Preparation and Characterization of Novel Polymer-Based Heterogeneous MPg-C₃N₄ Catalyst and Its Application in Multi-Component Reactions

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Abstract

Magnetic polyvinyl alcohol-based g-C₃N₄ composite (MPg-C₃N₄) was synthesized as a heterogeneous catalyst. It was characterized by various analyses such as FT-IR, XRD, FE-SEM, TGA, EDX, and VSM. For showing the catalytic merits of MPg-C₃N₄, it was used in the synthesis of acridinedione and 4H-chromene derivatives in a highly efficient yield. Various aldehyde derivatives were used to show the merits of the MPg-C₃N₄. High yield, short reaction time, easy separation, mild condition reaction, simple purification, non-toxic solvents, and reusability are the advantages of using polymer-based heterogeneous MPg-C₃N₄ catalyst to synthesize acridinedione and 4H-chromene derivatives. Also, the intended products were purified by simple crystallization.

Introduction

Today, nanocomposite catalysts are receiving much attention in organic synthesis due to various advantages such as chemical stability, high activity, reusability, and easy separation. Numerous factors affect the properties and performance of nanocomposite catalysts, such as surface area, porosity, morphology, and stability. Therefore, using proper support can improve the performance of these catalysts. Among organic polymer compounds, graphitic carbon nitride (g-C₃N₄), due to its particular structure and attractive electronic properties, has attracted much attention in various fields such as sensing, solar cells, photocatalysis, and catalysis. g-C₃N₄ can be easily synthesized at a low price with chemical stability and an environmentally friendly nature.

Graphitic Carbon nitrides have recently been suggested as candidates for new hard materials. These materials are expected to include a combination of extreme chemical inertness, hardness, and oxidation resistance[1]. The most notable material in this family is the covalent carbon-nitrogen solid, beta-C₃N₄, which would have hardness comparable to or greater than the diamond. Furthermore, the cohesive energy of beta-C₃N₄ was found to be reasonably large, indicating that it might be an energetically favorable phase in the C₃N₄ system[2]. In one study, small crystallites were found embedded in amorphous C₃N₄ films; Electron diffraction suggested that beta-C₃N₄ is an applicable structure for these crystallites[3]. Due to the unique properties of g-C₃N₄, they can be used as fillers in polymer nanocomposites.

In the last decades, polymeric nanocomposites have gained more attention due to the unique properties obtained with these materials. Polyvinyl alcohol (PVA) is an excellent polymer candidate for polymer nanocomposites. It has unique properties such as good biocompatibility, processability, biodegradability, and chemical resistance. For improving the properties of PVA, it is advisable to add an inorganic filler to create a composite that may be elastic, soft, and well-formed. Polymer nanocomposites with 2D nanofillers usually perform much differently or better than bulk polymers. Due to the high thermal and chemical stability of polymer nanocomposites[4], they are a candidate as heterogeneous catalysts in synthesizing organic compounds through various reactions.

Multi-component reactions have been employed as an effective, simple, economic, eco-friendly tactic to prepare numerous organic and pharmacological compounds[5]. The mechanism of multi-component reactions goes through a one-pot condensation reaction of three or more components to generate new materials containing the starting components in their skeletal arrangement. Hantzsch, Biginelly, Strecker, and synthesis of acridinedione and 4H-chromene derivatives are examples of multi-component reactions[6, 7].

Nowadays, 4H-chromene derivatives are attracted to scientists due to various activities such as biology and pharmaceutical [8]. Also, they are one of the essential classes of heterocyclic compounds due to their biological properties like spasmolytic[9], anti-cancer[10], and anticoagulant[11]. So, 4H-chromene derivatives can be employed in neurodegenerative diseases such as Parkinson's disease[12] and Alzheimer's disease[13].

Another important class of heterocyclic compounds is acridinedione derivatives that possess the ring of the 1,4-dihydropyridine(1,4-DHP) compound. These compounds represent several significant properties such as laser activity[14], laser dyes[15], photoinitiators[16], photophysical[17], electrochemical[18], and fluorescence properties[19].

The 1,4-DHP derivatives are valuable pharmaceutical agents and active intermediates in organic and medical chemistry[20]. Furthermore, these materials contribute very effective biological activities such as antimicrobial[21], anticancer[22], anti-inflammatory[23], anti-diabetic[24], vasodilator[25], and DNA binding properties[26]. Therefore, tremendous interest has been devoted to the synthesis of these compounds using heterogeneous or homogeneous catalysts.

