Arylaminomaleimides as a New Class of Aggregation-induced Emission-active Molecules Obtained from Organoarsenic Compounds

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Heating 1,4-dihydro-1,4-diarsininetetracarboxylic acid dianhydride with excess amounts of aniline and toluidine provided 3-anilino-*N*-phenylmaleimide and 3-*p*-toluidino-*N*-*p*-tolylmaleimide, respectively, which showed aggregation-induced emission (AIE) properties. Not only are the present aminomaleimide derivatives simple-structured AIE-active molecules, but they also exhibit pH responsive properties without introducing additional functional units.

Recently, luminophores displaying aggregation-induced emission (AIE) have attracted attention as promising materials for optical and electronic devices,¹ because high loading of dves in a matrix can be achieved without self-quenching to increase light-emitting efficiency.² After Tang and co-workers developed a series of propeller-shaped molecules that are nonemissive in solution and are induced to emit efficiently in the solid state,^{2a} several examples of AIE-active dyes have been reported. Researchers have realized that restricted intramolecular vibrational and rotational motions in the solid state are responsible for AIE phenomena, and their occurrence in sterically crowded molecules has been presented. In solution, intramolecular rotation is active and serves as a relaxation channel for decay of the excited state. The extremely large fluorescence enhancement in the solid state is attributed not only to the spatial confinement effect, but also to the formation of specific supramolecular stacking architecture associated with the unique electronic and geometric characteristics of the designed molecules.

Maleimide is an electron-deficient heterocyclic ring that is similar to phthalimide, naphthalimide, and peryleneimide derivatives, which are known to be n-type semiconducting materials for organic transistors. A series of maleimide-based fluorophores exhibit a large variation of emission spectra spanning the entire visible range.³ Emission intensity of these dyes, however, decreases with increasing solution concentration. Only some limited maleimide-based dyes show solid-state luminescence.^{3b} However, no AIE-type maleimide-based molecules have been reported until now. Here, we found that the aminomaleimide derivatives show AIE properties as well as essential pH responsive properties. No luminescence properties have been reported for the aminomaleimide derivatives, since they were regarded as having fungistatic, herbicidal, insecticidal, and antitumor activity.⁴

We also found that the aminomaleimide derivatives were unexpectedly obtained by heating a 2,3-bisarsenic-substituted maleic anhydride derivative, i.e., 1,4-dihydro-1,4-diarsininetetracarboxylic acid dianhydride (1), with excess amounts of arylamines. Some aminomaleimide derivatives can be synthesized by the reactions of acetylenedicarboxylic acid methyl esters with excess amounts of amines at relatively high temperature in comparison with our present reaction.⁴ The chemistry of organoarsines has been developed and their use in organic synthesis arouses much interest.⁵ For example, arsonium ylides prepared from triphenylarsine and other organoarsines are stronger nucleophiles than the corresponding phosphonium ylides.⁶ A transition-metal-catalyzed aryl-aryl exchange reaction between metal-bound aryl and arsenic-bound aryl compounds is an attractive strategy for the synthesis of organoarsenic compounds.⁷ However, the number of reports disclosing the use of organoarsines in organic synthesis has been rather limited until now. This is because most organoarsenic compounds are prepared from arsenic chlorides or arsenic hydrides and require extreme caution in handling because of their volatility and toxicity. We have developed the facile synthesis of a series of 1,4-dihydro-1,4-diarsinine derivatives as cyclic organoarsenic compounds starting from methylarsonic acid, a nonvolatile organoarsenic compound.8

The reaction of 1,4-dihydro-1,4-diarsininetetracarboxylic acid dianhydride (1)^{8c} with aniline or toluidine at moderate temperature produced the corresponding 1,4-dihydro-1,4-diarsininetetracarboxylic acid diimides 2. However, 3-anilino-*N*-phenylmaleimide (3a) and 3-*p*-toluidino-*N*-*p*-tolylmaleimide (3b) were obtained by heating 1 with an excess amount of aniline at 130 °C for 7 h and toluidine at 150 °C for 9.5 h, respectively (Scheme 1, Path A). After the excess amines were removed under reduced pressure, the residues were recrystallized to give yellow crystalline products, 3a and 3b in 39 and 42% yield, respectively. Formation of the maleimde structures was confirmed by ¹H and ¹³C NMR spectra, and elemental analysis (Figures S1 and S2).¹⁴ Both structures were further confirmed by X-ray crystallography (Figure S3).^{9,14}

Aminomaleimide derivative **3a** also formed in 30% yield by heating N,N'-diphenyl-1,4-dihydro-1,4-diarsininetetracarboxylic acid diimide (**2a**) with excess amounts of aniline. This result suggests that the reaction of **1** with excess amounts of amines occurred via formation of **2**. This reaction pathway is supported by the fact that 3-*p*-toluidino-*N*-phenylmaleimide (**3c**) can be



Scheme 1. Synthesis of arylaminomaleimides.

