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Mechano-fluorochromic behavior of AEE polyurethane films and their high sensitivity to halogen acid gas†

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Three polyurethanes with different contents of tetraaryl-but-1,3-diene derivatives in the soft segment (STMPU-25/STMPU-50/STMPU-75) have been synthesized and found to present aggregation-enhanced emission features. The fluorescence intensity of polymer films was greatly enhanced with increasing tensile stress. Also, polyurethanes with higher aggregation-induced emission fluorogen content had stronger mechano-fluorochromic behavior in the same tension state. Moreover, the resulting polyurethane films possessed high sensitivity for halogen acid gas, suggesting their potential applications in environmental monitoring fields.

In contrast to traditional fluorescent compounds with the property of aggregation-caused quenching (ACQ), aggregation-induced emission (AIE) or aggregation-enhanced emission (AEE) molecules show strong emission in aggregation states, and do not emit fluorescence in solution.^{1–3} These AIE small molecules have been found in many luminescence systems such as silole,¹ tetraphenylethene,^{4,5} styrylbenzene⁶ and their derivatives.⁷

Interestingly, many AIE compounds have been proved to be piezo- or mechano-fluorochromic materials.⁸ In 2008, Tang *et al.* found that the photoluminescence of hexaphenylsilole was enhanced by pressure in the solid state.⁹ In 2010, Park *et al.* reported a cyano-substituted distyryl benzene derivative, which showed reversible multi-stimuli luminescence switching.¹⁰ At the same time, Chi *et al.* firstly put forward the concept of piezofluorochromic aggregation-induced emission (PAIE) materials. They synthesized several PAIE materials and proposed that AIE compounds containing a twisted conformation would exhibit piezofluorochromic activity.¹¹ Till now, numerous reported AIE compounds, such as typical triphenylethylene,¹² tetraphenylethylene (TPE),^{13–17} silole,¹⁸ cyano-distyrylbenzene,^{19–21} 9,10-distyrylanthracene and their derivatives^{22–31} were found to possess PAIE feature.

However, AIE/AEE polymers possessing mechano-fluorochromic feature were rarely studied.^{32–34} Kokado *et al.* found that the AIE elastomer based on PDMS and TPE exhibited stimuli-sensitive fluorescence against organic solvents and temperature.³⁵ Tang *et al.* reported a TPE-containing memory

chromic polyurethane, which showed that the emission intensity of resulting polyurethane gave negative correlation with shape fixity, temperature, and existence of solvent.³⁶ In our previous work, an AEE polyurethane containing 4,4'-((1Z,3Z)-1,4-diphenylbuta-1,3-diene-1,4-diyl) dibenzaldehyde (TABDAA2) was prepared and it was found that the fluorescence of polyurethane films was enhanced in the tension state.^{37,38} So far, the effect of tension on the fluorescent intensity of polymer films was poorly understood.

Meanwhile, the detection of halide is important for monitoring excessive halide levels in the environment (*i.e.* pollution in air and water). There are many ways to determine the concentration of the halide in the solutions, such as amperometry and chemistry titration,^{39–42} but few researches are about detecting the presence of halide gas in air.

Considering that the content of AIE molecules TABDAA2 might affect the fluorescence behavior of polyurethane films, three polyurethanes with different mass fraction (0.25%, 0.5% and 0.75%) of TABDAA2 in the soft segments (STMPU-25/STMPU-50/STMPU-75) have been synthesized in this work. And their mechano-fluorochromic behavior were investigated. Meanwhile, the polyurethane film was sensitive to halogen acid gas like hydrogen iodide (HI), proving that it could be good solid probe to halogen acid gas.

