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Solvent Selective Polyacrylonitrile Fiber as a Recyclable Catalyst for the Knoevenagel-Michael Reaction in Water

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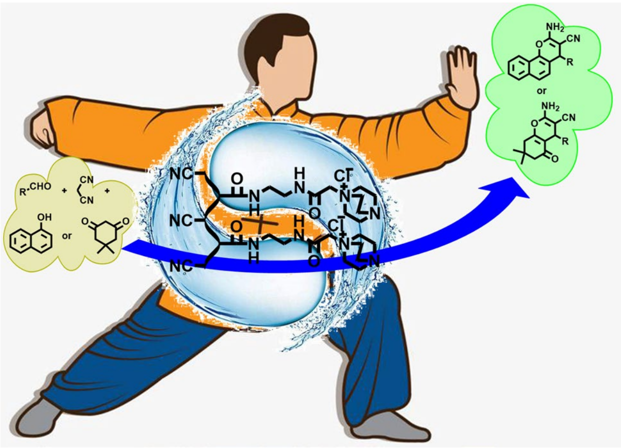
Abstract

Heterogeneous catalysis is an important branch of sustainable chemistry. In this work, a series of polyacrylonitrile fiber (PANF) fiber catalysts (PANF-E, PANF-EDs, and PANF-D) with different catalytic micro-environments are developed and characterized by elemental analysis, Fourier-transfer infrared spectroscopy, x-ray diffraction, thermogravimetric/differential scanning calorimetry analysis, scanning electron microscopy, and mechanical strength measurements to demonstrate the successful immobilization of the different amines as well as evaluate the physical strength and thermal stability of the fiber catalysts at different stages. The catalytic activities of the fiber catalysts are tested by one-pot three-component Knoevenagel-Michael reaction to the synthesis of substituted 2-amino-4*H*-chromenes in which the influences of surface polarities, kinds and proportions of functional groups on the fiber catalysts activities were investigated. Among the prepared catalysts, the PANF-D with higher density of tertiary amino group and hydrophilic micro-environment exhibited the best catalytic activity to efficiently catalyze the three-component reaction in water with excellent substrate suitability (92-98%). In addition, the catalyst can be easily separated from the catalytic system and conveniently reused at least ten times. Moreover, the PANF-D performs well in scaled-up experiment in a simple fixed-bed reactor with a yield of 97% which allows it to have great potential for further cleaner industrial applications.

Graphic Abstract



Keywords Green chemistry · Heterogeneous catalysis · Polyacrylonitrile fiber · Fixed-bed reactor

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1 Introduction

Chemistry has provided more than one hundred million artificial chemical substances that are in widespread use to maintain or even promote the living standards of our society [1]. However, environmental problems like ozone hole, river eutrophication, acid rain, heavy metal contamination, and so on have also been caused by chemicals over the last 50 years. The crisis also prompts people to explore new energy sources and environmentally friendly chemicals and chemical processes [2]. The "10 Key Green Chemistry Research Areas" [3] in Table 1 and "12 Green Chemistry Principles" [4, 5] show the main research areas of green chemistry in recent years and, to some extent, indicate the direction of green chemistry in the future. Among them, the 10 key catalyst immobilization without significant loss in kinetics principles is still an important direction for the research of green chemistry.

Nowadays, varieties of heterogeneous catalysts had been developed to realize green chemistry and multifarious materials like zeolite [6, 7], metal oxides [8, 9], polymer [10, 11], silica [12], biochar [13, 14] and so on had served as supports. Due to the unique microenvironment, polymer-based heterogeneous catalysts often show superior catalytic activity, excellent regioselectivity, and many other unique properties [15–17].

Polyacrylonitrile fiber (PANF) with advantages of light density, high strength, and low cost, is a common and widely used material in the industry and our daily life. Moreover, the abundant cyano groups in PANF can be easily transformed into aminocarbonyl, carboxyl, and other functional groups [18]. To date, various modified PANF have been prepared and applied to remove contaminants in water [19–21], synthesize phase change [22, 23], antimicrobial [24], and pH-sensitive materials [18, 25], etc. However, the application of PANF based heterogeneous catalysis in organic synthesis has been very rare. In our previous works, PANF has well modified to prepare heterogeneous base [26, 27], acid [28, 29], phase transfer [30], metal [31], bifunctional catalysts [32], etc. After the in-depth research, it was found that the immobilization of the PANF is a high-density, deep-seated modification, which constructs a specific micro-environment by immobilized functional groups and polymer block in the fiber catalyst. The micro-environment influences the catalytic activity of the fiber catalyst to a great extent by adsorption of organic substrate and increasing their contact area. Besides, PANF can be knitted into different shapes to suit for the application of fixed bed in industry, which indicate that PANF is an excellent support for heterogeneous catalyst.

In recent years, 2-amino-4*H*-chromenes have amused increasing interest due to their pervasive biological activities such as anticancer, antibacterial, anticoagulant, antidiabetic and antianaphylaxis activities [33–35]. A number of catalysts have been developed for the synthesis of 2-amino-4*H*-chromenes, including ionic liquids [36], metal bromide [37, 38], metal complex [39], amines [40], piperazine-functionalized nickel ferrite nanoparticle [41], Schiff base complex functionalized-magnetic nanoparticles [42]. Despite their potential utility, those methods have limitations, like long reaction time, hazardous solvents, tedious handle approaches, and unsatisfactory yields, which restrict their further practical applications. Therefore, it is still of extreme necessity to explore simpler, greener, and efficient catalytic systems for the synthesis of 2-amino-4*H*-chromenes.

