

## Solvatochromism of near infrared photoluminescence from molecularly functionalized carbon nanotubes

(<sup>1</sup>Department of Applied Chemistry, Kyushu University, <sup>2</sup>WPI-I2CNER, Kyushu University, <sup>3</sup>CMS, Kyushu University) ○Yoshiaki Niidome,<sup>1</sup> Tsuyohiko Fujigaya,<sup>1,2,3</sup> Tomohiro Shiraki<sup>1,2</sup>

**Keywords:** Carbon Nanotube; Near Infrared Photoluminescence; Chemical Functionalization; Solvatochromism; Exciton

Solvatochromism is a molecularly optical phenomenon, in which absorption or photoluminescence (PL) wavelengths are changed by surrounding solvents. This phenomenon is significant in single-walled carbon nanotubes (SWCNTs).<sup>1</sup> The one-dimensional nanostructures afford quantum confinement and weak dielectric screening to enhance Coulombic interactions, which result in the stable exciton formation and their sensitive solvatochromism.<sup>2</sup> Local chemical functionalization of SWCNTs has been developed for doping defects to the crystalline sp<sup>2</sup> carbon lattices for enhancement of their PL functions.<sup>3</sup> The doped sites have narrower bandgaps and trap mobile excitons to be localized states. The locally functionalized SWCNTs (lf-SWCNTs), therefore, emit red-shifted and brighter  $E_{11}^*$  PL (~1150 nm) compared to original  $E_{11}$  PL (~980 nm) observed for non-functionalized SWCNTs.

Here, we investigated the solvatochromism of PL from lf-SWCNTs in terms of structural dependency of the doped site. We used *Mono*-aryl doped (lf-SWCNTs-*mA*, Fig. 1a) and *bis*-aryl doped lf-SWCNTs (lf-SWCNTs-*bA*, Fig. 1b) that were solubilized by sodium dodecylbenzenesulfonate micelles in D<sub>2</sub>O. Each of water-immiscible solvents (*e.g.* *o*-dichlorobenzene) was added to the lf-SWCNTs solutions to make organic solvent atmospheres around the solubilized lf-SWCNTs.  $E_{11}^*$  PL and  $E_{11}$  PL from lf-SWCNTs-*mA* red-shifted according to changes of the orientation polarity parameter of added organic solvents. Importantly, shift values of  $E_{11}^*$  PL were always greater than those of  $E_{11}$  PL by 6 meV.<sup>4</sup> In the case of the lf-SWCNTs-*bA* emitting largely red-shifted  $E_{11}^{2*}$  PL (~1250 nm),<sup>5</sup>  $E_{11}^{2*}$  PL shift values were decreased compared to those of  $E_{11}^*$  PL. The observed difference in the solvatochromic behaviors would be due to the variation of exciton localization degree at the doped sites, which change the strength of interactions with solvents. This result indicates excitonic property modulation for lf-SWCNTs based on molecular structure designs of the doped sites.

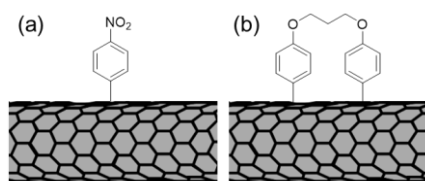


Fig. 1. Structural images of lf-SWCNTs-*mA* (a) and lf-SWCNTs-*bA* (b).

1) Y. Ohno *et al.*, *Phys. Status. Solidi. B* **2007**, 244, 4002. 2) Y. Miyauchi, *J. Mater. Chem. C* **2013**, 1, 6499. 3) a) R. B. Weisman *et al.*, *Science* **2010**, 330, 1656. b) Y. Wang *et al.*, *Nat. Rev. Chem.* **2019**, 3, 375. c) T. Shiraki *et al.*, *Acc. Res. Chem. Res.* **2020**, 53, 1846. d) T. Shiraki, *Chem. Lett. in press*. 4) T. Shiraki *et al.*, *Chem. Commun.* **2019**, 55, 3662. 5) T. Shiraki *et al.*, *Chem. Lett.* **2019**, 48, 791.