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REVIEW ARTICLE

Modification of single molecule fluorescence using external fields

Rui-Yun Chen, Guo-Feng Zhang, Cheng-Bin Qin, Yan Gao, Lian-Tuan Xiao†, Suo-Tang Jia

State Key Laboratory of Quantum Optics and Quantum Optics Devices, Institute of Laser Spectroscopy,
Shanxi University, Taiyuan 030006, China
Collaborative Innovation Center of Extreme Optics, Shanxi University, Taiyuan 030006, China
Corresponding author. E-mail: †xlt@sxu.edu.cn

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Controlling and manipulating the fluorescence of single fluorophores is of great interest in recent years for its potential uses in improving the performance of molecular photonics and molecular electronics, such as in organic light-emitting devices, single photon sources, organic field-effect transistors, and probes or sensors based on single molecules. This review shows how the fluorescence emission of single organic molecules can be modified using local electromagnetic fields of metallic nanostructures and electric-field-induced electron transfer. Electric-field-induced fluorescence modulation, hysteresis, and the achievement of fluorescence switch are discussed in detail.

Keywords single molecules, fluorescence, modification, external fields

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Contents

1 Introduction

Single molecule spectroscopy has proven to be a powerful tool in physics, biology, chemistry, and materials science over the past 25 years [1–3]. Since the first groundbreaking study by Orrit in 1990 [4], the efficient detection of individual molecules through their fluorescence has resulted in the majority of the field using this approach, particularly in the rapidly growing area of super-resolution imaging. Single-molecule fluorescence detection removes the usual ensemble averaging in bulk detection and enables the investigation of complex and heterogeneous systems [5–8]. Although fluorescence imaging is a highly sensitive technique, the detection of a single fluorophore is usually limited by its fluorescence quantum yield, background noise from the matrix, and the photostability and brightness of emitters. The fluorescence can easily be obscured by the background and suffers from irreversible photobleaching. For this reason, single-molecule fluorescence detection is usually performed on robust single chromophores that are doped in a proper host matrix with low background noise. However, variable or switchable fluorescence intensity can facilitate the use of single organic molecules in molecular photonics, molecular electronics, and even biological imaging. The principle of single-molecule-based super-resolution fluorescence imaging is to fluorescently activate a small fraction of molecules at a given time or to reconstruct the photobleached molecules in the image. The ability to manipulate and control the fluorescence of single emitters, therefore, will promote their application in related fields.

In addition to single organic molecules, some artificial molecules such as quantum dots (QDs) and nitrogen-vacancy (NV) centers in diamond are good candidates for single emitters. The photoluminescence of single QDs is size dependent. One can easily control the absorption and emission spectra of single QDs simply by changing their size. NV centers in diamond can undergo strong, spin-sensitive optical transitions under ambient conditions. Many studies have reported manipulating the photoluminescence of NV centers and single QDs by means of optical [9, 10], temperature [11, 12], and plasmonic [13, 14]. Although NV centers and single QDs have perfect photostability, they suffer from a broad emission spectrum. Organic molecules show a number of red-shifted fluorescence lines, which are nearly absent in semiconductor nanocrystals, making it possible to record sharp zero-phonon lines in fluorescence exaction spectra.

The fluorescence emission of single organic molecules can be easily modified by carefully controlling the external environment. Many external stimuli, such as pH-triggers [15], temperature [16], and photo-activation [17] have been reported to modify the fluorescence of single molecules. The interface dielectric environment can also affect the fluorescence emission by guiding spontaneous emission into directional emission to enhance the collection efficiency [18, 19]. Metallic nanostructures have had important applications in modification of fluorescence because of their antenna properties, which lead to local-field enhancement of absorption or radiation decay rate. The widest application has been surface-enhanced Raman scattering (SERS), in which the weak Raman signals of molecules are strongly amplified by the evanescent field of nanostructures. However, it is also interesting to investigate the use of metallic nanostructures to modify the fluorescence properties of single molecules. Another method for modifying the fluorescence properties of single molecules is based on electron transfer [20–27]. Electron transfer is an elementary process in physics and chemistry that occurs when an electron moves from one species to another. Once the single molecule is excited from the electronic ground state to the electronic excited state by absorbing a photon, the excited state can relax via several pathways: radiative transition from the excited state to the ground state with emission of fluorescence, intersystem-crossing to the spin-forbidden triplet state, internal conversion into heat without emitting a photon, and electron transfer from single molecules to traps inside the surrounding matrix. Electron transfer is a controllable phenomenon that can be affected by the environment and the external applied field. By reversibly controlling electron transfer events in single molecules or between single molecules and the surrounding environment, the fluorescence of single molecules can be manipulated using an external electric field.

In this review, we present an overview of recent studies into the modification of single-molecule fluorescence using an external field, primarily either a local electromagnetic field of metallic nanoantennas or an electric field.

2 Modification of single-molecule fluorescence using the local electromagnetic field of metallic nanostructures

There have been many efforts to investigate the fluorophore-metal interaction using ensembles of molecules and metal films. However, for planar metallic surfaces, fluorophores have diverse orientations and distances toward the surface. For non-continuous thin metal films that have metal islands of various particle sizes and shapes, the interaction is uncontrolled and the modification of fluorescence has inherent inhomogeneity. Clusters or hotspots on the metal surface can be effective nanostructures for the enhancement of molecular fluorescence. Strong fluorescence enhancements of single molecules, by up to 54 and 136 times, respectively, have been observed on the surface of aluminum thin films and silver nanoparticle clusters. Based on this surface enhancement effect of single-molecule fluorescence, Cang *et al.* [28] probed the electromagnetic field of a 15-nm hotspot using single-molecule imaging. The hotspots appeared when light illuminated a rough metallic surface. The concentration of the light on the nanometer scale produced an intense electromagnetic field. Individual fluorescent molecules can be localized with nanometer accuracy in the optical far field. However, multiple emitters in the diffraction limited spot cannot be distinguished from each other. To probe the field within a diffraction-limited spot, one must ensure that the emitters emit one at a time. Cang *et al.* used Brownian motion of single dye molecules in a solution to scan the hotspots one molecule at a time in a stochastic manner. Using this method, images of the fluorescence enhancement profiles of single hotspots as small as 15 nm with an accuracy of 1.2 nm can be obtained (Fig. 1). The fluorescence enhancement factor has a peak point, ranging from a few nanometers to several tens of nanometers. The quenching effect due to energy transfer from the molecule to the metal nanostructure dominates near the surface, whereas the local field dominates farther away from the surface. Both the material and the geometry of the nanostructures affect the enhancement factor.

