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## Short note

## Emission properties of diazines chromophores: Structure-properties relationship



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## ABSTRACT

This article presents the photophysical properties of a series of diazine chromophores. The influence of five parameters has been studied: the presence of a diazine/benzodiazine fragment, the nature of the diazine fragment (1,3-diazine/1,4-diazine), the presence or not of a vinyl linker between diazine ring and phenylene fragments of the  $\pi$ -conjugated bridge, the presence of a phenylene/biphenylene linker and the nature of electron donating group (dimethylamino/diphenylamino). Taguchi's design of experiment combined with analysis of variance methodologies have been employed to highlight the main structural parameters influencing the position of absorption and emission maxima of dichloro-methane solution and the extend of emission solvatochromic range exhibited by this family of chromophores.

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## 1. Introduction

Since the beginning of the 2000's, there has been a great interest in the photophysical properties of diazine chromophores [1,2]. Diazines are six-membered aromatic heterocycles with two nitrogen atoms. Depending of the position of the nitrogen atoms, the pyridazine (1,2-diazine), the pyrimidine (1,3-diazine) and the pyrazine (1,4-diazine) can be distinguished. Due to the significant  $\pi$ -deficient character of diazine rings, diazinyll fragments can be used as electron-withdrawing group in push-pull structures in which intramolecular charge transfer (ICT) process occurs.  $\pi$ -conjugated diazine derivatives, especially when substituted by electron-donating group such as amino group, generally exhibit intense fluorescence properties with strong emission solvatochromism [3–9].

The main applications of diazine fluorophores include sensing (polarity [3–9], pH [7–10], metal cations [11,12], nitroaromatic explosives [13], biological materials [14,15]...), two photon excitation biological imaging [16,17] and organic light emitting diodes [18,19].

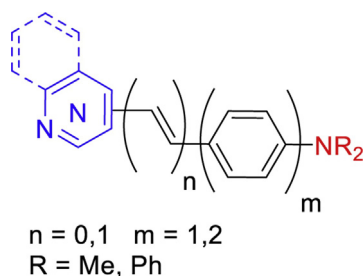
Emission properties of diazine chromophores can be easily tuned by structural modification regarding the diazine fragment itself, the  $\pi$ -conjugated bridge and the electron-donating group. In this context, defining precisely structure-property relationship

appears as a key point. Taguchi's design of experiment and analysis of variance (ANOVA) statistical methodologies can be useful to evaluate the influence of various factors on a defined parameter [20,21]. In principle, the Taguchi's design of experiments is used to get information such as main effects and interactions effects of design parameters from minimum number of experiments. Fewer experiments are required to study all levels of all factors and filters out some effects due to statistical variations. Taguchi methodology is well developed to optimize chemical process [22] or device performance [23,24]. Recently we have described the prediction of photophysical properties (position of absorption and emission maxima, extend of the emission solvatochromic range) of a series of pyrimidine chromophores [25]. The influence of three parameters were studied: the nature of the electron-donating group and of the  $\pi$ -conjugated linker as well as the substituted position of the pyrimidine core.

The aim of the work described in this communication is to extend this methodology to other diazines chromophores (pyrimidine, pyrazine and their benzo-analogues: quinazoline and quinoxaline) and other  $\pi$ -conjugated bridge combinations (Chart 1). The influence of five parameters on absorption and emission maxima of dichloromethane solution of chromophores and the extend of solvatochromic range have been studied. The five structural modifications of the chromophores are the following one: the presence of a diazine/benzodiazine fragment, the nature of the diazine fragment (1,3-diazine/1,4-diazine), the presence or not of a vinyl linker between diazine ring and phenylene fragment of the  $\pi$ -conjugated bridge, the presence of a

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**Chart 1.** General structure of studied chromophores.

phenylene/biphenylene linker and the nature of the amino electron donating group (dimethylamino/diphenylamino).

## 2. Experimental

### 2.1. Method

In order to predict the absorption maxima, the five previously listed factors have been studied. For each factor, two levels have been considered. The orthogonal array of  $L_8$  type was used and is represented in Table 1. Affection of each factor to the column of the orthogonal array are given in Table 2. Columns B and E are not affected and are used as control to check if there are interactions between studied factors. The corresponding compounds are represented in Chart 2.

### 2.2. General experimental

All solvents were reagent grade for synthesis and spectroscopic grade for photophysical measurements. The starting materials were purchased from Sigma-Aldrich or Alfa Aesar and used without further purification. For air and moisture-sensitive reactions, all glassware pieces were flame-dried and cooled under nitrogen. NMR spectra were recorded in  $\text{CDCl}_3$ , on a Bruker Advance 300 spectrometer ( $^1\text{H}$  at 300 MHz and  $^{13}\text{C}$  at 75 MHz). The

**Table 1**

Experimental layout using the  $L_8$  orthogonal array.

