Electronic supplementary information (ESI)

Room-temperature Y-type emission of perylenes by encapsulation within single-walled carbon nanotubes

Masayoshi Tange,* Toshiya Okazaki, Zheng Liu, Kazu Suenaga and Sumio Iijima

National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba 305-8565, Japan

*e-mail: masa-tange@aist.go.jp

Experimental Section.

We used single-walled carbon nanotubes (SWCNTs) of different diameters for perylene encapsulation. The first sample of SWCNTs had relatively small diameters (less than 1.3 nm); these were produced by the high-pressure carbon monoxide (HiPco) process (Carbon Nanotechnologies, Inc.). The other sample consisted of large-diameter SWCNTs synthesized by the arc discharging of a Ni–Y carbon rod (APJ-SSA, Meijo Nano Carbon Co., Ltd.). The SWCNTs were purified according to the procedure reported by Okubo *et al.*,[1] and the diameters (d_t) of the purified HiPco-SWCNTs and Arc-SWCNTs were 0.8–1.3 nm and 1.2–1.6 nm, respectively. Next, using the vapor-phase doping technique[2,3,4] for molecular encapsulation, we encapsulated perylenes, which were purchased from Tokyo Chemical Industry Co., Ltd., into the SWCNTs. First, the purified SWCNTs were heated at approximately 500 °C for 20 min, in order to open their ends. Next, the open-ended SWCNTs were placed along with perylenes in a quartz tube under vacuum (~1 × 10^{-4} Pa), and the quartz tube was sealed. In order to encapsulate the perylene molecules within the individual SWCNTs through sublimation, we heated the sealed quartz tube at 450 °C for 48 h. After the encapsulation of perylenes, in order to remove the excess perylenes adhering to the outsides of the SWCNTs, we rinsed the SWCNTs doped with the encapsulated perylenes (perylenes@HiPco-SWCNTs and perylenes@Arc-SWCNTs) with *n*-hexane and acetone. Next, we formed sheets of perylenes@SWCNTs via the filtration of the acetone solutions. Finally, the sheets were annealed at approximately 280 °C under vacuum.

The procedure used for preparing the solutions of the encapsulated perylene samples was as follows. The annealed perylenes@SWCNTs sample (approximately 0.1 mg) was added to D_2O (3 mL) along with 1 wt% sodium dodecylbenzene sulfonate (SDBS), and dispersed using a bath-type ultrasonicator. In addition, the dispersion was homogenized using a probe-type ultrasonicator (Sonics VCX130) operated at 65 W for 20 min. After further sonication in a bath, the resulting solution of well-dispersed perylenes@SWCNTs was ultracentrifuged at 147000 ×g for 1 h. The supernatant (i.e., upper 80% of the solution) was collected and used as the sample solution of encapsulated perylenes.

A mechanical mixture of SWCNTs and perylenes was prepared by grinding a control sample (approximately 0.2 mg) of SWCNTs, heating it at 450 °C for 48 h under vacuum, and adding perylenes (approximately 0.5 mg) to it using an agate mortar and pestle set. The mixture was added to D_2O (3 mL) along with 1 wt% SDBS and dispersed using the bath-type ultrasonicator. The solution was then homogenized using the probe-type ultrasonicator for 10 min. After further sonication in a bath, the solution of the well-dispersed mechanical mixture was ultracentrifuged at 147000 ×g for 1 h. The supernatant (upper 80% of the solution) was collected and used as the solution sample of the mechanical mixture.

High-resolution transmission electron microscopy (HRTEM) images of the encapsulated perylene samples were taken with a JEM-2010F transmission electron microscope (JEOL), operated at an acceleration voltage of 120 kV, according to a previously published protocol on molecular encapsulation.[4] The fluorescence spectra of the solution samples were measured with a spectrofluorometer (Horiba, SPEX fluorolog-3 TRIAX). Even though perylene exhibits an absorption peak centered at approximately 390 nm, for these measurements, we chose radiation with a wavelength of 380 nm as one of the excitation lights to avoid the effects of Raman scattering arising from the O–D stretching mode at 2500 cm^{-1} (in D_2O) on the shapes of the fluorescence spectra. The emission and excitation spectra of the encapsulated perylene samples were measured with a fluorescence spectrophotometer (Hitachi, F-4500). Further, the fluorescence decay curves were measured with a fluorescence lifetime spectrofluorometer (Horiba, FluoroCube) using pulsed light with wavelengths of 460 nm and 390 nm; the pulse duration was 1.2 ns.

