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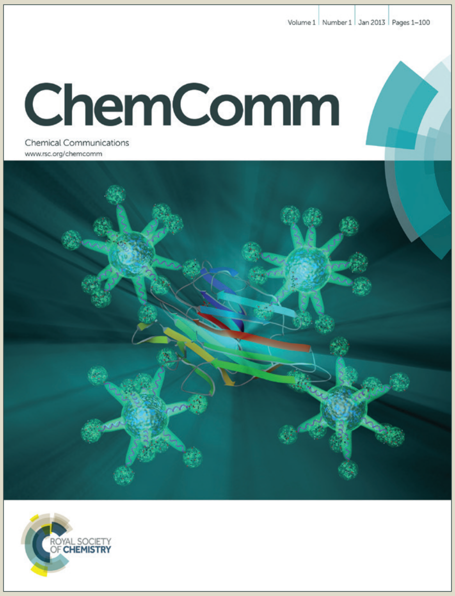

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COMMUNICATION

Mechanically inducible fluorescence clolour switching in formation of organic nanoparticles of an ESIPT molecule

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Electrostatic interaction between an ESIPT molecule 2-(5'-amino-2'-hydroxyphenyl)benzothiazole (AHBT) and a phenylborate derivative gives blue-green emission in acetic acid solution, but interestingly, vigorous (or mechanical) shaking of the solution leads to formation of organic AHBT nanoparticles, which results in fluorescence colour switching from blue-green to yellow-orange.

Excited-state intramolecular proton transfer (ESIPT) refers to phototautomerization in an excited state that occurs in heterocyclic molecules such as hydroxyphenylbenzothiazole (HBT) derivatives.[1] It is well-known that ESIPT molecules are normally more stable as enol forms in the ground state and more stable as keto forms in the excited state (Fig. 1). In the ESIPT process, irradiation of the dye molecule converts the enol to the excited-state keto species in a very fast time scale.[2] The resulting emission from the excited keto form exhibits an unusually large Stokes shift, and thus, ESIPT has attracted much attention due to applications in fluorescent molecular probes,[3] bioimaging,[4] and light-emitting materials,[5] as well as for photophysical studies.[1,2]

Meanwhile, fluorescent organic nanoparticles (FONs) are expected to play roles in a wide variety of applications such as organic light emitting diodes and biologics.[6] To obtain high quality FONs, their fluorescence should be much enhanced by, for example, "specific" intermolecular aggregation or intramolecular rotational restriction,[7] because many organic materials are emissive in their dilute solutions but become weakly luminescent when fabricated into solids. Hence luminescent behavior in the solid state is a major current topic.[8] So far, there have been some reports of solid-state ESIPT emission,[9] but the development of such systems remains a challenge because compounds exhibiting efficient solid-state ESIPT emission have been still limited to date.[10]

In this communication, fabrication of organic nanoparticles of an ESIPT chromophore 2-(5'-amino-2'-hydroxyphenyl)benzothiazole (AHBT, chemical structure is shown in Fig. 1) is reported. For preparing the organic nanoparticles, a new synthetic route based on ion-association which has advantages in simplicity and versatility, is applied.[11] This method utilizes the formation of water-insoluble ion-pair aggregates in aqueous phases by association of a chromophoric ion with a hydrophobic counterion to fabricate organic nanoarchitectures. In the course of exploring the synthesis of organic AHBT nanoparticles using the ion-association method, surprisingly, we found shaking-induced (that is, mechanically inducible) fluorescence colour switching from blue-green to yellow-orange. This finding provides a very rare example of high-contrast fluorescence switching that is driven by a change in the intermolecular interactions between the chromophore and its counterpart species, enabling a piezochromic response.

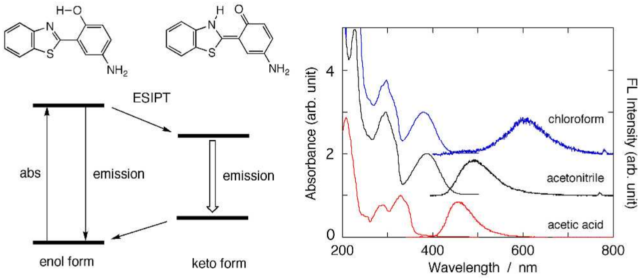

Fig. 1 (Left) Schematic representation of the ESIPT process of AHBT. (Right) Absorption and fluorescence spectra of AHBT in various solvents.

