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A high contrast tri-state fluorescent switch: properties and application

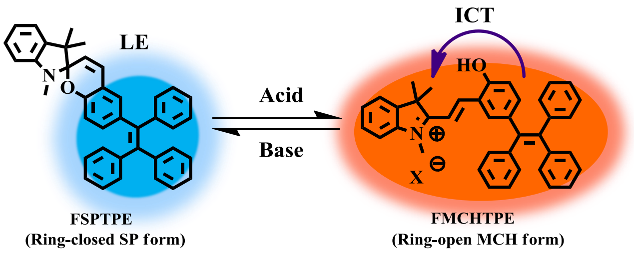
Xing Su,[ab] Yi Wang,[b] Xiaofeng Fang,[b] Yu-Mo Zhang,[b] Ting Zhang,[b] Minjie Li,[b] Yifei Liu,*[b] Tingting Lin*[a] and Sean Xiao-An Zhang[b]

Abstract: A high contrast tri-state fluorescent switch (FSPTPE) with both emission color change and on/off switching is achieved in a single molecular system by fusing the aggregation-induced emissive tetraphenylethene (TPE) with a molecular switch of spiropyran (SP). In contrast to most of the reported solid state fluorescent switches, FSPTPE only exists in amorphous phase in the ring-closed form due to its highly asymmetric molecular geometry and weak intermolecular interactions, which leads to its grinding-inert stable cyan emission in solid state. Such an amorphous phase facilitates FSPTPE with fast response to acidic gases and induces the structural transition from ring-closed form to ring-open form, accompanied with the "Off" of fluorescence. The structural transition leads to the planar molecular conformation and high dipole moment, which further result in strong intermolecular interactions and good crystallinity, so when the acid is added together with a solvent, both the ring-opening reaction and re-crystallization can be triggered to result in an orange emissive state. The reversible control between any two of the three states (cyan/orange/dark) can be achieved with acid/base or mechanical force/solvent treatment. Because of the stable initial state and high color contrast (Δλ=120 nm for cyan/orange switch, dark state Φ_F <0.01%), the fluorescent switch is very promising in applications of display, chemical or mechanical sensing, and anti-counterfeiting.

Introduction

Fluorescent molecular switches have been in the limelight recently because of their smart multi-stimuli responsive fluorescence switching characteristics.[1] The distinct change in emission colours upon a diverse of triggers, such as UV/Vis, heat, mechanical/hydrostatic force, acid/base, chemical vapour, etc. has broadened their applications in optical data recording,[2] chemical sensor,[3] display[4] and bio-imaging.[5] Fluorescent switches that can show multi-colour states and on/off states have been reported,[6] however, realizing both emission color switch and on/off switch in a single molecular system is not easy. Integration of a fluorophore chemically with a molecular switch is a plausible method toward fluorescent switch, which can take advantages of manipulating both the chemical structure and the molecular packing in aggregated state, and thus has more possibility in emission state control.[7] And the single molecular system can avoid the complexity in energy matching as in the mixed double chromophores system.[8]

In our previous work, several TPE integrated molecular switches have been developed by a double bond linkage, and high color contrast has been achieved with these fluorescent switches due to the significant change in chemical structure.[9] As we know that the properties of molecules are greatly related to their molecular structures and subsequent aggregation structures,[10] here we report a new and very small tetraphenylethene (TPE) functionalized spiropyran (SP) molecular switch (FSPTPE, meaning fused SP with TPE) by sharing a mutual benzene (Scheme 1), which achieves both emission color change and on/off switching. In contrast to most of the reported solid state fluorescent switches, FSPTPE only exists in amorphous phase in the ring-closed form due to its highly asymmetric molecular geometry and weak intermolecular interactions. FSPTPE has three well-distinguishable high-contrast states of cyan (amorphous ring-closed form, ARCF), orange (crystalline ring-open form, CROF) and dark (amorphous ring-open form, AROF). The contrast of cyan and orange emissive states comes to 120 nm with negligible overlap, and the dark state is complete (ΦF: <0.01%). The reversible switch between any two of the states can be achieved with acid/base or mechanical force/chemical vapour stimuli. Because of the stable initial state and high color contrast, FSPTPE is very competitive in display, chemical or mechanical sensing, and anti-counterfeiting. As an example, high contrast fluorescent display and multi-channel anti-counterfeiting were demonstrated in this article.



Scheme 1. Molecular structure of FSPTPE and its acid/base triggered isomerization.

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Supporting information for this article can be found via a link at the end of the document. It contains characterization of FSPTPE. ^{1}H NMR, ^{13}C NMR, UV-Vis, PL spectra, PXRD, etc.

Results and Discussion

Reversible isomerization in solution

It's known that the molecular switch of spiropyran can be triggered to isomerize from ring-closed SP form to ring-open merocyanine (MC) form or protonated MC (MCH) form with UV light or acid.[11] Firstly, the isomerisation behaviour of the FSPTPE was studied in solution. When FSPTPE was dissolved in acetonitrile, the absorption bands began at about 400 nm. Upon adding HCl acid, new absorption bands at less than 545 nm appeared gradually, indicating the ring-opening reaction has been triggered with acid. When enough base such as NaOH was added into the aforementioned solution, the absorption changed back (Fig. 1A). This indicates that FSPTPE preserved reversible acid/base isomerization property in solution. However, UV light cannot be used to get stable MC form of FSPTPE in some typical organic solvents, such as THF, acetonitrile, DMF, ethyl acetate and DMSO et al. Only a little proportion of isomerized FSPTPE can be observed in these solutions. For example, the absorbance at around 450 nm for the MC form is no more than 0.02 after irradiated with 254 nm UV light for 3 min in acetonitrile (Fig. S1, ESI†). This is because the zwitterionic MC form with high dipole moment is unstable in these neutral solvent when there is no stabilizing electron-withdrawing, such as nitro and cation groups at the para-position of phenolate, and MC form converted back to the SP form very quickly.[11e,f] Only in dichloromethane, UV irradiation can result in a broad absorption band up to 650 nm corresponding to the MC form, which redshifts about 100 nm compared with acid triggered MCH form (Fig. 1B). MC form in DCM solution could only partly convert back to SP form after removal of UV light and exposure to ambient light even for 5 hours. This indicates that DCM may have special stabilization effects for the MC form. The phenomenon has been observed in our previous work;[9b] however, the reason is still not very clear.

