Development of Near-Infrared Rare Earth Doped Organic Materials for Nanophotonics Applications

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Abstract: We have synthesized a series of near-infrared rare-earth doped organic materials for nanophotonics applications and studied their absorption and emission properties. The developed materials show promise as research tools and (meta)device components.

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Many active nanophotonic meta-devices and research tools critically depend on availability of emitters that can be brought to close vicinity of resonating plasmonic nanostructures or other electric and magnetic hot spots. Trivalent Rare Earth ions are particularly attractive in many photonics applications because of unparalleled richness of their energy spectra, availability of metastable states with millisecond life-times, and co-existence of both electric-dipole and magnetic-dipole absorption and emission transitions. The latter property, found in the visible part of the spectrum in Eu^{3+} ions, allowed the authors of Ref. [1] to study electric field and magnetic field enhancements in arrays of plasmonic nanoholes. Availability of both magnetic-dipole ($\lambda\approx590$ nm) and electric-dipole ($\lambda\approx614$ nm) emission transitions stimulated the development of a series of Eu^{3+} doped organic materials, including Eu(NO3)3·Bpy2, Eu(TTA)3(L18) and Eu(TTA)3(L1a) complexes, and multiple related studies [2-6].

Many photonic applications (*e.g.* optical fiber communication) and unique photonic environments (*e.g.* epsilon near zero transition in conductive transparent oxides [7,8]) lie in the near-infrared part of the spectrum. Therefore, in the present study, we have synthesized and optically studied several Rare Earth organic materials doped with Yb^{3+}, Nd^{3+}, Er^{3+} and Tm^{3+} ions.

To synthesize Rare Earth (or lanthanide) doped 2,2'-Dipyridyl crystals (also known as Ln(NO3)3·Bpy2), ethanol solutions of the 2,2'-Dipyridyl and lanthanide nitrate Ln(NO3)3·6(H2O) were mixed in the 2:1 molar ratio and sonicated. Small transparent crystals (of ≈ 1 mm in size) precipitated and grown over course of several hours or several tens of hours. Samples consisting of several tens of small crystallines were pressed between two microscope cover glasses and used in the absorption and emission studies discussed below. In order to fabricate thin films, two solutions were prepared: (A) 6 mg of grown Ln(NO3)3·Bpy2 crystals was dissolved in a mixture of 0.2 ml ethanol and 0.1 ml of deionized water and (B) 6 mg of PVP (8k) was dissolved in 1 ml of ethanol. The solutions A and B were mixed in the 6:1 to 3:1 ratios and vigorously sonicated in an ultrasonic bath for 1 hour. The resultant mixed solution was spin coated onto a glass substrate (Specialty Coating System's 6800 Spin Coater Series). The film thicknesses were measured using the DektakXT stylus profilometer (from Bruker).

Transmission spectra of the crystalline and thin film samples studied were measured using the Lambda 900 spectrofluorimeter from PerkinElmer and the emission and excitation measurements were carried out using the Flurolog fluorometer (Horbia). The spectra consisted of distinct lines, many of which were easy to identify [9]. As an example, the spectra of Er(NO3)3·Bpy2 and Tm(NO3)3·Bpy2 are depicted in Figs. 1a and 1b, respectively. They show strong emission lines ranging between ≈1100 nm and ≈1900 nm. The emission can be excited by pumping directly into the absorption lines of Rare Earth ions or the strong absorption band of Dipyridyl located at ~325 nm [5]. The emission signals were stronger in crystalline samples than in ≈100 nm films, primarily due to larger volume of the material. The emission kinetics excited with tunable 4 ns laser (Surelite III OPO and Panther Ex Plus from Continuum) were rather short. Thus, the emission lifetime of Yb^{3+} was ≈10 μs, instead of expected ≈1 ms [10], suggesting the quantum yield of ≈1%. Therefore, the emission intensity and the emission quantum yield have room for improvement through systematic optimization of the synthesis procedure.

We believe that the developed series of Rare Earth doped organic materials emitting in the near-infrared range of the spectrum will benefit applications and fundamental studies of metamaterials and metadevices.

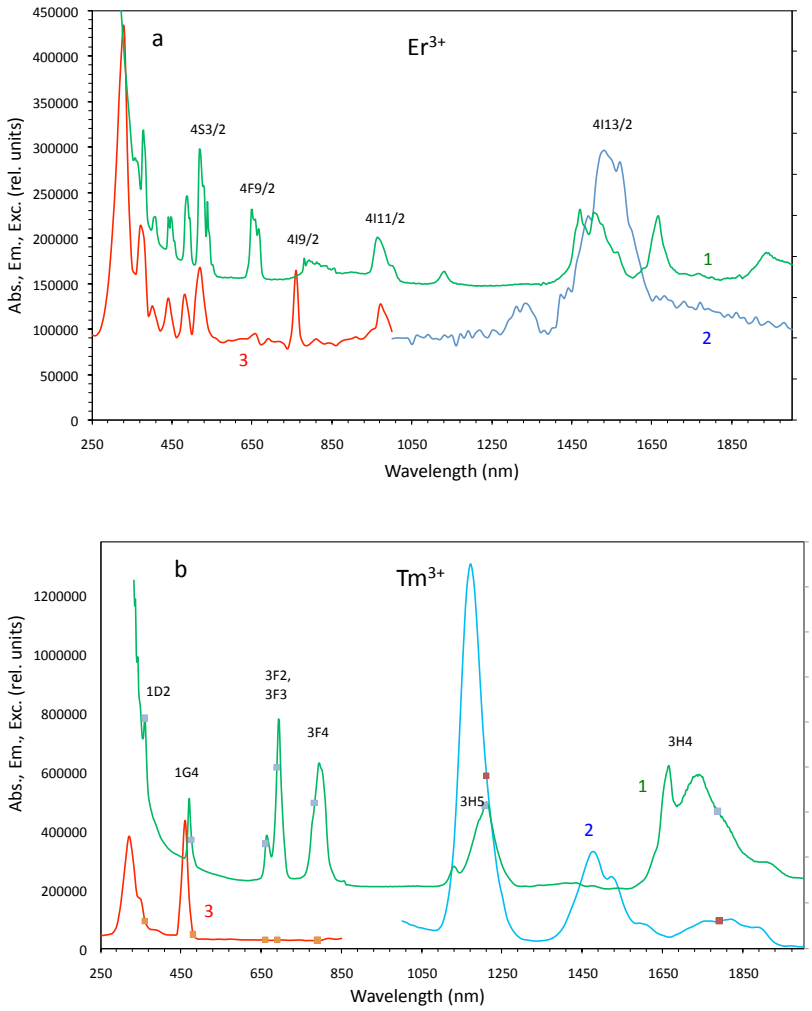

Fig. 1. Absorption (1), emission (2) and excitation (3) spectra of Er^{3+}:2,2'-Dipyridyl crystals (a) and Er^{3+}:2,2'-Dipyridyl crystals (b).

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