For ensemble measurement on thin-film matrices, the modification of fluorescence suffers from an inhomogeneous distribution in size, shape, and surface roughness of the nanostructures. The space and orientation of the molecules relative to the nanostructures also have wide distributions. The heterogeneity is overwhelmed by ensemble-averaged data. In past decades, the de-

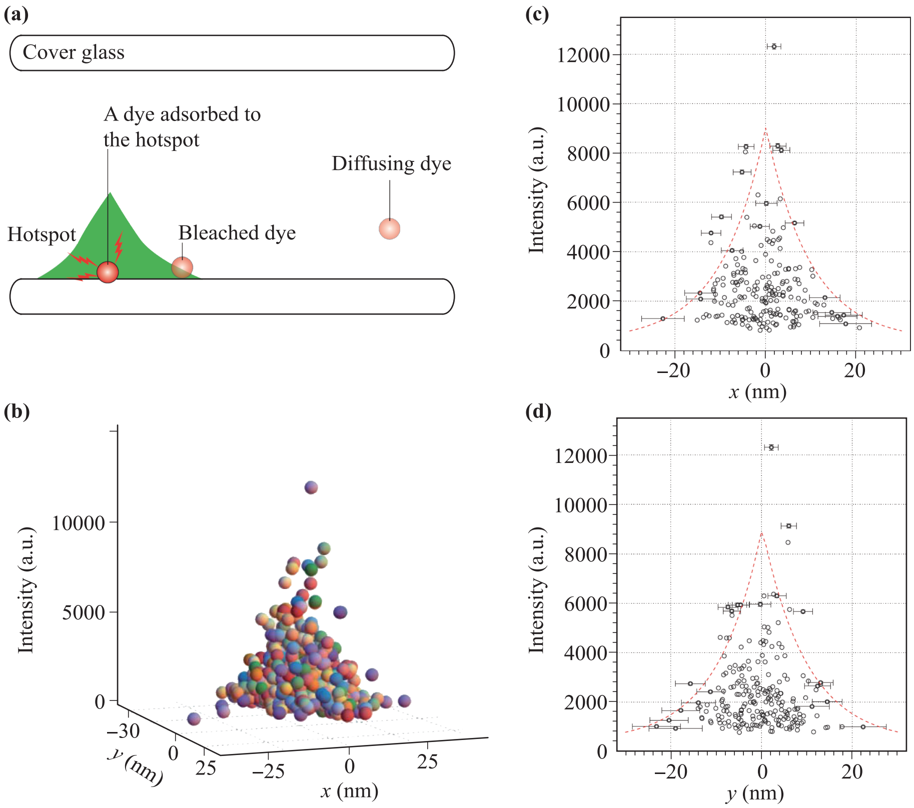

Fig. 1 **(a)** The principle of Brownian motion single molecule scaning the hotspots on the surface of a thin aluminum film. **(b)** 3D scatter plot of the fluorescence enhancement profile of the hotspot, with each sphere representing one single molecule event. **(c)** The molecules within -2 nm $< y < 2$ nm, which represents a cross-section of the hotspot at $y = 0$ nm. **(d)** A similar plot of the cross-section of the hotspot at $x = 0$ nm. Reproduced with permission from Ref. [28].

velopment in nanotechnology has made control of the nanoscale processes much available. It is interesting to modify the photophysical properties of single emitters at desired locations in the device. One of the most important developments has been the discovery of SERS down to the single-molecule level in the interactions of single molecules with metallic nanostructures or nanoparticles. However, SERS is not the only application of novel metallic nanostructures that has been investigated. The fluorescence spectrum of a single molecule has been shown to be very sensitive to its surrounding nanoenvironment, such as the shape, size, and material properties of metallic nanostructures.

A majority of studies considering interaction between metallic nanostructures and single molecules have focused on so-called plasmon-enhanced fluorescence (PEF) [28–58]. Reviews beyond the scope of this article can be found in Refs. [59, 60]. For a single molecule with ground and excited states $|g\rangle$ and $|e\rangle$, the fluorescence intensity S can be expressed as $S = D \cdot k_{exc} \cdot \phi_f$, where D is the overall detection efficiency of the system, k_{exc} is the excitation rate of a single molecule, and ϕ_f is the fluorescence quantum yield. The overall detection efficiency of the system is well defined for a given setup. The excitation rate $k_{exc} \propto |\mu \cdot E|^2 \cdot \rho_e$ depends on the absorption transition moment μ, light field E, and excited state density ρ_e. The quantum yield ϕ_f can be described by $\phi_f = k_r/(k_r + k_{nr})$, where k_r and k_{nr} denote the radiative and non-radiative decay rates of the excited state, respectively. In the vicinity of a metallic nanostructure, the plasmonic effect may modify the fluorescence emission in two ways. One way is increasing the excitation rate via local-field enhancement. In essence, this method is dependent on the overlap of the absorption spectrum of a single molecule and the plasma resonance wavelength of a metallic nanostructure. The other way is based on the modification of radiative and non-radiative decay rates by changing the localized density of photonic states using a plasmon. The modification of k_r and k_{nr} is conducted in a distance- and orientation-dependent manner.

Modification of single-molecule fluorescence has been observed when coupling to a single metal nanoparticle acting as an optical antenna [32, 33]. Figure 2 shows the schematics of the experimental arrangement. The optical antenna in the form of a spherical nanoparticle is attached to the end of an optical fiber. By varying the distance between molecules and gold nanoparticles, single-molecule fluorescence can be enhanced or quenched. The fluorescence of a single molecule is proposed to be the product of excitation influenced by the environment and the emission of radiation influenced by radiative and non-radiative decay. At longer distances, the local-field enhancement induced by gold nanoparticles leads to an increased excitation rate, which results in fluorescence enhancement. However, at very short distances, the decrease in quantum yield due to non-radiative energy transfer to the nanoparticle is stronger than the increase of the excitation rate, thereby quenching the fluorescence of the molecule. The agreement between experiment and theory is surprisingly good. Figure 3 shows the fluorescence rate as a function of particle-surface distance z. The fluorescence enhancement reaches its maximum at a distance of $z \approx 5$ nm. In similar work by the Sandoghdar group [32], more than a 20-time enhancement for fluorescence and 20-fold shortening of the excited state lifetime were observed. Furthermore, the plasmon resonance of gold nanoparticles was found to play a central role in the enhancement process. The quantum efficiency of single molecules was found to be reduced at very short distances; however, no fluorescence quenching was discussed.

The local-field-enhancement factors and sizes of regions depend on the size, shape, composition, arrangement, and surrounding environment of metallic nanostructures. In the past decade, great effort has been made to prepare metallic nanostructures with well-defined sizes, uniform shapes, and fine arrangements. The fluorescence enhancement effect of metallic nanostructures with diverse patterns has been investigated, such as nanoprisms [36, 47], nanorods [42, 43, 56, 58, 61], nanobowties [44, 51, 55], nanodimers [40, 41], nanoporous materials [46], nanoshells [52], and nanoparticle arrays [50, 54]. One of which is bowtie-like nanoantennas [44]. Using lithographically fabricated gold bowtie nanoantennas (Fig. 4), enhancement of single-molecule fluorescence by up to 1000 times has been reported. Additionally, the single molecules investigated were well chosen for the overlap of absorption and emission spectra with the plasmon resonance of the bowtie nanoantennas. Therefore, both the absorption and radiative emission rate can be affected by the local field of the bowtie. The enhancement effect is highly dependent on the bowtie gap size. The smaller gaps yield higher enhancement factor values, which are consistent with the higher local field strengths induced by smaller gaps. It is found that the enhancement of absorption rate in the center of the bowtie gap is excitation wavelength dependent. Basically, the maximal local-field enhancement can be obtained only when the plasmon resonance is excited at its peak wavelength. The detuning of excitation wavelength from the peak will reduce the enhancement effect. The overlap between the plasmon wavelength peak and the emission wavelength of the Stokes-shifted fluorescence can also affect the enhancement. It is difficult to obtain simultaneous overlap of the plasmon peak with absorption and emission. However, if the plasmon resonance spectrum is sufficiently wide, absorption and emission enhancement can be obtained, although neither is optimal.

