

Progress on photochromic diarylethenes with aggregation induced emission

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Abstract Among various photochromic compounds, diarylethenes (DAEs) have been widely studied and applied due to their excellent thermal bistability and fatigue resistance. Most researches are focused on the properties and applications of DAEs in solution. However, they meet the problem of fluorescence quenching at high concentration or at solid state which limits their performance in the practical applications. Fortunately, the DAE based photochromic aggregation-induced emission (AIE) materials do well in addressing this problem. This work here reviews the current research progress on the structures, properties and applications of the DAE based photochromic AIE materials and points out some existing problems so as to promote subsequent development of this field in the future.

Keywords aggregation-induced emission (AIE), photochromism, diarylethene (DAE), fluorescence photoswitching, optical memory, super-resolution imaging

1 Introduction

Since first introduced in 1988 by Irie and Mohri [1], the photochromic diarylethenes (DAEs) have received increasing attention owing to their excellent thermal bistability and fatigue resistance as well as efficient photoisomerization [2–6]. Multiple responsive DAEs with controllable photochromism properties are desirable since they can provide wide potential applications in bioimaging [7,8], optical transistors [9], nondestructive readout [10–12], chemical/biosensors [13–16], optical memory and storage

[17,18], super-resolution imaging [19,20] and so on. In most cases, the integration of both fluorophore and DAE moieties in molecule structure are normally employed to construct photoswitchable fluorescent DAE molecules where the two moieties are near enough to ensure an efficient photochromic energy transfer between them and only the closed form DAE can quench the excited energy of the fluorophore moieties as its absorption spectrum has a significant overlap with that of the fluorescence spectrum of fluorophore moieties [21]. The easiness of introducing functional groups to DAE units results in great progress of photoswitchable fluorescent DAEs with large on/off switching ratio and speed in recent three decades [22–25]. However, “concentration quenching”, the general problem in the fluorescence signal, are also faced by DAEs, which would inevitably limit their application in high-density optical systems [26]. Fortunately, in 2001, a novel kind of fluorophores exhibiting aggregation-induced emission (AIE) effect were first observed by the group of Tang [27], which is exactly opposite to the aggregation caused quenching (ACQ) phenomenon: the emission of AIE-gens is very weak in solution but become bright when aggregates are formed, opening a new window to design high-performance organic fluorescence materials with more widely and greater practical applications [28]. Within the last few years, a great deal of effort has been made to investigate this extraordinary phenomenon and a variety of AIE systems (tetraphenylethenes (TPE) [29,30], hexaphenylsilole (HPS) [31], cyanostilbenes [32,33], salicylaldazine (SA) [34], etc. are reported in succession.

Recently, great progress has been made in DAE based photochromic AIE materials showing enhanced emission as well as reversible fluorescence switching. Compared to the DAE materials without AIE effect, the AIE-based photochromic DAEs would exhibit strong fluorescence in aggregate state and solid state avoiding effectively ACQ problem. The enhanced bright emission would be irreversibly switched on and off accompanying with the photochromism reaction induced by UV/Vis irradiations.

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Specially, the AIE-based photochromic DAEs show none or very weak fluorescence emission in solution, but only keep high activity of photochromism, i.e., the color could be changed upon irradiations. Thus there will be at least four combinations of absorption and fluorescence states by controlling phases of matter and light irradiations. This kind of materials are naturally useful for multiple address recording, logical gate and so on. Besides, the Stokes shift of AIE materials are usually larger than 100 nm, which are benefit for fluorescence imaging and other optical applications. The above excellent optical properties make AIE-based photochromic DAE showing great potential in practical applications. However, as far as we know, there are no comprehensive reports on the AIE-active photochromic DAE materials up to date. This article attempts to review the current research progress and summarize the structure, properties and application of the photochromic DAE with AIE materials, so as to promote subsequent development of this field.

2 Structures of photochromic DAE with AIE

2.1 Small molecules with typical AIE-gens

The simplest strategy to endow DAEs with AIE effect is to introduce an AIE group onto the photochromic structure unit. In 2004, Park et al. [35] first introduced a cyano-based aggregation-induced enhanced emission (AIEE) fluorophore to photochromic DAE, named CN-MBE, the multifunctional fluorescent molecules not only maintain enhanced fluorescence emission, but also exhibit bistable photochromism (Fig. 1). A moderate fluorescence on/off contrast (larger than 10:1) was successfully realized in both nanoparticles and polymethyl methacrylate (PMMA) film. However, the maximum fluorescence intensity was approximately 29% loss after 5 cycles of alternative 365 nm UV and > 520 nm visible light irradiations.

Known as the most famous AIE-active materials, compounds based on TPE are facile to be synthesized and modified, exhibiting large AIE effect values and bright fluorescence at solid state. Taking advantage of the above TPE's attractive properties, Li et al. first designed and

synthesized TPE-based photochromic material DTE-TPE [36] that enables AIE behavior and fluorescence photo-switching (Fig. 2). The blue-green fluorescence ranges from 520 to 540 nm can be quenched by irradiating with 365 nm ultraviolet light, the quenching efficiency reached 90% in the photostationary state, the maximum fluorescence switching ratio was about 53:1. In addition, it was found that effective photochromism can also occur within the visible light region between 400 and 440 nm. The fluorescence intensity was almost no change after 440 nm irradiation that can be said to be “quasi-nondestructive readout wavelength”. The responsiveness to short visible light makes it potentially useful in information storage and bioimaging applications without UV light.

Recently, four novel DAEs derivatives presenting both photochromism and AIE properties have been prepared by conjugating tetraphenylethene and triphenylethene [37] to the bithienylethene (BTE) [38] (Fig. 3). Their photochromism and fluorescence properties have been explored detailedly. All the four compounds exhibits prominent AIE properties, i.e., almost not emissive in solutions but displaying bright yellowish green fluorescence in the aggregate and solid state. As expected, all the compounds show effectively photochromic property with alternating UV and visible light irradiations, in the meantime, their fluorescence is nearly completely quenched upon 254 nm UV irradiation. Moreover, it was discovered that the compounds in which tetraphenylethene connects to BTE display brighter emission in the aggregate and solid state than the ones in which triphenylethene connects to BTE.

Though both tetraarylethylene and photochromic DAE materials possess a core structure of ethylene bridge in common, they perform distinguished behaviors and represent two kind of functional materials. Interestingly, TPE has similar structure with *cis*-stilbene (Fig. 4). It is well-known that stilbene undergoes *trans*-*cis* isomerization upon UV irradiation, and the subsequent photocyclization of *cis*-stilbene forms dihydrophenanthrene, which is unstable. Early in 1993, tetraphenylethylene had been observed to undergo photochemical reactions both in solution and solid state upon ultraviolet light irradiation [39]. Zhu's group [40,41] found the substituted TPEs show non-negligible photo-oxidation behavior, and the electron-

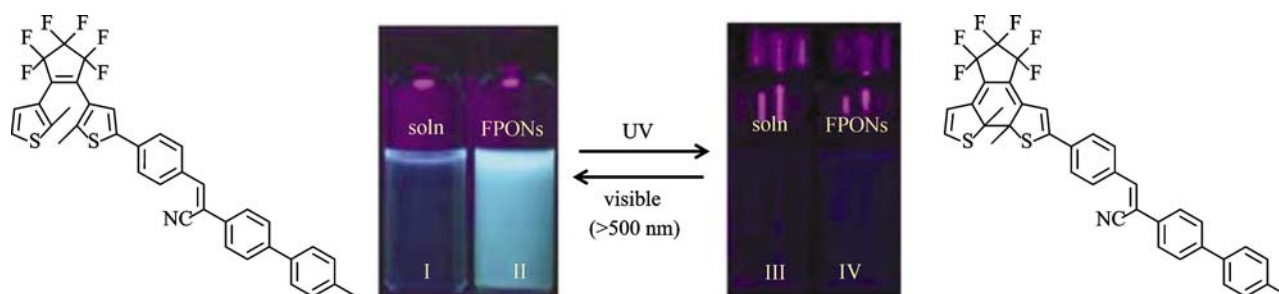


Fig. 1 Chemical structure of CN-MBE based diarylethene (DAE) and fluorescence photos of its THF solution (soln) and the colloidal suspension (II, IV) of fluorescent photochromic organic nanoparticles (FPONs). The concentration is 2×10^{-4} mol/L [35]

