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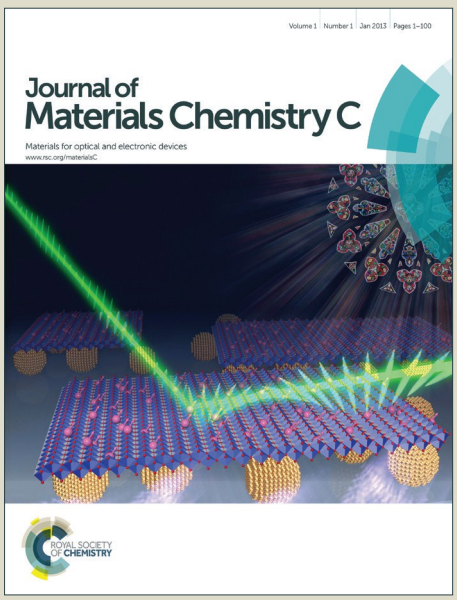

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EDGE ARTICLE

An ESIPT fluorophore with a switchable intramolecular hydrogen bond: for applications of solid-state fluorochromism and white light generation†

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A novel excited state intramolecular proton transfer (ESIPT) fluorophore of BTImP, in which benzothiazole (BT) and imidazole (Im) rings are respectively linked to the 2,6 positions of a phenol, was designed and synthesized. The switching of two intramolecular hydrogen bonds from the phenol proton to either the BT or Im nitrogen was reversibly induced by external acid/base stimuli due to protonation/deprotonation of the Im site. The fluorescence color of BTImP was thus changed with high contrast between green and orange, which could be achieved even in a BTImP-doped Nafion film. Writing a letter on the film using acidic or basic water as ink was demonstrated. Furthermore, the property that the protonated state of BTImP is sensitive to the surrounding anions provides other possibilities not only for blue/orange fluorochromism in Nafion film by dry-wet treatments, but also for white light generation in solution by tuning of the excitation wavelength.

Introduction

Photoinduced proton tautomerization from enol (E^*) to keto (K^*) tautomers is associated with proton migration within an intramolecular hydrogen bonding (H-bonding) site and is known as excited state intramolecular proton transfer (ESIPT). Molecules that undergo ESIPT often emit intense fluorescence from K^* with a large Stokes shift. The photocycle (E-E^*-K^*-K-E) provides a distinct four-level laser scheme to achieve population inversion; therefore, ESIPT fluorophores are useful as laser dyes.[1] Although conventional laser dyes cannot fluoresce efficiently unless they are in solution, ESIPT fluorophores have an advantage in that concentration quenching does not readily occur, even in the solid-state,[2] so that highly fluorescent powders can be easily obtained.[3] On the other hand, ESIPT fluorophores are sensitive to surrounding factors (i.e., pH, solvent polarity and the presence of ions) as a result of their influence on the intramolecular H-bonding site, which sometimes results in dual-wavelength ratiometric fluorescence that involves ESIPT emission from K^* and non-ESIPT emission from E^*. Such a phenomenon has attracted attention for applications such as fluorescent sensing probes.[4] We recently reported that under certain solvent conditions, the ESIPT fluorophore exhibits a panchromatic spectrum that consists of triple emissions from K^*, E^* and a deprotonated anionic form, which led to an almost white emission.[3a] Therefore, ESIPT fluorophores are also promising candidates for single-component white light generation.[5,6]

With those characteristics in mind, we have been trying to create stimuli-responsive fluorescent solids using ESIPT fluorophores. Organic solids that can change their emission color by external stimuli such as mechanical pressure, heat, light, guest molecules, and pH have attracted significant interest in recent years.[7] In many reports, a mechanical force such as grinding or rubbing causes a drastic change in emission color, and subsequent heating or exposure to organic vapor restores the initial emission color. Such mechano(piezo)chromism is the result of mechanical force-induced morphological change of the molecular assemblies from a stable to metastable phase or from an ordered to disordered (amorphous) phase. To achieve emission color switching and intense emission in the solid, there has been a focus on the development of compounds that exhibit an aggregation-induced emission enhancement (AIEE) effect.[8] However, it seems difficult to design such compounds in anticipation of the solid-state morphology and fluorescent properties. In contrast, ESIPT fluorophores have the potential to not only exhibit intense emission by themselves, even in the solid-state, but to also fluoresce with different color if the intramolecular H-bond is affected in a different manner by neighboring molecules within the solid. There has been a report of an ESIPT fluorophore that exhibits polymorph-dependent thermofluorochromism.[9] However, the fluorochromism of the ESIPT fluorophore we present here (BTImP), shown in Fig. 1a, originates from switching of the