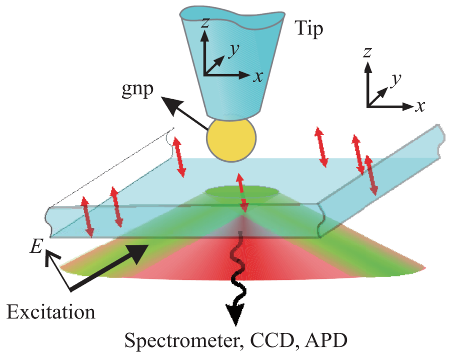

Fig. 2 Schematic of an optical antenna scanning across a single molecule. Reproduced with permission from Ref. [32].

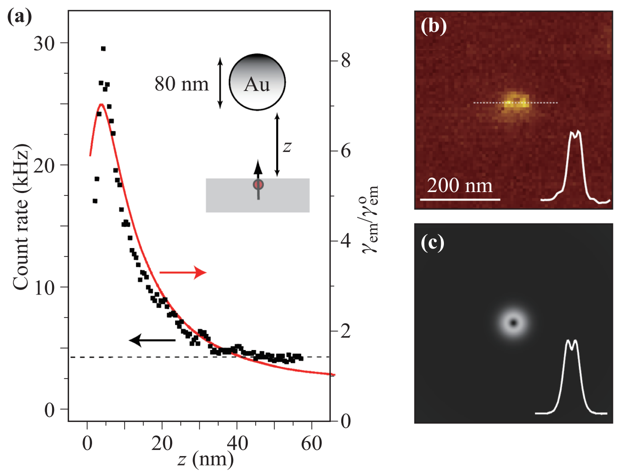

Fig. 3 **(a)** Fluorescence rate of a vertically oriented single molecule as a function of distance z between particle and surface (solid curve: theory, dots: experiment). The horizontal dashed line shows the background level. **(b)** Fluorescence image of a single molecule acquired for $z \approx 2$ nm. The dip in the center shows fluorescence quenching. **(c)** Theoretical simulation image. Reproduced with permission from Ref. [33].

The sizes of the local-field-enhancement regions, field enhancement factors, and the plasmon resonance wavelength vary with the geometry, size, and arrangement of metallic nanostructures [59]. Thus, the preparation of nanostructures plays an important role in studies of PEF. Several novel metal (Ag and Au) nanostructures

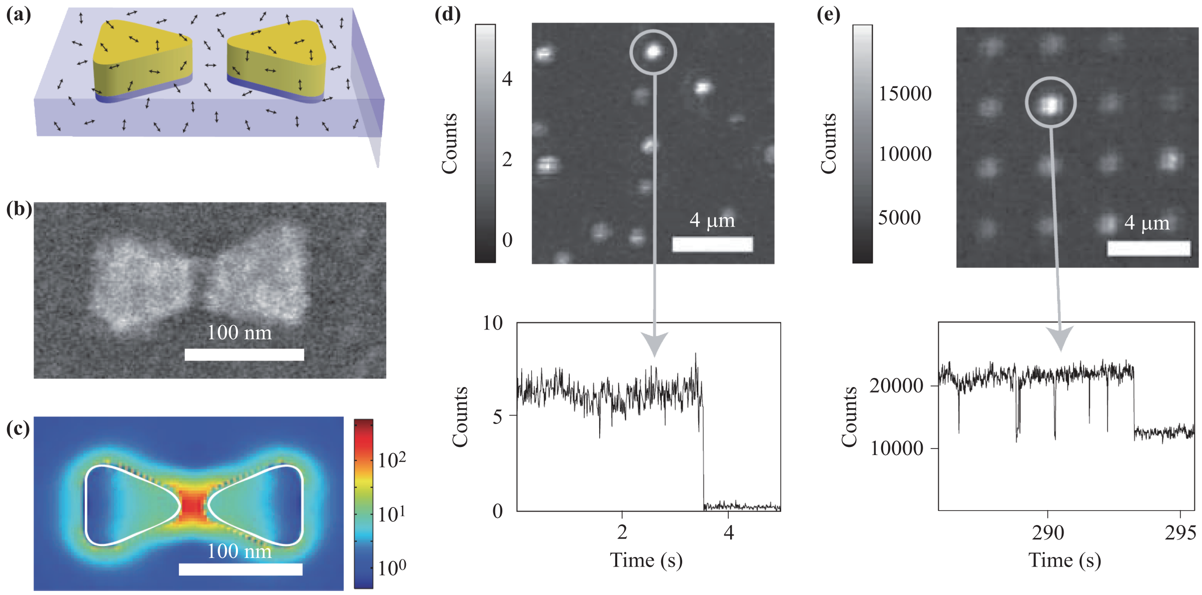

Fig. 4 **(a)** Schematic of gold bowtie nanoantenna spin-coated with N,N'-bis(2,6-diisopropylphenyl)-1,6,11,16-tetra-[4-(1,1,3,3-tetramethylbutyl)phenoxy]quaterrylene-3,4: 13,14-bis(dicarboximide) (TPQDI) molecules (*black arrows*) in poly(methyl methacrylate) (PMMA) (*light blue*) matrix. **(b)** Scanning electron microscopy image of a gold bowtie nanoantenna. **(c)** Theoretical simulation of local intensity enhancement of a bowtie nanoantenna with finite-difference time-domain calculation. **(d, e)** Confocal fluorescence imaging and fluorescence time trace of TPQDI in PMMA without and with bowtie nanoantennas, respectively. Reproduced with permission from Ref. [44].

have been prepared using wet chemical methods [62–67]. Plasmon resonance wavelength ranging from the ultraviolet to near-infrared region can be obtained by controlling the geometries of the nanostructure. The space between molecules and nanostructures, and the patterns of nanostructures, should be precisely controlled to facilitate PEF. In the control of space, great progress has been made in near-field optics, which can also improve the spatial resolution. For diverse patterns of nanostructures on the substrate, coupling between single molecules and the metal nanostructure is difficult. The concentration of single-molecule samples should be sufficiently large that one can find appropriate couples with optimal interaction, which may be a barrier to specific applications.

