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# A water–ethanol on–off fiber catalyst for the synthesis of substituted 2-amino-2-chromenes

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A DMAP (4-dimethylaminopyridine) functionalized polyacrylonitrile fiber catalyst ($PAN_{DMAP}F$) was prepared and used to efficiently catalyze three-component condensation reactions among an aldehyde, malononitrile and α-naphthol in water to afford the corresponding substituted 2-amino-2-chromenes. The $PAN_{DMAP}F$ exhibited excellent catalytic activities in water and methanol, but failed to show any catalytic activity in ethanol and solvents with low polarity. In other words, water can turn the reaction on but ethanol shuts it off. This differs greatly from the same reaction catalyzed by free DMAP or by a tertiary amine functionalized polyacrylonitrile fiber. The $PAN_{DMAP}F$ catalyst is applicable to a wide range of aromatic aldehydes (80–99%). Moreover, this newly developed fiber catalyst also exhibited excellent recyclability and reusability (up to seven times) without any additional treatment.

## 1. Introduction

In accordance with sustainable development strategies, much attention has been given to performing organic transformations in benign media, especially multi-component condensation reactions in which two or more steps are combined in one pot without isolation of any intermediates. The use of toxic and volatile organic solvents as reaction media has aggravated ever-increasing environmental concerns. Therefore, environmentally friendly processes that can be conducted in green solvents are of urgently needed. The low cost of water along with its non-toxic nature, makes it an ideal media for chemical synthesis and transformations. Further, using a multi-component one-pot condensation approach could result in tremendous, potential cost savings in the areas of raw materials, energy, equipment, labor and time. These advantages become even more attractive if such reactions can be conducted using heterogeneous recyclable catalysts.

Substituted 2-amino-chromenes are widely employed as pigments, cosmetics, photoactive materials,[1] biodegradable agrochemicals, and represent an important class of chemicals which are the main constituents of many natural products. However, most of the reported synthesis methods require prolonged reaction times, stoichiometric reagents, toxic solvents, and the yields are only moderate.

Generally, for the synthesis of the substituted 2-amino-2-chromenes, DMAP (4-dimethylaminopyridine)[2] and DBU(1,8-diazabicyclo[5.4.0]undec-7-ene)[3] are used in homogeneous catalytic systems and nano-sized MgO[4] are used in heterogeneous catalytic systems. Heterogeneous catalysts have several advantages over conventional homogeneous catalysts, such as simpler post-treatments, reusability and the generation of less pollution. Thus the development of new heterogeneous catalysts is very important.

DMAP is an efficient catalyst that has been studied intensively since it was first reported.[5,6] Some homogeneous catalysts have used soluble polymers as a support to immobilize DMAP or its analogues.[7–12] These homogeneous catalysts have a similar efficiency to free DMAP, however, the separation is difficult. Heterogeneous catalysts based on epoxy resins or mesoporous silica[13–16] have overcome this disadvantage, but their catalytic efficiencies are lower than that of free DMAP. Thus the development of heterogeneous catalysts with high catalytic efficiencies is of particular interest.

In our previous work, functionalized fibers were successfully used to catalyze a three-component Bigineili reaction[17] and the synthesis of thiophene derivatives.[18,19] In this paper, a DMAP functionalized polyacrylonitrile fiber ($PAN_{DMAP}F$) was prepared and used to catalyze the synthesis of substituted 2-amino-chromenes in water. This fiber catalyst showed an on–off characteristic in water–ethanol system, and an excellent reusability and recyclability.

## 2. Experimental

### 2.1 Reagents

Polyacrylonitrile fibers with lengths of 10 cm and diameters of 30 ± 0.5 mm were purchased from the Fushun Petrochemical Corporation of China. All aldehydes, naphthols, malononitrile, *N*,*N*′-dimethyl-1, 3-propanediamine and the other reagents were

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of analytical grade and used without further purification. The water was deionized.

### 2.2 Apparatus and instruments

Elemental analysis was determined with an Elementar vario EL analyzer. A model XL-30 scanning electron microscope (Philips) was employed to characterize the surface of the modified fibers. FTIR spectra were collected with an AVATAR360 FTIR spectrometer (Thermo Nicolet). $^1$H NMR spectra were recorded on an AVANCE III (600 MHz) instrument using TMS as the internal standard. Melting points were taken on a Yanagimoto MP-500 apparatus.

### 2.3 Preperation of the fiber catalyst

As the fiber catalyst works through the DMAP moiety immobilized on the fiber, so *N*,*N*′-dimethyl-*N*-(4-pyridyl)-1,3-propanediamine was introduced to chemically bond the DMAP part on the fiber by –NH group.

**2.3.1 *N*,*N*′-Dimethyl-*N*-(4-pyridyl)-1, 3-propanediamine.** First, 4-chloropyridine hydrochloride (30 g, 0.2 mol) was added in batches to a mixture of *N*,*N*′-dimethyl-1,3-propanediamine (62.5 mL), water (125 mL) and sodium carbonate (42.4 g, 0.4 mol) over a course of 6 h. Then the mixture was refluxed for 12 h using TLC (Thin Layer Chromatography) to track the reaction. After completion of the reaction, the aqueous phase was extracted with $CH_2Cl_2$ three times and the organic layers were combined. The solvent was removed by evaporation and the residue was distilled under reduced pressure to obtain a pale yellow oily substance (bp: 178–180 °C/40 mmHg, yield: 53.8%) which was determined to be *N*,*N*′-dimethyl-*N*-(4-pyridyl)-1, 3-propanediamine.

