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Control of the Photoluminescence Properties of Single-walled Carbon Nanotubes by Alkylation and Subsequent Thermal Treatment

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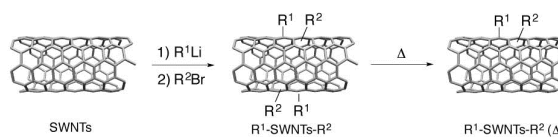
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Dibutylated single-walled carbon nanotubes (Bu-SWNTs-Bu) with varying degrees of functionalization were prepared by two-step reductive alkylation and subsequent thermal treatment. New photoluminescence peak around 1240 nm was observed and was increased drastically after the thermal treatment. The results indicate that thermally treated Bu-SWNTs-Bu are promising NIR photoluminescent materials.

Single-walled carbon nanotubes (SWNTs) have excellent mechanical and electrical properties, and have therefore been proposed for use in many applications.^[1-4] In 2002, the near-infrared (NIR) photoluminescence (PL) spectra of semiconducting SWNTs dispersed in D₂O were observed and characterized.^[5,6] Since then, PL spectroscopy has become a very powerful tool for the investigation of semiconducting SWNTs because the E₁₁ PL peaks of different kind of SWNTs are observed individually by the excitation of E₂₂ depending on their electronic structures, in which E₁₁ and E₂₂ are the optical absorption bands corresponding to the first and second excitons in semiconducting SWNTs, respectively. The PL of semiconducting SWNTs in the NIR region has received significant attention for application in biological imaging,^[7-9] because NIR light from 1000 to 1400 nm, which is known as the second NIR window, has high transparency in biological tissues.^[10] To improve the PL performance of SWNTs as biological imaging materials, chirality enriched semiconducting SWNTs have been investigated, and have shown better PL performance than unsorted SWNTs.^[11] Recently, it has been reported that sidewall functionalization of SWNTs induces a newly bright PL peak in red-shifted region.^[12-17] On the basis of density functional theory calculations, the new PL is considered to be derived from splitting of the frontier orbitals of SWNTs by sidewall functionalization.^[12,15,16] At this point, sidewall functionalization is advantageous for practical applications because it can improve their dispersibility and additional functionality.^[18] However, the electronic and optical properties of SWNTs are diminished upon excessive functionalization.^[19] Therefore, it is important to control the degree of functionalization in SWNTs if they are to be used as luminescent materials. Studies on the influence of reaction time and reactant ratio have indicated that the degree of functionalization, which depends on these parameters, is an important factor in controlling the PL property of SWNTs.^[12-17]

For instance, in the case of reaction of SWNTs with aryl diazonium salts, new PL peak intensity is increased with decrease of original PL peak intensity by the addition of adequate amount of the diazonium salts. On the other hand, new PL peak intensity is decreased by the addition of large amount of the diazonium salts.^[16] Meanwhile, we have previously reported that the substituents on SWNTs, and their bulkiness, strongly affect the degree of functionalization during the reductive alkylation of SWNTs.^[20,21] Thus, we envisage the reductive alkylation with the appropriate choice of substituents, can be used to control the PL properties of SWNTs. Herein, we report the PL properties of dialkylated SWNTs with varying degrees of functionalization. In this study, we demonstrate that the degree of functionalization can be precisely controlled by introducing a thermal treatment step in the preparation of these materials.

Dialkylated SWNTs (R¹-SWNTs-R²) were synthesized using butyllithium (R¹Li) and butyl bromide (R²Br) according to previously reported methods.^[20,21] (Scheme 1) In *n*Bu-SWNTs-R (R = *n*Bu, *iso*Bu, *sec*Bu, and *t*Bu) and *t*Bu-SWNTs-R (R = *n*Bu, *iso*Bu, and *sec*Bu), the characteristic E₁₁ and E₂₂ absorption peaks were mostly diminished by the alkylation, indicating sidewall functionalization proceeded effectively. On the other hand, the absorption spectrum of *t*Bu-SWNTs-*t*Bu exhibited relatively small changes, as shown in Fig. 1. The results indicate that the degree of functionalization of *t*Bu-SWNTs-*t*Bu is much lower than those of the other Bu-SWNTs-Bu, owing to the bulkiness of the *t*Bu group. The degree of functionalization was estimated from the D/G ratios in the Raman spectra of Bu-SWNTs-Bu, shown in Fig. S1, which was consistent with the results observed in the absorption spectra. The



Scheme 1 Reductive alkylation and subsequent thermal treatment.

