RSC Advances

Volume 1 | Number 1 | Jan 2013 | Pages 1–100

RSC Advances

www.rsc.org/advances

ROYAL SOCIETY OF CHEMISTRY

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

RSC Advances

Dynamic Article Links ►

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

PAPER

Synthesis and characterization of dicationic 4,4′- bipyridinium dichloride ordered mesoporous silica nanocomposite and its application in the preparation of 1*H*-Pyrazolo[1,2-*b*]phthalazine-5,10-dione derivatives

Aigin Bashti, Ali Reza Kiasat* and Babak Mokhtari

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

The sol–gel method was used for the synthesis of dicationic 4,4′-bipyridine silica hybrid nanocomposite. In order to introduce 4,4′-bipyridine into the skeleton framework of the ordered mesoporous silica (SBA-15), first, the (N,N′-bis(triethoxysilylpropyl)-4,4′-bipyridinium dichloride precursor was synthesized by the reaction of 3-chloropropyltriethoxysilane with 4,4′-bipyridine, $(TEOS)_2$ $BiPy^{+2}2Cl^-$. The organic–inorganic hybrid nanocomposite, SBA@$BiPy^{+2}$ $2Cl^-$, was then synthesized by hydrolysis and polycondensation of the precursor and tetraethylorthosilicate under mild acidic conditions. The nanocomposite was characterized by FT-IR spectroscopy, scanning electron microscopy (SEM), Transmission electron microscopy (TEM), Thermogravimetric analysis (TGA) and Brunauer Emmett Teller (BET). The characteristics results of FT-IR, XRD and TGA confirmed the coexistence of silica and 4,4′-bipyridinium dichloride networks. The catalytic ability of SBA@$BiPy^{+2}$ $2Cl^-$ as a novel environmentally safe heterogeneous nanoreactor towards the preparation of 1H-Pyrazolo[1,2-b]phthalazine-5,10-dione derivatives via one-pot multicomponent method under solvent-free conditions have been described. The catalyst can be reused without an obvious loss of the catalytic activity.

1. Introduction

Application of microporous materials was greatly restricted due to their small pore sizes. This limitation has been overcome by the discovery of mesoporous materials in 1992.[1] In last decade, ordered mesoporous silicas such as SBA-15 and its functionalized family with a tunable pore structure and tailored composition have received considerable interest due to their potential applications such as adsorbents and guest–host chemical supports for large organic molecules.[2] However, the nature of the neutral framework of SBA-15 with few lacuna, poor ion-exchange ability and lack of active sites, limits its applications in catalysis.[3] In this context, very recently, organized hybrid xerogel mesoporous materials, where the organic component is bonded to a polymeric silica skeleton framework, have attracted significant attention due to their outstanding properties.[4,5]

Green chemistry has attracted considerable attention to overcome the problem pertaining to the environmental pollution being encountered by the global population. In this context, Multi-component reactions (MCRs) under solvent free conditions are gaining more and more attention from organic, medicinal and synthetic chemists especially in the total synthesis of natural products, and medicinal heterocyclic compounds.[6]

1H-Pyrazolo[1,2-b]phthalazine-5,10-dione derivatives, which are nitrogen-containing fused hydrazine-based pyrazole heterocycles, represent an important class of pharmaceutical compounds and exhibit a wide spectrum of biological activities such as anti-inflammatory,[7] antifungal,[8] anticancer,[9] antiviral,[10] antitumor,[11] anticoagulant[12] and antibacterial[13] activity. Several three-component reactions have been reported for the synthesis of these compounds in the presence of an acid or base[14-21] via condensation of an aromatic aldehyde, phthalhydrazide, and malononitrile. Many of the reported synthetic methods have drawbacks such as the harsh reaction condition, the poor yields, the prolonged reaction times and application of toxic or hazardous catalysts, or costly reaction procedure. Thus novel methodologies which could overcome these drawbacks are still needed.

Taking all these facts into account, the aim of the presented protocol is to highlight the synergistic effects of the combined use of MCRs and solvent-free conditions with application of an organized mesoporous tunable pore nanocomposite, SBA@$BiPy^{+2}$ $2Cl^-$, for the development of a green strategy for the preparation of 1*H*-Pyrazolo[1,2-*b*]phthalazine-5,10-dione derivatives (Scheme 1).

