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### Nano BF<sub>3</sub>.SiO<sub>2</sub>: a green heterogeneous solid acid for synthesis of formazan

### dyes under solvent-free condition

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**Abstract:** A solvent-free, efficient and rapid approach for synthesis of formazan dyes was developed by diazotization of aromatic amines with NaNO<sub>2</sub>, nano silica-supported boron trifluoride (nano BF<sub>3</sub>.SiO<sub>2</sub>), then diazo coupling with aldehyde phenylhydrazones by grinding method at room temperature. This study aimed to overcome the limitations and drawbacks of the previous reported methods such as: low temperature, using corrosive and toxic acids and solvents, using buffer solutions, instability of aryl diazonium salts, modest yields, and long reaction times.

Keywords: Formazan; Nano BF<sub>3</sub>.SiO<sub>2</sub>; Solid acid; Solvent-free; Diazotization

#### 1. Introduction

Formazans are coloured compounds due to their  $\pi$ - $\pi$ \* electronic transitions and form a distinct class of organic dyes with certain properties. These compounds have received much attention for their applications in analytical chemistry [1,2], biological applications [3,4] and as dyestuffs [5]. Their antiviral [6,7], antimicrobial [8,9], anti-inflammatory, analgesic [10], antifungal [11], anticancer, anti-HIV [12], photochromic and thermochromic activities [13] are also of utmost importance. In recent years, the progress in the field of solvent-free reactions which are based on grinding has reached significance [14-19] due to

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their high efficiency and selectivity, operational simplicity, mild reaction conditions, reduction in waste and benefit to the industry as well as the environment. As synthesis of formazan dyes requires some special conditions such as low temperature and concentrated liquid acids (for synthesis of aryl diazonium salts) [20-31], in addition to high costs, it leads to corrosion of reactors and equipments, too. However, the main limitation of such synthetic processes is environmental incompatibility. Nowadays, solid acids have resolved these problems and improved activity and selectivity [32-46]. In this regard, nano structure solid acids exhibit higher activity and selectivity than their corresponding bulk materials due to their large surface to volume ratio [47-50]. BF<sub>3</sub>.SiO<sub>2</sub> is an excellent proton source in terms of convenience, cheapness, ease of production, and insolubility in all organic solvents, so it can be used for the synthesis of many organic compounds [51-58]. On the other hand, nano BF<sub>3</sub>.SiO<sub>2</sub>, in addition to the mentioned properties, has high surface to volume ratio that makes the application to catalyze many chemical reactions [59-62].

So far, a lot has been known about numerous synthesized formazans and their structural, spectral features and reaction mechanisms of their formation [20-31]. Based on our knowledge, none of the reported syntheses of formazan derivatives were carried out by grinding under a solvent-free condition and in the presence of a solid acid. On the other hand, formazans have not gained widespread use in the industry because of their hard synthetic methods and modest yields. Thus, the development of novel and simple synthetic methods for the efficient preparation of formazans is an interesting challenge. All these facts have prompted us to employ a new and eco-friendly grinding methodology for the synthesis of formazan dyes in solvent-free environment at room temperature. The findings of this research may have implications for an effective synthesis on a larger scale in dyeing and medical industries.

#### 2. Experimental

### 2.1. Materials and apparatus

Chemicals and solvents were purchased from Merck Company. Commercial nano silica gel was prepared from Sigma-Aldrich Company. Transmission electronic microscopy (TEM) micrographs of nano silica gel

and nano BF<sub>3</sub>.SiO<sub>2</sub> were taken using a LEO 912 AB OMEGA instrument (Germany) with a LaB6 cathode and accelerating voltage of 100 kV. X-ray diffraction (XRD) patterns were acquired using a Philips Xpert MPD diffractometer equipped with a Cu K $\alpha$  anode ( $\lambda$ =1.54 A°) in the 2 $\theta$  range from 10 to 80°. Ultravioletvisible (UV–Vis) spectra of formazan dyes were taken by a double beam Perkin-Elmer 550S spectrophotometer in the range of 200-600 nm, using spectrophotometric grade ethanol as the blank. Fourier transform infrared (FT–IR) spectra were run on a Nicolet Magna 550 spectrometer. Proton nuclear magnetic resonance (<sup>1</sup>H NMR, 400 MHz) spectra were recorded on a Bruker DRX-400 Avance spectrometer. Tetramethyl silane (TMS) was used as an internal reference and deuterated chloroform (CDCl<sub>3</sub>) used as solvent. Melting points were obtained with a micro melting point apparatus (Electrothermal, Mk3) and are uncorrected.

