



## Synthesis and Fluorescence properties of Schiff bases of 4-hydroxy-3-methoxy-5-nitrobenzaldehyde

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### ABSTRACT

Vaniline (**1**) is nitrated by using known literature method to 4-hydroxy-3-methoxy-5-nitrobenzaldehyde (**2**). The haloanilines (**3a-g**) used for the synthesis of Schiff bases was synthesized by known literature methods and by referring Vogel's Practical Organic Chemistry, 5<sup>th</sup> Edition. The nitrovaniline is reactive towards amine and forming 4-*[(E)-(4-aryl)imine]methyl*-2-methoxy-6-nitrophenol (**4a-g**). The final compounds 4-*[(E)-(4-aryl)imine]methyl*-2-methoxy-6-nitrophenol (**4a-g**) and are further subjected to fluorescence study.

**Key Words:** 4-hydroxy-3-methoxy-5-nitrobenzaldehyde, Haloanilines, Schiff Bases, nitrovaniline, Fluorescence.

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### INTRODUCTION

The compounds containing azomethine (-C=N-) group are known as Schiff bases, are formed by the condensation of a primary amines with a carbonyl compounds such as aldehydes or ketones. The Schiff bases of aliphatic aldehydes are relatively unstable and are readily undergoes polymerization while those of aromatic aldehydes having an effective conjugation system are more stable. Schiff bases play very important role in many biological and chemical reactions; because of the imine linkage. Schiff bases[1] are generally bi- or tri- dentate ligands capable of forming very stable complexes with transition metals[2].

The word phosphor was invented in the early 17<sup>th</sup> century. There are some characteristics of typical phosphor as must survive hazardous chemical environment, cannot be water soluble, durable, easy to apply, not easily detected or noticed without specialized equipment, etc. Phosphors become technologically and industrially important with the introduction of fluorescent lamps in 1938. Thermometry was suggested in the German patent in 1938. First peer-reviewed article, to our knowledge appeared in 1949. Between 1950 to 1980, it was not widely used. Its most common use was aerodynamic applications. Advances in lasers, microelectronics, and other supporting technologies enable additional commercial as well as scientific use. The physics and chemistry of luminescence materials and their applications become and still is the core area covered by Luminescence symposia.

In the small molecules organic light emitting diodes, the family of carbazoles[03] could be extended to be suitably fit for red[04-06], green[07-09], and blue light[10-12] triplet emitters and therefore, they can be used in full color displays[13-16, 18-21]. More recently studies of Thompson, Forrest and co-workers shows that the use of electron blocking layers (EBLs) consisting of Ir<sup>III</sup> complexes with picolinate ligands[22] produced improved color purities in

the case of blue light emitting device[13]. Some of the organic molecules are used as EBLs as- fluorinated phenylenes[17], and oxadiazole as well as triazole containing molecules such as trimer of N-arylbenzimidazoles (TPBi)[23,24], 2-tert-butylphenyl-5-biphenyl-1,3,4-oxadiazole (PBD)[25], 3-phenyl-4-(1'-naphthyl)-5-phenyl-1,2,4-triazole (TAZ)[26,27], 1,8-Naphthalimides[28], polyquinolines[29], or carbon nanotubes doped in PPV[30] were also found to be useful as hole blocking layers (HBLs).

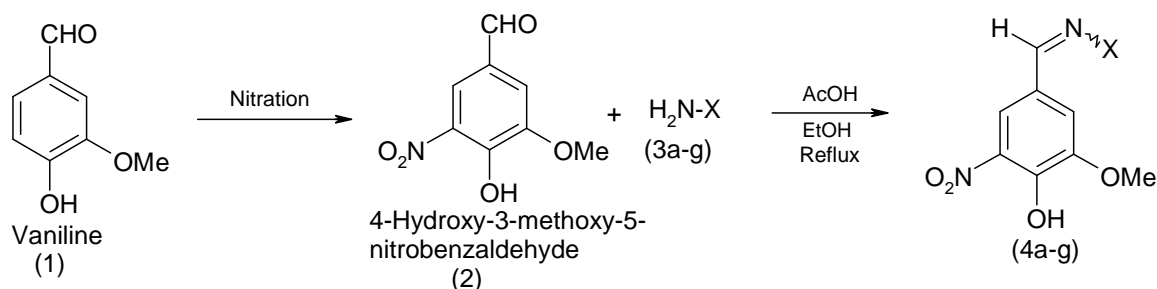
Searching for highly efficient fluorescence organic compounds (Schiff bases) is a topic of current interest. The aromatic based ligand having electron donating or withdrawing groups has been increased or decreased the intensity of absorption or shifted absorption wavelength on either side. Luminescence properties of the various Schiff bases of nitrovaniline has been checked by using Spectrofluorometer model number RF5301. A Xe laser lamp was used for excitation and emission spectra were scanned from the range 220 nm to 750 nm.