Herein, we have introduced MPg-C₃N₄ (Scheme 1) as a novel polymer-based heterogeneous catalyst and characterized it with various analyses. Also, we have used MPg-C₃N₄ in two different multi-component reactions with high yields and short reaction times for showing its catalytic property.

Result And Discussion

The synthesized MPg-C₃N₄ is a Polymer-based heterogeneous catalyst and has both the advantages of polymers and nanoparticles. The contact surface of MPg-C₃N₄ has increased by the hydrophilicity of PVA, and the extraction would easily be done due to magnetic properties.

Figure 1 is for the MPg-C₃N₄ FT-IR analysis. The absorption band at 550-660 cm⁻¹ is related to Fe-O modes. The relatively weak absorption band in the 886 cm⁻¹ is related to the bending vibration of the tri-s-triazine ring system. The presence of an absorption band of about 1072 cm⁻¹ indicates the tensile vibrations of the Fe-O-C bond[27]. The band specified in the range 1240-1637 cm⁻¹ corresponds to the C-NH-C and N-(C)₃ vibration modes[28]. The band about 1315 is related to C-H deformation vibration[29]. The bands about 2800 cm⁻¹ and 2900 cm⁻¹ are related to the stretch vibrational of C-H. The presence of broadband of about 3100 to 3400 cm⁻¹ is related to -NH and -OH groups and hydrogen bondings[30].

For the compositional study of MPg-C₃N₄, the EDS analysis has been done and shown in Fig. 2. The EDS spectrum revealed C, N, O, Fe elements in synthesized polymer-based heterogeneous MPg-C₃N₄ that refer to the presence of Fe₃O₄ particles amongst magnetic PVA/ g-C₃N₄.

Structural analysis of synthesized polymer-based heterogeneous MPg-C₃N₄ catalyst was performed using X-ray diffraction (XRD), and the results were shown in **Fig 3**. As you can see, the peaks about 30.62°, 36.35°, 43.74°, 57.82°, and 63.41° are related to Fe₃O₄ nanoparticles (JCPDS database, PDF#99-0073)[31]. Moreover, there is a peak of about 19° that is related to PVA. The peaks for g-C₃N₄ nanosheets are disappeared, which should be related to the low amount of filler in the MPg-C₃N₄[32].

The illustration related to the morphology, size, and structure of the catalysts must also be explored; therefore, we adopt FE-SEM to examine the morphology of the prepared polymer-based heterogeneous catalyst in different scales (Fig. 4-a 100 nm, Fig. 4-b 200 nm, Fig. 4-c and Fig. 4-d 500 nm in different angles). As can be seen, Fe₃O₄ spherical nanoparticles are seen between g-C₃N₄ nanosheets and polymer-based PVA/ g-C₃N₄, and loaded aggregation is distributed uniformly on the surface.

The thermal behavior of the prepared polymer-based heterogeneous MPg-C₃N₄ was investigated by thermogravimetric analysis (TGA) over the temperature range of 20-800 °C under the air atmosphere. The TGA curve in **Fig 5** presented 3 main weight loss regions. The first weight loss (from 50 to 150 °C) denotes the evaporation of adsorbed water on the surface of the Fe₃O₄ nanoparticles[33]. The second weight loss (from 250 to 397 °C) occurs when the PVA/ g-C₃N₄'s functional groups are decomposed and up to 397 °C related to degradation of the PVA backbone[34]. The remaining, in the end, is related to Fe₃O₄.

The magnetic properties of MPg-C₃N₄ were determined using the VSM analysis at room temperature and shown in Fig. 6. Magnetic coercivity (HC) and magnetic residue (Mr) are negligible for polymer-based heterogeneous MPg-C₃N₄. Therefore, the ultra-magnetic behavior of the MPg-C₃N₄ is confirmed. In fact, in the field of the applied intensity with KOe10 intensity, the magnetic saturation (Ms) of the synthesized MPg-C₃N₄ is about 32/94521 emu/g, which is less than Fe₃O₄ nanoparticles. The observed decrease in magnetic saturation is due to the composite's involvement of some Fe₃O₄ levels, which have no magnetic nature. Despite the observed reduction in magnetic saturation, the MPg-C₃N₄ as a catalyst is easily separated from the reaction mixture by an external magnet.

