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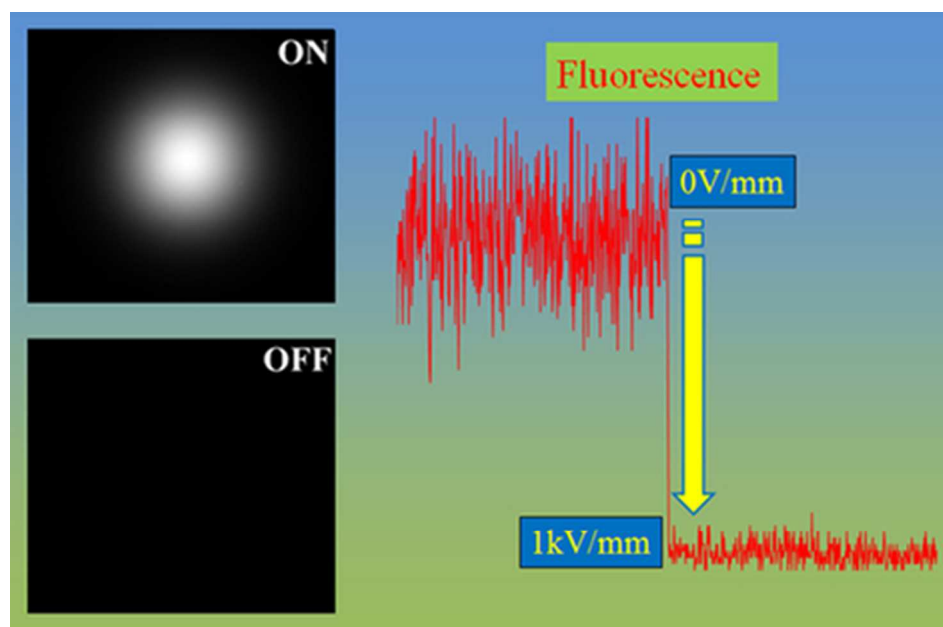
Based on the intramolecular electron transfer within a single molecule, we have achieved fluorescence switch induced by the electric field.
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ARTICLE TYPE

Electric Field Induced Reversible Single-Molecule Fluorescence Switch

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We report that by applying an electric field to single squaraine-derived rotaxane (SR) molecule on bare glass, the fluorescence can be completely quenched. The molecule undergoes a reversible fluorescence switch between a zero-
10 **field "on" state and a high-field "off" state, which is attributed to intramolecular electron transfer within SR molecule.**

Single molecule (SM) reversibly changed between two different states can serve as a molecular switch.[1-3] Of particular
15 interest are those molecules[4-6] which could be repeatedly switched between fluorescence "on" and "off" states or different colours, considering their potential applications in fields as sensors, optical memories, security inks and super-resolution fluorescence imaging.[7-10] A typical application of such SM
20 fluorescence switch is that the fluorescence image with ~20 nm resolution by stochastic optical reconstruction microscopy has been achieved by combining a photo-switchable "reporter" and an "activator" which facilitated photo-activation of the reporter.[10] Many external stimuli, such as PH-triggering,[11] temperature-
25 guiding[12] and photo-switching,[13] have been discovered for controlling the SM fluorescence switch. Electric field (EF) has been widely used to modulate SM fluorescence,[14-16] revealing a candidate for SM fluorescence switch. Lupton group reported that the EF could shift the fluorescence spectrum of a single
30 chromophore on an MEH-PPV polymer molecule at 5 K due to linear *Stark effect*.[14] Sugimoto et al. pointed that the *conformational change* of single polythiophene chain could be occurred by the EF with amplitude of ~10 MV/mm and the fluorescence intensity of about 20% single chains was
35 modulated.[15] Ohta and coworkers observed that the fluorescence of ethylcarbazole doped in PMMA polymer film was quenched by the external EF because of the enhancement of *intermolecular electron transfer* between SM and PMMA matrix.[16]

Early in 1986, Bigelow and Freund have pointed out that the
40 *intramolecular electron transfer* would occur within the squaraine dye molecule.[17] Recently, one-step ON-OFF fluorescence switch of a synthesized diarylethene-perylenebisimide dye molecule has been observed upon visible and UV light irradiation based on intramolecular electron transfer
45 between donor perylenebisimide and acceptor diarylethene units.[18] In this communication, we present a reversible EF-induced fluorescence switch between a zero-field "on" state and a high-field "off" state, which is attributed to the intramolecular

