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Interactions of functionalized carbon nanotubes with tethered pyrenes in solution

Liangwei Qu, Robert B. Martin, Weijie Huang, Kefu Fu, Daniel Zweifel, Yi Lin, and Ya-Ping Sun[a]
Department of Chemistry and Center for Advanced Engineering Fibers and Films, Howard L. Hunter Chemistry Laboratory, Clemson University, Clemson, South Carolina 29634-0973

Christopher E. Bunker, Barbara A. Harruff, and James R. Gord
Air Force Research Laboratory, Propulsion Directorate, WPAFB, Ohio 45433-7103

Lawrence F. Allard
High Temperature Materials Laboratory, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6062

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Single-wall carbon nanotubes (SWNTs) were functionalized by oligomeric species containing derivatized pyrenes. Absorption and emission properties of the pyrene moieties tethered to the functionalized SWNTs were studied in homogeneous solution. The absorption spectra suggest no significant ground-state complexation between the pyrenes and nanotubes. The fluorescence and fluorescence excitation results show that the tethered pyrenes form ‘‘intramolecular’’ (intra-nanotube) excimers and that the excimer formation is predominantly dynamic in nature. The time-resolved fluorescence results show that the pyrene monomer and excimer emissions are significantly quenched by the attached SWNTs. The quenching is explained in terms of a mechanism in which carbon nanotubes serve as acceptors for excited-state energy transfers from the tethered pyrene moieties. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1510745]

INTRODUCTION

Carbon nanotubes have attracted much recent attention for a variety of potential technological applications.[1,2] For example, carbon nanotubes have been used as physical dopants with conjugated polymers for the development of novel opto-electronic materials.[3,4] The doping effects are strongly dependent on interactions of aromatic moieties in the polymers with the nanotube graphitic surface. It has also been reported that pyrene derivatives could be attached to the graphitic surface of a single-wall carbon nanotube (SWNT) via π-stacking type interactions.[5] The functional groups on the nanotube-attached pyrene moieties were used to link natural proteins for the biological modification of carbon nanotubes.[5] These examples have demonstrated the need for a fundamental understanding of interactions between carbon nanotubes and aromatic molecules on the nanotube surface.

The solubilization of carbon nanotubes via chemical functionalization offers unique opportunities to study the nanotube-molecule interactions in homogeneous solution.[6] Carbon nanotubes are known to contain surface-bound carboxylic acids,[7–9] which have been used to attach functional groups via amide or ester linkages.[6,9–20] We have previously shown that carbon nanotubes can be functionalized with lipophilic and hydrophilic dendron species to be made soluble in a variety of common solvent systems.[16,17] Here we report the preparation and spectroscopic study of the functionalized SWNTs with tethered pyrene moieties. The fluorescence results show that there are significant emission contributions from pyrene excimers in the functionalized SWNTs in solution and that the carbon nanotubes serve as efficient quenchers for the pyrene photoexcited states.

EXPERIMENT

Materials

Methyl 3,5-dihydroxybenzoate (98%) and 18-crown-6 (98%) were purchased from Avocado Research Chemical Ltd., 1-bromohexadecane (99%) and thionyl chloride (99.5+%) from Acros, 1-pyrenemethanol (98%) from Aldrich, and lithium tetrahydridoaluminate (95%) from Alfa Aesar. Solvent grade THF was distilled over sodium before use, and other solvents were either of spectrophotometry/HPLC grade or purified via simple distillation. Poly(methyl methacrylate) (PMMA) with an average molecular weight of 350 000 was also purchased from Acros. Deuterated NMR solvents were obtained from Cambridge Isotope Laboratories.

The SWNT sample was supplied by Professor A. M. Rao of Physics Department, Clemson University.[21] It was purified by using an established procedure already reported in the literature.[7,22]

Methyl 3-hydroxy-5-hexadecoxy benzoate (I)

1-Bromohexadecane (1.83 g, 6 mmol) was added to a solution of methyl 3,5-dihydroxybenzoate (2 g, 11.9 mmol), potassium carbonate (8.1 g, 58.6 mmol), and 18-crown-6 (0.25 g, 0.94 mmol) in THF-acetonitrile (150 mL–30 mL). After the mixture was refluxed for 10 h, the solvent was removed on a rotary evaporator. The sample was redissolved