In this paper we tried to synthesis of various Schiff bases of nitrovaniline of haloamines which has general name as 4-{(E)-[(4-aryl)imine]methyl}-2-methoxy-6-nitrophenol (**4a-g**) study their fluorescence study.

### EXPERIMENTAL SECTION

#### Experimental Work:

Vaniline (**1**) is nitrated by using known literature method to 4-hydroxy-3-methoxy-5-nitrobenzaldehyde (**2**). The haloanilines (**3a-g**) used for the synthesis of Schiff bases was synthesized by known literature methods and by referring Vogel's Practical Organic Chemistry, 5<sup>th</sup> Edition. The nitrovaniline is reactive towards amine and forming 4-{(E)-[(4-aryl)imine]methyl}-2-methoxy-6-nitrophenol (**4a-g**).



*H<sub>2</sub>N-X* – 4-iodoaniline, 4-iodo-2-methylaniline, 4-bromoaniline, 4-chloroaniline, 3-chloroaniline, 2,4,5-trichloroaniline, 4-chloro-3-trifluoromethylaniline.

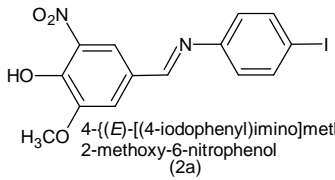
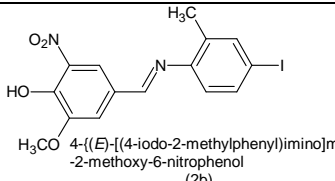
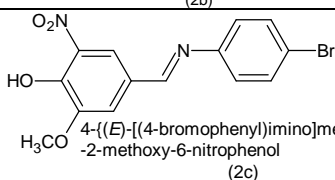
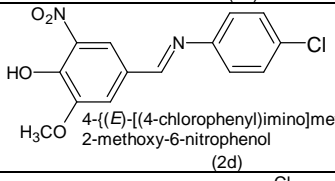
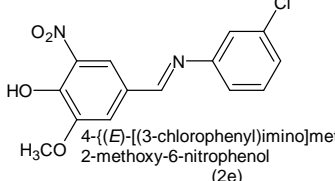
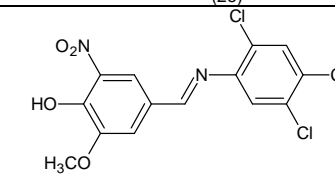
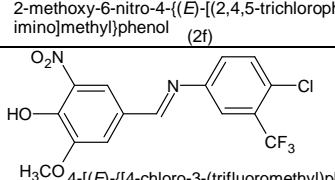
#### Synthesis of Schiff bases:

Add 200 mg of 4-hydroxy-3-methoxy-5-nitrovaniline (1.015 mmol) (**2**) in 10 ml of absolute alcohol and for few minutes till all aldehyde get dissolve. Add 1.02 mmol of haloanilines (**3a-g**) in above reaction mixture with constant stirring and finally add catalytic amount of acetic acid. Reflux the reaction mixture with stirring for about 30 – 50 minutes and check the completion of reaction with help of TLC (in pet ether and ethyl acetate). Cool the reaction mixture and filter the resulting solid 4-{(E)-[(4-aryl)imine]methyl}-2-methoxy-6-nitrophenol (**4a-g**) on Buckner funnel, wash with cold ethanol. Record the yield, M.P and recrystallized from absolute ethanol.

