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# On water synthesis of pyran-chromenes *via* multicomponent reaction catalyzed by fluorescent *t*-ZrO<sub>2</sub> nanoparticles

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Here, we have demonstrated fluorescent tetragonal ZrO<sub>2</sub> nanoparticles (*t*-ZrO<sub>2</sub> NPs) catalyzed green one-pot multicomponent protocol for the synthesis of diverse pyran fused chromene analogous such as 2-aminochromenes, dihydropyrano[3,2-*c*]chromene, chromeno[4,3-*b*]chromene derivatives in water. The rate of the reactions and yields of the products have increased significantly in water. In addition, *t*-ZrO<sub>2</sub> NPs showed higher reactivity than monoclinic ZrO<sub>2</sub> NPs. The *t*-ZrO<sub>2</sub> NPs were recycled and the gradual decrease in yield of the product using recycled catalyst could be possibly due to the decrease in zrconium content associated with decrease in oxygen vacancies which were evident from fluorescence and atomic absorption studies. However, the tetragonal phase of the catalyst remained intact even at 10<sup>th</sup> cycle.

#### Introduction

The development of green alternative multicomponent reactions (MCRs) has attracted much attention as these reactions produced important biological scaffolds<sup>1</sup> and various designers as well as marketed drugs<sup>2</sup> in en environmentfriendly pathway. The reaction parameters such as, solvent, catalyst etc. of a MCR determines the selectivity, versatility and environmental acceptability. Water is the greenest solvent among all and consequently it has been widely used as reaction media for elementary organic transformations<sup>3a-e</sup> as well as in MCRs.<sup>4</sup> It has also been reported that water accelerates the rate of the reaction due to its high polarity, hydrogen bonding in the transition state and hydro-phobic effect.<sup>3,4</sup> On other side, catalyst also plays a crucial role in determining the yield and selectivity. Thus, synthesis of bioactive scaffolds via MCR using a mild and inexpensive catalyst in green solvent like water is appreciated.

Recently, heterogeneous nano-catalysis have attracted much interest due to their unique properties of large and reactive surface areas, selective reactivity, reusability, greener reactions reaction conditions<sup>5</sup> and providing advantages of both homogeneous and heterogeneous catalysis.<sup>6</sup> Very recently, metal oxide nanoparticles (NPs) have been widely applied as catalysts because of their dual Lewis acid and Lewis base nature and red-ox properties on the surface.<sup>7</sup> As a part of our continuous interest in catalysis by metal oxide

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nanoparticles,<sup>8</sup> we have reported excellent catalytic activity of  $ZrO_2$  NPs in MCRs leading pyrano[2,3-c]pyrazoles and bezylpyrazolyl coumarins.<sup>81</sup> In this paper, we have explored the catalytic activity of  $ZrO_2$  NPs in one-pot MCRs leading various bioactive pyran fused chromene scaffolds namely, 2-aminochromenes, dihydropyrano[3,2-c]chromenes and chromeno[4,3-b]chromenes (scheme 1).



Scheme 1  $ZrO_2$  NPs catalyzed synthesis of functionalized pyran annulated chromene analogues.

#### **Results & Discussion**

At first we have tried to synthesize pyran fused 2aminochromene derivatives using ZrO<sub>2</sub> NPs. These moieties exhibited various biological and pharmaceutical activites<sup>9</sup> such as antimicrobial,<sup>10a</sup> mutagenicity,<sup>10b</sup> antiviral,<sup>10c</sup> antiproliferative,<sup>10d</sup> sex pheromonal,<sup>10e</sup> antitumor,<sup>10f</sup> central

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<sup>+</sup>Electronic Supplementary Information (ESI) available: [details of experimental procedure for preparation of catalysts and synthesis of pyran fused chromenes, supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

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nervous system activity<sup>10g</sup> etc. agent and influenza virus sialidases inhibitors.<sup>10h</sup> Some selected bioactive 2aminochromene derivatives are shown in Fig. 1. In addition, these moieties are present as essential component in many natural products and used as valuable constituent for the fabrication of commercially important products.<sup>11</sup>



