

## Fluorescence Tuning Using Conjugated Aromatic Imine Systems

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The fluorescent conjugated aromatic imine derivatives are systematically designed and synthesized as the high yield through the simple one-pot condensation reaction. The emission of the synthesized conjugated aromatic imine derivatives can be tuned efficiently in the range of about 100 nm by the change of electron donating groups constituting parent molecule, which shows the considerable quantum yields from 0.38 to 0.56.

**key words:** fluorescence tuning, one-pot condensation reaction, conjugated aromatic imine derivatives

### INTRODUCTION

More recently, the photofunctional fluorescent compounds have already been utilized in various fields and the increasing demand for those having superior and multi-functionality is attracting further research interest [1,2]. For example, one of the most exciting developments in molecular electronics is the utilization of organic materials for optoelectronic applications, particularly light-emitting devices [3-5]. The critical elements in designing and fabricating those compounds are the control of their emission wavelength and sometimes their photo-switching responded by the external stimuli [6]. Conjugated aromatic derivatives, oligomers and polymers, such as 1,10-phenanthroline, poly(p-phenylene vinylene) and polythiophenes, allow color tuning through changes in their length, substitution, regioregularity and degree of conjugation [6-8]. In fact, those compounds showing a fine fluorescence tuning and a desired function have been reported limitedly because those syntheses are sometimes problematic as the several reaction steps and the inconvenient work-up, and no emission is often showed in the obtained compounds.

Therefore, we simply and systematically synthesized the aromatic conjugated systems showing the multi-functionality such as the the fluorescence tuning as well as the high fluorescence property by the connection of imine bond through one-pot condensation reaction. The introduction of various functional groups from the electron withdrawing group (X=F, Cl, I) to electron donating group (X=NH<sub>2</sub>, CH<sub>3</sub>, OCH<sub>3</sub>, and N(CH<sub>3</sub>)<sub>2</sub>) in the para-position of the ending aromatic ring is possible to control the fluorescence finely. Herein, we report on the fluorescence tuning of the highly fluorescent materials prepared as the high yield through the investigation of the spectroscopic behavior.

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### MATERIALS AND METHODS

#### Materials

P-Phenylenediamine, p-anisidine, and N,N-dimethyl-p-phenylenediamine, were obtained from Acros Organics, USA. p-Toluidine, p-fluoroaniline, p-chloroaniline, p-iodoaniline and terephthalic acid were obtained from Aldrich Chemical Co. Benzaldehyde was purchased from Kanto Chemical Co., Japan. Aniline was purchased from Duksan Pharmaceutical Co., Korea. Spectrophotometric grade methanol, methylene chloride, acetonitrile and chloroform were purchased from Aldrich Chemical Co. and used as received.

#### Synthesis of conjugated aromatic imine system

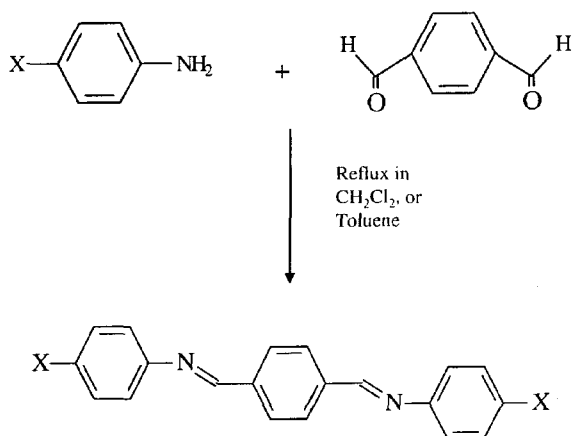
The key starting materials were used the aniline derivatives and terephthalic acid. The aromatic imine derivatives were synthesized by refluxing 1 eq. of terephthalic acid and 3 eq. of aniline derivatives or methylene chloride. As shown in Figure 1, various aromatic imine derivatives were simply prepared for the systematical investigation toward the fluorescence tuning. In order to characterize the conjugated aromatic imine derivatives, <sup>1</sup>H-NMR spectral data were obtained on a Varian Mercury 400 (400 MHz) NMR spectrometer. Chemical shifts were given in ppm using tetramethylsilane (TMS) as internal standard. All compounds were dissolved in chloroform-*d*. The melting points of the samples were measured by Fisher-Johns melting apparatus. Elemental analysis was performed with a Fisons EA-1108 Elemental Analyzer.

