

Tetracene Inclusion in Boron Nitride Nanotubes for Photoluminescence Property Modulation Based on Aggregated State Control in Their Nanocavity

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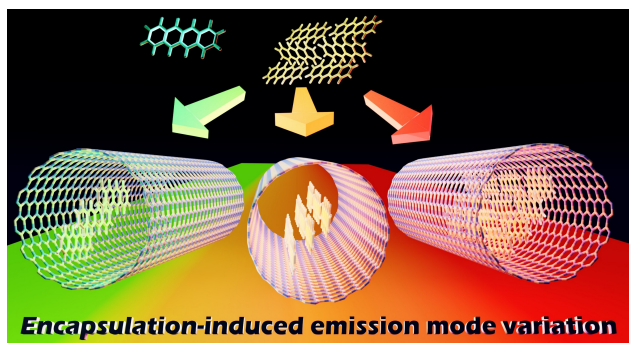
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ABSTRACT.

Boron nitride nanotubes (BNNTs) are used for the self-assembly of tetracene (Tc) molecules without chemical modification in their one-dimensional nanocavities. The Tc aggregated state can be changed depending on the encapsulated Tc amount that is controlled by the sublimation condition of Tc molecules for the complexation (Tc@BNNTs). As a result, the photophysical processes including singlet fission in the Tc assemblies are varied, which enables the emission mode switching of the aggregation-based fluorescence and the excimer emission for Tc@BNNTs. Consequently, the host-guest complexation using BNNTs allows not only the fabrication and evaluation of optically functionalized molecular assemblies in the nanocavity but also the modulation of their photophysical processes, by which the emission colors of Tc@BNNTs are also tuned.

TOC Graphic



Boron nitride nanotubes (BNNTs) are nanocylinders composed of rolled-up hexagonal boron nitride (hBN) sheets with ~ 100 nm diameter and $\sim \mu\text{m}$ length. The boron and nitrogen atoms in BNNTs are covalently bound with sp^2 hybridisation, wherein their atomic electronegativity difference enhances the chemical bonds by adding an ionic bond character.¹ Accordingly, BNNTs have wide bandgaps of 5–6 eV, independent of their tube diameter and chirality.² The photoabsorption and photoluminescence (PL) of BNNTs typically appear in the ultraviolet (UV) region, implying they are mostly transparent in the visible to near-infrared regions. Nanotubes, including BNNTs, can be used as host materials to encapsulate guest molecules in their cavities. Carbon nanotubes (CNTs),^{3, 4} structural analogues of BNNTs, have been widely studied. For example, photosensitization of CNTs through energy transfer from photo-absorbing guest dye molecules^{5, 6} and air-stabilization of carrier dopants for CNTs^{7, 8} in the host–guest complexes have been reported. BNNTs could offer an optically transparent host space that allows the spectroscopic evaluation of encapsulated molecules and the fabrication of optically functional nanomaterials through the host–guest chemistry approach. For example, sexithiophene (6T) has been encapsulated in BNNTs and spectral red-shifts of its photoabsorption and PL have been observed due to π conjugation expansion of conformationally elongated 6T in the nanocavity.^{9–11} Polyoxometalates have been encapsulated in BNNTs by an electron transfer process, as confirmed by the PL quenching of the BNNTs.¹² In another study, BNNTs were used as a template to synthesize other inorganic nanotubes in the cavity, and spectroscopic property evaluation of the synthesized materials was conducted.¹³

We selected tetracene (Tc) as a guest molecule for molecular aggregate formation in BNNTs because polyacenes, including Tc, show good singlet fission (SF) properties in solid states^{14, 15} and form J- and H-aggregates exhibiting optical properties different from those of its monomers.¹⁶ Thus far, the aggregated state control of polyacenes has been examined by the substituent modification in the polyacene skeletons¹⁷⁻¹⁹ and host-guest complexation using host materials of small molecules and metal-organic frameworks.²⁰⁻²⁴

We employed the one-dimensional (1D) nanocavities of BNNTs for Tc molecule assembly, wherein the sublimation of non-modified Tc was used to form the host-guest complex (Tc@BNNTs) (**Figure 1**). This approach helps avoid the possible problems associated with the existing methods, including the substituted Tc synthesis that may accompany complex synthesis and intrinsic property changes due to the introduced substituent effects. In the Tc@BNNTs, the Tc molecules formed different aggregated states depending on the encapsulated Tc amount in the BNNTs. Two types of emissions with longer wavelengths compared to that of monomeric Tc in the solution were generated for the Tc@BNNTs based on the Tc amount-dependent aggregate and excimer formation, respectively.