Table 1 Key green chemistry research areas

Rank	Research area
1	Development of effective and versatile methodology utilizing cheap/sustainable metals.*
2	General methods for catalytic/sustainable (direct) amide or peptide formation.
3	Aliphatic and aromatic C–H activation, using green oxidants and giving predictable site selectivities.
4	Amide reductions avoiding $LiAlH_4$ and diborane.
5	Direct substitution of alcohols.
6	Catalyst immobilization without significant loss in kinetics.*
7	Asymmetric hydrogenation of unfunctionalized olefins/enamines/imines.
8	Improved fluorination/trifluoromethoxylation.
9	Wittig chemistry without Ph_3PO.‡
10	Alternatives for oxidations, C–O or C–N redox processes.

*New research area

‡New research area, but on the 2006 long list

In this work, based on our previous researches on polyacrylonitrile fiber catalysts, two 1,4-diazabicyclo[2.2.2]octane (DABCO) derivate functionalized polyacrylonitrile fiber catalysts were developed for the synthesis of substituted 2-amino-4*H*-chromenes by catalyzing one-pot Knoevenagel-Michael multi-component tandem reactions. The influences of surface polarities, kinds, and proportions of functional groups on the fiber catalysts activities were detailedly investigated. Furthermore, scaled-up experiment in simple fixed-bed reactor demonstrates the industrial application potential of the fiber catalyst.

2 Experimental Section

2.1 Synthesis of the PANF Catalysts

2.1.1 Synthesis of the DABCO Derivate (DABCO-COOMe)

DABCO (0.1 mol) was dissolved into 200 mL EtOAc, 0.08 mol methyl chloroacetate was dropped into the solution above, and the mixture was stirred at RT for 24 h. After the reaction was completed, the mixture was filtered and the white solid was washed by anhydrous ether (30 mL × 3). Then, the white solid was dried overnight at 60 °C to give the DABCO derivate of DABCO-COOMe (Scheme 1).

2.1.2 Synthesis of the Ethylenediamine Functionalized Polyacrylonitrile Fiber (PANF-E)

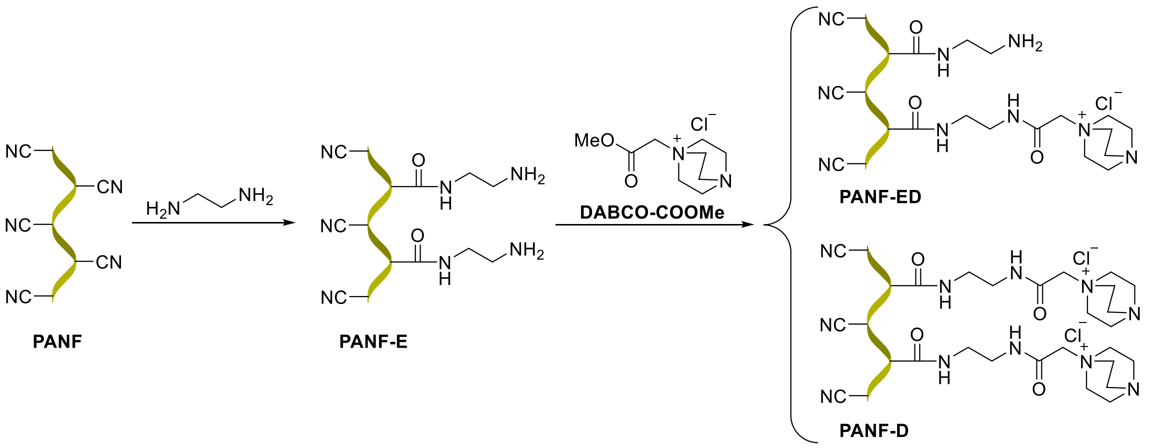
A mixture of dried PANF (1.0 g), ethylenediamine (10 mL) and water (20 mL) was added into a 100 mL round-bottom flask and the mixture was stirred and refluxed at 105 °C for the appropriate time, then the fiber was filtered out and washed repeatedly with deionized water (60–70 °C) until the pH of the filtrate was neutral. After that, the modified fiber was dried overnight under vacuum at 60 °C to give the PANF-E.

2.1.3 Synthesis of the Fiber Catalysts PANF-ED and PANF-D

A mixture of dried PANF-E (0.5 g), DABCO-COOMe (15 eq. of the amino group in PANF-E), Na_2CO_3 (0.5 g), and water (30 mL) was added into a 100 mL round-bottom flask and the mixture was stirred and refluxed at 105 °C for the appropriate time, then the fiber was filtered out and washed repeatedly with deionized water (60–70 °C) until the pH of the filtrate was neutral. After that, the modified fiber was dried overnight under vacuum at 60 °C to give the PANF-ED or PANF-D.

2.2 General Procedure for the PANF-D Catalyzed One-Pot Knoevenagel-Michael Multicomponent Reaction

A mixture of aldehyde (1.0 mmol), malononitrile (1.0mmol), 1-naphthol, or 5,5-dimethyl-1,3-cyclohexanedione (1.0 mmol), H_2O (20 mL), and PANF-D (15 mol%, based on DABCO group) were stirred and refluxed for the appropriate time. Then, the fiber catalyst was filtered out and washed with EtOAc (3 × 10 mL). The organic phase was combined and concentrated, and the crude product was purified by recrystallization from EtOH to afford the pure product. For the recyclability test, the recycled catalyst was dried and used directly for the next cycle.



Scheme 1 Synthesis of different fiber catalysts

3 Results and Discussion

3.1 Syntheses of Fiber Catalysts

The PANF-E was synthesized by directly refluxing the mixture of PANF, water, and ethylenediamine. Then, the PANF-ED was easily prepared by the reaction of PANF-E with DABCO-COOMe for the appropriate time. When the amino groups are consumed completely and the PANF-D is obtained (Scheme 1). The functional degrees of the fiber catalysts are determined by weight gain and acid exchange capacity, and the results are listed in Table 2. Compared with PANF-E, the preparation of PANF-ED is a time-consuming process caused by the low concentration of DABCO-COOMe (Table 2, entries 2-5).

