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Strong Luminescence of Solubilized Carbon Nanotubes

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Since their discovery in 1991,[1] carbon nanotubes have attracted significant scientific attention.[2,3] Many potential applications of carbon nanotubes require an understanding of their photoexcited-state properties, but the insolubility of nanotubes in any solvent has hindered quantitative investigations.[4,5] We have been able to solubilize carbon nanotubes by covalently attaching them to highly soluble linear polymers. Here we report an interesting finding that the polymer-bound carbon nanotubes in homogeneous organic and aqueous solutions are luminescent or strongly luminescent.

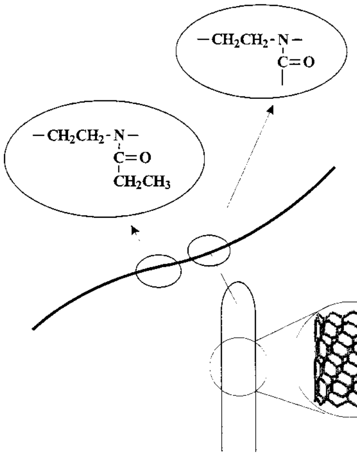

Figure 1. A cartoon illustration of the PPEI-EI polymer-bound carbon nanotubes.

Table 1. Luminescence Parameters of the Polymer-Bound Carbon Nanotubes in Solution

sample	solvent	λ_{EX} (nm)	Φ^a	τ_1 (ns)	τ_2 (ns)	a_1/a_2
S-MWNT−PPEI-EI	$CHCl_3$	632		2.2	5.6	1.2
		400	0.11	2.3	8.0	2.9
	Water	400	>0.03	2.3	8.9	4
S−SWNT−PPEI-EI	$CHCl_3$	632		1.9	5.8	1.2
		440	0.06			
SWNT−PPEI-EI	$CHCl_3$	400	>0.003	1.5	7.3	4.2
	Water	365		2.1	9.8	2.3
S-MWNT−PVA-VA	$CHCl_3$	365	>0.03	1.6	6.0	7.3

[a] 9,10-Bis(phenylethynyl)anthracene as the standard.

Multiple-wall (MWNT) and single-wall (SWNT) carbon nanotubes were purified using the methods reported in the literature.[3,9−11] Shortened MWNT (S-MWNT) and shortened SWNT (S-SWNT) were obtained via the procedures reported by Hiura, et al.[9] and Liu, et al.,[3] respectively, and were characterized using FT-IR, Raman, and SEM. The S-MWNT, S-SWNT, and SWNT samples were treated with HCl solution to fully recover the carboxylic acid groups on the nanotube surface, followed by reflux in neat $SOCl_2$ for 24 h to convert the carboxylic acids into acyl chlorides.[5] These functionalized nanotubes were then mixed well with poly(propionylethylenimine-*co*-ethylenimine) (PPEI-EI, $M_W \approx 200\,000$, EI mole fraction ≈ 15%)[12] and reacted at 165 °C for 20 min.[13] The reaction mixtures were repeatedly extracted with chloroform to obtain the soluble fractions, which were then purified via repeated precipitations. According to the STM results, it appears that the polymer attachment is at the end of nanotube, as illustrated in the cartoon diagram in Figure 1. The same reaction conditions were used to attach S-MWNT to poly(vinyl acetate-*co*-vinyl alcohol) (PVA-VA, MW ≈ 110 000, alcohol mole fraction ≈ 40%) via ester linkages.[14,15] These samples of polymer-bound nanotubes are soluble in both organic solvents and water, forming highly colored homogeneous solutions. After being repeatedly filtered through 0.2 μm Teflon filters, the chloroform and aqueous solutions were used for spectroscopic measurements. UV−vis absorption spectra of the chloroform solutions at room temperature (∼22 °C) are compared in Figure 2, and spectra of the aqueous solutions are similar.

The polymer-bound nanotubes are luminescent, with similarly broad Gaussian-like bands among different samples (Figure 2), and the luminescence spectra are dependent on excitation wavelengths in a progressive fashion (Figure 3). As shown in Table 1, luminescence quantum yields of the nanotubes are substantial: for example, 11% for S-MWNT−PPEI-EI in chloroform at 400 nm excitation. Among different nanotubes, luminescence yields of the polymer-bound S-SWNT and S-MWNT are on the same order of magnitude. However, the unshortened SWNT bound to the same polymer is less luminescent, although the observed yield is still higher than that of [60]fullerene by at least an order of magnitude.[16,17] The luminescence excitation spectra monitored at different emission wavelengths are consistent with the broad UV−vis absorption of the polymer-bound carbon nanotubes (Figure 2).

