Supporting Information

Synthesis and Photophysics of Quaterrylene Molecules in Single-Walled Carbon Nanotubes: Excitation Energy Transfer between a Nanoscale Cylinder and Encapsulated Materials

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Supporting results for encapsulation of quaterrylene molecules in SWNTs

We prepared rylene/SO-SWNT samples by heat treatment at 200 °C for 72 h. A Raman spectrum (blue curve) for a sample obtained using an excitation photon energy of 1.96 eV is shown in Figure S1. For comparison, the Raman spectrum for a rylene/SO-SWNT sample produced using a heat treatment of 400 °C for 15 h is shown by the red curve, and strong peaks attributed to quaterrylene molecules are observed at 1256, 1287, and 1361 cm^{-1} (for details, see the main text). The blue spectrum shows no strong Raman peaks due to quaterrylene molecules, indicating that such molecules were not synthesized in this sample. After the sample was annealed at 400 °C for 15 h, however, these peaks did appear, indicating the synthesis of quaterrylene molecules. Since quaterrylene molecules could not be synthesized by simply heating perylene powder in a sealed glass tube at 400 °C for 15 h, the one-dimensional confinement imposed by the SWNT is required.
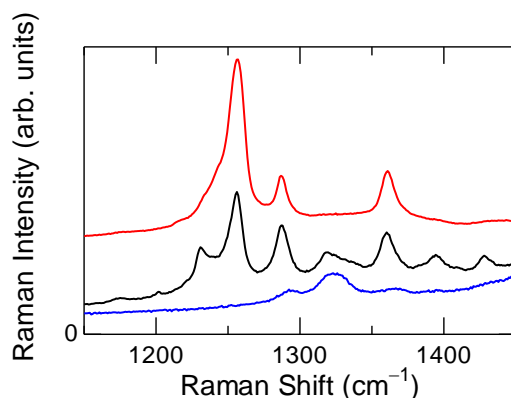

Figure S1. Raman spectra for rylene/SO-SWNT samples prepared by heat treatment at 400 °C for 15 h (red) and at 200 °C for 72 h (blue). The spectrum shown in black is that for a rylene/SO-SWNT sample prepared by heat treatment at 200 °C for 72 h, and then annealed at 400 °C for 15 h.

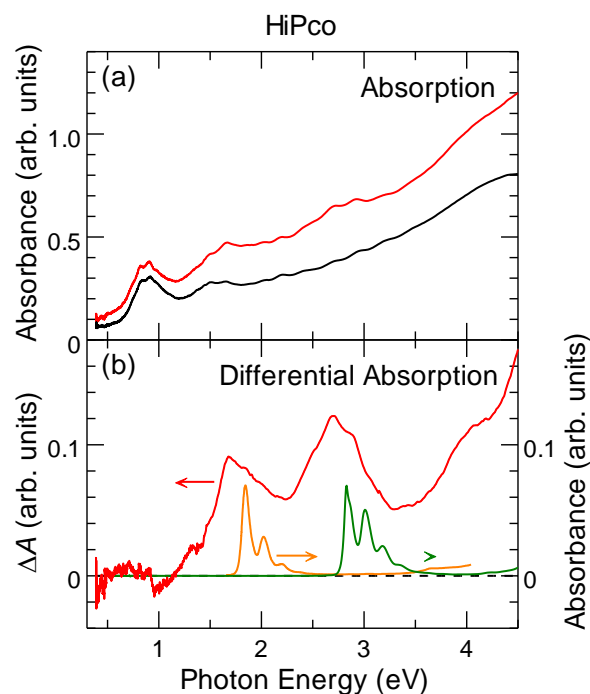**Absorption spectra for rylene/HiPco-SWNT and reference samples**

Figure S2. (a) Absorption spectra for rylene/HiPco-SWNT (red curve) and reference (black curve) samples. (b) Differential absorption spectrum (red curve) obtained by subtracting the absorption spectrum for the reference sample from that for the rylene/HiPco-SWNT sample in (a). Before subtraction, the spectrum for the reference sample is multiplied by a normalization factor and a background is added, to be fitted to the spectrum for the rylene/HiPco-SWNT sample below 1.2 eV. Absorption spectra for quaterrylene (orange curve) and perylene (green curve) molecules in 1,2,4-trichlorobenzene and tetrahydrofuran solvents, respectively, are also shown. The spectrum for the quaterrylene molecule is taken from ref [S1].

