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Multistep Wavelength Switching of Near-infrared Photoluminescence Driven by Chemical Reactions at Local Doped Sites of Single-walled Carbon Nanotubes

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Abstract: Local chemical functionalization is used for defect doping of single-walled carbon nanotubes (SWNTs), to develop near-infrared photoluminescence (NIR PL) properties. We report the multistep wavelength shifting of the NIR PL of SWNTs through chemical reactions at local doped sites tethered to an arylaldehyde group. The PL wavelength of the doped SWNTs is modulated based on imine chemistry. This involves the imine formation of aldehyde groups with added arylamines, imine dissociation reaction, exchange reaction of bound arylamines in the imine, and the Kabachnik-Fields reaction of imine groups using diisopropyl phosphite. Using doped sites as a localized chemical reaction platform can exploit the versatile molecularly-driven functionality of carbon nanotubes and related nanomaterials.

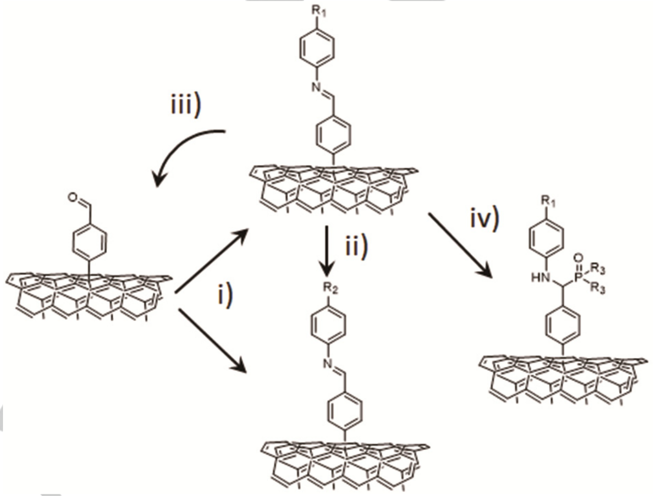

Figure 1. Schematic diagram of the range of chemical pathways for inducing versatile spectral shifts based on the synthesized lf-SWNTs-CHO: i) imine bond formation, ii) R_1-R_2 exchange reactions, iii) imine dissociation, and iv) Kabachnik-Fields reaction using dialkyl phosphite.

Doping-induced defect engineering is a fascinating strategy for functionalizing semiconducting nanomaterials, including nanocarbons and quantum dots, to achieve or enhance their optical, electronic, and magnetic functionality.[1] One such nanocarbon is single-walled carbon nanotubes (SWNTs). SWNTs exhibit semiconducting features depending on the tube structure. The structure is determined by the chiral index (n,m), which is classified by the manner in which a single graphene sheet is rolled up to form the tube.[2] Defect doping into SWNTs was recently reported to result in near-infrared (NIR) photoluminescence (PL) that was red shifted and had an enhanced quantum yield (named as E_{11}*) compared with the original PL (E_{11}).[3] E_{11}* PL at wavelengths above 1000 nm is promising for the development of high-resolution and high-depth imaging techniques in biomedical applications[1b] and secure telecommunication devices.[4] Defect doping has been achieved through oxygen-doping using ozonization treatment,[3a, 3b, 5] and also through sp^3 defect doping using aryl modification (diazonium chemistry)[3c, 6] and reductive alkylation.[7] The key is achieving a small amount of chemical modification (local functionalization) that produces doped sites on the SWNTs.[3b, 3c] E_{11}* PL then emerges on the locally functionalized SWNTs (lf-SWNTs) owing to changes in the local electronic properties. These changes are based on partial symmetry breaking of the tube structure, and allow exciton trapping at the doped sites that suppresses exciton quenching processes like collision with the tube edges.[3b, 8]

Recent reports have demonstrated wavelength shifts of the E_{11}* PL via the two-state switching of functionalized molecules at the doped sites of lf-SWNTs. Therein, the second state was formed by molecular binding at doped sites, through molecular recognition using phenylboronic acid[9] or an azacrown ether,[10] and by protonation of arylamine groups.[7a, 10-11] These results suggested that local chemical events at doped sites could potentially manipulate the PL functionality of lf-SWNTs, without further modification of the SWNT structure. The observed molecular-driven switching function can be considered as a mimic of receptors in living cells, in which chemical signaling controls and activates various biological functions in the cell.