**2.3.2 DMAP Functionalized polyacrylonitrile fiber ($PAN_{DAMP}F$).** The dried PANF (1 g) was put into a mixture of water (50 g) and *N*,*N*′-dimethyl-*N*-(4-pyridyl)-1, 3-propanediamine (50 g) in a 250 mL three-neck flask and heated to reflux for 18 h. The modified PANF was filtered out and washed with deionized water at 60–70 °C until the pH of the wash water was 7. Then the fiber catalyst $PAN_{DAMP}F$ was dried overnight under vacuum at 60 °C. And the process was shown as Scheme 1.

### 2.4 Acid exchange capacities of the fiber catalyst

The dried $PAN_{DAMP}F$ (0.200 g) was immersed into 20 mL of 0.100 mol $L^{-1}$ HCl for 12 h. The neutralized fiber was then filtered out. The HCl concentration of the remaining solution was determined by titration with 0.100 mol $L^{-1}$ NaOH. The exchange capacity was calculated based on the amount of acid consumed.[20]

### 2.5 General procedure for the synthesis of 2-amino-2-chromenes

A mixture of an aldehyde (1 mmol), malononitrile (1 mmol), α-naphthol (1 mmol) and $PAN_{DMAP}F$ (20 mol%) in 15 mL of water was refluxed for 1 h (Scheme 2). After completion of the reaction, the $PAN_{DMAP}F$ was filtered and extracted with ethanol for 3 h using a Soxhlet extractor in order to collect all the adsorbed products. The extracted ethanol was combined with the filtrate. After removing the solvent with a rotary evaporator, the residue was recrystallized with ethanol to give 2-amino-2-chromenes.

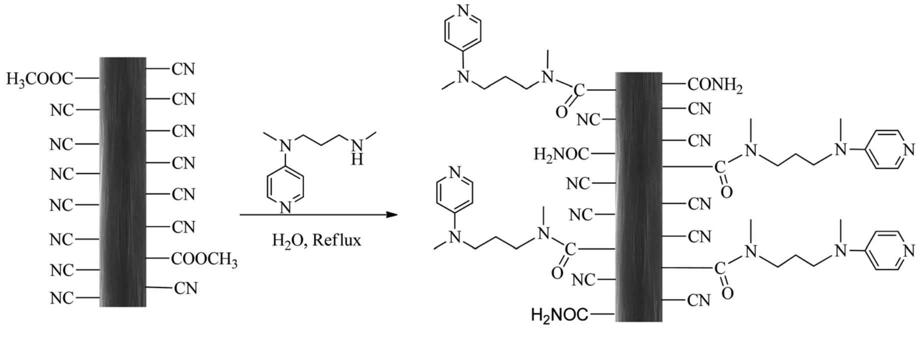
## 3. Results and discussions

In this paper, a simple and efficient protocol for the synthesis of 2-amino-2-chromenes using $PAN_{DMAP}F$ as a novel and eco-friendly heterogeneous catalyst is described. The $PAN_{DMAP}F$ has selectivity to the solvent and the yields could be controlled by adjusting the ratio of water to ethanol.

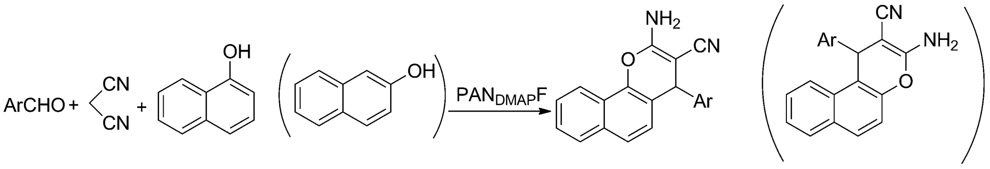
### 3.1 Synthesis of $PAN_{DAMP}F$

The fiber catalyst $PAN_{DMAP}F$ was synthesized by grafting *N*,*N*′-dimethyl-*N*-(4-pyridyl)-1,3-propanediamine onto the surface of PANF using water as the solvent. The extent of the modification was determined from the acid exchange capacity and the weight gain of the fiber catalyst, where, the weight gain = (the weight of $PAN_{DMAP}F$ − the weight of PANF)/(the weight of PANF). The reaction conditions were optimized and the results are shown in Table 1.

Table 1 shows that the weight gain increased with reaction time and with w(amine)/w($H_2O$) ratio. Taking the strength of the fiber into consideration, entry 5 was selected as the optimal condition. The acid exchange capacities of the fiber catalysts were determined as described in the Experimental section and then used to determine the effective number of functional groups. The titration result (0.67 mmol $g^{-1}$) was in good accordance with the result calculated from the weight gain (0.66 mmol $g^{-1}$).



Scheme 1 Preparation of fiber catalyst $PAN_{DMAP}F$.



Ar= Phenyl, 4-Chlorophenyl, 3-Nitrophenyl, 2-methoxyphenyl, etc.