Estimation of energy separation between the H-type dimer and monomer transitions

We consider the point dipole approximation for simplicity. The energy of the dipole-dipole interaction E is given by $\frac{\mu_1 \mu_2}{4\pi\varepsilon\varepsilon_0 r^3}(2\cos\theta_1 \cos\theta_2 - \sin\theta_1 \sin\theta_2 \cos\phi)$, where $\mu_1(\mu_2)$ is the dipole moment of dipole 1(2), ε is the dielectric constant, ε_0 is the permittivity of the vacuum, r is the distance between the two dipoles, $\theta_1(\theta_2)$ is the angle of dipole 1(2) from the center-to-center direction of two dipoles, and ϕ is the rotation angle between the two dipoles. We consider the interaction between dipoles of the lowest excited states in two quaterrylene molecules; $\mu_1 = \mu_2 \equiv \mu$. (The dipole moment is parallel to the long axis of the molecule.) The TEM images indicate that the two quaterrylene molecules are in a face-to-face configuration; $\theta_1 = \theta_2 \equiv \theta$. Owing to the large aspect ratio of the quaterrylene molecule, the rotation angle between the two molecules is negligible in SWNTs; $\phi = 0$.

Consequently, E can be rewritten as $\frac{\mu^2}{4\pi\varepsilon\varepsilon_0 r^3}(1 - 3\cos^2\theta)$. The relationship among these parameters, μ, r, and θ, for the two molecules is schematically shown in Figure S3.

When we use the theoretical values of the transition energy $\hbar\omega$ (1.88 eV) and the oscillator strength per molecule f (1.17) of the quaterrylene molecule [S2], μ is obtained to be 2.47 C m. Assuming $\theta = 80°$, $r = 0.5/\sin\theta$ nm, and the dielectric constant is 1.5 [S3], we estimate $E = 0.16$ eV. When we use the experimental values of $\hbar\omega = 1.88$ eV and $f = 0.87$ for the quaterrylene derivative estimated from the molar absorption spectrum [S4], $E = 0.12$ eV is obtained. For various values of θ, E is calculated as listed in Table S1, indicating that the roughly estimated E is in the range ~0.1–0.2 eV. As two electrons are in the highest occupied molecular orbital, the energy separation between the H-type dimer and monomer transitions is $2E$, and is in the range ~0.2–0.4 eV.
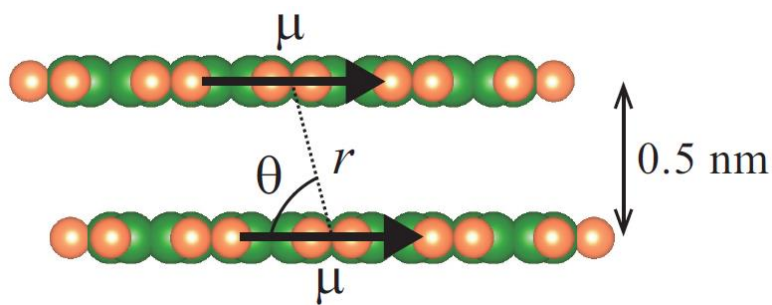
Figure S3. Schematic of two quaterrylene molecules.

Table S1. Energy of Dipole-Dipole Interaction E for Various Angles θ

θ	65°	70°	75°	80°	85°	90°
E_{theo} (eV)	0.063	0.098	0.13	0.16	0.18	0.18
E_{exp} (eV)	0.047	0.073	0.097	0.12	0.13	0.14

E_{theo} (E_{exp}) is calculated using the theoretical (experimental) values of the transition energy and oscillator strength.

