

## Ultrasmall Far-red Emitting Polymer Dots

Hubert Piwonski,<sup>1</sup> Tsuyoshi Michinobu,<sup>2</sup> Satoshi Habuchi<sup>1</sup>

<sup>1</sup> King Abdullah University of Science and Technology (KAUST), Biological and Environmental Sciences and Engineering Division, P.O. Box 4700 KAUST, Thuwal 23955-6900, Saudi Arabia.

<sup>2</sup> Tokyo Institute of Technology, Department of Organic and Polymeric Materials, 2-12-1 O-okayama, Meguro-ku, Tokyo 152-8552, Japan.

E-mail : [satoshi.habuchi@kaust.edu.sa](mailto:satoshi.habuchi@kaust.edu.sa)

**KEY WORDS:** conjugated polymer nanoparticles, fluorescent nanoparticles, fabrication, photophysical properties, polymer chain packing

New fluorescence microscopy methods often require fluorophores with specific spectroscopic properties. The development of new fluorophores is thus increasingly important. Various types of fluorophores, including organic dyes, fluorescent proteins, and semiconductor quantum dots (QDs), have been used in fluorescence microscopy. Conjugated polymer nanoparticles (Pdots) have recently emerged as a new class of fluorescent nanoparticles because their fluorescent properties can be fine-tuned by an appropriate molecular design of conjugated polymers (CPs). Given their superior fluorescent brightness and photostability as well as low cytotoxicity, the applicability of Pdots as fluorescent tags and sensors has been expanding significantly during the last few years. Recent studies have demonstrated that, in some cases, the performance of Pdots as fluorescent tags surpasses that of conventional organic dyes and QDs. Their applications critically depend on the size of the nanoparticles, the brightness of the fluorescence, and the intraparticle energy transfer. The molecular design of CP has thus far been the main focus of the development of Pdots.

Here, we demonstrate that proper control of the physical interactions between the chains in the particles is as critical as the molecular design to fabricating desirable Pdots. The unique design of twisted CP molecules and fine-tuning of the reprecipitation conditions allow us to fabricate ultrasmall (diameter  $\approx 3.0 - 4.5$  nm) Pdots with excellent photostability (photobleaching yield  $\approx 1.7 - 3.3 \times 10^{-11}$ ) in a controlled manner that emit fluorescence in far-red spectral region [1]. Extensive photophysical and structural characterization revealed the essential role played by the packing of the polymer chains in the particles in the intraparticle spatial alignment of the emitting sites, which regulate the fluorescence brightness and the intraparticle energy migration efficiency. Our findings significantly enhance understanding of the relationship between chain interactions and the photophysical properties of conjugated polymer nanomaterials, providing a framework for designing and fabricating functional Pdots for advanced imaging applications.

[1] H. Piwonski, T. Michinobu, and S. Habuchi, "Controlling photophysical properties of ultrasmall conjugated polymer nanoparticles through polymer chain packing" *submitted*.