In this work, the properties of different fiber catalysts were determined by water uptake content, which is a key factor in determining the hydrophilic properties of the fiber surface [43]. The PANF has low water uptake content of 10.9% for the dense surface (Table S1, entry 1). Because of the primary, tertiary amines, and quaternary ammonium are hydrophilic groups, the water uptake contents of PANF-E, PANF-ED, and PANF-D rise to 32.6%, 54.7%, and 66.9% (Table S1, entries 2–4), respectively as expected.

3.2 Elemental Analyses (EA)

The elemental analysis data of PANF, PANF-E, PANF-D, PANF-D-1 (the PANF-D have been used one time) and PANF-D-10 (the PANF-D have been used ten times) were tested three times and the average values were calculated (Table 3). For the ethylenediamine has lower carbon content (39.97%), higher hydrogen and nitrogen contents (13.42% and 46.61%, respectively), the carbon content of PANF-E is decreased, and the hydrogen content is increased as expected (Table 3, entry 2). The nitrogen content is decreased to 22.87% may be caused by the hydrolysis of -CN to -CONH$_2$.

Table 2 Preparation of different fiber catalysts

Entry	Raw fiber	Time (h)	WG (%)^a	F (mmol/g)	Catalyst
1	PANF	3	8.21	1.06^b	PANF-E
2	PANF-E	7	6.72	0.36^c	PANF-ED$_{2/1}$
3	PANF-E	8	9.92	0.53^c	PANF-ED$_{1/1}$
4	PANF-E	9	13.37	0.71^c	PANF-ED$_{1/2}$
5	PANF-E	10	16.79	0.99^c	PANF-D

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[a] Weight gain = [(W2–W1)/W1] × 100%, in which W1 and W2 are the weights of original and modified fibers, respectively

[b] Determined by titration

[c] Determined by weight gain

Table 3 Elemental analysis data of different fibers

Entry	Fiber	C (%)	H (%)	N (%)	S (%)
1	PANF	70.75	5.94	26.12	0.09
2	PANF-E	62.93	6.32	22.87	0.08
3	PANF-D	63.22	6.14	20.36	0.06
4	PANF-D-1	63.29	6.17	20.30	0.07
5	PANF-D-10	65.63	6.28	18.74	0.08

Compared to those of PANF-E, EA data of PANF-D has similar changes, which demonstrate the successful immobilization of DABCO (Table 3, entry 3). After being used one time, the EA data of PANF-D-1 almost the same as those for PANF-D (Table 3, entry 4). When the PANF-D was used ten times, the EA data of PANF-D-10 only slightly changed which may be caused by the absorption of some intermediates or products during the reaction process.

3.3 Fourier-Transform Infrared Spectroscopy (FTIR)

Samples of different fibers are pulverized and mixed into KBr pellets and the spectra are shown in Fig. 1. For the FTIR spectrum of PANF (Fig. 1a), the peak at 2942 cm^{-1} is assigned to the C–H stretching vibration of methyl and methylene in PANF. The 2245 cm^{-1} absorption band is attributed to the stretching vibration of –C≡N. The adsorption peak at 1733 cm^{-1} indicates the existence of methyl acrylate units. After modified by ethylenediamine (Fig. 1b), the peaks at 2245 cm^{-1} and 1733 cm^{-1} are reduced in size as expected for the reaction of -CN and -COOMe groups with -NH$_2$ in ethylenediamine. The broad peak that appears at 3404 cm^{-1} is assigned to N–H in the –CONH– and –NH$_2$ moieties formed during