ΔA spectra for rylene/semiconducting-SO-SWNT and reference samples

Figures S4a and S4b show the linear absorption and ΔA spectra for the reference sample, respectively. Figures S4c and S4d show the linear absorption and ΔA spectra for the rylene/semiconducting-SO-SWNT sample, respectively. The ΔA spectra for both samples were measured under resonant excitation conditions at 1.86 eV, corresponding to the quaterrylene absorption band. The ΔA spectra for the reference sample at different delay times in Figure S4b show five dips at 2.04, 2.18, 2.32, 2.48, and 2.62 eV, superimposed on the broad component with a positive sign in the spectral range from ~1.6 to 2.9 eV. The energies of the dip positions correspond to those of the peaks and shoulders in the linear absorption spectrum in the top panel (Figure S4a). These features are similar to those of the spectra observed in the previous study, and are attributed to spectral broadening and shift of the absorption bands of E_{33} and E_{44} excitons in the SWNTs [S5]. In the ΔA spectra for the rylene/semiconducting-SO-SWNT sample shown in Figure S4d, absorption changes due to the SWNTs are observed; in addition, remarkable differences are also observed in the range ~1.5−1.8 eV. The spectra for the rylene/semiconducting-SO-SWNT sample show an absorption decrease in this range, while those for the reference sample show an absorption increase. Since this spectral region corresponds to the quaterrylene absorption band (Figure S4c), the absorption decrease for the rylene/semiconducting-SO-SWNT sample may be attributed to bleaching of the quaterrylene absorption. Similar behavior of ΔA in the spectral range ~1.5−1.8 eV was observed for the rylene/DIPS-SWNT and reference samples, as shown in Figures S5a−S5d.
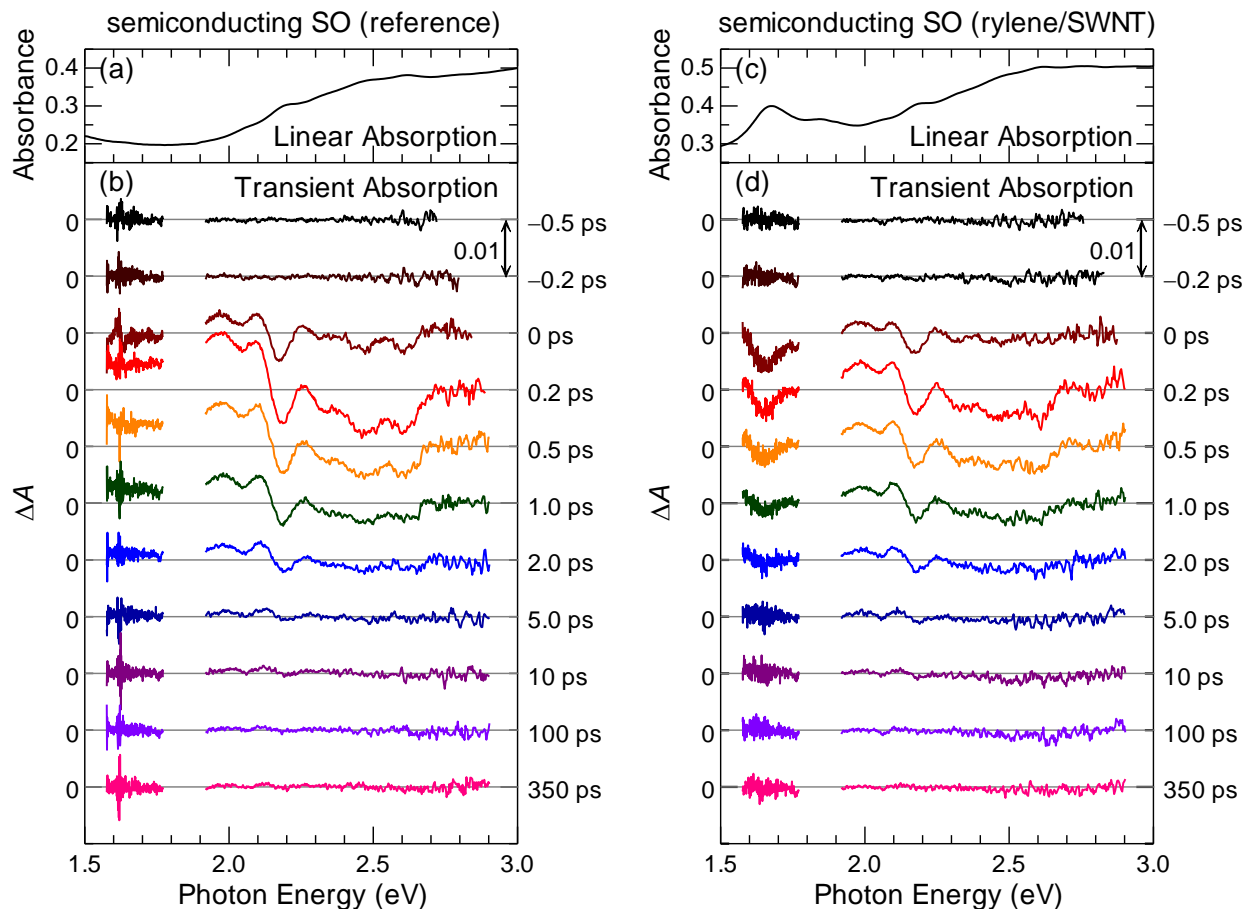
Figure S4. (a) Linear absorption spectrum and (b) differential absorption spectra ΔA for the reference sample. (c) Linear absorption spectrum and (d) differential absorption spectra ΔA for the rylene/semiconducting-SO-SWNT sample. The delay times are indicated on the right of the figures. The excitation photon energy is 1.86 eV, corresponding to the quaterrylene absorption band, and the pump fluence is 1.6×10^{16} photons cm^{-2} per pulse (4.8 mJ cm^{-2} per pulse). Because of the strong scattering of pump pulses, the absorption change in the region of ~1.8–1.9 eV cannot be observed.