2. Results and Discussion

At first, the (N,N′-bis(triethoxysilylpropyl)-4,4′-bipyridinium dichloride precursor was synthesized by the reaction of 3-chloropropyltriethoxysilane with 4,4′-bipyridine, $(TEOS)_2$ $BiPy^{+2}2Cl^-$. The organic–inorganic hybrid nanocomposite, SBA@$BiPy^{+2}$ $2Cl^-$, was then synthesized by hydrolysis and polycondensation of the precursor and tetraethylorthosilicate under mild acidic conditions in the presence of Poly(ethyleneoxide)-b-poly(propyleneoxide)-b-poly(ethylene-oxide), Pluronic P123, (Scheme 2). The processes are the self-assembly of the amphiphilic surfactant P123 that serves as template, the interaction at the interface between P123 and mixture of TEOS and $(TEOS)_2$ $BiPy^{+2}2Cl^-$, and the sol–gel process that introduce 4,4′-bipyridine into the skeleton framework of the ordered mesoporous silica. The template is subsequently removed by soxhelt extraction with ethanol to generate SBA@$BiPy^{+2}$ $2Cl^-$.

In order to characterize the catalyst, and to confirm the incorporation of bipyridinium moiety into the skeleton framework of the ordered mesoporous silica, FT-IR spectroscopy was utilized. As it is apparent from Fig. 1, The FT-IR spectrum of SBA@$BiPy^{+2}$ $2Cl^-$ shows the band from 807 and 1100 cm^{-1} is due to Si-O-Si bond vibrations and the band at about 960 cm^{-1} is assigned to the Si-OH bond. Meanwhile a broad peak is obvious at 3417 cm^{-1} which is relevant to surface OH groups of silica stretching vibration. Furthermore the quaternary nitrogen has a characteristic peak at 1641 cm^{-1}. Aromatic pyridinium rings are also responsible for the stretching vibrations at 1503 and 1561 cm^{-1}.

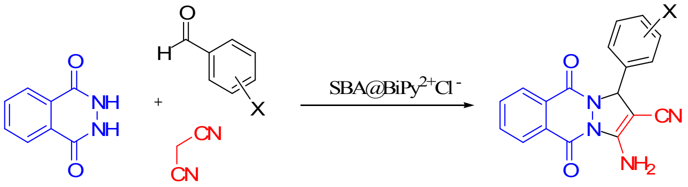
Thermogravimetric (TG) analysis of the SBA@$BiPy^{+2}$ $2Cl^-$ is presented in Fig. 2. The TG curve shows two weight losses. The first weight loss at around 100 ˚C is attributed to the loss of physically adsorbed water, representing approximately 0.18 g/g of the sample. The second weight loss is concentrated in the range of 300–700 ˚C, resulting from the decomposition of the organic parts of skeleton framework during hydrothermal treatment. The weight losses of the organic parts are 0.19 g/g of the sample. Therefore, the nanocatalyst is completely stable below 300 °C and can be applied without degradation.

Fig. 3 illustrates the SEM images of SBA-15 and SBA@$BiPy^{+2}$ $2Cl^-$. The SEM image (Fig. 3b) shows a dominant lengthy rod-like morphology for SBA@$BiPy^{+2}$ $2Cl^-$, in a bundle arrangement with a diameter of approximately 1 µm. The same morphology is observed for SBA-15 (Fig. 3a), indicating that the morphology was maintained without change.

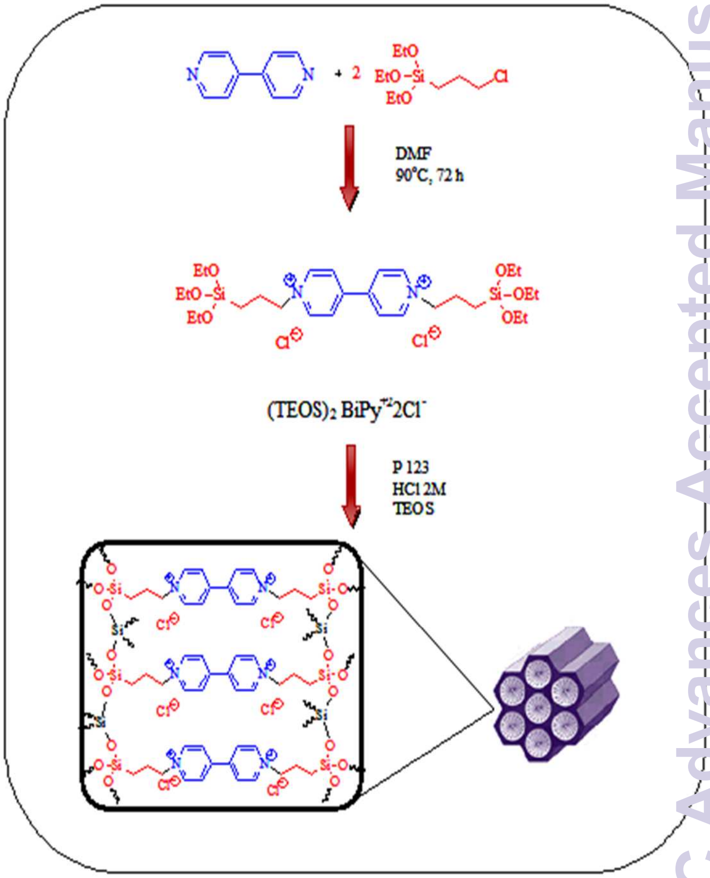
Fig. 4 shows TEM images of SBA@$BiPy^{+2}$ $2Cl^-$. It can be clearly seen that the uniform mesoporous structure of SBA-15 was not destroyed after introduction of functionalization organic parts onto skeleton framework of SBA.

