

# Post modification approach for photoluminescence modulation of locally functionalized single-walled carbon nanotubes

Tamehito Shiga<sup>1</sup>, Tsuyohiko Fujigaya<sup>1,2,3</sup>, Naotoshi Nakashima<sup>2</sup>, Tomohiro Shiraki<sup>1,2</sup>

<sup>1</sup> Department of Applied Chemistry, Graduate School of Engineering, Kyushu University, 744 Motoka, Nishi-ku, Fukuoka, 819-0395, Japan

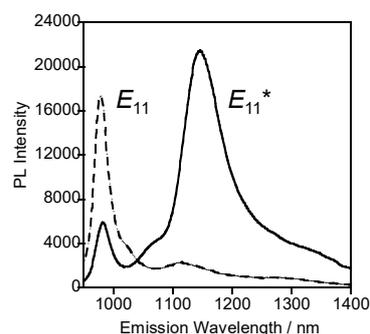
<sup>2</sup> WPI-I2CNER, Kyushu University, 744 Motoka, Nishi-ku, Fukuoka, 819-0395, Japan

<sup>3</sup> PRESTO-JST, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

Single-walled carbon nanotubes (SWNTs) show photoluminescence (PL) in the near infrared (NIR) region and, are applicable to a wide range of applications including optoelectronic devices and imaging materials. Recently, local chemical functionalization of SWNTs has been reported to create red-shifted PL ( $E_{11}^*$ ) with enhanced quantum yields compared to  $E_{11}$  PL [1-5]. The PL properties emerge by the formation of new emissive sites that have narrower band gaps and can trap excitons generated on the tubes. We have been synthesizing molecularly-designed modifiers to modulate the  $E_{11}^*$  PL and, recently have succeeded in a selective  $E_{11}^*$  wavelength shift of the locally functionalized SWNTs (lf-SWNTs) based on binding of a specific molecule on the modified sites through a molecular recognition technique [2].

In this study, as a new modulation technique using molecular systems, a post modification approach is developed for  $E_{11}^*$  PL modulation, in which the post modification occurs locally at the chemically-modified sites on lf-SWNTs. Herein, we employ imine bond formation, which is based on a condensation reaction between aldehyde and amine groups, at the modified site by using the synthesized aromatic aldehyde-modified lf-SWNTs (**PhCHO-SWNTs**) and their post modification upon addition of amine compounds.

Fig. 1 shows PL spectra of pristine SWNTs and **PhCHO-SWNTs**. For **PhCHO-SWNTs**, a new PL peak appeared at 1140 nm ( $E_{11}^*$ ) which was red-shifted than  $E_{11}$  PL at 980 nm. When *p*-methylaniline, *p*-bromoaniline or *p*-nitroaniline was mixed with **PhCHO-SWNTs**, peak shifts of the  $E_{11}^*$  PL were observed, resulting in different wavelength shift values ( $\lambda(E_{11}^*) - \lambda(E_{11})$ ) of 154, 163 and 165 nm, respectively. The results indicate that the wavelength shift occurs with strong dependence on the chemical structures of the added aniline derivatives. Our present technique, therefore, is expected to achieve versatile modulation of the wavelength of  $E_{11}^*$  PL.



**Fig. 1** PL spectra of pristine SWNTs and **PhCHO-SWNTs** ( $\lambda_{\text{ex}} = 570$  nm).

- [1] Y. Wang, *et al.*, Nat. Chem. **5**, 840 (2013). [2] T. Shiraki, *et al.*, Chem. Commun. **52**, 12972 (2016). [3] T. Shiraki, *et al.*, Sci. Rep. **6**, 28393 (2016). [4] T. Shiraki, *et al.*, Nanoscale, **9**, 16900 (2017). [5] T. Shiraki, *et al.*, Chem. Commun. **53**, 12544 (2017).