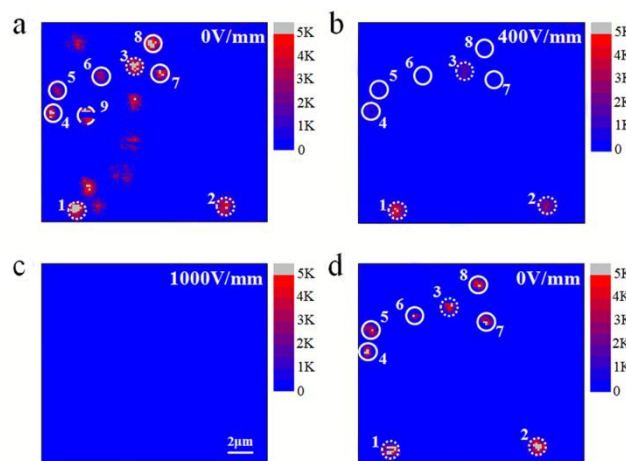electron transfer within squaraine-derived rotaxane (SR)
50 molecule.

Fig. 1 Confocal fluorescence images of single SR dye molecules on bare glass substrate within the same area (18 µm × 18 µm) are quenched by the external EF of (a) 0 V/mm, (b) 400 V/mm, (c) 1000 V/mm, and (d) the
55 recovered 0 V/mm in sequence. Note that the different fluorescence intensity amongst the molecules: molecules 1-3 give a weaker fluorescence at 400 V/mm, while the fluorescence of molecules 4-8 is absent. All molecules are fluorescence quenching completely at 1000 V/mm.

60 Single SR molecules (Fig. S1, see the detail in the Electronic Supplementary Information (ESI)) were spin-coated on bare glass substrate to perform the experiment. The fluorescence of SR molecule was measured based on a home-built scanning confocal microscope[19-21] (see Fig. S3). Figure 1 presents that the
65 fluorescence images of SR molecules on bare glass are quenched by the external EF with the amplitude of 0, 400, 1000 and the recovered 0 V/mm in sequence, respectively. Each image is raster scanned within the same area (18 µm × 18 µm) in the focal plane. In Fig. 1b, the fluorescence of molecules 4-8 are completely
70 quenched by the EF of 400 V/mm, while molecules 1-3 give weaker fluorescence. What amazing is that when the amplitude of the EF increases to 1000 V/mm, the fluorescence of all SMs could be completely quenched, as shown in Fig. 1c. Figure 1d indicates that the fluorescence of SMs could recover to the initial
75 intensity when the EF is turned off. There are some SMs, such as the molecule 9, which could not recover owing to photobleaching. The effect that the fluorescence of SMs could be completely quenched by a high EF as well as it could recover with the EF

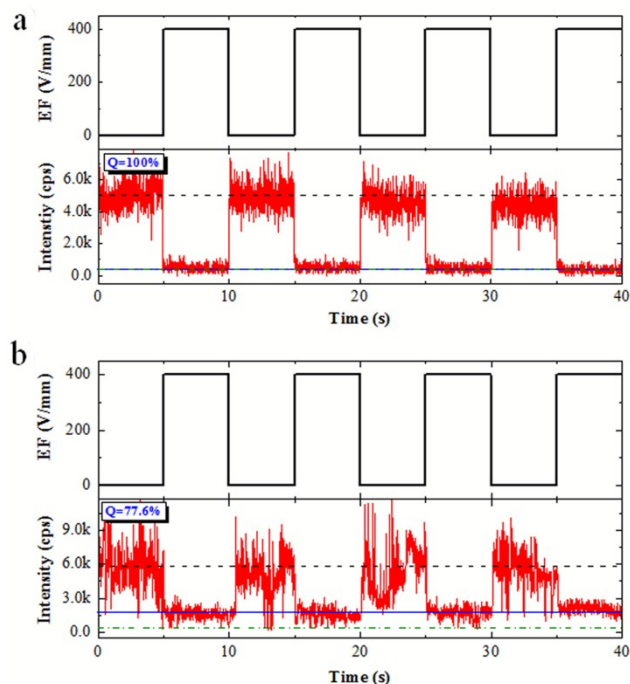turning off could serve as EF-induced SM fluorescence switch.