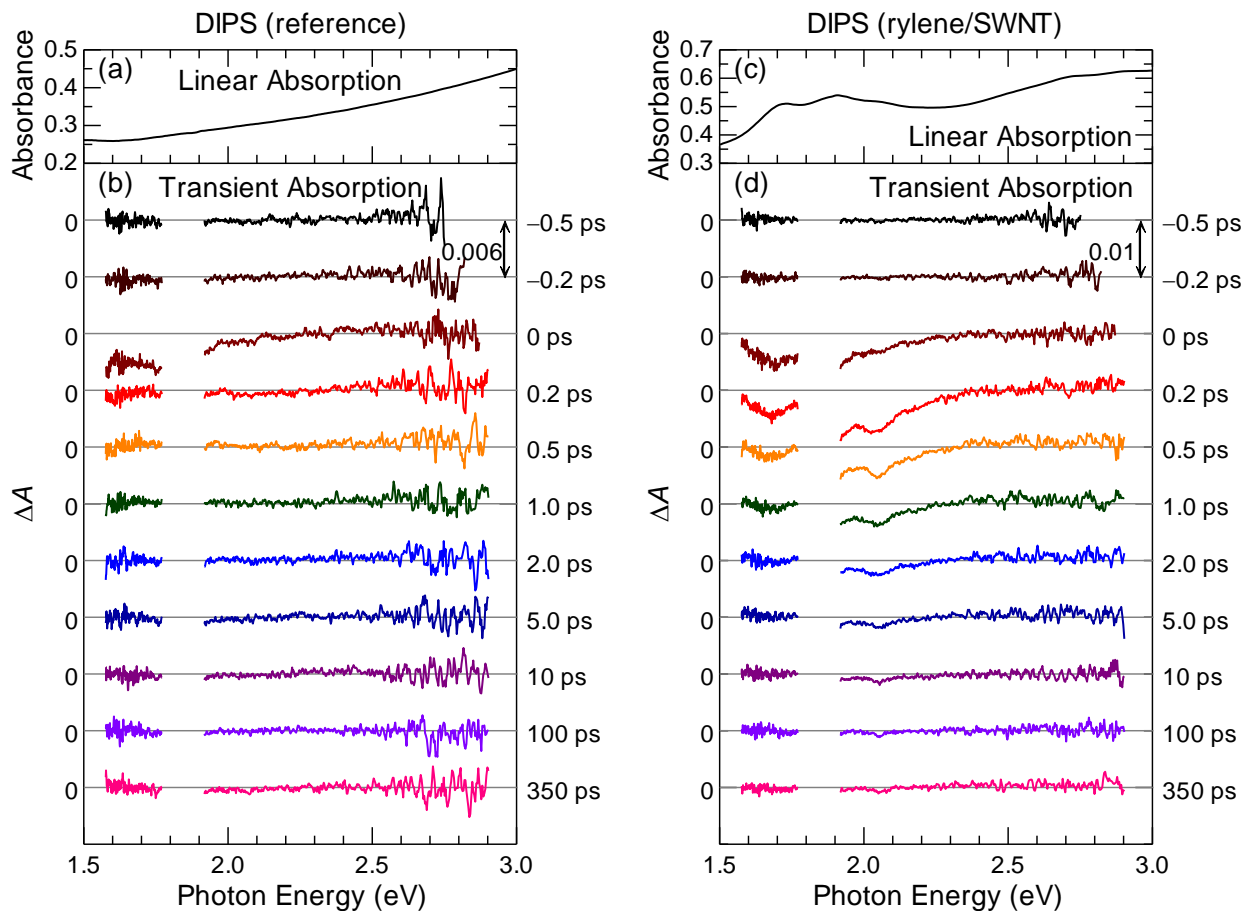## ΔA spectra for rylene/DIPS-SWNT and reference samples

