NON-LINEAR EFFECTS IN THE QUENCHING OF FLUORESCENT QUANTUM DOTS BY PARAMAGNETICSPECIES IN SOLUTION AND IN PHOTONIC CRYSTAL FIBERS

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Photonic crystal fibers (PCFs) have received considerable attention because of their unique light transmission characteristics, but only limited attention from the point of view of their potential performance in the construction of microdevices, particularly sensors; such devices will require the incorporation of additional functionality. Photonic crystal fibers contain a geometric array of uniform sized channels; these microchannels confer the fibers their distinct optical properties. The important properties of PCFs relate to their two-dimensional microstructure and the large refractive index contrast between silica and air. In our initial studies we have used single mode photonic crystal fibers of 125 μm in diameter silica core coated with a single layer of acrylate cladding for a total diameter of 220 μm. They contain 54 microchannels of 6.2 μm in diameter separated by 8.0 μm spacings; the holey region is 57.4 μm in diameter including a fiber core of 12.0 μm.

The fibers were filled by capillarity with solutions of fluorescent quantum dots. Exposure of the fiber tip to a toluene solution of TEMPO (Figure 1) leads to immediate quenching of the quantum dot fluorescence near the tip region. Much to our surprise the fluorescence is restored to a very considerable extent within minutes (see Figure 1), and remains essentially unchanged for at least one week.

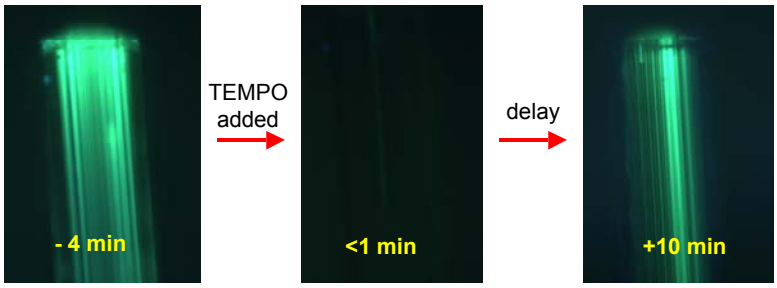

Figure 1: PCF with green Q-dots showing immediate rapid quenching by paramagnetic TEMPO, followed by spontaneous fluorescence recovery.

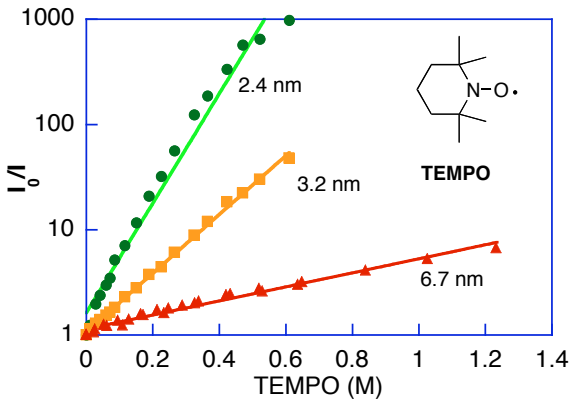

Figure 2: Semilogarithmic Stern-Volmer type plot of Q-dot luminescence quenching by TEMPO. The exponential dependence is unusual for quenching plots of this type.

The reason for the unexpected recovery of the luminescence mentioned above can be attributed to the remarkable non-linearity of the quenching of quantum dot luminescence by paramagnetic species. We have examined the quenching of CdSe Q-dots by TEMPO in toluene solutions. In our case we use Q-dots of 2.4 nm (green, λ_{max} 525 nm), 3.2 nm (orange, λ_{max} 575 nm) and 6.7 nm (red, λ_{max} 630 nm), in diameter. The plot of Figure 2 provides a simple explanation for the recovery of most of the luminescence over a few minutes in the studies involving photonic crystal fibers. A localized initial high concentration of TEMPO extinguishes the quantum dot emission, while diffusion over a few minutes decreases the concentration moving the system into the less efficient region with concurrent recovery of enough luminescence to readily reveal the internal channel structure under conditions of fluorescence microscopy. The unusual exponential nature of the quenching process allows major emission changes with relatively minor changes in TEMPO concentration.