Near Infrared Photoluminescence Modulation of Biotinfunctionalized Single-walled Carbon Nanotubes Based on Avidin Binding

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Photoluminescence (PL) in near infrared (NIR) regions from single-walled carbon nanotubes (SWCNTs) is useful for biomedical applications such as imaging and sensing due to the advantages of NIR light that show low-autofluorescence and high transparency to biological tissues.¹ The PL properties of SWCNTs can be enhanced by local chemical functionalization that allows sp³ carbon doping to their sp² carbon networks.² The resultant locally functionalized SWCNTs (lf-SWCNTs) emit red-shifted and bright E_{11} * PL over 1000 nm regions. Recently we have reported that E_{11} * PL of lf-SWCNTs showed larger spectral shifts than E_{11} PL of nonfactionalized tubes by differences in polarities of surrounding environments.³ The enhanced wavelength shifts of E_{11} * PL are expected to develop new sensing systems based on adsorption of analyte molecules on the lf-SWCNT surfaces.

Here, we investigate E_{11} * PL wavelength shifts of lf-SWCNTs by the adsorption of proteins using a selective biomolecular binding system that is based on avidin-biotin interactions (dissociation constant is ~10⁻¹⁵ M). The lf-SWCNTs tethering biotin groups (lf-SWCNTs-b) were synthesized through the chemical functionalization using an aryldiazonium

salts, followed by its post-modification (Fig. 1). When neutravidin was mixed with a lf-SWCNTs-b solution, E_{11} * PL peak was redshifted, indicating the higher polarity environment formation by neutravidin adsorption on the lf-SWCNTs-b. When avidin or streptavidin was used for lf-SWCNTs-b binding experiments, wavelength shifting behaviors of E_{11} * PL from lf-SWCNTs-b were clearly changed depending on the used avidin derivatives. The results would be due to different polar environment formation deriving from structural differences of each avidin derivative. Therefore, lf-SWCNTs are expected for development of advanced protein detection devices using NIR PL.



Fig. 1. Structural images of lf-SWCNTs-b

J. H. Choi *et al.*, J. Mater. Chem. B 2017, 5, 6511. 2) a) Y. Wang *et al.*, Nat. Rev. Chem. 2019, 3, 375.
S. Tretiak *et al.*, Acc. Chem. Res. 2020, 53, 1791.c) T. Shiraki *et al.*, Acc. Chem. Res. 2020, 53, 1846.
T. Shiraki, Chem. Lett. 2021, 50, 397. 3) a) T. Shiraki *et al.*, Chem. Commun. 2019, 55, 3662.b) T. Shiraki *et al.*, J. Phys. Chem. C 2021, 125, 12758.