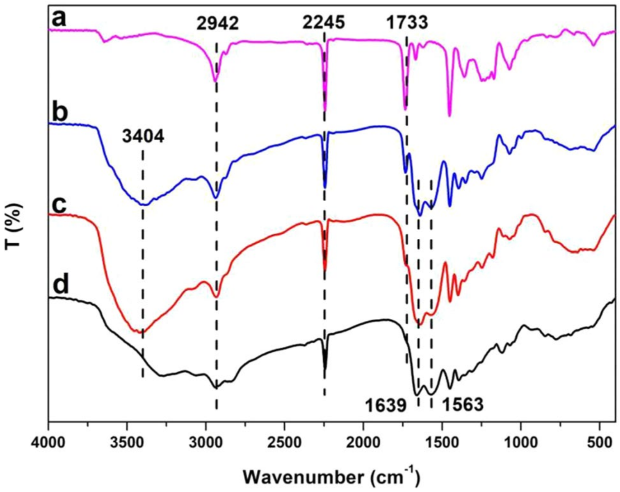


Fig. 1 FTIR spectra of **a** PANF, **b** PANF-E, **c** PANF-D, **d** PANF-D-10

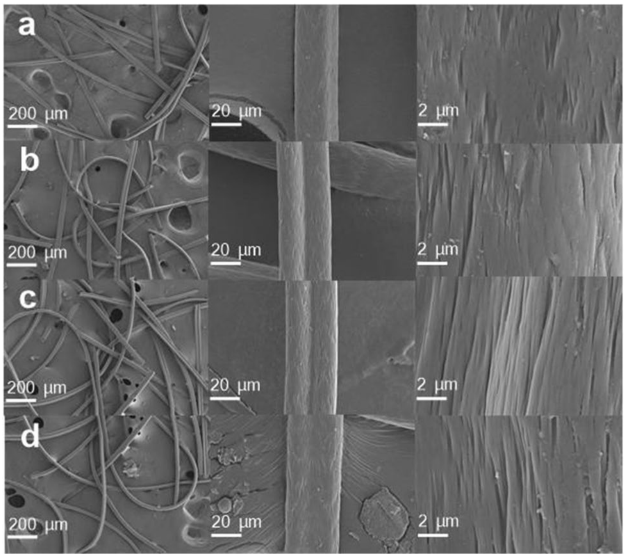


Fig. 2 SEM images of **a** PANF, **b** PANF-E, **c** PANF-D, **d** PANF-D-10

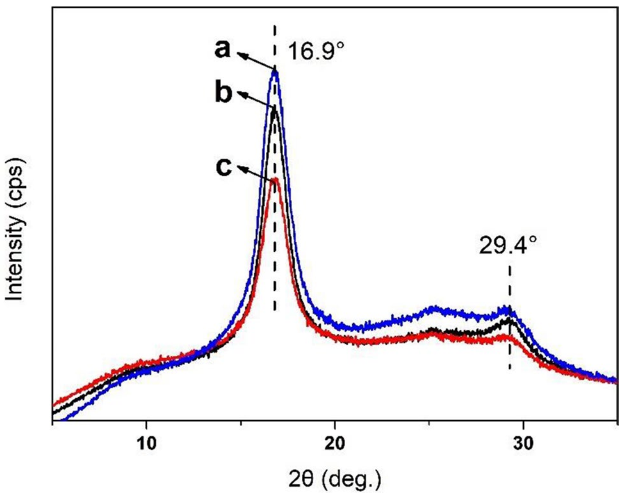


Fig. 3 XRD spectra of **a** PANF, **b** PANF-D, **c** PANF-D-10

the aminolysis of the cyano and ester groups with ethylenediamine. In addition, two new bonds at 1639 cm^{-1} and 1563 cm^{-1} are superpositions of C=O, C–N stretching vibration and N–H bending vibration in –CONH– and –$CONH_2$. For the spectrum of PANF-D (Fig. 1c), the peaks at 3404, 1639, and 1563 cm^{-1} are all enhanced which indicates the successful grafting of DABCO on PANF. After used ten times, the spectrum of PANF-D-10 only has minor changes, which suggests the excellent recoverability of the fiber catalyst (Fig. 1d).

3.4 Scanning Electron Microscopy (SEM)

The SEM images of PANF, PANF-E, PANF-D, and PANF-D-10 are illustrated in Fig. 2. Compare to the SEM image of PANF, the surface of PANF-E and PANF-D become slightly rougher, and their diameters increase remarkably, which caused by the swelling effect during the modification processes (Fig. 2a–c). After being used ten times (Fig. 2d), the fiber catalyst PANF-D was swelled further and its surface becomes rougher. At last, the basic structure of the PANF-D is still retained with considerable mechanical strength (Table 3) to meet the need for further applications (Fig. 3).

3.5 X-Ray Diffraction (XRD)

XRD spectra of PANF, PANF-D, and PANF-D-10 are exhibited in Fig. 4. For PANF (Fig. 3a), two peaks at $2\theta = 16.9°$, 29.4° are corresponded to strong diffraction of (100) face and weak diffraction of (110) face, respectively. The hexagonal lattice formed by parallel close packing of the molecule rods caused the peak at $2\theta = 16.9°$, which indicates that PANF adopts a stiff rod-like conformation due to the intermolecular repulsion of the nitrile dipoles. After being modified by DABCO-COOMe (Fig. 3b), the reflection peak at $2\theta = 16.9°$ was decreased, which demonstrates that part of the crystalline

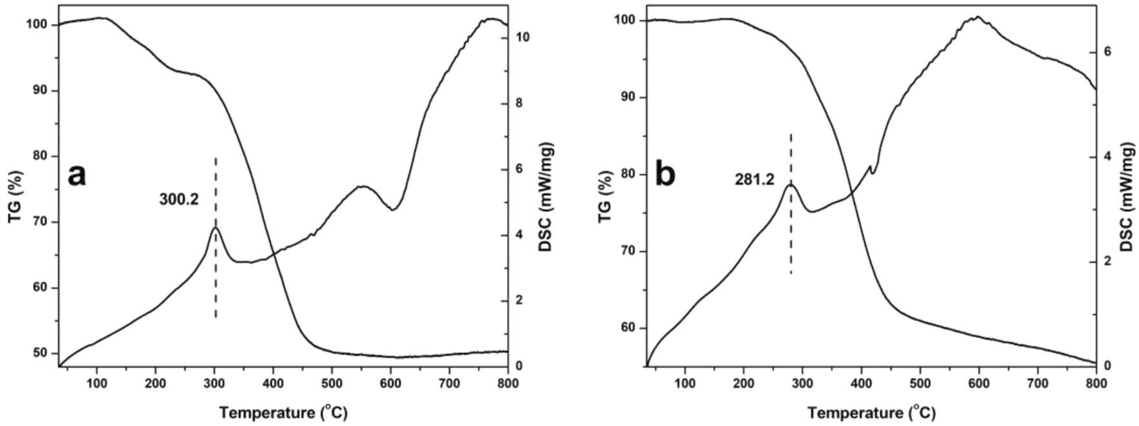


Fig. 4 TG/DSC curves of **a** PANF-D, **b** PANF-D-10

Table 4 Mechanical strength of different fibers

Entry	Fiber	BS (cN)	RBS (%)
1	PANF	11.0	100
2	PANF-E	10.2	93
3	PANF-D	9.5	86
4	PANF-D-10	8.9	81

phase of the fibers has been damaged during the modified processes. When the fiber catalyst was used ten times (Fig. 3c), the peak at $2\theta = 16.9°$ was further weakened for the continuous breakage of bonds in the inner crystal region. However, the basic structure of the PANF-D-10 is still retained (Fig. 2d).