BNNTs used in this study were multiwalled tubes (the common layer number is double-wall) with a diameter of 2-6 nm.²⁵ Tc@BNNTs were fabricated by a sublimation method, wherein a mixture of purified and end-opened BNNTs (5.0 mg, Figure S1) and Tc (10.0 mg) was heated in a glass tube at 200 °C under a vacuum (~5 Pa). The resultant product was washed with methanol to remove Tc molecules attached to the outer surfaces of the Tc@BNNTs. As shown in the TEM images of Tc@BNNTs (Figure 1b), crystalline or

amorphous organic residues were hardly observed around the BNNTs. The magnified TEM images (Figure 1c and Figure S2) similarly showed that most of the outer surfaces of BNNTs were clean and the encapsulated molecules inside BNNTs were observed. These results indicate that the optical signals of Tc@BNNTs originate primarily from the Tc molecules encapsulated within the BNNTs. The Fourier- transform infrared (FT-IR) spectrum of the Tc@BNNTs (Figure S3 and Table S1) showed peaks

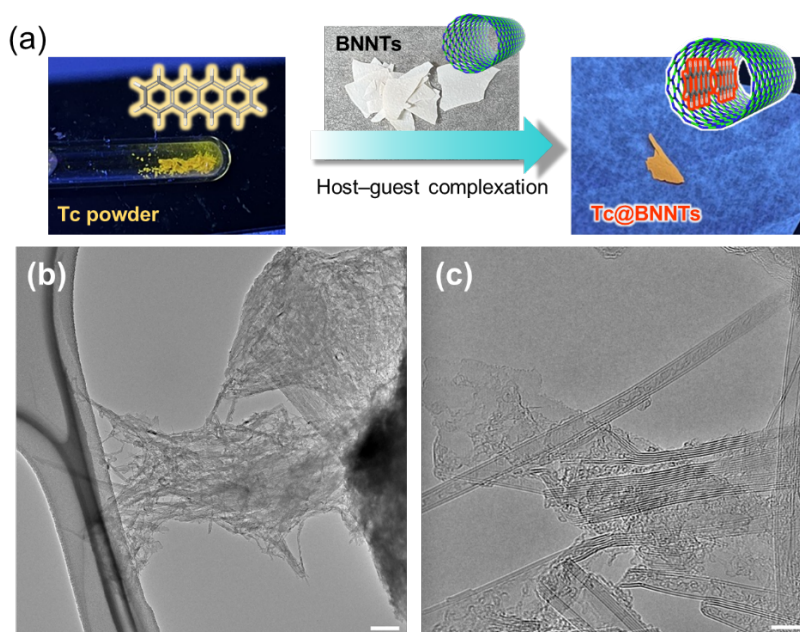
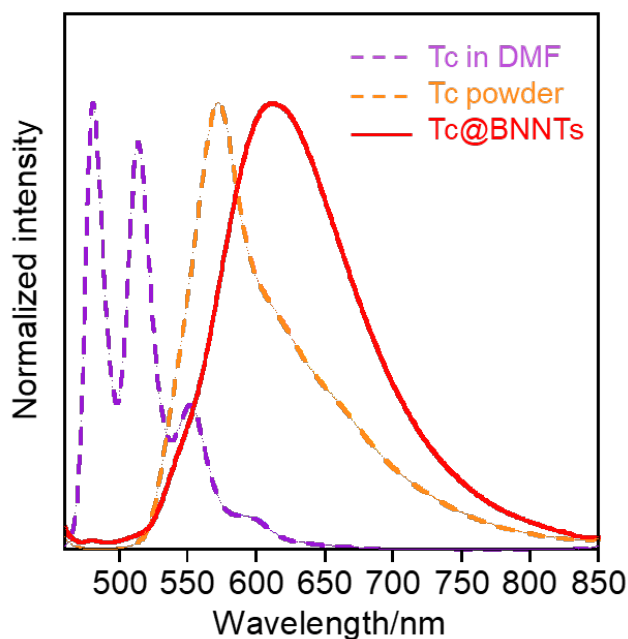