### 2.2. Preparation of 15 mol % nano BF<sub>3</sub>.SiO<sub>2</sub>

Nano BF<sub>3</sub>.SiO<sub>2</sub> was easily prepared from nano silica gel and BF<sub>3</sub>.Et<sub>2</sub>O according to the literature [59]. In short, BF<sub>3</sub>.Et<sub>2</sub>O (2.65 mL) was added drop-wise to a slurry containing nano silica gel (7 g) and ethanol (30 mL, instead of chloroform). The mixture was stirred for 1h at room temperature. The resulted suspension was filtered to obtain the white solid named nano BF<sub>3</sub>.SiO<sub>2</sub> (15 mol %). The acidic capacity of nano BF<sub>3</sub>.SiO<sub>2</sub> was 2.07 mmol.g<sup>-1</sup> and determined *via* titration of 0.2 g of solid acid with standard solution of NaOH.

#### 2.3. Typical procedure for the synthesis of formazan derivatives (7a-s)

In order to synthesize aryl diazonium salts (2a-g), aromatic amines 1a-g (2 mmol) was ground with NaNO<sub>2</sub> (3 mmol) and 15 mol % nano BF<sub>3</sub>.SiO<sub>2</sub> (0.4 g) in a mortar with a pestle. Aldehyde phenylhydrazones (5a-k) were also synthesized from solvent-free grinding of phenylhydrazine 3 (2 mmol) and aldehyde derivatives 4a-k (2 mmol) in another mortar. The excellent yields of aldehyde phenylhydrazone derivatives caused no need to more purification. In the next step, synthesized aryl

diazonium salt was added to a ground mixture of aldehyde phenylhydrazone and NaOH to reach pH: 7 or more. The residual acidic sites on nano BF<sub>3</sub>.SiO<sub>2</sub> in diazotization step can partially decompose aldehyde phenylhydrazones to the starting materials in non- basic medium. So, NaOH amount should be sufficient and fully ground with aldehyde phenylhydrazones, before adding of aryl diazonium salts. Medium pH of 10-12 is suitable for formazan formation. If the mixed NaOH amount with aldehyde phenylhydrazone before diazo coupling is not sufficient to achieve pH of 10-12, we can re-add NaOH after coupling of aldehyde phenylhydrazone with diazonium salt. Anyway, the mixture was ground at room temperature for 1-2 min. After completion of the reaction (TLC), the mixture was washed by distilled water (50 mL) for naturalization of additional NaOH and then by acetone (30 mL) for separation of nano BF<sub>3</sub>.SiO<sub>2</sub>. Evaporation of the solvent followed by flash column chromatography (in the case of compounds **7d**, **7e** and **7j**, washing by hot ethanol was performed instead of flash column chromatography) that gave formazans in high yields. The structures of formazan dyes were characterized by spectroscopic methods such as UV–Vis, FT–IR and <sup>1</sup>H NMR.

#### 2.3.1. Spectroscopic data for some selected formazans

**2.3.3.1** 3-(3-Methoxyphenyl)-1,5-diphenylformazan (7d): Bright red colour; UV–Vis (ethanol)  $\lambda_{max1}$  ( $\pi$ – $\pi^*$ ): 484 nm,  $\lambda_{max2}$  (n– $\pi^*$ ): 323 nm; FT–IR (KBr) v (cm<sup>-1</sup>): 2924 (N–H), 1599 (C=C), 1511 (C=N), 1452 (N=N), 1032-1242 (C–O); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 15.51 (1H, s, NH), 6.93-7.77 (14H, m, CH), 3.92 (3H, s, OCH<sub>3</sub>).

**2.3.3.2** *1-(2-Chlorophenyl)-3-(3-nitrophenyl)-5-phenylformazan (7j):* Red colour; UV–Vis (ethanol) λ<sub>max1</sub> (π–π\*): 470 nm, λ<sub>max2</sub> (n–π\*): 341 nm; FT–IR (KBr) *v* (cm<sup>-1</sup>): 2925 (N–H), 1589 (C=C), 1522 (C=N), 1452 (N=N), 1348 (NO<sub>2</sub>), 675 (C–Cl); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ: 15.67 (1H, s, NH), 7.16-9.01 (13H, m, CH).