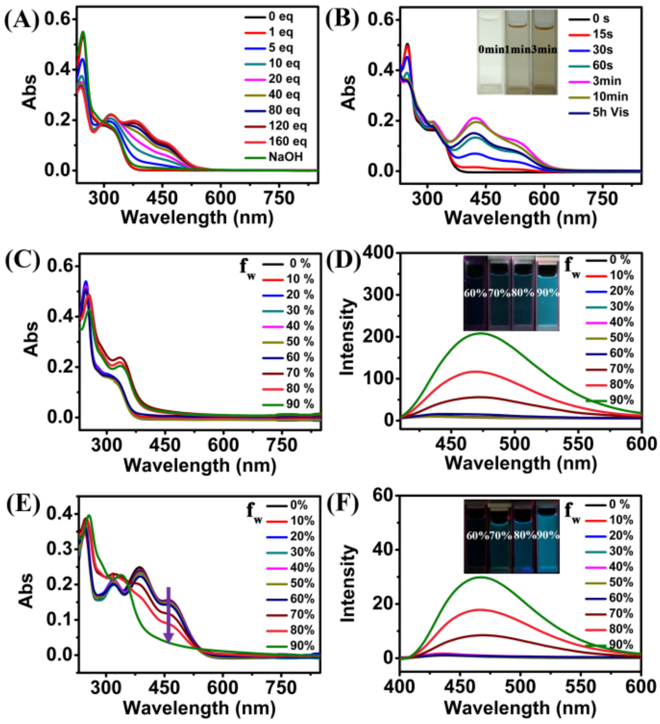


Figure 1. (A) Absorption spectra of FSPTPE in acetonitrile solution (1×10^{-5} M) with addition of HCl (from 0 to 160 eq.), then adequate NaOH treatment. (B) Absorption spectra of FSPTPE in dichloromethane (1×10^{-5} M) irradiated with 254 nm UV light for different time, then irradiated with visible light for 5 hours. (Insets: Corresponding photos of UV-irradiated FSPTPE) (C) Absorption spectra and (D) PL spectra of FSPTPE in different acetonitrile–water (v/v) mixtures (1×10^{-5} M, Ex: 253 nm). (E) Absorption spectra and (F) PL spectra of FMCHTPE (obtained from acidizing FSPTPE with 40 eq. HCl for 12 h) in different acetonitrile–water (v/v) mixtures (1×10^{-5} M, Ex: 253 nm).

Aggregation-induced emission (AIE) property

Due to the free-rotating of the benzene group, both FSPTPE and FMCHTPE do not show emissions in good solution and AIE property is observed accompanied with increment of poor solvent proportion. For FSPTPE, when water proportion of solution reaches 70 %, it begins to aggregate and the absorption red shifts due to the molecular environment change (Fig. 1C). Simultaneously, a cyan emission centred at 475 nm appears, and the emissive intensity continuously increases with water proportion (Fig. 1D). The aggregates formed in acetonitrile/water mixture are amorphous, which was confirmed with PXRD characterization of the precipitates (Fig. S2, ESI†). For FMCHTPE, when the water proportion of the solution reaches 70 %, the cyan emission from FSPTPE aggregates appears rather than orange emission of FMCHTPE (the emission of FMCHTPE will be further discussed in later). This phenomenon indicates a ring-closing process of FMCHTPE has happened, which was confirmed by the UV and PL spectra (Fig. 1E, 1F, Fig. S3, ESI†). The water induced ring-closing reaction is because water can capture the proton and reduce the acidity of the solution, which has been described before.[9a] If acid was largely excessive, the ring-closing process would be suppressed and the ionic FMCHTPE can still be dissolved in high water content solution and does not show emission (Fig. S4, ESI†). Therefore, different from other AIE molecules that do not have structural transition properties, for our fluorescent molecular switch, poor solvent of water not only has the function to precipitate the organic molecules, but also has effects on structural transition, and leads to more complicated phenomena.

The stability of FSPTPE in initial solid state

It has been reported that TPE does not have mechanochromic property because of its symmetric spherical molecular conformation and quick re-crystallization rate.[12] However, FSPTPE exists only in amorphous state because of its high asymmetry structure and weak intermolecular interactions, which are different from other TPE derivatives and the reported fluorescent molecular switches.[13] Re-crystallization was carried out in various solvents, such as n-hexane, acetone, ethanol and toluene, but none of the solvents was successful. Thermal annealing also failed to induce the amorphous to crystalline transition even when the temperature arrived at the melt point (80.4 °C). Emission of the powder red shifts 6 nm after 4 h of annealing at 75 °C, which could not be distinguished by naked eyes (Fig. 2). DSC measurement also confirms that no exothermic process of crystallization occurred (Fig. S5, ESI†). The low melt point proves that the intermolecular interactions in solid are extremely weak. Theoretical calculation by Gaussian 09 also shows that the optimized FSPTPE structure is of high asymmetry and strong steric repulsion (Fig. S6, ESI†), and the small molecular switch with low molecular weight has very weak dispersion force. So it is not easy for the asymmetrical FSPTPE to crystallize through extremely weak intermolecular interactions.

Existing in only amorphous state, the FSPTPE does not have mechanochromic property. When the pristine powder [obtained by slowly evaporating its methanol solution, Em=480 nm Φ_F= 10.27 %, τ_1= 1.3 ns (A1 = 38.07 %), τ_2 =3.7 ns (A2 = 61.93 %)] is subjected to grinding, the emission of the powder only red shifts a negligible 2 nm. This means that FSPTPE is insensible to mechanical force. Besides, freeze-drying was applied to FSPTPE solution to get amorphous FSPTPE powder, in which the cyan emission (485 nm) was also obtained. The above experiments suggest when the molecules exist in only amorphous phase without the regular intermolecular interactions, the processing methods (such as solvent evaporation, annealing, grinding and freeze-drying) will not have strong contributions to the control of molecular conformations as in the polymorph crystals, and the conformations of molecules from different processing methods are very close to each other, resulting in the nearly fixed emission position.

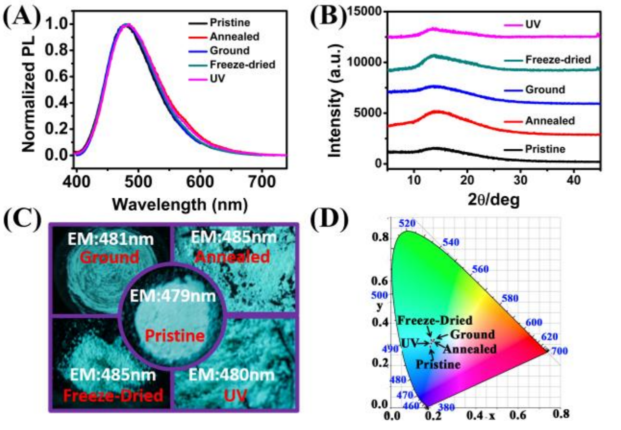


Figure 2. (A) PL spectra, (B) PXRD pattern, (C) fluorescent images and (D) CIE graph of ARCF after different treatment. Photos were taken under 365 nm UV light.