The XRD pattern of SBA@$BiPy^{+2}$ $2Cl^-$ was also provided in Fig 5. X-ray diffraction patterns of the SBA-15 materials reveal the 2D hexagonally structured pores at low angles, whereas no diffraction pattern can be observed at high angles due to the amorphous nature of the pore walls.[22]

The mesoporous nature of the synthesized sample was studied by N_2 adsorption desorption isotherm (Fig. 6). The sample exhibited type IV isotherms. The main structural characteristics determined experimentally are listed in Table 1. The BJH pore size distribution analysis shows that the material posses uniformly sized mesopores centered at ca. 61.8 Å. The BET surface area of SBA@$BiPy^{+2}$ $2Cl^-$ was found to be 339 m^2 g^{-1} and the pore volume of 0.3 cm^3 g^{-1}. The characteristic data on the sample are summarized in Table 1.



Scheme 1 One-pot preparation of 1*H*-Pyrazolo[1,2-*b*]phthalazine-5,10-dione derivatives



Scheme 2 Preparation of the SBA@$BiPy^{+2}$ $2Cl^-$

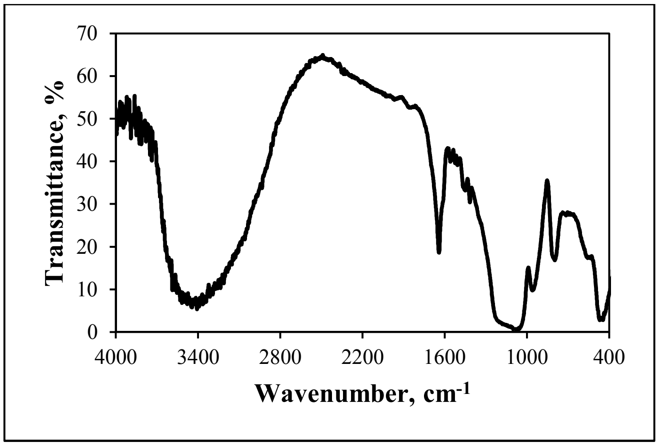


Fig. 1 The FT-IR spectrum of synthesized mesoporous SBA@BiPy^{+2} 2Cl^{-}

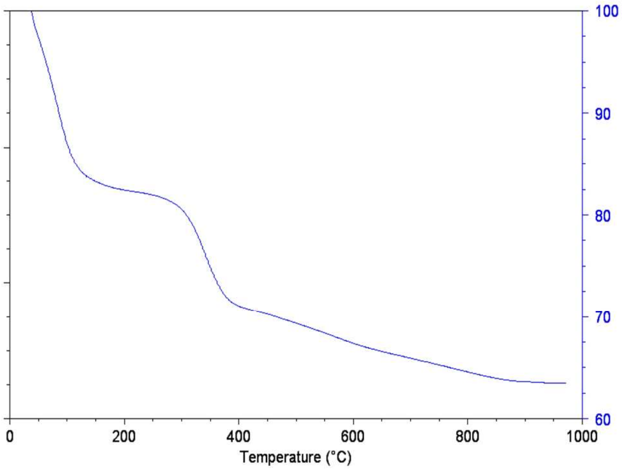
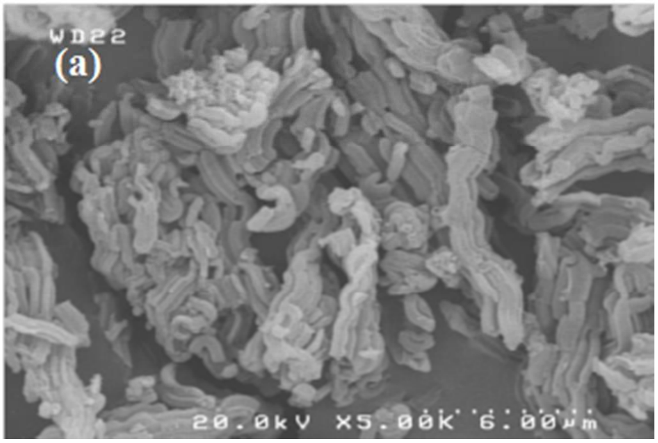