Scheme 2 The three-component condensation reaction.

Table 1 Optimization of the synthesis conditions

| Entry | w(amine)/w($H_2O$) | Time (h) | Weight gain (%) |
|---|---|---|---|
| 1 | 1/2 | 14 | 2.1 |
| 2 | 3/4 | 14 | 6.5 |
| 3 | 1/1 | 12 | 7.8 |
| 4 | 1/1 | 14 | 9.1 |
| 5 | 1/1 | 18 | 15.8 |
| 6 | 1/1 | 20 | 19.4 |

## 3.2 Characterization of the fiber catalyst

**3.2.1 Elemental analysis.** The elemental analysis of PANF, $\text{PAN}_{\text{DMAP}}\text{F}$, $\text{PAN}_{\text{DMAP}}\text{F}$-1 ($\text{PAN}_{\text{DMAP}}\text{F}$ used one time), and $\text{PAN}_{\text{DMAP}}\text{F}$-7 ($\text{PAN}_{\text{DMAP}}\text{F}$ reused seven times) are shown in Table 2.

Compared with PANF, $\text{PAN}_{\text{DMAP}}\text{F}$ has less nitrogen and carbon and more hydrogen. The formation of $-\text{CONH}_2$ and $-$CONMeR (R = $\text{PyNMeCH}_2\text{CH}_2\text{CH}_2-$, the DAMP moiety) groups from the hydrolysis of the cyano groups and the immobilization of the DAMP moiety account for this. In entries 3 and 4, the carbon content increased and the hydrogen content decreased which is probably due to the adsorption of the reaction intermediates and product during the reaction.

**3.2.2 Scanning electron microscopy (SEM).** To distinguish the differences among PANF, $\text{PAN}_{\text{DAMP}}\text{F}$ and $\text{PAN}_{\text{DAMP}}\text{F}$ used for times, SEM photographs were taken. The SEM photographs show that the PANF has a smooth surface, and that the surface became slightly rougher after it was modified with *N*,*N*′-dimethyl-*N*-(4-pyridyl)-1,3-propanediamine. The surface of $\text{PAN}_{\text{DMAP}}\text{F}$ was unchanged after it was used once and after it was used seven times. These results indicate that the fiber catalyst maintained its integrity after being reused many times (Fig. 1).

**3.2.3 Fourier-transfer infrared spectroscopy (FTIR).** FTIR is a useful tool to prove whether the *N*,*N*′-dimethyl-*N*-(4-pyridyl)-1,3-propanediamine was grafted onto the surface of PANF. Compared to the IR spectrum of PANF, the spectrum of $\text{PAN}_{\text{DMAP}}\text{F}$ has a new emerging broad peak at 3000–3700 cm$^{-1}$. This peak is evidence for the existence of $-\text{CONH}_2$ groups which is formed by the hydrolysis of $-$CN. In addition, the C–N absorption peak at 2242 cm$^{-1}$ is weaker in $\text{PAN}_{\text{DMAP}}\text{F}$ than in PANF, which suggests that part of the cyano groups have disappeared. The ester C=O stretching vibration at 1731 cm$^{-1}$ is smaller in $\text{PAN}_{\text{DMAP}}\text{F}$ than in PANF which is due to the aminolysis and hydrolysis reactions. The new peak at 1554 cm$^{-1}$ in the $\text{PAN}_{\text{DMAP}}\text{F}$ spectrum is due to the frame vibrations of pyridine which demonstrates the successful grafting of *N*,*N*′-dimethyl-*N*-(4-pyridyl)-1, 3-propanediamine onto the surface of PANF. The characteristic peaks in $\text{PAN}_{\text{DMAP}}\text{F}$-7 are all weakened due to the absorption of the reaction intermediates and product during the reaction (Fig. 2).

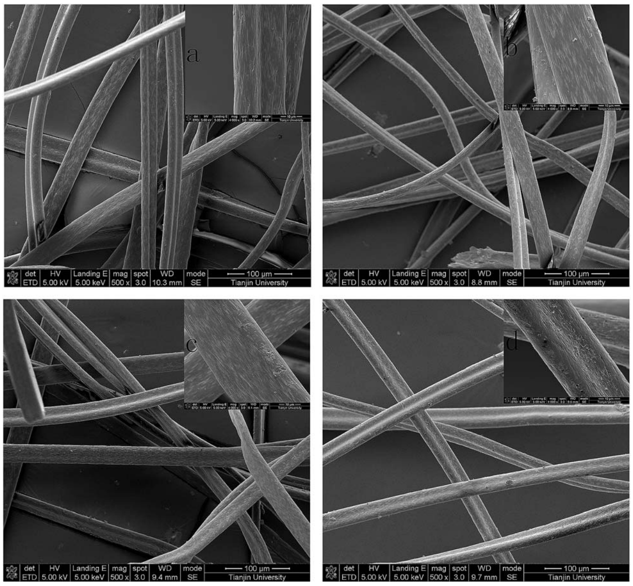


Fig. 1 The SEM photograph of (a) PANF, (b) $\text{PAN}_{\text{DMAP}}\text{F}$, (c) $\text{PAN}_{\text{DMAP}}\text{F}$-1, (d) $\text{PAN}_{\text{DMAP}}\text{F}$-7.

