

# Near-Field Time-Resolved Fluorescence Studies of Poly(phenylmethyl Silane) with Subwavelength Resolution

D. A. McL. Smith,<sup>1</sup> S. A. Williams,<sup>1</sup> R. D. Miller,<sup>2</sup> and R. M. Hochstrasser<sup>1,3</sup>

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We present an example of the first time-correlated single-photon counting (TCSPC) near-field optical measurement. The aperture size of our prepared aluminum-coated fiber-optic probe was approximately 50 nm, which represents a spatial resolution of  $\lambda_{exc}/7$  for our UV measurements. Near-field fluorescence decays of poly(phenylmethyl silane) in solid thin films excited in the range 325–360 nm were obtained and the steady-state excitation spectra compared with the excitation spectral information obtained in the far field. Fluorescence decays showed single exponential lifetimes ranging from 45 to 277 ps, which was dependent on the excitation wavelength and the selected near-field tip. The proximity of the metal-coated tip to the sample may be the reason for the modulation in fluorescence lifetime.

**KEY WORDS:** Time-correlated single-photon counting; near-field fluorescence; poly(phenylmethyl) silane; subwavelength resolution.

## INTRODUCTION

Recent advances in nanopositioning technology [1,2] have made new forms of ultrahigh-resolution scanning microscopies possible, such as scanning tunneling and atomic force microscopy. In addition to the new imaging advantages, near-field scanning optical microscopy is the first such method that demonstrates the potential for spectroscopic applications with a combined high spatial resolution of an order much greater than  $\lambda/10$  [3–6]. There have been already several applications of this microscopy [7–9] including the most recent reports on single molecule detection and spectroscopy [10,11].

Our effort is aimed toward achieving high signal-to-noise fluorescence signals with both fast (picosecond) time resolution and single-molecule optical resolution. The pres-

ent study shows, clearly, that near-field optical microscopy combines naturally with TCSPC methods with the result that a 20-ps time resolution can be obtained at the highest achievable spatial resolutions by near-field techniques. The effect of the large range of photon momenta, in the near-field region, on electronic spectra is discussed.

## THE NEAR-FIELD MICROSCOPE WITH SHEAR FORCE DISTANCE REGULATION

Our near-field fiber-based scanning optical microscope arrangement (Fig. 1) was modeled after the design of Betzig and Trautman [5] with specific modifications which will be detailed in a subsequent publication. Distance regulation was achieved by using the shear force technique [12]. A transmission optical configuration of the microscope was used for these experiments with the fiber tip in illumination mode. An optical-fiber probe, mounted inside a piezo tube, was caused to oscillate with an amplitude of approximately 10 nm at 79 kHz, a frequency of high-resonance quality ( $Q$ ). Scattered light,

<sup>1</sup> Chemistry Department, University of Pennsylvania, Philadelphia, Pennsylvania 19104.

<sup>2</sup> IBM Research Division, Almaden Research Center, San Jose, California 95120.

<sup>3</sup> To whom correspondence should be addressed.

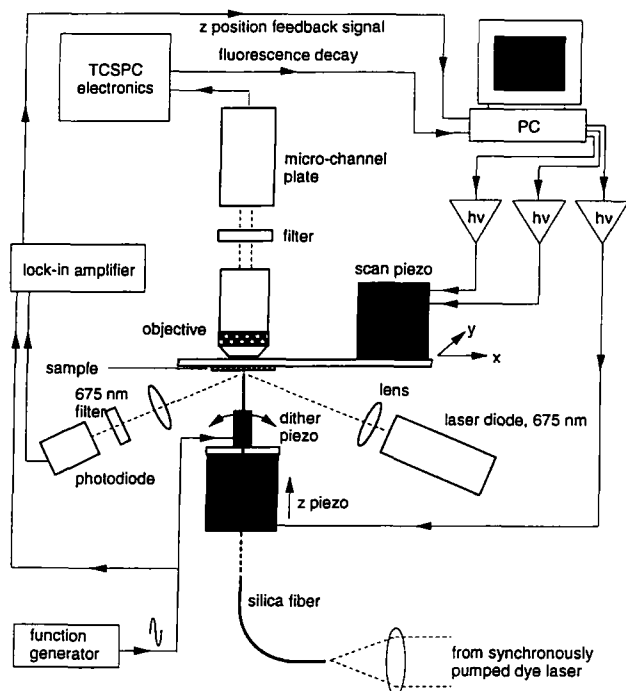


Fig. 1. RLBL near-field scanning optical microscope/TCPSC spectrometer. Transmission presentation is illustrated. The RLBL instrument design accommodates both transmission and reflection collection geometries.

originating from the 5-mW, 675-nm laser diode focused at the tip, was modulated by the oscillation, and the amplitude and phase of this dither signal were compared with those of the driving signal using a lock-in amplifier. Typical dither lock-in signals, with oscillation amplitudes of 10 nm, are 20 mV peak to peak. The tip was manually positioned to within a few microns from the sample surface. Further advance of the tip toward the sample was carried out using a second piezo tube and was computer controlled. After characterizing the tip-sample distance versus the lock-signal profile for our fiber tip, a nominal tip-sample distance of 10 nm was maintained.