Fig. 2 The TGA curve of SBA@BiPy^{+2} 2Cl^{-}



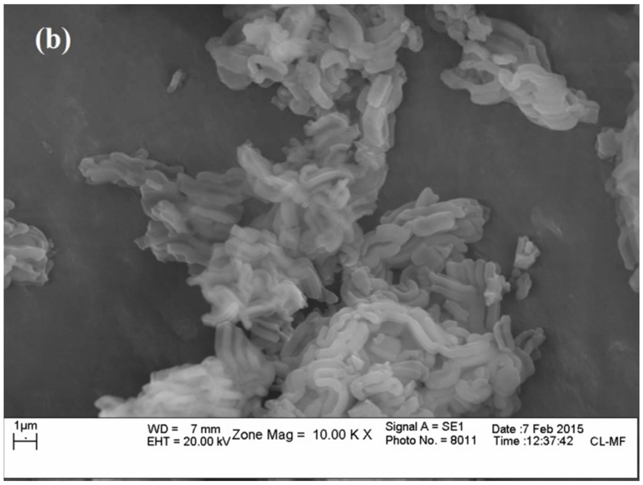


Fig. 3 SEM images of (a) SBA and (b) SBA@BiPy^{+2} 2Cl^{-}

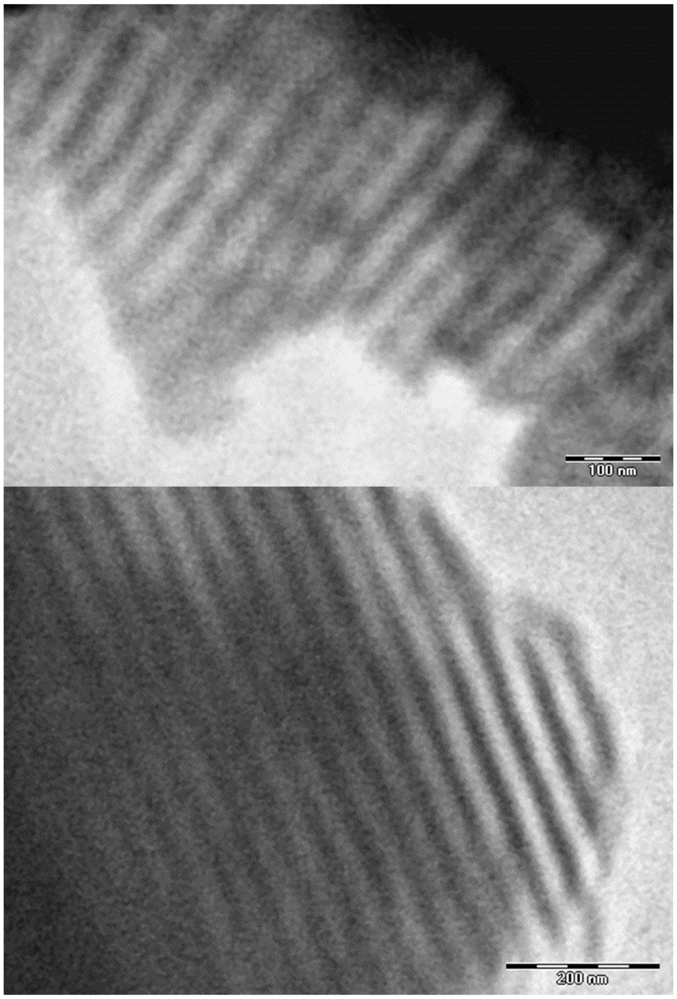


Fig. 4 TEM images of SBA@BiPy^{+2} 2Cl^{-}

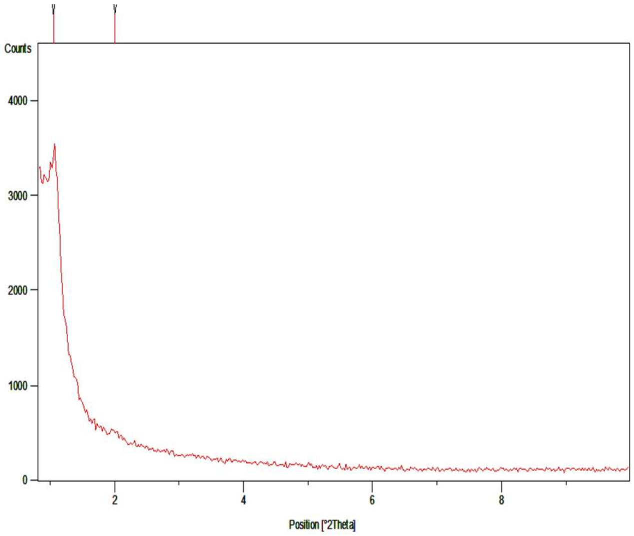