Photochromic property of amorphous FSPTPE was also investigated. UV light can hardly induce the isomerization of FSPTPE from SP form to MC form in solid state. There was no emission position change even after UV light (254 nm) radiation for 10 min (Fig. S7, ESI†). Actually, only a few spiropyran derivatives were observed to isomerize upon light irradiation in solid or crystal state.[14] This is because the restriction of molecular vibration in the solid not only blocks the non-radiation transition, but also constrain the cis-trans transition which is needed to stabilize the MC form. So the photo-stationary MC form is not easy to be obtained in solid.

From the above experiment, it is obvious that the emissions of the FSPTPE have no distinguishable change (within 6 nm shift) after different stimuli such as grinding, annealing, freeze-drying and UV irradiation. So FSPTPE has very stable initial emission state and it is insensibility to most physical stimuli, which can supply a very stable initial emissive colour as observed from the CIE graph(Fig. 2D, Fig. S8, ESI†).

Solid state ring-open/ring-closed isomerization regulated by acid/base and the fluorescence mechanism

Although acid/base has been used to trigger the isomerisation of FSPTPE in solution, the resultant SP and MCH forms do not have emissions due to the free rotating of the benzenes in TPE. To achieve fluorescent switch, triggers of acid/base were added to the solid sample. When FSPTPE powder was fumed with a mixture of HCl and EtOAc, its color changed from white to orange under ambient light, and the emission turned simultaneously from cyan to orange [601 nm, Φ_F= 10.17 %, τ_1=1.4 ns (A1 =65.14 %), τ_2=3.2 ns (A2 =34.86 %)] (Fig. 3A). The UV-Vis absorption of the orange powder is the same with FMCHTPE, suggesting the occurrence of isomerization. ^{1}H NMR spectrum also confirmed the generation of FMCHTPE (Fig. S9, ESI†). After fuming with HCl/EtOAc mixture, the resultant FMCHTPE existed in crystal phase as proved with PXRD (Fig. S2, ESI†). The reverse process was achieved by fuming the orange powder with a mixture of Et_3N/MeOH, and FMCHTPE converted to FSPTPE again with the fluorescence changing back to cyan (Fig. 3A). Methanol here was used to enhance the penetrability of Et_3N into the crystal and improve the converting rate of crystalline FMCHTPE to FSPTPE. The process can be repeated at least four cycles without obvious colour and intensity change in each state. This indicates that FSPTPE in solid state can isomerize reversibly with acid/base stimuli in the presence of appropriate solvents. The high emission contrast from cyan to orange (about 120 nm spectral shift) and the negligible spectral overlap make it more competitive in real application.

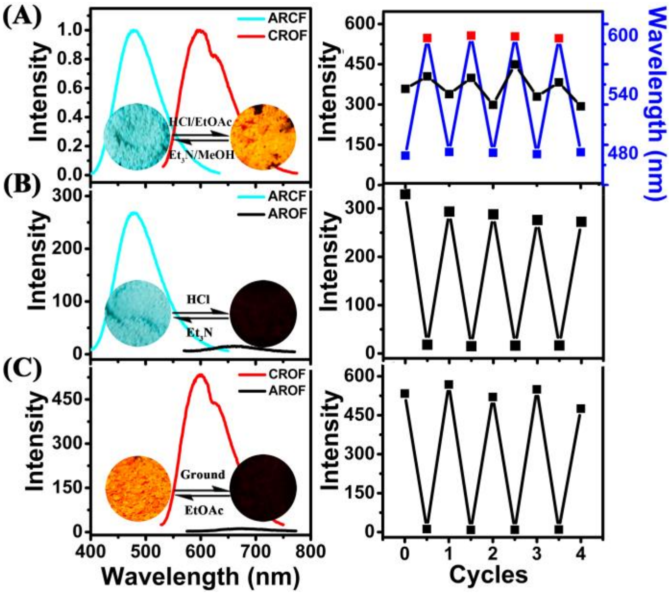


Figure 3. Left: Fluorescent images and PL spectra of FSPTPE converting reversibly between different solid states. Right: PL intensity and wavelength contrast profiles for several cycles. (A) FSPTPE-crystalline FMCHTPE (ARCF-CROF) switching, (B) FSPTPE- amorphous FMCHTPE (ARCF-AROF) switching, (C) crystalline FMCHTPE- amorphous FMCHTPE (CROF-AROF) switching.

Spiropyran usually has no/weak emission in solution or solid state either in SP form or MCH form. Fusion with TPE changes its molecular orbital, making it a fluorescent molecular switch with high luminescent property in solid and aggregate states. Theoretical calculations were performed to investigate the origin of the cyan and orange emissions.[15] For FSPTPE, although the HOMO and LUMO are distributed on indole and TPE moiety respectively, its emission is very similar to TPE itself in aggregate state (Fig. S10, ESI†). Considering the fact that poor conjugation between indole and TPE, the cyan emission should be assigned as the localized excited (LE) emission of TPE moiety, while electronic transition occurs between HOMO-1 and LUMO (Fig. 4). As for FMCHTPE, HOMO distributes on TPE, while LUMO locates on the indolium moiety, suggesting that the intramolecular charge transfer (ICT) is responsible for the orange emission. Therefore, the TPE moiety not only enable the AIE property of FSPTPE in SP form, but also acts as electron donor and offer the molecule a new emission from ICT state in MCH form.

The ICT emission of FMCHTPE depends on the degree of crystallization. Without the assistance of solvent, hydrogen chloride gas alone can also achieve ring-opening process quickly. But the corresponding PXRD (Fig. S2, ESI†) indicates that the obtained orange powder is in amorphous state. However, amorphous FMCHTPE has no emission under 365 nm UV light [ΦF <0.01 %]. When the amorphous FMCHTPE is fumed with Et3N, it converts back to FSPTPE and the cyan emission is lightened up again. The process exhibits good reversibility without obvious emission position or intensity change. So the cyan/off switching is realized (Fig. 3B). The conversion from either crystalline or amorphous FMCHTPE only results in amorphous FSPTPE, which also confirms the stability of the amorphous state for FSPTPE.

