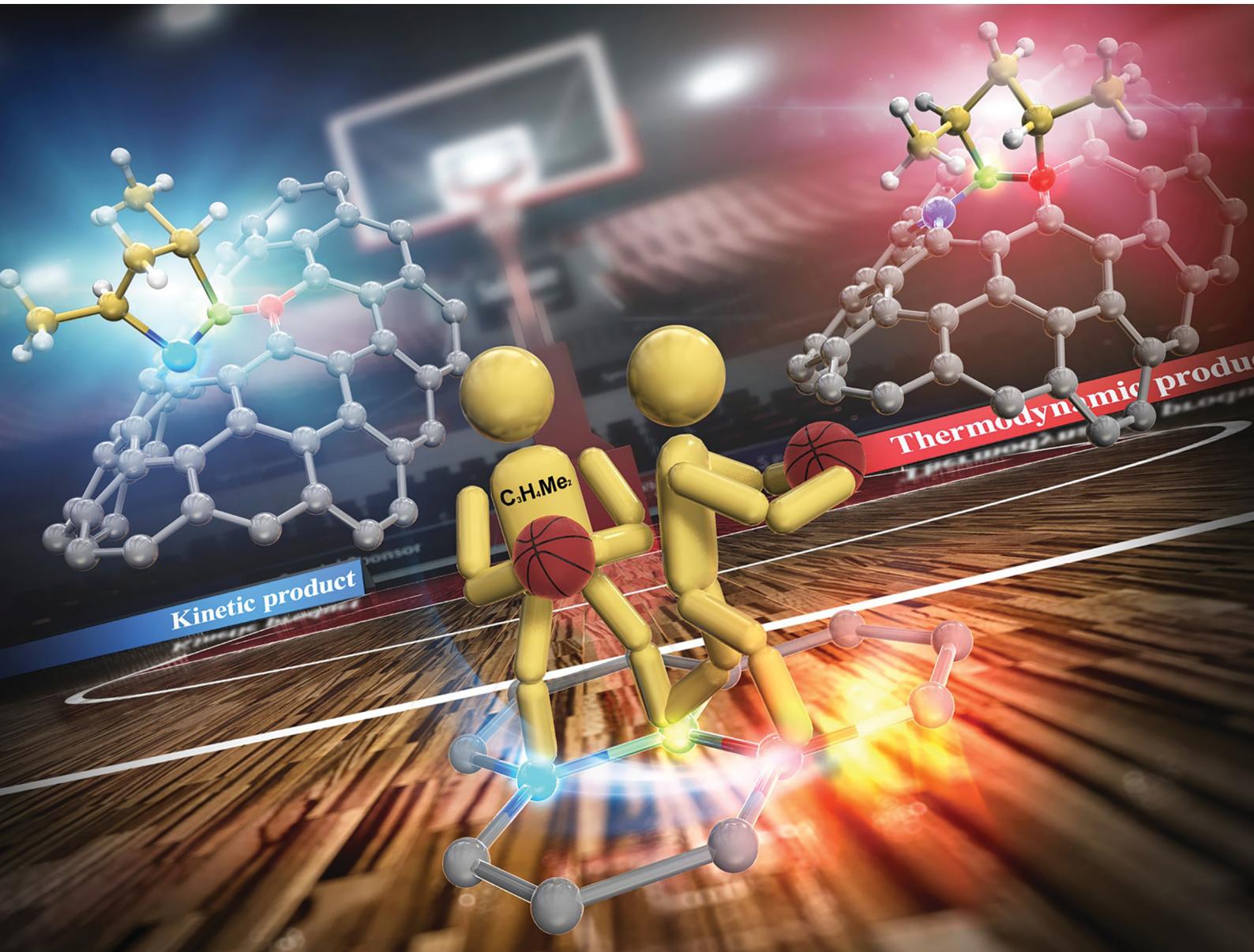


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Control of functionalized single-walled carbon nanotube photoluminescence *via* competition between thermal rearrangement and elimination[†]

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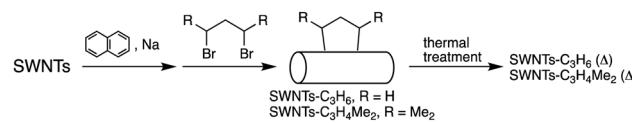
We conducted the chiral separation of functionalized single-walled carbon nanotubes (SWNTs) with dibromopropane derivatives. Depending on their chirality and diameter, the thermal treatment of functionalized SWNTs leads to a shift in the emission radiation to longer wavelengths owing to rearrangement reaction in competition with elimination reaction.

