Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Electric Field Induced Reversible Single-Molecule Fluorescence Switch

Ruixiang Wu, Ruiyun Chen, Chengbing Qin, Yan Gao, Zhixing Qiao, Guofeng Zhang, Liantuan Xiao,* and Suotang Jia

State Key Laboratory of Quantum Optics and Quantum Optics Devices, Institute of Laser Spectroscopy, Shanxi University, Taiyuan 030006, China

Email: xlt@sxu.edu.cn

1. Introduction of SR Molecule

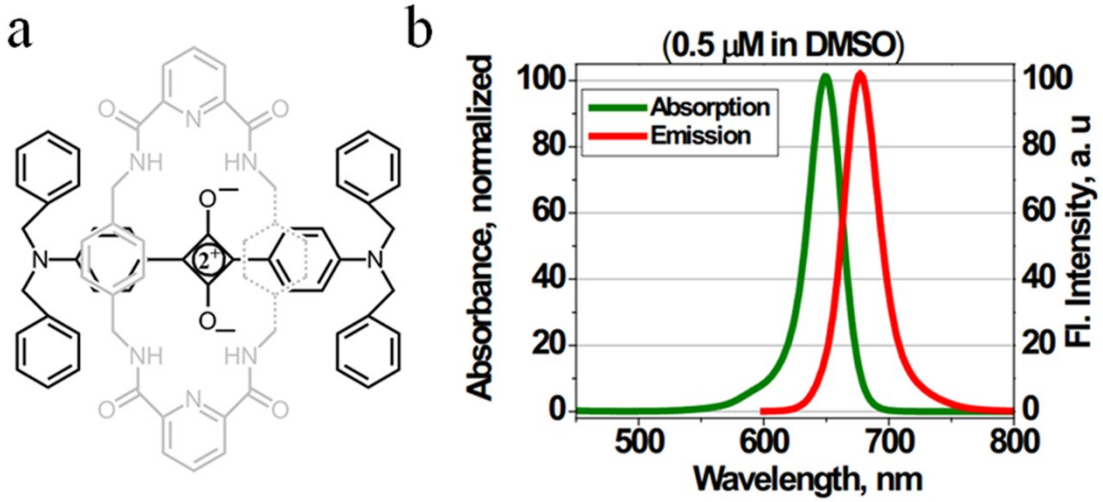

Fig. S1 (a) The chemical structure of SR molecule. (b) Absorption and fluorescence emission spectra of SR molecule. (The data is from www.mtarget.com)

From the perspective of squaraine-derived rotaxane (SR) (SRflour@680 Phenyl, Molecular Targeting Technologies Inc., SR-1001, purity: > 95% by HPLC at 650nm) molecular structure (Fig. S1a), the 2, 6-pyridine dicarboxamide-derived macrocyle，which is indicated as gray, is used to be encapsulated the squaraine dyes inside a protective molecular container.[1] Owing to the internal hydrogen bonding, the macrocycle wraps more tightly to the central four-membered carbon moiety of the squaraine thread and molecular chemical stability is enhanced. SR molecular absorption and fluorescence emission maximum values are 650nm and 678nm, respectively (Fig. S1b). The linewidth of SR absorption and fluorescence emission spectra are both about 50nm, which corresponds to ~10^4GHz.

2. Sample Preparation

The cover glass substrates were cleaned by sonication successively in acetone, potassium hydroxide solution, milliQ water, and then irradiated for one hour using an ultraviolet lamp. SR molecules were dissolved and diluted in the milliQ water at a concentration of 10^{-10}-10^{-9}M without any further chemical purification and spin-coated 50μL solution onto pre-covered slip with rotation at a rate of 3000rpm for 1min. The concentration of SR molecules solution was dilute enough to ensure that

molecules were separated from each other and there was no more than one molecule appeared in the confocal area. Two aluminum electrodes were fixed to the glass substrate and the distance between them was 2mm (Fig. S2). The triangle- or square-wave voltage was applied to two arms of the electrodes at a frequency of 0.1Hz.

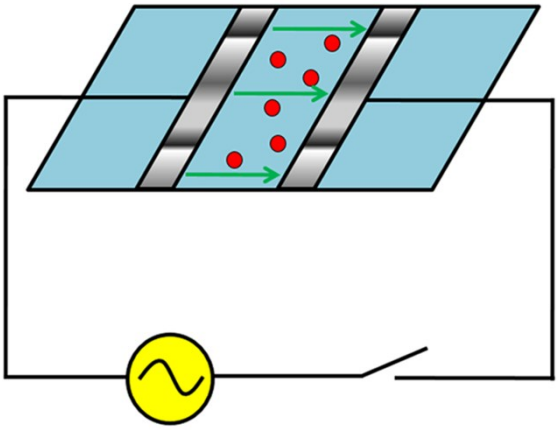

Fig. S2 The pattern of sample. The distance between the electrodes is about 2mm, and the red points indicate the single SR dye molecules.