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intramolecular H-bond, and is not dependent on morphological change, which opens a new possibility for single-molecule-based solid-state fluorochromism. BTImP possesses a switchable intramolecular H-bond from the central phenol proton to either the imidazole (Im) ring nitrogen or to the benzothiazole (BT) ring nitrogen. Depending on which side the H-bond is formed, the emission color is assumed to be different because ESIPT occurs at different H-bonding sites. As a result of protonation/deprotonation of the Im ring, the emission color of BTImP is drastically and reversibly changed by the addition of acid or base, which can be confirmed in a Nafion film doped with BTImP. It was also determined that under the presence of bulky anions such as ClO_4^- and BF_4^- in solution, BTImP exhibits dual fluorescence that consists of blue and orange emissions, of which the color is tunable from blue to white to orange by tuning the excitation wavelength.

Results and discussion

Fluorescence properties of BTImP

BTImP was obtained as a crystalline yellow powder (ESI†). Fig. 2 shows that BTImP fluoresces yellowish green with an emission maximum ($\lambda_{max,Fl}$) at 545 nm. Almost the same spectrum is observed in a typical solvent such as tetrahydrofuran (THF) ($\lambda_{max,Fl}$ = 542 nm). Thus, the fluorescence of BTImP is not significantly affected by the type of solvent, even polar aprotic solvents with high basicity, such as dimethylsulfoxide (DMSO) and N,N-dimethlyformamide (DMF), which often deprotonate ESIPT dyes.[3a] However, only in acetic acid (AcOH) solution, the fluorescence color is significantly changed to orange, with a $\lambda_{max,Fl}$ shift to 586 nm. In contrast to $\lambda_{max,Fl}$, there is only a subtle difference in the absorption wavelength maxima ($\lambda_{max,Abs}$) for spectra measured in THF and in AcOH (Fig. 2, left-hand side), where $\lambda_{max,Abs}$ is 378 nm and 372 nm, respectively. The Stokes shifts calculated from $\lambda_{max,Abs}$ and $\lambda_{max,Fl}$ are large in both cases (8,005 cm^{-1} and 9,817 cm^{-1} in THF and in AcOH, respectively), which suggests that

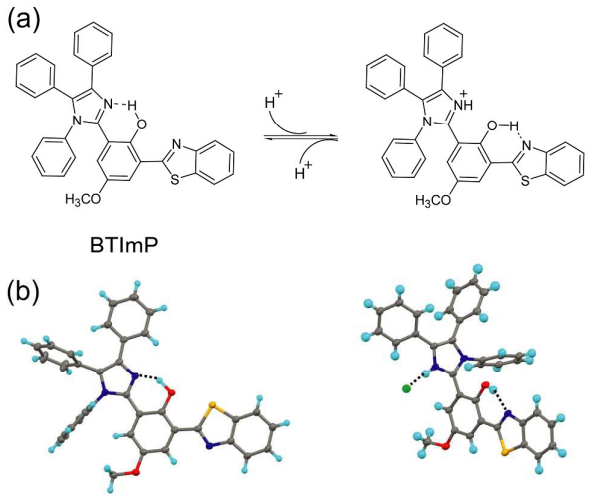

Fig. 1 (a) Structural formula of BTImP and its protonated form. (b) Crystal structures of BTImP (left) and its HCl salt (right).

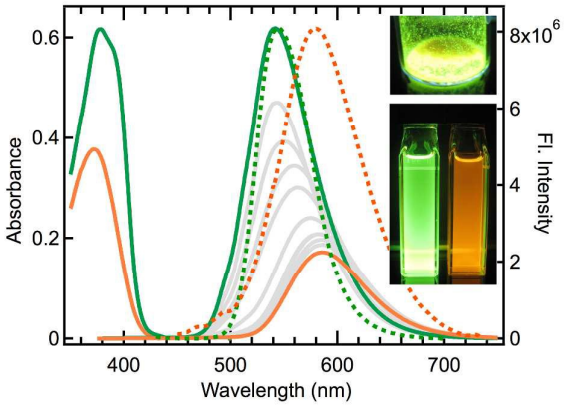

Fig. 2 Absorption and fluorescence spectra of BTImP in THF (green solid lines) and in AcOH (orange lines). Grey lines are fluorescence spectra when changing the THF/AcOH (v/v) ratio from 9:1 to 1:9. The green and orange dotted lines are the fluorescence spectra of BTImP and BTImP-HCl salt in powder, respectively. The fluorescence spectra were obtained by excitation at 365 nm and inset photographs were taken under irradiation by a 365 nm ultraviolet lamp.