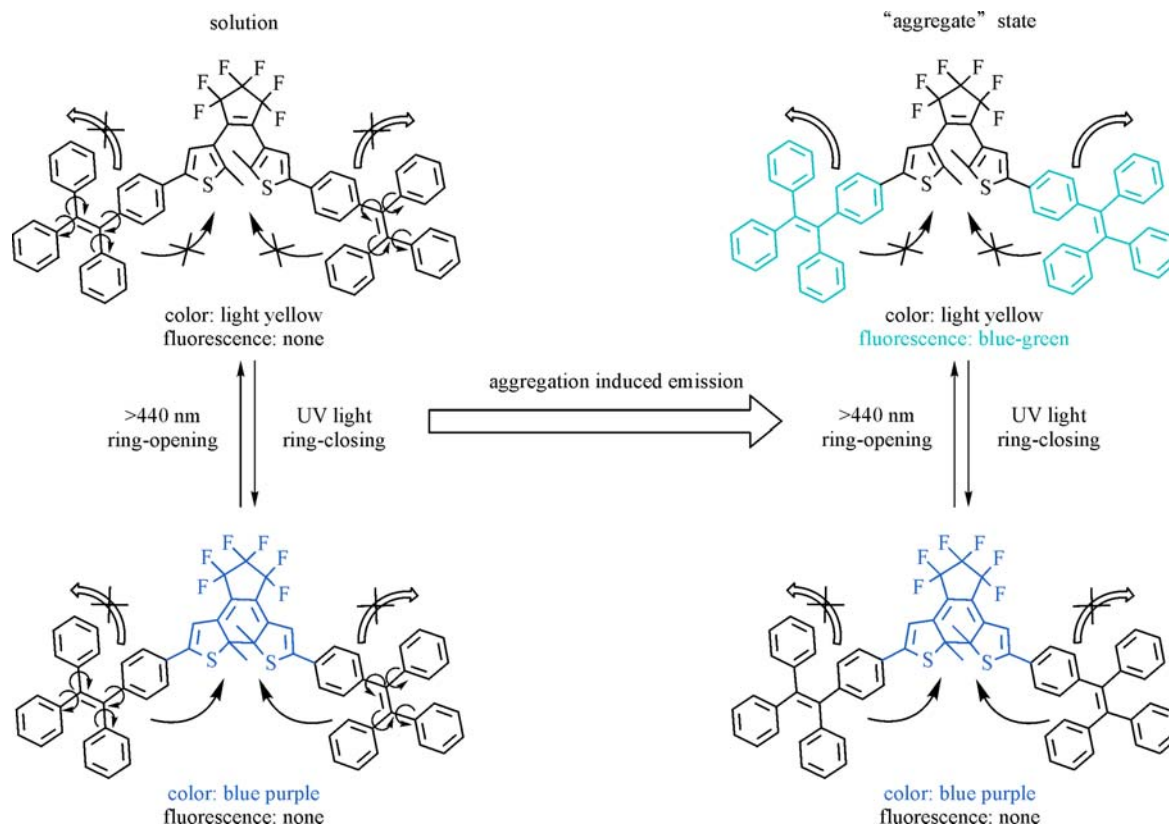


Fig. 2 Photochromism and fluorescence on/off in solution and the "aggregate" state of dithienylethene-tetraphenylethene (DTE-TPE) [36]

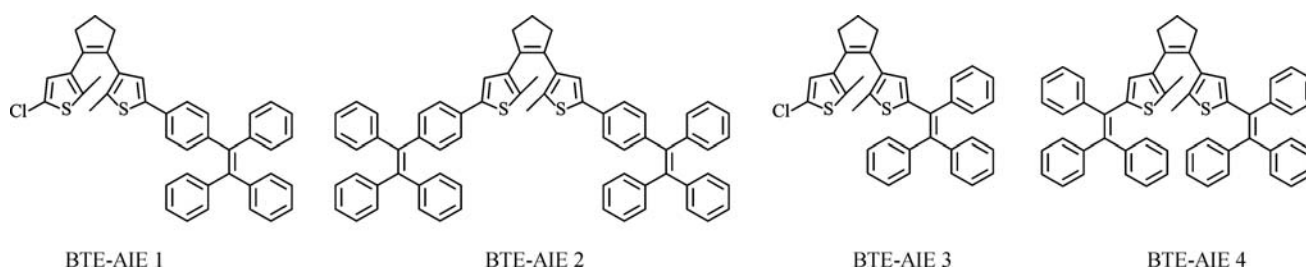


Fig. 3 Structures of tetraphenylethene and triphenylethene-based bisthienylethene (BTE) [38]

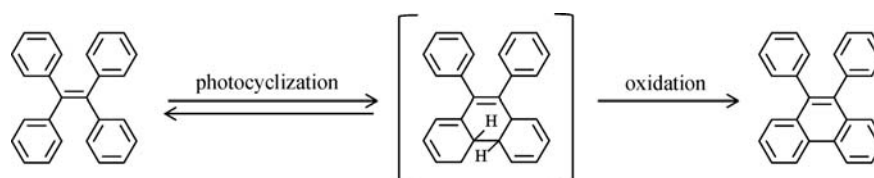


Fig. 4 Typical photo-cyclization process of tetraphenylethylene

donating groups were proved to be able to increase the rate of oxidation. What's more, aggregation-promoted photochromism [42–44] has been reported very recently. Chi and coworkers [43] explored combined AIE and aggregation promoted photochromism properties in dichloro-substituted triphenylethylene derivatives which show rapidly responsive photochromism behavior and moderate

on/off reversibility (Fig. 5). What's more, the authors can adjust the surface morphology of TrPECl₂ microcrystalline using UV light irradiation. After irradiation, the contact angle of a water droplet on the surface of TrPECl₂ is changed from 73° to 118°. In 2005, two tetrathienylethylene were designed and synthesized, and their photochromism and fluorescence properties were also reported

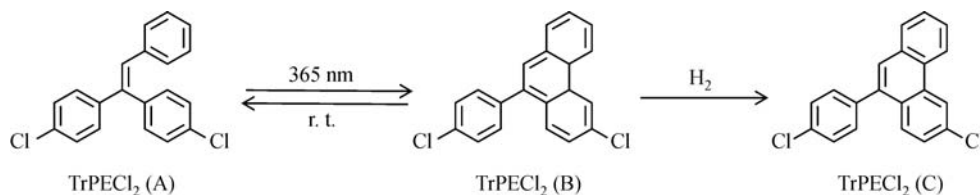


Fig. 5 Proposed mechanism of the photochromism of TrPECl₂ [43]

[45]. However, there are no data involving in AIE.

It is the most common protocol to design the multi-functional compounds by connecting more than one functional units together with various physical or chemical modifications. Frequently, the different building moieties may be interfered with each other in function. Also, usually the synthesis procedures will be unavoidably more and more complex as well the molecular structures would become bigger and bigger. Luo et al. [46] constructed a kind of simple structure where two thiophene rings construct dithienylethene structure with photochromism function while the rest two benzenes are the structural components of tetraarylethene showing AIE function. These two functional structures share the same ethene bridge (Fig. 6). This design takes the atom economy into account so that the *cis*- and *trans*-tetraarylethenes are conveniently gotten by one pot synthesis under mild conditions. It is observed that both the *cis*- and *trans*-isomers display reversible photochromism and switchable fluorescence in solution, PMMA film, solid powder, and single crystal. Furthermore, these hybrid *cis*-*trans* tetraarylethenes could be considered as photoswitchable media to adjust the behavior of AIE and ACQ. Their above versatile properties are promising for potential applications in fluorescence photoswitching, logic gates and nondestructive readout.