3 Modification of single-molecule fluorescence using an electric field

Molecular electronics has attracted much attention over the past several decades. The possibility of using single organic molecules as active elements in organic optoelectronic devices for a variety of applications has led to a great deal of research. With the goal of examining physical processes at the molecular scale of functioning electronic components, the effect of the electric field on the fluorescence of single molecules is an active research area in molecular electronics.

3.1 Electric-field-induced fluorescence modulation of single molecules

Conjugated polymers and organic dye molecules have been widely applied in a range of devices such as light-emitting diodes [68], field-effect transistors [69, 70], and solar cells [71]. As the performance of these organic devices is largely dependent on the properties of the components down to the molecular level, the behavior of molecule-scale units, i.e., single conjugated polymer molecules or single organic molecules, under the influence of an external electric field is of particular interest recently.

Poly[2-methoxy,5-(2′-ethyl-hexyloxy)-*p*-phenylene vinylene] (MEH-PPV) is one of the most commonly used conjugated polymers among organic materials; it has the advantages of chain folding and self-aggregation (unlike rigid molecules) [72–74]. The effect of an electric field on the fluorescence of MEH-PPV has been studied for both bulk films and individual molecules in a matrix. In ensemble measurements, it was found that the fluorescence of neat PPV film can be quenched by the electric field [75–77]. Commonly, this phenomenon is attributed to the field-induced dissociation of electron-hole pairs into off-chain charge pairs. The quadratic dependence of fluorescence quenching on the strength of the electric field was found; it can be explained using Marcus electron transfer theory [78]. Linear relationships between fluorescence quenching yield and photoinduced free charges were found at strong fields [77]. In 2001, Barbara *et al.* found field-induced fluorescence modulation of an MEH-PPV thin film [79]. They proposed that the modulation of fluorescence is due to the change in the local carrier density induced by the electric field. Smith *et al.* [80] studied the electrofluorescence of MEH-PPV oligomers under an applied electric field. They found that field-induced quenching is comparable to that of thin films and that quenching magnitude decreases with decreasing chain length. They concluded that inter-chain contacts facilitate charge separation and that the polarizable environment formed by oligomer chain was capable of stabilizing the charge separation state.

Single-molecule detection removes the ensemble averaging effect in bulk investigations and can be used to obtain more detailed information than ensemble experiments. The fluorescence of single conjugated polymer molecules placed in an electric field has been studied in detail [81–84]. In 2004, Park *et al.* [81] studied the charge injection and photo-oxidation of single conjugated polymer molecules by applying a repeated triangle voltage to the single MEH-PPV molecules. They showed that the electrical bias can reversibly modulate the fluorescence of a single MEH-PPV molecule, particularly when the fluorescence quantum yield of single MEH-PPV was reduced by photo-oxidation (Fig. 5). The electrical bias was thought to control the charge injection events that influence the fluorescence quantum yield, which reveals the direct correlation of photobleaching and charge carrier effects in a single molecule. Hania *et al.* [82] found that the electric field can induce quenching and blinking of fluorescence of single conjugated molecules. They attributed this effect to electric-field-induced long-living charged species, which act as quenchers for excitations. In a further study [83], Hania *et al.* studied the response of the fluorescence of single MEH-PPV molecules to an oscillating electric field. Obvious fluorescence modulation was found in their work. To investigate the origin of the fluorescence modulation effect, the responses of single MEH-PPV molecules dispersed in two different matrix PMMA and polystyrene (PS) were compared. They defined modulation depth M to quantify the response of fluorescence to the electric field. M is defined as $(I_{max} - I_{min})/I_{max}$, where I_{max} and I_{min} are the maximum and minimum fluorescence intensity, respectively. They found that the modulation depth of single molecules in PMMA is more pronounced than those in PS (Fig. 6). They attributed this phenomenon to the full of suitable electron acceptor sites which contribute to the quenching of single-molecule fluorescence in PMMA.

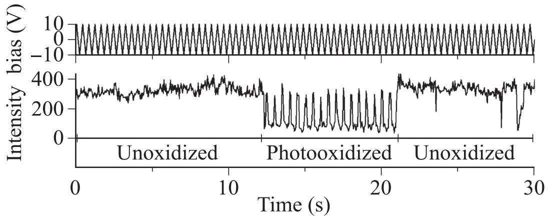

Fig. 5 Photooxidation and electrical bias induced fluorescence modulation of a single MEH-PPV molecule. Reproduced with permission from Ref. [81].

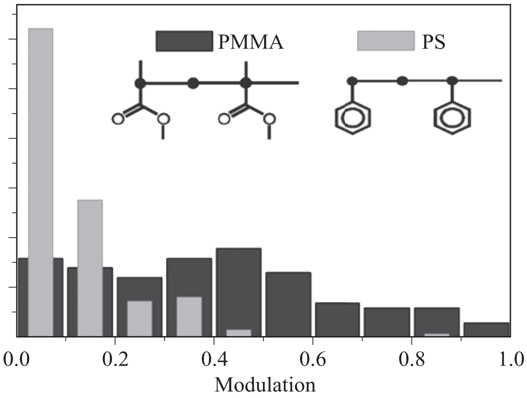

Fig. 6 Distribution of electric-field-induced fluorescence modulation for single MEH-PPV molecules in PMMA and PS matrices. Reproduced with permission from Ref. [83].

Compared to single conjugated polymer molecules with hundreds of chromophores, and thus, inter-chain electron transfer events that complicate the investigation of fluorescence modulation, single organic dye molecules have the advantage of having individual chromophores, which removes the effect of large conformation changes and facilitates the study of local environments.

By applying the electric field to the sample, Chen *et al.* [85, 86] evaluated the fluorescence modulation of single organic molecule by measuring the single-molecule fluorescence trajectories versus the change in amplitude of the field. Figure 7 shows the typical response of single molecules to the electric field. The fluorescence of some single molecules was found to be enhanced when the electric field was applied, whereas some single molecules showed fluorescence quenching when the electric field was applied. There were also several single molecules that had no response to the electric field. For single molecules responding to the field, the response times are quite different. Some single molecules showed an instantaneous change versus the electric field, whereas others showed a delay effect.