The current study proposes the concept of multistep spectral shifts, as shown in Figure 1. This is achieved by creating doped sites with arylaldehyde groups that form dynamic imine bonding. This dynamic bonding allows for multiple reaction pathways. Specifically, E_{11}* PL shifts occur via the following steps: 1) Imine bond formation between the arylaldehyde group and added aniline derivative, in which the resulting wavelength shift is determined by the chemical structure of the bound aniline derivative; 2) Dissociation of the imine bond and exchange

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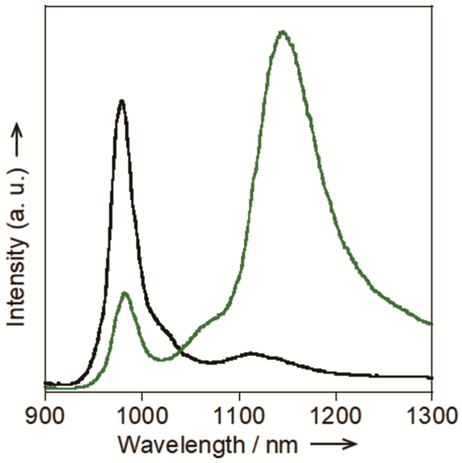

Figure 2. PL spectra of the pristine SWNTs (black) and lf-SWNTs-CHO (green). The concentration of CHO-Dz was 22.7 μM for the synthesis of the lf-SWNTs-CHO. λ_{ex} = 570 nm.

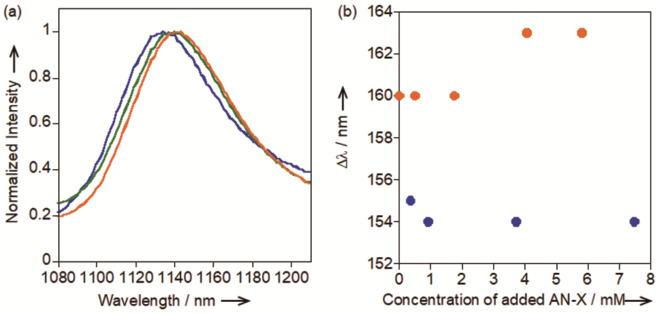

Figure 3. (a) Normalized PL spectra of lf-SWNTs-CHO before (green) and after adding AN-CH$_3$ (blue) or AN-Br (orange). [AN-CH$_3$] = 3.73 mM and [AN-Br] = 5.81 mM, λ_{ex} = 570 nm. (b) Plot of Δλ for the mixture of lf-SWNTs-CHO with AN-CH$_3$ (blue) or AN-Br (orange) as a function of the added AN-X concentration.

reaction of the bound aniline derivative based on the equilibrium of the dynamic imine bond; 3) The Kabachnik-Fields reaction, in which a dialkyl phosphite selectively and covalently binds at the imine-formed sites to produce an α-amino phosphonate.

Aldehyde-tethering aryldiazonium tetrafluoroborate (CHO-Dz) was synthesized by one-step diazotization of a tert-butoxycarbonyl group (BOC)-protected aniline derivative, through reaction with nitrosyl tetrafluoroborate (see Supporting Information, Experimental section). For local functionalization using CHO-Dz, SWNTs (CoMoCAT, (6,5) rich) were dissolved in D$_2$O containing sodium dodecylbenzene sulfonate (SDBS), which was mixed with CHO-Dz, providing arylaldehyde-modified lf-SWNTs (lf-SWNTs-CHO).

