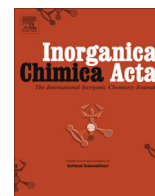




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Evidence of dexter energy transfer in NO photolability of dye-sensitized ruthenium nitrosyls

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ABSTRACT

Direct attachment of light-harvesting dye molecules to the ruthenium center of designed {Ru–NO}⁶ nitrosyls has been shown to exhibit enhanced light-induced NO photorelease upon exposure to visible light. Theoretical studies have indicated that orbital overlap between the MOs of the dye and the nitrosyl units are key for such sensitization. In order to check whether altering the electronic conjugation between these two units causes reduction in the extent of sensitization, we have synthesized a pyridinyl-oxy-fluorescein dye **PyFIET** and attached it to two designed ruthenium nitrosyls through the pyridine-N donor of the pyridinyl-oxy-end. The quantum yield values of NO photodissociation at 500 nm (ϕ_{NO}) and fluorescence quantum yield values (ϕ_{FI}) of these two nitrosyl-dye conjugates namely, [(Me)₂-bpb)Ru(NO)(PyFIET)]ClO₄ (**1-PyFIET**) and [((OMe)₂IQ1)Ru(NO)(PyFIET)]BF₄ (**2-PyFIET**) have been compared with those of [(Me)₂bpb)Ru(NO)(FIET)]ClO₄ (**1-FIET**) and [((OMe)₂IQ1)Ru(NO)(FIET)]BF₄ (**2-FIET**) in which the same FIET dye is directly attached through the phenolato-O donor. This minor alteration in the linkage between the dye and the nitrosyl unit has caused significant reduction in the ϕ_{NO} values of **1-PyFIET** and **2-PyFIET** while their ϕ_{FI} values have shown moderate improvement. These results strongly suggest that the light energy absorbed by the dye unit is transferred to the Ru–NO moiety through the Dexter pathway. If the electronic overlap is disrupted, only part of the energy is used in NO photorelease and a significant portion is lost through fluorescence.

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1. Introduction

Research during the past three decades has delineated the role of nitric oxide (NO) as a signaling molecule in a number of physiological and pathological pathways [1–3]. This odd-electron diatomic molecule is endogenously generated by the enzyme nitric oxide synthase (NOS) through catalytic oxidation of L-arginine to citrulline [4]. The constitutive isoforms of NOS (endothelial NOS and neuronal NOS) mediate physiological pathways such as blood pressure regulation and neurotransmission at nM levels of NO while higher concentrations (μM or above) of NO, generated by the inducible isoform of NOS of macrophages, play an important role in thwarting pathogens as part of our innate immune system [5,6]. The diverse biological roles of this gaseous molecule have prompted the development of exogenous NO-donors as potential therapeutic agents [7]. Most of the compounds developed in such pursuit are systemic NO donors that afford NO through enzyme mediated degradation and/or pH changes. As a consequence, these NO donors cannot be employed to deliver NO selectively to a specific biological target under controlled conditions.

To this end, we have synthesized a number of metal nitrosyls that can deliver NO under the control of light [8–14]. Although the iron and manganese nitrosyls of the type {M–NO}⁶ exhibit excellent NO photolability [15], the {Ru–NO}⁶ nitrosyls remain of central interest due to their superior stability in biological media [16–19]. Unfortunately, many ruthenium nitrosyls maintain characteristic metal-to-ligand charge transfer bands (MLCT, $d_{\pi}(\text{Ru}) \rightarrow \pi^*(\text{NO})$) within the UV region, a feature unfavorable for potential biomedical applications. To address this complication we have designed a set of ligands with the aid of density functional theory and time-dependent density functional theory (DFT and TD-DFT, respectively), and synthesized a series of ruthenium nitrosyls that resulted in the systematic red shift of the MLCT photoband to the visible region [16,20]. Many of these nitrosyls were of type [(L)Ru(NO)(Cl)], where L represents an equatorial tetradentate ligand frame that was carefully altered to move the photoband. Examples of such nitrosyls are [((Me)₂bQb)Ru(NO)(Cl)] (λ_{max} of the photoband = 455 nm), [((OMe)₂IQ1)Ru(NO)(Cl)] (λ_{max} of the photoband = 475 nm), and [((OMe)₂bQb)Ru(NO)(Cl)] (λ_{max} of the photoband = 490 nm), derived from the designed ligands of Fig. 1 [17,21].

While the MLCT bands were shifted to the visible region in such a set of {Ru–NO}⁶ nitrosyls, the respective molar extinction

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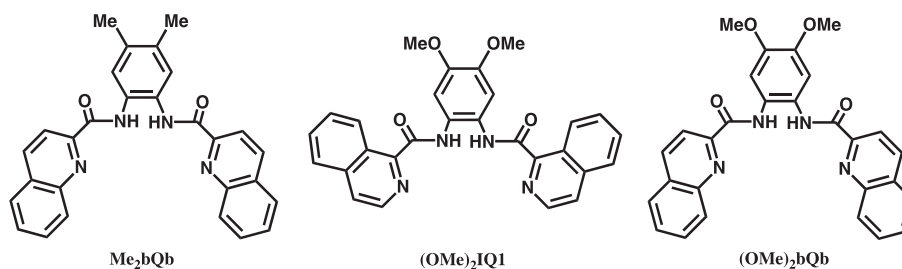


Fig. 1. Structures of the designed tetradentate ligands used to synthesize photoactive ruthenium nitrosyls.