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[a] Author to whom correspondence should be addressed. Electronic mail: syaping@clemson.edu

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in chloroform. The chloroform solution was washed with water several times and then dried with anhydrous $MgSO_4$. The crude product was purified using silica gel column chromatography with chloroform as eluting solvent (43% yield). ^{1}H-NMR (500 MHz, $CDCl_3$): δ=0.88 (*t*, *J*=7.10 Hz, 3*H*), 1.20–1.40 (*m*, 24*H*), 1.40–1.55 (*m*, 2*H*), 1.7–1.79 (*m*, 2*H*), 3.90 (*s*, 3*H*), 3.97 (*t*, *J*=6.9 Hz, 2*H*), 5.22 (*s*, 1*H*), 6.60 (*s*, 1*H*), 7.11 (*s*, 1*H*), 7.15 (*s*, 1*H*) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$): δ=14.21, 22.78, 26.00, 29.45, 29.65, 29.68, 29.74, 29.78, 32.01, 52.36, 68.45, 107.05, 107.91, 108.95, 132.11, 156.65, 160.50, 166.92 ppm.

1-Pyrenemethanchloride (II)

Thionyl chloride (0.98 g, 7.6 mmol) was added to a solution of 1-pyrenemethanol (1.5 g, 6.4 mmol) in toluene (50 mL). After it was refluxed for 12 h, the solution was washed with water several times and then dried with anhydrous $MgSO_4$. The product was obtained after the removal of toluene on a rotary evaporator (~100% yield). ^{1}H-NMR (300 MHz, $CDCl_3$): δ=5.33 (*s*, 2*H*), 8.0–8.40 (*m*, 9*H*). ^{13}C-NMR (75 MHz, $CDCl_3$): δ=44.98, 123.0, 124.96, 125.88, 126.00, 127.50, 127.80, 128.25, 128.50, 129.0, 130.8, 131.0, 131.5, 132.0 ppm.

Methyl 3-hexadecoxy-5-pyrenemethoxyl benzonate (III)

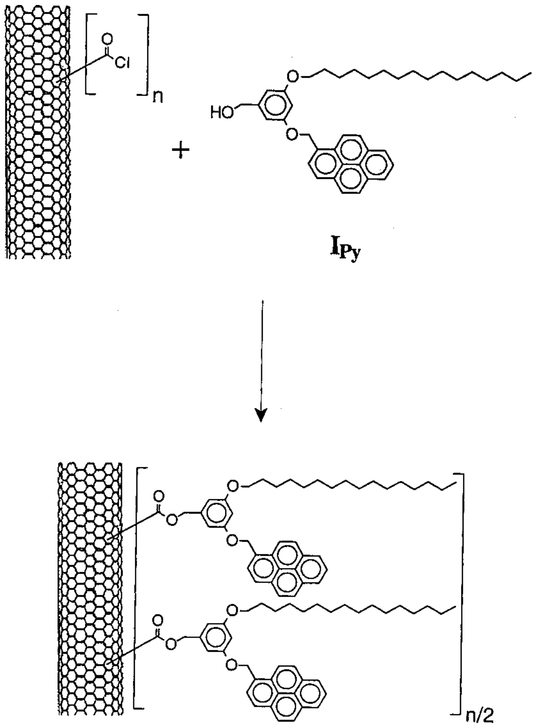
A solution of **I** (1 g, 2.6 mmol), **II** (0.64 g, 2.6 mmol), potassium carbonate (0.42 g, 3 mmol), and 18-crown-6 (0.2 g, 0.75 mmol) in THF-acetonitrile (20 mL–100 mL) was refluxed for 20 h. After the removal of solvent on a rotary evaporator, the solid sample was redissolved in chloroform. The chloroform solution was washed with water several times and then dried with anhydrous $MgSO_4$. The crude product was purified using silica gel column chromatography with chloroform as eluting solvent (98% yield). ^{1}H-NMR (500 MHz, $CDCl_3$): δ=0.88 (*t*, *J*=7.05, 3*H*), 1.25–1.50 (*m*, 26*H*), 1.70–1.90 (*m*, 2*H*) 3.85–4.10 (*m*, 5*H*), 5.75 (*s*, 2*H*), 6.83 (*s*, 1*H*), 7.25 (*s*, 1*H*), 7.43 (*s*, 1*H*), 7.90–8.40 (*m*, 9*H*) ppm, ^{13}C-NMR (125 MHz, $CDCl_3$); δ=14.22, 22.79, 26.00, 29.46, 29.66, 29.69, 29.79, 32.02, 52.36, 68.48, 69.14, 107.12, 107.88, 108.47, 123.08, 124.75, 125.04, 125.52, 125.56, 126.14, 127.07, 127.46, 127.82, 128.24, 129.39, 130.82, 131.30, 131.75, 132.10, 159.97, 160.36, 167.01 ppm.