Single-walled carbon nanotubes (SWNTs) are cylindrical carbon nanomaterials that have attracted special attention owing to their unique electronic and optical properties.^{1,2} Various chemical functionalization methods have been developed, and unique chemical reactivity depending on the electronic structure and diameter has been reported.^{3–7} The functionalization degree of SWNTs significantly impacts their intrinsic properties because excessive functionalization disturbs the π -electron system of SWNTs.^{8,9} The functionalization degree of SWNTs can be estimated by spectroscopic analysis, the decrease of their intrinsic absorption and photoluminescence (PL) peaks, and the increase of the D- to G-band intensity ratio (D/G) in the Raman spectra.^{7,8} SWNTs with smaller diameters were shown to have higher reactivity because of their higher strain energy, and their adducts are thermodynamically more stable than those of SWNTs with larger diameters.^{10,11}

The functionalization of SWNTs was recently reported to reduce the band gap locally at the addition site, as revealed by PL measurements at an appropriate functionalization degree.^{12,13} New PL peaks in the near-infrared (NIR) region were emerged in high quantum yield by functionalization, enabling excitation at the E₁₁ energies and thus facilitating the application of SWNTs as an NIR light source in fields such as bioimaging and sensing.¹⁴ Systematic theoretical calculations using model compounds

revealed that the binding configuration of addenda is an important factor for the local band gap energy.^{15–17} In other words, it is expected that the PL wavelength of SWNT adducts provides insight into their local structure. Previously, we reported that functionalization of (6,5) SWNTs with 1,3-dibromoalkanes, Br(CH₂)_nBr ($n = 3–5$), emerged a new PL peak at 1215–1231 nm depending on the alkyl lengths; the PL intensity was affected by the functionalization degree, which was modified through the partial elimination of the addenda *via* thermal treatment.¹⁸ In contrast, the PL wavelength of (6,5) SWNTs functionalized using 2,4-dibromopentane (mixture of stereoisomers) changed from 1219 to 1268 nm after the thermal treatment, indicating thermal rearrangement, *i.e.*, changing of binding configuration (Scheme 1 and Fig. S1, ESI[†]).¹⁹ The combination of functionalization and thermal treatment extended the PL wavelength range of (6,5) SWNTs^{19–22} to 1268 nm, reaching the original-band in the optical communication wavelength bands. He *et al.*, demonstrated that SWNTs with PL controlled by arylation produce room-temperature single-photon emission in the telecom band. The development of new methods for effectively and selectively generating new PL peaks in the telecom band has a high potential for applications.²³

As previously mentioned, theoretical calculations indicated that the PL wavelength of functionalized SWNTs isomers is governed by the binding configuration of the addenda. Therefore, the PL wavelength after functionalization can be a probe for the binding configuration of the functionalized SWNTs. Herein, we investigated how the thermal treatment and chiral separation of SWNTs-C₃H₄Me₂ can expand the excitation and emission wavelengths of SWNTs. The results showed that the emission of various chiral semiconducting SWNTs can be



Scheme 1 Functionalization of SWNTs and subsequent thermal treatment.

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shifted to longer wavelengths by the thermal rearrangement competing with the elimination reaction, in a diameter dependent manner.

Fig. 1 and 2 depict the PL spectra of the separated SWNTs-C₃H₆ and SWNTs-C₃H₄Me₂ before and after thermal treatment. For a detailed explanation of separation of SWNTs, see ESI† (Fig. S2–S16).^{24–29} The characteristic PL peaks were assigned based on the relationship between the excitation wavelengths and the E₂₂ and E₁₁ energies for each chiral SWNTs (Table 1).²⁷ The chiral index assignment for each PL peak is shown in PL mapping (Fig. S17–S23, ESI†). A single new PL peak was observed selectively for each chiral SWNTs-C₃H₆ adduct. In (6,4), (7,3), and (6,5) SWNTs-C₃H₆, no significant change in PL wavelengths was observed after thermal treatment at 400 °C. In contrast, in (8,3), (7,5), and (8,4) SWNTs, the intensity of E₁₁ PL peaks at respectively 957, 1035, and 1122 nm, respectively, increased after thermal treatment with a decrease of the PL peaks emerged by functionalization (Fig. 1d–f). The results suggest that the thermal treatment resulted in an elimination reaction. In addition, (8,3) and (7,5) SWNTs-C₃H₆ (400 °C) exhibited new PL peaks at 1249 and 1266 nm, respectively. Therefore, the thermal treatment of SWNTs-C₃H₆ is effective in diameter-selectively controlling the PL intensities emerged after functionalization. Moreover, the emergence of new PL peaks in (8,3) and (7,5) SWNTs-C₃H₆ (400 °C), for which (mod(n-m, 3) = 2), indicates competing rearrangement and elimination reactions.