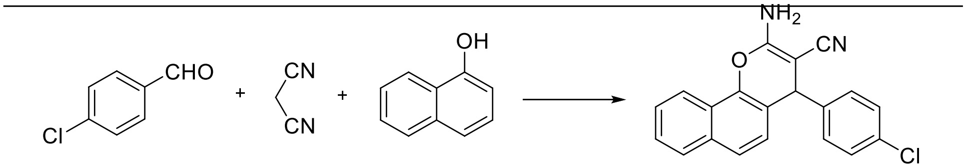
3.6 Thermal Stability Analysis

Thermal stabilities of PANF-D and PANF-D-10 are tested by TG/DSC and the results are presented in Fig. 4. The DSCmax (maximum thermal decomposition temperature) of the PANF-D is 309.4 °C [32]. After a two-step modification, the DSCmax of PANF-D is decreased to 300.2 °C (Fig. 4a), which indicates little structural damage happening on the fiber catalyst. When the fiber catalyst was used ten times, the PANF-D-10 was further swelled and its DSCmax was declined to 281.2 °C (Fig. 4b), which can still meet the thermal stability requirement for the one-pot Knoevenagel-Michael multi-component tandem reaction.

3.7 Mechanical Strength

Appropriate breaking strength (BS) is an important parameter for the fiber catalyst as fixed-bed material in the industry. The mechanical strengths of different fibers are tested and the results are listed in Table 4. The PANF has a BS of 11.0 cN and its retention of breaking strength (RBS) is 100% (Table 4, entry 1). After modified by ethylenediamine, the breaking strength of PANF-E decreases to 10.2 cN with 93% RBS (Table 4, entry 2), and the mechanical strength of PANF-D is further declined to 9.5 cN BS and 86% RBS (Table 4, entry 3). When the fiber catalyst was

Table 5 Optimization of the three-component condensation reaction reaction[a]



Entry	Fiber	Dosage (mol%)	T (°C)	Time (min)	Yield (%)[b]	TOF (h^{-1})
1	PANF	----	80	60	20	----
2	PANF-E	15	80	60	46	3.1
3	PANF-$ED_{1/2}$[c]	15	80	60	61	4.1
4	PANF-$ED_{1/2}$[c]	15	80	60	69	4.6
5	PANF-$ED_{1/2}$[c]	15	80	60	78	5.2
6	PANF-D	15	80	60	84	5.6
7	PANF-D	15	90	60	93	6.2
8	PANF-D	15	refluxed	60	98	6.5
9	PANF-D	15	refluxed	80	98	4.9
10	PANF-D	10	refluxed	60	81	8.1
11	PANF-D	20	refluxed	60	98	4.9

[a] Reaction conditions: 4-chlorobenzaldehyde (1.0 mmol), malononitrile (1 mmol) and 1-naphthol (1 mmol) in the presence of PANF-D in water (10 mL) are refluxed for appropriate time

[b] Isolated yield after recrystallization with ethanol

[c] The subscripted number indicates the proportion of primary amine to DABCO groups