Figure 8(a) shows the typical fluorescence trajectory

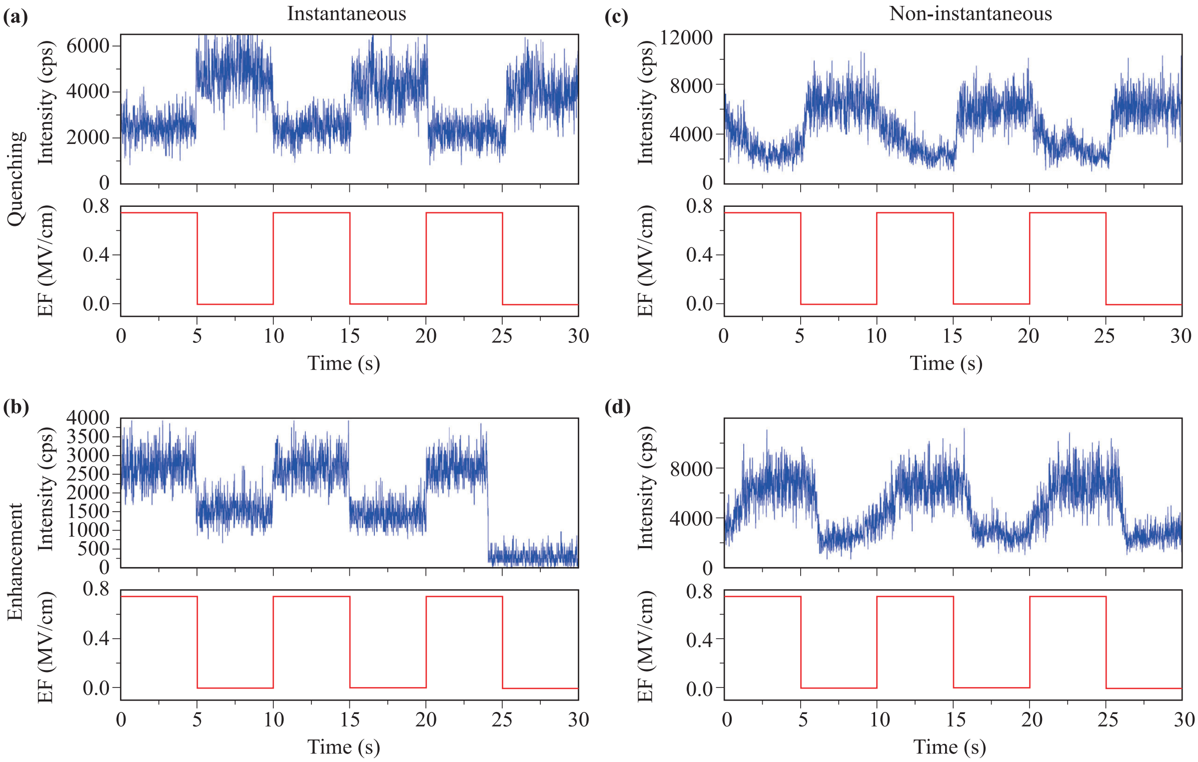

Fig. 7 Diverse fluorescence response of single squaraine-derived rotaxane (SR) molecules in PMMA matrix under square wave electric field with maximum field of 0.75 MV/cm. Reproduced with permission from Ref. [85].

of a single molecule for which fluorescence was quenched when the electric field was turned on and recovered when the electric field was turned off. The average response times achieved by exponential fitting are 1.22 s for quenching and 0.28 s for recovery, as shown in Figs. 8(b) and (c), respectively. Figure 8(d) shows the time constants of molecules that have non-instantaneous responses to the electric field. Figure 8(d) implies that under smaller electric fields, more time is needed for the reorientation of polymer chains toward the direction of the electric field, thus the redistribution of electron acceptors requires more time to form a new equilibrium. However, under large electric fields, the reorientation of the polymer chain will be easier, which leads to less polarization time with respect to the electric field. When the electric field is turned off, the slow relaxation of fluorescence is attributed only to the viscosity of the polymer, resulting in similar recovery times under both larger and smaller electric fields.

Electron transfer is an important fluorescence-quenching pathway that can be reversibly controlled using an external electric field. PMMA has an ester group $-\mathrm{COOCH_3}$ with a dipole moment of 1.6 Debye [87]. The carbonyls in the ester group can serve as electron acceptors, which induce the quenching of single-molecule fluorescence [83]. The electron acceptors have an anisotropic distribution around the single molecules, which diversifies the interaction between single molecules and electron acceptors, and thus, creates a diverse response of fluorescence to the electric field. If the coupling between single molecules and surrounding electron acceptors is enhanced by the electric field, the forward electron transfer rate is increased and the backward electron transfer rate is decreased. The fluorescence quantum yield is reduced. However, if the coupling strength is suppressed by the electric field, the fluorescence would be enhanced. The alternating electric field would induce fluorescence modulation of single molecules. The response of single-molecule fluorescence to the external electric field also suggests a sensitive method for investigating the electric-field-induced polarization dynamics of the PMMA matrix [86]. Because of the polar character of the PMMA polymer, we expect two main types of polarization effects when the electric field is applied: electronic polarization and orientational polarization. Both types of polarization effects can cause distribution of the electron acceptors surrounding the single molecules. However, the redistribution of electron acceptors induced by electronic polarization is much faster than that induced by orientational polarization. Therefore, if electronic polarization dominates, the fluorescence will show an instantaneous response to the electric field, and vice versa.

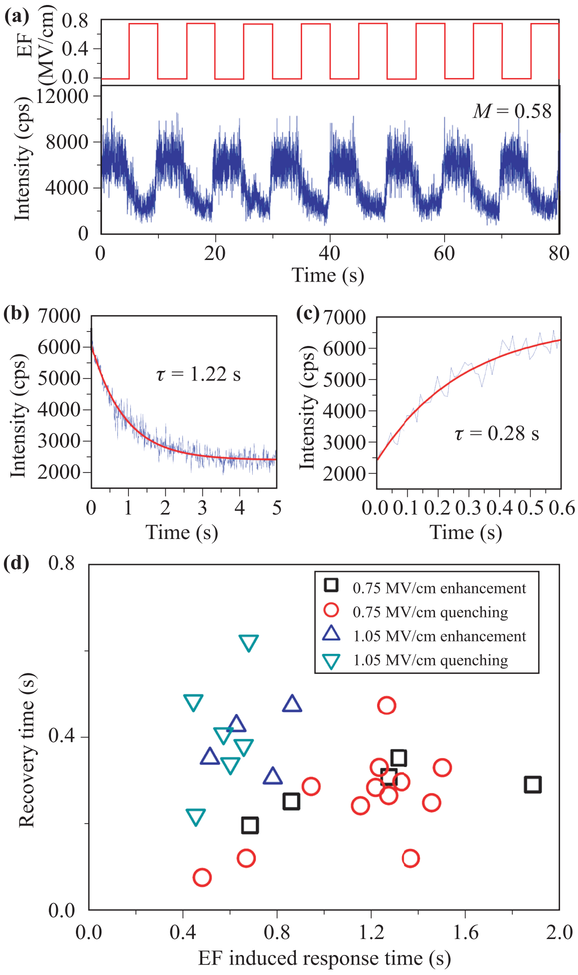

Fig. 8 **(a)** Fluorescence trace of individual SR molecule under square wave electric field with maximum field of 0.75 MV/cm. The field resulted in a quenching in the fluorescence and a slow decay time. A faster recovery of the fluorescence was found after the field was turned off. **(b, c)** Exponential fits of quenching and recovery time constants of same molecule, respectively, averaged over 7 complete cycles. **(d)** Distribution of the transient response time for field-induced fluorescence quenching molecules and field-induced fluorescence enhancement molecules under square wave electric field with two different maximum field strength, where horizontal axis is the electric-field-induced response time of fluorescence and vertical axis is the recovery time of fluorescence when the field is turned off, respectively. Reproduced with permission from Ref. [86].