All the materials, instruments and synthesis procedure for STMPUs polyurethanes with modified reactant molar ratios have been shown in the previous articles and the ESI.[†]^{37,38} In brief, the mixture of TABDAA2 (0.25%, 0.5% and 0.75% mass fraction) and poly(tetrahydrofuran) ($M_n = 1000$, PTMG1000) was used as soft segments, and reacted with 4,4-diphenylmethane diisocyanate (MDI) and 1,4-butanediol (BDO) in the molar ratio of 1 : 2 : 1 to give the product polyurethanes STMPUs (STMPU-25/STMPU-50/STMPU-75). The reaction molar

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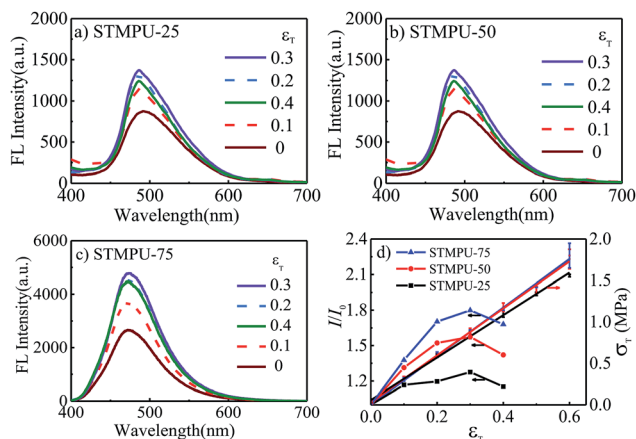


Fig. 2 Fluorescence emission spectra of (a) STMPU-25, (b) STMPU-50 and (c) STMPU-75 films at different tensile strains; (d) true stress-strain curves and fluorescence peak intensity-true strain curves of three AEE polyurethanes.

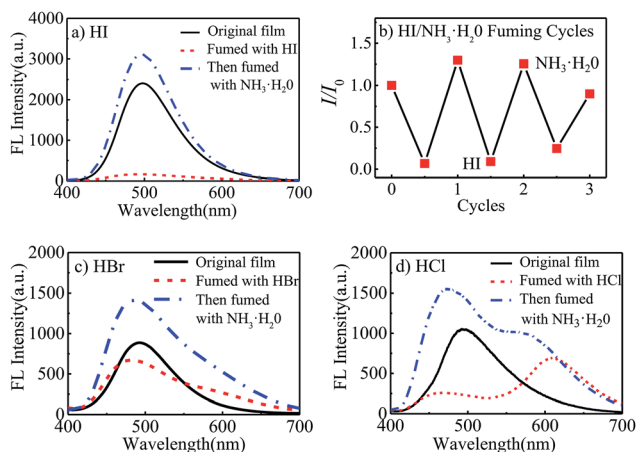


Fig. 3 (a) Fluorescence emission spectra of STMPU-50 film before and after fumed with hydroiodic acid and then fumed with $\text{NH}_3 \cdot \text{H}_2\text{O}$; (b) the quenching and recovery test by HI- $\text{NH}_3 \cdot \text{H}_2\text{O}$ fuming cycles; fluorescence emission spectra of STMPU-50 film before and after fumed with (c) hydrobromic acid and (d) hydrochloric acid, and then fumed with $\text{NH}_3 \cdot \text{H}_2\text{O}$.

enhanced, but the new emission peak in 610 nm became shoulder peak. Therefore, it could be assumed that the polyurethane film had different and obvious response to hydrogen iodide and hydrochloric acid.

Simultaneously, this phenomenon could be observed visually in Fig. 4(a) and (b). The STMPU-50 film was deep yellow after smoked with hydroiodic acid, then turned to pale yellow when fumed with $\text{NH}_3 \cdot \text{H}_2\text{O}$. Under 365 nm ultraviolet lamp, the original film exhibited blue fluorescence, then got dim greenish blue after fumigated with hydroiodic acid. The fluorescence of film became bright blue when fumigated with $\text{NH}_3 \cdot \text{H}_2\text{O}$. In contrast, the film was painted reddish brown after smoked with hydrochloric acid, and then turned to pale yellow when fumed with $\text{NH}_3 \cdot \text{H}_2\text{O}$. Under 365 nm ultraviolet lamp, the original film exhibited blue fluorescence, and yellow after smoked with