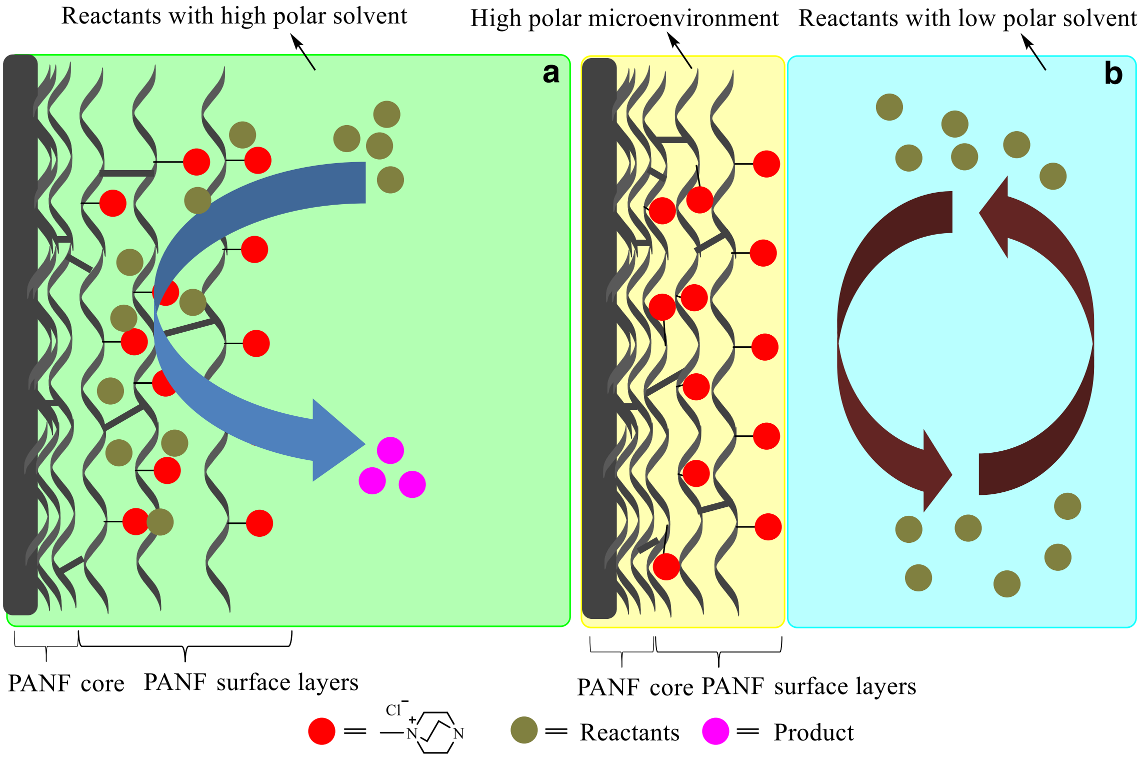


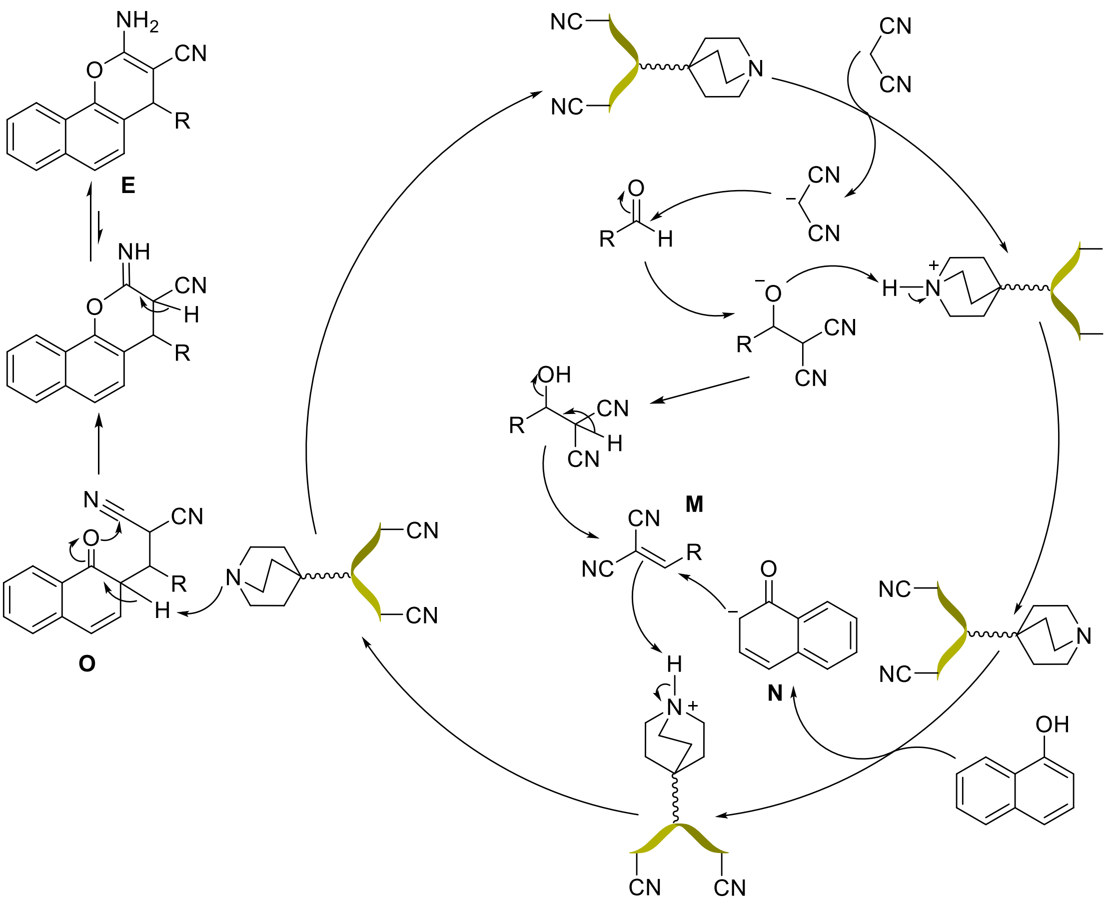
Fig. 5 Knoevenagel-Michael at **a** high polar solvent, **b** low polar solvent.

used ten times (Table 4, entry 4), the PANF-D-10 still has 8.9 cN BS and 81% RBS mechanical strength, which indicates the fiber catalyst has excellent mechanical strength for further researches.

3.8 Catalytic Activities

The catalytic activities of different fiber catalysts were tested using the template reaction of 4-chlorobenzaldehyde, malononitrile, and 1-naphthol in water (Table 5). When the reaction was carried out at 80 °C for 60 min with PANF as catalyst, only 20% yield was obtained (Table 5, entry 1). In the case of PANF-E as catalyst, the yield was 46%. For PANF-ED, the yields were grown from 61 to 84% as proportions of the DABCO group in the fiber catalysts were increased (Table 5, entries 3–6), which suggests that the DABCO group is the dominating catalytic unit. With PANF-D as catalyst, the yields were increased from 84 to 98% as the reaction temperature enhanced from 80 °C to refluxing condition (Table 5, entries 7 and 8). Reaction time is another reaction parameter, when the reaction time was prolonged to 80 min, the yield was kept unchanged (Table 5, entry 9). When dosage of the catalyst was reduced to 10 mol%, the reactants were consumed incompletely, and the yield was reduced to 81%. However, the yield was unaffected if the catalyst dosage was increased to 20 mol%. Finally, 15 mol% of catalyst dosage, refluxed 60 min at 80 °C in water were selected as the optimal reaction conditions.

Furthermore, the solvent effect on the Knoevenagel-Michael reaction had been studied in this work. As we can see from Table S2, the polarities of solvents have significant impacts on the reaction yields. The reaction can only proceed effectively in strongly polar solvents like H_2O which can get a yield of 98% (Table S2, entry 1). CH_3OH solvent, whose polarity is 6.6, the yield was declined to 12% rapidly. However, when the PANF-D was performed in solvents with less polarity than CH_3OH, like CH_3CN, 1,4-dioxane, C_2H_5OH, and toluene, the reaction even can't occur (Table S1, entries 3-6). It is a strange phenomenon for common organic reactions. In order to understand this phenomenon, we proposed a high polar micro-environment promote mechanism (Fig. 5). This phenomenon can be explained by the relative polarity of solvent and the surface of fiber catalyst. The tertiary amine group, quaternary ammonium group, and polymer block construct a high polar micro-environment in fiber catalyst. In high polar solvent like water (Fig. 5a), the micro-environment can be stretched, and the mixture of solvent and reactants can access the active catalytic sites in the micro-environment to generate the product. On the contrary, the high polar micro-environment will be shrunk in a less polar solvent (Fig. 5b), the mixture of solvent and reactants can hardly access to the active catalytic sits, resulting in the failure of