3.2 Electric-field-induced fluorescence hysteresis of single molecules

Hysteresis is an effect that is widely applied in physics, material science, and biology [88–90]. Research on the hysteresis effect in single molecules suggests methods of designing memory elements at the single-molecule level. Recently, the hysteresis effect has been found in research regarding the electric field effect on the fluorescence of single MEH-PPV molecules. In single MEH-PPV molecules, the fluorescence spectrum can be modulated using an electric field [84]. Figure 9 shows the electric-field-induced Stark shift of the fluorescence spectrum of single MEH-PPV molecules at 5 K and the corresponding linear and hysteresis responses of the emission. The hysteresis effect found in the Stark shift suggests the development of single-molecule switches and memory elements. Similarly, the hysteresis effect was found in the electric-field-induced fluorescence intensity modulation of single MEH-PPV molecules [83]. Various types of hysteresis were observed, including crossing and non-crossing curves. The independence of hysteresis from the electric field oscillation frequency suggests that the local conformational change in the MEH-PPV chain or its surrounding matrix contributes to the hysteresis.

In work of Zhou *et al.* [91], hysteresis was found in the electric-field-induced fluorescence modulation of single organic molecules in polymer film. The single SR molecules were dispersed in PMMA polymer film. An alternating voltage was applied to electrodes between which the single molecules were dispersed. By recording the fluorescence intensity of single molecules versus the alternating electric field, hysteresis of the fluorescence intensity was found. Figure 10 shows the fluorescence modulation of single molecules with a sine-wave electric

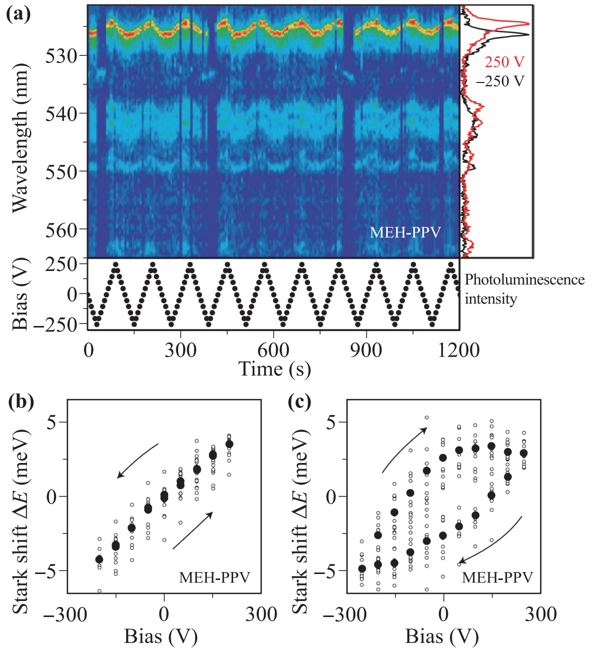

Fig. 9 **(a)** Modulation of fluorescence spectrum of a single MEH-PPV molecule using voltage applied to the electrodes. **(b, c)** Linear and hysteretic response of the spectrum of single MEH-PPV molecule. Reproduced with permission from Ref. [84].

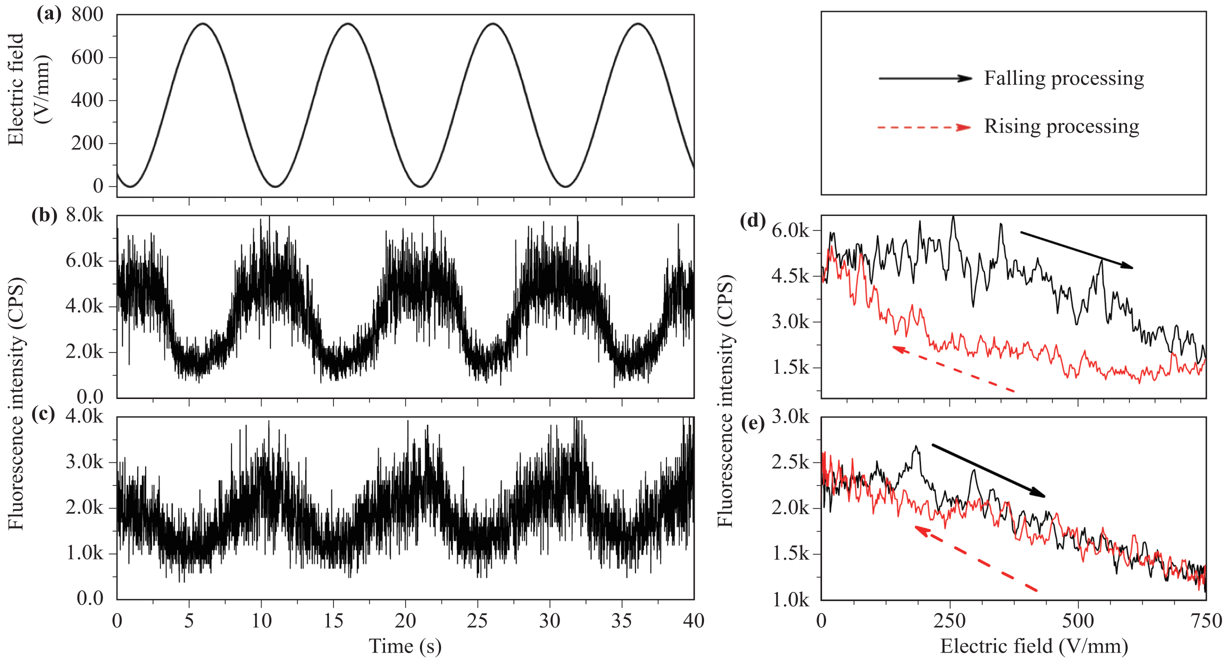

Fig. 10 **(a)** Sine wave electric field applied on single molecules. **(b, c)** are two types of fluorescence trajectories of single molecules response to electric field with maximum strength of 750 V/mm. **(d, e)** are the corresponding asymmetric and symmetric response of fluorescence intensity versus electric field, achieved by averaging the profiles of **(b)** and **(c)**, respectively. Reproduced with permission from Ref. [91].

field. Figure 10(d) shows obvious asymmetric fluorescence quenching and recovering versus the electric field, exhibiting the hysteresis effect.

A model based on electron transfer and space charge relaxation processes to explain the hysteresis effect was proposed. The model considers electron transfer between the single molecule and electron acceptors in its surrounding matrix, which has been proven to be an important cause of fluorescence quenching. The fluorescence modulation induced by electron transfer can be expressed as

$$\Delta I_1(F(t)) = I_0 \cdot \eta \cdot F^2(t), \tag{1}$$

where I_0 represents the initial fluorescence intensity without an applied electric field, $F(t)$ is the electric field, and η is a coefficient that depends on both the concentration of acceptors in the matrix and the standard Gibbs free energy gap of individual molecules [78]. The electron-transfer-induced fluorescence variation shows a dependence of the square of the field strength.