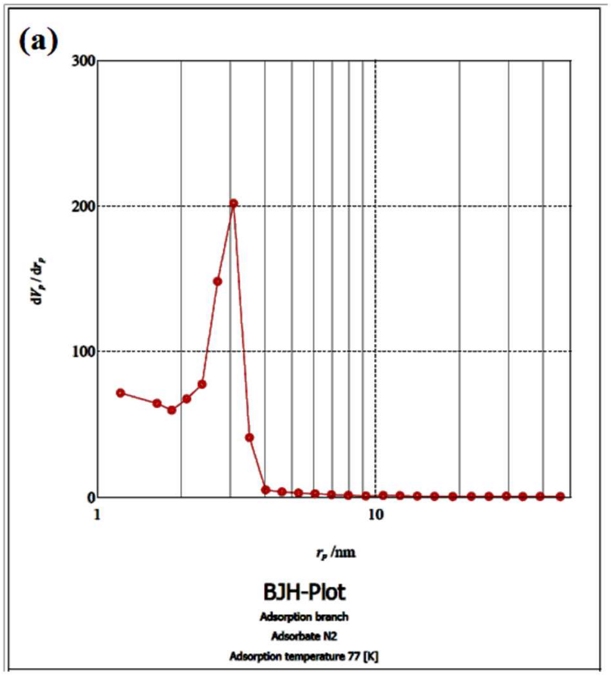


Fig. 5 XRD pattern of SBA@BiPy^{+2} 2Cl^{-}



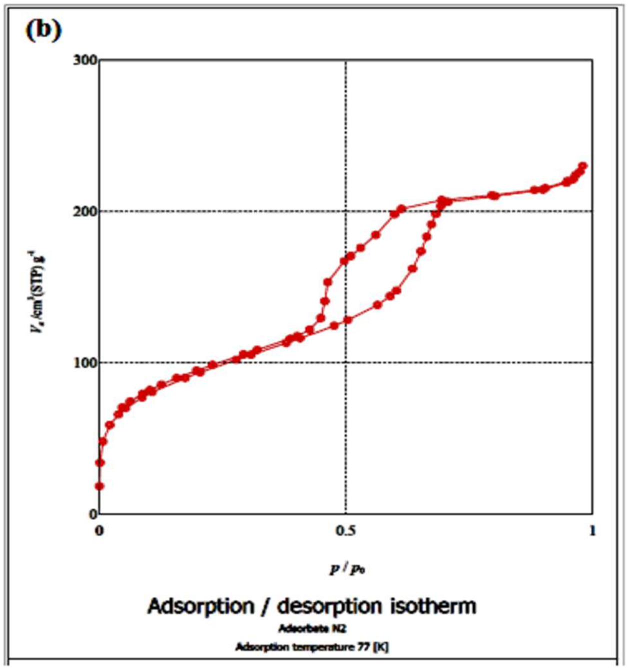


Fig. 6 Pore size distributions of and Nitrogen adsorption-desorption isotherms of SBA@BiPy^{+2} 2Cl^{-}

Table 1 Specific surface area (S_{BET}), diameter pore and total pore volume.