Figure 1. Schematic image of Tc@BNNT formation with fluorescence photos obtained for Tc powder and Tc@BNNTs under UV light (365 nm). TEM images of Tc@BNNTs at (b) low and (c) high magnification. Scale bars: (b) 100 nm and (c) 5 nm, respectively.

at 740, 799, 903, 1368, and 3045 cm^{-1} , assigned to the vibrational modes of Tc²⁶ and BNNTs,²⁷ indicating the coexistence of Tc and BNNTs in the prepared Tc@BNNTs. The PL spectra of Tc in a *N,N*-dimethylformamide (DMF) solution, Tc powder, and Tc@BNNTs in a solid state are presented in Figure 2. The Tc in DMF shows peaks at 481, 514, and 552 nm, attributed to the vibrational PL signals of Tc.²⁸ For the Tc powder, a peak appears at 572 nm, which is red-shifted compared to those of the Tc in DMF owing to the aggregation of Tc molecules in the solid state²⁸. For the Tc@BNNTs, PL appears at 612 nm, which is further red-shifted compared to the PL wavelength of the Tc powder. In the absorption spectrum of Tc@BNNTs (Figure S4), the absorption band was red-shifted compared to those for the Tc solution and Tc powder, with an absorbance increase in the ≥ 600 nm wavelength region. Typically, factors that induce spectral red-shifts for molecular aggregates with a J-type arrangement are the sharpening of the aggregate angles and an increase in the number of molecules forming the aggregates.^{29,30} Thus, the observed spectral red-shifts of the Tc@BNNTs suggest different Tc molecular packing in the Tc aggregates between the Tc@BNNTs and Tc powder.

To investigate the origin of the 612 nm emission observed for the Tc@BNNTs, PL lifetime



and PL quantum yield (PLQY) measurements were conducted. For the PL lifetime estimation, the obtained PL decay curves of Tc in DMF, Tc powder, and Tc@BNNTs were analyzed based on first-, second-, and third-order fitting models, respectively (Table S2 and Figure S5). For the Tc in DMF, a single lifetime $\tau_1 = 4.08$ ns was detected, identical to the reported value.²⁸ The small τ_1 values for the Tc powder and Tc@BNNTs (< 1 ns) indicated the existence of an SF process

Figure 2. PL spectra of Tc in DMF solution (purple), solid-state of Tc powder (orange), and Tc@BNNTs (red). $\lambda_{\text{ex}} = 441$ nm.

forming a T_1 pair from an S_1 state.³¹ Characteristically, the Tc@BNNTs had relatively large contributions from the long-lifetime components of τ_2 and τ_3 (39% and 10%, respectively), and $\tau_3 = 8.87$ ns was longer than $\tau_1 = 4.08$ ns for the Tc in DMF. In addition, the PLQY for Tc@BNNTs was 0.012, compared to 0.006 for the Tc powder. In the literature,^{19, 32} such long-lived components were generated based on excimer emission because, in excimers, energetic stabilization of the excited state occurs compared to the monomeric state.³³ In a previous study,¹⁹ a tetracene dimer embedded in a polymer matrix showed excimer state stabilization, resulting in a PL red-shift. Therefore, in Tc@BNNTs, the excimer state would stabilize through Tc encapsulation in the rigid BNNT cavity for the observed longer wavelength PL. The shorter lifetime compared to those (> 20 ns) of typical excimers^{34, 35} may be due to slight disorder from the face-to-face Tc molecular packing in the Tc@BNNTs.³⁴ In the time-resolved photoluminescence (TR-PL) measurements for the Tc@BNNTs (Figures S6 and S7),