Another reason is the space charge relaxation of the polymer film induced by the electric field. The effect of space charge relaxation is not to create distinct point-like charges, but rather, to create a continuous charge distribution over a region of space; this distribution changes the local density of electrons or holes around single molecules. Relative to direct electron transfer, the effect of space charge relaxation on the fluorescence variation should be slow. The fluorescence variation is dependent not only on the immediate electric field at the moment t but also on the effect of the electric field at previous times:

$$\Delta I_2(F(t)) = I_0 \cdot k \cdot \int_{-\infty}^{t} F(t_i) \cdot \mathrm{e}^{-\frac{t-t_i}{\tau}} \mathrm{d}t_i, \tag{2}$$

where $F(t_i)$ is the electric field at time t_i, τ is the attenuation constant, and k is the coefficient decided by the surrounding environment of the single molecule. The sign of k depends on the electron accumulation or hole accumulation surrounding the single molecule.

For a periodic sine wave electric field (as used in the experiment) $F(t) = A[\sin(\omega t) + 1]$, the total effect of electron transfer and space charge relaxation on the fluorescence variation can be expressed as

$$\begin{aligned} I(F(t)) &= I_0 + \Delta I_1(F(t)) + \Delta I_2(F(t)) \\ &= I_0 \cdot \eta \cdot A^2[\sin(\omega t) + 1] \\ &\quad + I_0 \cdot k \cdot A \left[\frac{\tau\sqrt{1+\omega^2\tau^2} \cdot \sin(\omega t - \delta)}{1+\omega^2\tau^2} + \tau \right]. \end{aligned} \tag{3}$$

Figure 11 shows the stimulation results of hysteresis and linear fluorescence trajectories versus the electric field. The hysteresis effect dependents primarily on the

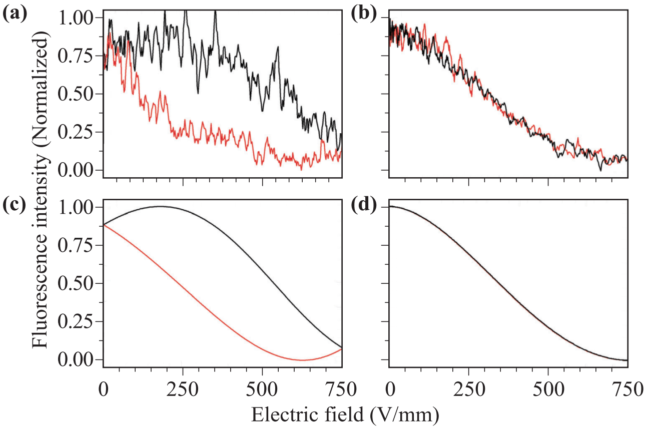

Fig. 11 **(a, b)** are the hysteresis and linear response of single-molecule fluorescence versus the electric field, respectively. **(c, d)** are the simulation to **(a)** and **(b)**. The simulation parameters in the case **(c)** are $\tau = 0.65$ and $k = -100$, while in the case **(d)** are $\tau = 0$ and $k = -100$. Reproduced with permission from Ref. [91].

space charge relaxation of the PMMA polymer. The parameters k and τ are variables that are influenced by the environment surrounding single molecules, for example, the concentration of PMMA and the temperature of the environment. The combination of electron transfer and the space charge relaxation effect fully explains the electric-field-induced hysteresis of single-molecule fluorescence.

3.3 Electric-field-induced single molecular fluorescence switch

With the development of nanotechnology and optoelectronics in recent years, much attention has been focused on the feasibility of molecular photonic switches and optical data storage elements based on single fluorescent molecules. To achieve this goal, the fluorescence intensity of single molecules should be switched in a reversible manner between two distinct states that are controllable using external stimuli. Generally, controllable single-molecule fluorescence on/off switch demands efficient competing pathways to counter the emission from the excited state of single molecules via, for example, spectral diffusion and spectral jumps due to the surrounding environment, intersystem crossing to dark triplet states, electron transfer to trap sates, and excitation energy transfer. Once these factors can be reversibly controlled, molecular switching can be achieved.

Many schemes for single molecular switches are based on light-induced changes in the photophysical phenomena of single molecules. By controlling the photon-induced spectral jumps of a single molecule at low temperature, reproducible single molecular switch between two absorption states was achieved [92, 93]. At low temperatures (< 3 K), the excitation spectra of individual molecules is narrower than that at ambient temperature. Light-induced reversible frequency jumps cause the absorption of single molecules on/off-resonance with an excitation laser, leading to on/off state of single-molecule fluorescence. Based on the optical switching of fluorescence resonance energy transfer pairs, Irie *et al.* [94] created the first room temperature single-molecule photoswitch. In their experiment, the fluorescence of donor chromophore can be turned on and off by light activating or deactivating a quenching unit acting as an energy acceptor, which is connected to the donor. Light at 488 nm was used to de-active the quenching unit. Light at 325 nm was used for activation. Similar single-molecule optical switching based on two-color excitation was achieved by Heilemann *et al.* [95] in commercially available single carbocyanine dyes (e.g., Cy5). Rather than donor/acceptor energy transfer, the photo-switch developed in this work is based on alternating excitation at 633 nm and 488 nm to obtain a fluorescent and non-fluorescent state of individual Cy5 molecules, as illustrated in Fig. 12. A reproducible and reliable single-molecule photo-switch with millisecond responses was shown.

The electric field is a significant external stimulus used for controllable single-molecule switching. Using an external electric field, the fluorescence of single quantum nanorods was directly controlled in a reversible on-off optical switch [96]. The field-induced spectral red shift was proposed to explain emission intensity reduction. An additional occurrence induced by the applied field, i.e., the controlled charging of single quantum nanorods, was found. The electric field can also induce conformation changes of single molecules, which provides another category of molecular switch. By applying a bias voltage to a single molecule, Meded *et al.* [97] found that the current-voltage characteristics of single molecules can be switched between "on" and "off" traces. They found that

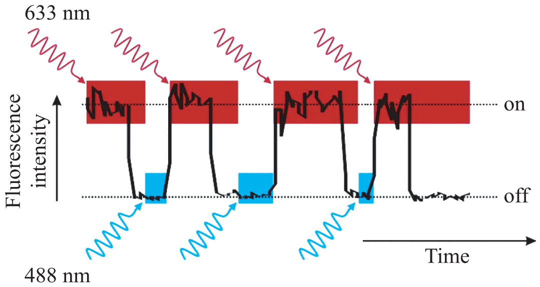

Fig. 12 Principle schematic of Cy5 single molecule as efficient reversible single-molecule optical switch, where the molecular fluorescence intensity is switched between an on and off state by applying alternating excitation at 633 and 488 nm. Reproduced with permission from Ref. [95].

the bias voltage can control the conformation change of single molecules. Rather than the fluorescence switch, the alternative mechanism of the conductance switch was presented.