Figure S5. (a) Linear absorption spectrum and (b) differential absorption spectra ΔA for the reference sample. (c) Linear absorption spectrum and (d) differential absorption spectra ΔA for the rylene/DIPS-SWNT sample. The delay times are indicated on the right of the figures. The excitation photon energy is 1.86 eV, corresponding to the quaterrylene absorption band, and the pump fluence is 1.6×10^{16} photons cm^{-2} per pulse (4.8 mJ cm^{-2} per pulse). Because of the strong scattering of pump pulses, the absorption change in the region of ~1.8−1.9 eV cannot be observed.

Time evolution of $\Delta(\Delta A)$ at various photon energies for rylene/DIPS-SWNT samples

Figure S6 shows the time evolution of $\Delta(\Delta A)$ at 1.65, 1.70, 1.74, 1.95, 2.00, 2.05, 2.10, 2.15, and 2.20 eV for the rylene/DIPS-SWNT samples. The decay curves at 1.65, 1.70, and 1.74 eV are fitted to a single exponential function $\propto \exp(-t/\tau)$ (black curve), and the curves at 1.95, 2.00, 2.05, 2.10, 2.15, and 2.20 eV are fitted to a double exponential function $\propto C\exp(-t/\tau_f) + (1-C)\exp(-t/\tau_s)$ (black curve). The obtained time constants and coefficients for the fast and slow components are listed in Table S2. The ratio of the coefficient for the fast component to that for the slow component decreases with increasing photon energy, which qualitatively corresponds to the absorption band of the quaterrylene monomer that has a peak at 1.65 eV (Figure 2). This correspondence suggests that bleaching of the absorption band of the quaterrylene monomer is occurring for the fast component above 1.95 eV.
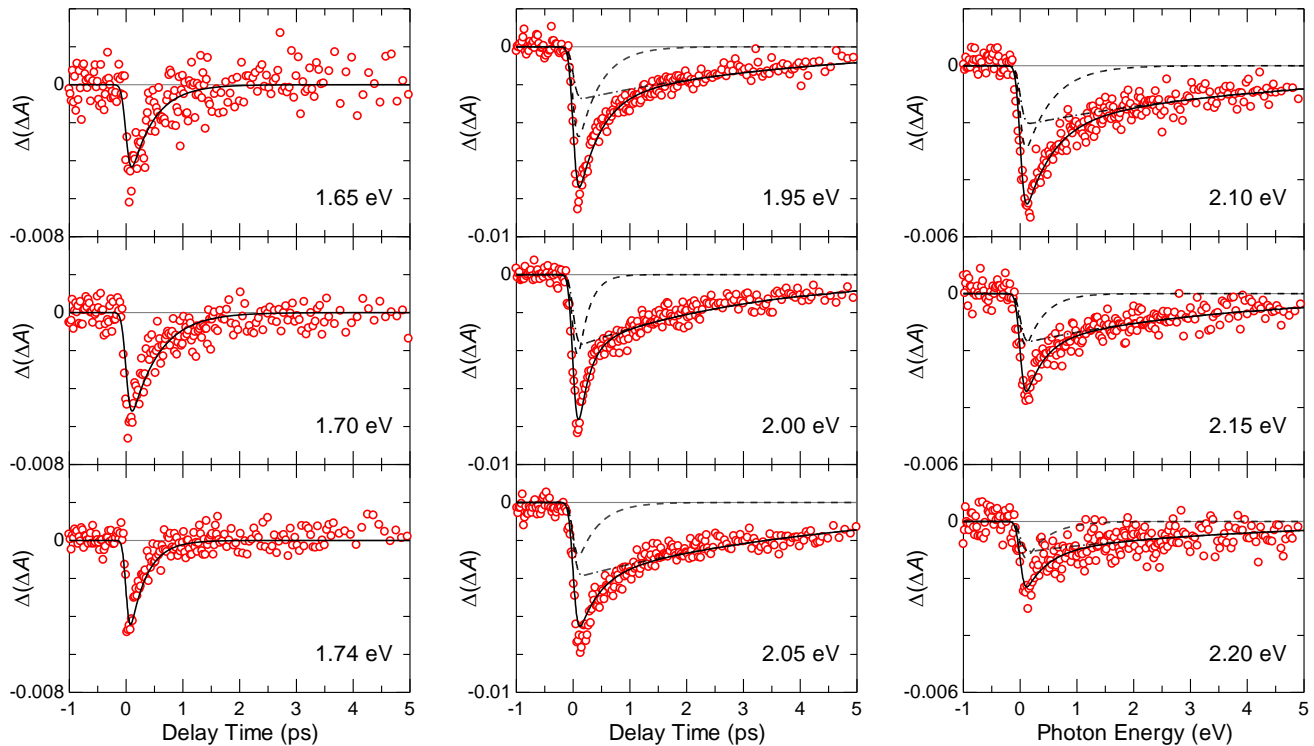