The separated (7,3), (6,5), and (8,4) SWNTs-C₃H₄Me₂, for which (mod(n-m, 3) = 1), each exhibited a single new PL peak at similar wavelengths to those of SWNTs-C₃H₆ (Fig. 2). After thermal treatment at 300 °C for 6 h, PL peaks at 1317 and 1268 nm were observed in (7,3) and (6,5) SWNTs-C₃H₄Me₂ (300 °C, 6 h), respectively, accompanied by an increase of the intrinsic E₁₁ PL peak. In contrast, after thermal treatment at

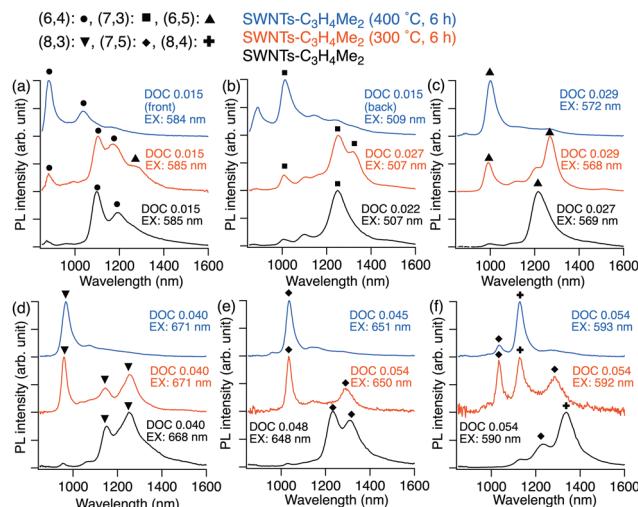


Fig. 2 PL spectra of separated SWNTs-C₃H₄Me₂ before and after thermal treatment dispersed in D₂O solution containing 1 wt% SC. Black line: SWNTs-C₃H₄Me₂. Red line: SWNTs-C₃H₄Me₂ (300 °C, 6 h). Blue line: SWNTs-C₃H₄Me₂ (400 °C, 6 h). Excitation wavelengths and peak assignment are shown in each spectrum.

Table 1 PL wavelengths of separated SWNTs-C₃H₄Me₂ before and after thermal treatment

	(6,4)	(7,3)	(6,5)	(8,3)	(7,5)	(8,4)
SWNTs-C ₃ H ₄ Me ₂	1098 1192	1249 1251	1213 1210	1151 1157	1234 1237	1337 1310
SWNTs-C ₃ H ₄ Me ₂ (200 °C, 6 h)	1104 1190	1252 1268	1210 1146	1157 1146	1237 1298	1337 1299
SWNTs-C ₃ H ₄ Me ₂ (300 °C, 6 h)	1104 1174	1252 1317	1210 1268	1146 1146	1237 1298	1337 1255
SWNTs-C ₃ H ₄ Me ₂ (400 °C)	1102 1157	1246 1323	1269 1269	1130 1130	1290 1251	1337 1251
SWNTs-C ₃ H ₄ Me ₂ (400 °C, 6 h)	1032	1142	1121			
SWNTs-C ₃ H ₆ ³¹	1101	1251	1215	1146	1231	1339
SWNTs-C ₃ H ₆ (350 °C)	1105	1249	1204		1225	1338
SWNTs-C ₃ H ₆ (400 °C)	1105	1252	1204	1249	1225	1334
						1266