two PL peaks were detected depending on the detection time scale; specifically, the 612 nm emission assignable to the excimer emission mainly appeared after 1 ns, and the 572 nm emission assignable to the aggregate fluorescence occurred before 1 ns. For the Tc powder, while a similar tendency was observed, the main PL peak was the 572 nm emission in the different detection time scale measurements. The PL intensity of the Tc@BNNTs increased under magnetic fields (Figure S8), indicating that, in Tc molecules assembled in BNNTs, SF produces triplet pair states, and the magnetic fields inducing Zeeman splitting of the triplet pair states enhance triplet–triplet annihilation to increase the radiative relaxation efficiency for the observed PL brightening.³⁶ The maximum relative PL intensity for the Tc@BNNTs was smaller than that for the Tc powder, probably due to the existence of the excimer emission process for the Tc@BNNTs. Furthermore, in the excitation spectrum of the Tc@BNNTs (Figure S9, $\lambda_{em} = 612$ nm), peaks were observed at 414, 440, and 469 nm, possibly corresponding to the photoabsorption of monomeric-state Tc. In contrast, the emission of the Tc powder ($\lambda_{em} = 572$ nm) was generated by more red-shifted photoabsorption corresponding to the Tc aggregate.³⁷ These results indicate that the 612 nm emission observed for the Tc@BNNTs can be assigned to the excimer emission of Tc.

A control experiment using hBN instead of BNNTs confirmed the importance of the BNNT nanocavity for the excimer generation from the encapsulated Tc molecules. Specifically, Tc molecules were sublimated to be mounted on a two-dimensional sheet of hBN via the same experimental method used for Tc@BNNT preparation. In the PL measurements, the resultant complex (Tc/hBN) showed a peak at 571 nm assignable to the Tc aggregate. Both the PL and

excitation spectra for the 571 nm emission were mostly identical to those of the Tc powder (Figure S10 and S11). These results indicate that the Tc molecules on hBN form a herringbone arrangement³⁸ like the behaviour observed for the Tc powder possessing a crystalline structure (Figure S12). In contrast, for the Tc@BNNTs, the BNNT 1D nanocavity offers a unique molecular assembly space for the formation of the Tc aggregates showing excimer emission (Figure S11), probably due to interfacial interactions with the BNNT walls in the confined nanospace.

The encapsulated Tc amount dependency was also studied using Tc@BNNTs fabricated under different mixing ratios of Tc to BNNTs ($x:1$, $x = 0.05, 0.1, 1, 2$). The products were denoted as Tc@BNNTs($x:1$); Tc@BNNTs(2:1) is the sample discussed above. In the thermogravimetric analysis (TGA), the encapsulated Tc molecule amounts for Tc@BNNTs($x:1$) were estimated from the observed weight loss at 200–500°C corresponding to Tc degradation (Figure S13 and Table S3). The results show that the encapsulated Tc molecule amounts for Tc@BNNTs($x:1$) increased when the mixing ratio of Tc was increased from 0.05:1 to 2:1. Based on the weight loss values in the Table S3, the actual Tc:BNNT weight ratios were calculated to be 0.02:1, 0.06:1, 0.14:1, and 0.15:1 for Tc@BNNTs(0.05:1), (0.1:1), (1:1), and (2:1), respectively. In the absorption spectra of the solid-state Tc@BNNTs($x:1$) (Figure S14), the absorbance in the >500 nm region increased for all Tc@BNNTs($x:1$) compared to that of the Tc in DMF based on the aggregated formation. In addition, absorption peak red-shifts occurred according to the increase in the encapsulated Tc molecule amount for Tc@BNNTs($x:1$). Figure 3 shows the PL spectra of Tc@BNNTs($x:1$).