Before the nanoparticle synthesis, the amino group in AHBT should be first protonated to form ammonium cation by adjusting the pH of the solution using acetic acid ([CH_3COOH] = 10 mM; pH ~3.3: *Cf.* p*K*a of hydroxyaniline is ranged in 4.2–5.5 whereas that of benzothiazole counterpart is ~1.16).[12] Typically, rapid addition of acetic acid solution (1–2 mL) containing polyvinylpyrrolidone (PVP) and tetrakis(4-fluorophenyl)borate (TFPB) anions into the ultrasonicated acetic acid solution of 1–2 mL containing protonated AHBT cations (0.1 mM), at the molar ratio ρ (= [TFPB]/[AHBT]) changing from 1 to 4, produced almost clear transparent suspension. At this stage, almost no Tyndall scattering was observed, suggesting the absence of nanoparticle formation. However, vigorous shaking of the solution made the suspension pale yellow with characteristic Tyndall scattering, giving confirmatory evidence of nanoparticle formation. It should be noted that TFPB is indispensable because no change was detected in the absence of TFPB. Therefore, all measurements were carried out for samples (i) just after mixing the solution of protonated AHBT and TFPB (referred to as AHBT *composites*), and (ii) with 1-day storage after vigorous shaking for about 30 sec (referred to as AHBT *nanoparticles*). It is of note that the *composite* samples did not change their spectroscopic properties even after keeping still for 1 day.

The absorption and fluorescence spectra of molecularly dispered AHBT in various solvents are shown in Fig. 1. In chloroform and acetonitrile, the absorption typically has two bands at 295–300 and 380–390 nm, which are attributed to the pure benzothiazole moiety and the coupling between the benzothiazole and substituted phenyl ring, respectively.[2,13] In weak acetic acid solution (pH ~3.3), we found the band at longer wavelength region shifted to blue (~330 nm). It is known that the absorption band at longer wavelengths is strongly affected by the functional group in the substituted phenyl ring, in contrast with the small change in shorter wavelengths around 295–300 nm,[13] so the blue shift proves protonation of animo group in the substituted phenyl ring. On the other hand, in chloroform, fluorescence from the excited keto tautomer formed via ESIPT process was observed with a large Stokes shifts, whereas in polar and protic solvents (acetonitrile or acetic acid solution), normal (smaller) Stokes-shifted fluorescence bands were observed, which can be attributed to the enol form of AHBT.

Scanning transmission electron microscopy (STEM) images were obtained to determine the sizes of the AHBT *nanoparticles* (Fig. 2). Note that, for the AHBT *composites*, almost no nano-sized objects could be seen. From Fig. 2, the diameters of AHBT *nanoparticles* prepared at $\rho = 1$ and 4 are in the range of 45–80 nm and 25–45 nm, respectively. In addition, when $\rho = 1$, we could see relatively large nanoparticles with slight aggregation.

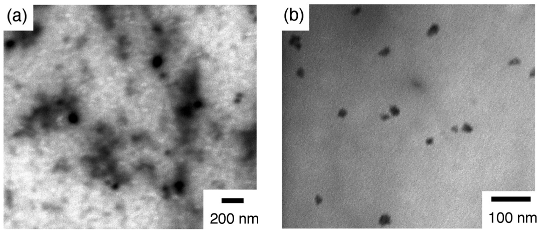

Fig. 2 (a) and (b) STEM images of the AHBT *nanoparticle* samples prepared at $\rho = 1$ and 4 (with vigorous shaking), respectively.

Figs. 3a and 3c show absorption spectra of AHBT *composites* and *nanoparticles*, respectively. Spectral profiles of the *composites* are very similar to that of AHBT in aqueous acetic acid solution (Fig. 1) at $\lambda \geq \sim 280$ nm. Note that peaks at 270–280 nm can be ascribed to pure (fresh) TFPB$^-$. However, the absorption spectra of AHBT *nanoparticles* are significantly different compared to those of the corresponding *composites*. In particular, the strong appearance of a tailing peak at 390–400 nm accompanied by a large decrease of band intensity at 330 nm is remarkable.