**2.3.3.3** *3-(4-Pyridyl)-1,5-diphenylformazan (7q):* Red-brown colour; UV–Vis (ethanol)  $\lambda_{max1}$  ( $\pi$ – $\pi^*$ ): 470 nm,  $\lambda_{max2}$  (n– $\pi^*$ ): 327 nm; FT–IR (KBr) v (cm<sup>-1</sup>): 2924 (N–H), 1636, 1402 (C=C), 1594, 1499 (C=N), 1453 (N=N); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 15.80 (1H, s, NH), 7.30-8.65 (14H, m, CH).

**2.3.3.4** *3-Propyl-1,5-diphenylformazan (7r):* Red colour; UV–Vis (ethanol)  $\lambda_{max1}$  ( $\pi$ – $\pi$ \*): 416 nm,  $\lambda_{max2}$  (n– $\pi$ \*): 325 nm; FT–IR (KBr) v (cm<sup>-1</sup>): 2963 (N–H), 1626 (C=C), 1491 (C=N), 1460 (N=N); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 10.84 (1H, s, NH), 7.20-8.04 (10H, m, CH), 2.76 (2H, dt, CH), 1.67 (2H, dm, CH), 1.01 (3H, t, CH<sub>3</sub>).

#### 3. Results and discussion

This research was performed in two stages. Initially, nano  $BF_3.SiO_2$  was prepared through stirring a mixture of nano silica gel and  $BF_3.Et_2O$  in ethanol. The size and structure of nano particles were identified by TEM and XRD. In the second stage, formazan derivatives with electron-withdrawing substituents as well as those with electron-donating groups were synthesized by mixing aryl diazonium salts prepared in the presence of nano  $BF_3.SiO_2$  and basic aldehyde phenylhydrazones at room temperature.

#### 3.1. Nano BF<sub>3</sub>.SiO<sub>2</sub> characterization

The final structure of  $BF_3.SiO_2$  (Scheme 1) [62] and its nano particles morphology determined by Scanning electron microscopy (SEM) images [59] have been previously reported. Herein, the properties of  $BF_3.SiO_2$  nano particles were characterized by two other techniques including TEM and XRD.



Scheme 1. The structure of BF<sub>3</sub>.SiO<sub>2</sub>.

Inspection of the TEM images in Figure 1 indicated involvement of nano particles with an average size distribution of 20 nm for nano silica gel and 25 nm for nano BF<sub>3</sub>.SiO<sub>2</sub>.



Figure 1. TEM micrographs of a) nano silica gel, b) nano BF<sub>3</sub>.SiO<sub>2</sub>.

Nano silica gel XRD pattern displayed a broad strong peak in 20 value of 21.8024 with full width at half maximum (FWHM) equal to 0.1771. Nano  $BF_3.SiO_2$  XRD pattern showed three main sharp peaks in 28.4516 with FWHM of 0.1771, 27.9718 with FWHM of 0.2952 and 14.5404 with FWHM of 0.2362. In addition, there was a short broad peak in 21.9895 with FWHM of 0.1771 related to amorphous nano silica gel. The broadness of peak in Figure 2a verified the amorphous nature of nano silica gel and peaks sharpness in Figure 2b represented the crystal-like structure of nano  $BF_3.SiO_2$ .



Figure 2. XRD patterns of a) nano silica gel, b) nano BF<sub>3</sub>.SiO<sub>2</sub>.

#### 3.2. Synthesis and characterization of formazan dyes

The most common synthetic route to the formazan compounds involves coupling of aryl diazonium salts with aldehyde phenylhydrazones in basic medium. As synthesis of formazans is a three-step reaction and highly time-consuming with modest yields which requires special conditions such as low temperature, using buffer solutions to adjust pH and liquid acids to synthesize diazonium salts [20-31], we tried to solve these problems by development a green and facile procedure for the synthesis of formazans.

At first, the efficiency of nano  $BF_3.SiO_2$  in diazotization reaction, followed by diazo coupling with aldehyde phenylhydrazones, was explored *via* a model reaction. 4-Chloro aniline (1d) was selected as a model substrate and screened for a range of parameters such as effect of various solid acids, stability of diazonium salt (2d) at room temperature, reaction time of diazotization, and yield of resulted formazan (7h). The observed results are summarized in Table 1.