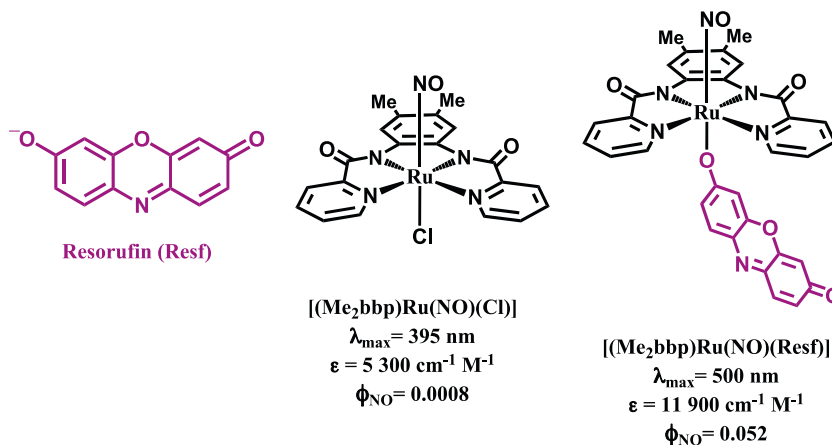


Fig. 2. Structures and spectral parameters of the pendant dye chromophore resorufin (**Resf**), the parent ruthenium nitrosyl chloride $[(\text{Me}_2\text{bbp})\text{Ru}(\text{NO})(\text{Cl})]$ (**1-Cl**) and the metal nitrosyl–dye conjugate $[(\text{Me}_2\text{bbp})\text{Ru}(\text{NO})(\text{Resf})]$ (**1-Resf**).

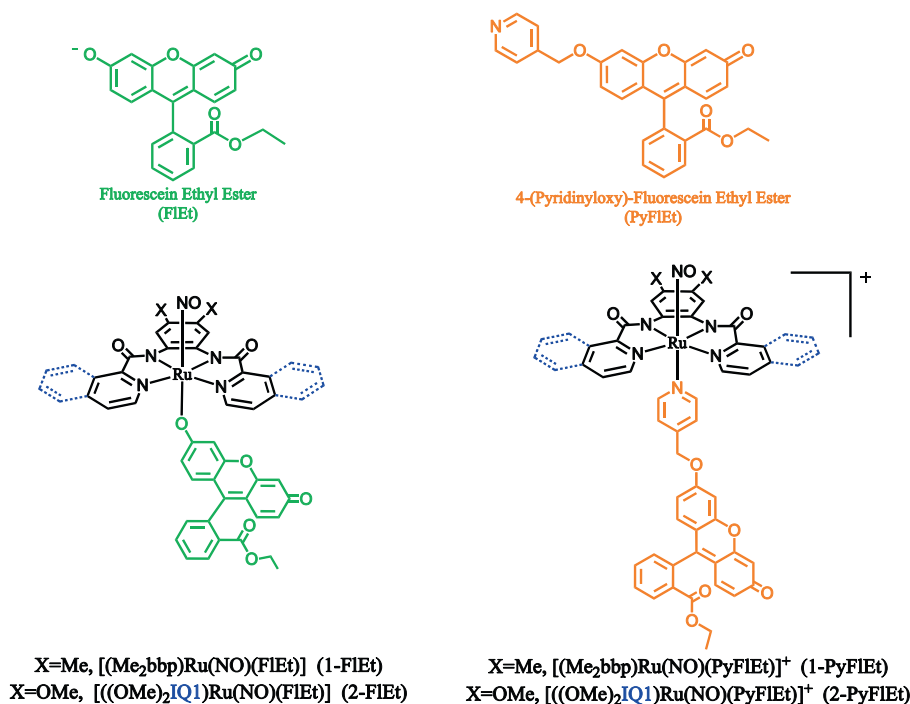


Fig. 3. Structures of fluorescein ethyl ester (**FIEt**) and 4-(pyridinyloxy)-fluorescein ethyl ester (**PyFIEt**) (top panel), and the nitrosyl–dye conjugates $[(\text{Me}_2\text{bbp})\text{Ru}(\text{NO})(\text{FIEt})]$ (**1-FIEt**), $[((\text{OMe})_2\text{IQ1})\text{Ru}(\text{NO})(\text{FIEt})]$ (**2-FIEt**), $[(\text{Me}_2\text{bbp})\text{Ru}(\text{NO})(\text{PyFIEt})]\text{ClO}_4$ (**1-PyFIEt**), and $[((\text{OMe})_2\text{IQ1})\text{Ru}(\text{NO})(\text{PyFIEt})]\text{BF}_4$ (**2-PyFIEt**) (bottom panel).

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