fluorescence in both occur via ESIPT. The fluorescence quantum yield (Φ_{Fl}) is determined to be 0.75 in THF and 0.23 in AcOH. Changing the volume ratio of AcOH to THF can gradually change the fluorescence color from green to yellow to orange.[10] However, when trifluoroacetic acid (TFA), a stronger acid (pK_a = 0.23) than AcOH (pK_a = 4.76), was instead used, the fluorescence color became orange by adding a small amount of TFA (Fig. S1†). Furthermore, with successive addition of HCl to THF solution, the similar color change was also observed (Fig. S2†). These results suggest that the orange emission is ascribed to protonation of BTImP. We estimated the pK_a values of BTImP by using the ACD/Percepta program.[11] The obtained pK_a (base) values for the nitrogen atoms at Im and BT rings are 3.0 ± 0.1 and -0.5 ± 0.1, respectively, suggesting that the Im ring is far more likely to be protonated in acidic solution. The BT ring nitrogen of BTImP is suggested to be much harder to protonate, as compared to 2-(2-hydroxyphenyl)benzothiazole whose pK_a (base) is 1.3 ± 0.1. In fact, as shown in Fig. 2, we do not see any spectral changes that imply the formation of deprotonated dication of BTImP under the condition we applied.

Crystal structures of BTImP and its protonated form

The prediction that acid induces switching of the intramolecular H-bonding positions is verified by X-ray crystallography (Fig. 1b). In the green fluorescent crystal, the hydroxyl group of the central phenol ring is directed toward the Im ring, whereby the same H-bond configuration as that of Im-based ESIPT dyes is formed.[12] On the other hand, in the orange fluorescent crystal obtained from THF-HCl solution, the direction of the phenolic hydroxyl group is changed to the BT side due to protonation of the Im moiety, which results in the same H-bond configuration as that of BT-based ESIPT dyes.[3b] Its fluorescence spectrum (Fig. 2, orange dotted line) is almost

the same as that in AcOH. It is thus concluded that Stokes-shifted green and orange fluorescence is mainly emitted when ESIPT occurs at the Im and BT side, respectively, and these are switchable with each other by protonation/deprotonation of the Im moiety. Before protonation, the three π-units (phenol, Im and BT rings) are almost coplanar, while after protonation causes a twisting of the Im plane with respect to the other planes (dihedral angle = 65.53°). In addition, the frontier π-orbitals spread over the entire π-units become restricted only on the phenol and BT rings (Fig. S4†). These results indicate that protonation of the Im moiety cause structural and electronic changes of BTImP. However, considering that there is only a subtle difference in $\lambda_{max,Abs}$ between the spectra measured in THF and in AcOH (Fig. 2), we speculate that such twisting is not likely to occur in AcOH, and is induced only in the presence of a chloride ion that can form an ion-pair with the Im proton (N···Cl distance = 3.02 Å).[13] To our knowledge, this is the first example of fluorescence color switching based on the switching of ESIPT sites by acidic stimuli, although there is a report of acid-induced fluorescence on/off switching in an ESIPT dye that originates from the structural transformation of a built-in rhodamine moiety.[14]