3-Decyloxy-5-pyrenyloxyphenylmethan-1-ol (I_{Py})

Lithium tetrahydridoaluminate (0.12 g, 3.1 mmol) was added to a solution of **III** (1.6 g, 2.6 mmol) in dry diethyl ether (25 mL). After the solution was refluxed for 8 h, water (2 mL) was added to quench the reaction. The reaction mixture was filtered to yield the crude product, followed by purification using silica gel column chromatography with chloroform as eluting solvent (93% yield). ^{1}H-NMR (500 MHz, $CDCl_3$): δ=0.88 (*t*,*J*=7.0 Hz, 3*H*), 1.25–1.44 (*m*, 26*H*), 1.72–1.79 (*m*, 2*H*), 3.94 (*m*, 2*H*), 4.66 (*s*, 2*H*), 5.72 (*s*, 2*H*), 6.59–6.74 (*m*, 3*H*), 7.90–8.60 (*m*, 9*H*) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$): δ=14.24, 22.80, 26.00, 29.47, 29.68, 29.71, 29.80, 32.03, 65.51, 68.23, 68.90, 101.10, 105.36, 105.78, 122.0–132.0 (15*C*), 143.48, 160.37, 160.72 ppm.

I_{Py}-SWNT

The functionalization of SWNTs with $\mathbf{I_{Py}}$ was accomplished via the esterification of the nanotube-bound carboxylic acids.[16,17] In a typical experiment, a purified SWNT sample (15 mg) was treated in concentrated HCl solution to fully recover the carboxylic acid groups on the nanotube surface, followed by refluxing the sample in thionyl chloride for 24 h to convert the carboxylic acids into acyl chlorides. After a complete removal of residual thionyl chloride on a rotary evaporator with a vacuum pump, the nanotube sample was mixed well with carefully dried $\mathbf{I_{Py}}$ (150 mg, 0.26 mmol) in a flask, heated to 90 °C, and vigorously stirred for 24 h under nitrogen protection. The reaction mixture was extracted repeatedly with chloroform to obtain a dark-colored homogeneous solution. After the evaporation of solvent chloroform, the mixture was purified to remove unreacted $\mathbf{I_{Py}}$ by Soxhlet extraction with acetone for 48 h. The $\mathbf{I_{Py}}$-SWNT sample was obtained by drying under vacuum at 60 °C for 24 h. ^{1}H-NMR (500 MHz, $CDCl_3$): δ=0.4–1.9 (broad), 3.0–7.0 (broad), 7.0–9.0 (broad) ppm; ^{13}C-NMR (500 MHz, $CDCl_3$): δ=14.22, 22.8, 26.0, 29.47, 29.80, 32.0, 120.0–134.0 (broad) ppm.



The $\mathbf{I_{Py}}$-SWNT sample is soluble in common organic solvents such as chloroform, THF, and toluene. Results from the characterization using transmission electron microscopy (TEM, Fig. 1), defunctionalization in thermal gravimetric analysis (TGA), and Raman spectroscopy confirm that the sample contains functionalized SWNTs.