Solid acids such as silica phosphoric acid and silica chloride gave the formazan with yields of 43% and 48%, respectively (Table 1, entries 1 and 2). The stability of aryl diazonium salt supported on above mentioned acids was maximum 2 days. Silica gel and BF<sub>3</sub>.Et<sub>2</sub>O sources were also tested individually. There was no reaction neither in the presence of silica gel nor BF<sub>3</sub>.Et<sub>2</sub>O (Table 1, entries 3 and 4), while BF<sub>3</sub>.SiO<sub>2</sub> afforded an improved yield of 63% for formazan (Table 1, entry 5). These results clearly indicated that the

7

presence of Brønsted acid sites on the solid acid surface is essential factor for promoting diazotization reactions. Also, the rate of diazotization in the presence of BF<sub>3</sub>.SiO<sub>2</sub> was much higher than silica phosphoric acid and silica chloride.

In another comparative study (Table 1, entries 6-10), the effect of nano silica gel loading by  $BF_3.Et_2O$  on the acidic performance of nano  $BF_3.SiO_2$  was investigated. Although the time of diazotization and the stability of diazonium salt supported on nano  $BF_3.SiO_2$  with different loadings in the same conditions were approximately identical, but 15 mol % nano  $BF_3.SiO_2$  resulted in the highest yield of formazan. In conclusion, 15 mol % nano  $BF_3.SiO_2$  is the most ideal solid acid for synthesis of formazans among those listed in Table 1.

<b>Table 1.</b> Comparison of efficiency of various solid acids in synthesis of formazan dyes.					
	NH <sub>2</sub> NH <sub>2</sub> Cl	$\begin{array}{c} aNO_2 \\ \hline id acid \\ nt-free, r.t. \\ Cl \end{array}$	anion		
	1a-g	2a-g		<b>X7• 1 1</b> 8	
Entry	Solid acid (mol %)	Stability at r.t.	diazotization	Yield" (%)	
1	Silica phosphoric acid (20)	$\sim 2 \text{ day}$	35 min	43	
2	Silica chloride (20)	$\sim 2 \text{ day}$	30 min	48	
3	Silica gel		No reaction		
4	BF <sub>3</sub> .Et <sub>2</sub> O		No reaction		
5	BF <sub>3</sub> .SiO <sub>2</sub> (20)	$\sim 25$ month	1 min	63	
6	Nano $BF_3$ .SiO <sub>2</sub> (10)	$\sim 30$ month	13 sec	75	
7	Nano $BF_3$ .SiO <sub>2</sub> (15)	$\sim 30$ month	10 sec	81	
8	Nano BF <sub>3</sub> .SiO <sub>2</sub> (20)	$\sim 30$ month	10 sec	77	

9	Nano BF <sub>3</sub> .SiO <sub>2</sub> (25)	$\sim 30 \text{ month}$	10 sec	73			
10	Nano $BF_3.SiO_2$ (30)	$\sim 30$ month	10 sec	70			
<sup>a</sup> The yields	refer to the isolated pure formazan (7	7h) after adding fresh diazoni	um salt (2d) into basic	benzaldehyde			
phenylhydrazone (5c).							

To explore the reasons for stability of diazonium salt supported on nano  $BF_3.SiO_2$ , its FT–IR spectrum was studied (Figure 3). In this spectrum, the ethanolic OH and existing moisture in nano silica gel and  $BF_3.Et_2O$  caused a broad O–H stretching band at wavenumber of 3221 cm<sup>-1</sup>. The appearance of the band at 2278 cm<sup>-1</sup> clearly demonstrated N=N stretching vibration and verified the formation of diazonium salt. The absorption bands of B–O and Si–O vibrations were observed at 1377 and 1090 cm<sup>-1</sup>, respectively. The absorption band of B–F was hidden under Si–O band. Aromatic C–H bending vibrations and C–Cl stretching band were revealed at 731 cm<sup>-1</sup> and 652 cm<sup>-1</sup>.



Figure 3. FT-IR spectrum of 4-chlorophenyl diazonium salt (2d) supported on nano BF<sub>3</sub>.SiO<sub>2</sub>.

According to this information, the structure of diazonium salts supported on nano BF<sub>3</sub>.SiO<sub>2</sub> was guessed. Scheme 2 reveals that in this probable structure, aryl diazonium cations are located on the surface of negatively charged particles called nano silica triflouroborate. So, the presence of bulky anions and favorable charge–charge interactions between nitrogen and boron atoms are the possible reasons of unusual

stability of these salts. In addition, the small size of nano particles and large surface to volume ratio in nano  $BF_3.SiO_2$  can be the reason of greater stability of diazonium salt in comparison to that supported on the bulk  $BF_3.SiO_2$ .