Figure 2 shows PL spectra of non-modified (pristine) SWNTs and lf-SWNTs-CHO. The pristine SWNTs showed a PL peak at 980 nm (E_{11}). After reaction with CHO-Dz, an additional PL peak appeared at 1140 nm (E_{11}*). The observed wavelength of E_{11}* is in agreement with the expected value from the reported linear relationship between wavelength shifts (ΔE_{11}/eV = $E_{11}^* - E_{11}$ and Δλ/nm = $\Delta\lambda(E_{11}^*) - \Delta\lambda(E_{11})$), and the Hammet substituent constants (σ)[12] of the para-substituted aryl group on the lf-SWNTs (Figure S1).[3c, 6] The Raman spectra of the lf-SWNTs-CHO (Figure S2) showed a decrease in the ratio of the G band (1581 cm^{-1}) to D band (1304 cm^{-1}) with increasing CHO-Dz concentration. These bands related to vibration of the graphitic carbon lattice and defect sites, respectively.[13] This ratio decrease indicated the introduction of defects on the tube walls. Vis/NIR absorption spectra (Figure S3) showed slight bleaching with increasing CHO-Dz concentration. In contrast, remarkable PL changes were observed after chemical functionalization, similarly to reports of local functionalization.[3c, 4, 6-7, 9, 11] These results show that the chemical modification largely preserved the sp^2 carbon network of the tubes, and therefore, the local functionalization using CHO-Dz resulted in the defect-induced PL of E_{11}* for lf-SWNTs-CHO.

Figure 3 shows the PL spectral changes of the lf-SWNTs-CHO upon the addition of aniline derivatives (AN-X; where X represents the substitution group). AN-Br and AN-CH$_3$ induced peak wavelength shifts of E_{11}* to 1145 nm and 1134 nm, respectively (Figure 3a). In a control experiment using *p*-nitroaryl-modified lf-SWNTs without aldehyde groups, no E_{11}* shift was induced by the added AN-CH$_3$ (Figure S4). For lf-SWNTs-CHO, the E_{11} wavelength showed slight changes (0–2 nm) upon the addition of AN-Xs. SWNTs exhibit PL shifts depending on the surrounding microenvironment such as solvents, surfactants, and additives.[15] The lf-SWNTs showed two PL peaks of E_{11} and E_{11}*, and both could be shifted by additives. Thus, the Δλ or Δ*E* is useful for gauging PL changes induced by chemical reactions at the doped sites, because such environmental effects are reflected in the wavelength shifts of E_{11}. The resulting Δλ values were 154 nm and 163 nm for the addition of AN-CH$_3$ and AN-Br, respectively, which were varied from the Δλ of 160 nm for the lf-SWNTs-CHO. The observed blue shifts and red shifts of the E_{11}* PL were related to the electron-donating CH$_3$ group and the electron-withdrawing Br group in the aryl moieties, respectively (Table 1). This was consistent with the expected shift directions from the aforementioned trend between Δλ and σ. The added AN-Xs showed different concentration dependency on the spectral shifts; that is, AN-CH$_3$ induced the spectral shift at a relatively low concentration of 0.50 μM, while AN-Br required a concentration of >2.0 μM to induce the wavelength shift (Figure 3b). The addition of AN-Xs in this concentration range showed no pH change. For the formation of the imine bond, the acidity of amine groups (p*Ka*) affects their reactivity.[16] The p*Ka* values of the amine groups of AN-CH$_3$ and AN-Br are 5.08 and 3.89, respectively,[14] from which imine bond formation preferentially favors AN-CH$_3$ over AN-Br. AN-NO$_2$ showed low reactivity due to its strong electron-withdrawing properties (p*Ka* = 1.02[14]).

Table 1. p*Ka* and σ for AN-Xs (X = CH$_3$, Br, or NO$_2$) and observed Δλ for each lf-SWNTs-I-X.

X group in AN-X	CH$_3$	Br	NO$_2$
p*Ka*[14]	5.08	3.89	1.02
σ for X-substituted aryl[12]	–0.17	0.23	0.78
Δλ / nm	154	163	165

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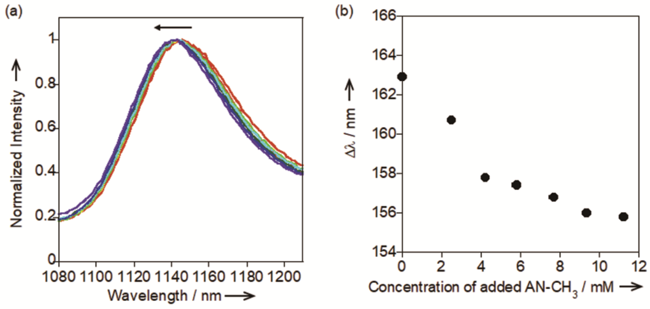

Figure 4. (a) Normalized PL spectra and (b) plot of Δλ as a function of the added AN-CH_3 concentration for lf-SWNTs-I-Br. [AN-CH_3] = 0 (red) – 11.2 mM (blue), λ_{ex} = 570 nm.