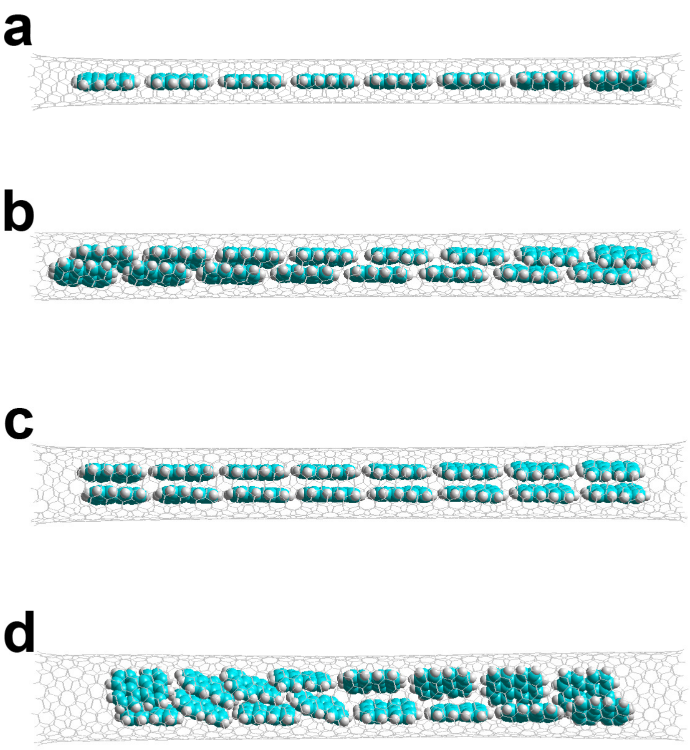

Fig. S1. Molecular arrangements of perylenes encapsulated within SWCNTs with different tube diameters (d_t) identified by chiral indices (n,m): (a) a monomeric chain in a (8,6) SWCNT (d_t=0.97 nm), (b) a dimeric chain in a (12,4) SWCNT (d_t=1.15 nm), (c) a dimeric chain in a (12,7) SWCNT (d_t=1.32 nm), and (d) a disordered dimeric structure in a (14,6) SWCNT (d_t=1.41 nm). The molecular arrangements were simulated by a molecular mechanics method with the Amber99 force field using HyperChem (Hypercube, Inc., version 8.0.10). For simulation, SWCNTs of about 10 nm in length were used; the ends of the structure of each SWCNT were capped with bonds to hydrogen atoms. The energy of the hybrid system consisting of perylene molecules and an SWCNT was minimized using conjugate gradient minimization to a root mean square (RMS) gradient of 0.001 kcal Å^{-1} mol^{-1}.