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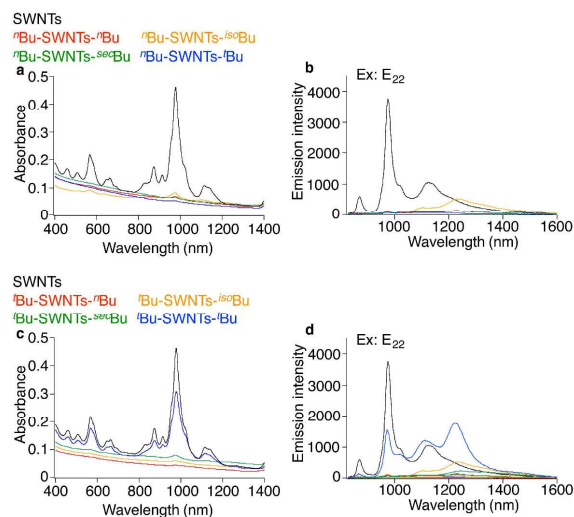


Fig. 1 Absorption spectra (a,c) and PL spectra with E22 excitation (b,d) of SWNTs and Bu-SWNTs-Bu.

characteristic peak changes in absorption and Raman spectra after functionalization corresponds to the degree of functionalization.^[19]

In situ PL measurements of the SWNTs during the two-step reductive alkylation reaction is difficult due to the low dispersibility of SWNTs under the reaction conditions employed. Thus, in order to compare the PL peak intensity before and after functionalization, SWNT dispersions having similar absorption intensities at a local minimum of ~ 775 nm after centrifugation (140,000g, 1 h) were used for discussion (Table S1). Based on our previous study, we have found that the absorption intensity around 775 nm shows little change after the photochemical reaction of SWNTs with aliphatic amines.^[22] After functionalization, most of original PL peaks decreased and new PL peak around 1240 nm appeared slightly in *n*Bu-SWNTs-R (R = *n*Bu, *iso*Bu, *sec*Bu and *t*Bu) and *t*Bu-SWNTs-R (R = *n*Bu, *iso*Bu, and *sec*Bu) inferred from the weak E_{11} and E_{22} absorption peak intensities (Fig. 1). The alkylation experiments suggest that the number of the introduced functional group was too much to induce the new PL by the applied condition. Hence, it is required to adjust the functionl degree to control the PL properties of SWNTs. On the other hand, *t*Bu-SWNTs-*t*Bu exhibited both the original and new PL peak around 1240 nm in moderate intensities (Fig. 1d). The particularity of *t*Bu-SWNTs-*t*Bu observed in the PL spectrum comes from the much lower degree of functionalization on the SWNT sidewall compared to those of the other Bu-SWNTs-Bu.

Thermogravimetric analysis (TGA) of functionalized SWNTs has been used to estimate the degree of functionalization based on the weight loss observed as the substituents on the SWNT sidewall are eliminated by thermal treatment under inert gas atmosphere.^[23-25]

Hirsch et al studied thermal defunctionalization of *n*hexyl-SWNTs using TG/MS and Raman spectroscopy. Ion peaks of hexyl group were detected between 150 and 350°C in TG/MS analysis, and the sample mass loss in this region was correlated with the

corresponding D/G ratio of respective sample.^[25] Encouraged by this report, thermal treatment of Bu-SWNTs-Bu was conducted at various temperatures to control the degree of functionalization more precisely by removing substituents gradually. This is a much easier and more efficient method for controlling the degree of functionalization than monitoring and adjusting the amount of highly reactive reagents in the reductive alkylation.

After thermal treatment, the characteristic absorption and Raman spectra of the SWNTs were recorded, and their temperature dependence is shown in Fig. 2 and Fig. S3-S6. Characteristic absorption and Raman peak intensities of SWNTs were recovered with increase of the temperature. These results are consistent with the result of thermal treatment of *n*hexyl-SWNTs reported by Hirsch et al and indicate that the degree of functionalization of alkylated SWNTs can be tuned depending on the temperature employed in the subsequent thermal treatment.^[25] A strong PL peak around 1240 nm is observed in the spectra of Bu-SWNTs-Bu after thermal treatment when the D/G_{633nm} value of Bu-SWNTs-Bu are between 0.1 and 0.2 (Fig. 2, 3, S5, S6, and S13). The relative peak areas in the 827 – 1600 nm, estimated in eV unit, range for pristine SWNTs and Bu-SWNTs-Bu with E_{22} excitation are summarized in Table S1. The peak areas of *n*Bu-SWNTs-*iso*Bu (Abs_{773nm} : 0.077), *n*Bu-SWNTs-

