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# Reversible colour changes of binary films composed of azobenzene-based amorphous molecular materials and p-toluene sulfonic acid in response to exhaled breath

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## COMMUNICATION

# Reversible colour changes of binary films composed of azobenzene-based amorphous molecular materials and *p*-toluene sulfonic acid in response to exhaled breath

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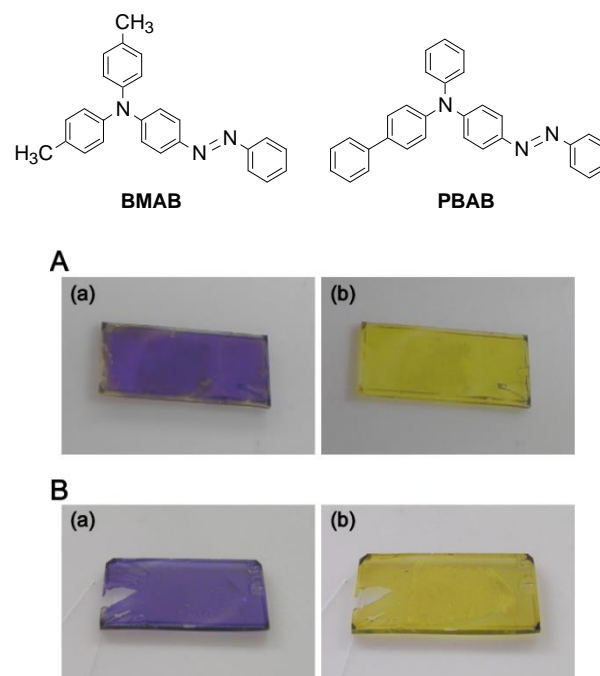
**Binary films composed of azobenzene-based amorphous molecular materials and *p*-toluene sulfonic acid were found to exhibit drastic colour change when we breathed onto their films. When pausing the breath, the colour returned to the original immediately. Moisture in the breath was suggested to play a role for such phenomena.**

In recent years, a variety of stimuli-responsive materials have been extensively studied from both viewpoints of fundamental materials science and practical applications to e.g. chemical sensors. Among a variety of organic materials, azobenzene family seems to be quite attractive since they provide not only colouring agents like food pigments but also a variety of stimuli-responsive materials such as pH-indicators,<sup>1</sup> photochromic and photo-responsive materials,<sup>2</sup> etc. Very recently, photomechanical effects observed for azobenzene-based materials have been attracting a great deal of attentions.<sup>3,4</sup> We have been performing studies of a variety of photomechanical effects using azobenzene-based amorphous molecular materials, namely low molecular-mass materials that readily form amorphous glasses.<sup>5</sup>

As well as our foregoing studies using single component system of azobenzene-based amorphous molecular materials, binary systems together with other low molecular-mass molecules are expected to provide novel functional organic films. We report here binary films composed of azobenzene-based amorphous molecular materials together with *p*-toluene sulfonic acid (TsOH) that exhibited drastic and reversible colour change when we breathed onto their films. The azobenzene-based amorphous molecular materials used here were 4-[bis(4-methylphenyl)amino]azobenzene (BMAB) and 4-[phenyl(biphenyl-4-yl)amino]azobenzene (PBAB), prepared by reported methods written in our previous papers.<sup>6</sup> TsOH could be purchased commercially as the monohydrate (TsOH·H<sub>2</sub>O).

Binary films of BMAB–TsOH and PBAB–TsOH were prepared onto glass substrates by spin-coating method from 1,2-dichloroethane solutions of the mixture of corresponding amorphous molecular

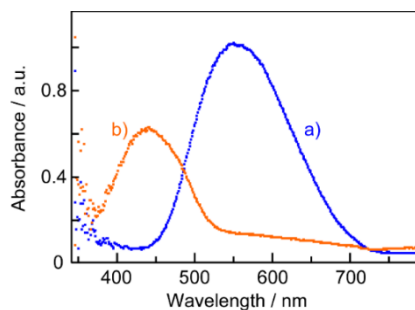
materials and TsOH·H<sub>2</sub>O with a molar ratio of ca. 1:2. As-prepared films were brilliant bluish purple in colour. When we breathed onto these films, their colours were found to change drastically to yellow as shown in Fig. 1. When pausing the breath, the colour returned to original bluish purple immediately. The reversible colour change of the BMAB–TsOH film is also shown in Supplementary Video 1.<sup>†</sup>



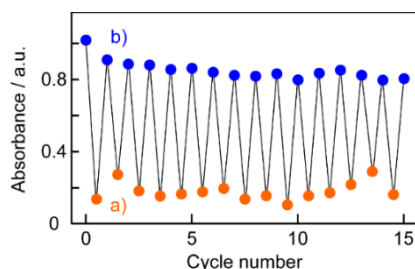
**Fig. 1** Photographs of (A) BMAB–TsOH and (B) PBAB–TsOH films. (a) at ambient atmosphere. (b) when breathing onto their films.

