

Comment on "Single Pentacene Molecules Detected by Fluorescence Excitation in a *p*-Terphenyl Crystal"

In a recent Letter, Orrit and Bernard¹ show the fascinating result that the use of fluorescence excitation for single-molecule detection (SMD) and spectroscopy in solids can yield excellent signal-to-noise ratio, thus confirming earlier SMD using absorption techniques.² We obtain similar results using fluorescence excitation, and wish to comment on two points.³

Orrit and Bernard find anomalously large linewidths of 10–15 MHz for single pentacene molecules at 25 mW/cm². We find similar widths at similar intensities; however, at lower intensity (0.5 mW/cm²) the lifetime-limited width⁴ of 7.8 ± 0.2 MHz is reached (Fig. 1). We find a measured saturation intensity L_s of 1.8 ± 0.8 mW/cm² which is a factor of 40 below the three-level L_s calculated from known photophysical parameters.⁴ Apparently, while the power-broadening characteristic of single pentacenes is modified, the excited-state lifetime is not.

Orrit and Bernard observe sudden drops and surges in some emission peaks which are interpreted as photoinduced spectral hole burning of single molecules.¹ While photoinduced changes may occur, we find that two distinct classes of molecules are present: class I, which are stable in time, and class II, which show spontaneous, discontinuous jumps in resonance frequency of 20–60 MHz on a 1–420-s time scale. The occurrence of class-II defects is quite common in the wings of the inhomogeneous line (increasing to 40% at +0.23 nm from the

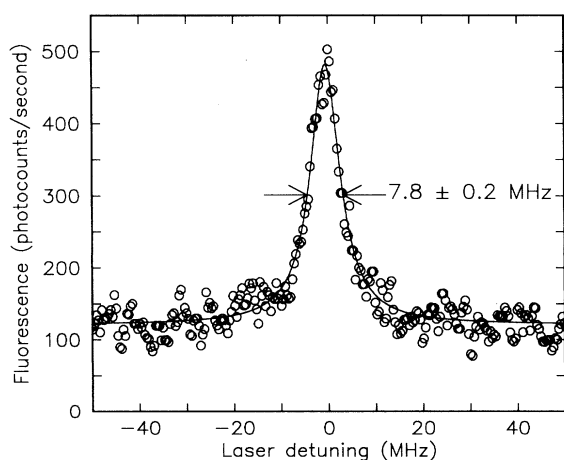


FIG. 1. Fluorescence excitation spectrum for a single pentacene molecule in a sublimed crystal of *p*-terphenyl at 1.5 K. $0 \text{ MHz} \equiv 592.407 \text{ nm}$; laser drift removed by shifting and averaging seven fast scans. The solid line is a Lorentzian fit.

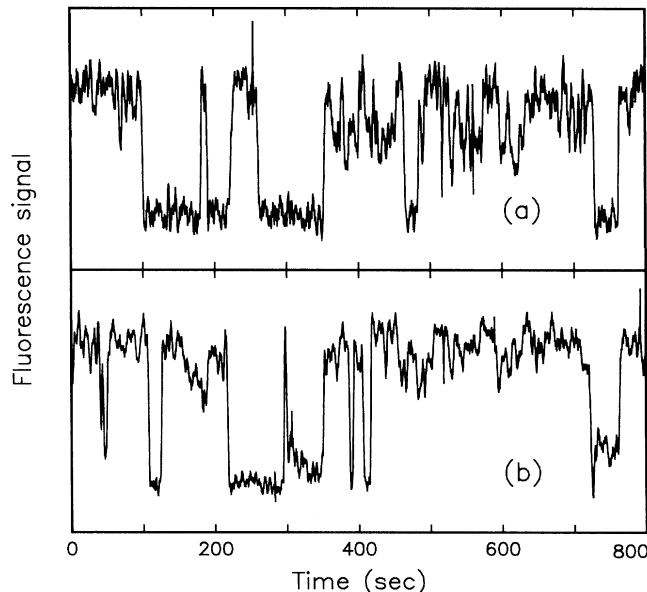


FIG. 2. Spectral jumps in the resonance frequency of a class-II single defect detected with a fixed frequency laser at 592.362 nm. (a) 0.9 nW and (b) 36 nW.

line center), but only class-I defects have been observed in a spectral region from 0.003 to 0.01 nm from the line center. Figure 2 shows that for fixed laser frequency, the fluorescence of a class-II defect turns on and off in a stochastic fashion as the molecule jumps into and out of resonance. Moreover, the jump rate changes little with laser power [Figs. 2(a) and 2(b)]. We find no evidence that the jumping transitions are laser driven; the dominant effect appears to be spectral diffusion of class-II molecules perhaps because they are coupled to an (unidentified at present) ensemble of two-level systems in the host undergoing phonon-assisted tunneling.

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