#### Luminescence Properties:

Luminescence properties of the schiff bases of 4-hydroxy-3-methoxy-5-nitrobenzaldehyde with various haloanilines (fluoro, chloro, bromom and iodoanilines) has been checked by using Spectrofluorometer model number RF5301. A Xe laser lamp was used for excitation and emission spectra were scanned from the range 220 nm to 750 nm. For fluorescence study of the Schiff bases, dimethylformamide is used as solvent and reference material. The excitation of the molecule is occurred due to the  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transitions.

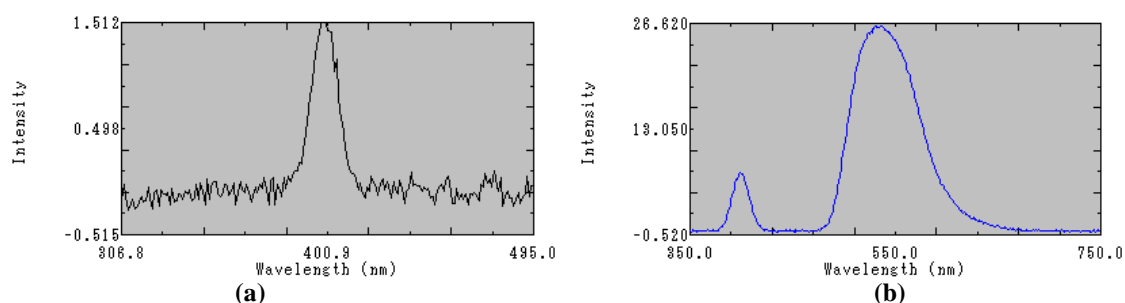
**Table 01: Starting amines, Structure and IUPAC name of product, Yield, m.p. and NMR data of the product.**

Starting Amines	Name and structure of Product	Yield	M.P. °C	NMR data ( $\delta$ in ppm) in DMSO-D <sub>6</sub> (300 MHz)
4-Iodoaniline	 4-((E)-[(4-iodophenyl)imino]methyl)-2-methoxy-6-nitrophenol (2a)	82%	135	<b>3.94 (s, 3H)</b> ; 6.43 (d, 1H); 7.2 (dd, 2H); 7.7 (dd, 2H); 8.1 (d, 1H); <b>8.6 (s, 1H)</b> ; <b>10.90 (bs, 1H)</b> .
4-Iodo-2-methylaniline	 4-((E)-[(4-iodo-2-methylphenyl)imino]methyl)-2-methoxy-6-nitrophenol (2b)	74%	105	2.26 (s, 3H); <b>3.96 (s, 3H)</b> ; 6.87 (d, 1H); 7.55 (d, 1H); 7.62 (s, 1H); 7.60 (s, 1H); 8.01 (s, 1H); <b>8.46 (s, 1H)</b> ; <b>10.95 (bs, 1H)</b>
4-Bromoaniline	 4-((E)-[(4-bromophenyl)imino]methyl)-2-methoxy-6-nitrophenol (2c)	78%	145	<b>3.94 (s, 3H)</b> ; 7.25 (dd, 2H); 7.61 (dd, 2H); 7.74 (s, 1H); 8.05 (s, 1H); <b>8.61 (s, 1H)</b> ; <b>10.90 (bs, 1H)</b>
4-Chloroaniline	 4-((E)-[(4-chlorophenyl)imino]methyl)-2-methoxy-6-nitrophenol (2d)	81%	143	<b>3.94 (s, 3H)</b> ; 7.32 (dd, 2H); 7.48 (dd, 2H); 7.75 (s, 1H); 8.05 (s, 1H); <b>8.61 (s, 1H)</b> ; <b>10.95 (bs, 1H)</b>
3-Chloroaniline	 4-((E)-[(3-chlorophenyl)imino]methyl)-2-methoxy-6-nitrophenol (2e)	67%	125	<b>3.95 (s, 3H)</b> ; 7.2-7.6 (m, 4H); 7.75 (s, 1H); 8.10 (s, 1H); <b>8.64 (s, 1H)</b> ; <b>10.90 (bs, 1H)</b>
2,4,5-Trichloroaniline	 2-methoxy-6-nitro-4-((E)-[(2,4,5-trichlorophenyl)imino]methyl)phenol (2f)	76%	142	<b>3.96 (s, 3H)</b> ; 7.62 (s, 1H); 7.78 (s, 1H); 8.04 (s, 1H); 8.11 (s, 1H); <b>8.59 (s, 1H)</b> ; <b>11.22 (bs, 1H)</b>
4-Chloro-3-trifluoromethyl-aniline	 4-((E)-[(4-chloro-3-(trifluoromethyl)phenyl)imino]methyl)-2-methoxy-6-nitrophenol (2g)	85%	168	<b>3.96 (s, 3H)</b> ; 7.60 (s, 1H); 7.73 -7.78 (m, 3H); 8.05 (s, 1H); <b>8.70 (s, 1H)</b> ; <b>10.95 (bs, 1H)</b>