Table 2 Elemental analysis of PANF, $\text{PAN}_{\text{DMAP}}\text{F}$, $\text{PAN}_{\text{DMAP}}\text{F}$-1, $\text{PAN}_{\text{DMAP}}\text{F}$-7

| Entry | Sample | N (%) | H (%) | C (%) |
|---|---|---|---|---|
| 1 | PANF | 23.68 | 6.52 | 65.55 |
| 2 | $\text{PAN}_{\text{DMAP}}\text{F}$ | 21.32 | 7.12 | 61.04 |
| 3 | $\text{PAN}_{\text{DMAP}}\text{F}$-1 | 21.75 | 5.67 | 62.61 |
| 4 | $\text{PAN}_{\text{DMAP}}\text{F}$-7 | 21.68 | 6.81 | 63.13 |

## 3.3 Catalytic activities

**3.3.1 Catalytic activities.** The catalytic activity of $\text{PAN}_{\text{DMAP}}\text{F}$ for the three-component condensation reaction was investigated in different solvents and the results are listed in Table 3.

As shown in Table 3, in the absence of any catalyst, the three-component condensation with α-naphthol gave a low yield of 28% (Table 3, entry 1), whereas in the presence of PANF, the yield decreased to 14% (Table 3, entry 2). This might be due to

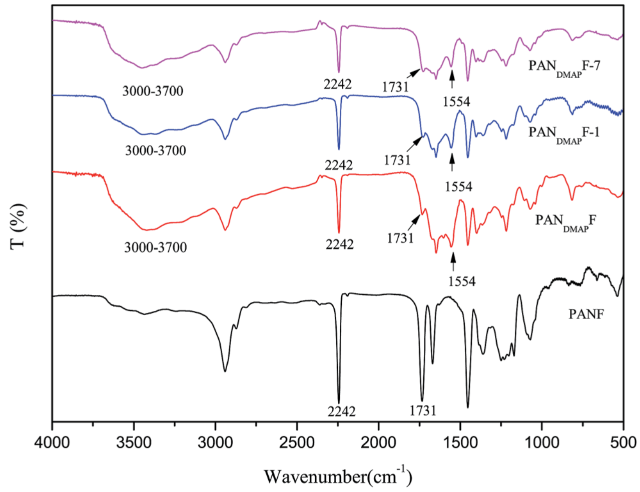


Fig. 2 Fourier-transfer infrared spectra of the fibers.

Table 3 Catalytic activities of catalysts

| Entry | Catalyst | Solvent | Yield[a] (%) | Yield[b] (%) |
|---|---|---|---|---|
| 1 | None | $H_2O$ | 28 (0)[d] | 0 |
| 2 | PANF | $H_2O$ | 14 (0)[d] | 0 |
| 3 | DMAP | $CH_3CH_2OH$ | 81 | 61 |
| 4 | DMAP | $H_2O$ | 72 | 51 |
| 5 | $PAN_TF$ | $CH_3CH_2OH$ | 94 | 62 |
| 6 | $PAN_TF$[c] | $H_2O$ | 90 | 76 |
| 7 | $PAN_{DMAP}F$ | $CH_3CH_2OH$ | 0 | 0 |
| 8 | $PAN_{DMAP}F$ | $H_2O$ | 97 | 51 |

[a] Reactions were carried out with 4-chlorobenzaldehyde (1 mmol), malononitrile (1 mmol) and α-naphthol (1 mmol) in the presence of different catalysts (0.20 mmol) in water or ethanol (15 mL) under reflux for 1 h. [b] Reactions were carried out under the same conditions with β-naphthol instead of α-naphthol. [c] $PAN_TF$ was prepared by grafting *N*,*N*-dimethyl-1,3-propanediamine onto PANF.[21] [d] The yields in () were obtained with ethanol as the solvent.

the adsorption of the reactants onto the surface of PANF, which would reduce the collisions among the reactants. When ethanol was used as the solvent, with either the PANF catalyst or no catalyst, there is no reaction. Using free DAMP as the catalyst gave good catalytic activity in both water and ethanol (Table 3, entries 3 and 4), but ethanol is much better due to the good solubility of the reactants in ethanol. Good solubilities ensure sufficient collisions which facilitates the reaction. In addition, a tertiary amine functionalized PANF ($PAN_TF$) gave excellent catalytic activity, both in water and ethanol (Table 3, entries 5 and 6). The yields were relatively low when β-naphthol was used as the reactant which due to steric hindrance.

Surprisingly, $PAN_{DAMP}F$ did not show any catalytic activity in ethanol (Table 3, entry 7), but exhibited excellent catalytic activity in water (Table 3, entry 8). In ethanol, the reaction stopped at the Knoevenagel intermediate **A** (Scheme 3). In water, the reaction proceeded to the end with a high yield of 97% which indicates that the grafted DMAP is very important to the catalytic activity and to solvent selectivity. To the best of our knowledge, this is the first catalyst to quantitatively catalyze an organic reaction in water[22] which can also be completely turned off in ethanol. This result demonstrates that it is possible in some cases to effectively catalyze an organic reaction in water and that expensive and poisonous organic solvents are not necessary.