For Tc@BNNTs(0.05:1), a PL peak is observed at 545 nm. In its excitation spectrum (Figure S15), sharp absorption bands accompanying the vibrational structures were observed at 436, 464, and 495 nm, indicating dimer or several-molecule aggregation.³⁸ In sharp contrast, Tc@BNNTs(x:1) with $x \geq 0.1$ showed PL signals with decreased intensities for the ~ 550 nm emission originating from the Tc aggregates and increased intensities for the > 600 nm emission originating from the Tc excimer. Consequently, the peak wavelength is red-shifted from 550 to 612 nm (Figure 3). Similar PL changes from aggregate to excimer emission were reported in a Langmuir–Blodgett film composed of an indocarbocyanine dye and stearic acid when high surface pressures resulted in dense molecular packing.³⁹ Figure 4 depicts a schematic image of the relationship between the encapsulated Tc amount and the observed emission modes of the aggregate and excimer for Tc@BNNTs(x:1). The numbers of Tc molecules per a 10 nm length of BNNT were calculated using the estimated encapsulated Tc amounts for Tc@BNNTs(x:1) in the TGA measurements (for the detailed calculation method, see the Supporting Information). This analysis suggests that the typical Tc aggregation occurs for Tc@BNNTs(0.05:1), which contain two Tc molecules per 10 nm length of BNNT. Additionally, when the number of encapsulated Tc molecules per a 10 nm length of BNNT is more than six, i.e. Tc@BNNTs(x:1) ($x > 0.1$), a pronounced PL red-shift accompanied by spectral broadening was

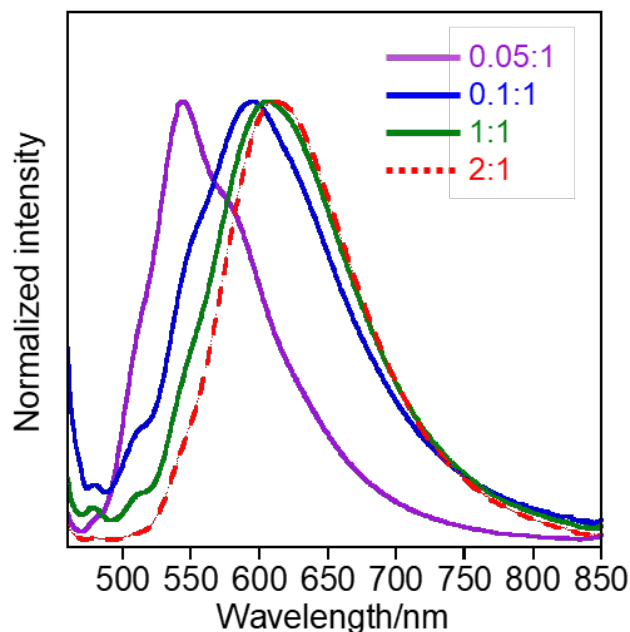


Figure 3. PL spectra ($\lambda_{\text{ex}} = 441 \text{ nm}$) of Tc@BNNTs(0.05:1, purple), Tc@BNNTs(0.1:1, blue), Tc@BNNTs(1:1, green), and Tc@BNNTs(2:1, red).

observed. This behaviour is characteristic of H-type aggregation, as described by Spano.⁴⁰ Given that the transition dipole moment of Tc lies along the short axis of the molecular backbone, a face-to-face stacking arrangement is required for the formation of H-aggregates.¹⁹ Therefore, the face-to-face aggregation of Tc in the BNNT nanocavity is suggested rather than the conventional herringbone crystalline structure of Tc.