These behaviours could be detected spectroscopically by using BLUE-Wave miniature spectrometers (StellarNet, Inc.). A large absorption bands around 545 nm were observed for both as-prepared

films of BMAB-TsOH and PBAB-TsOH. When we breathed onto these films, the spectra changed immediately, that is, the band around 545 nm almost disappeared and a new band around 440 nm appeared as shown in Fig. 2 and Fig. S1(A)<sup>†</sup> for BMAB-TsOH and PBAB-TsOH films, respectively. When pausing the breath, the spectra immediately recovered to their originals. On the other hand, such colour change could not be observed for BMAB without TsOH as shown in Fig. S1(B)<sup>†</sup>. Absorbance of the BMAB-TsOH film around 545 nm was found to change repeatedly upon on-off cycles of the breath as shown in Fig. 3. Although these films seemed to be somewhat deteriorated, these colour changes were clearly visible after more than 100 cycles.



**Fig. 2** Electronic absorption spectral changes of BMAB-TsOH film. (a) at ambient atmosphere. (b) when breathing onto the film.



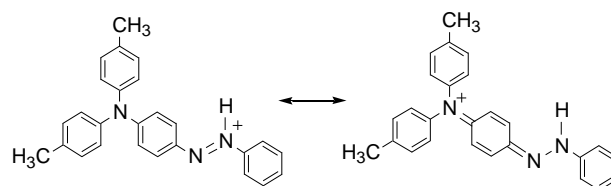
**Fig. 3** Change in absorbance of a BMAB-TsOH film at 545 nm upon on-off cycles of the breath. (a) when breathing onto the film. (b) when pausing the breath.

When their films were in the stream of dry and hot air by means of a hair dryer, no colour changes of these films could be observed. Colour change could neither be observed when the films were exposed to hexane vapour. On the other hand, these films turned yellow in colour when they were exposed to water vapour as shown in Supplementary Video 2.<sup>†</sup> These results suggested that moisture played a role for present phenomena of reversible colour changes of BMAB-TsOH and PBAB-TsOH films. Preliminary results showed that the electronic absorption spectrum of the film depended upon the humidity in the humidity range between ca. 40% and ca. 70% as shown in Fig. S2(A),<sup>†</sup> the colour of the film changing gradually from bluish purple to yellow with the increasing in the humidity in this range. The spectrum of the film at relatively low humidity was depending upon the molar ratio of BMAB and TsOH as shown in Fig. S2(B).<sup>†</sup> The film of BMAB-TsOH with a molar ratio of 1:2 exhibit more brilliant bluish purple in colour than the films with molar ratios of ca. 1:0.5 and ca. 1:1.

Recently, reflection colour changes of the humidity-sensitive photonic crystal and cholesteric liquid crystal films have been investigated.<sup>7</sup> It was suggested that the colour changes of these

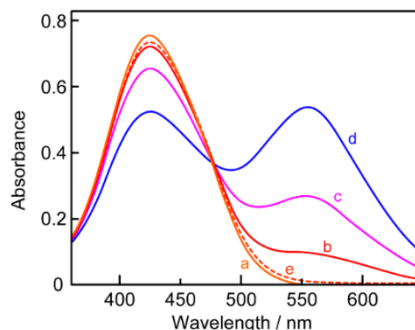
materials were due to variation in their photonic band gaps caused by changing in content of moisture in their films. Relative to these films, binary films in the present study seemed to be superior in terms of ready fabrication using easy-to-use low molecular-mass compounds. The film can be obtained readily by just spin-coating of their mixed solution onto a substrate. It is also expected that the film can be fabricated onto a variety of substrate by just brush coating of the solution of the mixture like painting a picture. As far as we know, the present study provided the first examples of binary films based on low molecular-mass organic compounds that exhibit such drastic colour changes in response to moisture.