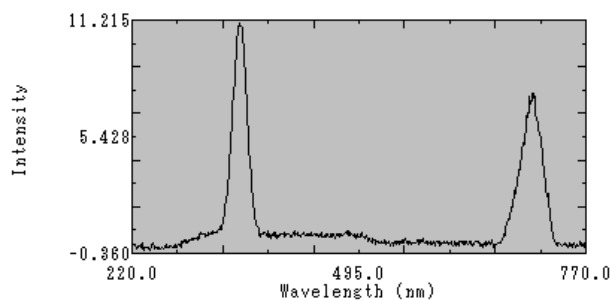
The fluorescence data can be shown in following data:

Slit width: Excitation and emission is 5 nm; Concentration of solution is 500 ppm; Solvent used is DMF.

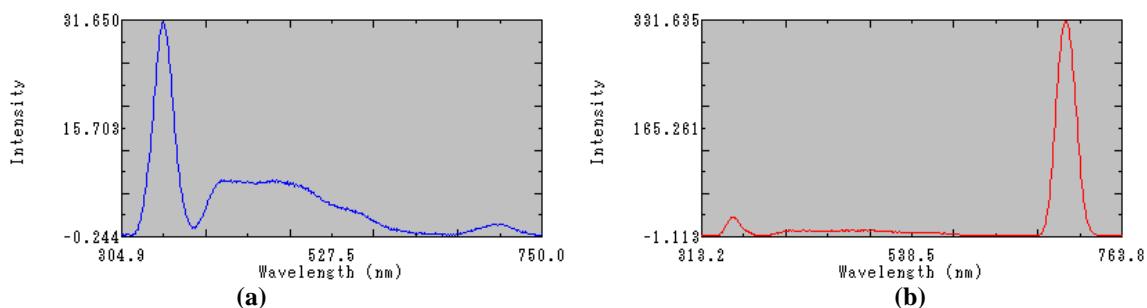
Sample Name	Excitation wavelength (nm)	Emission wavelength (nm)
4-{(E)-[(4-iodophenyl)imine] methyl}-2-methoxy-6-nitrophenol	399 ( $\epsilon$ 1.559)	399 ( $\epsilon$ 7.3); 531 ( $\epsilon$ 26.35)
4-{(E)-[(4-Iodo-2-methyl phenyl)imine]methyl}-2-methoxy-6-nitrophenol	350 ( $\epsilon$ 11.102) 705 ( $\epsilon$ 7.59)	348 ( $\epsilon$ 31.33); 413 ( $\epsilon$ 8.18); 347 ( $\epsilon$ 29.21); 470 ( $\epsilon$ 9.38); 705 ( $\epsilon$ 330.49)
4-{(E)-[(4-bromophenyl)imine] methyl}-2-methoxy-6-nitrophenol	279 ( $\epsilon$ 5.1) 361 ( $\epsilon$ 2.2) 480 ( $\epsilon$ 2.1)	300 ( $\epsilon$ 7.0); 599 ( $\epsilon$ 1.26); 361 ( $\epsilon$ 10.0); 540 ( $\epsilon$ 1.0) 551 ( $\epsilon$ 505.0)
4-{(E)-[(4-chlorophenyl)imine] methyl}-2-methoxy-6-nitrophenol	401 ( $\epsilon$ 3.5) 481 ( $\epsilon$ 1.1)	403 ( $\epsilon$ 4.5); 525 ( $\epsilon$ 11.0); 554 ( $\epsilon$ 129.2)
4-{(E)-[(3-chlorophenyl)imine] methyl}-2-methoxy-6-nitrophenol	402 ( $\epsilon$ 7.88)	405 ( $\epsilon$ 11.19); 515 ( $\epsilon$ 27.58)
4-{(E)-[(2,4,5-trichlorophenyl)imine] methyl}-2-methoxy-6-nitrophenol	402 ( $\epsilon$ 97.23)	406 ( $\epsilon$ 131.33); 439 ( $\epsilon$ 57.83); 467 ( $\epsilon$ 59.21)
4-{(E)-[(4-Chloro-3-trifluoromethylphenyl)imine] methyl}-2-methoxy-6-nitrophenol	263 ( $\epsilon$ 2.90) 328 ( $\epsilon$ 3.84) 401 ( $\epsilon$ 91.14) 681 ( $\epsilon$ 4.014)	266 ( $\epsilon$ 3.38); 401 ( $\epsilon$ 3.2); 331 ( $\epsilon$ 3.51); 406 ( $\epsilon$ 5.23); 404 ( $\epsilon$ 111.36); 508 ( $\epsilon$ 31.20); 340 ( $\epsilon$ 1.98); 402 ( $\epsilon$ 5.34); 474 ( $\epsilon$ 1.17); 684 ( $\epsilon$ 150.9)