Fig. 2 The fluorescence of single SR molecule is quenched with the quenching ratio Q of (a) 100% and (b) 77.6%, respectively, by a square-
5 wave EF with the amplitude of 400 V/mm. The three lines in bottom part of each figure represent the different intensity levels. Dash line: initial fluorescence intensity; solid line: quenched fluorescence intensity; dash dot line: background.

An efficiently reversible SM fluorescence switch could be
10 directly observed by applying a square-wave EF as the external stimulus. Figure 2 shows that the fluorescence of SR molecule on bare glass substrate is quenched by the EF with the amplitude of 400 V/mm at the frequency of 0.1 Hz. In order to quantitatively describe the degree of SM fluorescence quenching, we define a
15 quenching ratio (Q) as $(I_i-I_q)/(I_i-I_b)$, where I_i, I_q and I_b are initial fluorescence intensity, quenched fluorescence intensity and background, respectively. It is found that the quenched fluorescence intensity of the molecule 6, selected from Fig. 1, is equal to background ($I_q=I_b$), and the Q can reach 100%, as shown
20 in Fig. 2a. The fluorescence intensity tends to background ("off" state) immediately when the field is turned on, and it instantly recovers to the initial intensity ("on" state) as soon as the EF is turned off. The respond time is below 0.1 ms, which is the time resolution of photon counting here. The fluorescence trajectory of
25 SR molecule on bare glass could be reversibly converted between "on" and "off" states by the square-wave EF, indicating a perfect fluorescence switch at the SM level.

From Fig. 1b, it can be found that not all of the SMs could be completely quenched by the EF with the amplitude of 400 V/mm.
30 As shown in Fig. 2b, the fluorescence of the molecule 1, selected from Fig. 1, is not completely quenched to the background and the Q is just 77.6%. In order to study the response characteristic with the varying EF, we perform an experiment in which the SM fluorescence is quenched as a function of the triangle-wave EF,
35 as shown in Fig. 3a. The fluorescence intensity gradually tends to background with the rising EF, and it recovers to the initial intensity with the falling EF. Particularly, the amplitude of the EF,

which quenches the fluorescence of SMs on bare glass with the Q being 90%, is defined as turn-off EF (E_{off}). The E_{off} of the
40 molecule in Fig. 3a is 578.3 V/mm. Note that photoblinking is observed at 49.32 s in the fluorescence trajectory of the SR molecule, which could be used to recognize SM. A histogram of E_{off} for 371 SM fluorescence switches is shown in Fig. 3b. The data is fitted by Gaussian function, which is shown as the red
45 curve with the most probable E_{off} of 593 V/mm and the full width at half maximum (FWHM) of 259 V/mm. In the case, two adjacent SMs with different E_{off} can be distinguished by applying the proper EF to achieve the super-resolution fluorescence imaging.[10]
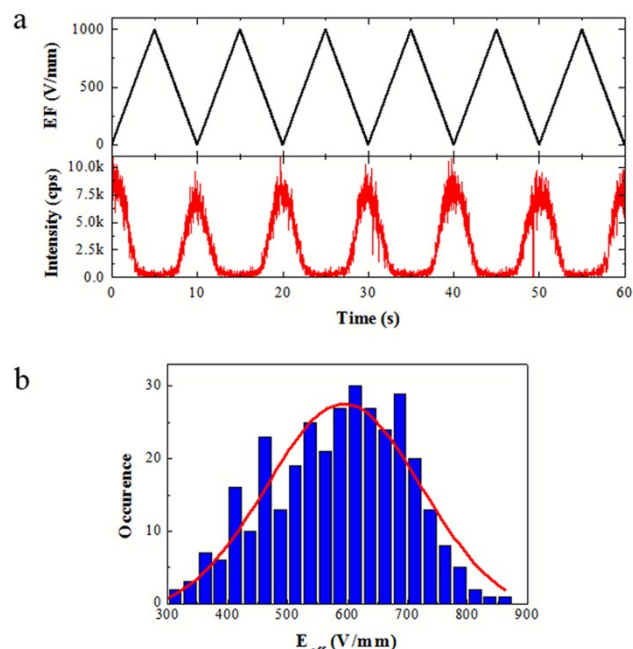

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Fig. 3 (a) The periodic triangle-wave EF-induced fluorescence quenching of SR molecule on bare glass. The fluorescence is gradually quenched with the rising EF. (b) The histogram of E_{off} for 371 SM fluorescence switches. The most probable E_{off} is 593 V/mm and the FWHM is 259
55 V/mm.

