

**Microwave Assisted, Catalyst Free One-Pot Green Synthesis and Aggregation-Induced Emission Study of (*E*)-3-(4-hydroxy-3-methoxyphenyl)-2-(1*H*-tetrazol-5-yl) acrylonitrile**

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**Abstract**

Microwave assist green and effective synthesis of (*E*)-3-(4-hydroxy-3-methoxyphenyl)-2-(1*H*-tetrazol-5-yl) acrylonitrile derivative by Knoevenagel condensation and chemo selective facile intermolecular [2+3] cycloaddition between an azide and a nitrile group in presence of water as a solvent with excellent yields. This approach offers quick purification without using chromatography. Under microwave irradiation, [2+3] cycloaddition has the advantages of clean and straightforward process, mild temperatures, and little environmental effect. The synthetic material performed well in experiments of aggregation-induced emission. Synthesized compound was characterized by NMR, LCMS and FT-IR spectral studies.

## 1.Introduction

Microwave-assisted organic synthesis is regarded as a "green" method, owing to the fact that a variety of organic reactions can be carried out without the use of solvents.<sup>1,2</sup> Microwaves have been employed as a new procedure for combinatorial chemistry in recent years,<sup>3,4</sup> with the goal of lowering reaction time, eliminating side products, boosting product yield, and simplifying reaction pathways.<sup>5</sup> In combinatorial synthetic organic chemistry, multicomponent reactions are crucial. Great atom economy and the highest efficiency compared to traditional chemical reactions are MCRs' main advantages.<sup>6,7</sup> Tetrazoles are becoming increasingly popular as metabolically stable surrogates for carboxylic acid groups, as precursors to a wide range of nitrogen-containing heterocycles, and as acceptable lipophilic spacers in medicines.<sup>8,9</sup> In recent years, aggregation-induced emission (AIE),<sup>10</sup> which provides a new mechanism for researchers to investigate new types of luminogens, has piqued scientific curiosity.<sup>11,12</sup> The ability to emit light is a unique characteristic of luminescent materials with AIE.<sup>13,14,15</sup> Research into optical-conjugated organic composite materials<sup>1</sup> has received a lot of attention due to their potential applications in organic light-emitting diodes (OLEDs),<sup>16</sup> cellular imaging,<sup>17</sup> detection of micro environmental changes,<sup>18</sup> solar energy conversion,<sup>19</sup> organic lasers,<sup>20</sup> optical data storage media,<sup>21</sup> field-effect transistors (FETs),<sup>22</sup> and other fields.<sup>23,24</sup> It is known as concentration quenching or aggregation-caused quenching<sup>25,26</sup> when the emissions of many traditional organic fluorophores with large delocalized conjugated moieties diminish at high concentrations or in aggregated forms (ACQ).<sup>27</sup> Organic compounds exhibiting solid state fluorescence are still uncommon among the several ACQ molecules,<sup>28</sup> and this is thought to be due to the fact that the aggregates' excited states frequently decay via non-radiative pathways due to strong intermolecular vibronic interactions.<sup>29</sup> The family of AIE molecules and their uses has exploded since Tong reported a series of salicylaldehyde azine derivatives that belong to the excited state intramolecular proton transfer (ESIPT) compounds.<sup>30</sup> Because of their huge stokes shift, chromophores with ESIPT often exhibit high quantum effectiveness at concentrated states, reducing self-quenching in fluorescence significantly. AIE is influenced by hydrogen bonds, -stacking, and other monovalent interactions.<sup>31</sup> Molecules containing ESIPT can self-assemble into aggregates of varying colours, structures, and fluorescence proficiency, resulting in color-

tunable morphology controlled nanostructures.<sup>32</sup> By this inspiration on AIE we report the synthesis of interesting tetrazole derivative by Knoevenagel condensation and regioselective facile intermolecular [2+3] cycloaddition between an azide and a nitrile group in water under microwave irradiation as an eco-friendly benign protocol with aggregation induced emission property.

## 2. Materials and method

### 2.1 Materials

All the chemicals were purchased from Aldrich, Alfa-Aesar and local companies used as received. The solvents were purified and dried as per the literature methods prior to the use. The target molecules were purified by recrystallization technique choosing appropriate mixture of solvents.