Measurements

UV/vis absorption spectra were recorded on either a Shimadzu UV2101-PC or a Perkin Elmer Lambda 900 spectrophotometer. Fluorescence spectra were measured on either a

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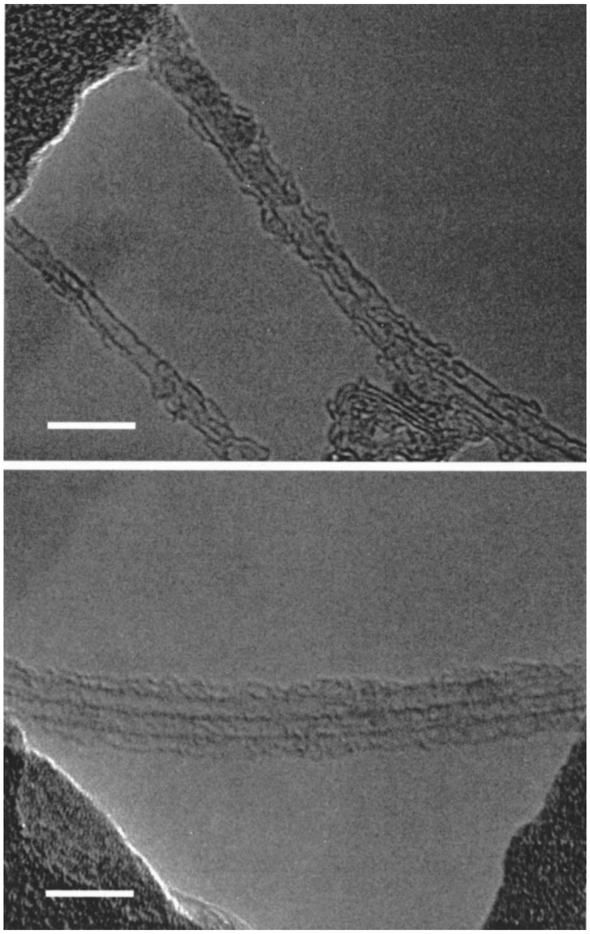

FIG. 1. TEM images of $\mathbf{I}_{\mathbf{Py}}$-SWNT on a stainless steel grid coated with holey $LaCrO_3$. The sample on the grid was heat-treated in air at 400 °C for 30 min before imaging. Both scale bars represent 5 nm.

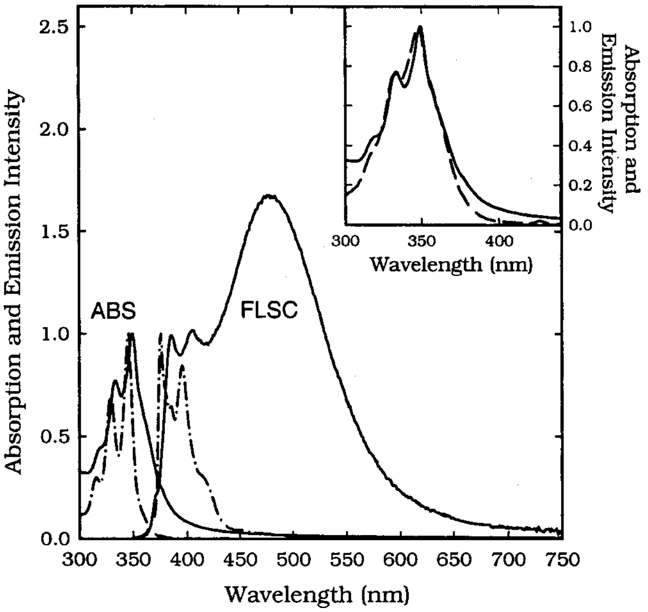

FIG. 2. Absorption and fluorescence (FLSC, excitation wavelength 337 nm) spectra of $\mathbf{I}_{\mathbf{Py}}$ (-.-.-.-) and $\mathbf{I}_{\mathbf{Py}}$-SWNT (—) in room-temperature toluene solutions. Shown in the inset is a comparison of the fluorescence excitation (emission wavelength 490 nm) spectrum of $\mathbf{I}_{\mathbf{Py}}$-SWNT (-----) with the corresponding absorption spectrum.

Spex Fluorolog-2 or a Spex Fluorolog-3 photon-counting emission spectrometer. The Fluorolog-2 is equipped with a 450-W xenon source, a Spex 340S dual-grating and dual-exit emission monochromator and two detectors. The two gratings are blazed at 500 nm (1200 grooves/mm) and 1000 nm (600 grooves/mm). The room-temperature detector consists of a Hamamatsu R928P PMT operated at −950 V, and the thermoelectrically cooled detector consists of a near-infrared-sensitive Hamamatsu R5108 PMT operated at −1500 V. The Fluorolog-3 is equipped with a 450-W xenon source, double monochromators for excitation and emission, and a Hamamatsu R928P PMT operated at −950 V as detector. Unless specified otherwise, all emission spectra were corrected for nonlinear instrumental response by use of predetermined correction factors.