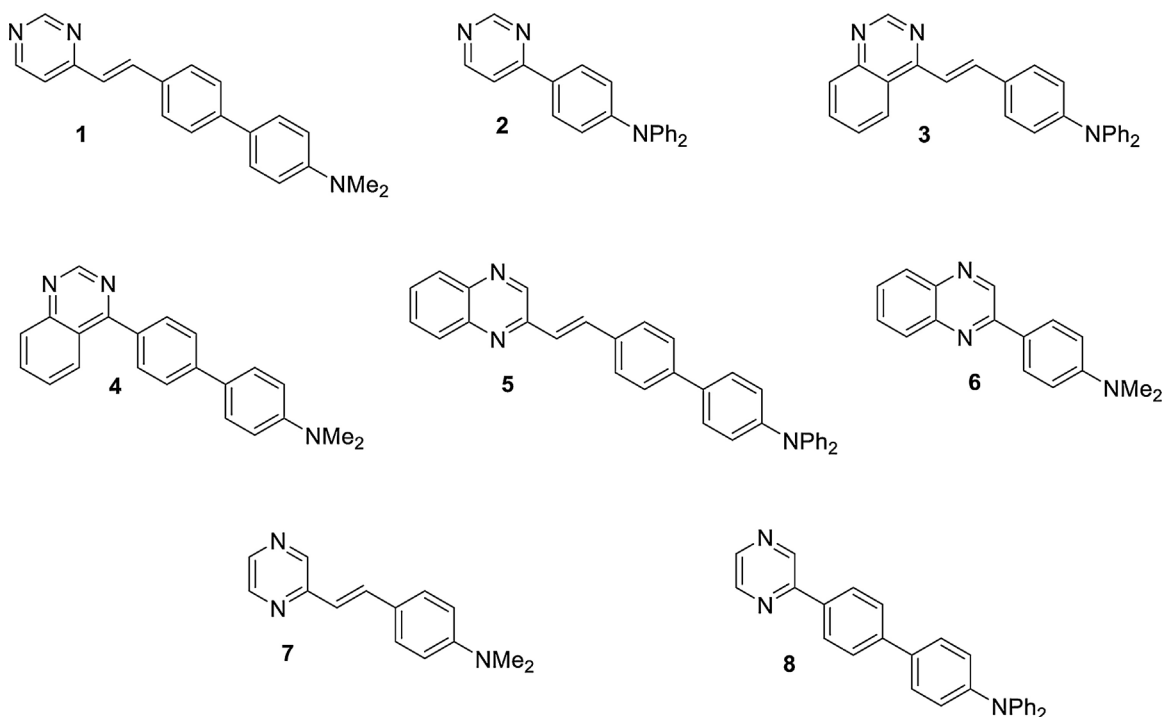
Compd	A	B	C	D	E	F	G
1	1	1	1	1	1	1	1
2	1	1	1	2	2	2	2
3	1	2	2	1	1	2	2
4	1	2	2	2	2	1	1
5	2	1	2	1	2	1	2
6	2	1	2	2	1	2	1
7	2	2	1	1	2	2	1
8	2	2	1	2	1	1	2

**Table 2**

Factor and their corresponding level to be studied in experiments.

Column	Level 1	Level 2
A: Nature of the diazine ring	Pyrimidine	Pyrazine
B: Free		
C: Diazine/Benzodiazine	Diazine	Benzodiazine
D: Presence of an ethenyl linker between diazine and phenyl rings	Yes	No
E: Free		
F: number of phenyl rings in the $\pi$ -conjugated bridge	2	1
G: nature of electron donating group	$\text{NMe}_2$	$\text{NPh}_2$

chemical shifts  $\delta$  are reported in ppm relative to the residual solvent ( $\text{CHCl}_3$ ). The coupling constants  $J$  are given in Hz. In the  $^1\text{H}$  NMR spectra, the following abbreviations are used to describe the peak patterns: s (singlet), d (doublet), dd (doublet of doublet), t (triplet), m (multiplet). In the  $^{13}\text{C}$  NMR spectra, the nature of the carbons (C, CH,  $\text{CH}_2$  or  $\text{CH}_3$ ) was determined by performing a JMOD experiment. Melting points ( $^\circ\text{C}$ ) were measured on a Kofler hot-stage with a precision of  $2^\circ$  ( $\pm 2^\circ\text{C}$ ). High-resolution mass analyses were performed at the "Centre Régional de Mesures Physiques de l'Ouest" (CRMPO, University of Rennes1) using a Bruker MicroTOF-Q II apparatus. Analytical thin layer chromatographies (TLC) were performed on silica gel plates (Merck 60F254) and compounds



**Chart 2.** Structure of studied chromophores 1–8.

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