### 2.2 Instruments

Melting points were determined with sigma melting point apparatus. <sup>1</sup>H NMR spectra were recorded using Bruker (300MHz) spectrometer. For the <sup>1</sup>H NMR spectra, the chemical shifts are reported in ppm relative to SiMe<sub>4</sub>(TMS) as an internal standard and coupling constants are presented in Hz. ESI-MS analysis was performed in the negative ion mode on a liquid chromatography–ion trap mass spectrometer (LCQ Fleet, Thermo Fisher Instruments Limited, US). All fluorescence measurements were made on a Fluoromax-4 Spectrofluorometer (HORIBA JOBIN YVON) with excitation slit set at 5.0 nm band pass and emission at 5.0 nm band pass in 1 cm × 1 cm quartz cell. UV–vis absorption spectra were recorded using JASCO-spectra manager (V-630) in 1 cm path length quartz cuvette with a volume of 2 mL at room temperature.

## 3. General Procedure

### 3.1. Synthesis of (*E*)-3-(4-hydroxy-3-methoxyphenyl)-2-(1*H*-tetrazol-5-yl) acrylonitrile

A mixture of carbonyl compounds (1 mmol), malononitrile(1mmol), and sodium azide(2 mmol) in H<sub>2</sub>O was irradiated at 100°C for 2minutes. After completion of reaction the mixture

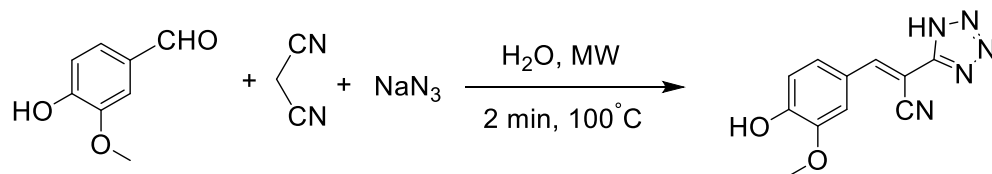
is added with 20 ml of 2N HCl with vigorous stirring causes the tetrazole to precipitate. The precipitate was filtered and recrystallized with absolute ethanol give pure product.

### 3.1.1. (E)-3-(4-hydroxy-3-methoxyphenyl)-2-(1H-tetrazol-5-yl) acrylonitrile

Yellow solid, yield: 90%, mp 195-197°C; IR,  $\nu$  max (KBr, cm<sup>-1</sup>): 3448.54 (NH), 2220.14 (C≡N), 1566.25 (N=N), 3394.83 (OH), 1026.16 (C-O). <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 7.60(s, 2H,ene & ArH), 7.32(d, *J*=9.0Hz, 1H, ArH), 6.80(d, *J*=9.0Hz, 1H, ArH), 4.48(s, 1H, NH), <sup>13</sup>C NMR (75 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 159.42, 152.29, 147.18, 128.99, 124.04, 115.35, 114.50, 113.72, 110.64, 78.06, 56.29.

## 4. Results and discussion

In the present investigation, a mixture of carbonyl compound (1 mmol), malononitrile (1 mmol) and sodium azide (2 mmol) in H<sub>2</sub>O (5 mL) was irradiated in microwave for two minutes, after completion of the reaction, as indicated by TLC, the reaction mixture was filtered. To the filtrate 30 mL of 2N HCl was added with vigorous stirring causing the tetrazole to precipitate. The precipitate was filtered and dried in a drying oven to furnish the tetrazole with good yield. (Scheme 1)