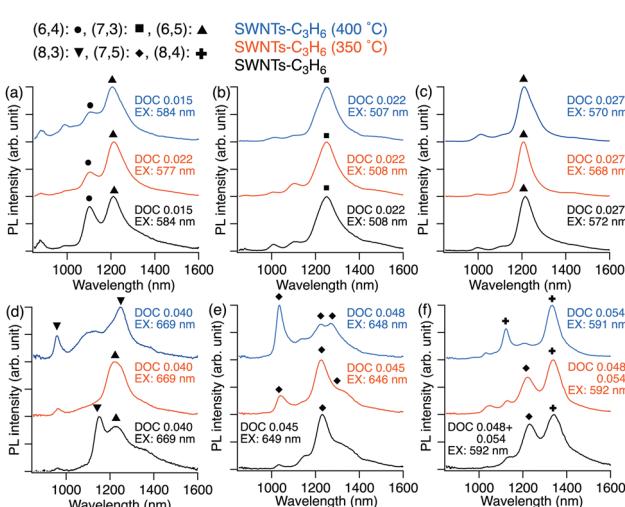


Fig. 1 PL spectra of separated SWNTs-C₃H₆ before and after thermal treatment dispersed in D₂O solution containing 1 wt% SC. Black line: SWNTs-C₃H₆. Red line: SWNTs-C₃H₆ (350 °C). Blue line: SWNTs-C₃H₆ (400 °C). Excitation wavelengths and peak assignment are shown in each spectrum.

300 °C for 6 h, (8,4) SWNTs-C₃H₄Me₂ exhibited only the E₁₁ PL peak. The emergence of new PL at red-shifted wavelengths and the increase in E₁₁ PL intensity indicate competing rearrangement and elimination reactions. The results indicate that adducts of SWNTs with smaller diameter are thermally stable towards elimination, and the rearrangement reaction has the effect of shifting the PL peak to longer wavelengths.

In contrast, the separated (6,4), (8,3), and (7,5) SWNTs-C₃H₄Me₂, (mod(n-m, 3) = 2), exhibited new PL peaks at 1192, 1251, and 1310 nm, respectively, without thermal treatment, in addition to the PL peaks observed in SWNTs-C₃H₆ (Fig. 2a, d, and e). Relatedly, the chirality-selective emergence of NIR PL was reported to occur in the hydrobutylation of SWNTs.²⁵ Hydrobutylated (7,3) and (6,5) SWNTs ("Bu-SWNTs-H) exhibited two new PL peaks, whereas ⁷Bu-(6,4), (8,3), and (7,5) SWNTs-H exhibited one new PL peak, respectively. Diameter-selective increases in the E₁₁ PL intensities were also observed after thermal treatment in (6,4), (8,3), and (7,5) SWNTs-C₃H₄Me₂. In



addition, (6,4) SWNTs-C₃H₄Me₂ (400 °C, 6 h) exhibited a new PL peak at 1032 nm, indicating a change in binding configuration (Fig. 2a). The change in PL wavelength selectivity and promotion of the elimination and rearrangement reactions in SWNTs-C₃H₄Me₂ may be attributed to the increased steric repulsion between SWNTs and addenda, and the higher stability of the SWNTs-C₃H₄Me₂ radical, the plausible intermediate in the reactions, compared to that of the SWNTs-C₃H₆ radical.

Fig. 3 depicts the emission energy difference (ΔPL) between functionalized and pristine SWNTs plotted as a function of the squared diameter of SWNTs. Two PL peaks observed in SWNTs-C₃H₄Me₂ before and after thermal treatment showed similar diameter dependence to the reported results of arylated and alkylated SWNTs,^{22,30} with ΔPL values decreasing as SWNT diameters increase (Fig. 3. Black and red lines). The similar ΔPL trends for SWNTs-C₃H₆ and SWNTs-C₃H₄Me₂ suggest identical binding configurations for each (Fig. 3. Black and green lines). ΔPL values for (6,4) and (8,3) SWNTs-C₃H₄Me₂ and that after thermal treatment with the higher energy region, respectively, tended to be larger than those of others. The larger ΔPL value for the (8,3) SWNT adduct compared to those of other chiral SWNT adducts is consistent with previous reports on arylated SWNTs.³⁰

