



# Luminescence as a tool to investigate dendrimer properties

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## Abstract

Recent investigations have shown that coupling luminescence with dendrimer chemistry can lead to systems capable of exhibiting quite unusual and interesting properties. In this trend article we focus on: (i) interactions of luminescent units within a dendrimer, (ii) quenching of dendrimer luminescence by external species, (iii) sensitization of luminescent metal ions, and (iv) sensitization and quenching of dye luminescence. Several examples of dendrimers are discussed, including compounds capable of: (a) performing excimer and/or exciplex emission, (b) exploiting energy transfer for harvesting light, (c) undergoing electron transfer processes, (d) protecting with their branches the luminescence of the core, (e) down and up converting light frequency, (f) playing the role of ligands for luminescent and non-luminescent metal ions, and (g) performing as hosts for luminescent dyes.

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*Keywords:* Dendrimers; Luminescence; Photochemistry; Light-harvesting; Sensors; Host–guest systems; Metal complexes

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## 1. Introduction

Luminescence, the emission of light by electronic excited states of molecules, is an important phenomenon from a basic viewpoint (e.g. for monitoring excited state behaviour) [1] as well as for applications (lasers, displays, sensors, etc.) [1–3].

Recent investigations have shown that coupling luminescence with dendrimer chemistry can lead to systems capable of exhibiting quite unusual and interesting properties [4–7]. In this trend article we briefly summarize some fundamental concepts concerning photophysical processes in dendrimers and then we focus on: (i) interactions of luminescent units within a dendrimer, (ii) quenching of dendrimer luminescence by external species, (iii) sensitization of luminescent metal ions, and (iv) sensitization and quenching of dye luminescence. Illustration of these processes will offer us the opportunity to discuss some important topics like: (a) multiple luminescence, (b) light harvesting, (c) conversion of incident UV light into visible or infrared emission, and (d) sensing metal ions with signal amplification. Several of the discussed examples are taken from work performed in our laboratory. We will only deal with bulk properties in fluid solution. Processes related to dendrimer fluorescence at the single molecule level are discussed elsewhere [8].

## 2. Luminescence and related processes

From a topological viewpoint, dendrimers contain three different regions: core, branches, and surface.

Luminescent units can be covalently incorporated in each region of a dendritic structure and can also be non-covalently hosted in the cavities of a dendrimer or associated at the dendrimer surface [9].

Fig. 1a shows a schematic energy level diagram for a molecule that could be a chromophoric and luminescent unit of a dendrimer. In most cases the ground state of a molecule is a singlet state ( $S_0$ ), and the excited states are either singlets ( $S_1$ ,  $S_2$ , etc.) or triplets ( $T_1$ ,  $T_2$ , etc.). In principle, transitions between states having the same spin value are allowed, whereas those between states of different spin are forbidden. Therefore, the electronic absorption bands observed in the UV–visible spectrum of molecules usually correspond to  $S_0 \rightarrow S_n$  transitions. Excited states are unstable species that undergo fast deactivation by intrinsic (first order kinetics) processes. When a molecule is excited to upper singlet excited states, it usually undergoes a fast and 100% efficient radiationless deactivation (internal conversion, i.c.) to the lowest excited singlet,  $S_1$ . Such an excited state undergoes deactivation via three competing processes: non-radiative decay to the ground state (internal conversion, rate constant  $k_{ic}$ ); radiative decay to the ground state (fluorescence,  $k_f$ ); conversion to the lowest triplet state  $T_1$  (intersystem crossing,  $k_{isc}$ ). In its turn,  $T_1$  can undergo deactivation via non-radiative (intersystem crossing,  $k'_{isc}$ ) or radiative (phosphorescence,  $k_{ph}$ ) decay to the ground state  $S_0$ . When the molecule contains heavy atoms, the formally forbidden intersystem crossing and phosphorescence processes become faster.

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