

## Review

# Two-photon absorption properties of 1,10-phenanthroline-based Ru(II) complexes and related functionalized nanoparticles for potential application in two-photon excitation photodynamic therapy and optical power limiting



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## ABSTRACT

In this review, we report and discuss the specific linear and nonlinear optical properties (two-photon absorption) of original 5-substituted-1,10-phenanthroline-based Ru(II) complexes. The perspective of applications in optical power limiting (OPL) and (two-photon excited) photodynamic therapy (2PE)-PDT, are presented together with our strategy developed in collaboration, towards the elaboration and the use of the related functionalized nano-edifices obtained by encapsulation or covalent grafting. Multifunctional nano-platforms (NPs) with potential new properties or applications are described and particularly explained by the confinement of the molecular complexes within (or at the surface of) these NPs. The stability, inertness and versatility of the involved Ru(II) complexes are more particularly highlighted in order to fit the requirements.

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## 1. Introduction

In this review, the specific linear and nonlinear optical properties (two-photon absorption phenomena) of polypyridyl Ru(II)

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complexes are presented and discussed in the perspective of potential applications in optical power limiting and (two-photon excited) photodynamic therapy (2PE-PDT).

## 2. Octahedral polypyridyl-based Ru(II) complexes

Octahedral polypyridyl-based Ru(II) complexes have been intensively studied for their stability, kinetic inertness, biological activity such as interaction with DNA [1], and optical properties such as  $^3\text{MLCT}$  (metal-to-ligand charge transfer) triplet excited-state properties [2], second-order [3], and third order [4] nonlinear optical properties, and more recently for two-photon absorption (2PA) [5]. Their unique photophysical properties have opened avenues to a wide range of applications in organic light-emitting diodes (OLEDs), dye-sensitized solar cells (DSSCs) [6], therapy [7], biological imaging (two-photon excited fluorescence (2PEF) emission), optical power limiting (OPL) [8], and singlet dioxygen sensitization [9]. To achieve these purposes, one can particularly take advantage of (i) the synthetic tailorability of the ligands and the

related Ru(II) complexes [10], (ii) the long-lived triplet character of the excited-state reached by one or two-photon absorption, allowing emission, excited state absorption or energy transfer to triplet dioxygen [11]. We have employed molecular engineering to develop this family of complexes, both for the fundamental interest of these systems in 2PA phenomena and for the potential applications in two-photon induced photodynamic therapy (2PE-PDT) and 2PA-based OPL in the near infrared (NIR). This work and the related results are summarized in this manuscript. It does not intend to be an exhaustive review, rather provide a general overview of the literature in this particular domain in connection with our work. Therefore, the 2PA properties of several homo- and heteroleptic ruthenium complexes involving 5-substituted-1,10-phenanthroline ligands (see Fig. 1, bottom, for general molecular structures) will be discussed both at the molecular level and at the nanometer scale, via pertinent functionalization of selected nanoparticles (encapsulation or grafting), and the elaboration of specific heteroleptic complexes bearing one ligand as an anchor.

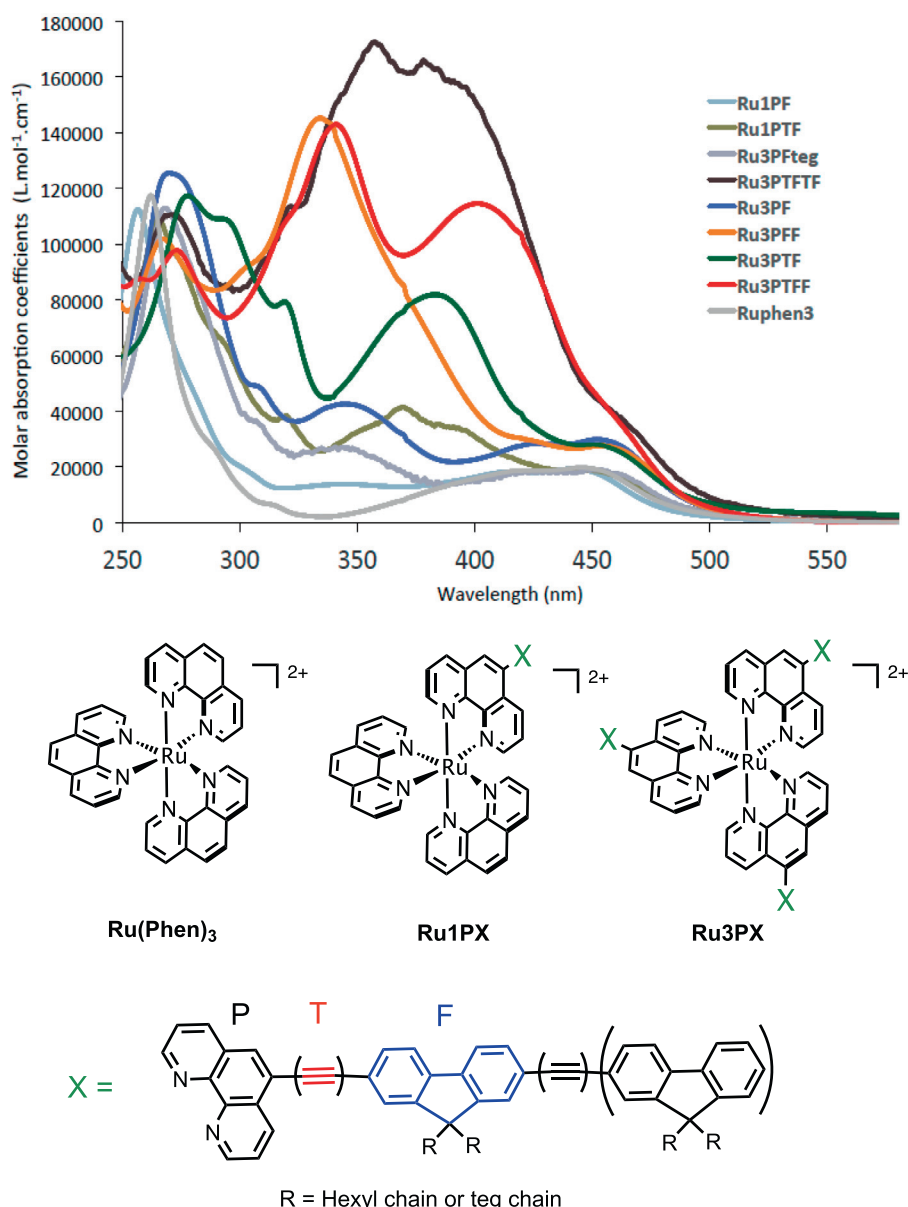


Fig. 1. UV-vis spectra of hetero- and homoleptic Ru(II) complexes and general molecular structure (Figure adapted from Ref. [12b]).

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