Mechanism for this three-component reaction is depicted in Scheme 3. In this three-component one-pot reaction, $PAN_{DMAP}F$ acts as the Brønsted proton scavenger and two steps of this reaction take place on the surface of $PAN_{DMAP}F$. The first step is to form the Knoevenagel intermediate **A.** $PAN_{DAMP}F$ would take a proton away from naphthol which is adsorbed on the $PAN_{DMAP}F$ and generate the intermediate **B** by which naphthol is activated. Then the final product **C** was produced.

$PAN_TF$ is different from the $PAN_{DMAP}F$ in that it can undergo long-range interactions with the anions. This may be the reason why the three-component condensation reaction could be conducted in both water and ethanol when $PAN_TF$ was used as the catalyst (Table 3, entries 5 and 6).

**3.3.2 Effect of the solvent.** The effect of several commonly used solvents on the three-component reaction of 4-chlorobenzaldehyde, malononitrile and α-naphthol catalyzed by $PAN_{DMAP}F$ was then investigated and the results are shown in Table 4. Proton donating solvents with higher polarities such as methanol and $H_2O$ afforded fairly high yields (Table 4, entries 1 and 2). Among these solvents, water is the best choice in terms of yield, expense, availability and being environmentally benign. In solvents with aprotic and weaker polarities (Table 4, entries 3–10), no final products were obtained.

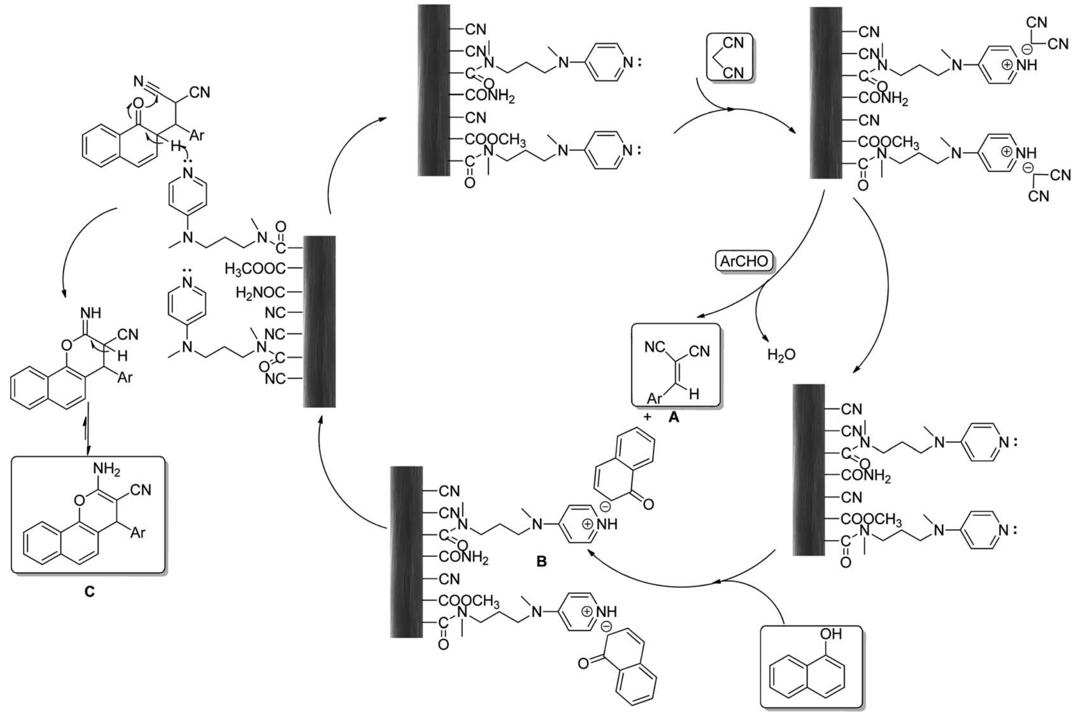
Next the effect of the solvent polarity was studied in more details. Solvents with different polarities were obtained by adjusting the ratio of water to ethanol and the results are shown in Table 4 (entries 11–15). As the polarity of the solvent increased, so did the yield. This is because naphthol is insoluble in highly polar solvents, which forces it to accumulate on the $PAN_{DMAP}F$ surface, thus facilitating the activation of naphthol to produce the final product. These results demonstrate that the reaction can be turned on just by adding enough water to the system.

The experimental results prove that in ethanol, the reaction terminates at step of the formation of Knoevenagel intermediate **A.** This is because naphthol has a good solubility in ethanol which made it difficult to access the fiber catalyst and undergo the next step.

## 3.4 Optimization of the reaction conditions

**3.4.1 Effect of catalyst amount.** The effect of the amount of catalyst loading on the three-component reaction was explored and the results are shown in Fig. 3. The yields of the condensation reaction increased greatly from 65% to 97% as the amount of catalyst increased from 5 to 20 mol%. However, no further increase in the yield was observed when the amount of catalyst was increased from 20 to 30 mol%. Therefore 20 mol% of $PAN_{DMAP}F$ was selected for all subsequent reactions.

**3.4.2 Effect of reaction time.** The effect of reaction time (from 10 to 70 min) on the yield was also investigated and the results are shown in Fig. 4. There was a sharp increase in the



Scheme 3 The possible reaction mechanism.