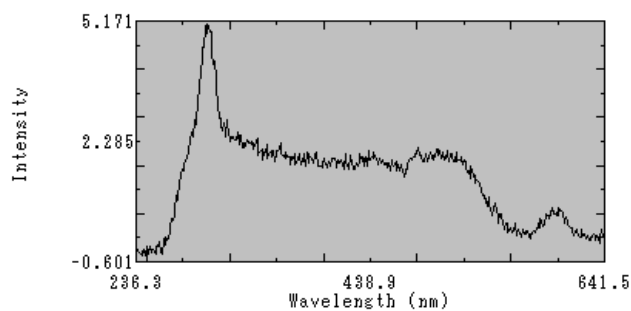
**Fig. 1 (a) Excitation spectra of 4-{(E)-[(4-iodophenyl)imine]methyl}-2-methoxy-6-nitrophenol. (b) Emission spectra of 4-{(E)-[(4-iodophenyl)imine]methyl}-2-methoxy-6-nitrophenol at 399 nm**



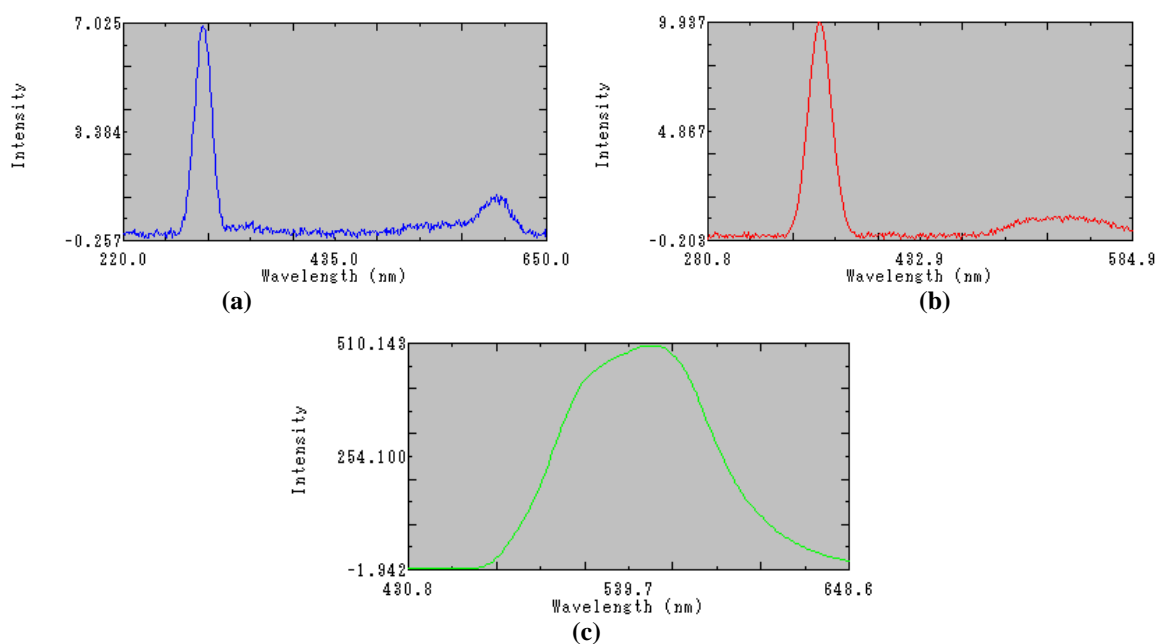
**Fig. 2 Excitation spectra of 4-{(E)-[(4-iodo-2-methylphenyl)imine]methyl}-2-methoxy-6-nitrophenol.**