Scheme 2. The structure of aryl diazonium salt supported on nano BF<sub>3</sub>.SiO<sub>2</sub>.

On the other hand, synthesis of aldehyde phenylhydrazone derivatives (**5a-k**) was carried out by a simple grinding without any use of solvent and acidic catalyst at room temperature. It is expected that aldehyde derivatives (**4a-k**) with electron-withdrawing substituent as a strong electrophile should be more reactive than those containing electron-donating groups. But, as shown in Table 2, the reaction was done so rapidly that the substituent type could not influence the reaction time and even yield of aldehyde phenylhydrazones. Totally, excellent yields and purity, short reaction times, solvent- and catalyst-free medium and practically of the procedure at room temperature were the main advantages of this new method for the synthesis of aldehyde phenylhydrazone derivatives.



**Table 2.** Condensation of phenylhydrazine with various aldehydes for the synthesis of aldehyde phenylhydrazones.

4-OCH <sub>3</sub> -phenyl	4a	5a	8	98
4-CH <sub>3</sub> -phenyl	4b	5b	10	97
Phenyl	4c	5c	12	98
3-OCH <sub>3</sub> -phenyl	4d	5d	19	96
3-NO <sub>2</sub> -phenyl	4e	5e	40	97
4-NO <sub>2</sub> -phenyl	4f	5f	17	98
2-Furyl	4g	5g	11	97
2-Thienyl	4h	5h	8	96
4-Pyridyl	4i	5i	6	98
Propyl	4j	5j	23	95
1-Phenylethyl	4k	5k	18	96
<sup>a</sup> Isolated yield		NO		

Diazo coupling of aldehyde phenylhydrazones (**5a-k**) with diazonium salts (**2a-g**) in basic medium was the final step of formazan dyes (**7a-s**) formation.

Formazans are usually synthesized around 0-5 °C [20-31], because temperatures above 5 °C causes decomposition of diazonim salts and conversion to side products before coupling with aldehyde phenylhydrazones and formation of formazan dyes. This is the main reason for the modest yield of formazans. To overcome this limitation, we decided to use nano BF<sub>3</sub>.SiO<sub>2</sub> as a solid acid to be able to do the reaction at room temperature. In conclusion, the stability of diazonium salts supported on nano BF<sub>3</sub>.SiO<sub>2</sub> at room temperature, significantly increased the efficiency of formazans synthesis. Final results of reaction times and yields are clarified in Table 3.

**Table 3.** Diazo coupling of aldehyde phenylhydrazones with diazonium salts for the synthesis of formazan derivatives.



		Diazonium	Aldehyde		Yield <sup>a</sup>	Mp.
R	$\mathbf{R}^{1}$	salt	phenylhydrazone	Formazan	(%)	Found/Reported
TT	Dhamal	2.	5 c	7.	0.1	172-174/
п	rnenyi	Za	30	7 a	01	172-173 [23]
Ц	4 OCH phonyl	2.	50	71	0.2	171-173/
п	4-OCH <sub>3</sub> -pilenyi	28	Ja	10	83	170-171 [23]
TT	4 CII mhanvil	20	5 h	7	85	153-155/
п	4-CH <sub>3</sub> -phenyl	28	50	70		154-157 [23]
TT	2 OCU shared	2-	51	7.1	0.1	159-161/
Н	3-OCH <sub>3</sub> -pnenyl	Za	50	/d	81	160-162 [23]
ц	4 NO phonyl	20	5 f	70	80	196-198/
11	4-NO <sub>2</sub> -phenyi	2a	51	70		196-198 [24]
A CH	Dhonyl	2h	50	7f	84	154-156/
4 <b>-</b> CH <sub>3</sub>	Flienyr	20	50	/1	04	154 [30]
1 Br	Dhanyl	20	50	7~	83	188-190/
4-DI	Flienyi	20	30	/g		189 [30]
4 (7)		1 01	-	71	01	117-119/
4 <b>-</b> Cl	Pnenyl	2 <b>d</b>	50	/ <b>h</b>	81	119 [30]
4 D=		nhonyl 2a	5	7:	95	176-178/
4 <b>-</b> BI	5-mO <sub>2</sub> -pnenyl	20	36	/1	00	176.5-177.5 [27]