Sample	BET surface area (m^2 g^{-1})	diameter (nm)	pore volume (cm^3 g^{-1})
SBA@BiPy^{+2} 2Cl^{-}	339	6.18	0.3

In addition, the presence of organic parts in skeleton framework was also confirmed by CHN analysis (14.51, 3.23, 3.62 for C, H, N respectively)

After qualification of the catalyst, it was decided to evaluate the catalytic activity of SBA@BiPy^{+2} 2Cl^{-} in the preparation of 1*H*-Pyrazolo[1,2-*b*]phthalazine-5,10-dione derivatives. A model three-component coupling reaction of phthalhydrazide, malononitrile and aromatic aldehydes under solvent-free conditions at 100°C in the presence of SBA@BiPy^{+2} 2Cl^{-} was examined.

In order to evaluate the appropriate catalyst loading, a model reaction was carried out using 0.004-0.03 g of the catalyst at different temperatures under solvent-free conditions (Table 2). It was found that 0.005 g of the catalyst shows maximum yield in minimum time. In the next step, the effect of temperature was evaluated for the model reaction. It was observed that the reaction did not proceed at low temperatures, while the reaction proceeded to the desired product in high yield, at elevated temperatures. We were fortunate to find that the reaction proceeded effectively, and almost complete conversion to the desired product was observed at 100°C, affording 3-amino-5,10-dioxo-1-phenyl-5,10-dihydro-1*H*-Pyrazolo[1,2-*b*]phthalazine-2-carbo-nitrile in 96% yield within shorter reaction time (Table 2. Entry 6).

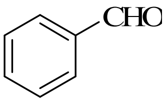
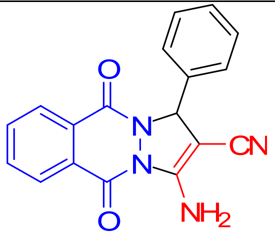
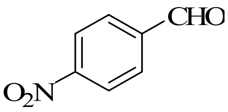
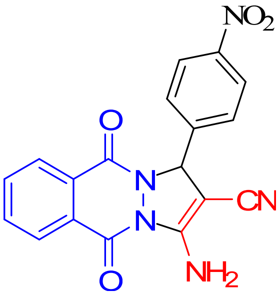
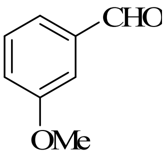
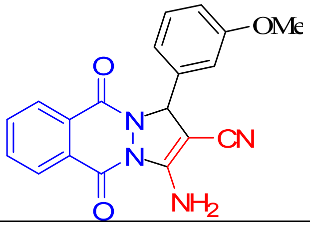
Table 2 Optimum conditions for the three-component condensation reaction of phthalhydrazide (1 mmol), malononitrile (1 mmol) and benzaldehyde (1 mmol) under thermal solvent-free conditions

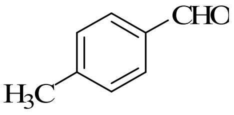
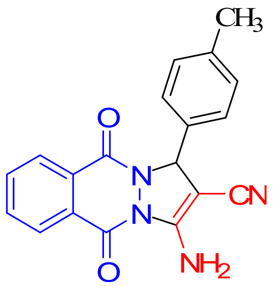
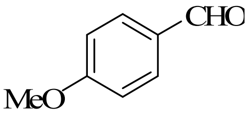
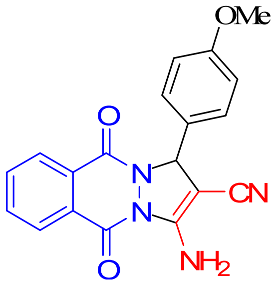
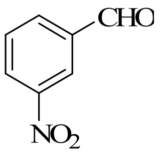
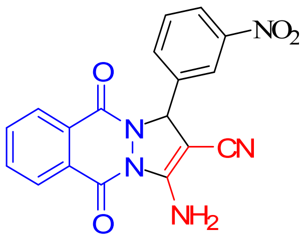
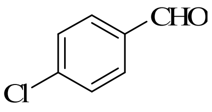
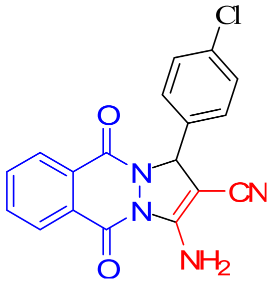
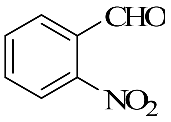
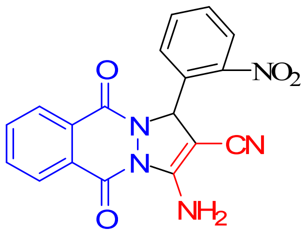
Entry	Catalyst (g)	Temp. (°C)	Time (min)	Yield (%)
1	0.003	60	90	60
2	0.001	60	90	58
3	0.005	60	90	55
4	0.004	60	90	65
5	0.005	90	70	82
6	0.005	100	40	96
7	-	100	60	48
8	0.005	110	40	90