Adding deuterium chloride accelerated this reaction, and a larger spectral red shift was observed (E_{11}* = 1150 nm, E_{11} = 985 nm), providing a Δλ = 165 nm (Figure S5). X-ray photoelectron spectroscopy (XPS) was used to investigate the product of lf-SWNTs-CHO reacting with AN-Br, in which the specimen was collected as a solid through filtration after rinsing with ethanol. As shown in Figure S6, a peak of the Br 3d state was detected at 70.6 eV. A mixture of the pristine SWNTs with AN-Br showed no signal after the same filtration procedure. This result indicated that the AN-Br group was attached on the lf-SWNTs-CHO in a stable manner via imine bond formation. In aqueous systems, imine bonds rarely form due to the abundance of water. However, the lf-SWNTs-CHO provided a hydrophobic microenvironment around the doped arylaldehyde group by the SDBS micelle coating of the tube walls. This hydrophobic microenvironment promoted imine formation through the exclusion of water molecules. Such effect of the hydrophobic domain was observed in a control experiment, in which the imine product preferentially formed in aqueous SDBS micellar solutions (Figure S7).

Thus, the observed E_{11}* shifts originate from imine bond formation at the doped sites on lf-SWNTs-CHO, which produces imine-formed lf-SWNTs (lf-SWNTs-I-X). The system realizes PL shifts towards shorter wavelengths (blue shift) and longer wavelengths (red shift), depending on the chemical structure of the added AN-Xs. This versatile switching differs from reported wavelength shifts of the E_{11}* PL for lf-SWNTs, in which shifting occurred between the two states of before and after protonation at amine groups or sugar binding at phenylboronic acid groups.[7a, 9-11]

Imine bonds are highly dynamic, so controlling the equilibrium state could be a driving force for further wavelength shifts of the PL of lf-SWNTs-I-X. As shown in Figure 4, when AN-CH_3 was mixed with lf-SWNTs-I-Br, the E_{11}* peak blue shifted, resulting in changes in the Δλ from 163 nm to 156 nm. Based on the observed blue shift and the higher binding ability of AN-CH_3 than AN-Br, an exchange reaction of the bound aniline derivative is proposed to have occurred at the imine bond of doped sites, generating lf-SWNTs-I-CH_3.

The dilution with water could potentially shift the equilibrium from the imine bond state to the bond dissociation state. Dialysis of lf-SWNTs-I-CH_3 using SDBS solution was therefore conducted. Specifically, heating at 70 °C was applied to enhance the reaction kinetics, through heat-induced loosening of the surfactant packing structure.[17] This would allow water molecules to access the embedded imine bonds on the tubes. The resulting PL spectrum was almost identical to that of lf-SWNTs-CHO (Figure S8), which showed that the imine dissociation reaction induced the spectral shift.

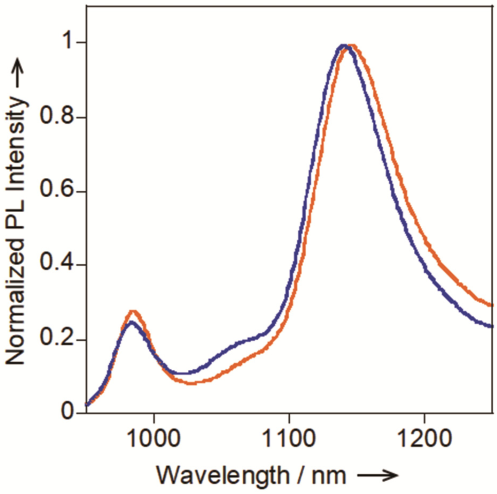

Figure 5. Normalized PL spectra of lf-SWNTs-I-Br before (orange) and after (blue) adding 21.3 mM DIPP. λ_{ex} = 570 nm.