2-Cl	3-NO <sub>2</sub> -phenyl	2e	5e	7j	78	174-176/	
						175.5-176.5 [27]	
4-Cl	3-NO <sub>2</sub> -phenyl	2d	5e	7k	80	175-177/	
						177.5-179 [27]	
4-OCH <sub>3</sub>	4-OCH <sub>3</sub> -phenyl	2f	5a	71	87	187-189/	
						187-188 [27]	
4-CH <sub>3</sub>	4-OCH <sub>3</sub> -phenyl	2b	5a	7m	84	242-244/	
						242-243 [27]	
3-OCH <sub>3</sub>	4-OCH <sub>3</sub> -phenyl	2g	5a	7n	86	204-206/	
						205-206.5 [27]	
Н	2-Furyl	2a	5g	70	86	116-118/	
						118 [20]	
Н	2-Thienyl	2a	5h	7p	83	138-140/	
				_		138 [25]	
Н	4-Pyridyl	4-Pyridyl 2a	5i	7g	88	191-193/	
						192 [26]	
Н	Propyl	2a	5j	7r	84	86-88	
Н	1-Phenylethyl	I-Phenylethyl 2a	5k	7s	82	82-84/	
						81-82 [21]	
<sup>a</sup> Overall isolated yield after column chromatography							

After purification of formazans, their structures were determined by spectroscopic methods. The FT–IR spectra of formazan derivatives showed characteristic absorption bands at 2921-3066 (N–H), 1586-1638 (aromatic C=C), 1487-1524 (C=N) and 1443-1487 (N=N) cm<sup>-1</sup>. Based on <sup>1</sup>H NMR spectroscopic data, all products synthesized from aromatic or heteroaromatic aldehydes (**7a-q**) exhibited a singlet at 14.28-15.80 ppm for NH proton. Two formazans prepared from aliphatic aldehydes (**7r**, **7s**) showed NH proton at higher

fields (10.84, 11.60 ppm). Also, formazans (**7a-s**) indicated signals at 6.53-9.01 for aromatic protons dependent on substituent effect. According to Scheme 3, formazan dyes have two tautomeric forms that quickly interconvert. The participation of the NH proton in rapid intramolecular tautomeric conversions in formazans has been demonstrated by means of <sup>1</sup>H NMR spectroscopy with isotopically enriched samples [64,65].



Scheme 3. Tautomerization in formazan via intramolecular proton transfer.

According to the proposed mechanism in Scheme 4, for full conversion of intermediate (6) to formazan, medium pH should be changed from 7 to 10-12. In order to control and fixate the medium pH, different buffer solutions have been used in the literature [20-31], while in our research by using grinding procedure in the absence of solvent, there is no need to buffer solution for pH adjustment. Hence, one of the significant results of our methodology compared to previous methods, there was no requirement for buffering solution to adjust medium pH.



Scheme 4. The plausible mechanism of formazan formation.

Overall, the advantages of our methodology in comparison to the previous reported methods [20-31] included rapid and solvent-free synthesis of aryl diazonium salts in high conversion at room temperature, long-term stability of aryl diazonium salts supported on nano BF<sub>3</sub>.SiO<sub>2</sub>, not use of toxic solvents, acid catalysts, and short reaction times in synthesis of aldehyde phenylhydrazones, no need to more purification of aldehyde phenylhydrazones because of excellent yields, eco-friendly synthesis of formazan dyes at room temperature, no need to solvent, buffer solution and control of temperature below 5 °C, short reaction times and high yields using grinding methodology.

Finally, the full consumed time for all three steps was less of 5 minutes and the yields of formazan derivatives obtained between 78-88%, regardless of the type and position of substituents.

#### 4. Conclusion

A green and highly effective methodology for the synthesis of formazan derivatives (**7a-s**) was developed by solvent-free diazo coupling of diazonium salts (**2a-g**) with basic aldehyde phenylhydrazones (**5a-k**) at room temperature. Using nano BF<sub>3</sub>.SiO<sub>2</sub> in diazotization step and solvent-free procedure caused the experimental simplicity, compatibility with environment, no use of special conditions such as buffer solution and low temperature, efficient yields, short reaction times, and made this procedure attractive to synthesize a variety of these dyes. The structure and stability of diazonium salt supported on nano BF<sub>3</sub>.SiO<sub>2</sub> were studied, too.

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Highlights:

Nano  $BF_3$ .SiO<sub>2</sub> efficiency in synthesis of aryl diazonium salts and their stability. Solvent- and catalyst-free methodology for synthesis of aldehyde phenylhydrazones. Room temperature synthesis of formazans *via* coupling of above mentioned reactants. No need to buffer solution, solvent, and liquid acid for synthesis of formazans.