As shown in Fig. 4, the 1,2-isomers are distinguished by the binding configuration of the two carbon atoms relative to the axis of SWNTs as L₊₊, L₊, and L₋, according to a pioneering report by He *et al.*¹⁶ Previously, we calculated the relative energy and transition energy of the model compounds of (6,5) SWNTs-C₃H₄Me₂ isomers using density functional theory (DFT) at the level of B3LYP/3-21G.^{19,34} The wavelength shift after the thermal treatment may be attributed to the formation of 1,2-L₊₊ (6,5) SWNTs-C₃H₄Me₂ as a kinetically preferred isomer during the functionalization reaction, while the 1,2-L₊ (6,5) SWNTs-C₃H₄Me₂ is formed as the thermodynamically favored product after the thermal treatment.³¹ The higher spin density at 1,2-L₊₊ carbon atom in the butylated SWNTs radical supported the hypothesis that the 1,2-L₊₊ adduct is the kinetically preferred product.³¹

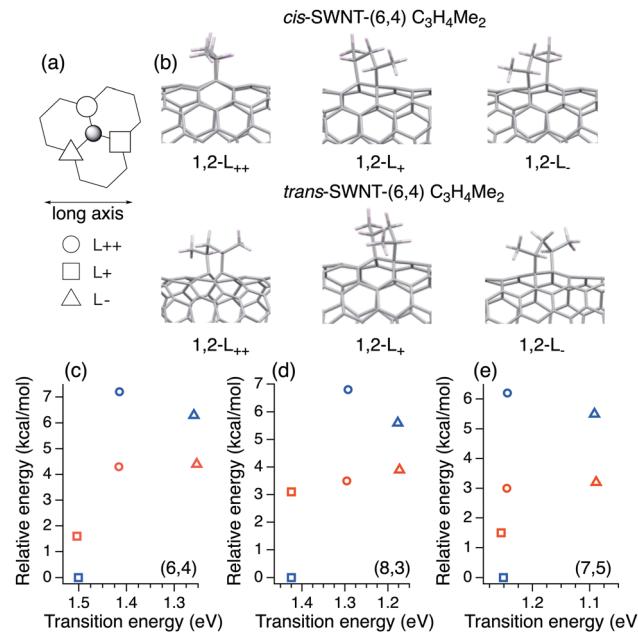


Fig. 4 (a) Three different binding configuration, marked as (○): L₊₊, (□): L₊, and (△): L₋, relative to the central addition site (gray circle). (b) Optimized partial structures of (6,4) SWNT-C₃H₄Me₂ isomers. Calculated transition energies (eV) and relative energies (kcal mol⁻¹) of model compounds of (b) (6,4), (c) (8,3), and (d) (7,5) SWNT-C₃H₄Me₂ isomers. Blue: trans-isomer. Red: cis-isomer.

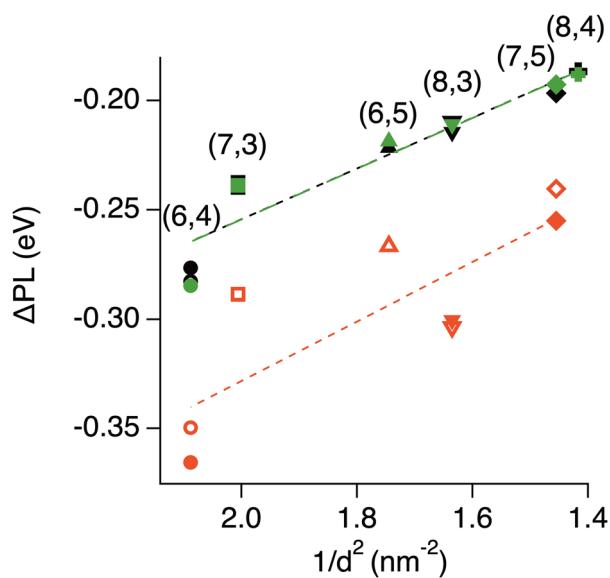


Fig. 3 Emission energy difference (ΔPL) between the functionalized and non-functionalized SWNTs as a function of the squared diameter of SWNTs.²⁶ SWNTs-C₃H₆ (green mark). SWNTs-C₃H₄Me₂ (filled black and red mark). SWNTs-C₃H₄Me₂ (300 °C, 6 h) (opened black and red mark). Black and red lines exhibit the linear fitting of ΔPL values for the PL peaks observed with the lower (black mark) and higher energy regions (red mark), respectively.