#### *N,N'*-diphenylbenzal-1,4-diimine(a)

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ, ppm 8.52 (s, 2H, C=N), 8.02 (s, 4H), 7.40-7.44(m, 4H), 7.25-7.28(m, 6H); mp 158°C, yellow powder. EA calc. for C<sub>20</sub>H<sub>16</sub>N<sub>2</sub> C 84.48, H 5.67, N 9.85, found C 84.30, H 5.83, N 10.14

#### *N,N'*-di(p-fluorobenzene)benzal-1,4-diimine(b)

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ, ppm 8.45 (s, 2H, C=N), 8.01 (s, 4H), 7.37-7.39 (m, 4H), 7.18-7.2(m, 4H); mp 150°C, ivory white powder. EA calc. for C<sub>20</sub>H<sub>14</sub>N<sub>2</sub>F<sub>2</sub> C 74.99, H 4.40, N 8.74 found C 74.72



**X = H, F, Cl, I, CH<sub>3</sub>, OCH<sub>3</sub>, NH<sub>2</sub> and N(CH<sub>3</sub>)<sub>2</sub>**

Figure 1. Synthesis of conjugated aromatic imine derivatives.

H 4.42, N 8.87

*N,N'*-di(*p*-chlorobenzene)benzal-1,4-diimine(c)

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ, ppm 8.51 (s, 2H, C=N), 8.00 (s, 4H), 7.23-7.27 (m, 4H), 7.08-7.13(m, 4H); mp 180°C. yellow needle. EA calc. for C<sub>20</sub>H<sub>14</sub>N<sub>4</sub>Cl<sub>2</sub> C 68.99, H 3.99, N 7.93 found C 67.86 H 4.12, N 8.05

*N,N'*-di(*p*-iodobenzene)benzal-1,4-diimine(d)

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ, ppm 8.48 (s, 2H, C=N), 8.00 (s, 4H), 7.71-7.74 (m, 4H), 6.99-7.01(m, 4H); mp 255°C. pale brown powder. EA calc. for C<sub>20</sub>H<sub>14</sub>N<sub>4</sub>I<sub>2</sub> C 44.80, H 2.63, N 5.22 found C 44.81 H 2.63, N 5.41

*N,N'*-di(*p*-aniline)benzal-1,4-diimine(e)

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ, ppm 8.54 (s, 2H, C=N), 7.95 (s, 4H), 7.19-7.21 (m, 4H), 6.71(d, 4H), 3.74(s, 4H -NH<sub>2</sub>); mp >300°C, orange powder. EA calc. for C<sub>20</sub>H<sub>18</sub>N<sub>4</sub> C 76.41, H 5.77, N 17.82 found C 76.27, H 5.87, N 10.05

*N,N'*-di(*p*-toluene)benzal-1,4-diimine(f)

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ, ppm 8.54 (s, 2H, C=N), 8.0 (d, 4H), 7.17-7.26 (m, 4H), 2.29 (s, 6H -CH<sub>3</sub>); mp 168°C, orange powder. EA calc. for C<sub>22</sub>H<sub>16</sub>N<sub>2</sub> C 84.58, H 6.45, N 8.97, found C 84.78, H 6.52, N 9.17

*N,N'*-di(*p*-anisole)benzal-1,4-diimine(g)

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ, ppm 8.54 (s, 2H, C=N), 7.99 (s, 4H), 7.27-

7.29 (m, 4H), 6.94-6.97(d, 4H), 3.85(s, 6H, -OCH<sub>3</sub>); mp 227°C, yellow powder. EA calc. for C<sub>22</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub> C 76.72, H 5.85, N 8.13 found C 77.20, H 5.84, N 8.28

*N,N'*-di(*p*-dimethylaniline)benzal-1,4-diimine(h)