Application

The catalytic potential of prepared polymer-based heterogeneous MPg-C₃N₄ for multi-component reactions was investigated. Appropriate conditions were developed by using environmental solvents, the optimal amount of catalyst at the optimum time. The synthesis of acridinedione derivatives was carried out using 4-chlorobenzaldehyde (1 mmol), dimedone (2 mmol), ammonium acetate (1 mmol), and MPg-

C₃N₄ (20 mg) in ethanol as model reaction (Reaction 1, Scheme 2). Also, the 4H-chromene reaction was carried out by 4-chlorobenzaldehyde (1 mmol), dimedone (1 mmol), malononitrile (1 mmol), MPg-C₃N₄ (20 mg), and ethanol as model reaction (Reaction 2, Scheme 3). In addition, the progression of the reaction is monitored by thin-layer chromatography (TLC). The obtained product was determined by nuclear magnetic resonance spectroscopy (NMR) analysis.

Reaction conditions were optimized for reactions **1** and **2** using 4-chlorobenzaldehyde, dimedone, ammonium acetate, and 4-chlorobenzaldehyde, dimedone, malononitrile, respectively (Table 1). Initially, the reaction was performed at room temperature (RT), and the reaction progression was controlled at different time intervals (Table 1, **entries 1-3**). It was observed that within 15 minutes, no significant product was formed. No significant increase in product performance was observed with increased time. In addition, to increase the yield of the product, the temperature has risen to 80°C, leading to high yields (Table 1, **entry 4**).

Moreover, in addition to ethanol, other benign environmental solvents, such as water, methanol, and acetonitrile, were also investigated for model reaction. (Table 1, **entries 5-7**). It was found that the highest yield of the product was observed in ethanol compared to other solvents. In addition, the reaction was also carried out in non-green solvents such as dichloromethane (DCM) and dimethyl sulfoxide (DMSO), and it was observed that the reaction resulted in relatively lower yields (Table 1, **entries 8 and 9**). Therefore, it was concluded that optimum reaction conditions with ethanol as solvent at 80°C (Table 1, **entry 4**) were used as model reaction conditions for further reactions. Also, the optimal catalyst amount was determined according to Table 2. The best result was found with 20 mg of MPg-C₃N₄ as a catalyst, and a further increase in the amount of it did not increase the reaction speed. Under optimum reaction conditions, different control reactions were performed with g-C₃N₄ nanosheets and without any catalyst to show the importance of the catalyst (Table 1, entries 10 and 11). Therefore, it was found that MPg-C₃N₄ can catalyze multicomponent reactions with high product yield under optimum conditions.

Table 1. Optimization of MPg-C₃N₄ catalyzed reaction 1 and reaction 2^(a)

Entry	Catalyst	Temperature ()	Time (min)	Solvent	Yield (%) (Reaction 1)	Yield (%) (Reaction 2)
1	MPg-C ₃ N ₄	RT	5	EtOH	33	28
2	MPg-C ₃ N ₄	RT	10	EtOH	48	43
3	MPg-C ₃ N ₄	RT	20	EtOH	58	55
4	MPg-C ₃ N ₄	80	20	EtOH	96	93
5	MPg-C ₃ N ₄	80	20	H ₂ O	71	66
6	MPg-C ₃ N ₄	80	20	MeOH	84	78
7	MPg-C ₃ N ₄	80	20	Acetonitrile	51	46
8	MPg-C ₃ N ₄	80	20	DCM	38	36
9	MPg-C ₃ N ₄	80	20	DMSO	30	28
10	g-C ₃ N ₄	80	30	EtOH	19	16
11	-	80	45	EtOH	-	-

(a) Model reaction (1): 4-chlorobenzaldehyde (1mmol), dimedone (2mmol), and ammonium acetate (1mmol) for synthesis of acridinedione derivatives. Model reaction (2): 4-chlorobenzaldehyde (1mmol), malononitrile (1mmol), and dimedone (1mmol) for synthesis of 4H-chromene derivatives.

Table 2. Different amount of MPg-C₃N₄ used for model reaction 1 and model reaction 2^(a).