3. Experimental Setup

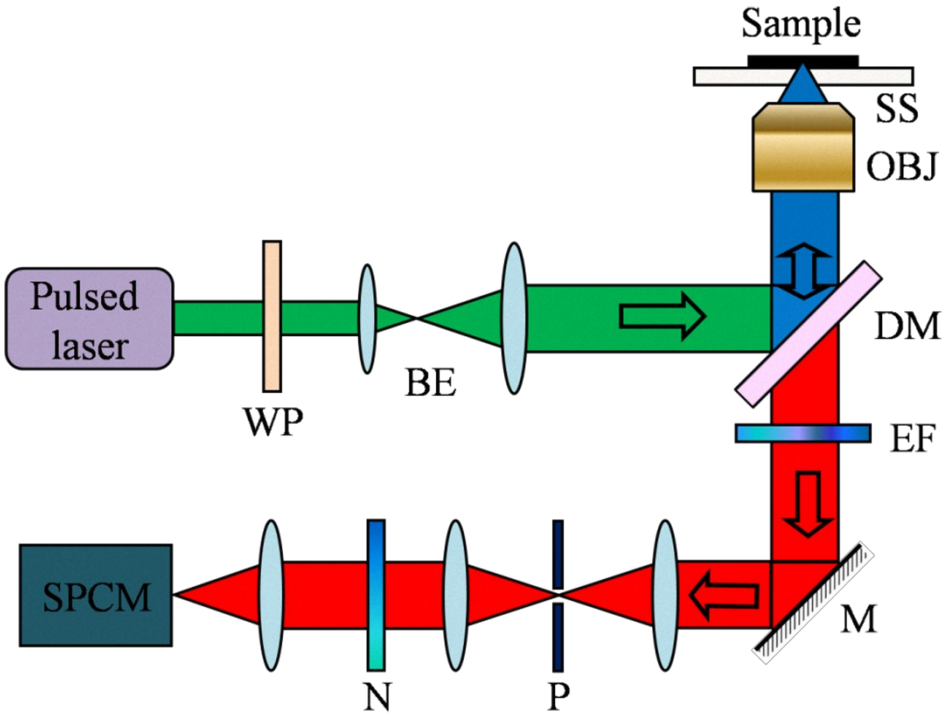

Fig. S3 Schematic of the experimental setup. WP, wave plate; BE, beam expander; DM, dichroic mirror; OBJ, objective; SS, piezo-scan stage; EF, emission filter; M, mirror; P, pinhole; N, notch filter; SPCM, single photon counting module.

Figure S3 displayed the experimental setup which was a home-built scanning

confocal microscope based on an inverse microscope (Nikon ECLIPSE TE200-U). Single molecules (SMs) were excited with a 70-picoseconds-pulse diode laser (repetition rate is 40MHz, PicoQuant, PDL808). The full width at half maximum (FWHM) of laser is about 3nm, which corresponds to ~10^3GHz. The laser was turned into a circularly polarized light by a combination of a half wave plate and a quarter wave plate, collimated by an expander. The beam was adjusted to the back aperture of an oil immersion objective (Nikon, 100×, NA=1.3), reflected by a dichroic mirror (BrightLine, Semrock, Di01-R635-25×36). The excitation light was focused to a diffraction limited spot on SMs, which were distributed randomly on the glass cover slip (Ted Pella, 260168). Using an x-y-z piezo-scan stage (Piezosystemjena, Tritor 200/20 SG) with nanometers resolution, the confocal fluorescence image of SR molecules was obtained point-by-point by scanning the sample. The fluorescence of SM was collected by the same objective and passed through the dichroic mirror. The backscattered laser light in the signal was blocked by using an emission filter (BrightLine, Semrock, FF01-642/LP-25-D) and a notch filter (BrightLine, Semrock, NF03-633E-25). The fluorescence was then focused onto an 100μm spatial filter and collected by an avalanche photodetector (PerkinElmer, SPCM-AQR-15, Germany). The emission time traces were recorded by exciting with the 635nm diode laser at 70μW excitation power measured in the front of the inverse microscope. All measurements were conducted under ambient conditions.