Table 4 Effect of solvents

| Entry | Solvent | Polarity | Yield of A[a,b] (%) | Yield of product[a,b] (%) |
|---|---|---|---|---|
| 1 | Water | 10.20 | — | 97 |
| 2 | Methanol | 6.60 | — | 94 |
| 3 | Acetonitrile | 6.20 | 98 | 0 |
| 4 | 1,4-Dioxane | 4.80 | 99 | 0 |
| 5 | Ethanol | 4.30 | 99 | 0 |
| 6 | Ethyl acetate | 4.30 | 93 | 0 |
| 7 | Tetrahydrofuran | 4.20 | 98 | 0 |
| 8 | Dichloromethane | 3.40 | 97 | 0 |
| 9 | Toluene | 2.40 | 99 | 0 |
| 10 | Cyclohexane | 0.10 | 97 | 0 |
| 11 | Water–ethanol (1 : 14)[c] | 5.41[d] | 99 | 0 |
| 12 | Water–ethanol (3 : 12)[c] | 6.94[d] | 28 | 68 |
| 13 | Water–ethanol (6 : 9)[c] | 8.33[d] | 17 | 80 |
| 14 | Water–ethanol (9 : 6)[c] | 9.19[d] | — | 97 |
| 15 | Water–ethanol (12 : 3)[c] | 9.78[d] | — | 96 |

[a] Reactions were carried out with 4-chlorobenzaldehyde (1 mmol), malononitrile (1 mmol) and α-naphthol (1 mmol) in the presence of $PAN_{DMAP}F$ (0.2700 g, containing 0.20 mmol of effective group) in different solvents (15 mL of each) under reflux for 1 h. [b] Isolated yield after recrystallization with ethanol. [c] The proportion is a volume ratio. [d] Calculated value.

yield when the time was increased from 10 to 60 min. No further increase in yield was observed if longer reaction times were applied. So 60 min of reflux was chosen as the optimal reaction time for the condensation reaction.

### 3.5 Recyclability of $PAN_{DMAP}F$

$PAN_{DMAP}F$ was reused for the three-component reaction to test its recyclability. After each run, the fiber catalyst was filtered out and washed with ethanol to remove any residue that had adhered onto the $PAN_{DMAP}F$. The fiber catalyst was then reused directly in the next cycle without any additional treatment. The yields were 97%, 96%, 97%, 97%, 91%, 81%, 80% for the first seven cycles respectively. The decrease in the sixth and seventh cycle may be due to the deactivation of catalyst which was caused by the accumulation of micromolecules on the surface. Nevertheless, compared to homogeneous catalysts[2,3,23,24] and other heterogeneous catalysts,[4,25] this new fiber catalyst has advantages of a simple work-up procedure and good recyclability.

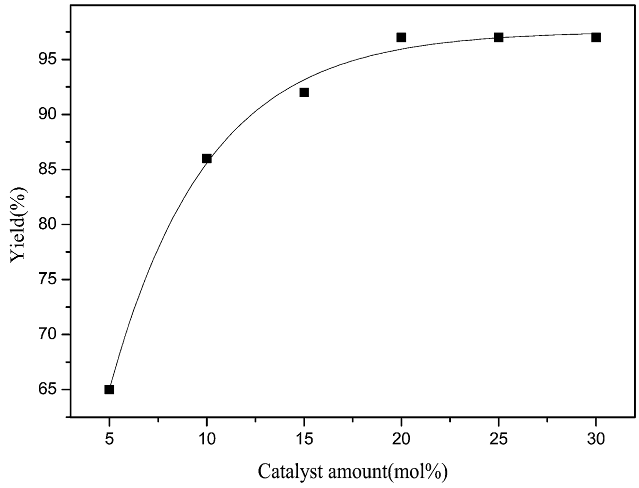


Fig. 3 Effect of catalyst amount on the three-component condensation reaction with 4-chlorobenzaldehyde (1 mmol), malononitrile (1 mmol) and α-naphthol (1 mmol).

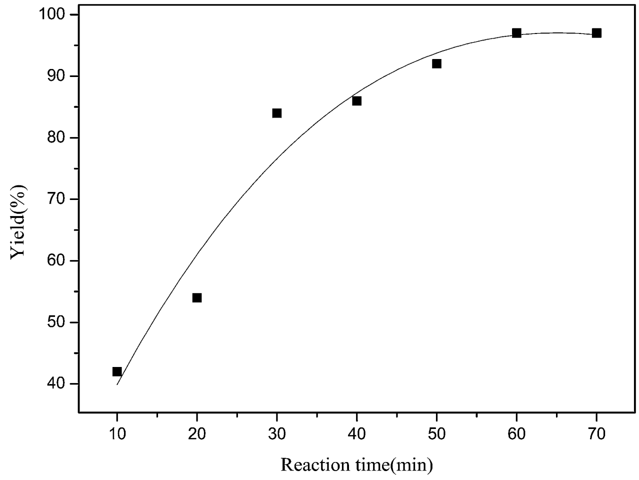


Fig. 4 Effect of reaction time on the three-component condensation reaction with 4-chlorobenzaldehyde (1 mmol), malononitrile (1 mmol) and α-naphthol (1 mmol).