Entry	Amount of MPg-C ₃ N ₄ (mg)	Temperature ()	Time (min)	Yield (%) (Reaction 1)	Yield (%) (Reaction 2)
1	5	80	20	67	63
2	10	80	20	74	69
3	20	80	20	96	93
4	30	80	20	96	93

(a) Model reaction (1): 4-chlorobenzaldehyde (1mmol), dimedone (2mmol), and ammonium acetate (1mmol) for synthesis of acridinedione derivatives. Model reaction (2): 4-chlorobenzaldehyde (1mmol), malononitrile (1mmol), and dimedone (1mmol) for synthesis of 4H-chromene derivatives.

The generality and amplitude of the MPg-C₃N₄ catalytic system were investigated using various substrates. The substrate range for multi-component reactions was investigated by changing different electron-withdrawing groups (EWG) and electron-donating groups (EDG) on carbonyl substrates according to Table 3 and Table 4. Reactions led to high product yield. It was observed that different EWG and EDG affect the rate of reactions and product efficiency. It was also observed that carbonyl compounds with EWG are more reactive than EDG, which shows electronic and steric changes.

Table 3. Different substrates for the synthesis of acridinedione derivatives^(a,b)

Entry	R	Amine	Product	Mp (°C, [Ref])	Yield (%)
1a		NH ₄ OAc		280 - 282[35]	90
2a		NH ₄ OAc		302 - 304[36]	96
3a		NH ₄ OAc		244 - 245[37]	82

4a		NH ₄ OAc		301 - 303[38]	85
5a		NH ₄ OAc		299 - 300[39]	94
6a		NH ₄ OAc		294 - 296[40]	91
7a				245 - 247[41]	85
8a				304 - 306[42]	88

9a				333 - 335[43]	81
10a				279 - 280[44]	83

^(a)Reaction condition: aldehyde (1mmol), dimedone (2mmol), ammonium acetate (1mmol), catalyst (20 mg), and ethanol (5mL) refluxed in 80 °C

^(b)Yields referred to pure products

Table 4. Different substrates for the synthesis of 4H-chromene derivatives^(a,b)

Entry	R	Product	Mp (°C, [Ref])	Yield (%)
1c			235 - 237[45]	87
2c			212 - 213[46]	85

3c			179 - 181[47]	91
4c			205 - 206[48]	89
5c			211 - 212[49]	93
6c			210 - 212[50]	90
7c			227 - 228[51]	89
8c			222 - 224[52]	83

9c			251 - 252[35]	81
10c			198 - 199[53]	88

^(a)Reaction condition: aldehyde (1mmol), dimedone (1mmol), ammonium acetate (1mmol), malononitrile (1mmol) catalyst (20 mg), and ethanol (5mL) refluxed in 80 °C

^(b)Yields referred to pure products

Mechanism

A plausible mechanism for the synthesis of acridinedione derivatives in the presence of MPg-C₃N₄ has been shown in Scheme 4. In this mechanism, hydrogen bonding is very effective. Firstly, MPg-C₃N₄ binds with the oxygen of dimedone's carbonyl group (I) and thus increases carbonyl activity, making alpha hydrogen highly acidic (II), thereby facilitating the adaptation and attack of the friend nucleus to aromatic aldehydes leading to obtaining a knoevenagel product (III). Then the knoevenagel product reacted in Michael's reaction with another molecule of the active molecule C-H (IV), and an intermediate has produced. Then, with the help of MPg-C₃N₄ and ammonium acetate (V), cyclization occurs (VI), creating one of the highest yields for the desired products (VII). The intermediate (I) (Figure 8) was synthesized (2-[(4-chlorophenyl)methylene]-5,5-dimethylcyclohexane-1,3-dione (MP: 125 °C [54])) and the reaction was initiated from step (IV). The intended product was obtained that shows this mechanism is acceptable.

The plausible mechanism for synthesizing 4H-chromene derivatives in the presence of MPg-C₃N₄ is presented in Scheme 5. Hydrogen bonding is very effective in this mechanism either. In the first step, the Knoevenagel condensation between malononitrile and aldehyde would occur (I). Next, MPg-C₃N₄ binds with the oxygen (II) and makes the alpha-hydrogen carbonyl group highly acidic, thereby incorporating the Knoevenagel product reacts with dimedone in a Michael addition (III). After intramolecular cyclization by helping MPg-C₃N₄ (IV), the desired product would obtain (V). The intermediate (II) (Figure 9) was synthesized (Benzylidenemalononitrile (MP: 82 °C [55])), and the reaction was initiated from step (III). The intended product was obtained that shows this mechanism is acceptable.