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ, ppm 8.56 (s, 2H, C=N), 7.95 (s, 4H), 7.26-7.32 (m, 4H), 6.76-6.78(d, 4H), 3.00(s, 6H, -N(CH<sub>3</sub>)<sub>2</sub>); mp 320°C dec. yellow powder. EA calc. for C<sub>24</sub>H<sub>26</sub>N<sub>4</sub> C 77.80, H 7.07, N 15.12 found C 77.46, H 7.10, N 15.20

#### Measurements

UV-Vis absorption spectra were measured using a Hitachi U-3300 spectrophotometer. The fluorescence spectra were obtained on a SLM8100 spectrofluorometer (AMINCO, USA) with a Xe-arc lamp light source using 4 nm or 8 nm band pass excitation and emission monochromators. The rhodamine B solution was used as a reference to correct for variation of the Xe light source with time and wavelength. The fluorescence data of the samples were normalized. Fluorescence quantum yields ( $\phi_F$ ) were measured by using a same spectrofluorometer as described above and calculated according to Equation (1) [9], where  $\phi_{unk}$  is the fluorescence quantum yield of the sample,  $\phi_{std}$  is the quantum yield of the standard ( $\phi_F=0.27$ , anthracene in ethanol) [10,11],  $I_{unk}$  and  $I_{std}$  are the integrated emission intensities of the sample and the standard, respectively,  $A_{unk}$  and  $A_{std}$  are the absorbances of the sample and the standard at the excitation wavelength, respectively, and  $\eta_{unk}$  and  $\eta_{std}$  are the refractive indexes of the corresponding solutions.

$$\phi_{unk} = \phi_{std} \left( \frac{I_{unk}}{A_{unk}} \right) \left( \frac{A_{std}}{I_{std}} \right) \left( \frac{\eta_{unk}}{\eta_{std}} \right)^2 \quad (1)$$

## RESULTS AND DISCUSSION

The electronic spectral data of the conjugated aromatic imine derivatives in various solvents are collected in Table 1. The solvent effects of every compounds are not much large, but it has shown that the substituent group having the stronger electron donating ability has totally influenced on blue shift in  $\pi$ - $\pi^*$  absorption band while red shift in  $n$ - $\pi^*$  absorption band. From the electronic spectra of all derivatives (Figure 2), it was known that the shorter absorption band (220-330 nm) is caused by  $\pi$ - $\pi^*$  state and the longer absorption band (330-550 nm) is

Table 1. Electronic spectral data of conjugated aromatic imine derivatives in various solvents

Compound	$\lambda_{max}$ (nm)							
	Chloroform		Methylene chloride		Acetonitrile		Methanol	
	$\pi$ - $\pi^*$	$n$ - $\pi^*$	$\pi$ - $\pi^*$	$n$ - $\pi^*$	$\pi$ - $\pi^*$	$n$ - $\pi^*$	$\pi$ - $\pi^*$	$n$ - $\pi^*$
X = N(CH <sub>3</sub> ) <sub>2</sub>	268	435	271	436	267	429	269	433
X = NH <sub>2</sub>	255, 280	402	252, 298	401	253, 295	407	253, 285	405
X = OCH <sub>3</sub>	286	377	241, 293	378	237, 294	373	236, 290	373
X = CH <sub>3</sub>	291	355	236, 303	355	233, 295	350	226, 290	351
X = H	291	344	300	348	228, 296	341	289	334

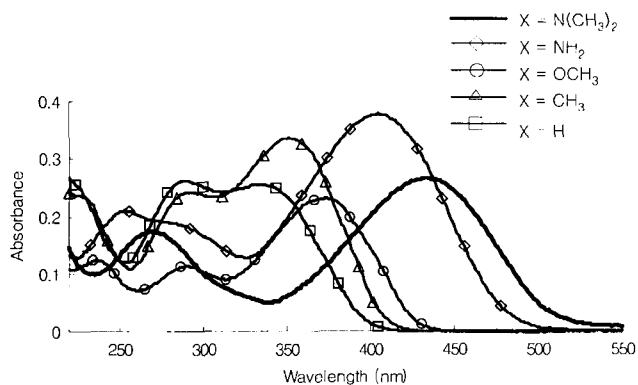


Figure 2. UV-Vis absorption spectra of conjugated aromatic imine derivatives with X=H, CH<sub>3</sub>, OCH<sub>3</sub>, NH<sub>2</sub>, and N(CH<sub>3</sub>)<sub>2</sub> in methanol.