Solid-state fluorochromism in BTImP-doped Nafion films

Since BTImP is insoluble in water, acidic water as a stimulus cannot penetrate into BTImP neat films or BTImP-doped hydrophobic polymer films. Thus, to achieve the green/orange fluorescent color switching of BTImP in the solid-state, we first attempted to incorporate BTImP into a hydrophilic Nafion film. Nafion is a well-known ion-exchange polymer used for various applications.[15] Dynamic hydrated nanopore structures are formed inside the Nafion film by negatively charged sulfonic groups on the polymer side chains;[16] therefore, it is likely that not only protonated cations of BTImP are incorporated, but that protons and hydroxyl ions are also introduced into the film. A Nafion film cut into 2×2 cm^2 square was immersed in a DMSO solution of BTImP (1 mg/mL) for 30 min and then rinsed with water (Fig. 3a, upper left inset photograph). Under UV irradiation at 365 nm, the film fluoresces orange (lower right), which indicates that BTImP is incorporated into the nanopores of Nafion in the protonated cationic state. The color changes to green by soaking the film in 1N NaOH solution (upper right), and then back to orange by soaking in 1N HCl solution. Therefore, switching of the fluorescent color is successfully achieved in a BTImP-doped Nafion film. The green and orange fluorescence spectra of the films are almost in agreement with those in THF and in AcOH, respectively (Fig. 3b). The response rate for the color change is determined by the diffusion rate of water in the film. Although such reversible fluorescence color change was clearly confirmed during at least several cycles (ESI video†), the fluorescence intensity was gradually reduced with each acid/base treatment cycle. This is because BTImP gradually leaches out from the Nafion film to the soaking solution. Thus, immobilization of the fluorophore inside a hydrophilic film such as Nafion is the next subject of our study and is currently underway. Here, a tentative demonstration of writing letters is presented (Fig. 3c). On the green fluorescent Nafion film after basic treatment, orange fluorescent letters can be written using acidic water as an ink. On the contrary, green fluorescent letters can be written on the orange fluorescent Nafion film after acidic treatment using basic water. Both letters are erasable by immersion of the film into either acidic or basic water. In most of the recent studies on morphology change-based mechanofluorochromism, the transition back to the initial phase (i.e., to erase letters) typically requires a high temperature beyond 100 °C or the use of organic solvent vapors. For applications such as rewritable data recording, water-based operations are more desirable from an eco-friendly perspective.[17]

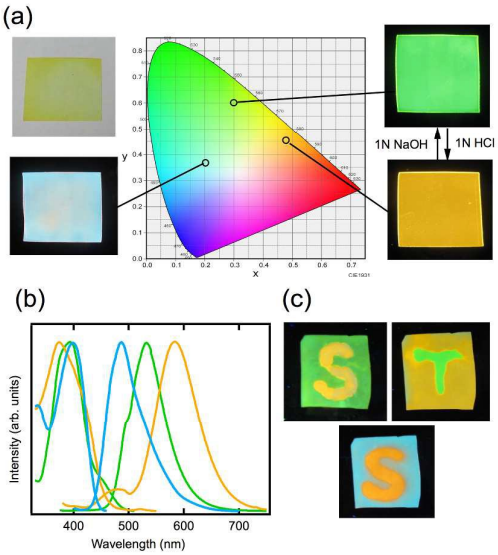

Fig. 3 (a) CIE coordinated for the fluorescent colors observed in BTImP-doped Nafion films and each photographs under a 365 nm UV lamp: green fluorescence after 1N NaOH treatment (upper right), orange fluorescence after 1N HCl treatment (lower right), and blue fluorescence after drying of the orange fluorescent film (lower left). The upper left photograph is taken under room light. (b) Fluorescence and excitation spectra for each of the Nafion films. The fluorescence spectra were obtained by excitation at 365 nm and the excitation spectra were monitored at the fluorescence maximum wavelength. (c) An attempt to write a letter by using acidic or basic water as ink (upper) and by wetting (lower).

Although the fluorescent color of the Nafion film after acidic treatment remained orange as long as it was wet, the fluorescence color gradually changed to light blue as drying progressed under ambient conditions (Fig. 3a, lower left inset photograph). The fluorescence spectrum had a maximum at 487 nm, and the excitation spectrum for this emission almost overlaps with that for the orange emission of the wet Nafion film (Fig. 3b). This suggests that the origin of both the orange and blue emissions is the same excited species, and thus the blue emission is a non-ESIPT E^* emission. Soaking the dried film in water restored the original orange color; orange/blue fluorescent color switching is reversible by alternating the wetting and drying processes. In contrast, the green fluorescence of the film after basic treatment remains unchanged even after it is dried. Therefore, with the orange fluorescent state of BTImP due to protonated cations, it is

likely to be affected by negatively charged sulfonic groups on the Nafion side chains, especially in the dry state, by which the ESIPT efficiency is lowered, rendering the blue E^* emission. In fact, it has been reported that the fluorescence properties of dyes encapsulated in the nanopores of a Nafion film are sensitive to the associated water content.[18] BTImP is thus demonstrated as a promising fluorophore for rewritable film with multicolor fluorescence switching properties.[19]