It is interested in the field of supramolecular chemistry of pillararene that the AIE-gens and pillararenes are assembled together to form a host-guest assembly with AIE property. Ma et al. [47] designed and synthesized a pillar [5]arene host (**H**) with AIE via grafting tetraphenylethene groups onto a pillar [5]arene structure by the Williamson etherification reaction. It can be composited with the dithienylethene guest (**G**) containing two cyano-triazole branches in each molecule, forming a photo-switchable fluorescent pseudo [3]rotaxane (Fig. 7). The fluorescence of **H** in H₂O/THF binary solutions with the water fraction $f_w = 50\%$ and 60% is intensely enhanced when assembled with **G**. The authors claimed that this is attributed to the restriction of intramolecular motions of tetraphenylethene by the host-guest interaction of the host and guest molecules. In a high water fractions of 60% , the **G**⊂**H** complex are assembled to a cake-like nanostructures which can be reversibly tuned to a shuttle-like nanostructures upon UV light irradiation which induce the photocyclization reaction. As the energy transfer between the closed form DTE and the tetraphenylethene in guest **G** is allowed, both in solution and solid state the enhanced emission of this novel **G**⊂**H** complex could be quenched OFF (higher than 68%) and turned ON reversibly upon alternative ultraviolet and visible light irradiations. Using its photoswitching properties, the applications of **G**⊂**H**

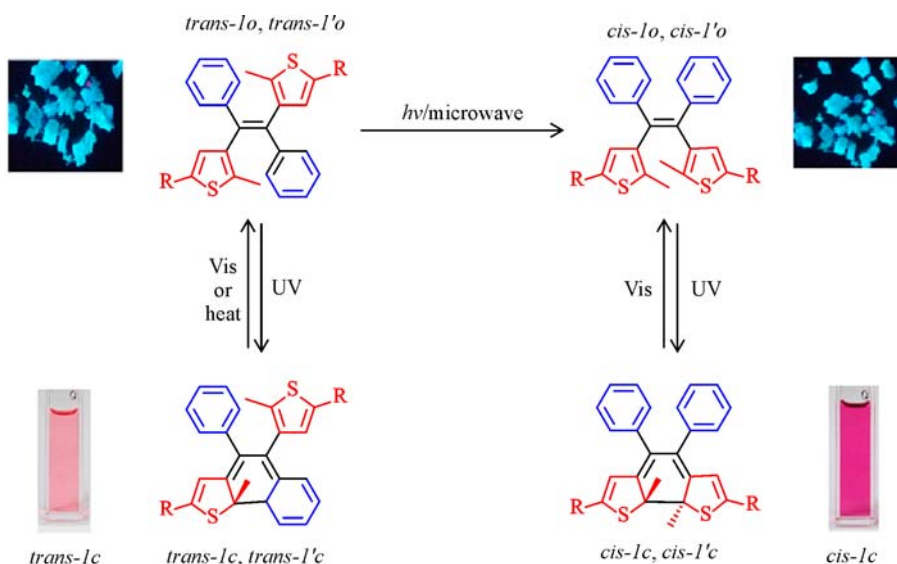


Fig. 6 Hybrid tetraarylethenes with photoswitchable aggregation-induced emission (AIE) and reversible photochromism [46]

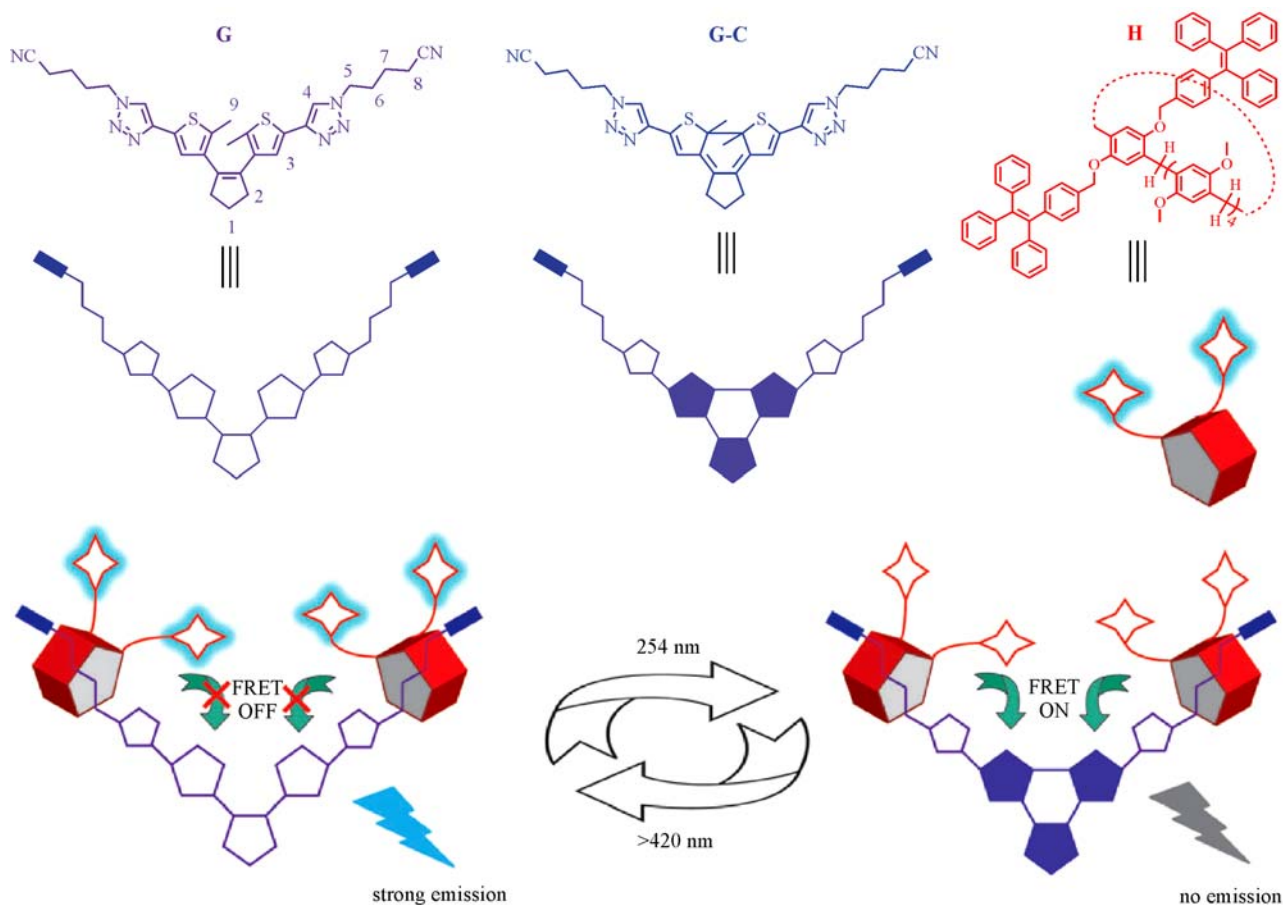


Fig. 7 Chemical structures of **H** and **G** and the photoresponsive fluorescence switching process of the complex [47]

complex doped PMMA film in soft recording and rewritable printing was also investigated and there is no obvious signal loss after repeating the recording/erasing cycles for several times.

However, the emission peaks of above molecules are commonly shorter than 550 nm, limiting its application in some degree. This is probably on account of the inherent feature of traditional TPE-type AIE moieties which usually exhibit an emission peak around 500 nm. In consequence, there are rare reports on the far-red or near-infrared AIE-active photoswitchable materials. Very recently, Zhu's group developed this novel kind of DAE compounds based on quinolinemalononitrile (EQ) fluorophore [48]. By conjugating BTE with EQ, the formed BTE-EQ (Fig. 8) shows bright long-wavelength emission at 613 nm at aggregation state. Interestingly, an unanticipated aggregation-controlled photochromism has been observed. The photoisomerization reactivity could be reversibly tuned ON and OFF via adjusting the aggregation state during the AIE process.