Typically, these moieties have been synthesized *via* three components condensation reactions of aryl aldehyde, malononitrile and activated phenols using a catalyst or reagent. However, most of them utilized homogeneous<sup>12:13</sup> catalyst/reagent such as toxic nitrogen containing bases like piperidine/triethylamine,<sup>12</sup> basic reagents *e.g.* ammonium salts,<sup>13a</sup> NaOH,<sup>13b</sup> K<sub>2</sub>CO<sub>3</sub>,<sup>13c</sup> I<sub>2</sub>/K<sub>2</sub>CO<sub>3</sub>,<sup>13d</sup> or Lewis acids (e.g. TiCl<sub>4</sub>,<sup>13e</sup> InCl<sub>3</sub>,<sup>13f</sup>) and few have used heterogeneous catalyst.<sup>14</sup> Moreover, most of the methods utilized hazardous organic solvents *e.g.* DMF or acetonitrile.<sup>12</sup> Thus, the synthesis of 2-aminochromenes using a mild catalyst in green solvent like water is in demand. Here, we have observed remarkable catalytic activity of ZrO<sub>2</sub> NPs in one-pot three component reactions leading to 2-aminochromenes in water.

Initially, we have prepared  $ZrO_2$  NPs via sol-gel method by the condensation of  $ZrO_2Cl_2.8H_2O$  under basic medium<sup>8i</sup> (See †ESI 1 for details) and the material was analyzed by different analytical and spectroscopic techniques. The powder X-ray diffraction (XRD) pattern of the material indicates the formation of nano sized  $ZrO_2$  particles which contains purely tetragonal phase and the average sizes of 12 nm (calculated from XRD using Scherrer formula<sup>15</sup>). These results are in well accordance with our previous report<sup>8i</sup> as well as results reported by Xie *et al.*<sup>16</sup>

The morphology and particle size of the  $ZrO_2$  NPs were further confirmed by high resolution transmission electron microscopic (HRTEM) study. The HRTEM image (Fig. 2a) revealed the formation of spherical size  $ZrO_2$  NPs. The selected electron diffraction (SAED) pattern (inset, Fig.2b) reveals the *d* values corresponding to the four brightest rings are 3.39, 1.84, 1.61, and 1.25 Å (from the inner to the outer) which are associated with the {101}, {122}, {211} and {213} planes of t- $ZrO_2$  respectively (JCPDS no. 79-1771).<sup>17</sup> Fig. 3a shows the spare magnified image of  $ZrO_2$  NPs clearly illustrating the associated lattice fringes with lattice spacing 0.295 nm corresponding to {111} plane of *t*- $ZrO_2$  (JCPDS card no. 17-0923).<sup>18</sup> The size distribution of the NPs was measured from HRTEM study over 100 grains and a narrow size distribution of  $ZrO_2$  NPs was observed and the Gaussian plot shows the average particle size of 11.4 nm (See Fig. S1, †ESI 2a). Energy dispersive X-ray analysis (EDX) through HRTEM clearly indicates that the sample is highly pure and does not contain any impurity peaks (Fig. 3b). The EDX analysis also interprets that the Zr/O ratio is slightly higher than the expected value which may be due to the creation of oxygen vacancies that make the tetragonal phase more stable (See †ESI 2b).



Fig. 2 (a) HRTEM image of t-ZrO<sub>2</sub> NPs (b) SAED pattern of t-ZrO<sub>2</sub> NPs





Fig. 3 (a) Magnified HRTEM of t-ZrO<sub>2</sub> NPs shows lattice fringes with lattice spacing (b) HRTEM-EDX pattern of t-ZrO<sub>2</sub> NPs.

The optical properties of ZrO<sub>2</sub> NPs have been analyzed using electronic absorption (spectra not provided) and fluorescence spectroscopy. The ZrO<sub>2</sub> NPs showed maxima at 261 nm (band gap ~ 4.76 eV) in UV-Vis spectrum<sup>8i</sup> and exhibited a sharp emission peak at 546 nm ( $\lambda_{excitation}$  = 260 nm) in water in the fluorescence spectrum (Fig. 4).