Fluorescence decays were measured using the time-correlated single photon counting (TCSPC) method. The TCSPC setup consists of a nitrogen flash lamp (Edinburgh Instruments). The 337 nm light was isolated using a band-pass filter (10 nm FWHM). Fluorescence decays were monitored through band-pass filters. The detector consists of a Phillips XP2254/B (red-sensitive version of XP2020) PMT in a thermoelectrically cooled housing. The PMT was operated at −2 kV using an EG&G Ortec 556 power supply. The detector electronics from EG&G Ortec include two 9307 discriminators, a 457 biased time-to-amplitude converter, and a 916 A multichannel analyzer. The instrument response function of the setup was ~2 ns (FWHM).

All solutions used in emission measurements were deoxygenated in repeated freeze–pump–thaw cycles.

RESULTS AND DISCUSSION

The absorption spectra of $\mathbf{I}_{\mathbf{Py}}$ and $\mathbf{I}_{\mathbf{Py}}$-SWNT in room-temperature toluene solutions are compared in Fig. 2. Dominating both spectra is the characteristic absorption of derivatized pyrene in the 300–400 nm region. There is no evidence for any significant absorption contribution from pyrene ground-state complexes in the $\mathbf{I}_{\mathbf{Py}}$-SWNT sample, namely that the pyrene moieties in $\mathbf{I}_{\mathbf{Py}}$ and $\mathbf{I}_{\mathbf{Py}}$-SWNT samples have similar molecular environments, resembling simple pyrene derivatives. It has been reported in the literature that the planar pyrene structure interacts strongly (π-stacking) with the nanotube graphitic surface in the solid state.[5] The results presented here seem to indicate that the interactions between carbon nanotubes and the tethered pyrene species in solution are not strong enough to introduce any substantial changes to the pyrene absorption spectrum.

The fluorescence spectra of $\mathbf{I}_{\mathbf{Py}}$ and $\mathbf{I}_{\mathbf{Py}}$-**SWNT** in room temperature toluene solutions are obviously different, with the spectrum of $\mathbf{I}_{\mathbf{Py}}$-SWNT containing substantial contribution from the pyrene excimer emission.[23,24] The ratio of excimer to monomer emission intensities is independent of the solution concentration according to a dilution experiment (Fig. 3). The results suggest that the excimer formation is ''intramolecular'' (intra-nanotube), due to neighboring $\mathbf{I}_{\mathbf{Py}}$ moieties that are attached to the same piece of SWNT. This

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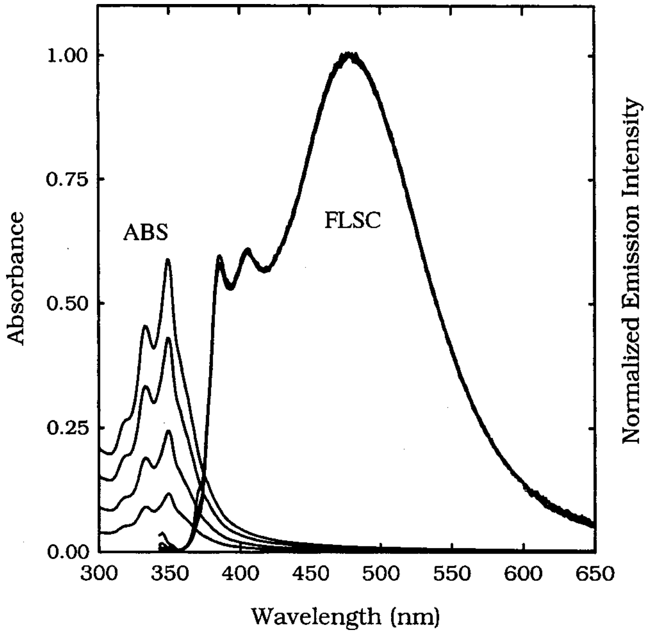

FIG. 3. Results from a dilution experiment on the concentration independence of pyrene fluorescence for $\mathbf{I}_{\mathbf{Py}}$-SWNT in room-temperature toluene. The fluorescence spectra are normalized.