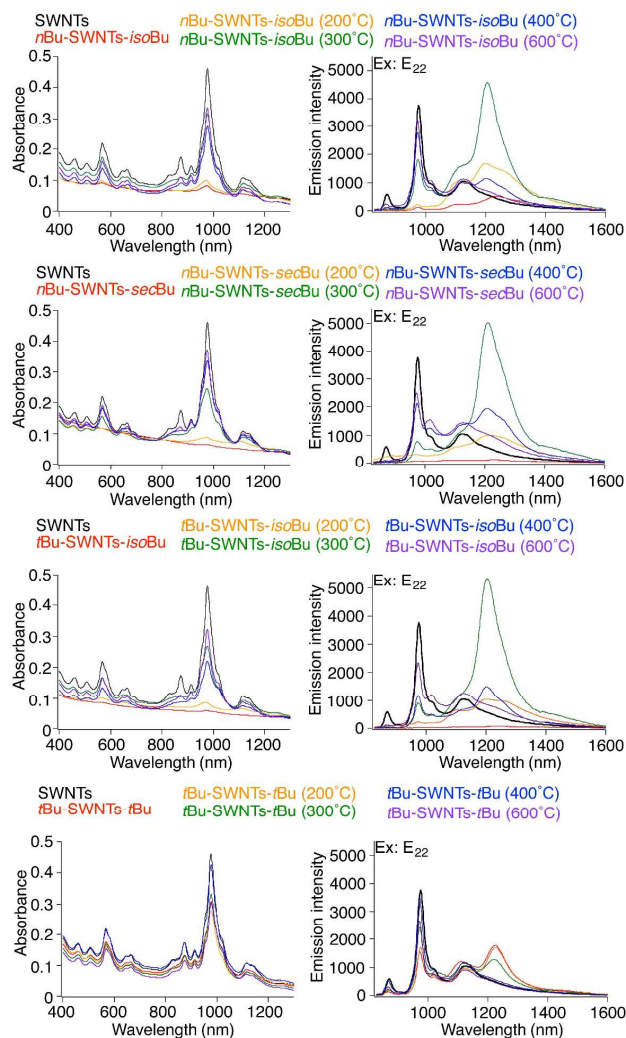


Fig. 2 Absorption spectra (left) and PL spectra with E22 excitation (right). SWNTs (black) and Bu-SWNTs-Bu (red) treated at 200 (orange), 300 (green), 400 (blue), and 600 °C (purple).

secBu (Abs_{768nm} : 0.077), and *tBu*-SWNTs-*isoBu* (Abs_{765nm} : 0.081) treated at 300 °C are 1.7 times larger than that of the pristine SWNTs (Abs_{779nm} : 0.084). There is a good correlation between the D/G ratio and the PL peak area of Bu-SWNTs-Bu. Although an excitation wavelength of 633 nm in the Raman measurements was not suitable for the detection of (6,5)-SWNT, these results indicate that the change in the D/G ratio can be used as an indicator in this study and the degree of functionalization of SWNTs is one of the important factors for the PL property of SWNTs. (Fig. S13). By controlling the thermal treatment condition, the degree of functionalization can be finely tuned, leading to strongly emissive materials for *nBu*-SWNTs-R (R = *nBu*, *isoBu*, *secBu*, and *tBu*) and *tBu*-SWNTs-R (R = *nBu*, *isoBu*, and *secBu*). On the other hand, for *tBu*-SWNTs-*tBu*, it is not achieved to introduce enough amount of the functional group by the alkylation at the first step. Therefore, the degree of functionalization before thermal treatment was too low in terms of new PL emission, and the thermal treatment reduce the degree of functionalization still more at the second step. Thus, it is rational that induction of the new bright PL around 1240 nm was no more desirable for *tBu*-SWNTs-*tBu* by the proposed protocol.

It should be emphasized that Bu-SWNTs-Bu can be excited by NIR light at the E_{11} absorption wavelength for NIR PL applications because the large Stokes shift after the functionalization allows easy separation from the Rayleigh scattering. In addition, it is noteworthy that the PL intensity excited at E_{11} is significantly increased compared to the PL intensity excited at E_{22} due to higher E_{11} absorption intensity. Excitation spectra of *nBu*-SWNTs-*isoBu*, *nBu*-SWNTs-*secBu*, and *tBu*-SWNTs-*isoBu* treated at 300 °C show good agreement with these absorption spectra, as shown in Fig. 4. The PL peak areas (between 1033 and 1600 nm, estimated in eV unit) excited at E_{11} of *nBu*-SWNTs-*isoBu*, *nBu*-SWNTs-*secBu*, and *tBu*-SWNTs-*isoBu* treated at 300 °C are 3.0 times larger than the PL peak area (between 827 and 1600 nm, estimated in eV unit) excited at E_{22} of the pristine SWNTs (Fig. 3 and 5). Importantly, NIR light,

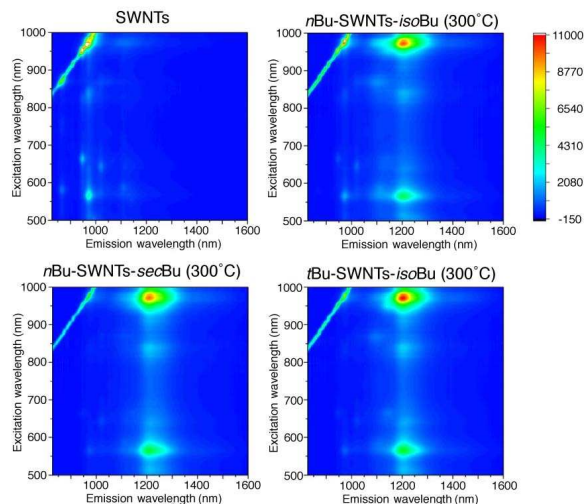


Fig. 3 Contour plots of fluorescence intensity versus excitation and emission wavelength of Bu-SWNTs-Bu after thermal treatment at 300 °C.