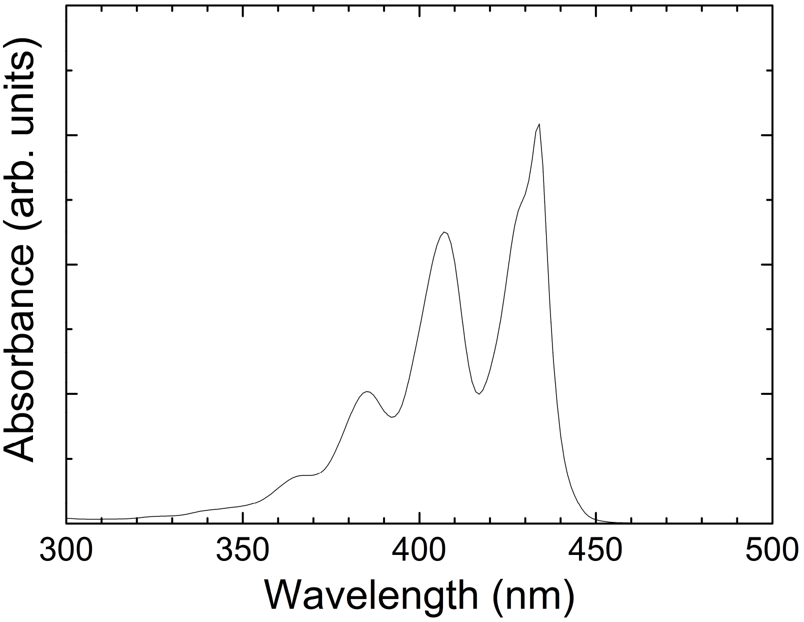

Fig. S2. Optical absorption spectrum of perylene in *n*-hexane (the concentration: 2×10^{-3} g/L). The spectrum was measured with a UV-VIS-NIR spectrophotometer (Shimadzu UV-3100PC).

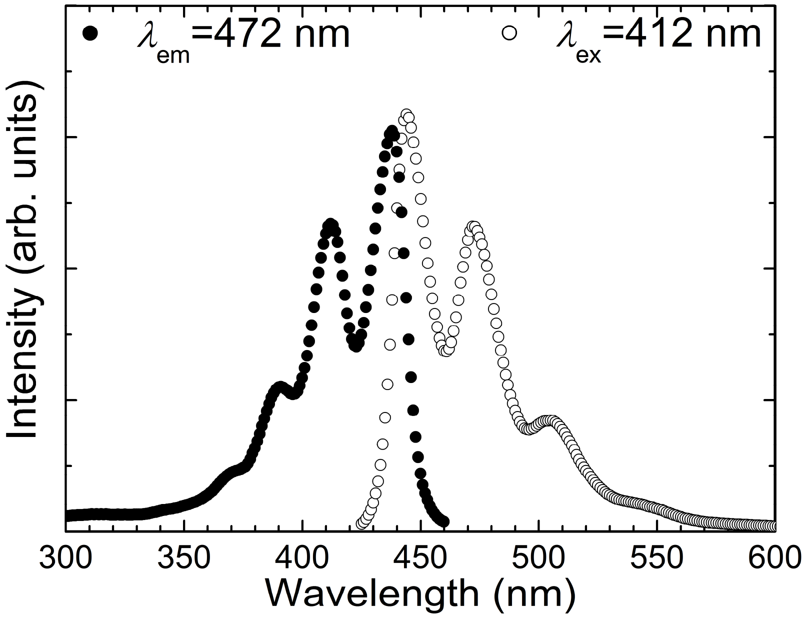

Fig. S3. Excitation and emission spectra of the mixture of perylenes and purified HiPco-SWCNTs in SDBS/D_2O. For the sample preparation, 1 wt% solution of SDBS was used following the dispersion process of perylenes@HiPco-SWCNTs.

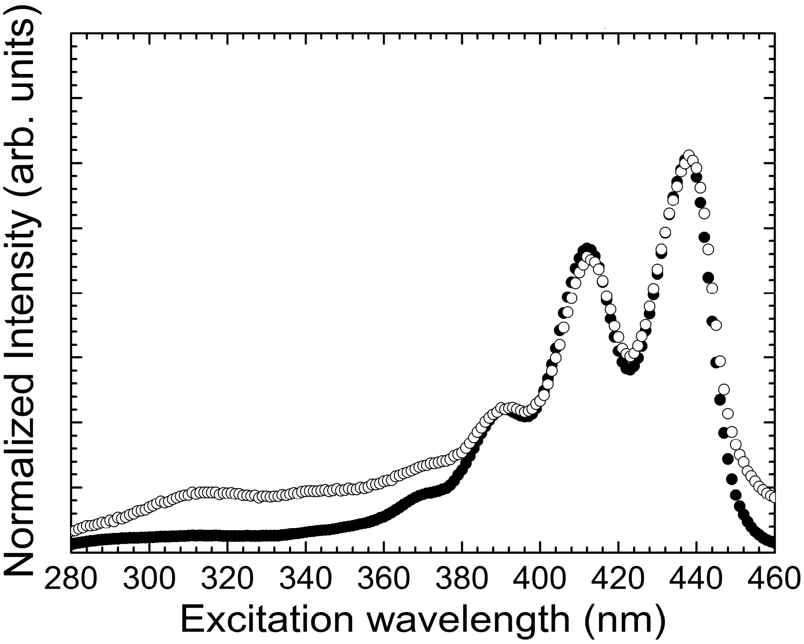

Fig. S4. Excitation spectra of perylenes@HiPco-SWCNTs (open symbols) and the mixture of perylenes and purified HiPco-SWCNTs (solid symbols) in SDBS/D_2O. The spectra were obtained at emission wavelengths of 473 nm (for perylenes@HiPco-SWCNTs) and 472 nm (for the mixture) at which the second vibronic peak of perylene emissions occurs.