The catalytic activity evaluation of MPg-C₃N₄ with other reported researches

For showing the efficiency of catalytic activity of MPg-C₃N₄ in the synthesis of acridinedione derivatives and 4H-chromene derivatives, it was compared with some other reported catalysts in Table 5 and Table 6. As you can see, the reaction condition and the yield of products for MPg-C₃N₄ is higher than other catalysts and shows that MPg-C₃N₄ is an efficient catalyst for multicomponent reactions.

Table 5. catalytic activity of MPg-C₃N₄ in the synthesis of acridinedione derivatives with other reported catalysts

Entry	Catalyst	Reaction condition	Time (min)	Yield (%)	Ref
1	Pd/AlO(OH)	DMF Ultrasonic bath	60	90	[56]
2	MCM-41-Pr-THEIC	EtOH:H ₂ O(1:2) Reflux	45	91	[57]
3	nano-Fe ₃ O ₄ @SiO ₂ -HBP-FeCl ₃	Solvent-Free 80 °C	30	95	[58]
4	MPg-C₃N₄	EtOH, 80 °C Reflux	20	96	This work

Table 6. catalytic activity of MPg-C₃N₄ in the synthesis of 4H-chromene derivatives with other reported catalysts

Entry	Catalyst	Reaction condition	Time (min)	Yield (%)	Ref
1	Fe ₃ O ₄ @SiO ₂	EtOH, rt	40	91	[59]
2	Fe ₃ O ₄ @GO-N-(pyridin)-4-amine	H ₂ O, Reflux	30	92	[60]
3	DAIL@SiO ₂	Solvent free, 100 °C	60	86	[61]
4	MPg-C₃N₄	EtOH, 80 °C Reflux	20	93	This work

Reusability

Catalyst recovery and reusability are the critical aspects in organic reactions and transformations in order to utilize in industrial applications. The catalyst was recovered by magnetization after completion of the reaction, washed with water and ethanol, and the recovered catalyst was reused for 4 cycles. The synthesized catalyst is detected with FT-IR spectrum and EDS analysis (Figure 10 and 11), which indicates no changes are investigated in the catalyst structure.

Conclusion

As a result, a highly efficient polymer-based heterogeneous catalyst, MPg-C₃N₄, has been synthesized and used in multicomponent reactions to show its merits for catalytic activity. The intended products obtained by the MPg-C₃N₄ catalyst resulted in high yields. Reactions were carried out at an optimum temperature, time, and in environmentally friendly solvents, making the developed protocol eco-friendly. Besides, the MPg-C₃N₄ catalyst is very stable and reused for 4 cycles with a slight reduction in catalytic activity. Consequently, MPg-C₃N₄ can be used effectively for various reactions under mild reaction conditions, and this research offers a metal-free, stable, and green approach for various multicomponent reactions.

Experimental

Material

All the materials were purchased from Merck and Sigma-Aldrich companies and used without any purification. The ultrasonic bath has been used by Becker vCLEAN company. For the synthesis of the desired materials, the furnace was used by the Exciton Company. The PIT320R model of Paul Ideal Equip Company was used to separate the materials from the high-speed centrifuge. Shimadzu Fourier was used for FT-IR spectra. CNMR and HNMR spectra were used by Varian INOVA 500MHz NMR. Melting points were measured with the 9100 electrothermal devices. Electron images were obtained by TE-SCAN Field Emission Scanning Electron Microscope.

General procedure for the synthesis of bulk g-C₃N₄

Melamine (10 g) was added to a crucible and placed in a furnace under an O₂ atmosphere at 550 °C with the rate of 5 °C/min and held for 4 h, and then the bulk g-C₃N₄ has obtained.

The general procedure of g-C₃N₄ nanosheets

Bulk g-C₃N₄ (2 g) was added to a 600 mL beaker with 40 mL H₂SO₄ and stirred at 90 °C. After 5 h, 400 mL ethanol was added to the mixture at room temperature. A white mixture is obtained and stirred for 2 h. Then, the beaker has rested for a day to settle the mixture. The upper liquid has overflowed, and the rest of it has ultrasounded for 6 h. The mixture was washed by centrifuge with ethanol and water and dried at 70 °C, and then the powder g-C₃N₄ nanosheets have obtained.