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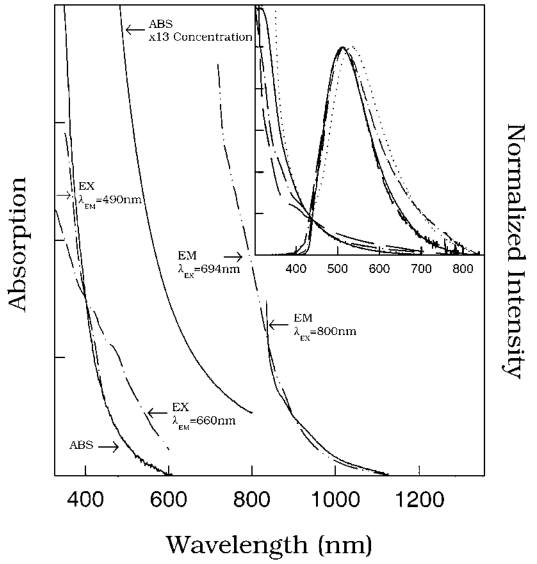

Figure 2. Absorption (ABS), luminescence (EM), and luminescence excitation (EX) spectra of the PPEI-EI polymer-bound S-MWNT in room-temperature chloroform. Inset: A comparison of absorption and luminescence (440 nm excitation) spectra of S-MWNT−PPEI-EI (—), S-MWNT−PVA-VA (···), S−SWNT−PPEI-EI (-·-·-), and SWNT−PPEI-EI (- - -) in homogeneous chloroform solutions at room temperature.

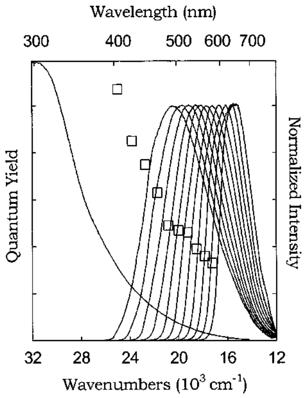

Figure 3. Progressive changes of the luminescence spectra and quantum yields of S-MWNT−PPEI-EI in homogeneous chloroform solution with excitation wavelengths (from left to right: 400−600 nm for the spectra and 400−580 for the quantum yields in 20 nm increment).

We were surprised by the strong luminescence of the polymer-bound carbon nanotubes[18] and, logically, concerned about possibilities of luminescent impurities or small aromatic species from the solubilization reactions, despite the fact that few small aromatic species or other impurities are fluorescent at 700−800 nm excitations.[22] With the aqueous solubility the polymer-bound nanotube samples were further purified via dialysis. After 3 days in a dialysis tube against fresh water, the sample solutions exhibited the same luminescence properties. The luminescence cannot be due to changes in PPEI-EI after being subject to the reaction conditions because the blank polymer sample treated under the same reaction conditions was colorless in chloroform solution and without emission at visible excitation. In addition, we prepared the same octadecylamine-functionalized carbon nanotube samples as reported in the literature,[5] and these samples in chloroform were similarly luminescent. However, because the polymer-bound and octadecylamine-functionalized carbon nanotube samples were prepared in essentially the same reaction procedure, they could in principle share the same artifacts if the luminescence were due to species produced in the solubilization reactions. Thus, we also prepared the soluble polymer-bound carbon nanotubes by using the diimide-catalyzed amidation reaction at room temeprature[12a,14] and again found similar luminescence from these samples.

The strong excitation wavelength dependence of luminescence indicates a distribution of emitters. Unlike fullerenes, which are only weakly fluorescent,[17] carbon nanotubes are considerably larger species and consist of defects (and cutting sites in shortened nanotubes). The luminescence could be due to the trapping of excitation energy at defect sites, which is phenomenologically similar to the emission observed in suspended semiconductor nanoparticles.[24] In this context, the shortened carbon nanotubes should be more luminescent, as observed. There is also another possibility. The solubilized carbon nanotubes might contain extended π-electronic structures that are isolated as a result of nanotube surface functionalzations. For fullerenes, multiple functionalized derivatives are more fluorescent,[17,25] or strongly fluorescent when the multiple functionalization is in a specific pattern.[26]

Luminescence decays of the polymer-bound carbon nanotubes in solution were measured using a time-correlated single photon counting method. Since the decays can be fitted well with a biexponential function, they may be considered as kinetically pseudo-two-component, despite the likelihood of multicomponent emissions. The lifetimes thus obtained are compared in Table 1.

Luminescence intensities of the polymer-bound carbon nanotubes can be quenched by electron donors such as *N*,*N*-diethylaniline (DEA). For S-MWNT−PPEI-EI in chloroform as an example, the luminescence intensity decreases with increasing DEA concentration, but the luminescence spectral profile undergoes only minor changes. The Stern−Volmer plots are curved downward. The limiting quenching rate constants obtained by including only those data points at low DEA concentrations are on the order of 10^9 M^{-1} s^{-1}, which suggest rather efficient quenching processes. The luminescence decays were also significantly faster in the presence of DEA. Mechanistically, the quenching of the nanotube luminescence by DEA is likely due to photoinduced electron transfer. Thus, similar to fullerenes, photoexcited carbon nanotubes may also serve as electron acceptors.

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Supporting Information Available: NMR spectra, STM images, and Stern−Volmer plots (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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