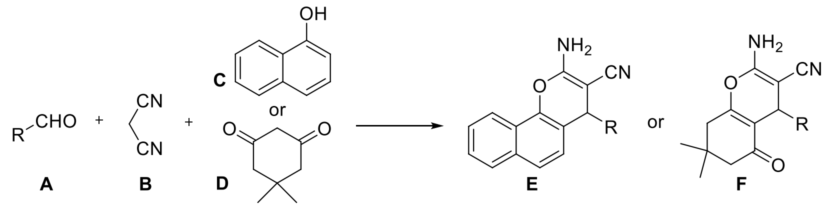
Scheme 2 The possible reaction mechanism

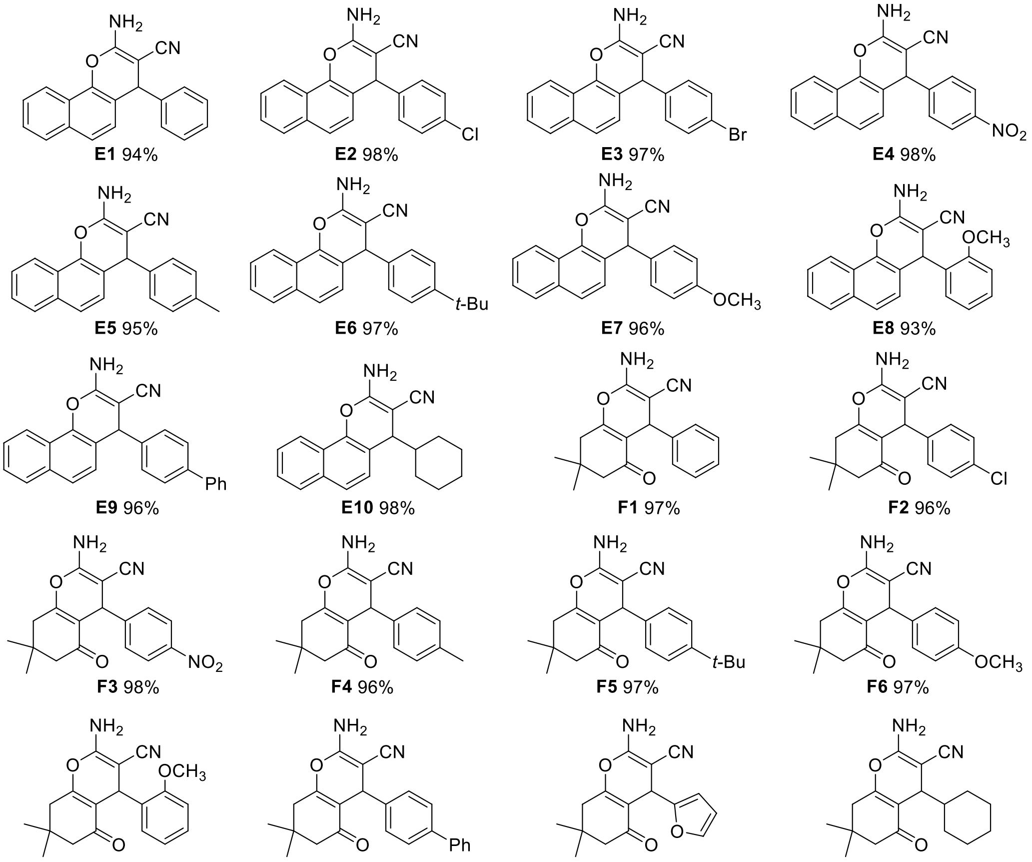
the reaction. The high selectivity to strongly polar solvents (especially for water, which is an environmentally friendly solvent) is one of the highlights for PANF-D.

A possible mechanism of the Knoevenagel-Michael cascade reaction catalyzed by PANF-D is depicted in Scheme 2. The ring structure of the DABCO group does not only make the lone pair electrons on the nitrogen atoms more exposed but also makes them more alkaline. For this three-component one-pot reaction, PANF-D acts as the Brønsted proton scavenger to promote the Knoevenagel reaction of aldehydes with malononitrile, and the intermediate product **M** is formed. At the same time, the 1-naphthol is activated by PANF-D to form the intermediate **N**. Then, the C=C bond in the intermediate product **M** is attacked by the intermediate **N** to form another intermediate **O**. In the end, after an intramolecular ring closure reaction facilitated by PANF-D, the final product **E** is produced.

PANF-D was then applied to the Knoevenagel-Michael cascade reaction of different aldehydes, malononitrile with 1-naphthol or 5,5-dimethyl-1,3-cyclohexanedione under the optimal conditions mentioned above, and the results are summarized in Table 6. Aldehydes with electron-donating or electron-withdrawing groups are all completed the reaction smoothly. However, the activity of 2-methoxybenzaldehyde is lower than that of 4-methoxybenzaldehyde which may be caused by the larger steric hindrance of the former (Table 6, E7, E8, F6, and F7). Furthermore, the three-component condensation reaction can also proceed successfully when the 1-naphthol was replaced by 5,5-dimethyl-1,3-cyclohexanedione (Table 6, E1-10, F1-10), which demonstrate the PANF-D has excellent substrate suitability for the Knoevenagel-Michael cascade reaction.

Table 6 Three-component reaction of aldehydes, malononitrile and ethyl cyanoacetate[a]





E1 94% **E2** 98% **E3** 97% **E4** 98%

E5 95% **E6** 97% **E7** 96% **E8** 93%

E9 96% **E10** 98% **F1** 97% **F2** 96%

F3 98% **F4** 96% **F5** 97% **F6** 97%

F7 92% **F8** 96% **F9** 95% **F10** 96%

[a] Reaction conditions: aldehydes (1.0 mmol), malononitrile (1 mmol) and 1-naphthol (1 mmol) in the presence of PANF-D (15 mol%) in water (10 mL) are reflux for appropriate time. Yield of isolated product

3.9 Scaled-Up Experiment in Simple Fixed-Bed Reactor

To demonstrate the potential industrial application of the fiber catalyst, the Knoevenagel-Michael reaction of 4-chlorobenzaldehyde, malononitrile and 1-naphthol was amplified 50 times in a simple fixed-bed reactor (250 mL, with the catalyst PANF-D intertwined on the stirring paddle, Fig. 6). The three-component one-pot reaction can be finished without any extension of the reaction time to obtain high product yields of 97% (16.1 g), which could meet the further preindustrial application research.