The procedure for the synthesis of polymer-based heterogeneous MPg-C₃N₄

For the synthesis of MPg-C₃N₄, (0.2 g) polyvinyl alcohol (72000 g/mol) and 7 mL H₂O have poured in a round bottom flask and stirred at 80 °C. After 3 h, g-C₃N₄ nanosheets (0.1 g) were added to the mixture and stirred for 5 h. The Co-precipitation method has been used for the deposition of magnetic ferrites over the layers of MPg-C₃N₄ composite. Therefore, FeCl₂.3H₂O and FeCl₃.2H₂O (2 : 1) were solved in water and poured in a round bottom flask in an inert atmosphere. Then, drop by drop, ammonia was added to the

mixture until pH reached approximately 12 and stirred for 2 h. After that, the obtained polymer-based heterogeneous MPg-C₃N₄ was washed with water and ethanol several times and dried in an oven at 70.

General procedure for the synthesis of acridinedione derivatives

A mixture of aldehyde (1mmol), dimedone (2mmol), ammonium acetate (1mmol), catalyst (20 mg), and ethanol (5mL) was poured in a 25 mL round bottom flask and refluxed at 80 °C for 20 min. TLC monitored the progress of the reaction. After completion of the reaction, the mixture was gradually cooled to room temperature. Then the catalyst was removed by external magnetic, and the intended product was obtained by simple recrystallization with ethanol.

General procedure for the synthesis of 4H-chromene derivatives

A mixture of aldehyde (1 mmol), dimedone (1 mmol), malononitrile (1 mmol) catalyst (20 mg), and ethanol (5mL) was poured in a 25 mL round bottom flask and refluxed at 80 °C for 20 min. TLC monitored the progress of the reaction. After completion of the reaction, the mixture was gradually cooled to room temperature. Then the catalyst was removed by external magnetic, and the intended product was obtained by simple recrystallization with ethanol.

Selected Spectral Data:

3,3,6,6-tetramethyl-9-(4-chlorophenyl)-10-phenyl-1,8-dioxodecahydroacridine (7a)

FTIR (KBr, cm⁻¹): 3035, 2954, 2882, 1630, 1579, 1487, 1361, 1265, 1221, 1142, 1087, 1013, 839, 704 cm⁻¹. ¹H NMR (500 MHz, DMSO): δ H (ppm)= 0.69(s, 6H, 2 CH₃), 0.86(s, 6H, 2 CH₃), 1.74(d, 2H, 2 CH), 1.99(d, 2H, 2 CH), 2.17(d, 2H, 2 CH), 2.20(d, 2H, 2 CH), 5.01(s, 1H, CH), 7.16-7.34(m, 4H, Ar-H), 7.41(b, 2H, Ar-H), 7.55-7.62(m, 3H, Ar-H).

2-amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (1c)

FTIR (KBr, cm⁻¹): 3396, 3326, 3214, 2961, 2889, 2200, 1680, 1661, 1605, 1371, 1214, 1037, 696 cm⁻¹. ¹H NMR (500 MHz, DMSO): δ H (ppm)= 0.96(s, 3H, CH₃), 1.05(s, 3H, CH₃), 2.09-2.57(m, 4H, 2CH₂), 4.17(s, 1H, CH), 7.01(s, 2H, NH₂), 7.13-7.32 (m, 4H, Ar-H).

Declarations

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Figures

Figure 1

The FT-IR spectra of MPg-C3N4

Figure 2

The EDS spectra of MPg-C3N4

Figure 3

The XRD pattern of MPg-C3N4

Figure 4

The FE-SEM images of MPg-C₃N₄ a) 100 nm b) 200 nm c , d) 500 nm

Figure 5

The TGA spectra of MPg-C3N4

Figure 6

The VSM spectra of MPg-C3N4

Figure 7

intermediate (I) of the mechanism of acridinedione derivatives synthesis.

Figure 8

intermediate (II) of the mechanism of 4H-chromene derivatives synthesis

Figure 9

The FT-IR spectra of recycled MPg-C3N4.

Figure 10

The EDS analysis of recycled MPg-C3N4.

Supplementary Files

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