level of B3LYP/3-21G.^{19,34} The wavelength shift after the thermal treatment may be attributed to the formation of 1,2-L₊₊ (6,5) SWNTs-C₃H₄Me₂ as a kinetically preferred isomer during the functionalization reaction, while the 1,2-L₊ (6,5) SWNTs-C₃H₄Me₂ is formed as the thermodynamically favored product after the thermal treatment.³¹ The higher spin density at 1,2-L₊₊ carbon atom in the butylated SWNTs radical supported the hypothesis that the 1,2-L₊₊ adduct is the kinetically preferred product.³¹

In this work, we evaluated the stability and transition energy of model compounds of three 1,2-addition isomers of (6,4), (8,3), and (7,5) trans- and cis-SWNT-C₃H₄Me₂ to consider their plausible binding configurations (Fig. S24, S25 and Table S1, ESI†).³⁵ As shown in Fig. 4, similar to previous findings on (6,5) SWNT-C₃H₄Me₂,¹⁹ the geometric isomerism of the methyl groups has a large effect on adduct thermodynamic stability and a small effect on transition energy. In all chiral SWNTs, 1,2-L₊-trans-SWNT-C₃H₄Me₂ is the most stable adduct with the highest transition energy. The 1,2-L₊₊-trans-isomer is the most unstable adduct with an intermediate transition energy compared to those of the 1,2-L₊ and 1,2-L₋ isomers. Assuming that 1,2-L₊₊ trans-SWNT-C₃H₄Me₂ is kinetically formed by the addition reaction, the PL peak shift in (7,3) and (6,5) SWNTs-C₃H₄Me₂ ($\text{mod}(n-m,3) = 1$) in red-shifted region can be explained by the thermodynamic rearrangement from the 1,2-L₊₊ isomer to 1,2-L₊.¹⁹ The two PL peaks exhibited by (6,4), (8,3), and (7,5) SWNTs-C₃H₄Me₂ may be attributed to the 1,2-L₊₊ and 1,2-L₋ isomers, which show small energy differences. Relatedly, it was reported that the spin densities at the 1,2-L₋ carbon

atoms of butylated (6,4), (8,3), and (7,5) SWNT radicals (0.1571, 0.1564, 0.1568) were slightly higher than those at the 1,2-L₊ carbon atoms of butylated (7,3), (6,5), and (8,4) SWNT radicals (0.1440, 0.1479, 0.1506), respectively.³⁰ However, further investigation is required to clarify the chiral index dependency. In addition, (6,4) SWNTs-C₃H₄Me₂ exhibited new PL peak at 1032 nm with an increase of the intrinsic E₁₁ PL; this can be explained by the thermodynamic rearrangement to the most stable 1,2-L₊ isomer. The PL wavelength is similar to that of a previously reported PL peak at 1015 nm in ⁷Bu-(6,4) SWNTs-H, for which the 1,2-L₊ binding configuration was proposed.²⁶ The thermal treatment of alkylated SWNTs^{11,36} and photo-irradiation of phenylated SWNTs³⁷ having two PL peaks emerged after functionalization was reported to increase the short- to long-wavelength PL intensity ratio. In contrast, a key factor in the thermal PL redshift is that cycloaddition affords kinetically controlled products, and the methyl groups promote the rearrangement reaction.

In conclusion, we demonstrate chirality- and diameter-dependent thermal rearrangement of addenda on SWNTs prompted by methyl groups competing with the elimination reaction. Functionalized SWNTs underwent chiral separation before and after thermal treatment and the optical properties of the products were analyzed. The results clarified that elimination reactions occur predominantly in adducts of large-diameter SWNTs, whereas competitive rearrangement reactions occur in smaller diameter (7,3) and (6,5) SWNTs-C₃H₄Me₂, resulting in redshifts in the PL wavelength. Conversely, without thermal treatment, (6,4), (8,3), and (7,5) SWNTs-C₃H₄Me₂ exhibited two PL peaks due to the substitution of methyl groups. The shift in PL wavelength beyond the optical communication wavelength range and the selectivity afforded by the substituent effect of methyl groups and thermal treatment provide a new perspective on the design and structural analysis of functionalized SWNTs.

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Conflicts of interest

There are no conflicts to declare.

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