Another important feature of lf-SWNTs-I-X is that the imine bond can be further modified by the Kabachnik-Fields reaction[18] using dialkyl phosphite, to generate an α-amino phosphonate. This reaction converts the dynamic imine bond to the irreversible α-amino phosphonate form. This would be useful as a technique for immobilizing the bound molecules and other materials, via imine bonds at local modified sites. Figure 5 shows PL spectra of lf-SWNTs-I-Br mixed with diisopropyl phosphite (DIPP). The addition of DIPP caused peak shifts of E_{11}*, which resulted in the Δλ changing from 163 nm to 157 nm.[19] The decrease in Δλ was in agreement with the expected change from imine bond to α-amino phosphonate that accompanied the variation in electronic properties upon changing from an electron-withdrawing to electron-donating substituent.[20] Mixing lf-SWNTs-CHO and DIPP resulted in a Δλ identical to that of lf-SWNTs-CHO itself (160 nm). However, the addition of AN-Br to the mixture resulted in a Δλ of 158 nm, which was almost the same as that for the mixture of lf-SWNTs-I-Br and DIPP. This indicated the formation of α-amino phosphonate regardless of the mixing order, as is typically observed in Kabachnik-Fields reactions. XPS measurements of the lf-SWNTs-I-Br/DIPP mixture showed a P 2p signal at 134 eV and a Br 3d signal at 70.4 eV, even after thorough rinsing with ethanol during filtration. These two signals were not observed in the spectrum of pristine SWNTs mixed with AN-Br and DIPP, followed by the same rinsing procedure (Figure S9). As another control experiment, the room temperature Kabachnik-Fields reaction was attempted using SDBS in a catalytic role,[18c] and the formation of diisopropyl(((4-bromophenyl)amino)(phenyl)methyl)phosphonate was observed (see Supporting Information, Experimental section). These results strongly suggested that the Kabachnik-Fields reaction occurred at defect sites that formed the imine bond on the tubes, and acted as a driving force to modulate the PL of lf-SWNTs-I-Br. This behavior could form the basis of spectral modulation techniques based on logic gate systems. It could be used as an "AND" gate that operates when the all three components coexist. The use of defect sites as chemical reaction platforms is therefore a powerful tool for versatile modulation of the E_{11}* PL of lf-SWNTs.

In conclusion, we have designed and synthesized arylaldehyde-modified lf-SWNTs (lf-SWNTs-CHO). Their E_{11}* PL showed bidirectional spectral shifts based on imine bond formation. The chemical structure of the bound aniline derivative determined the resulting E_{11}* wavelength. The E_{11}* PL of lf-SWNTs-I-X was subsequently modulated based on the dynamic imine bond, which enabled exchange reactions and dilution-induced dissociation. PL shifts in lf-SWNTs-I-X could also be induced through the Kabachnik-Fields reaction at doped sites. Our concept uses doped sites as a molecular reaction platform for modulating the functionality of a nanomaterial. Larger PL shifts may be possible using other types of doped site such as multipoint modification,[7, 21] and this forms the basis of our current research. The observed multistep PL shifting could be exploited in smart nanodevices and nanoprobes for NIR imaging and sensing with PL at wavelengths longer than 1000 nm. This would be useful for monitor biological/chemical events *in vivo*.

Acknowledgements

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Keywords: Single-walled carbon nanotubes • Photoluminescence • Imine bond • Doping • Nanotechnology

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[20] The considered electronic property changes is based on σ values of 0.42 for $–CH=N-C_6H_5$, 0.06 for $–CH_2PO(OEt)_2$, and -0.11 for $–CH_2NH_2$ from ref. 12.

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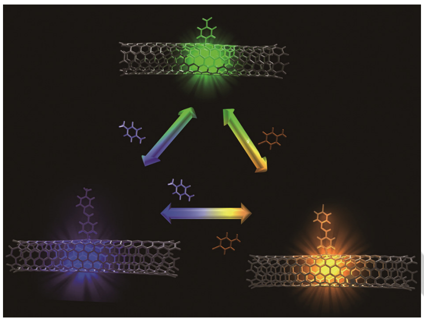
COMMUNICATION

A near-infrared photoluminescent nanomaterial with versatile emission is reported. Chemical reaction at local doped sites of single-walled carbon nanotubes shifts the emission to longer or shorter wavelengths, according to different chemical pathways. The doped sites allow for multiple chemical reactions, and realize the response based on dynamic imine bond formation and its further modification using the Kabachnik-Fields reaction.



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