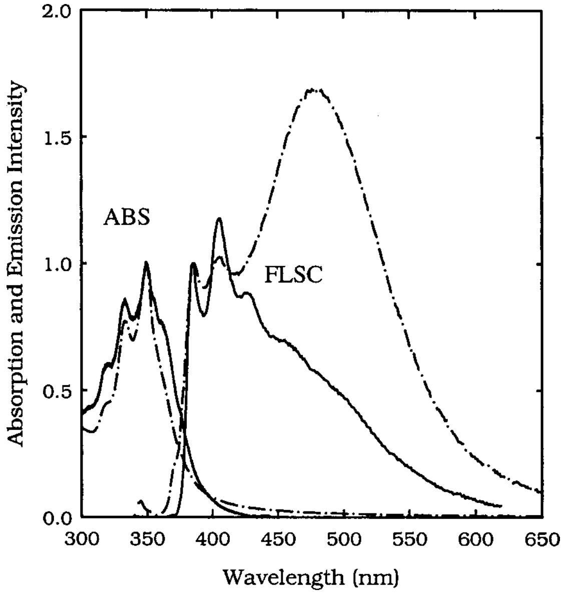

FIG. 4. Absorption and fluorescence spectra of $\mathbf{I}_{\mathbf{Py}}$-SWNT in toluene at 77 K (—) are compared with those in room-temperature toluene solution (-.-.-.-).

is conceptually similar to the formation of pyrene excimers in pyrene-tether-pyrene molecules[25] and in linear polymers with pendantly attached pyrene moieties.[26]

The fluorescence excitation spectrum of $\mathbf{I}_{\mathbf{Py}}$-SWNT monitored at the excimer emission maximum (490 nm) is rather similar to the absorption spectrum (Fig. 2). This agreement between absorption and excitation spectra suggests that the intramolecular excimer formation in solution is dynamic in nature, involving diffusional motions of the participating pyrene moieties that are not pre-associated in the ground state.[23,25,26] The predominantly dynamic nature of the excimer formation is confirmed by the results obtained from fluorescence measurements in a frozen solution at low temperature. The excimer emission is largely suppressed for $\mathbf{I}_{\mathbf{Py}}$-SWNT in toluene at 77 K (Fig. 4),[27] because the frozen solution hinders the diffusion of pyrene moieties required for the excimer formation.

A SWNT may be considered as a substrate with a large surface area. The pyrene species tethered to the functionalized SWNTs may be compared to the pyrenes adsorbed on a solid surface. For pyrene derivatives on various surfaces (such as silica), there is typically strong static pyrene excimer emission due to significant aggregation (pre-association) of pyrene structures in the ground state.[28,29] For $\mathbf{I}_{\mathbf{Py}}$-SWNT, the absorption and emission results suggest that the pyrene structures in neighboring $\mathbf{I}_{\mathbf{Py}}$ units (attached to the same piece of SWNT) are apparently not stacked together on the nanotube surface. This might be a result of steric hindrance in $\mathbf{I}_{\mathbf{Py}}$, due to the presence of a long alkyl chain and the relatively short tether linking the pyrene moiety. However, the spectroscopic results presented here do not necessarily preclude the possibility that the pyrene moieties in $\mathbf{I}_{\mathbf{Py}}$-SWNT interact strongly with the nanotube graphitic surface and perhaps undergo dynamic excimer formulation via diffusional motions along the surface.

Fluorescence decays of $\mathbf{I}_{\mathbf{Py}}$ and $\mathbf{I}_{\mathbf{Py}}$-SWNT were recorded and measured to evaluate the role of carbon nanotubes in the deactivation of the pyrene excited states. As shown in Fig. 5, the fluorescence of $\mathbf{I}_{\mathbf{Py}}$ in room-temperature toluene is long-lived, with the lifetime (~150 ns) comparable to those of other mono-functionalized pyrene molecules. After $\mathbf{I}_{\mathbf{Py}}$ is attached to nanotube to form $\mathbf{I}_{\mathbf{Py}}$-SWNT, the fluorescence decays of the pyrene moieties undergo significant changes. Both the monomer and excimer fluores-