Fig. 4 Fluorescence spectrum of  $ZrO_2$  NPs in water ( $\lambda_{excitation}$  = 260 nm).

The red-shift of the emission band as compared to the bulk  $ZrO_2$  (band gap 5.6 eV) indicates that the fluorescence involves extrinsic states or defect states *i.e.* due to the arrangement of oxygen vacancies.<sup>19-20</sup>

Next, the properly characterized t-ZrO<sub>2</sub> NPs were then used for the synthesis of pyrano fused 2-aminochromene derivatives. When a mixture of benzaldehyde (1 mmol), malononitrile (1 mmol), 1-napthol (1 mmol) and t-ZrO<sub>2</sub> (12 mg, 10 mol%) is heated at 80 °C in water (5 ml), excellent yield of 2-amino-3-cyano-4-phenyl-4*H*-benzo[*h*]chromene (92%) was obtained after 30 minutes (entry 1, Table 1). However, at room temperature the same reaction did not produce desired product even after 2 hrs (entry 2, Table 1). The reaction also failed to produce product in absence of the catalyst (entry 3, Table 1). The ZrO<sub>2</sub> NPs were found to be less reactive in organic solvents like acetonitrile, toluene and dimethyl formamide (DMF) (entries 4-6, Table 1). To study the effect of phase of the catalyst, we have studied the reaction using monoclinic ZrO<sub>2</sub> (m-ZrO<sub>2</sub>) NPs and cubic (bulk) ZrO<sub>2</sub> and it was observed that both cubic and m-ZrO<sub>2</sub> are less reactive than t- $ZrO_2$  (entries 7-8, Table 1). The phase pure monoclinic m- $ZrO_2$ NPs were prepared by following our previous report<sup>8i</sup> (See <sup>+</sup>ESI 3 for detailed preparation). The t-ZrO<sub>2</sub> NPs were also found to be more reactive compared to Fe<sub>3</sub>O<sub>4</sub>, SiO<sub>2</sub>, CuO and ZnO etc. NPs (entries 9-12, Table 1). Thus, the reaction using 10 mol% of t-ZrO<sub>2</sub> NPs in water at 80°C was considered as the optimized reaction conditions (see +ESI 4 for details experimental procedure).

Using optimized conditions, we have explored the scope of the methodology for the synthesis of 2-aminochromene derivatives. We have observed that the t-ZrO<sub>2</sub> NPs were able to produce a series of 2-aminochromene derivatives (1a-f, Table 2) by the condensation of variety of substituted aryl aldehydes with malononitrile and 1-napthol (entries 1-6, Table 2). Excellent yields of the products were obtained within practical time period (30-55 minutes).

**Table 1** Optimization of reaction conditions for the synthesis of

 2-aminochromene derivatives

	OH Ph				
	PhCHO + CN +	catalyst		JN	
	CN 🛰	Solvent		JH <sub>2</sub>	
			$\checkmark$		
Entry	Catalyst	Solvent/cond.	Time	Yield	
			(min)	(%) <sup>a</sup>	
1	<i>t</i> -ZrO <sub>2</sub> NPs	$H_2O/80^{\circ}C$	30	92	
2	<i>t</i> -ZrO <sub>2</sub> NPs	H <sub>2</sub> O/RT	240	-	
3	No catalyst	H₂O/80 <sup>°</sup> C	240	-	
4	<i>t</i> -ZrO <sub>2</sub> NPs	CH₃CN/80 <sup>°</sup> C	60	77	
5	<i>t</i> -ZrO <sub>2</sub> NPs	Toluene/80°C	60	62	
6	<i>t</i> -ZrO <sub>2</sub> NPs	DMF/80°C	60	60	
7	Bulk ZrO <sub>2</sub>	H <sub>2</sub> O/80 <sup>°</sup> C	60	41	
8	m-ZrO <sub>2</sub> NPs	$H_2O/80^{\circ}C$	30	52	
9	Fe <sub>3</sub> O <sub>4</sub> NPs	$H_2O/80^{\circ}C$	60	57	
10	SiO <sub>2</sub> NPs	$H_2O/80^{\circ}C$	60	51	
11	CuO NPs	$H_2O/80^{\circ}C$	60	79	
12	ZnO NPs	$H_2O/80^{\circ}C$	60	66	