mostly caused by  $n-\pi^*$  state. In particular, it was assumed that the absorption band (in any case, shoulder) appeared between 260 nm and 330 nm is caused by  $\pi-\pi^*$  state and  $n-\pi^*$  state of imine bond. The longer absorption peak at 435 nm in the derivative with X=N(CH<sub>3</sub>)<sub>2</sub> was shown an obvious red-shift with the long absorption tailing until 550 nm compared to that of the other derivatives. It indicates that this shift is obtained by introducing electron-donating group into the conjugated phenyl rings.

As shown in Figure 3, every fluorescence was shown by the excitation at the absorption peak appeared between 260 nm and 300 nm while the fluorescence appeared in the longer wavelength was not shown by the excitation at the longer absorption peak due to non-emitted property of  $n-\pi^*$  state. It was confirmed from the similar patterns between absorption spectra and excitation spectra of every compounds that two kinds of fluorescence emission bands are caused by the excitation (in any case, shoulder is appeared) of two kinds of absorption bands ( $\pi-\pi^*$ ). In particular, the fluorescence tuning ability appeared from about 300 nm to about 400 nm finely by the change of substituent group except for the halo-substituted compounds.

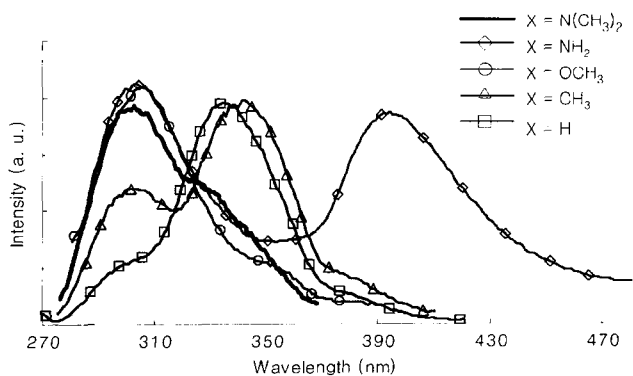


Figure 3. Fluorescence spectra of conjugated aromatic imine derivatives with X=H, CH<sub>3</sub>, OCH<sub>3</sub>, NH<sub>2</sub>, and N(CH<sub>3</sub>)<sub>2</sub> in methanol.

Table 2. Relative quantum yield of conjugated aromatic imine derivatives

Compound	X	$\phi_F$ in Chloroform
a	H	0.56
b	F	No emission
c	Cl	No emission
d	I	No emission
e	NH <sub>2</sub>	0.47
f	CH <sub>3</sub>	0.53
g	OCH <sub>3</sub>	0.41
h	N(CH <sub>3</sub> ) <sub>2</sub>	0.38

Table 2 showed that the fluorescence quantum yield ( $\phi_F$ ) of these compounds were greatly affected by the change of the substituent group. While the substitution of the electron withdrawing group such as X=F, Cl, I resulted in no emission because halogen-containing substances act as quenchers [12]. The substitution of the electron donating group such as X=NH<sub>2</sub>, CH<sub>3</sub>, OCH<sub>3</sub>, and N(CH<sub>3</sub>)<sub>2</sub> in the para-position of the ending aromatic ring including parent molecule (X=H) was markedly enhanced the quantum yields from 0.38 to 0.56. Joshi *et al.* [6] reported that fluorescence quantum yield was enhanced when introducing the electron donating group to the parent 1, 10-phenanthroline. Importantly, the emission of conjugated aromatic imine derivatives is blue or red-shifted (a shift range of approximately 100 nm) upon changing electron donating group compared to the emission of the parent molecule. Thus, these compounds provide a unique family of tunable intrinsic fluorophores. These synthesized compounds will be applied in the molecular sensing and switching and we are in part working on the molecular switching now.

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