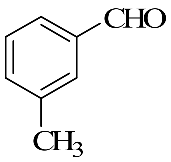
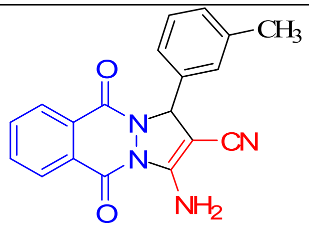
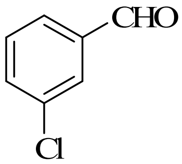
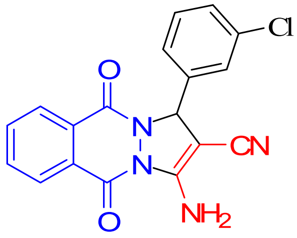
Subsequently, with optimal conditions in hand, 1:1:1 molar ratios of phthalhydrazide, malononitrile and aromatic aldehyde in the presence of 0.005 g of SBA@BiPy^{+2} 2Cl$^-$ at 100°C under solvent-free conditions, the synthetic scope of this procedure was demonstrated by synthesizing a series of 1*H*-Pyrazolo[1,2-*b*]phthalazine-5,10-dione derivatives (Table 3). Gratifyingly, a wide range of aromatic aldehydes were well tolerated under the optimized reaction conditions. The time taken for complete conversion and the isolated yields are recorded in Table 3. It is obvious that electron withdrawing groups promote the reaction rate due to their effect on carbonyl group; which make aldehyde to more electrophile in the subsequent Michael addition. All the compounds were characterized by comparison of their physical and spectral data with those of the authentic ones.

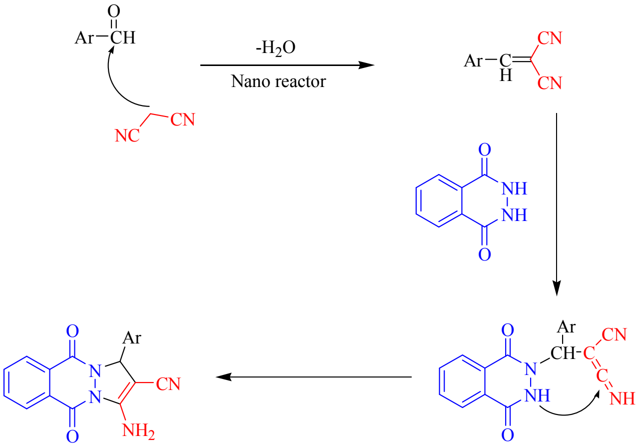
It is postulated that the reaction proceeds through a Knoevenagel condensation of malononitrile and aromatic aldehyde. In the next step the phthalhydrazide attaks to the adduct in a Michael type fashion, which in the subsequent steps yield the product (Scheme 3). The channels of mesoporous SBA@BiPy^{+2} 2Cl$^-$ represent a straightforward nanoreactor for these two steps condensation reaction.

Table 3 The one-pot three-component condensation reaction of phthalhydrazide (1 mmol), malononitrile (1 mmol), aromatic aldehydes (1 mmol) promoted by SBA@BiPy^{+2} 2Cl$^-$ (0.005 g) under solvent-free conditions at 100°C.

Entry	Substituted Benzaldehyde	Product	Time (min)	Yield (%)
1			40	96
2			30	94
3			54	90

4			50	86
5			60	89
6			30	91
7			30	87
8			50	90

9			50	86
10			30	88



Scheme 3 Postulated mechanism

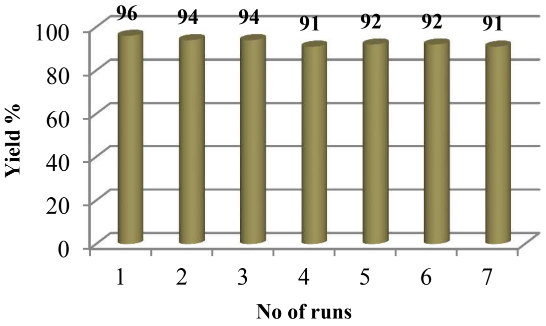


Fig. 7 Reusability of the catalyst in the reaction of phthalhydrazide (1.0 mmol), malononitrile (1.0 mmol), and benzaldehyde (1.0 mmol) at 100 °C under solvent-free conditions.

