Effect of the tether length of reagents with two reactive sites on the band gap of single-walled carbon nanotubes

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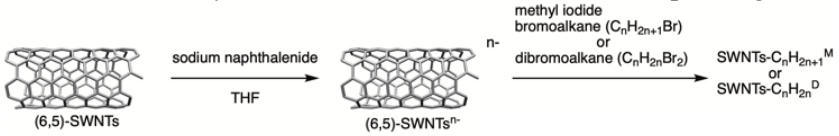
The structure of single-walled carbon nanotubes (SWNTs) can be defined by the chiral indices, (n,m), which specify its perimeter vector. Semiconducting SWNTs show characteristic photoluminescence (PL) peaks in the near-infrared region, with excitation and emission wavelengths dependent on the chiral index.[1] Recently, it has been revealed that the functionalization of SWNTs is effective to introduce quantum defects that emerge new PL in the red-shifted region. For instance, butylation of (6,5) SWNTs emerges PL at ~1100 nm (E_{11}^{*}) and ~1230 nm (E_{11}^{**}).[2] Additionally, (6,5) SWNTs functionalized using 1,2-bis(bromomethyl)benzene, which is structurally restricted to cycloadditions, resulted in the highly selective emergence of an E_{11}^{**} PL peak at 1231 nm. Recently, the reductive alkylation, as shown in the following scheme, SWNTs by using dibromoalkane ($C_nH_{2n}Br$, n = 3–5) showed a dominant peak in the range of 1215–1231 nm depending on the alkyl chain length of the dibromoalkane used.[3] These results suggested the cycloaddition to SWNTs by using dibromoalkanes.

Here, extending the previous scope in cyclization addition of SWNTs, SWNTs were reductively alkylated with a series of bromoalkanes ($C_nH_{2n+1}Br$, n = 1–4, 8) and dibromoalkanes ($C_nH_{2n}Br_2$, n = 3–8) to evaluate the effect of the length and bulkiness of the alkyl chain on the PL properties. The functionalization of SWNTs with dibromoalkanes ($C_nH_{2n}Br$, n = 3–5) exhibits a single E_{11}^{**} PL peak, whereas functionalization with dibromoalkanes with n = 6–8 emerged two new PL peaks (E_{11}^{*} and E_{11}^{**}PL), similar PL property with corresponding bromoalkanes. In addition, separation of functionalized SWNTs based on the chirality was conducted to reveal the effect of the functionalization on the PL properties in various SWNTs.[4,5] To gain insight into the origin of new PL peaks depending on the alkyl chain lengths of dibromoalkanes, the thermodynamic stabilities and transition energies of expected cyclization products were estimated by theoretical calculations for the corresponding model compound.



Scheme. Reductive alkylation of SWNTs.

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