2.2 Organic nanoparticles

In 2015, a class of photoswitchable dithienylethenes based

on coumarin fluorophore was reported. Interestingly, the compound B2C (Fig. 9) has been found to exhibit photochromic AIE properties [49]. Originating from the hydrophobic interactions, the open form B2C molecules are aggregated to form nanoparticles in organic solutions with high water fraction, which causes AIE emission. Specially, the emission intensity is increased progressively during the on-going photo-isomerization reaction. Here, any of the open-form and closed-form DTE could quench the excited state of coumarin because of the lack of overlap of their emission spectra and absorption spectra. Upon ultraviolet light exposure, the ring-closed isomers are generated. Compared to the open form B2C molecules, the more rigid structure of closed form B2C would certainly improve the aggregation effect and therefore nanoparticles in the high water fraction solution increase continuously as the photocyclization going on (Fig. 9). A continuous irradiation of 10 min could make the fluorescence enhanced by about 10%. Consequently, the above work affords a new approach for preparing a new member of DAE with both AIE character and photochromism property, which shows potential applications in optical storage and nonlinear optics.

It is a common way to prepare photoswitchable

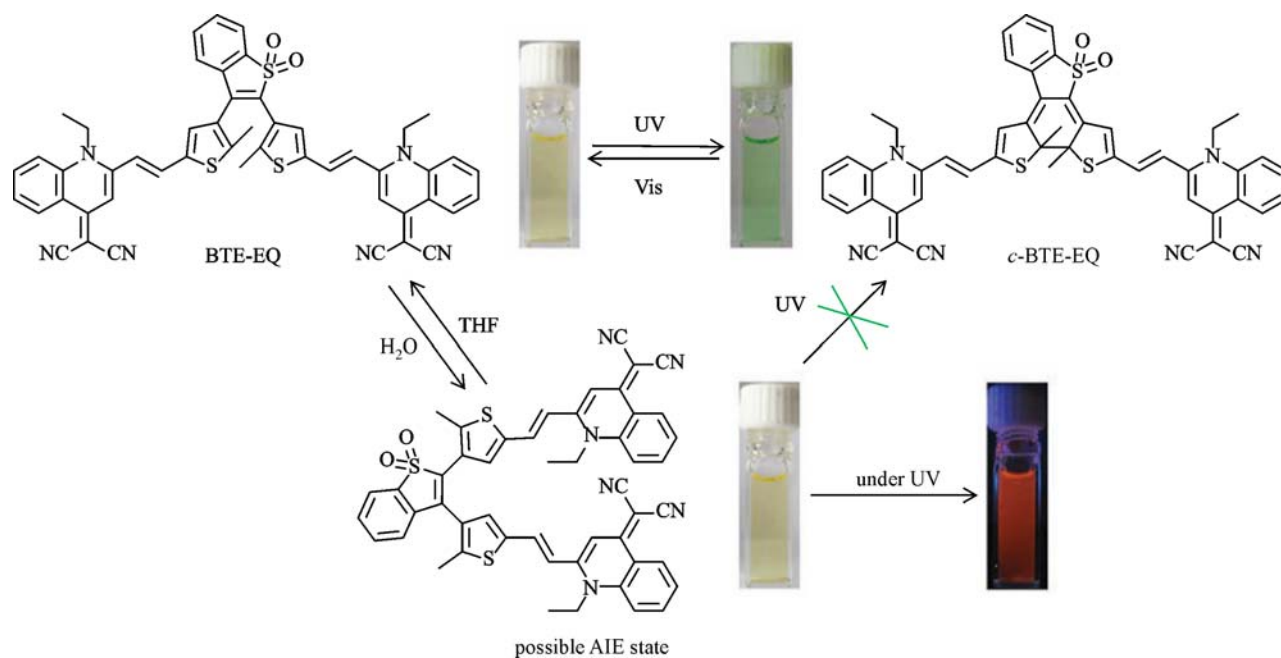


Fig. 8 Photochemical and reversible conversions between ring-opened BTE-EQ and ring-closure *c*-BTE-EQ by alternating ultraviolet and visible light irradiations. Specially, the aggregation at AIE state prevents BTE-EQ taking place the photocyclization reaction [48]

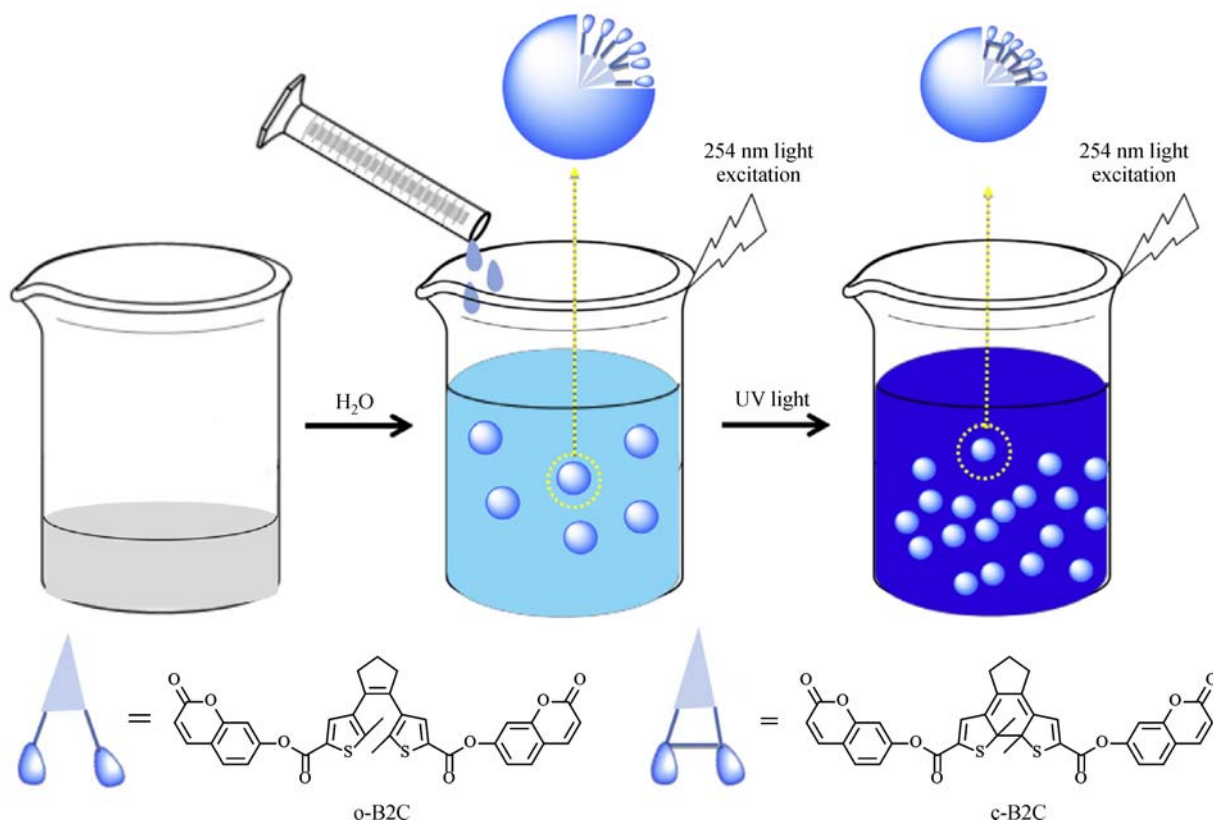


Fig. 9 Morphology and fluorescence change of B2C during H₂O addition and ultraviolet exposure [49]

fluorescence systems by hybridizing the photochromic acceptor component with fluorescent donor component into one material, e.g., nanoparticles. Lately, Fukaminato et al. [50] reported photoswitchable fluorescence nanoparticles using a diarylethene-benzothiadiazole dyad compound, which shows intense red fluorescence, ultra large on/off ratio as well as excellent fatigue resistance. The molecule exhibited ACQ effect in tetrahydrofuran solution below 60% water content. The continuous increase of the water content was accompanied by a sharp increase of fluorescence intensity. The fluorescence quantum yield is up to 0.65 when the water content is 90%. After continuous ultraviolet light irradiation, the fluorescence of nanoparticles was completely quenched at very low photochromic conversion levels ($< 5\%$), which also could be recovered under visible light irradiations. These outstanding properties is contributed by a “giant amplification of fluorescence photoswitching” which is induced by the high effective intermolecular Förster resonance energy transfer (FRET). As simulated, each switching event could quench more than 400 molecules at the origin of the collective quenching (Fig. 10). This work has proven and demonstrated such a photon-saving principle: using few photons to adjust/switch the optical signal from a huge set of molecules.