Difference in the fluorescence behaviors was much striking. Figs. 3b and 3d show fluorescence spectra of AHBT *composites* and *nanoparticles*, respectively. In the *composites*, spectra showed an enol emission at 450 nm together with an ESIPT (keto) emission at 490–500 nm with comparable intensity. Emergence of the keto emission suggests the presence of electrostatic interaction between the AHBT cations and TFPB anions, which could be confirmed by the excitation spectra (see ESI†). In this case, however, the interaction might be so weak that it did not grow to form nanosized objects. Intermolecular hydrogen bond between the OH group of protonated AHBT and water still prevents the ESIPT process.

In contrast, AHBT *nanoparticle* obtained by mechanical shaking at $\rho = 1$ exhibited strong enol emission along with relatively weak ESIPT (keto) emission, whereas that at $\rho = 4$ showed prominent ESIPT emission at longer wavelength together with a weak enol emission. We also present fluorescence pictures taken under 365 nm UV light irradiation (Figs. 3b and 3d). Importantly, fluorescence colour can be switched mechanically. It should be noted that the increase in the keto emission is associated with that in the absorption tail at 390–400 nm and the decrease in absorbance at 330 nm. According to Fig. 1, this behavior can be due to the formation of the deprotonated (or neutral) form of AHBT.[13] Excitation spectra monitored at the ESIPT emission also corroborate this mechanism (see ESI†). Moreover, absorption of *nanoparticles* for $\rho = 1$ can be approximately reproduced with a linear combination of three different spectra (spectra of molecularly dissolved AHBT in acetic acid, *nanoparticle* sample prepared at $\rho = 4$, and hydrolyzed (or modified) TFPB in acetic acid; see ESI†), strongly indicating that ρ dependence of absorption seen in Fig. 3c reflects a ρ dependence on the formation yield of AHBT *nanoparticles*. In any case, mechanical shaking can convert the AHBT-TFPB *composites* to *nanoparticles*, consisting of neutral AHBT and "modified" TFPB (see below). The mechanical shaking would help the proton of AHBT$^+$ attack to adjacent TFPB anion to form "modified" TFPB and subsequent nanoparticle formation. It is of importance to note here that thermal stimulation (or heating) has a similar effect to the mechanical shaking; in other words, mechanical shaking may act as local heating of the *composites* (see ESI†).

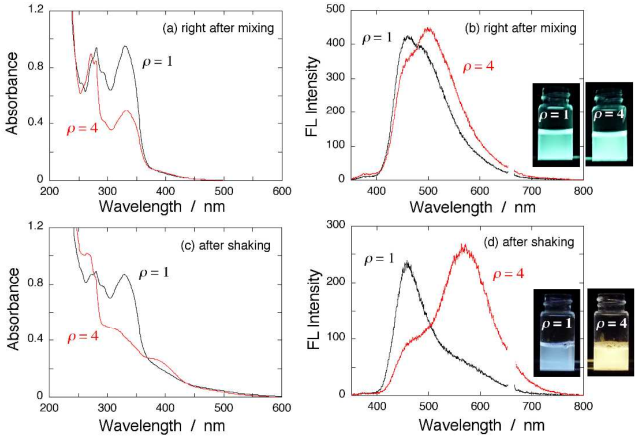

Fig. 3 (a) and (b) Absorption and fluorescence spectra of AHBT *composites* prepared at $\rho = 1$ and 4. (c) and (d) Absorption and fluorescence spectra of AHBT *nanoparticles* prepared at $\rho = 1$ and 4. The emission spectra were obtained upon excitation at 330 nm. Fluorescence images taken under 365 nm UV irradiation are also shown.