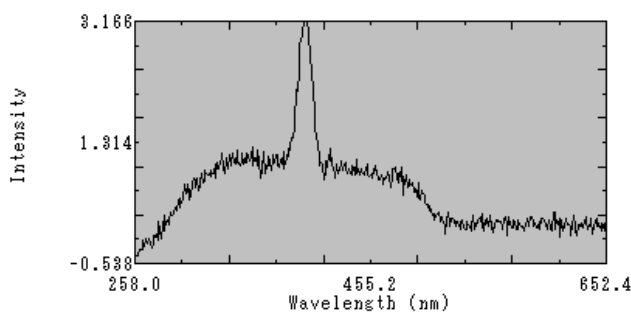
**Fig. 3 Emission spectra of 4-{(E)-[(4-iodo-2-methylphenyl)imine]methyl}-2-methoxy-6-nitrophenol at (a) 350 nm; (b) 705 nm.**



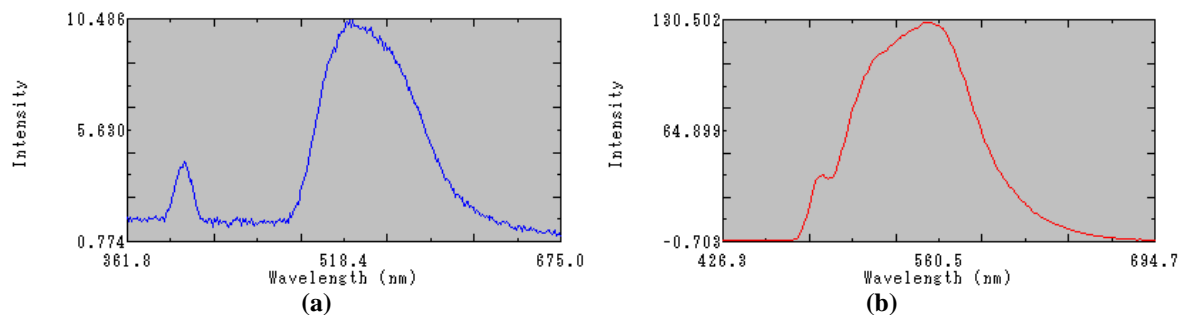
**Fig. 4** Excitation spectra of 4-((E)-[(4-bromophenyl)imino]methyl)-2-methoxy-6-nitrophenol.



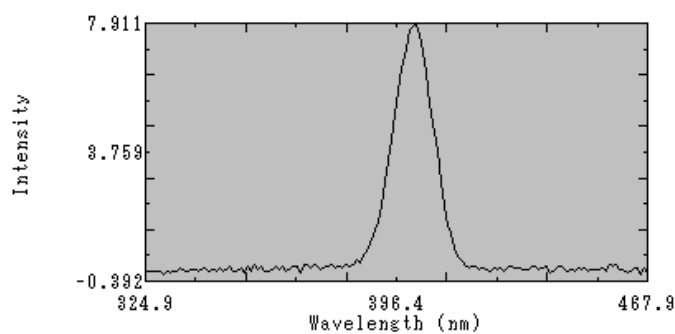
**Fig: 5** Emission spectra of 4-((E)-[(4-bromophenyl)imino]methyl)-2-methoxy-6-nitrophenol at (a) 297 nm; (b) 361 nm; (c) 480 nm.