Based on electric-field-induced electron transfer, we present a reversible single-molecule fluorescence switch [98]. In this work, single SR molecules were directly dispersed on a bare glass substrate and an external electric field was applied. At a given electric field, the fluorescence of single molecules was quenched to the background of the substrate. By repeatedly turning the electric field on and off, a reversible photo-switch was created. Figure 13 shows the fluorescence imaging of single SR molecules on bare glass at different electric field values. When there is no electric field applied to the sample, images of single molecules can be obtained, as shown in Fig. 13(a). The individual bright spots in the image represent single emitting molecules. Obvious photoblinking events can be found in certain single molecules during the image scanning period, e.g., molecule 9, which satisfies the basic properties of a single molecule. When an electric field of 400 V/mm was applied to the sample, the fluorescence of several single molecules was fully quenched, whereas others were not until a larger electric field (1000 V/mm) was applied. However, when the electric field was turned off, certain single molecules went back to emitting. The other single molecules disappeared because of light-induced photobleaching. The single molecules that survived during the experimental time scale showed reversible switching characteristics when an alternating electric field was applied.

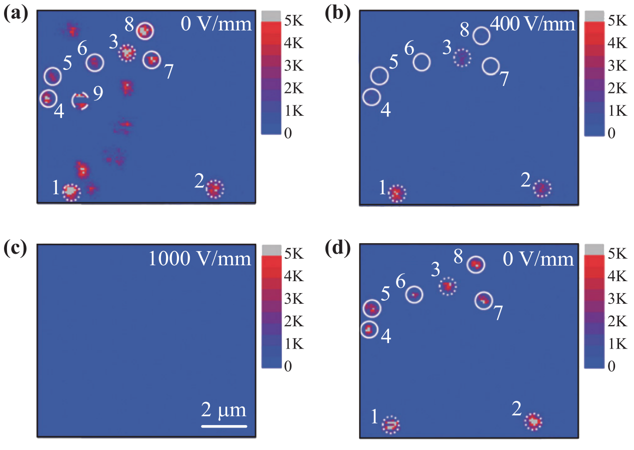

Fig. 13 Confocal fluorescence images of single SR molecules on a bare glass substrate within area of 18 μm × 18 μm under the external electric field of **(a)** 0 V/mm, **(b)** 400 V/mm, **(c)** 1000 V/mm, and **(d)** the recovered 0 V/mm, respectively. Molecules 1-3 show a weaker fluorescence at 400 V/mm, while the fluorescence of molecules 4-8 is absent. All molecules were completely quenched at the field strength of 1000 V/mm. Reproduced with permission from Ref. [98].

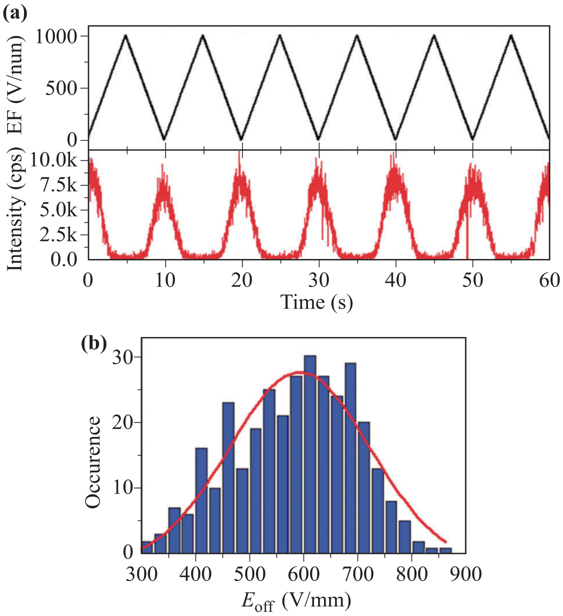

Fig. 14 **(a)** The periodic triangle-wave electric-field-induced fluorescence modulation of the SR molecule on bare glass. The fluorescence is gradually quenched with the increasing electric field strength. **(b)** The histogram of turned-off electric field E_{off} for 371 single-molecule fluorescence switches. The most probable value of E_{off} is 593 V/mm and the FWHM is 259 V/mm. Reproduced with permission from Ref. [98].

Figure 14(a) shows one fluorescence trajectory of a single molecule as a function of triangle-wave electric field. Note that the fluorescence intensity is gradually quenched when the electric field strength increases. We define the amplitude of the electric field under which 90% of single-molecule fluorescence is quenched as turned-off electric field (E_{off}). Figure 14(b) shows the distribution histogram of E_{off} for 371 single molecules. The most likely value is 593 V/mm; the full width at half maximum (FWHM) of the distribution is 259 V/mm.

Intermolecular and intramolecular electron transfer are usually considered to be controllable mechanisms that induce fluorescence quenching. Intermolecular electron transfer, however, could not contribute to complete quenching of the fluorescence intensity of single molecules, as was revealed in this work. The authors prefer that intramolecular electron transfer is the primary mechanism that responds for the controllable molecular switch. It is proposed that the anilino rings and carbonyl oxygens can act as electron donors while the four-membered carbon moiety can serve as electron acceptors in single SR molecules (Fig. 15). The applied electric field, therefore, would induce a charge density distribution of excited state of single molecules, and thus, the quenching of fluorescence.

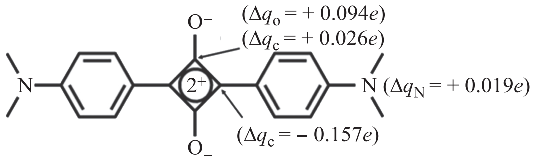

Fig. 15 The net electron transfer of the dominant atoms for bis(4-dimethylaminopheyl) squaraine at the one-electron level HOMO to LOMO excitation. Reproduced with permission from Ref. [98].

4 Conclusions and outlook

Single molecules possess a wide range of physical properties that make them attractive candidates for exploitation in molecular organic electronic and opto-electronic devices. The ability to modify the fluorescence emission of single molecules is crucial for single-molecule detection and for their use in molecular devices. In this review, we present the efforts to control and manipulate the fluorescence of single molecules using the local electromagnetic field of metallic nanostructures and external electric fields. The fluorescence is found to be modified by the presence of metallic nanostructures because of the local electromagnetic field effect. The fluorescence of single organic molecules can also be reversibly controlled using an alternating electric field, based on electron transfer between single molecules and the surrounding nanoenvironment. We demonstrate the effect of electron transfer and space charge relaxation processes on the hysteresis of single-molecule fluorescence. In addition, we show the design of a reversibly controlled single-molecule fluorescence switch using an electric field, where intramolecular electron transfer plays an important role in molecular switching.

The conclusions drawn support the possibility of the development of several applications. For example, studies of the external field effect on single-molecule fluorescence facilitate the application of single molecules in organic field-effect transistors, single photon electro-optic modulators, organic light-emitting diodes, and a variety of sensors based on single molecules. The hysteresis effect found in the electric-field-induced single-molecule fluorescence modulation also suggests a method of designing nanoscale memory elements, where information is written electrically and read optically. Controllable single-molecule fluorescence switches are good candidates for super resolution imaging in biosystems based on random bright/dark of single molecular labels. The photophysical behaviors should be further investigated for their potential use in increasing the brightness and photostability of single emitters and in next-generation molecular devices.

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