Why is the fluorescence of SMs quenched by the external EF? There are four possible mechanisms for EF-induced SM fluorescence quenching as discussed below.

Stark effect. The energy level of the SM, with the present of the
60 external EF, may be shifted and split, leading to the shift of absorption or emission spectrum.[14,22] Although the permanent dipole moment of the centrosymmetric molecule is zero, there is a small permanent dipole difference $\Delta\mu$ between the ground and excited state and $\Delta\mu$ is much lower than 1 D,[23] which corresponds
65 to the Stark shift of ~5 GHz/(kV/mm). However, the FWHM for SR absorption or fluorescence spectrum is about 10^4 GHz (see the detail in ESI), which is four orders of amplitude lager than 5 GHz. Therefore, Stark shift is too small to explain the fluorescence quenching completely here.
70 *Conformational change.* Molecular conformation could be changed by the EF, which has been proved to induce spectrum shift.[15,24] SR molecule used here is synthesized by encapsulating the squaraine dyes with a protective macrocyle, which wraps much more tightly around the central cyclobutene moiety and

enhances molecular chemical stability.[25] Compared to the EF of ~10 MV/mm which induced conformational change of conjugated polymer,[15] the EF of ~1 kV/mm we used here is not large enough to induce the conformation change of SR molecule considering its rigid structure.

Intermolecular (or Interfacial) electron transfer. The electron transfer between donor molecules and acceptor materials would induce the fluorescence quenching.[16,19,20,26-29] Based on the intermolecular electron transfer between single SR molecules and surrounding PMMA matrix, the fluorescence of SR molecules has been modulated by the EF, including quenching and/or enhancement, and the low Q was observed in our previous work.[20] Moreover, the interfacial electron transfer[27-29], which would induced "blinks",[27] could serve as a special case of intermolecular electron transfer. By applying the EF to the ITO electrode, we have also studied the interfacial electron transfer between SM and ITO, the obvious blinking behaviour has been observed.[19] Both of intermolecular and interfacial electron transfers show lower Q and bigger respond time (~0.1 s), comparing with the present results that the fluorescence of all single SR molecules can be completely quenched and the fluorescence is instantly response to the EF. Therefore, the SM fluorescence switch cannot be attributed to intermolecular (or interfacial) electron transfer.

Intramolecular electron transfer. Intramolecular electron transfer[30-33] is a nonradiative process, leading to fluorescence quenching. It would occur to SR molecule due to the containing of electron donor (the anilino rings and carbonyl oxygens) and electron acceptor (four-membered carbon moiety) in the squaraine structure.[19,31] An appreciable intramolecular electron transfer has been found in this squaraine structure by Salice et al.[32] The intramolecular electron transfer could be controlled by the external EF. The larger the EF, the larger the electron transfer rate. When the EF is higher than E_{off}, the radiative process is suppressed completely and the fluorescence of the SM is turned off. The results that the fluorescence quenched gradually with the rising EF, as shown in Fig. 3a, exactly showed the manipulation of intramolecular electron transfer by the varying EF.

The electron transfer rate is related to the electronic coupling, which depends on the distance between electron donor and electron acceptor.[27,28] The Q based on the intermolecular (or interfacial) electron transfer was extremely low, which have been presented in our previous works,[19,20] due to the weak electronic coupling between electron donor and electron acceptor with large distance. The extremely high Q in this experiment is attributed to efficiently intramolecular electron transfer, due to the strong electronic coupling between electron donor and electron acceptor within SR molecule.

In conclusion, we presented a reversible fluorescence quenching of SR molecules on bare glass substrate induced by the external EF. Analysis and comparison of different fluorescence quenching mechanisms, the SM fluorescence switch is attributed to the *intramolecular electron transfer* between distinct regions of single SR molecules. This reversibly and completely quenching behaviour could serve as EF-induced SM fluorescence switch, which would open the door for a broad range of applications in super-resolution fluorescence imaging, molecular electronics and photonics.[34-36]

Notes and references

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† Electronic Supplementary Information (ESI) available: [includes sample preparation, experimental setup, additional data and analyses]. See DOI: 10.1039/b000000x/

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