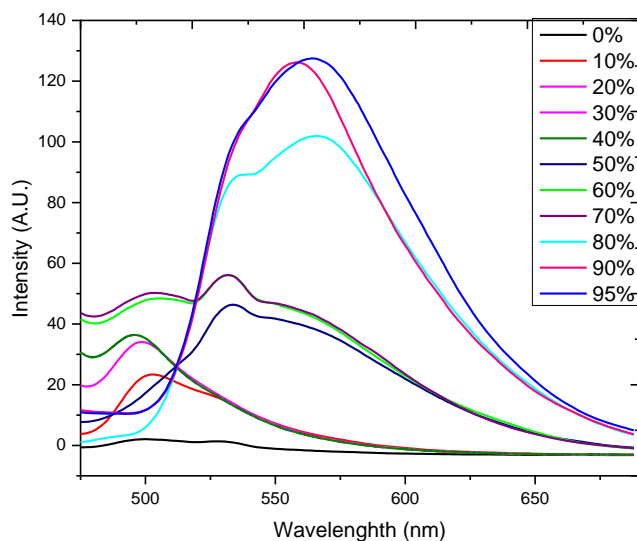


**Scheme 1.** Synthesis of (E)-3-(4-hydroxy-3-methoxyphenyl)-2-(1H-tetrazol-5-yl) acrylonitrile

The reaction is preceded very clearly under microwave irradiation with short reaction duration. This report describes the synthesis of 5-substituted 1H tetrazoles via region selective intramolecular [2+3] cycloaddition under microwave irradiation in short time duration. The catalyst 5 free reactions carried out under microwave irradiation are safe and time saving, on toxic to environment and inexpensive. The synthesized compound was confirmed by NMR, IR and mass spectral studies. The spectral data reported in the experimental procedure section.

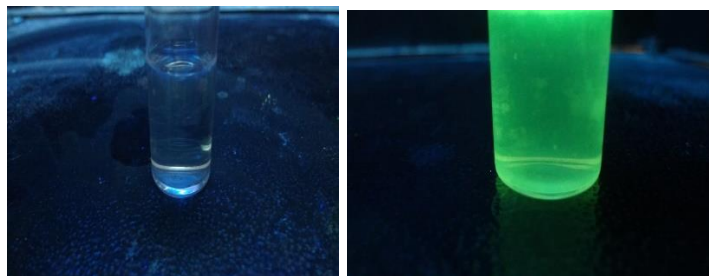
#### 4.1. Optical properties

Different amounts of poor solvent ( $H_2O$ ) was added to the solution of compound probe to study the AIE characteristics. We changed the water fractions ( $f_w$ ) from 0% to 95% and monitored the fluorescent spectra (FL) with the excitation wavelength of 475nm. PL spectra of compound of THF solution recorded under ultraviolet illumination and photo luminescent spectrum, a very small PL signals are recorded up to 40% of water fraction ( $f_w$ ) moreover the emission occurs tremendously up at 80% of water. Further addition of water fraction increases the fluorescent intensity up to 95%. It was shown in **figure 1**.

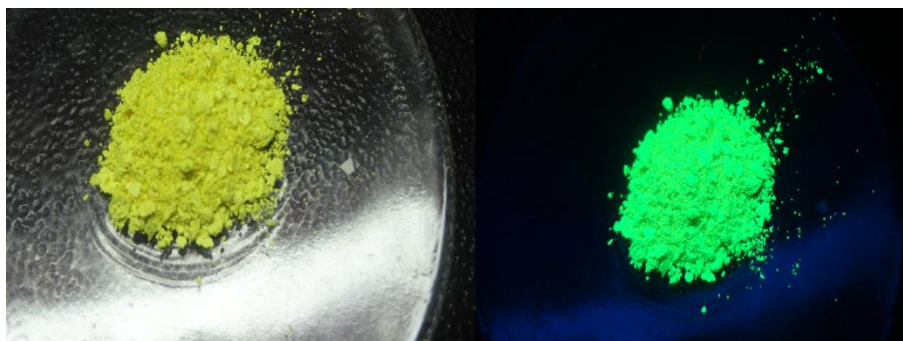


**Figure .1** Emission spectrum of 3b ( $1 \times 10^{-5}$ ) in a) THF- $H_2O$  (v/v)

Development of fluorescent intensity by the gradual addition of water fractions can be viewed by naked eye under long UV light shown in **figure 2**. Similarly the solid state photo emission of compound is shown in the **figure 3**.



**Figure 2. Photograph of compound h at 0% and 98% H<sub>2</sub>O fraction in long UV-light**



**Figure 3. Photograph of compound under visible and long UV light**

## 5. Conclusion:

We have developed a Microwave assisted one-pot green synthesis of 1*H*-tetrazoles via aqueous catalyst free multi-component Domino Knoevenagel condensation and [2+3] cycloaddition reactions. This cycloaddition offered products in better yields with higher regioselectivity using water as solvent. 1*H*-tetrazole derivatives with electron donor substitutions to change the degree of  $\pi$  conjugation cause the AIE was confirmed by solid state emission and emission spectral studies.

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