Electronic Supporting Information ESI†

Other origins for the fluorescence modulation of single dye molecules in open-circuit and short-circuit devices

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S1. Experimental

Materials and sample preparation. Glass cover slips (20 × 20 mm^2, thickness #1, mass of 0.14 g) and quartz cover slips (20 × 20 mm^2, thickness #1, mass of 0.18 g) were purchased from Menzel-Gläser and Trade 21, respectively. Polystyrene (PS, average M_n 130000, average M_w 290000), poly(methyl methacrylate) (PMMA, average M_w 120000), and toluene (spectrophotometric grade) were obtained from Sigma Aldrich. Polyvinyl alcohol (PVA, average M_w 57000-66000) was purchased from Alfa Aesar. Silver paint, indium tin oxide (ITO) coated glass cover slips (20 × 20 mm^2, thickness #1, resistance 8-12 Ω) and Atto647N dyes (see Fig. S1) were purchased from RS Components, SPI Supplies and ATTO-TEC GmbH, respectively.

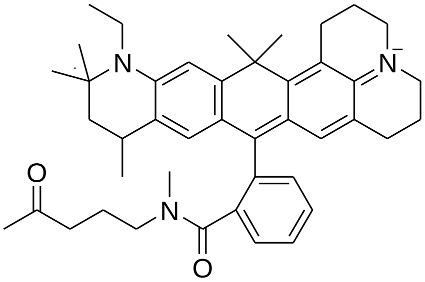

Fig. S1. Chemical structure of ATTO 647N.[S1]

For a short circuit device (Fig. 1a), a U-shaped silver electrode with a width of ~2 mm was painted on either a cleaned glass cover slip, quartz cover slip or glass petri dish (mass of 107 g). The device was then heated at 120 ^{o}C for 30 mins to achieve maximum conductivity. The thickness of the electrode was measured using a surface profiler (Dektek 150, Veeco). Single dye molecules and a bulk concentration of Atto647N molecules were deposited onto the center of the device by spincoating an aqueous solution of Atto647N of ~10^{-11} M and ~10^{-6} M, respectively. For an open-circuit device (Fig. 1b), a 450 nm PS layer was deposited onto an ITO coated cover slip by spincoating a 150 μL toluene solution of PS (50 mg/mL). Subsequently, a PVA layer (30 nm) containing single Atto647N molecules was prepared by spincoating a 150 μL aqueous solution of dye/PVA (10 mg/mL PVA, and ~10^{-11} M dye) onto the PS film. A PMMA film (55 nm) was then deposited from a 150 μL toluene solution of PMMA solution (10 mg/mL), followed by thermal evaporation (KCR-480S Evaporation Coating System) of an aluminum electrode (100 nm). The busbars on the ITO coated cover slip were protected using sticky tapes during the deposition of the polymer layers and Al electrode and the tapes were subsequently removed during measurements. The thicknesses of the polymer films were determined using an atomic force microscope AFM (D3100V, Veeco Digital Instruments). The electric field experienced by the single molecules was defined as the ratio of the applied voltage to the separation between the two opposite electrodes (ignoring the dielectric constant of the polymer layers).

The two parallel arms of the electrode in the short-circuit device and the ITO and Al electrodes in the open-circuit device were carefully connected *via* wires to a function generator (TG550, Thurlby Thandar Instruments) that provided a sinusoidal voltage at 0.1 Hz (Figs 2a and 6a). A digital multimeter (Mode1009, Kyoritsu) was used to determine if a device was short-circuited.

Single-molecule fluorescence spectroscopy. The device was held in place in a home-made sample holder by using sticky tape at the four corners, and then mounted onto a time-resolved confocal microscope (MicroTime 200, Pico Quant GmbH) equipped with an inverted microscope (IX71, Olympus). Excitation light from a pulse laser diode (635 nm, LDH-P-C-635B, PicoQuant) was passed through an excitation filter (Z636/10, Chroma) and focused through either an oil objective lens (1.4 numerical aperture, 100× magnification, Olympus) or air objective lens (0.9 numerical aperture, 60× magnification, Olympus). The fluorescence from single dye molecule was passed through a dichroic mirror (Z638rpc, Chroma) and an emission filter (HQ685/70, Chroma) before being detected by a single-photon avalanche diode (SPCM-AQR-15, Perkin Elmer). The backscattered excitation light was recorded by removing the emission filter before detection and the corresponding beam spot was captured using a CCD camera (GANZ ZC-F10C2). A confocal fluorescence image of single fluorescent Atto647N molecules from an open-circuit device (Fig. 1b) is given in Fig. S2.

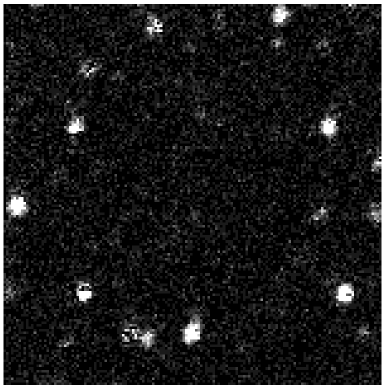

Fig. S2. A confocal fluorescence image of single fluorescent Atto647N molecules from an open-circuit device (Fig. 1b).

Ellipsometry and AFM. Refractive index measurement was done using a spectroscopic ellipsometer (Auto SE, Horiba Jobin Yvon). The integration time was set to be 60 s in each measurement. The displacement of the device with respect to the objective lens was quantified using an AFM in a non-contact mode (Nanosurf easyScan 2).

S2. Movie caption

Movie S1. Movie of the backscattered excitation light beam spot pattern with applied potential for a short-circuit device (Fig. 1a) that is subjected to a sinusoidal potential (at 0.1 Hz) ranging from +3 V to -3 V. The potential was applied after 4 s.

Reference

(S1) C. Eggling, C. Ringemann, R. Medda, G. Schwarzmann, K. Sandhoff, S. Polyakova, V. N. Belov, B. Hein, C. von Middendorff, A. Schönle, S. W. Hell, *Nature*, 2009, **457**, 1159-1163.