In order to gain further information about the phenomena of reversible colour changes of their films, electronic absorption spectra in acetonitrile solutions were investigated by means of Hitachi U-3500 spectrophotometer. The solution of BMAB without TsOH showed an absorption band around 430 nm (Fig. 4a). When TsOH-H<sub>2</sub>O was added to the solution, the band around 430 nm was reduced and a new absorption band around 550 nm increased with the increase in concentration of TsOH with an isosbestic point at 477 nm (Fig. 4b-d). When a few drops of water were added into the resulting solution in the sample cell, the spectrum almost recovered to the original (Fig. 4e). The absorption band around 550 nm was attributable to protonated BMAB (BMAB-H<sup>+</sup>), whose chemical structure is shown in Scheme 1) since the electronic absorption spectrum of BMAB-H<sup>+</sup> predicted by ab initio calculation based on density-function theory at B3LYP/6-31G(d,p) level performed with the Gaussian 09<sup>8</sup> showed a large absorption band around 550 nm (Fig. S3)<sup>†</sup>. Since resonance structures of BMAB-H<sup>+</sup> can be drawn as shown in Scheme 1, considerable red-shift of the electronic absorption spectrum by protonation may be caused by extension of the conjugation as well as change in electronic structure by protonation. Therefore, two equilibria were suggested to exist in the BMAB-TsOH-H<sub>2</sub>O system as indicated in Eqs. 1 and 2. When the concentration of TsOH was increased in the BMAB solution, the concentration of BMAB-H<sup>+</sup> increased and the solution turned to bluish purple in colour according to forward reaction of Eq. 1. When the water was added into the bluish purple solution, forward reaction of Eq. 2 proceeded and the concentration of BMAB-H<sup>+</sup> decreased, resulting in the recovery of the colour to the original yellow. Formation of BMAB-H<sup>+</sup> by addition of the TsOH and the following deformation by addition of the water were also suggested by <sup>1</sup>H NMR (Fig. S4).<sup>†</sup> When an excess amount of TsOH was added into the CD<sub>3</sub>CN solution of BMAB, NMR signals attributable to aromatic protons of BMAB were found to shift and a new broad signal appeared around 4.82 ppm attributable to proton attached to nitrogen of BMAB. When D<sub>2</sub>O was added into the resulting sample, signals for aromatic protons almost recovered to original positions and the signal for N-H proton disappeared accompanied with appearance of new sharp signal attributable to proton of H<sub>3</sub>O<sup>+</sup> at 3.23 ppm.

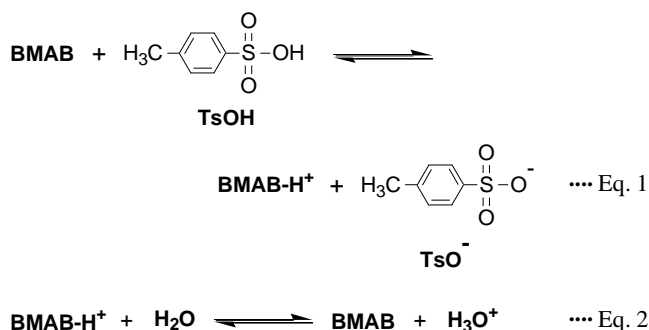


**Scheme 1** Resonance structures of BMAB-H<sup>+</sup>

Thus, present phenomena of reversible colour change of BMAB–TsOH and PBAB–TsOH films shown in Fig. 1 could be understood as follows. Due to considerably high concentrations of azobenzenes and TsOH, a large amount of protonated azobenzene existed in the film caused by forward reaction of Eq. 1, being bluish purple in colour. When we breathed onto their films, moisture in the exhaled breath was absorbed into their films and the colour turned to yellow according to forward reaction of Eq. 2. When pausing the breath, H<sub>2</sub>O evaporated immediately from their films, resulting in the recovery of the colour to original bluish purple according to the backward reaction of Eq. 2.



**Fig. 4** Electronic absorption spectra of acetonitrile solutions of BMAB ( $3.0 \times 10^{-5} \text{ mol dm}^{-3}$ ) and TsOH·H<sub>2</sub>O with a variety of concentration. [TsOH]/[BMAB] = (a) 0, (b) 1, (c) 3, (d,e) 7. (e) after addition of a few drops of water.



In summary, we have found that binary films composed of azobenzene-based amorphous molecular materials and TsOH exhibited reversible colour change when we breathed onto their films. They are applicable to e.g. simple humidity sensors which can be fabricated on a variety of substrates and paints for amusing arts whose colour changes by changing the surrounding humidity. The present study suggested that the mixture of azobenzene analogues whose electronic structures are altered together with conjugation of the molecule by protonation and organic acid with appropriate acidity may exhibit such behaviours of reversible colour change. The properties of the film were suggested to depend upon the kind of materials, ratio of the mixture, temperature, film thickness, etc. Further detailed studies are in progress.

## Notes and references

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† Electronic Supplementary Information (ESI) available: [Figs. S1–S4 and Videos 1–2 together with their legends]. See DOI: 10.1039/c000000x/

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