**Reaction conditions:** benzaldehyde (1 mmol), malononitrile (1 mmol), 1-napthol (1 mmol), catalyst (10 mol %), solvent (5 ml) with continuous stirring. <sup>a</sup>isolated yield, RT means room temperature.

We have also extended the scope of t-ZrO<sub>2</sub> NPs catalyzed reactions by using 2-napthol in place of 1-napthol and observed that corresponding 2-aminochromene derivatives (2a-c) were produced in good yields. Aryl aldehydes containing both electron donating (*e.g.* –OMe, –CH<sub>3</sub>, –Cl etc.) and electron withdrawing (e.g. –NO<sub>2</sub>) groups were participated in

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the reaction and no electronic effect was observed. The results were presented in Table 2. All the products are solid and were purified by recrystallization from ethanol and identified by their melting points determination and nuclear magnetic resonance spectroscopic study.





**Reaction conditions:** aryl aldehyde (1 mmol), malononitrile (1 mmol), 1- or 2-napthol (1 mmol), *t*-ZrO<sub>2</sub> NPs (10 mol%, 12 mg) and H<sub>2</sub>O (5 ml) with continuous stirring at 80 °C. <sup>a</sup>Yields refer to that of pure isolated products. <sup>b</sup>Melting points were determined for the pure and recrystallized products.

In order to compare the catalytic efficiency of *t*-ZrO<sub>2</sub> NPs for the synthesis of 2-aminochromene derivatives, a comparative study of catalytic performance of the present catalyst with the reported ones is presented in Table 3.

**Table 3** Comparative study of t-ZrO2 NPs for the synthesis of 2-aminochromene derivatives

ArCI	HO + NC CN +	OH (	Ar 0 (1)	CN NH <sub>2</sub>
Entry	Catalyst	Reaction	Yield	Time
		Conditions	(%)	(min.)
1	<i>t</i> -ZrO <sub>2</sub> NPs <sup>a</sup>	12 mg/H <sub>2</sub> O/ 80°C	88-94	35-55
2	Rochelle Salt <sup>14d</sup>	60 mg/ EtOH/reflux	75-90	240-480
3	TFMO-1 <sup>14e</sup>	40 mg/neat/ 110°C	86-92	240-360
4	Basic $Al_2O_3^{14c}$	500 mg/ H₂O/Reflux	83-96	180
5	$Na_2CaP_2O_7^{14f}$	H <sub>2</sub> O/Reflux	72-94	240-300

#### <sup>a</sup> Present work

The above comparison clearly indicates that the present method is better in terms of reaction time, environmental safety and catalyst loading.

The phase of played a significant role and the tetragonal phase of  $ZrO_2$  showed higher reactivity compared to its monoclinic phase. This phenomenon was in accordance with our previous report<sup>8i</sup> and also reported by others.<sup>21a,b</sup> The observed higher activity of the tetragonal phase was possibly due to the presence of oxygen vacancies, which are responsible for stability and higher surface activity for pure t- $ZrO_2$ .<sup>21a-c</sup> The presence of oxygen vacancies was also evident from the fluorescence study of t- $ZrO_2$  NPs.

# 38-40<sup>13h</sup> 88-80<sup>13h</sup>

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Next, we have investigated the stability of t-ZrO<sub>2</sub> NPs checking its reusability for the synthesis of 2-amino-3-cyano-4phenyl-4H-benzo[h]chromene (1a).