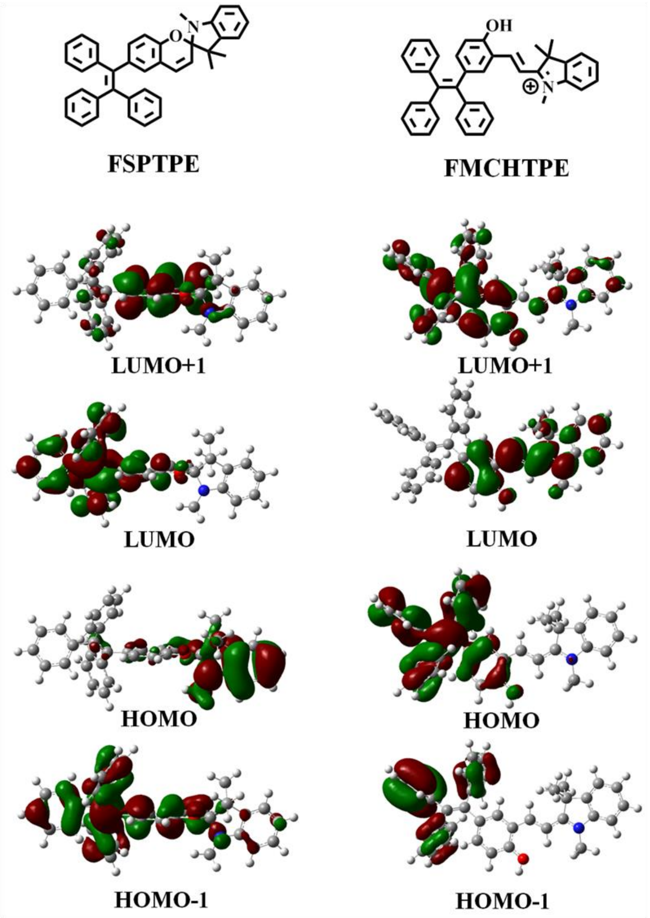


Figure 4. Calculated HOMO-LUMO orbitals of FSPTPE and FMCHTPE using B3LYP/6-31+g (d, p) basis set.

The mechnochromic property of FMCHTPE and mechanism of fluorescence quenching

Despite crystalline state of FSPTPE was not obtained, micro-crystals of FMCHTPE could be obtained by re-crystallization. But the amorphous FMCHTPE obtained from only HCl fuming is non-luminescent. This encouraged us to explore the mechanochromic property of FMCHTPE solid, since the mechanical forces are usually applied to induce the crystal to amorphous phase transition.[16]

The response of FMCHTPE to force is totally different from FSPTPE. When the orange crystalline powder was ground with pestle in a mortar, the orange emission vanished (Φ_F <0.01 %). Corresponding PXRD pattern indicates its crystal structure has changed to amorphous (Fig. S2, ESI†). The reverse process can be achieved through EtOAc fuming, and the fluorescence recovers. This is also a typical fluorescent on/off process.[17] Similarly, this process can be repeated for several cycles without obvious change of the quantum yield and emissive position of crystallized FMCHTPE (Fig. 3C). Thus, the orange/off emission switching is realized with high on/off ratio and can be detected easily by naked eyes. In fact, the fluorescence can be quenched gradually if the degree of grinding is controlled. As depicted in Fig. 5A, with increasing time of grinding, the fluorescence and absorption of crystallized FMCHTPE powder red shifted gradually. The emission peak of initial powder centered at 601 nm, went through 636 nm, 648 nm, 675 nm and nearly disappeared at 678 nm eventually (Fig. 5B). And the emission intensity descended quickly from 210 to no more than 10. The absorption red shifted nearly 100 nm after crystalline FMCHTPE entirely converted to amorphous (Fig. 5C). In most crystallization-induced emission systems, the reason for fluorescence quenching is that the non-irradiation transition channel is opened after the crystal is destroyed.[18] Herein, we attribute another main reason for the fluorescence quenching to the change of π-π interaction and dipolar interaction in FMCHTPE system. The existence of π-π stacking in ring-open form of spiropyran has been reported before.[19] It is a pity that we didn't get corresponding single crystal data, but we could obtain clues from the theoretical calculation by Gaussian 09. The MCH segment in optimized structure of FMCHTPE is nearly a planar conjugated system (Fig. S11, ESI†). The long conjugated plane facilitates the formation of intermolecular π-π stacking. In the crystal structure of FMCHTPE, we think that the molecules are interlocked by weak π-π interaction. In this condition, the non-radiation transition is blocked and the π-π stacking is not strong enough to quench the fluorescence of ICT. If the crystal is crushed or suffers from hydraulic force, the molecules will be more planar in conformation and the intermolecular distances will be closer,[20, 21] which results in the enhancement of π-π interaction and dipole-dipole interaction, so bathochromic effect and quenching of the fluorescence appear. The redshift of absorption spectra for the FMCHSP crystals (>100 nm) after grinding is consistent with the deduction that more planar conformation and enhancement of π-π interaction are induced (Fig. S12, ESI†). Based on the above experiment, it's shown FSPTPE is force-inert, and FMCHTPE is force-sensitive. Therefore, the mechanochromic behaviour of our fluorescent switch is changeable by structural tautomerization triggered by acid or base.

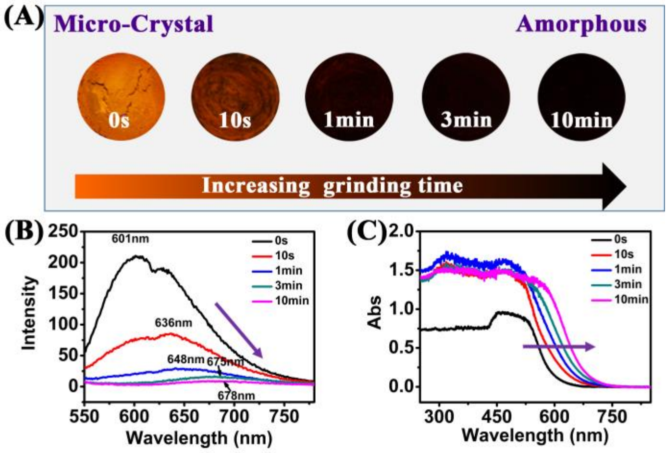


Figure 5. (A) The fluorescent photos of crystalline FMCHTPE powder converting to amorphous with different grinding time. (B) PL spectra and (C) Absorption spectra are corresponding optical data of force-induced fluorescence quenching process.

The cyan/off switching mechanism was also studied. Unlike orange/off switching, the cyan/off switching doesn't go through crystal-amorphous state conversion. It is the transition between the two amorphous states of FSPTPE and FMCHTPE. When FSPTPE powder exposed to HCl gas, FSPTPE changed into FMCHTPE quickly. As depicted in Fig. 6A, the cyan emission faded away gradually with different exposure time, which was confirmed by PL spectra. The loose stacking style of FSPTPE and the spatial support of TPE in microenvironment facilitate the reaction with acid and result in high conversion efficiency. The fluorescent intensity descends from 526 to no more than 5 within one minute (Fig. 6B, on/off ratio>100), and the fluorescence quenches completely after fumed 3 min. This indicates that FSPTPE is ultra-sensitive to acid. There is a weak shoulder emission at 580 nm accompanied with the main emission peak at 480 nm in acid fuming process, which may origin from a small amount of FMCHTPE molecules surrounded by FSPTPE. With increasing amount of FMCHTPE in the solid, the emission at 580 nm gradually quenched by stronger π-π interactions between FMCHTPE molecules. Different from orange/off switching, the absorption for amorphous FMCHTPE didn't have a bathochromic shift but enhanced gradually. (Fig. 6C). This meant that after captured HCl, FSPTPE promptly turned into FMCHTPE and formed strong π-π interactions in the relative slack amorphous solid state, and the orange fluorescence was directly quenched.