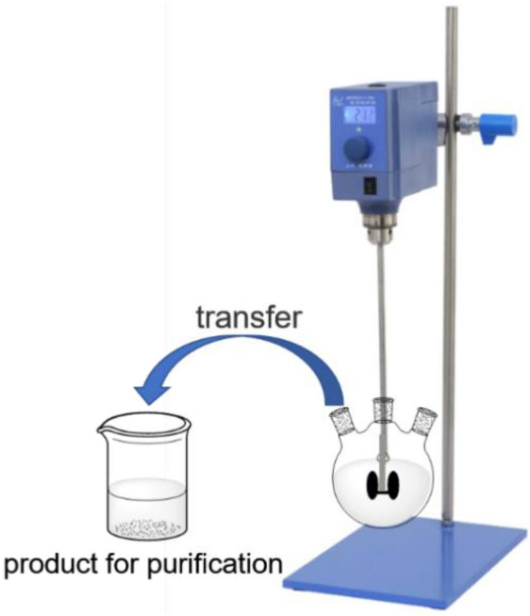


Fig. 6 Diagrammatic sketch of the simple fixed-bed reactor for Knoevenagel-Michael reaction

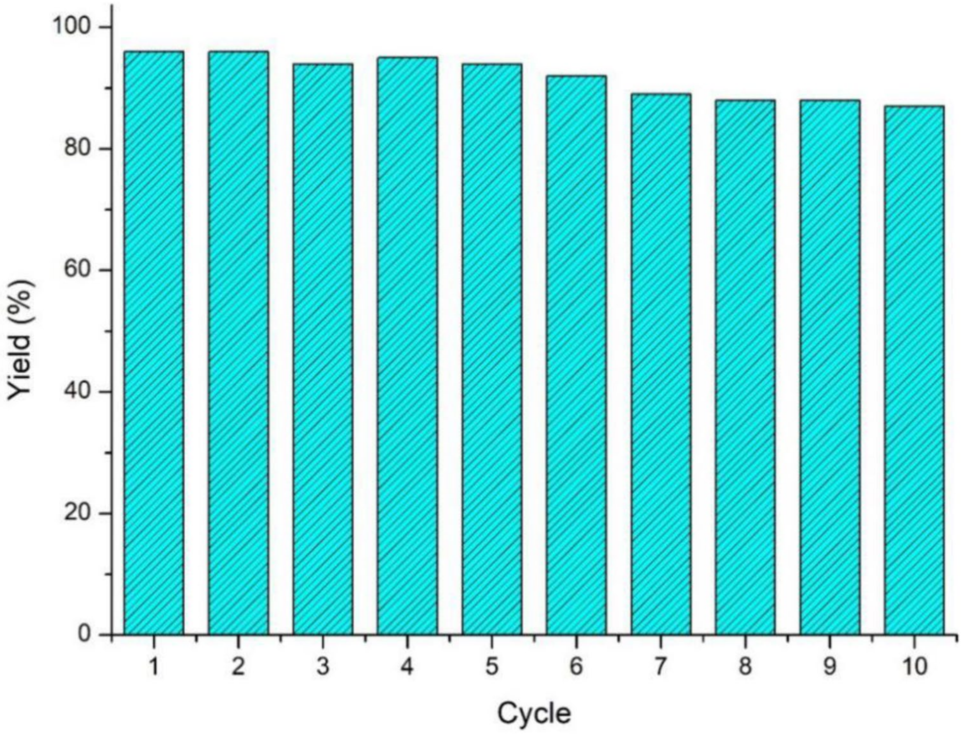
3.10 Recyclability Test

From the view of economical and sustainable chemistry, recyclability is one of the characteristic advantages of the heterogeneous catalyst. Therefore, the recyclability of PANF-D is tested with the Knoevenagel-Michael reaction of 4-chlorobenzaldehyde, malononitrile, and 1-naphthol under the optimal reaction conditions (Fig. 7). After each cycle, the PANF-D is separated out with tweezers and rinsed by EtOAc (3 × 10 mL). Then the fiber catalyst can be directly used for the next cycle and the results are shown in Fig. 6. After ten cycles, the reaction can still reach a yield of 90%, which indicates excellent recoverability of the fiber catalyst PANF-D.

4 Conclusion

In summary, a series of PANF fiber catalysts (PANF-E, PANF-ED$_{2/1}$, PANF-ED$_{1/1}$, PANF-ED$_{1/2}$, and PANF-D) with different functional groups are developed and applied to the synthesis of substituted 2-amino-4*H*-chromenes by three-component one-pot Knoevenagel-Michael reaction in water. The influences of surface polarities, kinds, and proportions of functional groups on the fiber catalysts activities were investigated. The experiments testify that the catalytic activity and solvent selectivity of synthesized PANF support catalyst is mostly dependent on the strong basicity and micro-environment polarity of the fiber catalyst. Among the fiber catalysts, the PANF-D has shown the best catalytic activity which can complete the Knoevenagel-Michael reaction with high yields of 92–98% in 1 h. Moreover, the PANF-D has excellent recyclability (at least ten times) and performs well in scaled-up experiment with a simple fixed-bed reactor (97%). It turns out that the

Fig. 7 Recyclability of PANF-D in the Knoevenagel-Michael reaction



catalyst has many advantages, such as easy preparation, highly efficient activity, broad substrate scope, green solvent, and excellent recyclability. It is believed that more new applications of PANF-D will be developed in value-added chemistry.

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Compliance with Ethical Standards

Conflict of interest There has no conflict of interest for each contributing author.

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