2.3 Organic/inorganic gels

A new strategy to integrate intramolecular photochromism with intermolecular AIE effect has been demonstrated by Liu et al. [51]. The authors designed and synthesized a novel kind of photochromic molecular turnstile (can be

looked as a kind of molecular rotor) by connecting two bipyridinium groups at the ends of dithienylethene (DTE), called as DTE-BP. The intramolecular rotation of central chemical bonds can be restricted by changing the environment, resulting in AIE phenomenon. DTE-BP turnstile exhibits outstanding AIE and photochromism performances in both high-viscosity and solid medium. Significantly, DTE-BP can be expediently embedded into polymer matrixs, such as polyvinylidene fluoride (PVDF) and PMMA, to prepare photo-rewritable fluorescent materials with good repeatability and easy manipulation. Liu et al. [52] also intercalated the DTE-BP dye into the inorganic clay of Laponite to procedure binary supramolecular hydrogel giving enhanced mechanical properties (Fig. 11). Fortunately, the photoisomerization ability of DTE is nearly wholly maintained in the DTE-BP/Laponite hybrid hydrogel. In addition, the intrinsic fluorescence of the open-form DTE-BP dye can be triggered in the gel state where the intramolecular rotation is restricted, which can be quenched upon UV light irradiation.

Gels fabricated from low-molecular-weight π -conjugated organic gelators shows tailorable and functionalizable properties by introducing stimuli-responsive groups as a part of the gelator molecule structure. Park et al. [53] designed a fluorescent supramolecular organogel system based on a thermally-responsive AIEE-active organogelator and photochromic DAE compounds with high compatible groups to the gelator. This organogel system can work as a binary “OR” logic gate whose fluorescence as the output signal show a response to dual inputs of light and thermal stimulations. Experimentally, a high-contrast fluorescence switching ratio of 166 is obtained. Also the

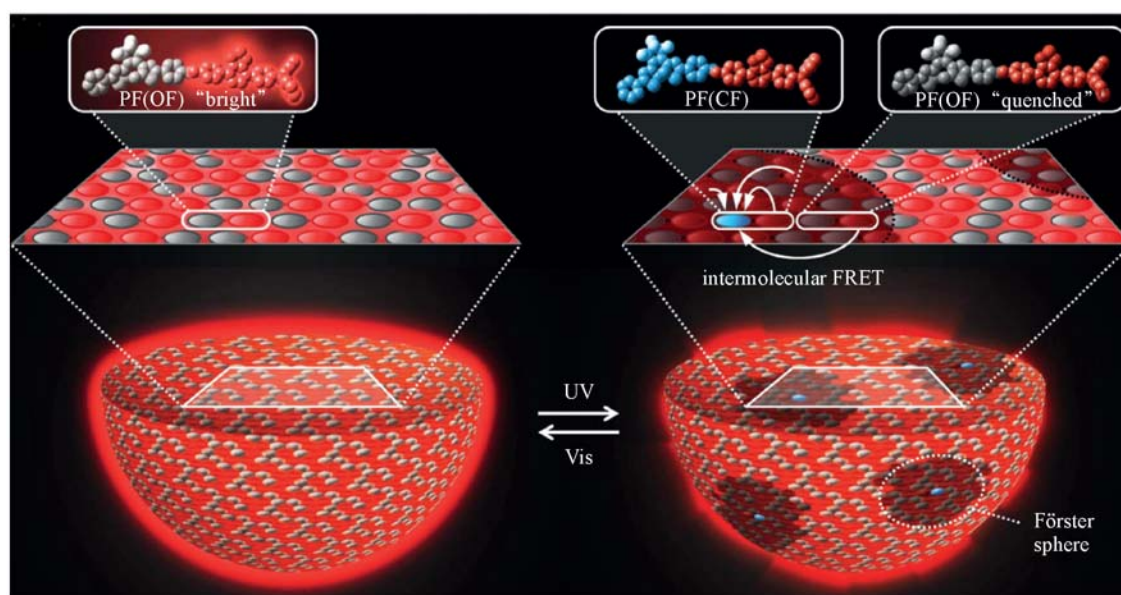


Fig. 10 Diagram of “giant amplification of fluorescence photoswitching” in nanoparticles induced by intermolecular Förster resonance energy transfer (FRET) [50]

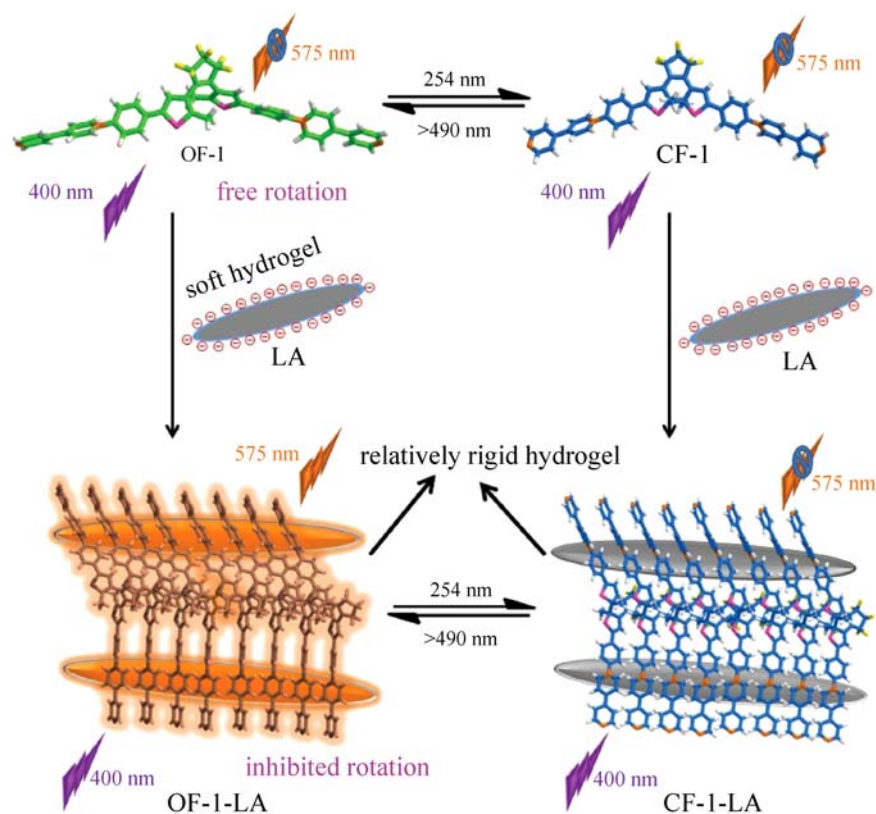


Fig. 11 Open-form DTE-BP (OF-1), closed-form DTE-BP (CF-1), inorganic clay of laponite (LA) construction of DTE-BP/laponite hybrid hydrogel and its fluorescence photoswitching process [52]

addressing of fluorescence image with light irradiations is achieved. It is suggested that the switchable smart fluorescent organogel materials will be promisingly applied in rewritable optical memory.