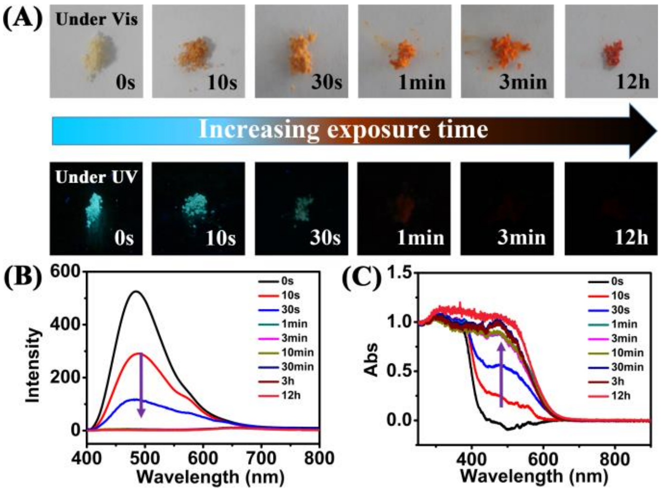


Figure 6. (A) Optical images of FSPTPE treated by HCl with different time; (B) PL spectra and (C) absorption spectra of the FSPTPE in HCl fuming process.

Application demonstration

The fluorescence of FSPTPE not only can be reversibly tuned between two states at one time, but also can be arbitrarily switched among cyan/orange/off in a stimuli-responsive circulation process without any crosstalk (Fig. S13, ESI†). So the solid state FSPTPE can be used for display, high-density information storage and consecutive sensing in situ.

To realize the processibility of the molecules, a polymer is used as a matrix. As FSPTPE is dispersed in polymer, intermolecular π-π interaction is avoided and the molecular free rotating is restricted, both FSPTPE and FMCHTPE can give strong emission without affected by grinding. When doped into PEG 20000 with mass ratio of 1/20 and tinted on paper, FSPTPE can reversibly convert emission between blue and orange under acid/base treatment (Fig. 7A). PL and absorption spectra of acid/base treated paper show characteristic emission and absorption of FSPTPE and FMCHTPE molecules (Fig. 7B, Fig. 7C). There is no obvious change of emission and absorption of the fluorescent paper after grinding or going through reversible acid/base stimuli. A distinct dove of peace was drawn on the paper, and it could be erased by base (Fig. 7D). So the high contrast and stable blue-orange fluorescent paper for writing and printing is accomplished.

FSPTPE also can be used in anti-counterfeiting (Fig. 7E). The characters on the practice notes were coated with FSPTPE/PEG mixture. The stable cyan fluorescence can be used as junior identification. As for senior identification, the note can be fumed with a volatile acid, such as edible acetic acid. The acid-sensitive FSPTPE changed to FMCHTPE quickly, and the absorption and fluorescence of character turned to orange. Although the fluorescent intensity of acetic acid treated FMCHTPE was not high, but the change of absorption could be clearly detected by naked eyes, and FMCHTPE spontaneously returned back to FSPTPE after the acid volatilizes, along with fluorescence and absorption recovering. All changes of the anti-counterfeiting coating can be detected by naked eyes both under ambient light and UV light, and the anti-counterfeiting method is convenient and recyclable without introduction of impurity into the discriminating system. So the weak edible acid responsiveness, reversibility and high color contrast make FSPTPE very competitive in real application.

Conclusions

In summary, a TPE functionalized spiropyran molecular switch FSPTPE with highly fused structure has been synthesized. This molecule exhibits isomerization and AIE properties in solution, and it possesses three emission states in solid phase. The three states are amorphous ring-closed form with high insensitivity towards external stimuli, force sensible crystal ring-open form and non-emissive amorphous ring-open form. These three states correspond to three different emissive states of cyan, orange and dark respectively. And these three states can be changed reversibly between each other under appropriate external stimuli. Cyan/orange switching possesses excellent reversibility with high emission contrast, while cyan/off and orange/off switching exhibit remarkable high on/off ratio. The optical stability of FMCHTPE will be enhanced greatly if doped into polymer. Based on the above properties, we could regulate the sensibility of FSPTPE to external force and change its fluorescence among cyan/orange/off states. The particular properties make the fluorescent molecular switch promising for the application of controllable chemical and mechanical sensing, high density data storage, display and anti-counterfeiting.

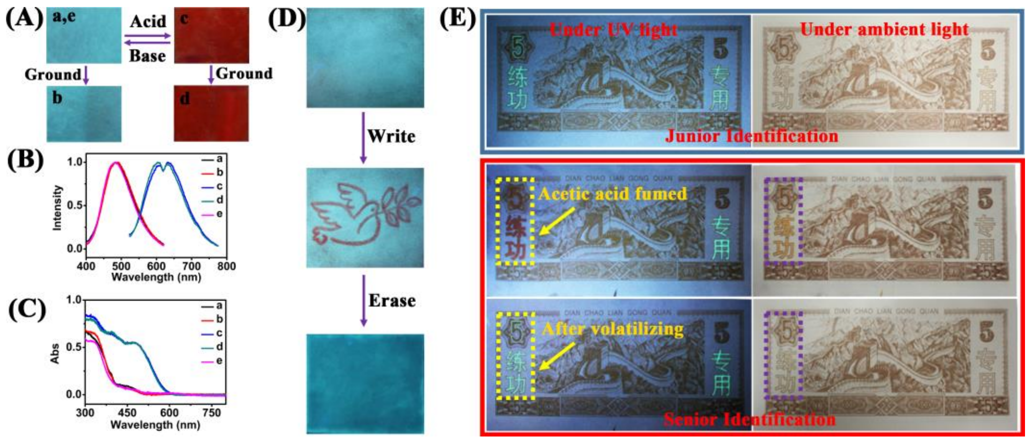


Figure 7. (A) The fluorescent photos of FSPTPE/PEG coated filter paper upon different stimuli, and their corresponding (B) PL spectra and (C) Absorption spectra. (D) Image of a peaceful dove drawn by brush pen on the FSPTPE/PEG coated filter paper. Ink: p-toluenesulfonic acid/ethanol solution, Eraser: NaOH/ethanol solution. (E) Image demonstration of the anti-counterfeiting application of FSPTPE/PEG coating on a practice note. Left: under 365nm UV light, and right: under ambient light.