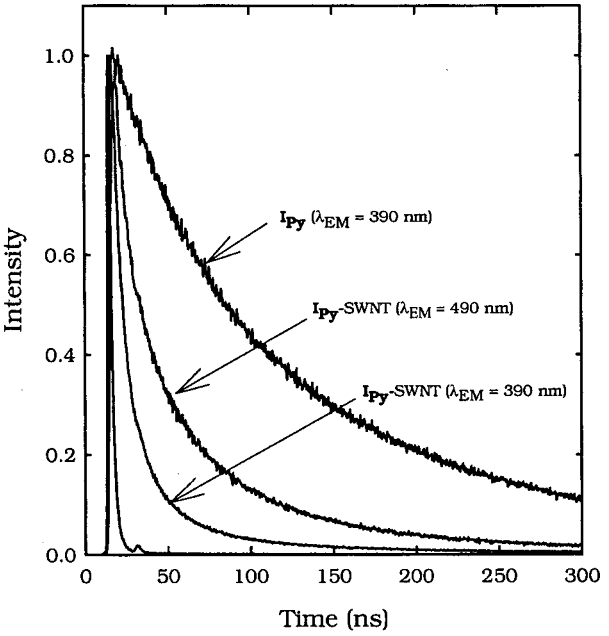

FIG. 5. Fluorescence decays of $\mathbf{I}_{\mathbf{Py}}$ and $\mathbf{I}_{\mathbf{Py}}$-SWNT (monomer at emission wavelength 390 nm and excimer at emission wavelength 490 nm) in room-temperature toluene solutions.

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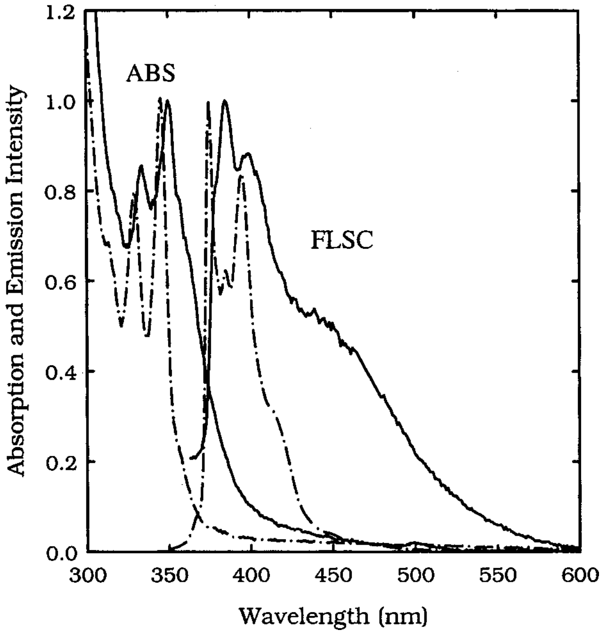

FIG. 6. Absorption and fluorescence spectra of $\mathbf{I_{Py}}$ (-.-.-.-) and $\mathbf{I_{Py}}$-SWNT (—) in PMMA polymer thin film matrix at room temperature.

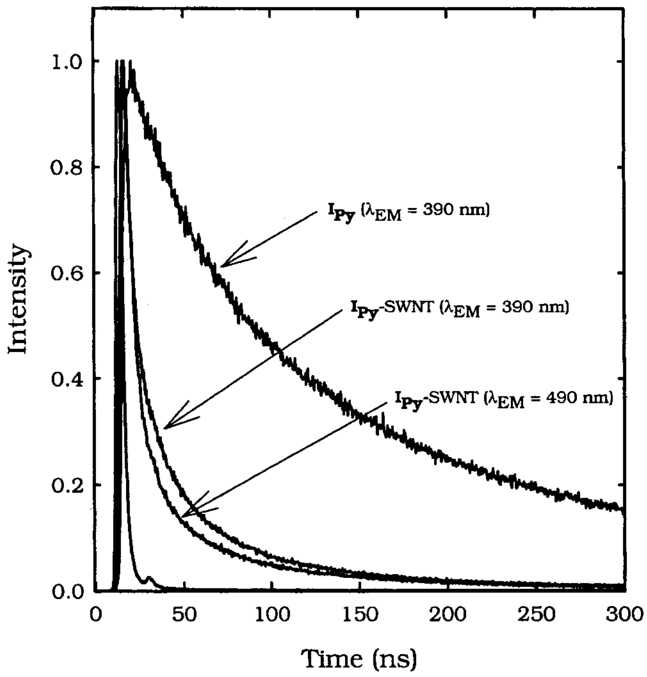

FIG. 7. Fluorescence decays of $\mathbf{I_{Py}}$ and $\mathbf{I_{Py}}$-SWNT (emission wavelengths of 390 nm and 490 nm) in PMMA polymer thin film matrix at room temperature.