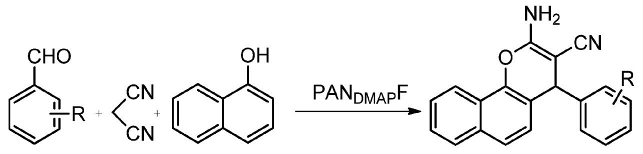
### 3.6 Extension of the substrate

$PAN_{DMAP}F$ was then applied to different kinds of aromatic aldehydes (Table 5) and the condensation products were obtained in excellent yields ranging from 80% to 99%. Relatively low yields were obtained for entries 7 and 9 because of steric effects. The lower yield for entry 11 is because of the protonation of the hydroxyl group on the benzene ring or the quinoid transformation of the molecular structure.

$^1H$ data for selected compounds are given below:

**2-Amino-4-phenyl-4*H*-benzo[*h*]chromene-3-carbonitrile (Table 5, entry 1).** $^1H$ NMR (600 MHz, DMSO) δ 8.25 (d, $J$ = 8.3 Hz, 1H), 7.85 (t, $J$ = 40.6 Hz, 1H), 7.77–7.44 (m, 3H), 7.32 (t, $J$ = 7.2 Hz, 2H), 7.29–7.16 (m, 5H), 7.12 (d, $J$ = 8.4 Hz, 1H), 4.91 (s, 1H).

Table 5 Three-component condensation reaction



| Entry | R | mp (°C) | Lit. mp (°C) | Yield$^{a,b}$ (%) |
|---|---|---|---|---|
| 1 | H | 208–210 | 211–212 | 93 |
| 2 | *p*-Cl | 237–239 | 231–232 | 97 |
| 3 | *p*-F | 224–225 | 230–232 | 88 |
| 4 | *m*-$NO_2$ | 210–211 | 210–212 | 98 |
| 5 | *p*-$OCH_3$ | 182–184 | 182–183 | 96 |
| 6 | *m*-$OCH_3$ | 232–233 | — | 96 |
| 7 | *o*-$OCH_3$ | 188–189 | 204 | 88 |
| 8 | *m*-$CF_3$ | 212–213 | 215.5–216.5 | 99 |
| 9 | *o*-$CF_3$ | 236–238 | 239–240 | 89 |
| 10 | *m*-OH | 242–244 | 250–253 | 98 |
| 11 | *p*-OH | 239–241 | 245–247 | 80 |

[a] Reactions were carried out with aldehyde (1 mmol), malononitrile (1 mmol) and α-naphthol (1 mmol) in the presence of $PAN_{DMAP}F$ (0.2700 g, containing 0.20 mmol of effective group) in different solvents (15 mL of each) under reflux for 1 h. [b] Isolated yield after recrystallization with ethanol.

**2-Amino-4-(4-chlorophenyl)-4*H*-benzo[*h*]chromene-3-carbonitrile (Table 5, entry 2).** $^1H$ NMR (600 MHz, DMSO) δ 8.25 (d, $J$ = 8.2 Hz, 1H), 7.90 (d, $J$ = 7.7 Hz, 1H), 7.76–7.52 (m, 3H), 7.38 (t, $J$ = 15.2 Hz, 2H), 7.34–7.19 (m, 4H), 7.10 (d, $J$ = 8.4 Hz, 1H), 4.96 (s, 1H).

**2-Amino-4-(4-fluorophenyl)-4*H*-benzo[*h*]chromene-3-carbonitrile (Table 5, entry 3).** $^1H$ NMR (600 MHz, DMSO) δ 8.24 (d, $J$ = 8.2 Hz, 1H), 7.90 (d, $J$ = 7.8 Hz, 1H), 7.62 (m, $J$ = 20.1, 14.8, 7.0 Hz, 3H), 7.29 (m, 2H), 7.21 (s, 2H), 7.15 (m, $J$ = 8.3 Hz, 2H), 7.11 (d, $J$ = 8.4 Hz, 1H), 4.96 (s, 1H).

**2-Amino-4-(3-nitrophenyl)-4*H*-benzo[*h*]chromene-3-carbonitrile (Table 5, entry 4).** $^1H$ NMR (600 MHz, DMSO) δ 8.27 (d, $J$ = 8.4 Hz, 1H), 8.19 (m, 2H), 7.92 (d, $J$ = 8.1 Hz, 1H), 7.76 (d, $J$ = 7.6 Hz, 1H), 7.70–7.58 (m, 4H), 7.36 (s, 2H), 7.17 (d, $J$ = 8.5 Hz, 1H), 5.22 (s, 1H).

**2-Amino-4-(4-methoxyphenyl)-4*H*-benzo[*h*]chromene-3-carbonitrile (Table 5, entry 5).** $^1H$ NMR (600 MHz, DMSO) δ 8.24 (d, $J$ = 8.4 Hz, 1H), 7.87 (d, $J$ = 23.5, 7.0 Hz, 1H), 7.69–7.48 (m, 3H), 7.17 (d, $J$ = 8.6 Hz, 2H), 7.14 (s, 2H), 7.09 (d, $J$ = 8.5 Hz, 1H), 6.89 (d, $J$ = 13.2 Hz, 2H), 4.85 (s, 1H), 3.71 (s, 3H).