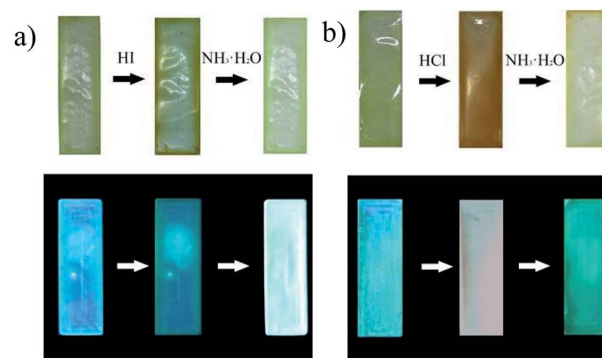


Fig. 4 (a) Color changes of the STMPU-50 film before and after fumigated with hydroiodic acid and then smoked with $\text{NH}_3 \cdot \text{H}_2\text{O}$ under normal light (top) and fluorescent changes upon irradiation by 365 nm ultraviolet lamp (bottom); (b) color changes of the STMPU-50 film before and after fumigated with hydrochloric acid and then fumed with $\text{NH}_3 \cdot \text{H}_2\text{O}$ under normal light (top) and fluorescence changes upon irradiation by 365 nm ultraviolet lamp (bottom).

hydrochloric acid. The fluorescence of film became green when fumigated with $\text{NH}_3 \cdot \text{H}_2\text{O}$.

According to the fluorescent color and brightness changes of the STMPU-50 film, the proposed sensing mechanism was illustrated in Fig. 5. Most of the Schiff base moiety of STMPU-50 with Cl^- formed a highly rigid fluorophore so that the conjugation extent of the molecular chain was enlarged, leading to a red shift peak at 610 nm. And for HBr, part of TABDAA2 molecules could form a rigid ring with the Schiff base moiety so that the new peak in 610 nm was weak as a shoulder peak. However, I^- ion was too large to insert into the space between $\text{C}=\text{N}$ and the benzene ring of the TABD. ^{46,47} Thus, I^- ion reacted with TABD fluorogen by electrostatic interactions and offered more diffusion channels for the excitons to migrate, allowing them to be more quickly annihilated by the hydrogen iodide. ⁴⁸ Next, when these films were fumed with ammonia gas, halogen ion could react with NH_4^+ due to the acid-base neutralization. Thus, the emission peak at around 470 nm was enhanced again.

In summary, three aggregation-enhanced emission polyurethanes with 0.25%, 0.5% and 0.75% of tetraaryl-but-1,3-diene derivatives in the soft segments, that is, STMPU-25/STMPU-50/STMPU-75, have been synthesized. The

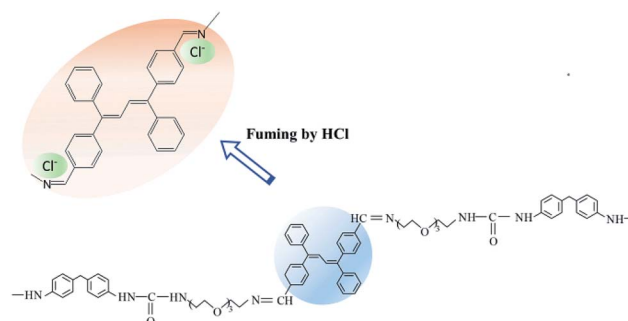


Fig. 5 The proposed sensing mechanism of the STMPU-50 for the detection of HCl gas.



fluorescence intensity of the polymer films was greatly increased with the increase of tensile stress. Also, polyurethanes with higher content of AIE fluorogen presented better positive correlation between fluorescent intensity and tensile strain when $\varepsilon_T \leq 0.3$. Moreover, the resulting polyurethane films had high sensitivity for halogen acid gas, suggesting their potential applications in environment monitoring fields.

Conflicts of interest

There are no conflicts to declare.

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