Nonlinear Intensity Dependence of Fullerene Nanotube Fluorescence

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Studies of the recently discovered intrinsic fluorescence of single-wall carbon nanotubes have revealed that the emission intensity depends nonlinearly on excitation intensity. As could be expected for macromolecular systems, the fluorescence increases more slowly than the excitation intensity. Only at intensities below ca. 10 kW/cm^2 was a linear intensity relation observed. This value correlates with the estimated size of a single nanotube and the ~10^{-9} s lifetime of a single exciton on the nanotube. At sufficiently high excitation intensities, approaching 5 MW/cm^2, the intensity dependence approaches a square-root function. Thus, over a wide range, the dependence is consistent with annihilation of nanotube excitons as they randomly diffuse in one dimension. It is estimated that more than one hundred excitations can be placed on a single nanotube by pulsed laser irradiation. Although no experimental time-resolved fluorescence data are yet available, the measured intensity dependence may be combined with a one-dimensional diffusion model to infer the underlying decay kinetics of nanotube excitons.

Because the fullerene nanotube samples are mixtures of nanotubes of different diameters and chiralities, even the shape of fluorescence spectrum depends on excitation intensity. At any fixed excitation wavelength, different nanotubes species are excited with different efficiencies. As the excitation intensity increases, the emission spectrum shows less excitation selectivity and more similar signals from different emitting centers, i.e. the various nanotube species. As a result, at higher intensities the emission spectrum contains information about all fluorescing nanotubes in the sample, becoming closer in shape to the absorption spectrum.