**2-Amino-4-(3-methoxyphenyl)-4*H*-benzo[*h*]chromene-3-carbonitrile (Table 5, entry 6).** $^1H$ NMR (600 MHz, DMSO) δ 8.24 (d, $J$ = 8.4 Hz, 1H), 7.88 (d, $J$ = 8.1 Hz, 1H), 7.65–7.54 (m, $J$ = 14.7, 12.6, 7.4 Hz, 3H), 7.20 (m, 1H), 7.16–7.09 (m, 3H), 7.08–6.99 (m, 2H), 6.88 (t, $J$ = 7.4 Hz, 1H), 5.26 (s, 1H), 3.81 (s, 3H).

**2-Amino-4-(2-methoxyphenyl)-4*H*-benzo[*h*]chromene-3-carbonitrile (Table 5, entry 7).** $^1H$ NMR (600 MHz, DMSO) δ 8.24 (d, $J$ = 8.4 Hz, 1H), 7.88 (d, $J$ = 8.1 Hz, 1H), 7.65–7.54 (m, $J$ = 14.7, 12.6, 7.4 Hz, 3H), 7.20 (m, 1H), 7.15–7.09 (m, 3H), 7.04 (m, 2H), 6.88 (t, $J$ = 7.4 Hz, 1H), 5.26 (s, 1H), 3.81 (s, 3H).

**2-Amino-4-(3-(trifluoromethyl)phenyl)-4*H*-benzo[*h*]chromene-3-carbonitrile (Table 5, entry 8).** $^1$H NMR (600 MHz, DMSO) $\delta$ 8.27 (d, $J = 8.3$ Hz, 1H), 7.91 (d, $J = 8.0$ Hz, 1H), 7.61 (m, $J = 29.9$, 20.9, 11.0 Hz, 7H), 7.31 (s, 2H), 7.14 (d, $J = 8.4$ Hz, 1H), 5.13 (s, 1H).

**2-Amino-4-(2-(trifluoromethyl)phenyl)-4*H*-benzo[*h*]chromene-3-carbonitrile (Table 5, entry 9).** $^1$H NMR (600 MHz, DMSO) $\delta$ 8.29 (d, $J = 8.4$ Hz, 1H), 7.90 (d, $J = 8.1$ Hz, 1H), 7.76 (d, $J = 7.9$ Hz, 1H), 7.67 (t, 1H), 7.60 (t, 3H), 7.44 (t, $J = 7.6$ Hz, 1H), 7.36–7.25 (m, 3H), 6.88 (d, $J = 8.5$ Hz, 1H), 5.21 (s, 1H).

**2-Amino-4-(3-hydroxyphenyl)-4*H*-benzo[*h*]chromene-3-carbonitrile (Table 5, entry 10).** $^1$H NMR (600 MHz, DMSO) $\delta$ 9.37 (s, 1H), 8.24 (d, $J = 8.3$ Hz, 1H), 7.90 (d, $J = 8.1$ Hz, 1H), 7.61 (m, $J = 23.0$, 15.0, 7.3 Hz, 3H), 7.23–7.01 (m, 4H), 6.72 (d, $J = 7.5$ Hz, 1H), 6.61 (s, 2H), 4.79 (s, 1H).

**2-Amino-4-(4-hydroxyphenyl)-4*H*-benzo[*h*]chromene-3-carbonitrile (Table 5, entry 11).** $^1$H NMR (600 MHz, DMSO) $\delta$ 9.36 (s, 1H), 8.23 (d, $J = 8.3$ Hz, 1H), 7.89 (d, $J = 8.0$ Hz, 1H), 7.76–7.51 (m, 3H), 7.14–6.96 (m, 5H), 6.70 (d, $J = 8.1$ Hz, 2H), 4.78 (s, 1H).

***N*,*N*′-Dimethyl-*N*-(4-pyridyl)-1,3-propanediamine.** $^1$H NMR (600 MHz, DMSO) $\delta$ 8.07 (d, $J = 3.6$ Hz, 2H), 6.58 (d, $J = 4.5$ Hz, 2H), 3.39 (t, $J = 7.0$ Hz, 2H), 2.91 (s, 3H), 2.44 (t, $J = 6.3$ Hz, 2H), 2.26 (s, 3H), 1.63 (m, 2H).

## 4. Conclusions

In this paper, a DMAP functionalized fiber catalyst PAN$_{\mathrm{DMAP}}$F was prepared for the first time and was employed as a novel and efficient catalyst for the synthesis of various substituted 2-amino-2-chromenes using a three-component condensation approach. The three-component reaction proceeded smoothly in water (80–97% yield) when catalyzed by PAN$_{\mathrm{DMAP}}$F, whereas in ethanol under the same conditions, no reaction took place. In ethanol the reaction was found to terminate after the formation of the Knoevenagel intermediate **A**. The reaction could be turned-on by adding enough water to the reaction system. This fiber catalyst is suitable for a wide range of aromatic aldehydes and can be easily recycled and reused up to seven times without any additional treatment. The attractive features of this fiber catalyst make it be an excellent choice for the green synthesis of 2-amino-2-chromenes.

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