



Facile construction of *N*-alkyl arylaminomaleimide derivatives as intensively emissive aggregation induced emission dyes



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ABSTRACT

Dimethyl acetylenedicarboxylate and one equivalent of aryl amines lead to dimethyl arylaminofumarates, and subsequent addition of alkyl amines readily gave arylaminomaleimide derivatives. Unsymmetrical structures were easily constructed without troublesome purification process. The obtained compounds showed aggregation induced emission (AIE) properties. The luminescence maximum wavelength at the obtained arylaminomaleimide derivatives in solid state were observed from 492 nm to 535 nm, and the quantum yields were up to 0.51. They also exhibited intense luminescence in a polymer matrix.

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1. Introduction

The solid state emission property of fluorescent molecules is, needless to say, of great importance in the viewpoint of application such as organic light emitting diodes (OLEDs),¹ semiconductor lasers,² and fluorescence sensors.³ To attain the solid state emission, aggregation induced emission (AIE) is one of the most effective strategy, where self-quenching can be avoided.⁴ In 2001, Tang and co-workers investigated emission behavior of 1-methyl-1,2,3,4,5-pentaphenylsilole, and advocated AIE phenomenon.^{4a} While the fluorescence is quenched by rotation of the phenyl groups and twist of the C=C bond in a good solvent, the emission can be observed in the situation where its molecular motion is regulated.⁵ After this report, various kinds of AIE dyes have been reported,⁶ and utilized as chemosensors, bioprobes, light-emitting materials, and so on.⁷ Almost all such molecules, on the other hand, need complicating synthetic routes from commercially available compounds.⁸ Their simple preparation method is still highly thirsted in not only academic research but industry.

Recently, we discovered *N*-aryl arylaminomaleimide derivatives such as 3-anilino-*N*-phenylmaleimide and 3-*p*-toluidino-*N*-*p*-tolylmaleimide showing AIE activity.⁹ Free rotation of the phenyl groups on the secondary amine probably shorten the conjugation length in solution, and meanwhile X-ray

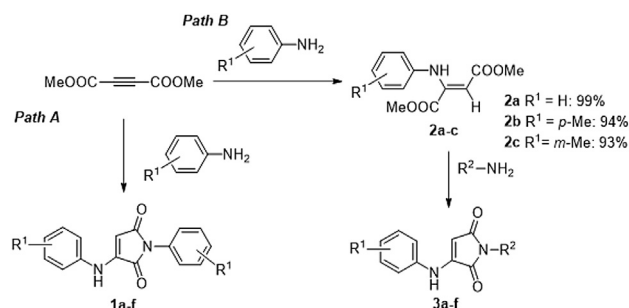
crystallography revealed that planar conformation was adopted in solid state. They were, however, synthesized from 1,4-dihydro-1,4-diarsininetetracarboxylic acid dianhydride,¹⁰ and a more practical synthetic route has been required. Indeed, several synthetic routes for arylaminomaleimide derivatives had been already developed in the field of organic synthesis.^{11,12} It is well known that dimethyl anilinoaminofumarates can be used as precursors for five- and six-membered heterocycles. Especially, Heindel's report¹² in 1970 was notable because arylaminomaleimide skeletons are readily constructed from dimethyl acetylenedicarboxylate and aryl amines. In this reaction, hydroamination gives a dimethyl arylaminofumarate at first, and subsequent *trans-cis* isomerization¹³ and imide ring formation at high temperature. However, no one-pot synthesis was applied.¹⁴ Moreover, the substituted groups on the nitrogen atom of the imide ring were investigated only on aryl groups. The solubility of the obtained arylaminomaleimides was poor, and their fluorescent quantum yields were low (up to 0.07 in the solid state). To improve the properties, other kinds of substituted groups should be employed. Herein we found that *N*-alkyl arylaminomaleimide derivatives from reaction of dimethyl acetylenedicarboxylate with arylamines and alkylamines show intensive emission in their aggregation states. We also prepared *N*-aryl arylaminomaleimide and studied their optical properties.

2. Results and discussion

The synthetic procedures in the present paper are shown in Scheme 1. If one kind of aryl groups on the secondary amine and the

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imide ring are required, only mixing dimethyl acetylenedicarboxylate and excess amount of an arylamine without solvent at 150 °C can lead a desired arylaminomaleimide (path A in Scheme 1). If different kinds of aryl groups are required, path B in Scheme 1 should be chosen. In this case, dimethyl acetylenedicarboxylate and one equivalent of a first arylamine were reacted at ambient temperature to give an adduct product, dimethyl arylaminofumarate **2a–c** almost quantitatively. Subsequently, unreacted compounds were removed in vacuo, and without further purification excess amount of a second amine was reacted at 150 °C in the case of an aryl amine. On the other hand, the reaction proceeded even at ambient temperature in the case of alkyl amines to obtain *N*-alkyl arylaminomaleimides. In both cases of path A and B, the purification process was only washing with methanol and recrystallization from dichloromethane and methanol. Especially, the unsymmetrical arylaminomaleimides can be obtained in a one-pot process with easy purification.



Scheme 1. Synthesis of *N*-arylmaleimides; path A is for one kind of aryl groups, and path B is for different kinds.