2.4 Polymers

The practical applications of photoswitchable fluorescent materials often require the materials at solid or aggregation state. High-vacuum vapor deposition is usually used for preparing solid films, but this method is very expensive and limited by the molecular weight. The other approach to solid film is doping the photochromic materials in a polymeric medium, however, the doped molecules are apt to aggregate spontaneously in polymer matrix in thermodynamics. These are common problems when practically apply low-molecular weight materials. Polymerizing the photoswitching molecules to get relatively large-molecular weight is an effective way to address above problems. That is owing to the polymers can be facilely made into large-area films simply by spin-coating process [54]. Up to date, most DAE based photochromic AIE materials are focused on small molecules, relatively few studies have been done on macromolecules or polymers. However, good film-forming and excellent coordination amplification properties of polymers make them better in functional composite

materials to small molecules and which can meet diversified application requirements.

In 2005, Park et al. [55] first designed a bistable photoswitchable fluorescent polymer named poly(DCS-BTE) (Fig. 12) which containing only AIEE and BTE repetitive structure units. The poly(DCS-BTE) was prepared via Knoevenagel condensation reaction, showing good mechanical and thermal properties with a glass transition temperature of 188°C. The resultant polymer exhibit great solubility but poor fluorescence in common organic solvents. Importantly, the polymer film exhibits an intensely increased fluorescence which is modulated reversibly by the bistable photoswitching of diarylethene units with a large switching ON/OFF ratio of more than 10:1 upon UV and visible light irradiations and was successfully demonstrated to be applicable in the erasable optical memory.

He's group [54] reported a novel photochromic AIE-active polymer poly(DTE-TPE) (Fig. 13(a)) containing photochromic dithienylethene and AIE-active tetraphenylethene structural units which are connected via oxygen bridges. The two moieties of the polymer retains both of their original properties. The emission of poly(DTE-TPE) could be photoswitched through the fluorescence resonance energy transfer (FRET) from the TPE to closed form DTE. The polymer film shows a fluorescence peak at 507

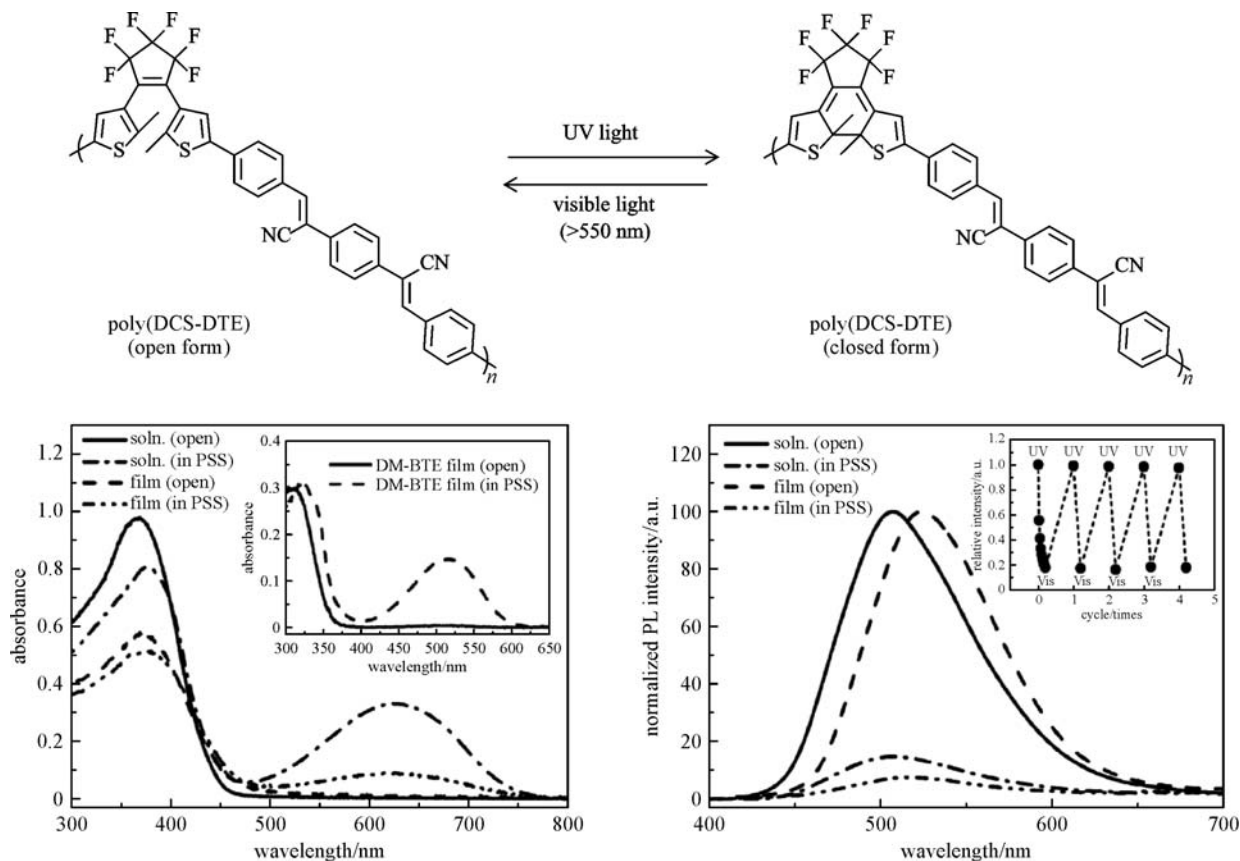


Fig. 12 Photochromic reaction of poly(DCS-BTE) and its absorption and fluorescence spectra at the open form and photostationary state (irradiated at 290 nm) [55]

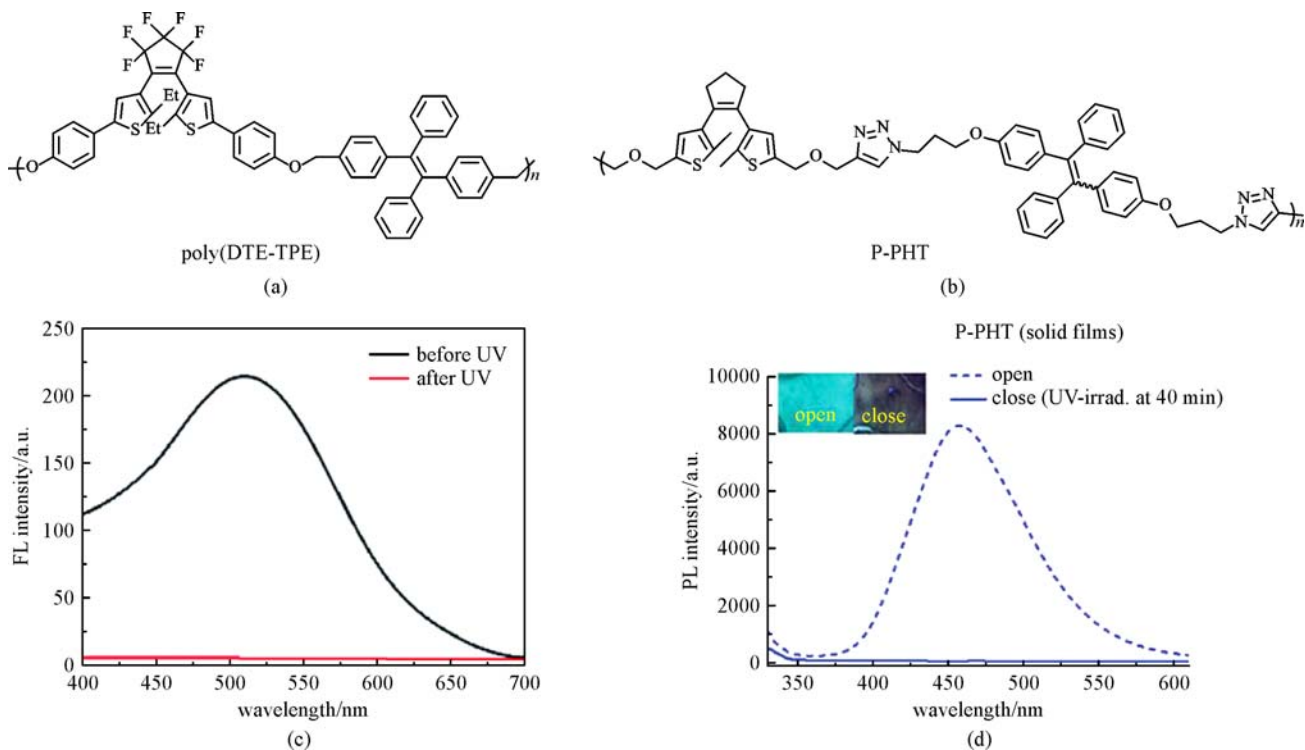


Fig. 13 Structures and photoluminescence (PL) spectra changes of (a, c) poly(DTE-TPE) and (b, d) P-PHT [54,56]