Excitation-energy dependent fluorescence

Fluorescence spectra were measured in the presence of anions (Cl^-, BF_4^-, ClO_4^-) to elucidate the influence of negatively charged species surrounding BTImP. The samples were prepared by the addition of each corresponding acid solution into a THF solution of BTImP.[20] As soon as was any of the acids added under UV irradiation at 365 nm, the green fluorescence changed to orange, which indicates the protonation of BTImP. However, $\lambda_{max,Fl}$ and the spectral shape are dependent on the type of anions present in the solution. For Cl^-, a single band with $\lambda_{max,Fl}$ at 583 nm was observed (Fig. 4a), whereas for BF_4^- and ClO_4^-, a dual band with $\lambda_{max,Fl}$ at 602 nm and a relatively weak second peak around 480 nm were confirmed (Fig. 4b and Fig. S5†, respectively). The band at 480 nm is similar to the band observed for the dry Nafion film in terms of position and shape (blue line in Fig. 3b), which suggests that it is due to the E^* emission. However, it should be noted that the origin of this peak is not the same as that of the ESIPT K^* emission at 602 nm, because the excitation spectral peak appears at 420 nm, which is different from that for the ESIPT band at 410 nm. A similar photoinduced product with absorbing absorption at 420 nm was identified in the presence of Cl^-, although without the E^* emission but instead the ESIPT K^* emission at 583 nm.

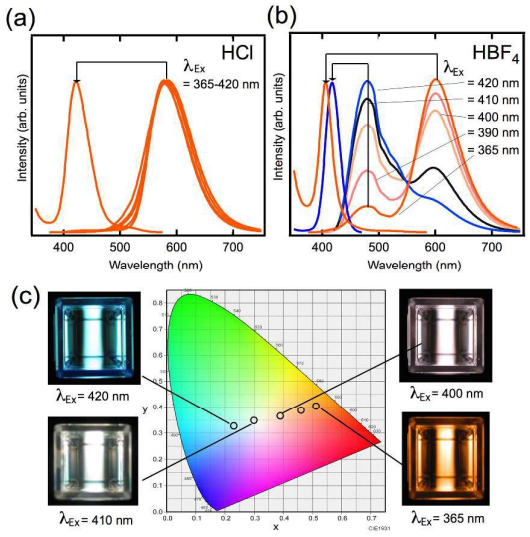

Fig. 4 Excitation wavelength dependent fluorescence of BTImP in (a) THF-HCl and (b) THF-HBF_4 solutions. Arrows indicate the excitation spectra for each of the fluorescence peaks. (c) CIE coordinates for the fluorescence spectra shown in (b), and photographs of the solution at their different excitation energies.

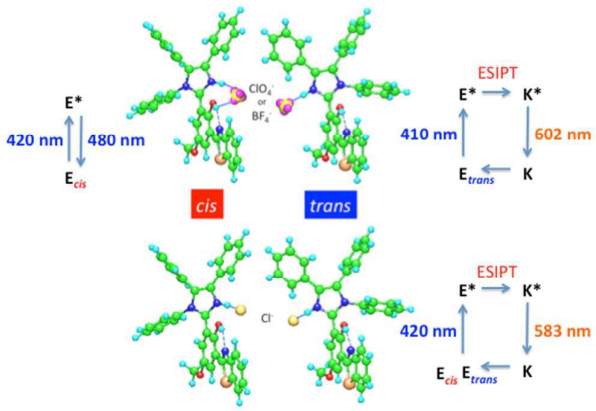

Fig. 5 Possible two rotamer structures of protonated BTImP (*cis* and *trans*) and their interaction modes with anions.

For an origin of such a photoproduct, a plausible explanation is presented by considering ion-pair formation between an anion and protonated Im, as observed in the X-ray results for the HCl salt of BTImP (Fig. 1b). With regard to the protonated BTImP, one can assume two rotamers arising from rotation about the bond between the Im ring and the central phenol (Fig. 5); one is a *cis* form where the N-H bond of Im and the O-H bond of the phenol are on the same side, and the other is a *trans* form where they are on the opposite side. In either rotamer, the binding of Cl^- to the Im moiety does not have an influence on the ESIPT process that occurs at the BT-side H-bond due to its relatively small ion size with an ionic radius (r) of 1.81 Å. However, the binding of a larger BF_4^- (r = 2.29 Å) or ClO_4^- (r = 2.40 Å) ion should make a difference in whether the dye is *cis* or *trans*. Namely, the binding to the *trans* form does not have an influence on the ESIPT process occurring at the BT-side H-bond, while the binding to the *cis* form disturbs it and results in the E^* emission at 480 nm. Within the dried Nafion film, sulfonic groups on the side chains might cause similar disturbance to protonated BTImP, giving rise to the 480 nm blue emission. Detailed titration experiments and theoretical support using DFT methods are the subjects of our ongoing work to verify the present model and will be reported in future.