4. The Recognition of SMs

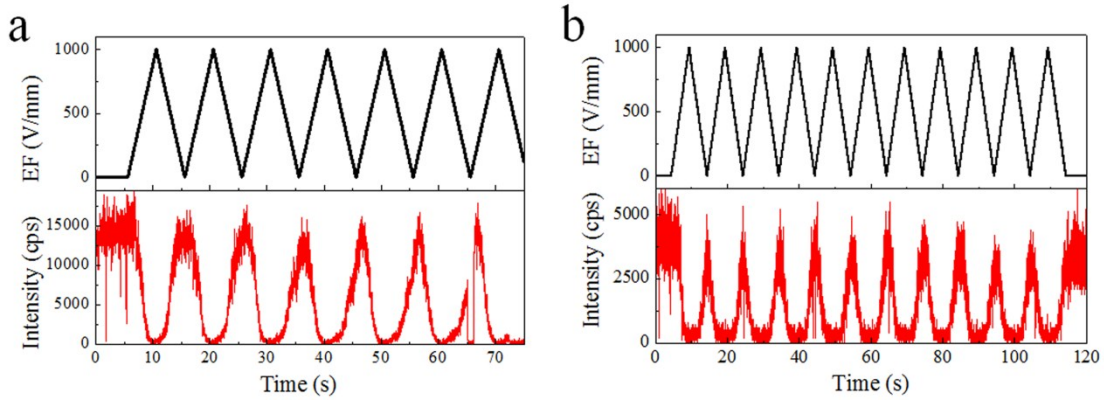

Fig. S4 The fluorescence quenching induced by a triangular EF in the complete measured process.

Except the traditional method of Hanbury-Brown-Twiss (HBT) interferometer,[2] the

phenomenon of photoblinking or photobleaching is also the way to identify the SM.[3] Photoblinking is the phenomenon of random exchanging between bright and dark states, which is usually thought as the result of the triplet state. Photobleaching is the vanishing of fluorescence due to photochemical destruction of the dye molecule by the light exposure for a certain time. In Fig. S4a, the triangular electric field (EF) is applied at 5.58s, and then the fluorescence is quenched, which has been described detailedly in the paper. Photoblinking appears at 1.83, 65.17-66.24s, respectively. Photobleaching appears at 72.45s. In Fig. 45b, photoblinking appears at 0.96, 24.50, 43.78, 44.92, 52.59, 52.59, 64.95, and 105.67s, respectively. At 114.40s, the EF is turned off and photobleaching appears at 121.68s. In our experiment, we recognize the SM by the appearance of photoblinking or photobleaching. The background is composed with the dark count of the detector and the backscattered laser light primarily in the experiment, which is the count value after the photobleaching of SM. As shown in Fig. S4b, the background is about 200cps.

5. Positive and Negative EF-Induced Fluorescence Quenching

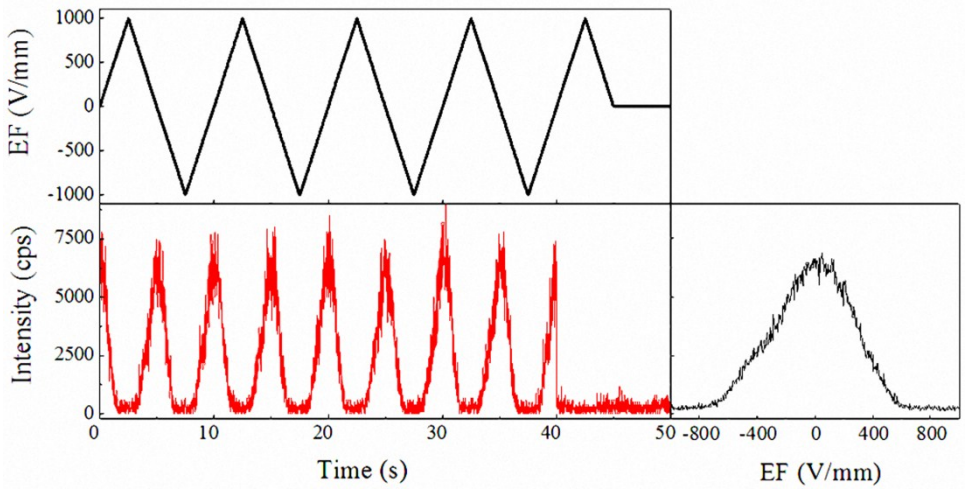

Fig. S5 The fluorescence quenching induced by a positive and negative triangular EF. The corresponding time averaged fluorescence-EF curve derived from the scans is shown in the right.

A triangular bias with a period being 10s is applied to two electrodes where the SMs are dispersed. Figure S5 shows the fluorescence quenching of a non-polar SR dye molecule induced by a positive and negative triangular EF. The SR molecule is bleaching when the tracing time is 39.94s. We find that the fluorescence of the SM

gradually tends to background with field magnitude increasing no matter the EF is positive or negative. The fluorescence is quenched consistently induced by the positive and negative EF. Averaging the data over a number of EF cycles and replotting as a function of applied EF yields the fluorescence quenching versus EF curves, displayed in the right. The fluorescence quenching is independent on the direction of applied EF because of the symmetric structure of SR molecules.