nm and is nearly completely quenched upon 302 nm UV irradiation, and could be recovered under a subsequent visible light irradiation. The above fluorescence photo-switching cycles of poly(DTE-TPE) by alternative UV/Vis light irradiations can be repeated for many time, displaying excellent fatigue resistance. Very recently, another new photoswitchable polymer named P-PHT comprising DAE moiety, tetraphenylethene moiety and triazole linkers (Fig. 13(b)) was prepared [56]. Its AIE property from TPE respectively in the case of the open and closed state of DAE in P-PHT was investigated. The irreversibly photocyclization of DAE in P-PHT is robust in pure THF, high water/THF binary solvents with high water fraction and solid films. The AIE of TPE in P-PHT at 90% water fraction in THF is completely quenched though the efficient energy transfer from TPE to the ring-closed DAE moiety, whereas there are still rarely reported monomeric emission from TPE at 385 nm in solutions especially under acidic conditions. No matter whether high water fraction was used before or after UV exposure, always solely the monomeric emissions without AIE was watched.

3 Application of photochromic DAE with AIE

3.1 Erasable optical memory

The absorption and fluorescence spectra of two forms of photoswitchable fluorescent DAE compounds change greatly before and after photoisomerization. This change can be used to create a simple optical information storage mode, where mask board recording information is coated on a film doped or coated with photochromic compounds, and then the information can be written, read or erased by employing corresponding irradiations. As well known, the photochromic AIE DAE materials can overcome the common problem of “concentration quenching” of fluorescent signal due to owning AIE-active structure in the molecule. Significantly, they could further perform as controlled rewritable optical materials deriving from its reversible photoswitchable fluorescence at solid state. As reported, a number of patterns can be light-written on the polymer films loaded photoswitchable fluorescent DAE with a simple hollowed-out mask [35,36,47,51]. As an example in Fig. 14 [51], when the mask was covered on the photochromic AIE-active DTE-BP embedded PVDF film, just the exposed parts can be exposed with ultraviolet light. Thus the irradiated open form DTE-BP converts to the closed form accompanied with the fluorescence quenching. Still the mask-sheltered parts will retain its original bright fluorescence of the open form. As a result, diversiform patterns can be recorded accurately on the DTE-BP films with large fluorescence switching ON/OFF contrast. Then, once the above obtained film was exposed by visible light whose emission wavelength is >490 nm,

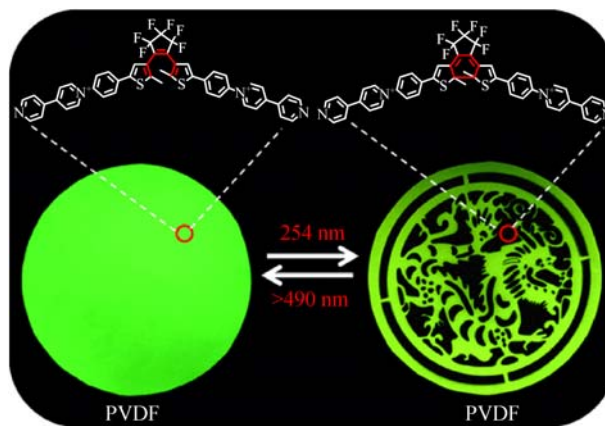


Fig. 14 Fluorescent photographs of DTE-BP embedded PVDF film upon alternating 254 nm UV and visible light irradiations [51]

the as-printed patterns would be totally removed, attributed to the reestablishment of the fluorescence quenching state.

3.2 Nondestructive readout

The non-destructive readout of information, namely, the recorded information are not changed or destroyed after reading, is promisingly realized by reading out the significant fluorescence signal rather than absorbance signal due to the avoiding of using the reading wavelength at the absorption range of both two isomers of DAE which will inevitably lead to the occurrence of photoisomerization reactions [35,36,57]. It requires the reading wavelength will not or at least negligibly participate in each of the photoisomerization reactions of DTE [11,58–61]. Keeping above in mind, Li et al. [36] employed the photochromic AIE TPE-DTE solid film covered with square-patterned contact mask to successfully demonstrate the microsized images could be efficiently and reversibly written (>440 nm), erased (UV light), and read out (~ 440 nm). Benefiting from the special red-edge effect of TPE-DTE, the irradiation at 440 nm could offers enough fluorescence for imaging but will not take part in any obvious photoisomerization reactions, thus resulting in pseudo-nondestructive readout. What's more, using the patterned illumination through the photomasks, the different patterns presenting different informations can be successfully stored and rewritten on the photochromic AIE-active poly(DCS-BTE) film (Fig. 15) [55]. Furthermore, all the recorded patterns in Fig. 15 could be nondestructively and repetitively read out with 400 nm light that is distinct with both the writing and erasing wavelengths which will induce either photocyclization of photocycloreversion reaction of poly(DCS-BTE). Fluorescence nondestructive readout is of great importance to high density information storage, optoelectronic devices and high resolution imaging. However, the researches

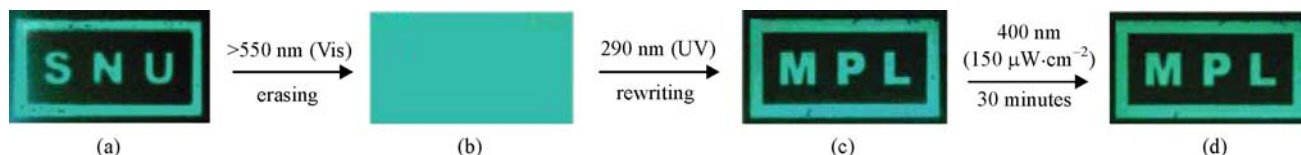


Fig. 15 Rewritable and nondestructive readout of fluorescent patterns recorded on poly(DCS-BTE) film prepared by spin-coating [55]

about it are relatively scarce, due to the balance of the fluorescence switch speed and contrast as well as fatigue resistance.

3.3 Logical gates

The two fluorescence “ON” and “OFF” states of DAE could be used to represent binary “1” and “0” which are analogical to the open and close of the logical gate. In Fig. 16 [53], a novel hybridized organogel material, named SS-TFMBE/TFM-BTE, shows intense luminescence due to the AIE effect. The organogel achieves the regulation of fluorescence on/off by dual modes, i.e., light irradiation driving photoisomerization and thermally induced gel-to-sol phase change. The thermal induced fluorescence switching acts on ring-opened TFM-BTE, while the material at either gel or sol forms is nonemissive in the case TFM-BTE are cyclized. This unique organogel system are able to perform as a binary OR logical gate. It takes fluorescence quenching as output signal which responds on the two inputs signal of “UV light” and “heat.” The resulted truth table is a) gel/visible light (0, 0), b) gel/UV light (1, 0), c) sol/visible light (0, 1), d) sol/UV light (1, 1).

