)₃Re(Br)(L)] (L = bis(benzimidazole) (BibzImH₂) and 4,7-phenanthroline-5,6:5',6'-pyrazine

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(ppz) has vacant diimine site, which can be utilized to coordinate with the Ln(III) unit. The photophysical properties of the monometallic rhenium complex and heterobimetallic d-f dyads were examined. Upon excitation, the luminescent rhenium center acts as

antenna, and the bis(benzimidazole) (BibzImH₂) and 4,7-phenanthroline-5,6:5',6'-pyrazine (ppz), by virtue of being of short bridges permits energy transfer to occur rapidly to Ln(III), thereby resulting in sensitized NIR emission.



Scheme 1. Synthesis of the rhenium-lanthanide bimetallic complexes.

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