cence emissions (monitored at 380 nm and 490 nm, respectively) for $\mathbf{I_{Py}}$-SWNT in room-temperature toluene are nonexponential, suggesting contributions from a distribution of emitting pyrene moieties with complicated excited state processes.[23] This is consistent with the known results for the intramolecular excimer formation and decay in pyrene-tether-pyrene molecules.[25] The observed decay curves can barely be deconvoluted using a three-exponential function, yielding lifetimes of ~40 ns and ~60 ns for the longest-living components in the monomer and excimer decays, respectively.[30] Despite the difficulty in the deconvolution of decay curves even with multi-exponential functions, it is obvious from the direct comparison of decays in Fig. 5 that the pyrene excited states become considerably shorter-lived upon the attachment of $\mathbf{I_{Py}}$ species to SWNTs.[30,31] However, an unambiguous mechanistic consideration of the fluorescence decays is complicated by the fact that there are excimer formation and decay processes in $\mathbf{I_{Py}}$-SWNT but not in $\mathbf{I_{Py}}$. More desirable would be a comparison of the flourescence decay results of $\mathbf{I_{Py}}$ before and after its attachment to SWNT without the complication associated with the excimer formation. As discussed above, the excimer formation in $\mathbf{I_{Py}}$-SWNT could be suppressed in a solid-like medium. Thus, polymer matrix was used for such a purpose.

The $\mathbf{I_{Py}}$ and $\mathbf{I_{Py}}$-SWNT samples were dispersed in polymer thin films. In the film preparation, to a toluene solution of $\mathbf{I_{Py}}$ or $\mathbf{I_{Py}}$-SWNT was added PMMA to form a highly viscous polymer blend, followed by casting on a slide. The fluorescence spectrum of $\mathbf{I_{Py}}$-SWNT in PMMA thin film at room temperature is broad, with the pyrene excimer emission largely suppressed (Fig. 6).[27] This is consistent with the results obtained in frozen solution as discussed above, because here the diffusional motions of the pyrene moieties are hindered by the solid-state polymer matrix. Shown in Fig. 7 is a comparison of the fluorescence decays of $\mathbf{I_{Py}}$ and $\mathbf{I_{Py}}$-SWNT in PMMA thin films at room temperature. Obviously, in the absence of any significant contributions associated with pyrene excimers in the polymer matrix, the fluorescence decay of $\mathbf{I_{Py}}$-SWNT is again considerably faster than that of $\mathbf{I_{Py}}$. On the other hand, the decays of $\mathbf{I_{Py}}$ in toluene solution and in PMMA thin film are quite similar, suggesting no fundamental medium dependence of pyrene excited state processes in $\mathbf{I_{Py}}$. The results of $\mathbf{I_{Py}}$-SWNT, however, point to the presence of additional excited state decay pathways in the SWNT-attached pyrene moieties, which are not available in known pyrene-tether-pyrene molecules.

One likely additional decay pathway is the quenching of pyrene excited states by the attached carbon nanotube, which may serve as an energy sink in an excited state energy transfer mechanism. Since SWNTs have significant absorptions in the visible and near-IR regions, there should be plenty of low-lying excited states with the nanotubes. As a result, the coupling between energy levels of the pyrene moieties and the attached SWNT might be responsible for the proposed energy transfer quenching of pyrene excited state decays in $\mathbf{I_{Py}}$-SWNT. However, structural details on the interactions between excited pyrene species and the attached nanotube (for example, the stacking of pyrene species on the nanotube surface vs other longer-distance couplings) remain to be explored. It seems less likely that π-stacking type interactions play a dominating role in the quenching of pyrene excited states by the attached nanotube, because such strong and specific interactions would probably have resulted in more significant static quenching. Long-distance coupling might be considered as a more likely mode of interactions between excited pyrene species and the nanotube graphitic surface in $\mathbf{I_{Py}}$-SWNT. Further experimental investigations are required.

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