Experimental section

Materials

Zinc powder was activated with dilute hydrochloric acid, then dried and stored under nitrogen. Trifluoroacetic acid, benzophenone, 4-hydroxybenzophenone were purchased from Energy Chemical. $TiCl_4$ and hexamethylenetetramine were purchased from Aladdin. Acetic acid, alcohol were purchased from Beijing Reagent. Acetonitrile, triethylamine were bought from Xilong Chemical. All these chemicals were used without any further purification.

Instruments

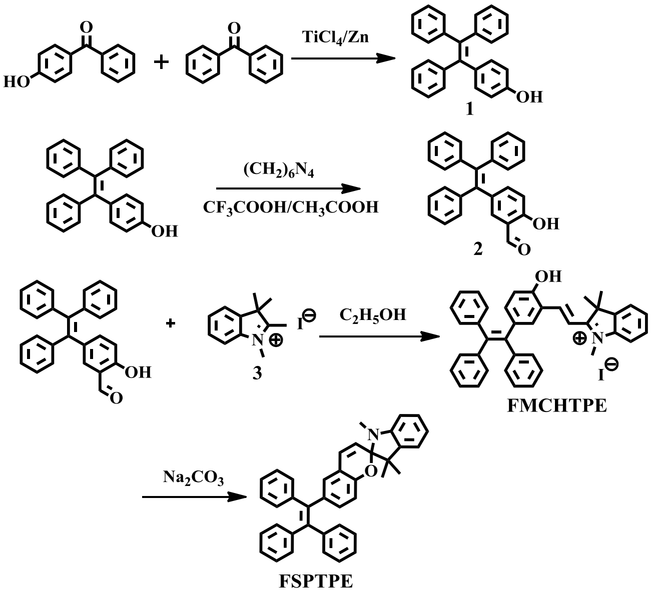
^{1}H NMR spectra were recorded on a 500 MHz BrukerAvance. ^{13}C NMR spectra were recorded on a 126 MHz BrukerAvance. The deuterated solvents of $CDCl_3$ and DMSO-d_6 were used for ^{1}H NMR and ^{13}C NMR. Tetramethylsilane (TMS, δ = 0.00 ppm) was used as an internal standard for ^{1}H NMR. $CDCl_3$ (δ = 40.03 ppm) and DMSO-d_6 (δ = 77.00 ppm) were used as internal standards for ^{13}C NMR. Fluorescence spectra of all samples (solid and solution) were measured with a RF-5301PC spectrofluorometer. Absorption spectra were measured on a Shimadzu UV-2550 spectrophotometer. Powder XRD patterns were obtained from a PANalytical B.V.Empyrean X-ray diffractometer with Cu-Kα radiation (λ = 1.5418 Å) at 20 ^{o}C (scan range: 5-45°). Fluorescence Lifetimes were measured using time-correlated single-photon counting method and collected on an Edinburgh FLS980, with an Edinburgh EPL-375 picosecond pulsed diode laser as the excitation source. Fluorescence quantum yield (Φ_F) was measured using an integrating sphere (C-701, Labsphere Inc.), with a 405 nm Ocean Optics LLS-LED as the excitation source. MS spectra were obtained with ITQ1100 (Thermo Fisher). DSC data were obtained from a NETZSCH DSC 204 instrument at a scanning rate of 10 ^{o}C min^{-1}. Thermogravimetric analysis (TGA) was performed on a Q500 at heating rate of 10 ^{o}C min^{-1} under nitrogen flow from 35 to 900 ^{o}C. Kubelka-Munk diffuse reflectance absorption spectra were obtained from a Maya 2000PRO fiber optical spectrometer with Ocean DH-2000-BAL UV-Vis-NIR light source using $BaSO_4$ as background.

General Synthesis and characterizations

FSPTPE was synthesized according to the synthetic routes shown in Scheme 2. Compound **1, 3** were obtained with the methods of literatures.[22] Corresponding characterizations were displayed in the ESI†.

2-hydroxy-5-(1,2,2-triphenylvinyl) benzaldehyde (2):

4-(1,2,2-triphenylvinyl)phenol **(1)** (3 mmol, 1.05 g) and hexa-methylenetetramine (9 mmol, 1.26 g) were added to a mixture of 8 mL acetic acid and 8 mL trifluoroacetic. The solution was heated to reflux under vigorous stirring. After 3 h, the reaction was quenched with 30 mL water and extracted with dichloromethane for three times (3×10 mL). The organic layers were combined and washed with water (15 mL) and brine (15 mL). Then the solution was evaporated to remove organic solvent and get the crude product. Column chromatography was used for further purification (EtOAc:PE =1:5) to get yellow powder product (0.78 g). Yield: 69 %. ^{1}H NMR (500 MHz, $CDCl_3$), δ 10.91 (s, 1H), 9.57 (s, 1H), 7.20–7.16 (m, 2H), 7.14–6.99 (m, 15H), 6.71 (d, J = 9.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.65 (s), 160.29 (s), 143.47 (d, J = 4.3 Hz), 143.16 (s), 141.61 (s), 140.22 (s), 139.00 (s), 136.53 (s), 135.76 (s), 131.56–131.23 (m), 128.11 (d, J = 14.4 Hz), 127.86 (s), 126.94 (d, J = 5.4 Hz), 126.75 (s), 120.28 (s), 117.08 (s).



Scheme 2. The synthetic route of FSPTPE.

FMCHTPE iodide and FSPTPE:

1,2,3,3-tetramethyl-3H-indol-1-ium iodide (3) (1 mmol, 0.30 g) and 2-hydroxy-5-(1,2,2-triphenyl vinyl) benzaldehyde (2) (1.2 mmol, 0.45 g) and 10 mL anhydrous EtOH were added into a flask. The reaction solution was refluxed for 36 h, and the solvent was evaporated to get orange powder. The orange powder was further purified by re-crystallization with DCM/EtOAc to get FMCHTPE iodide. Then FMCHTPE iodide was dissolved in DCM solution and washed with Na_2CO_3 aqueous solution to get FSPTPE. Then FSPTPE was separated from DCM and re-dissolved in MeOH to get white powder after drying. Yield: 62%. Melt point: 80.4 ^{o}C. ^{1}H NMR (500 MHz, DMSO), δ 7.09 (ddd, J = 16.5, 12.3, 6.8 Hz, 11H), 7.02 – 6.93 (m, 6H), 6.76 (d, J = 12.4 Hz, 3H), 6.66 (d, J = 2.0 Hz, 1H), 6.53 (d, J = 7.7 Hz, 1H), 6.43 (d, J = 8.4 Hz, 1H), 5.68 (d, J = 10.2 Hz, 1H), 2.60 (s, 3H), 1.17 (s, 3H), 1.05 (s, 3H). ^{13}C NMR (126 MHz, DMSO), δ 153.22 (s), 148.20 (s), 143.82 (d, J = 15.2 Hz), 143.57 (s), 140.58 (s), 140.40 (s), 136.76 (s), 135.69 (s), 132.63 (s), 131.14 (s), 129.95 – 129.72 (m), 129.60 (d, J = 26.9 Hz), 128.43 – 128.08 (m), 127.89 (s), 126.93 (d, J = 15.4 Hz), 121.85 (s), 119.91 (s), 119.36 (s), 118.78 (s), 114.36 (s), 107.19 (s), 104.29 (s), 51.75 (s), 28.99 (s), 26.14 (s), 20.32 (s). LC-HRMS (ESI) m/z: 532.2634 [$(M+H)^+$, calcd: m/z:532.2635].

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Keywords: fluorescent molecular switch• tetraphenylethene • spiropyran • aggregation-induced emission• mechanochromic

[1] a) S. Kim, S. J. Yoon and S. Y. Park, *J. Am. Chem. Soc.*, **2012**, 134, 12091-12097; b) C. Li, Y. Zhang, J. Hu. J. Cheng and S. Liu, *Angew. Chem. Int. Ed.*, **2010**, 49, 5120-5124; c) Z. Ma, Z. Wang, X. Meng, Z. Ma, Z. Xu, Y. Ma and X. Jia, *Angew. Chem. Int. Ed.* **2016**, 55, 519-522; d) H. Xia, Y. Xu, G. Yang, H. Jiang, G. Zou and Q. Zhang, *Macromol. Rapid Commun.* **2014**, 35, 303-308.

[2] a) M. Irie, T. Fukaminato, T. Sasaki, N. Tamai and T. Kawai, *Nature*, **2002**, 420, 759-760; b) A. Kishimura, T. Yamashita, K. Yamaguchi and T. Aida, *Nat. Mater.*, **2005**, 4, 546-549; c) X. Zhu, R. Liu, Y. Li, H. Huang, Q. Wang, D. Wang, X. Zhu, S. Liu and H. Zhu, *Chem. Commun.*, **2014**, 50, 12951-12954.

[3] a) X. Cheng, H. Jia, T. Long, J. Feng, J. Qin and Z. Li, *Chem. Commun.*, **2011**, 47, 11978-11980; b) Q. Zeng, P. Cai, Z. Li, J. Qin and B. Z. Tang, *Chem. Commun.*, **2008**, 9, 1094-1096; c) S. J. Toal, K. A. Jones, D. Magde and W. C. Trogler, *J. Am. Chem. Soc.*, **2005**, 127, 11661-11665; d) T. Han, J. W. Y. Lam, N. Zhao, M. Gao, Z. Yang, E. Zhao, Y. Dong and B. Z. Tang, *Chem. Commun.*, **2013**, 49, 4848-4850; e) R. Zhang, Z. Wang, Y. Wu, H. Fu and J. Yao, *Org. Lett.*, **2008**, 10**,** 3065-3068.

[4] a) H. Sun, S. Liu, W. Lin, K. Y. Zhang, W. Lv, X. Huang, F. Huo, H. Yang, G. Jenkins, Q. Zhao and W. Huang, *Nat. Commun.* DOI: 10. 1038/ncomms4601; b) S. Araki, K. Nakamura, K. Kobayashi, A. Tsuboi and N. Kobayashi, *Adv. Mater.*, **2012**, 24, OP122-OP126; c) H. Gu, L. Bi, Y. Fu, N. Wang, S. Liu and Z. Tang, *Chem. Sci.*, **2013**, 4, 4371-4377.

[5] a) M. Q. Zhu, L. Zhu, J. J. Han, W. Wu, J. K. Hurst and A. D. Q. Li, *J. Am. Chem. Soc.*, **2006**, 128, 4303-4309; b) Z. Tian and A. D. Q. Li, *Acc. Chem. Res.*, **2013**, 46, 269-279. c) G. Feng, D. Ding, K. Li, J. Liu and B. Liu, *Nanoscale*, **2014**, 6, 4141-4147.

[6] a) S. J. Yoon, J. W. Chung, J. Gierschner, K. S. Kim, M. G. Choi, D. Kim and S. Y. Park, *J. Am. Chem. Soc.*, **2010**, 132, 13675-13683; (b) Y. Sagara and T. Kato, *Angew. Chem.*, **2011**, 123, 9294-9298; c) C. Ma, B. Xu, G. Xie, J. He, X. Zhou, B. Peng, L. Jiang, B. Xu, W. Tian, Z. Chi, S. Liu, Y. Zhang and J. Xu, *Chem. Commun.*, **2014**, 50, 7374-7377; d) Y. Gong, Y. Zhang, W. Z. Yuan, J. Z. Sun and Y. Zhang, *J. Phys. Chem. C*, **2014**, 118, 10998-11005; e) J. W. Chung, S. J. Yoon, B. K. An and S. Y. Park, *J. Phys. Chem. C*, **2013**, 117, 11285-11291. f) C. Li, X. Tang, L. Zhang, C. Li, Z. Liu, Z. Bo, Y. Q. Dong, Y. H. Tian, Y. Dong and B. Z. Tang, *Adv. Optical Mater.*, **2015**, 3, 1184-1190; g) Z. Zhang, B. Xu, J. Su, L. Shen, Y. Xie and H. Tian, *Angew. Chem. Int. Ed.*, **2011**, 50, 11654-11657.

[7] a) Z. Ma, M. Teng, Z. Wang, S. Yang and X. Jia, *Angew. Chem. Int. Ed.*, **2013**, 52, 12268-12272; b) Q. Chen, D. Zhang, G. Zhang, X. Yang, Y. Feng, Q. Fan and D. Zhu, *Adv. Funct. Mater.*, **2010**, 20, 3244-3251; c) J. Garcia-Amorós, S. Swaminathan, S. Sortino and F. M. Raymo, *Chem. Eur. J.* **2014**, 20, 10276-10284; d) Y. Zhang, S. Swaminathan, S. Tang, J. Garcia-Amorós, M. Boulina, B. Captain, J. D. Baker and F. M. Raymo, *J. Am. Chem. Soc.* **2015**, 137, 4709-4719.