### THE OPTICAL FIBER TIP

A 100- $\mu\text{m}$  silica core fiber with a doped silica cladding of high numerical aperture (0.365), 3M FG-100-GLA, was vertically suspended by a 140-g mass with a cladding/buffer stripped segment positioned at the focus (10-cm focal length gold mirror) of a 30-W carbon dioxide laser (CW). The bared fiber was exposed to the focused 10- $\mu\text{m}$  radiation for less than a second, creating

two quickly tapering tip ends. Cross-sectional diameters at the tip ends were typically 1  $\mu\text{m}$  or less. The taper length from the nominal 100- $\mu\text{m}$  width was 0.5 to 1.0 mm. To obtain these tip dimensions repeatedly, motion and recoil effects on the suspended fiber were minimized by threading the bared fiber section through two opposing, 100- $\mu\text{m}$ -i.d., hypodermic needles separated by 5 mm. A 200-nm aluminum coating was applied to the fiber tip/taper region held at an angle of 5° and rotated by dc motors in an electron beam evaporation chamber. The fibers were held in hypodermic needle mounts to reduce eccentricity during rotation. At a 5° inclination, the uncoated tip ends defined an aperture of approximately 50 nm as determined by SEM. Conformation of the aperture sizes of the order of those seen in the SEM was confirmed by an experiment in which the light intensity measured from the near-field tip was compared with that of a cleaved fiber of known diameter. Determination of the spatial resolution by scanning the fiber probe over a sample of known dimension is currently being planned in our laboratory.

### TCSPC-NEAR-FIELD SYSTEM

The mode locked YAG pumped dye laser TCSPC instrument was described previously [13]. The 325 to 360-nm excitation wavelength range was obtained by second harmonic generation of the dye laser output using a 1-cm  $\text{LiIO}_3$  crystal. Fluorescence studies were performed on poly(phenylmethyl silane) (22,900 MW) thin film-coated quartz slides prepared by rapid evaporation of dilute sample solutions in THF. Typical excitation energies were 50  $\mu\text{W}$  before coupling into a fiber. Since the quantum yield ( $\Phi_f=0.11$ ) and absorption cross section ( $\sigma=3.6 \times 10^{-17} \text{ cm}^2/\text{molecule}$ ) are known for this polysilane sample of known thin-film concentration and fluorescence signal, we determined the excitation intensity, at the tip, to be  $6 \times 10^7$  photons/s. If the light intensity goes as the square of the tip diameter, then this tip intensity value corresponds to 300 photons/(s· $\text{Å}^2$ ). Pre-fiber coupled light intensity was estimated to be attenuated by a factor of  $1 \times 10^5$ . An instrument response, measured by direct transmission through a clean quartz substrate, was 25 ps (FWHM). The fluorescence was collected using an Olympus U Plan flint objective with a numerical aperture of 0.5 and working distance of 1.6 mm. Emission wavelength discrimination was achieved using a 380-nm interference filter having a 10-nm bandwidth. The fluorescence signal collected was between 200 and 2000 counts/s depending on the excitation wavelength. Significant photodegradation was measured dur-

ing the near-field measurement, and therefore, a new tip position was acquired with each excitation wavelength.

### NEAR-FIELD TIME-RESOLVED FLUORESCENCE DECAYS

The fluorescence lifetime decays for a poly(phenylmethyl silane) thin film were measured on a subnanosecond time scale from 325 to 360 nm. Similar to the decay obtained with an excitation wavelength of 340 nm (Fig. 2), the fitted fluorescence lifetimes were rigorously single exponential with decay times ranging from 45 to 277 ps ( $\chi^2 < 1.2$ ). In contrast to far-field measurements, where a 73-ps lifetime was wavelength independent [14], the fluorescence lifetimes in the near-field depended on both the excitation wavelength and the apparent tip morphology. That is, a lifetime dependence could be duplicated with the same tip, but was not consistent when a new tip was introduced. Dielectric coupling between the metal surface of the tip and the chromophore could account for the fluorescence lifetime modulation since we cannot exactly reproduce the tip morphology.