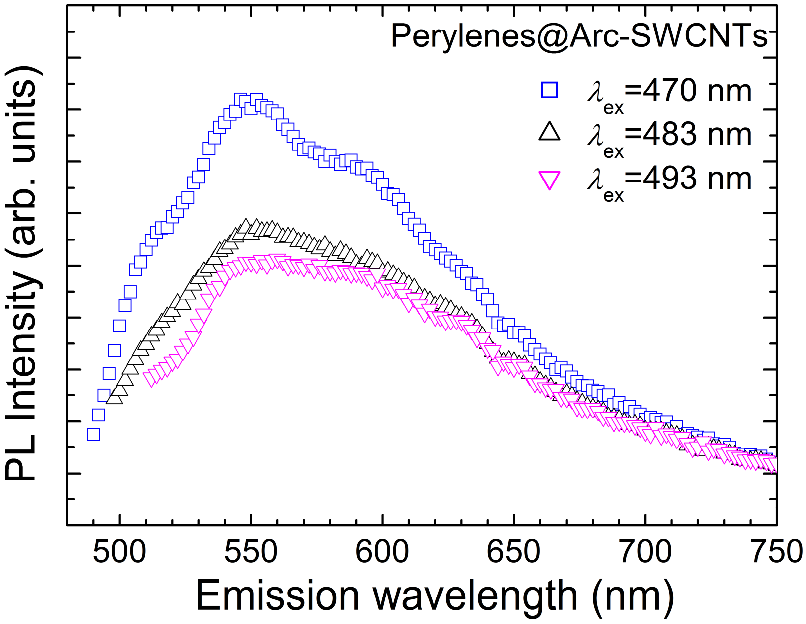

Fig. S5. Emission spectra of perylenes@Arc-SWCNTs in SDBS/D_2O obtained at different excitation wavelengths.

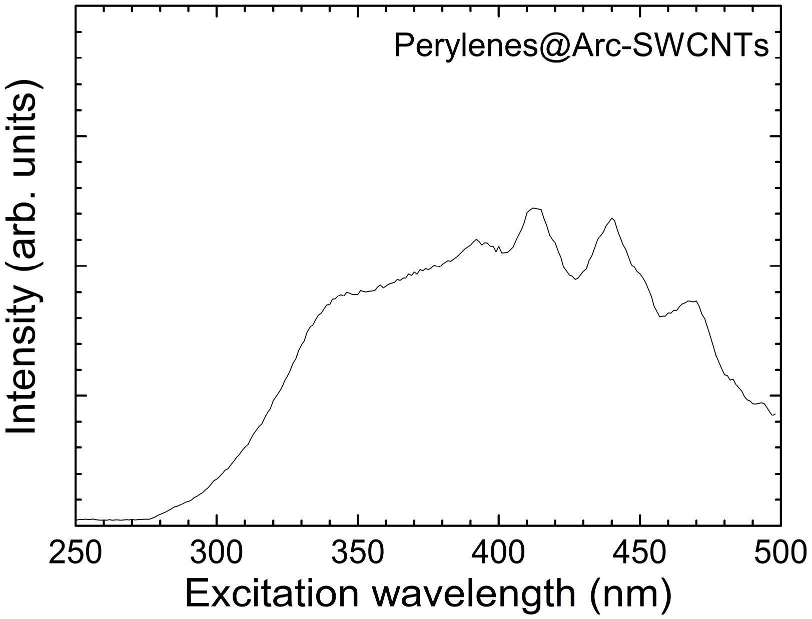

Fig. S6. Excitation spectrum of perylenes@Arc-SWCNTs in SDBS/D_2O. The spectrum for the disordered configurations of perylene was obtained at an emission wavelength of 508 nm.