6. Stark Effect

By Stark effect is meant the EF produced the shift and split of spectral lines of atoms or molecules. The Stark shift ΔE of SM fluorescence induced by the external EF could be formulated as follow

$$\Delta E = F \times \Delta\mu + F^2 \times \Delta\alpha \qquad (1)$$

where F is the EF, $\Delta\mu$ is the difference in permanent dipole of the ground and excited state. Under an external EF, $\Delta\mu$ of centrosymmetric molecules would be usually gained due to distortions induced by the surrounding solid matrix, leading to the linear Stark shift which is usually much stronger than the quadratic effect.[4] $\Delta\alpha$ is the difference in ground state and excited state polarisability of the system, and the second term is corresponding to the quadratic effect, which could be ignored in this work. Both the dipoles and the EF are vectors, whereas the polarisability is tensor. $\Delta\mu$ is around 0.3D in a Shpol'skii matrix, while it can be as large as 1D in disordered matrices, such as in polymers.[4] Assume $\Delta\mu$ is 1D, we calculate the Stark shift:

$$\Delta E = 1D \times 1KV/mm \approx 2.08e \cdot nm \times 1000V/mm = 2.08 \times 10^{-3} eV \approx 5GHz .$$

7. Intramolecular Electron Transfer

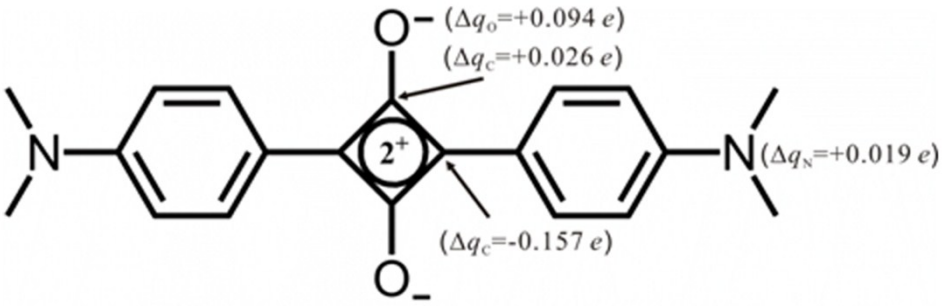

Fig. S6 The net electron transfer of the dominant atoms for bis(4-dimethylaminophenyl) squaraine at the one-electron level HOMO→LOMO excitation.

Intramolecular electron transfer is that the electron transfer between distinct regions within the molecule. In such intramolecular process, the reaction product is usually called an intramolecular electron-transfer state, which plays a fundamental role in photosynthesis in plants and molecular devices. The squaraines are a particularly promising class of near-IR dyes and the symmetric configuration is expected to lead to appreciable intramolecular electron transfer character.[5] The theoretical results by modified neglect of diatomic overlap (MNDO) semi-empirical method have showed that both ground state S_0 and excited state S_1 are intramolecular electron-transfer states.[6] The oxygen atoms and the anilino moieties are electron donors, and the central four-membered ring is an electron acceptor. The MNDO calculations further point that there is an electron transfer during the $S_0 \rightarrow S_1$ electron excitation, and electron transfer is primarily (~80%) localized within the squaraine part.[7] At the one-electron level HOMO→LOMO excitation of bis(4-dimethylaminophenyl) squaraine, as shown in Fig. S6, the largest electron transfer term occurs from the carbony groups to the squaraine carbons lying on the long molecular axis.[6] The net electron transfer for oxygen atom is ΔqO=+0.094e, and that for carbon atom in carbony group is ΔqC=+0.026e, as illustrated in Fig. S6. It is to say that both oxygen and carbon atoms in carbony group are electron donor. While the electron transfer for carbon atom lying on the long molecular axis is ΔqC= -0.157e, acting as electron acceptor. Besides, the nitrogen atom only gives 0.019e, and the net electron transfer for other atoms is very small. The back electron transfer would occur following by the transition $S_1 \rightarrow S_0$, and emitting the fluorescence. When applying the external EF to SR molecules on bare glass, the electron transfer process would be influenced and the charge density

distribution of excited state would be changed, resulting in the fluorescence of SR molecules quenched in our experiment.

References

1. E. Arunkumar, C. C. Forbes, B. C. Noll and B. D. Smith, *J. Am. Chem. Soc.,* 2005, **127,** 3288.
2. R. H. Brown and R. Q. Twiss, *Nature,* 1956, **177,** 27.
3. B. Kozankiewicz and M. Orrit, *Chem. Soc. Rev.,* 2014, **43,** 1029.
4. V. Puller, B. Lounis and F. Pistolesi, *Phys. Rev. Lett.,* 2013, **110,** 125501.
5. J. J. Gassensmith, J. M. Baumes and B. D. Smith, *Chem. Commun.,* 2009, **42,** 6329.
6. R. W. Bigelow and H.-J. Freund, *Chem. Phys.,* 1986, **107,** 159.
7. K.-Y. Law, *Chem. Rev.,* 1993, **93,** 449.