The origin of the E^* and K^* dual emission in the presence of BF_4^- or ClO_4^- was assigned to different excited species, which makes it possible to modulate the fluorescence color by tuning the excitation wavelength (λ_{Ex}). Orange fluorescence at λ_{Ex} = 365 nm subsequently changes to blue by tuning λ_{Ex} in the range of 365–420 nm (Fig. 4c). At λ_{Ex} = 410 nm, white emission was observed; the spectrum gives the CIE coordinates (0.30, 0.35), which is the closest to that for pure white (0.33, 0.33).

Conclusions

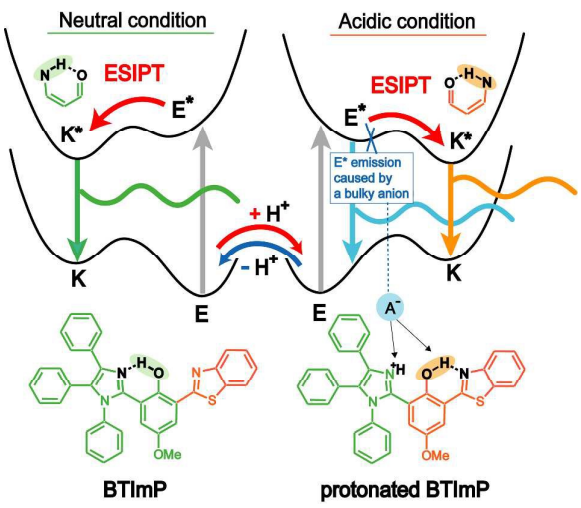

Fig. 6 Schematic diagram of the proposed mechanism for acid-induced fluorochromism in BTImP.

In summary, we have reported a novel ESIPT fluorophore of BTImP with switchable fluorescence color based on the switching of intramolecular H-bonding sites by external acid/base stimuli. Fig. 6 shows a schematic diagram of the mechanism for fluorochromism in BTImP. The green and orange fluorescence results from ESIPT emissions that occur at the Im- and BT-side H-bonds, respectively. Such fluorescence switching was maintained even when incorporated into Nafion films, and writing of a letter using acidic or basic water as an ink was demonstrated. Protonated BTImP is susceptible to influences from surrounding anionic species, such as the sulfonic groups within Nafion film and bulky BF_4^- and ClO_4^- ions in solution, thereby rendering blue E* emission due to the disturbance of ESIPT at the BT side. However, this can realize multicolor drawing on the Nafion film and single-component white emission in solution. These unique properties of BTImP open up new possibilities for applications such as rewritable data recording using water as ink, and multi-signal-responsive fluorescent probes that can emit a wide variety of colors including white.

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13 This speculation might be supported by the following results obtained under the same pH condition (pH 1.2): (1) The absorption spectrum in THF-HCl solution shows a weak rise in the region of 420 nm to 450 nm, although such a rise is not observed in AcOH (Fig. S2). (2) The excitation peak for orange emission appears at around 370 nm in AcOH, being almost in agreement with the absorption peak, while that in THF-HCl appears at 420 nm (Fig. 4a). Therefore, it is assumed that a Cl^- ion induces a twisting of the Im plane with respect to the other planes, giving rise to the band at 420 nm.
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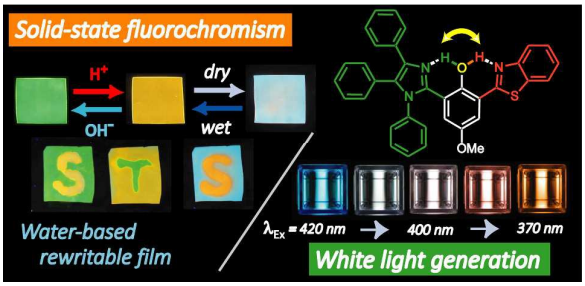
20 Orange fluorescence originated from protonated BTImP was observed by adding 0.1 ml of the acid solution (HCl 6 N, $HClO_4$ 9 N, HBF_4 6 N) to 3 ml of the THF solution of BTImP (1 mmol). The corresponding pH values are 0.7, 0.5 and 0.7, respectively. In each case, the molar ratio of H^+ to BTImP is almost equivalent.



Acid/base-switched solid-state fluorochromism and excitation-wavelength-dependent fluorescence color tuning have been demonstrated using an ESIPT fluorophore with a switchable intramolecular hydrogen bond.