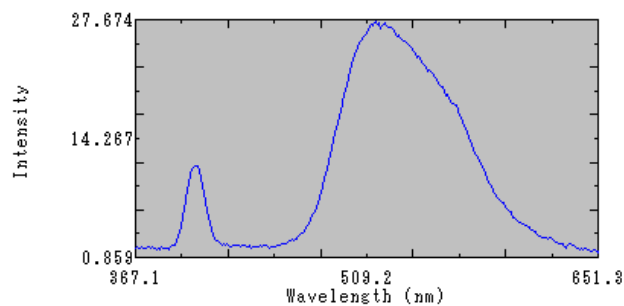
**Fig. 6** Excitation spectra of 4-((E)-[(4-chlorophenyl)imino]methyl)-2-methoxy-6-nitrophenol.



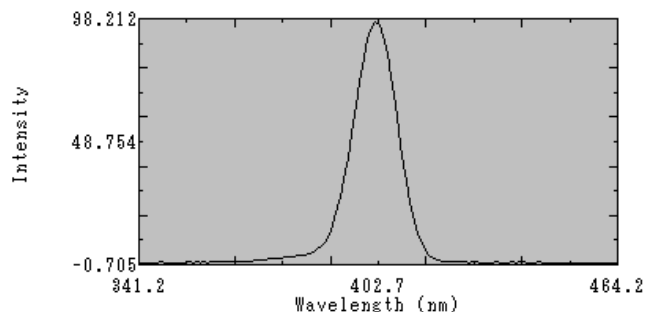
**Fig: 7** Emission spectra of 4-((E)-[(4-chlorophenyl)imino]methyl)-2-methoxy-6-nitrophenol at (a) 401 nm; (b) 481 nm.



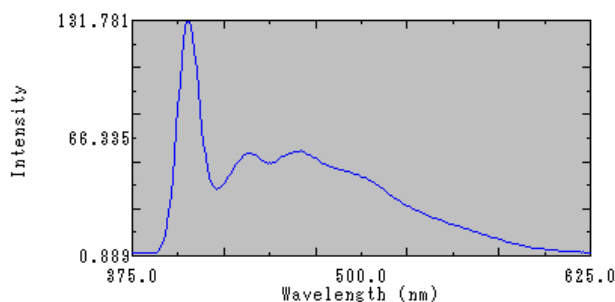
**Fig. 8** Excitation spectra of 4-((E)-[(3-chlorophenyl)imino]methyl)-2-methoxy-6-nitrophenol.



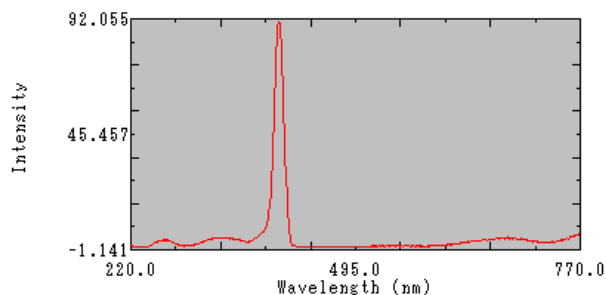
**Fig: 9** Emission spectra of 4-((E)-[(3-chlorophenyl)imino]methyl)-2-methoxy-6-nitrophenol at 297 nm.