The structures of the obtained products were confirmed by ¹H and ¹³C NMR analyses and high-resolution FABMS analysis for new compounds.¹⁵ Though aniline, *p*-toluidine, *m*-toluidine and *p*-bromoaniline gave correspondent arylaminomaleimides, *o*-toluidine and *p*-nitroaniline gave complex mixture (Table 1). Although the isolated yields of **1a** and **3b–f** were moderate, those of **1b**, **1c**, **1e** and **3a** were low and **1d** and **1f** were not isolated. In all cases, generation of the dimethyl arylaminofumarates were detected with ¹H NMR. In the case of using the aryl amines for formation of the imide rings, the *trans*-*cis* isomerization of the dimethyl arylaminofumarates accompanied with cyclization insufficiently proceed except for **1a** though the detail reaction mechanism is unclear. Employing the alkyl amines as a second amine allowed the reaction condition to be mild because nucleophilicity of the alkyl amines are much higher than that of the aryl amines.

Table 1
Arylaminoaleimides produced via Scheme 1

Route	Product	R ¹	R ²	Yield ^a [%]
Path A	1a	H	—	54
	1b	<i>p</i> -Me	—	6
	1c	<i>m</i> -Me	—	3
	1d	<i>o</i> -Me	—	n.d. ^b
	1e	<i>p</i> -Br	—	5
	1f	<i>p</i> -NO ₂	—	n.d. ^b
Path B	3a	H	<i>p</i> -BrPh	2
	3b	H	Propyl	22
	3c	H	Hexyl	26
	3d	H	Octyl	28
	3e	<i>p</i> -Me	Hexyl	27
	3f	<i>m</i> -Me	Hexyl	27

^a Isolated yield.

^b Complex mixture was obtained.

Solubility of **3b–f**, which have the alkyl groups on the nitrogen atoms of the imide rings, were higher in common organic solvents

such as chloroform and methanol than those of **1a–c**, **1e** and **3a**, whose substituents are aryl groups. The results for **1a** and **3b** are posted in Table 2. Solubility was drastically improved by exchange substituents on the nitrogen atoms of the imide rings from aryl groups to alkyl groups.

Table 2
Results of solubility test^a

Sample	CHCl ₃ [mol/L]	MeOH [mol/L]
1a	0.024	0.002
3b	0.621	0.050

^a Molar concentration of saturation.

All compounds showed AIE phenomena.⁹ Although no emission was observed in the solution states, addition of poor solvents such as water¹⁶ or removal of the solvents caused intense emission under UV irradiation at 354 nm (Fig. 1). To measure photoluminescence (PL) spectra in an aggregation state, powder samples were obtained by reprecipitation from cold chloroform and methanol. The UV–vis absorption and PL properties of the samples in solution and solid states are presented in Table 3. The absorption and PL properties were measured in chloroform ($c=1.0 \times 10^{-4}$ mol/L), and in solid state, respectively. The absorption spectra of **1a–c**, **1e** and **3a** show two absorption bands around 285–299 nm and 380–386 nm, and those of **3b–f** show two absorption bands around 267–275 nm and 380–386 nm (Fig. S22). The crystals of **1e** showed the longest luminescent wavelength at 535 nm, and those

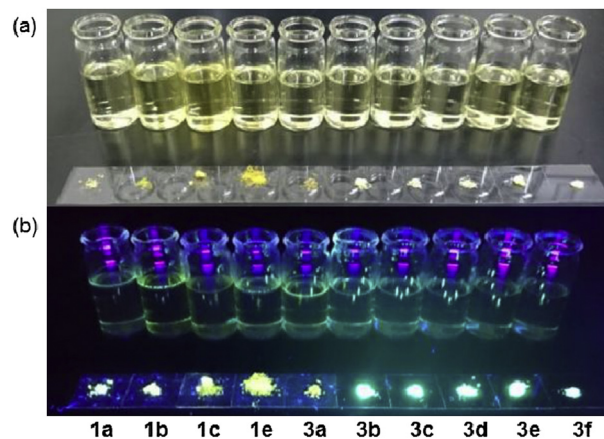


Fig. 1. Photographs of the obtained arylaminomaleimides in solution and solid state (a) with no irradiation, and (b) under UV (354 nm) irradiation.

Table 3
Optical properties of arylaminomaleimides

Sample	$\lambda_{\text{abs, sol}}^a$ [nm]	$\lambda_{\text{PL, solid}}^b$ [nm]	$\lambda_{\text{PL, film}}^c$ [nm]	$\Phi_{\text{PL, solid}}^d$
1a	380, 285	517	499	0.05
1b	386, 299	527	516	0.07
1c	382, 287	522	503	0.03
1e	382, 293	535	508	0.03
3a	383, 293	519	508	0.04
3b	380, 267	497	486	0.51
3c	380, 267	492	488	0.34
3d	380, 267	495	485	0.35
3e	386, 275	499	489	0.16
3f	383, 272	496	489	0.06

^a Absorption in chloroform solution ($c=1.0 \times 10^{-4}$ M).

^b PL in solid state.

^c PL in EVA film.

^d Absolute PL quantum efficiencies in solid state. PL spectra were measured under 350 nm irradiation for excitation.

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