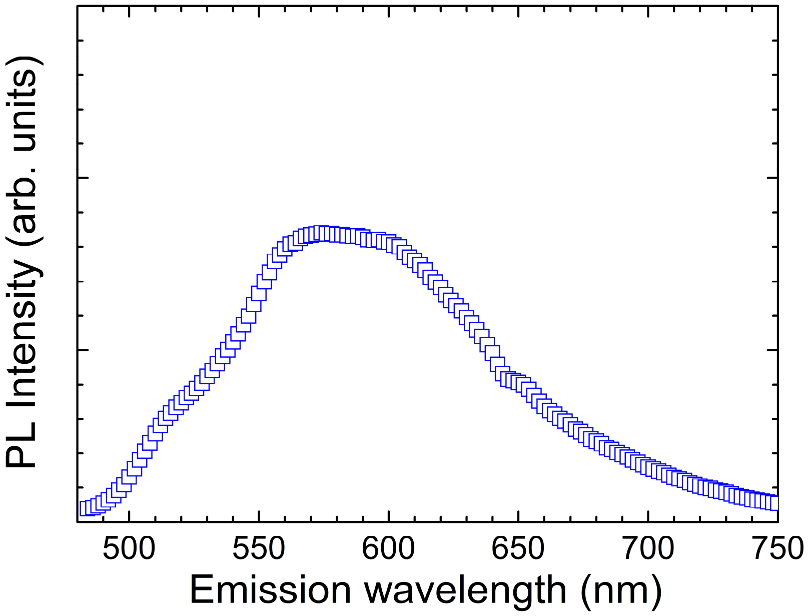

Fig. S7. Emission spectrum of a concentrated perylene solution (the concentration of perylene in SDBS/D_2O: 8×10^{-3} g/L). The E-emission was obtained at an excitation wavelength of 470 nm.

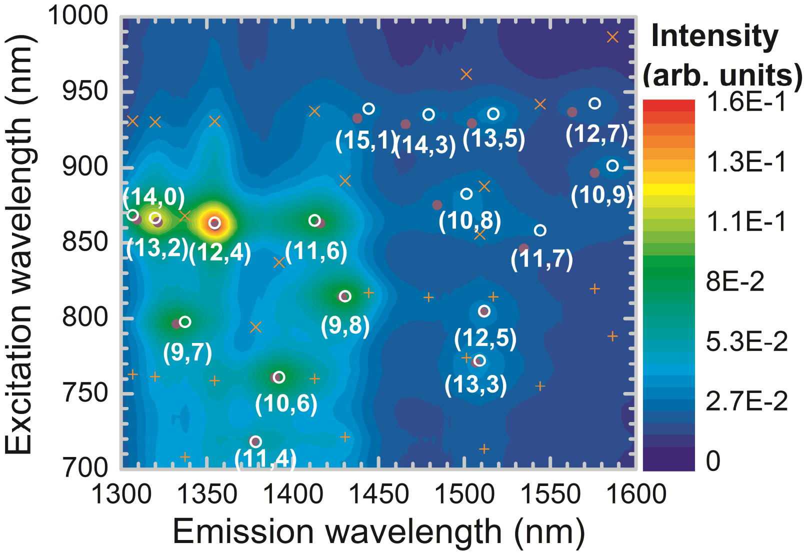

Fig. S8. Photoluminescence excitation (PLE) map of perylenes@HiPco-SWCNTs, with the PL peak positions of the different (*n*,*m*) types of SWCNTs. The PLE spectra were measured with a Shimadzu NIR-PL system with an IR-enhanced InGaAs detector (Princeton instruments, OMA-V2.2) for detection and a tunable Ti:sapphire laser (Spectra Physics, 3900S) for excitation. The open and closed circles represent the PL peak positions of perylenes@HiPco-SWCNTs and purified HiPco-SWCNTs in SDBS/D_2O, respectively. The observed PL peaks were assigned to different chiral indices (*n*,*m*) on the basis of a PLE spectroscopic study by Bachilo *et al.*[5] and the empirical functions by Weisman and Bachilo.[6] For each (*n*,*m*) SWCNT species in the PLE map, the positions related to the transverse excitonic resonance (the E_{12} and E_{21} transitions) and the phonon-coupled sideband (E_{22}+G)[7] are indicated by cross and plus symbols, respectively.

References.

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