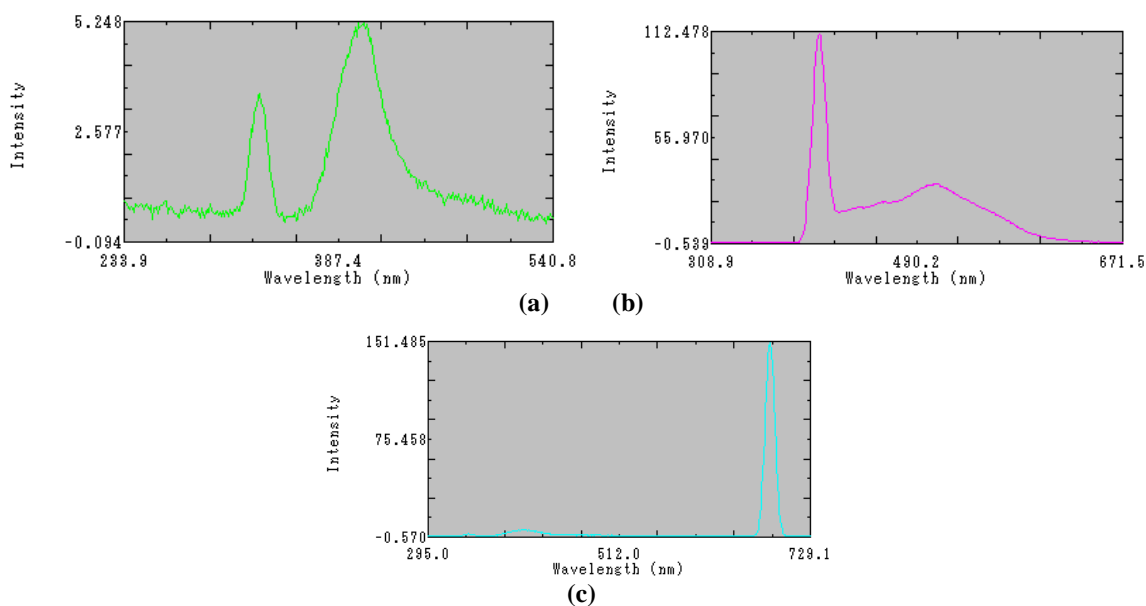
**Fig. 10** Excitation spectra of 4-((E)-[(2,4,5-Trichlorophenyl)imino]methyl)-2-methoxy-6-nitrophenol.



**Fig. 11** Emission spectra of 4-((E)-[(2,4,5-Trichlorophenyl)imine]methyl)-2-methoxy-6-nitrophenol at 402 nm.



**Fig. 12** Excitation spectra of 4-((E)-[(4-Chloro-3-trifluoromethylphenyl)imine]methyl)-2-methoxy-6-nitrophenol.



**Fig. 13** Emission spectra of 4-((E)-[(4-Chloro-3-trifluoromethylphenyl)imine]methyl)-2-methoxy-6-nitrophenol at (a) 328 nm; (b) 401 nm; (c) 681 nm.

## RESULTS AND DISCUSSION

Vaniline (**1**) is nitrated by using known literature method to 4-hydroxy-3-methoxy-5-nitrobenzaldehyde (**2**). The NMR spectra of the nitrovanillin shows  $\delta$  values at 3.96 (s, 3H) is for  $-\text{OCH}_3$  group protons and 11.22 (bs, 1H) is for deshielded phenolic  $-\text{OH}$  proton. The signal at 9.87 (s, 1H) is for aldehydic proton which is not observed in the final products. The nitrovaniline is reactive towards amine and forming 4-((E)-[(4-aryl)imine]methyl)-2-methoxy-6-nitrophenol (**4a-g**). The structures of the Schiff bases are confirmed by NMR spectra. The two signals of phenolic  $-\text{OH}$  and  $-\text{OCH}_3$  protons are present in final Schiff bases NMR with slight shielding/deshielding effect depending on

the aniline used for the coupling. The new peak at 8.4-8.7 ppm is due to azomethine proton confirm the formation of Schiff bases.

The vanillin shows excitation at 401 nm ( $\epsilon$  1.28) [very weak peak] and shows emission at 403 nm ( $\epsilon$  4.78). The Schiff bases of vanillin with various haloanilines (including fluoro, chloro, bromo and iodohaloanilines) shows shifting of some absorption bands (wavelengths) towards lower (in case of iodo, bromo and fluoroanilines) and in some cases towards higher wavelengths. The effect of shifting is considerable in case of para-substitution rather than meta-substitution.

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