3.4 Super-resolution fluorescent imaging

The conventional fluorescence imaging technology is difficult to obtain a resolution less than 200 nm according

to the Rayleigh criterion. The fluorescence of all molecules is lighted on at the same time and their emission spots overlapping seriously with each other of molecular fluorescence images. Unless the molecules are in a long enough distance with each other, the precision of localization of each molecules could be less than 1 nm [62]. In the super-resolution imaging techniques based on single-molecule localization such as photo-activated localization microscopy (PALM) [63] and stochastic optical reconstruction microscopy (STORM) [64], the luminescence emission of probe molecules is regulated to be in bright and dark state randomly by light irradiations and accurately positioned at nanoscale. After a great amount of the fluorescent molecules are localized in separated time domain, finally, the super-resolution image that breaks the diffraction limit could be reconstructed [65]. Super-resolution fluorescent imaging has become an important means to study the structure and function of biomolecules at nanoscale [66]. Photoswitching has always been regarded as the key element of it [67,68]. Recently, DAE based photochromic AIE material was first applied in the field by Zhu’s group [36]. As shown in Fig. 17, the authors could distinguish the very adjacent DTE-TPE emitters as well as their accurate distribution in PMMA matrix. Making comparison between the image of magnified super resolution image (Fig. 17(b)) with fluorescent one (Fig. 17(a)), obviously, the former is much clearer, in which the fluorescence spots are better distinguished with each other. The resolution of super-

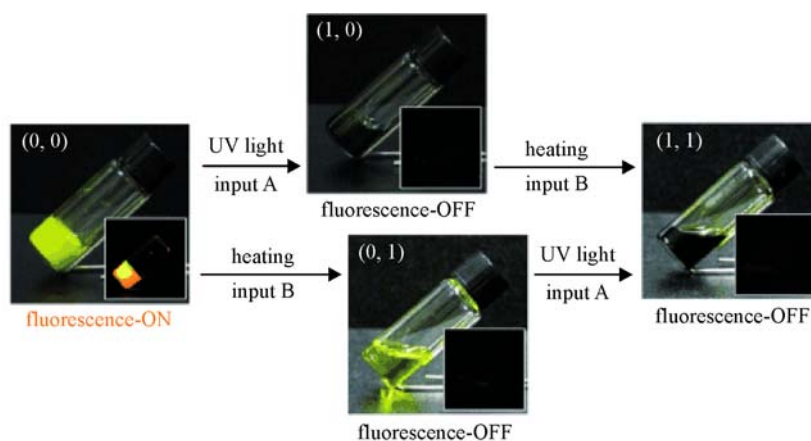


Fig. 16 Illustration of a binary logical gate based on the SS-TFMBE/TFM-BTE organogel system. It uses fluorescence quenching as output signal in response to two inputs signal of “UV light” and “heat,” giving a The resulted truth table: a) gel/visible light (0, 0), b) gel/UV light (1, 0), c) sol/visible light (0, 1), d) sol/UV light (1, 1) [53]

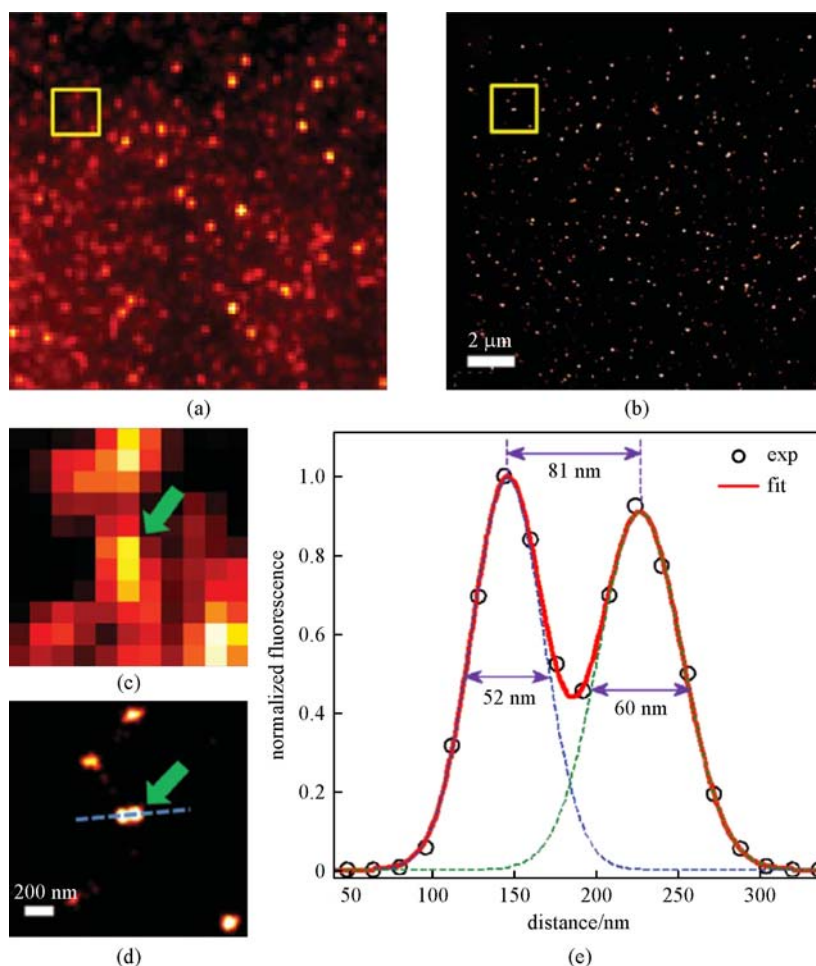


Fig. 17 (a) Conventional fluorescence imaging of DTE-TPE probes in PMMA matrix. (b) Super-resolution fluorescence imaging of the same area with (a). (c) Enlarged view and (d) super-resolution fluorescence images of the selected regions in (a) and (b), respectively. (e) Cross-sectional profiles along the dashed line across a couple of adjacent DTE-TPE emitting spots in (d), suggesting a spatial resolution of sub-81 nm [36]

resolution image is obtained sub-100 nm, which is adequate for distinguishing the adjacent emissive DTE-TPE spots (Fig. 17(d)) and determine the smallest distance of them. While the conventional image turns to be insufficient in resolution (Fig. 17(c)). It was measured that the two spots in DTE-TPE pairs are 81 nm in distance. Their full width in half maximum (FWHM) were 52 and 60 nm, respectively (Fig. 17(e)). This work demonstrated that photoswitchable fluorescent DAE compounds is a novel kind of probes for super-resolution imaging, which makes fluorescence imaging with a resolution sub-100 nm possible.

4 Summary and perspective

Photoswitchable fluorescent diarylethenes (DAEs) using fluorescence as the reading signal have a high detection sensitivity, but still suffer a challenging problem, that is the

general problem of aggregation caused quenching (ACQ) when using the fluorescence as the read out signal. ACQ has certainly restricted the practical applications of these functional photoswitching materials in high-density or high-precision optical systems. Very recently, a novel category of fluorophores exhibiting aggregation-induced emission (AIE) property was investigated and great efforts are being made to explore this special and practicable behavior. The integration of photochromic DAE with AIE has been proposed and studied to solve the ACQ problem in photochromic DAE system. Introducing AIE-gens to photochromic DAE structure is a convenient way to come true the DAE with aggregation induced emission properties. What's more, the preparation of organic nanoparticles, organic/inorganic gels and polymers containing DAE-AIE-gens structure units can also get DAE-based photochromic AIE systems. These novel photochromic systems exhibit excellent bistable photochromism, typical AIE behaviors, high fluorescent on/off ratio, and hence show

great potential for applications in optical memory, nondestructive readout, logic gate and bioimaging. At present, there are relatively few investigations on these photochromic systems and they are relatively not developed well enough to meet the practical application requirements, mainly for the low fluorescent quantum yield, the relatively short fluorescence wavelengths, hydrophobic and biological incompatibility, dependence strongly on ultraviolet light and so on. It is very important and urgent to design and synthesize the DAE based photochromic AIE materials with long wavelength luminescence, all visible light driving, water-soluble as well as high fluorescent quantum yield and fluorescent switching ratio in the future.

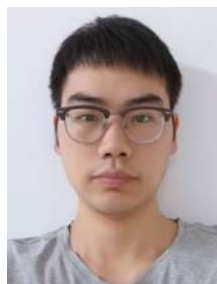
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