Figure S6. Time evolution of $\Delta(\Delta A)$ measured at 1.65, 1.70, 1.74, 1.95, 2.00, 2.05, 2.10, 2.15, and 2.20 eV for the rylene/DIPS-SWNT samples.

Table S2. Fitted Values of τ, τ_f, τ_s, and C

Photon Energy (eV)	1.65	1.70	1.74	1.95	2.00	2.05	2.10	2.15	2.20
τ (ps)	0.4	0.5	0.3						
τ_f (ps)				0.4	0.2	0.4	0.5	0.3	0.3
τ_s (ps)				4.1	3.3	4.9	5.2	3.8	3.8
C				0.70	0.65	0.50	0.64	0.60	0.60

Time evolution of $\Delta(\Delta A)$ at 2.15 eV for the rylene/semiconducting-SO-SWNT sample

Figure S7 shows the time evolution of $\Delta(\Delta A)$ at 2.15 eV for rylene/semiconducting-SO-SWNT sample. Similar to the rylene/DIPS-SWNT sample, the evolution exhibits double exponential decay and a slow decay component attributed to the dimers is certainly observed. The $\Delta(\Delta A)$ signal is smaller than that for the rylene/DIPS-SWNT sample, reflecting the low abundance of SWNTs encapsulating dimers. The smaller spectral weight in the energy range of 1.9–2.2 eV in the differential absorption spectrum for the rylene/semiconducting-SO-SWNT sample indicates that the amount of dimers in the ensemble of SO-SWNTs is smaller than that of DIPS-SWNTs. This is because the average tube diameters of SO-SWNTs (1.4 nm) is smaller than the threshold diameter (1.5 nm) at which dimers are formed in SWNTs. The small amount of dimers in SO-SWNTs causes the small absorption change due to dimers in pump-probe measurements.
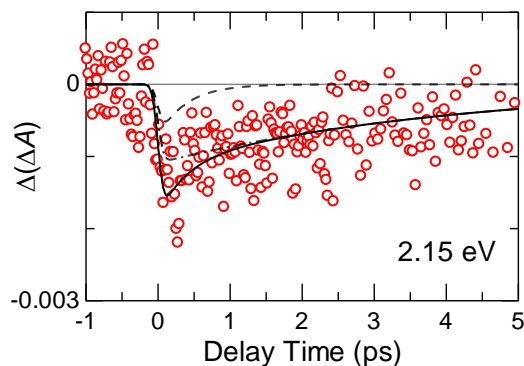

Figure S7. Time evolution of $\Delta(\Delta A)$ measured at 2.15 eV for the rylene/semiconducting-SO-SWNT sample.

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