### STEADY-STATE AND TIME-RESOLVED FLUORESCENCE EXCITATION SPECTRA

The photon momenta in the near-field evanescent field are given by the range (15)

$$\Delta p = h \left( \frac{1}{\lambda} \cdots \frac{1}{a} \right) \quad (1)$$

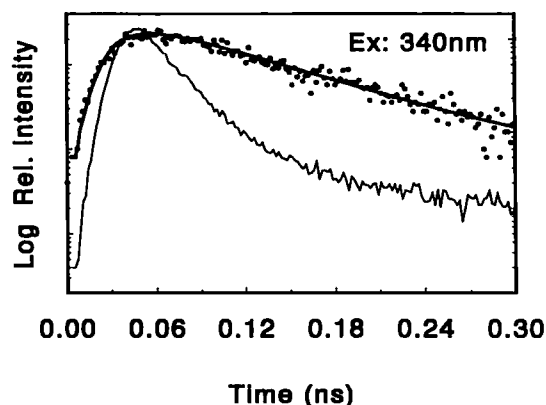


Fig. 2. Near-field time-resolved fluorescence decay of poly(phenylmethyl silane) thin film at 340-nm excitation. (●) Near-field fluorescence decay data (right y axis). (—) Instrument response function (left y axis). (---) One-exponential fit to the fluorescence decay ( $\chi^2 = 1.03$ ).

where  $h$  is Planck's constant,  $\lambda$  is the excitation wavelength, and  $a$  is the aperture radius. This large range of photon momenta, which satisfies the requirements of the uncertainty principle in the case of a very small aperture ( $\Delta x = 2a$ ), could be expected to result in a changed absorption spectrum of the polysilane obtained with such an arrangement. The excitations in the polysilanes are known to be spatially extended over 20 to 70 silicon atoms corresponding to momenta of  $h(1/L)$ , where  $L \leq 20$  nm [14]. The fluorescence excitation approach was used to determine the absorption spectrum. This produces a larger S/N than direct absorption when so few photons are absorbed.

The near-field fluorescence excitation spectrum (Fig. 3) was generated from the area under the time-resolved fluorescence decay, corresponding to the total fluorescence intensity, for each of the excitation wavelengths from 325 to 360 nm in 5-nm increments. Each decay was collected over the same time span and corrected for variation in the incident light intensity. The steady-state fluorescence spectrum was collected from the same thin-film sample using a Perkin-Elmer LS50 spectrofluorometer with the emission bandwidth set to 10 nm. The excitation spectrum bandwidth and center, measured in the far field, are consistent with previously published spectra [14]. As illustrated in Fig. 3, no spectral broadening was apparent in the near-field excitation spectrum, so the effect sought here may not be observable until apertures approaching the molecular size are produced. On the contrary, the excitation spectrum is apparently narrower in the near field and is reproducible (see Fig. 3). It is clear that some type of photoselection is occur-

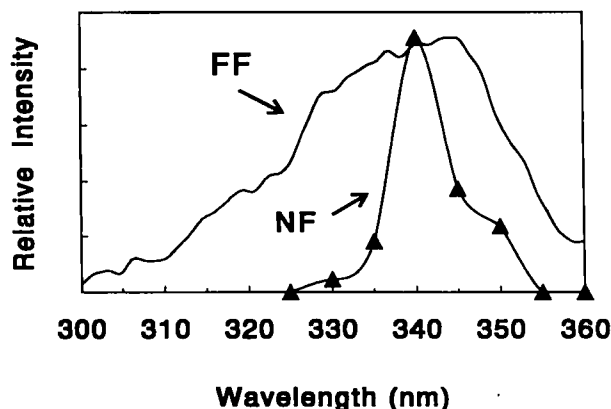


Fig. 3. Near-field integrated fluorescence intensity and steady-state fluorescence excitation spectra. (—) Steady-state fluorescence excitation spectrum; (▲) total integrated near-field fluorescence intensity.

ring in the near-field excitation configuration. It is well-known that the polysilane distributions can be hole burned [16] and that the size of the excitons is different at different parts of the inhomogeneous distribution. Since the polymer silanes exhibit such a photochemical susceptibility for hole burning and etching, precise micro-scale material processing applications, using this system, may be realized.

## CONCLUSIONS

Time-resolved fluorescence studies of poly-(phenylmethyl silane) have been presented using a near-field optical probe technique with subwavelength spatial resolution. In addition, there was no detectable temporal broadening of the 25-ps instrument response as a result of light propagation through the subwavelength near-field aperture. This promising result suggests that detailed time-resolved fluorescence studies are possible with the near-field optical technique. A broadening of the excitation spectrum, which was expected due to the large range of photon momenta in the evanescent near-field, was not observed with the current resolution but this predicted phenomenon may lead to a novel spectroscopy when smaller apertures are available.

## NOTE ADDED IN PROOF

Since we submitted our manuscript for publication, another application of near-field microscopy using time correlated single photon counting was reported by the research group of X. Sunney Xie and G. Holtom at the Pacific Northwest Laboratory (R.C. Dunn, et. al. (1994) *J. Phys. Chem.* **98**, 3094–3098).

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