Fig. 5 Represents reusability of t-ZrO<sub>2</sub> for the synthesis of 2amino-3-cyano-4-phenyl-4H-benzo[h]chromene (1a).

After each cycle, the *t*-ZrO<sub>2</sub> NPs were recovered by centrifugation, washed, dried and reused. The tetragonal phase of the t-ZrO<sub>2</sub> NPs (confirmed by powder XRD; see Fig. S3, <sup>+</sup>ESI 5) was remained intact even after 10<sup>th</sup> cycle (Fig. 5). The decrease in yield may possibly due to loss of surface hydroxyl groups<sup>8i</sup> or decrease of Zr-content which eventually associated with decrease of oxygen vacancies. The decrease of oxygen vacancies was evident from the fluorescence measurement of the recycled ZrO<sub>2</sub> NPs with a blue shift (~20 nm) of emission maximum of ZrO2 NPs (see Fig. S4, +ESI 5). Further, the decrease of Zr-content in recycled ZrO<sub>2</sub> NPs was evident from atomic absorption spectroscopic (AAS). The AAS results have been presented in table 1, †ESI 5. Moreover, no peak corresponding to the NPs were observed in the FT-IR spectra (Fig S5, ESI 5) of recycled product.

Motivated by the previous results next, we have tried to explore the catalytic efficiency of t-ZrO<sub>2</sub> NPs for synthesis of related pyran annulated heterocyclic compounds such as dihydropyrano[3,2-c]chromene (3) and chromeno[4,3b]chromene derivatives (4) by the condensation of aldehyde, malononitrile (for synthesis of 3) or 5,5-dimethyl-1,3cycloheadione (for the synthesis of 4) and 4-hydroxy-coumarin (Scheme 2).



Scheme 2 t-ZrO<sub>2</sub> NPs catalyzed synthesis of dihydropyrano[3,2c]chromene(3) and chromeno[4,3-b]chromene derivatives(4) derivatives.

Synthesis of coumarin fused pyran annulated 4Hchromenes, in particular, dihydropyrano[3,2-c]chromene and chromeno[4,3-b]chromene derivatives are of much interest as these moieties have shown diverse biological activities and act as anti-cancer,<sup>22a</sup> emetic,<sup>22b</sup> anti-HIV,<sup>22c</sup> anti-tumor,<sup>22d</sup> antianti-bacterial,<sup>22f</sup> anti-malaria,<sup>22g</sup> diuretic,<sup>22h</sup> alzheimer.<sup>22e</sup> spasmolytic,<sup>22i</sup> anti-leukemic,<sup>22j</sup> anti-anaphylactic<sup>22k</sup> and anticoagulant<sup>221</sup> agents. Few selected such bio-active molecules are shown in Fig. 6.



Fig. 6 Diverged bioactive coumarin fused 4H-chromenes.

When a mixture benzaldehyde (1 mmol), malononitrile (1 mmol), 4-hydroxy-coumarin (1 mmol) and t-ZrO<sub>2</sub> (12 mg) was reacted under the above mentioned optimized conditions *i.e.* heating in water at 80 °C, good yield (90%) of white solid product was isolated and identified as dihydropyrano[3,2c]chromene (3a) (see +ESI 6 for details experimental procedure).

The scope of this reaction for the synthesis of dihydropyrano[3,2-c]chromenes (3a-e) has been presented in Table 3. By replacing malononitrile with 5,5-dimethyl-1,3cyclohexanedione, in the said reaction, we have also synthesized chromeno[4,3-b]chromene derivatives (4a-d) (see +ESI 7 for details experimental procedure).

Table 4 t-ZrO<sub>2</sub> NPs catalyzed synthesis of dihydropyrano[3,2c]chromene and chromeno[4,3-b]chromene derivatives



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**Reaction condition:** aryl aldehyde (1 mmol), malononitrile or dimedone (1 mmol), 4-hydroxycoumarin (1 mmol), t-ZrO<sub>2</sub> NPs (10 mol%, 12.3 mg) and H<sub>2</sub>O (5 ml) with continuous stirring at 80 °C. <sup>a</sup> Yield of pure isolated products. <sup>b</sup> melting point was determined for the pure recrystallized products.