[8] a) M. S. Kwon, J. Gierschner, S. J. Yoon and S. Y. Park, *Adv. Mater.* 2012, **24**, 5487-5492; b) H. J. Kim, D. R. Whang, J. Gierschner, C. H. Lee and S. Y. Park, *Angew. Chem. Int. Ed.* **2015**, 54, 4330-4333.

[9] a) Q. Qi, X. Fang, Y. Liu, P. Zhou, Y. M. Zhang, B. Yang, W. Tian and S. X. Zhang, *RSC Adv.*, **2013**, 3, 16986-16989; b) Q. Qi, J. Qian, S. Ma, B. Xu, S. X. Zhang and W. Tian, *Chem. Eur. J.*, **2015**, 21, 1149-1155.

[10] a) Q. Qi, Y. Liu, X. Fang, Y. M. Zhang, P. Chen, Y. Wang, B. Yang, B. Xu, W. Tian and S. X. A. Zhang, *RSC Advances*, **2013**, 3, 7996-8002; b) J. Tong, Y. Wang, J. Mei, J. Wang, A. Qin, J. Z. Sun and B. Z. Tang, *Chem. Eur. J.* **2014**, 20, 4661-4670.

[11] a) G. Berkovic, V. Krongauz, V. Weiss, *Chem. Rev.*, **2000**, 100, 1741-1754; b) V. I. Minkin, *Chem. Rev.*, **2004**, 104, 2751-2776; c) I. Yildiz, E. Deniz, F. M. Raymo, *Chem. Soc. Rev.*, **2009**, 38, 1859-1867; d) S. Swaminathan, J. Garcia-Amorós, A. Fraix, N. Kandoth, S. Sortino, F. M. Raymo, *Chem. Soc. Rev.*, **2014**, 43, 4167-4178; e) S. Yagi, K. Maeda, H. Nakazumi, J. Mater. Chem. **1999**, 9, 2991-2997; f) J. T. C. Wojtyk, A. Wasey, P. M. Kazmaier, S.Hoz, E. Buncel, J Phys. Chem. A, **2000**, 104, 9046-9055.

[12] Y. Wang, I. Zhang, B. Yu, X. Fang, X. Su, Y. M. Zhang, T. Zhang, B. Yang, M. Li and S. X. A. Zhang, *J. Mater. Chem. C*, **2015**, 3, 12328-12334.

[13] a) B. Xu, Z. Chi, J. Zhang, X. Zhang, H. Li, X. Li, S. Liu, Y. Zhang and J. Xu, *Chem. Asian. J.* **2011**, 6, 1470-1478; b) H. Li, Z. Chi, B. Xu, X. Zhang, X. Li, S. Liu, Y. Zhang and J. Xu, *J. Mater. Chem.*, **2011**, 21, 3760-3767; c) R. Misra, T. Jadhav, B. Dhokale and S. M. Mobin, *Chem. Commun.,* **2014**, 50, 9076-9078.

[14] a) S. Benard and P. Yu, *Adv. Mater.*, **2000**, 12, 48-50; b) O. Godsi, U. Peskin, M. Kapon, E. Natan and Y. Eichen, *Chem. Commun.*, **2001**, 20, 2132-2133.

[15] M. J. Frisch, G. W. Trucks, H. B. Schlegel, etl., Gaussian 09, (Revision A. 02), Gaussian, Inc., Wallingford, CT 2009

[16] a) Z. Chi, X. Zhang, B. Xu, X. Zhou, C. Ma, Y. Zhang, S. Liu and J. Xu, *Chem. Soc. Rev.*, **2012**, 41, 3878-3896; b) X. Zhang, Z. Chi, H. Li, B. Xu, X. Li, W. Zhou, S. Liu, Y. Zhang and J. Xu, *Chem. Asian J.*, **2011**, 6, 808-811.

[17] a) Y. Zhang, J. Sun, G. Zhuang, M. Ouyang, Z. Yu, F. Cao, G. Pan, P. Tang, C. Zhang and Y. Ma, *J. Mater. Chem. C*, **2014**, 2, 195-200; b) X. Cheng, Z. Zhang, H. Zhang, S. Han, K. Ye, L. Wang, H. Zhang and Y. Wang, *J. Mater. Chem. C*, **2014**, 2, 7385-7391; c) J. Luo, L. Y. Li, Y. Song and J. Pei, *Chem. Eur. J.*, **2011**, 17, 10515-10519; d) Y. Lim, I. Choi, H. Lee, I. W. Kim and J. Y. Chang, *J. Mater. Chem. C*, **2014**, 2, 5963-5968.

[18] a) R. Zheng, X. Mei, Z. Lin, Y. Zhao, H. Yao, W. Lv and Q. Ling, *J. Mater. Chem. C,* **2015**, 3, 10242-10248; b) Y. Lin, G. Chen, L. Zhao, W. Z. Yuan, Y. Zhang and B. Z. Tang, *J. Mater. Chem. C*, **2015**, 3, 112-120; c) R. Yoshii, A. Hirose, K. Tanaka and Y. Chujo, *Chem. Eur. J.* **2014**, 20, 8320-8324.

[19] X. Wang, J. Hu, G. Liu, J. Tian, H. Wang, M. Gong and S. Liu, *J. Am. Chem. Soc.* **2015**, 137, 15262-16275.

[20] a) L. Wang, K. Wang, B. Zou, K. Ye, H. Zhang and Y. Wang, *Adv. Mater.*, **2015**, 27, 2918-2922; b) Y. Sagara, T. Mutai, I. Yoshikawa and K. Araki, *J. Am. Chem. Soc.*, **2007**, 129, 1520-1521.

[21] a) Y. Dong, B. Xu, J. Zhang, X. Tan, L. Wang, J. Chen, H. Lv, S. Wen, B. Li, L. Ye, B. Zou and W. Tian, *Angew. Chem. Int. Ed.* **2012**, 51, 10782-10785; b) R. R. M, C. W. Liao, W. L. Su and S. S. Sun, *J. Mater. Chem. C*, **2013**, 1, 5491-5501.

[22] a) L. Zhang, W. Hu, L. Yu and Y. Wang, *Chem. Commun.*, **2015**, 51, 4298-4301; b) J. A. Richard, *Org. Biomol. Chem.*, **2015**, 13, 8169-8172.

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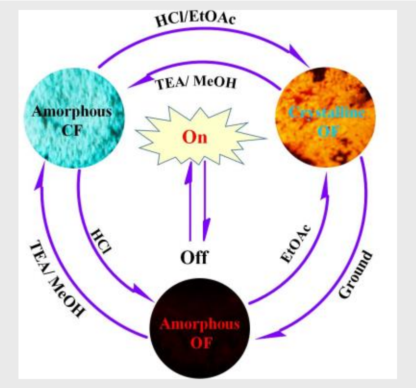

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A high contrast tri-state fluorescent switch: properties and application

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