Acid-catalyzed hydrolysis of tetraphenylborate anion is a well-known phenomenon and proceeds via a sequential loss of phenyl groups from the original material through triphenylborane, diphenylborinic acid, and phenylboronic acid.[14] Triphenylborane is very susceptible to air oxidation and thus rapidly decompose.[15] In the present cae, therefore, the "modified" TFPB that can interact with neutral AHBT should be either bis(4-fluorophenyl)borinic acid ($B(PhF)_2(OH)$) or 4-fluorophenylboronic acid ($B(PhF)(OH)_2$). Note here that p*K*a of diphenylborinic acid or phenylboronic acid is 6.2 and 8.8, respectively.[16] Here, $B(PhF)(OH)_2$ is unlikely because no spectroscopic change has been observed when AHBT was mixed (under vigorous shaking) with commercially available $B(PhF)(OH)_2$ in acetic acid solution. Hence $B(PhF)_2(OH)$ is the most plausible form of "modified" TFPB as the acid-catalyzed product. To confirm this, IR spectral analysis was carried out. We prepared "modified" (hydrolyzed) TFPB species by vigorously shaking the acidified solution (pH ~3.3) containing fresh TFPB. After keeping the solution for ~1 day, evaporation and subsequent purification was conducted. The IR spectra of the "modified" TFPB, fresh (pure) TFBP, and their difference spectra are shown in the ESI†. As expected, we found a change in the IR absorption properties. We then compared the experimental IR with that of the calculated $B(PhF)_2(OH)$ (see also ESI†. We have used density functional theory (DFT) to calculate the possible low energy structures and their IR spectra). In $B(PhF)_2(OH)$, a satisfactory agreement could be obtained between the IR spectra of experiment and calculation. Further support based on mass spectrometry is also presented in the ESI†. Hence we can couclude that the AHBT *nanoparticles* are formed between neutral AHBT and $B(PhF)_2(OH)$.

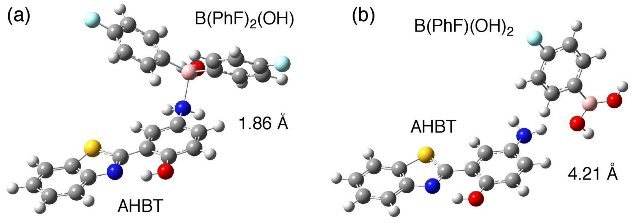

Fig. 4 Optimized geometries of (a) AHBT–$B(PhF)_2(OH)$ and (b) AHBT–$B(PhF)(OH)_2$ adducts calculated at the DFT/B3LYP level. The value (Å) in each figure indicates the B–N distance in each model.

The interaction between boron and nitrogen (Lewis acid-base interaction) has fascinated chemists for many years.[17] The B-N bond is isoelectronic with a carbon-carbon bond, but it is rather weak and has the strength of typical hydrogen bonds.[17] On the other hand, it is known that reaction of α-amino acid with diphenylborinic acid leads to the formation of a stable adduct at pH 2–5 in which B-N binding is involved.[18] Hence we propose that AHBT-based nanoparticle formation would result from B-N interactions, that is, interactions between the modified TFPB (borinic acid $B(PhF)(OH)_2$) and amino group in neutral AHBT. To understand the effect of B-N bonding, we calculated intermolecular geometrical models composed of AHBT and $B(PhF)_2(OH)$ or $B(PhF)(OH)_2$ based on DFT (Fig. 4). Solvent (Water) effect was also incorporated using the dielectric continuum model provided by the conductor polarizable continuum model (C-PCM). The calculations showed an optimized structure of AHBT–$B(PhF)_2(OH)$ adduct with B-N bonding (B-N length = 1.86 Å), but did not present that of AHBT–$B(PhF)(OH)_2$ adduct because the optimized B-N distance is too long (B-N distance = 4.21 Å). The result is in good agreement with our experimental data, suggesting that B-N bond formation and subsequent agglomeration of the adduct is responsible for the nanoparticle formation.[19] Hence shaking-induced fluorescence colour switching of AHBT dye from blue-green to yellow-orange can be due to (morphology) transformation from ion-pair adducts to Lewis acid/base-type nanoparticles. Importantly, this finding provides a rare example of stimuli-responsive organic nanoparticles with fluorescence switching.

Notes and references

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† Electronic Supplementary Information (ESI) available: [Excitation spectra of AHBT *composites* and *nanoparticles,* UV-vis absorption spectral simulation of AHBT *nanoparticles*, absorption and fluorescence spectra of AHBT *composites* evolved from the heating treatment (70 °C), IR and mass spectra of pure (fresh) and hydrolyzed TFPB (sodium salt) along with IR spectrum of the product (precipitate) composed of AHBT and hydrolyzed TFPB]. See DOI: 10.1039/b000000x/.

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isolated and purified the precipitate, and carried out the FT-IR measurements for identifying B-N bond formation. See the ESI†.