All the reactions listed in Table 3 are very clean and afforded excellent yields of the products. Although, various catalysts/reagents<sup>23</sup> have been used for the synthesis of dihydropyrano[3,2-c]chromene derivatives, however, only three reports<sup>24</sup> are available in literature for the synthesis of chromeno[4,3-*b*]chromene derivatives. The present protocol offered several advantages such as (i) use of mild  $ZrO_2$  NPs as catalyst, (ii) water as solvent, (iii) faster reaction rate (less than 1 hr), (iv) good to excellent yields of the products, (v) simple isolation and purification of products etc. The products were identified by their melting points determination and spectroscopic analysis (See ESI 8). These values are in well accordance with the values reported in literature.

Finally, a plausible mechanism has been suggested in Scheme 3 for the formation 2-amino-3-cyano-4-phenyl-4*H*-benzo[*h*]chromene (1a) in consultation with previously reported<sup>8i,14e</sup> mechanisms. The reaction believed to proceeds *via* initial Knoevenagel condensation to produce 2-phenylidenemalononitrile (I). Subsequently, the Michael addition reaction of the intermediate (I) with 1-napthol followed by tautomerization and intra-molecular cyclization furnished the desired product.



**Scheme 3** Plausible mechanism for *t*-ZrO<sub>2</sub> NPs catalysed synthesis of 2-aminochromene derivative (1a).

In our previous study,<sup>8i</sup> we have established that the surface of  $ZrO_2$  NPs contains active hydroxyl, oxide and  $Zr^{+4}$ ; which were reported to exhibit Lewis acidic or basic properties.<sup>21c</sup> Thus,

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these groups play an important role during the multicomponent synthesis of pyran fused 2-aminochromenes.

#### Conclusions

In conclusion, we have demonstrated MCRs leading to biologically active pyran fused chromene derivatives namely, 2-amino chromenes, dihydropyrano[3,2-c]chromene and chromeno[4,3-b]chromene derivatives using fluorescent t-ZrO<sub>2</sub> NPs as mild and reusable catalyst under aqueous medium. The fluorescent t-ZrO<sub>2</sub> NPs were characterized by analytical and spectroscopic methods. The present protocol offered several novelties such as (i) shorter reaction time (25-55 min.), (ii) high isolated yields of the products (88-95%), (iii) use of water as green reaction medium, (iv) the products were purified by recrystallization from ethanol and thus the use of organic solvents were avoided totally and finally, (v) reusability of ZrO<sub>2</sub> NPs made the protocol environmentally benign. Further, in addition to the stability of tetragonal phase of recycled ZrO<sub>2</sub> NPs, here we have established that the decrease of catalytic activities of recycled ZrO2 NPs associated with the loss of yield of the product was due to decrease of Zr-content which eventually associated with decrease of oxygen vacancies.

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#### **Graphical Abstract**

# On water synthesis of pyran-chromenes via multicomponent reaction catalyzed by fluorescent t-ZrO<sub>2</sub> nanoparticles

Here, we have demonstrated fluorescent tetragonal  $ZrO_2$  nanoparticles (t- $ZrO_2$  NPs) catalyzed green one-pot multicomponent protocol for the synthesis of diverse pyran fused chromene analogous such as 2-aminochromenes, dihydropyrano[3,2-c]chromene, chromeno[4,3b]chromene derivatives in water. The rate of the reactions and yields of the products have increased significantly in water. In addition, t- $ZrO_2$  NPs showed higher reactivity than monoclinic  $ZrO_2$  NPs. The t- $ZrO_2$  NPs were recycled and the gradual decrease in yield of the product using recycled catalyst could be possibly due to the decrease in zrconium content associated with decrease in oxygen vacancies which were evident from fluorescence and atomic absorption studies. However, the tetragonal phase of the catalyst remained intact even at 10<sup>th</sup> cycle.