1446



Figure 1. Normalized emission (black; $\lambda_{ex} = 400 \text{ nm}$, red; $\lambda_{ex} = 400 \text{ nm}$) and excitation spectra (black; $\lambda_{em} = 505 \text{ nm}$, red; $\lambda_{em} = 521 \text{ nm}$) of **3a** (black) and **3b** (red) in the solid state at room temperature.

obtained by the reaction of **2** and toluidine in 39% yield (Scheme 1, Path B). The reaction of Path B is regarded as hydroamination at the 2,3-position of the maleimide unit in 2^{10} . Although the mechanism of the present reaction is unknown, it is possible that the As–C bond, which is weaker than the N–C bond, triggers the exchang of As–C=C for N–C=C, allowing the hydroamination to proceed.¹¹

Both 3a and 3b were recrystallized from methanol to give yellow crystals. The crystalline solids of 3a and 3b exhibited very intense green ($\lambda_{max} = 505 \text{ nm}$) and yellow ($\lambda_{max} = 521 \text{ nm}$) luminescence at room temperature (Figure 1). However, no emission was observed for solutions in solvents such as CHCl₃ and THF. The solid-state structures of 3a and 3b were determined by X-ray crystallography (Figure S3).¹⁴ The crystal structure of **3b** was previously reported^{4f} and our crystal data are in agreement with the reported data. In 3a, the three rings are planar with the C(1) aryl ring twisted 44.3° from the N(1) maleimide ring, while the C(11) aryl ring is twisted 19.3° from the heterocyclic ring. In 3b, the three rings are planar with the C(1) aryl ring twisted 42.6° from the N(1) maleimide ring, while the C(12) aryl ring is twisted 12.7° from the heterocyclic ring. Because of the steric hindrance between the C(1) aryl ring and the N(1) maleimide ring, the planar conformation of the aminomaleimide moiety prevents them from suffering emission quenching due to $\pi - \pi$ stacking in the solid state. The emission maximum wavelength for 3b is red-shifted relative to that for 3a, because of its more planar structure. The torsion angle between the maleimide ring and the C(12) aryl ring for **3a** is larger than between the maleimide ring and C(11) ring for **3b**.

To better understand the photophysical properties of the present aminomaleimide derivatives, the HOMO and LUMO of **3a** and **3b** were calculated by using the B3LYP/6-31G(d) method. The optimized geometries¹² of **3a** and **3b** suggested that the conformations of the aminomaleimides are planar and the HOMOs of both molecules have significant orbital density at the same moieties, impying that π -conjugation is extended to the maleimide rings and the arylamine substituents (Figure S4).¹⁴ In contrast, the LUMOs of both molecules are dominated by orbitals from the maleimide rings. These electron distributions reveal intramolecular charge transfer in the aminomaleimide moieties of **3a** and **3b**.



Figure 2. Emission spectra of 0.8 mM **3a** in water/THF under 335 nm irradiation.

The emission properties of **3a** were studied in solutions of THF and water with different water/THF ratios, as **3a** is highly soluble in THF, but not in water. Although the emission spectrum of **3a** in a solution that was 56 vol % water was practically a flat line parallel to the abscissa (Figure 2), emission was observed when the solution was 58 vol % water. The emission was enhanced when the solutions were 58 to 66 vol % water and these solutions emitted green light of 493 nm. This result clearly indicates that **3a** is AIE active. The emission maximum wavelength in solution ($\lambda_{max} = 493 \text{ nm}$) is slightly blue-shifted relative to that in the crystalline state.

Arylaminomaleimide **3a** (2.6 mg, 0.98 mmol) was dissolved in toluene (2.6 mg) and the toluene solution was added to ethylene–vinyl acetate copolymer (EVA, 10 mg) to obtain a coating solution. The coating solution was cast on a Si substrate, heated at 70 °C, and baked at 130 °C for 20 min to form a paleyellowish, self-standing transparent film. Although the coating solution showed no luminescence, the film exhibited very intense green luminescence at 497 nm (Figure S6).¹⁴ The maximum luminescence wavelengths of the crystals, film, and aggregate were 505, 497, and 493 nm, respectively. The lower energy excitation maximum of the film was observed at 445 nm, which was blue-shifted from that of the crystalline compound at 460 nm (Figure S7).¹⁴ The planarity of the C(12) aryl ring relative to the maleimide ring might governed the HOMO– LUMO band gap energy.

The present aminomaleimides contain secondary amino moiety. The luminescence is expected to be turned "on" at high pH and "off" at low pH, because of ionization and deionizaion under acidic and basic conditions, respectively. When an aqueous 35% HCl solution (0.1 mL) was added to the emissive 66 vol % water/THF solution of **3a**, the emission immediately decreased and the solution was nonemissive within 30 min (Figures S8 and S9).¹⁴ In the aqueous medium with low pH, **3a** was converted to the salt form which is soluble in water, and hence, nonemissive and transparent. No emission was observed for the solid sample obtained after treatment with HCl. Thus, the aminomaleimide derivatives are not only simple-structured AIE molecules, but they also exhibit pH responsive properties without introducing additional functional units.¹³

In summary, we found that the arylaminomaleimide derivatives were obtained by hydroamination of 2,3-bisarsenicsubstituted maleic anhydride derivatives, i.e., 1,4-dihydro-1,4diarsininetetracarboxylic acid dianhydride (1), with arylamines. While they are practically nonluminescent when dissolved in solution, they are induced to emit intensely upon aggregate formation, clearly showing their AIE properties. They also exhibited pH responsive properties without introducing additional functional units. The present AIE-active maleimide-based fluorophores should be good candidates for spectral conversion films for solar cells and agricultural uses, since high loading of the dyes can be achieved to increase efficiency. Although the mechanism of the present reaction is unknown at the moment, the As-C bond, which is weaker than the N-C bond, possibly triggers the exchange of As-C=C for N-C=C, allowing hydroamination to proceed. Detailed studies of the reaction mechanism and synthesis of aminomaleimide derivatives with different structures are underway to gain an understanding of the chemistry of the present organoarsenic compounds. We expect that our work will stimulate the field of organoarsenic chemistry.

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