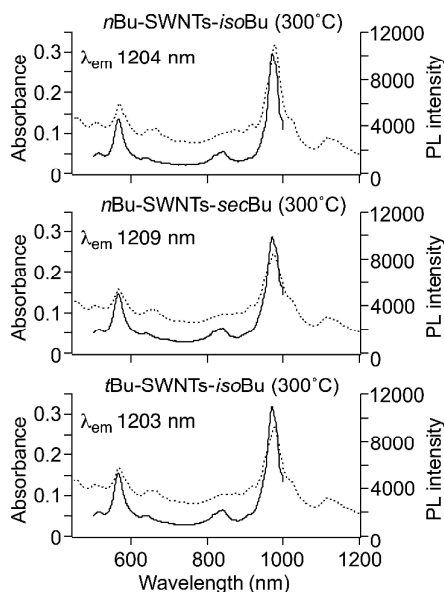


Fig. 4 Absorption (dashed line) and excitation spectra (solid line) of Bu-SWNTs-Bu after thermal treatment.

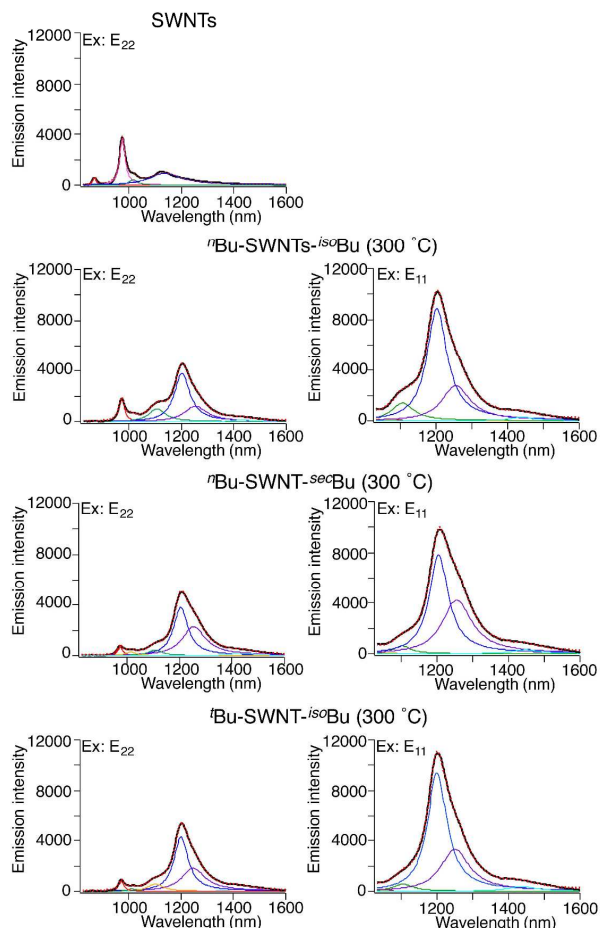


Fig. 5 Photoluminescence spectra excited at E_{22} (left) and E_{11} (right) of SWNTs and Bu-SWNTs-Bu after thermal treatment. Black line: PL spectra. Colored line: Lorentzian curve fitting. Dashed line: Sum of curve fitting data.

which has high transparency in biological tissue, can be used for the excitation, thus increasing analytical sensitivity for biological imaging applications.

In conclusion, we studied the PL properties of dialkylated SWNTs and found that the degree of functionalization of the dialkylated SWNTs was effectively controlled by substituent effects and thermal treatment under N_2 . After thermal treatment, strong PL around 1240 nm was observed depending on the degree of functionalization, which was estimated from the intensity of characteristic absorption peaks, and the D/G ratio. In addition, stronger PL occurred by E_{11} excitation than E_{22} excitation. This result indicates that thermally treated dialkylated SWNTs obtained as thermally stable materials have advantages as photoluminescent materials. The chemical functionalization of SWNTs as photoluminescent materials could lead to further practical applications. Their modification by these means could improve their bulk properties, such as their dispersibility, and add new therapeutic functionalities, such as pharmaceutical moieties or antibodies.

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Electronic Supplementary Information (ESI) available: Experimental details, spectra data, and SEM images.

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