We performed global analysis of the TR-PL data using a two-state sequential kinetic model (Figure S16) to quantitatively investigate differences in the excited-state dynamics. Tc powder exhibited a short PL lifetime ($\sim 260 \text{ ps}$) due to SF, as also observed in a PL lifetime measurement and low PLQY (Table S2 and Figure S5). This behavior is typically attributed to

the herringbone arrangement of the Tc crystalline structure which makes a significant matrix element between the S_1 state and the triplet pair state. In contrast, Tc@BNNTs exhibited qualitatively different PL behavior: the initial PL decays was elongated to >420 ps. This result indicates that the SF is suppressed in Tc@BNNTs compared to Tc powder, consistent with a less magnetic field effect observed for Tc@BNNTs (Figure S8). The suppression of SF in Tc aggregates by the BNNT encapsulation is explained by two contributions: (1) reduced electronic coupling in the face-to-face arrangement that is a different packing motif from the herringbone arrangement formed in the typical crystalline structure and (2) enlarged energy gap between S_1 and triplet pair states caused by lowering S_1 energy as evidenced by spectral red-shifts in Tc@BNNTs compared to Tc powder (Table S3). Consequently, the excitation energy is efficiently funneled into the lower-lying excimer state rather than SF, leading to enhanced excimer emission for Tc@BNNTs (Figure 4).

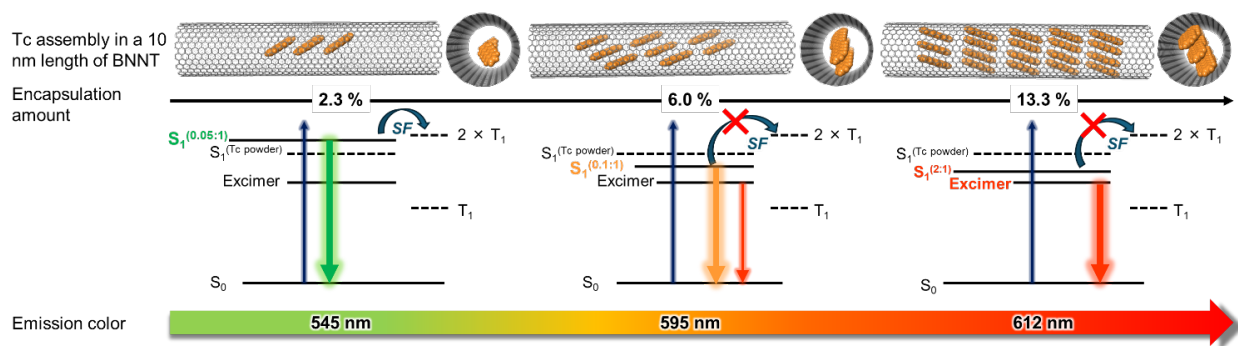


Figure 4. Schematic images of Tc@BNNTs($x:1$, $x = 0.05, 0.1$, and 2) showing different emission signals depending on the encapsulated Tc amount (wt%).

In this study, we used BNNTs as a 1D host nanomaterial for Tc molecule assembly. The BNNT transparency in the visible region enabled the optical characterization of the encapsulated Tc molecules. Absorption and PL spectral red-shifts for the Tc@BNNTs were observed compared to the monomeric Tc in DMF solution and the Tc powder forming the aggregate. Excitation spectroscopy results and spectral analyses using the fluorescence lifetime, PLQY, and TR-PL revealed that the largely red-shifted emission originated from the Tc excimer formation in the Tc@BNNTs. The comparison between the BNNTs and hBN revealed the importance of Tc molecule accumulation in the 1D nanocavity of BNNTs for producing the Tc molecular arrangement showing excimer emission. Moreover, in the Tc@BNNTs, the Tc assembled structures could be modulated simply by changing the amount of encapsulated Tc molecules through sublimation condition control. Consequently, different Tc emission modes of aggregates and excimers could be switched in the Tc@BNNTs based on the photophysical process control including SF, which provides emission color changes. Considering polyacenes have good optical and carrier transportation functions, our findings based on the host–guest chemistry using BNNTs will contribute to the development of 1D optoelectronic nanomaterials for device applications such as electronic devices with anisotropic carrier transport capability^{23, 41} and polarisation devices.¹⁰

ASSOCIATED CONTENT

Supporting Information.

Experimental details, experimental data including AFM images of BNNTs, FT-IR spectra, absorption spectra, PL lifetime decay, TR-PL spectra, magnetic field dependency of PL, excitation spectra, PL spectra, and TG curves (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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