

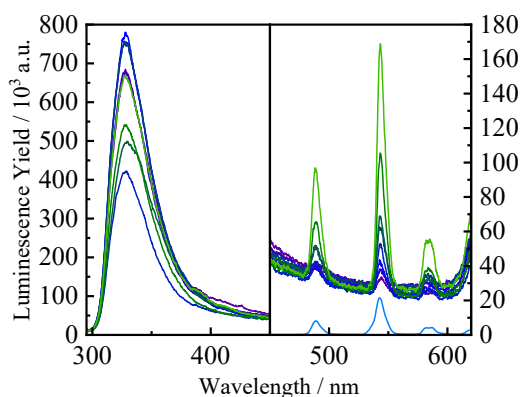
## Effects of Monomer in Ionic Nanospheres on Sensitized Luminescence from Terbium(III) Ion

(<sup>1</sup>Graduate School of Engineering, Kochi University of Technology) ○Nikita Madhukar,<sup>1</sup> Taizo Misato,<sup>1</sup> Akitaka Ito<sup>1</sup>

**Keywords:** f–f Transition; Photosensitization; Electrostatic Interactions; Ionic Nanosphere

Terbium(III) species have been used in a variety of applications, including sensing, photovoltaics, phosphor, bioimaging and others, owing to their high luminescence-color purity arising from narrow band shapes.<sup>1</sup> In contrast to such applicability, their luminescence is typically weak since both excitation and luminescence processes are Laporte-forbidden. An introduction of a photosensitizing unit(s) is one of the most popular strategies to compensate the weak absorption. In this study, we utilized ionic nanospheres, spherical ion-exchange resins with a diameter of <300 nm,<sup>2</sup> as solid-state media and photosensitizers for terbium(III) ion. Luminescence from terbium(III) ion was successfully sensitized upon doping in the ionic nanospheres with and without a ligating unit.

Ionic nanospheres were synthesized by copolymerizing sodium *p*-styrenesulfonate, divinylbenzene and poly(ethylene glycol)methacrylate methyl ether ( $M_n$ : 2000) in the absence and presence (1mol%) of 5-(4-vinylphenyl)-1,10-phenanthroline (vPPhen). Terbium(III) ion was doped in the ionic nanospheres (5–300 nmol/mg) by soaking the ionic nanosphere in an aqueous solution of  $TbCl_3$ . The terbium(III)-doped nanospheres without vPPhen exhibited several luminescence bands at 488, 544, 583 and 620 nm, which resemble to the luminescence originating in the  $^5D_4 \rightarrow ^7F_J$  ( $J = 3-6$ ) transitions in terbium(III) species, upon an excitation at 260 nm (Figure).<sup>3</sup> In the case of the nanosphere with vPPhen, an excitation at 300 nm resulted in the similar 4f–4f luminescence. Thus, the copolymerized vPPhen would help longer-wavelength excitation as a photosensitizer along with ligating moiety. Detailed effects of the monomer unit on the luminescence from terbium(III) ion will be discussed.



**Figure.** Luminescence spectra of terbium(III)-doped ionic nanospheres without vPPhen (5.04–299 nmol mg<sup>-1</sup>, purple → green,  $\lambda_{ex} = 260$  nm). Blue spectrum represents that of the aqueous  $TbCl_3$  solution.

1) D. Sarkar, S. Ganguli, T. Samanta, V. Mahalingam, *Langmuir* **2019**, *35*, 6211. 2) H. Yamamoto, M. Taomoto, A. Ito, D. Kosumi, *J. Photochem. Photobiol. A: Chem.* **2020**, *401*, 11277. 3) N. Madhukar, T. Misato, A. Ito, submitted.