To investigate the activity constancy of the catalyst, the catalyst was reused seven times in the one-pot multicomponent condensation of phthalhydrazide, malononitrile, and benzaldehyde at 100 °C under solvent-free conditions. In this procedure, after completion of each reaction, hot ethanol was added and the catalyst was filtered. The recovered catalyst was washed with ethanol, dried and reused (Fig. 7). As shown in Fig. 7, smooth loss of catalytic activity of SBA@BiPy^{+2} 2Cl$^-$ was observed.

3. Experimental

3.1 General

All commercially available chemicals were purchased from Fluka and Merck companies and used without further purification. Poly(ethyleneoxide)-b-poly(propyleneoxide)-b-poly(ethylene-oxide)[$EO_{20}PO_{70}EO_{20}$, Pluronic P123, Mw=5800] was purchased from Aldrich chemical company. IR spectra were recorded on a BOMEM MB-Series 1998 FT-IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded in DMSO-d$_6$ on a Bruker Advanced DPX 400 MHz spectrometer using TMS as internal standard. Reaction monitoring was accomplished by TLC on silica gel polygram SILG/UV 254 plates. The particle morphology was examined by SEM (LEO 1455VP Scanning Electron Microscope, operating at 1-30 KV) and TEM (ZEISS LEO 906E Transmission Electron Microscope; 80 kV).

3.2. Preparation of (N,N′-bis(triethoxysilylpropyl)-4,4′-bipyridinium dichloride precursor, (TEOS)$_2$ BiPy^{+2}2Cl$^-$

In a 25 mL three-neck round-bottom flask, bipyridine (8 mmol, 1.25 g) was added to DMF (5 mL), and stirred to make a clear solution. To this solution, (3-chloropropyl)triethoxy silane (16 mmol, 3.18 g) was added dropwise; and the mixture stirred at 90°C for 72 hours under argon atomosphere. Afterwards, the white solid, *$(TEOS)_2$ $BiPy^{+2}2Cl^-$*, was filtered and washed with methanol. This solid was dried for 2 hours in an oven at 90°C.

3.3. Preparation of dicationic 4,4′-bipyridine silica hybrid nanocomposite, SBA@BiPy^{+2} 2Cl$^-$

In a 110 mL round-bottom flask, Pluronic 123 (2.0g, 0.344 mmol, M_n=5800) was dissolved in HCl 2M (62.5 mL) at room temperature. Then tetraethyl orthosilicate (TEOS) (4.2g, 20 mmol) and $(TEOS)_2$ $BiPy^{+2}2Cl^-$ (0.65 g,1.0 mmol) was added and the mixture was stirred at 40°C for 20 hours. The mixture was hydrothermally treated at 95°C under static condition for 24 hours. The resulting solid was filtered and washed with excess water and dried at 100 °C. The solid was then soxhelt extracted with ethanol for 48 hours, to remove Pluronic 123 and then dried at 50 °C for 24 hours.

3.4. Typical procedure for the preparation of 1H-Pyrazolo[1,2-b]phthalazine-5,10-dione derivatives

A mixture of phthalhydrazide (1 mmol), malononitrile (1mmol), aromatic aldehyde (1 mmol), and *SBA@BiPy^{+2} 2Cl$^-$* (0.005 g) was heated at 100^{o}C in a test tube under solvent-free conditions (Table 3). Completion of the reaction was indicated by TLC [TLC acetone/n-hexane (3:10)]. After completion of the reaction the insoluble crude product was dissolved in hot methanol and the catalyst was filtered. The crude product was purified by recrystallization from methanol to afford the pure product.

3.5. Selected spectral data

3-Amino-1-(4-chlorophenyl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2 carbonitrile: Yellow powder; mp = 273-276 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 8.31-8.26 (m, 1H), 8.14 (brs, 2H, NH_2), 8.12-8.08 (m, 1H), 7.99-7.95 (m, 2H), 7.53 (d, J = 8.8 Hz, 2H), 7.45 (d, J = 8.8 Hz, 2H), 6.17 (s, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): 157.3, 154.2, 150.9, 150.7, 137.1, 134.8, 133.9, 133.3, 129.3, 129.4, 128.8, 128.1, 127.7, 126.9, 116.4, 62.7 ppm; IR (KBr): υ = 3377, 3259, 3109, 2187, 1656, 1560 cm $^{-1}$.

3-Amino-1-(4-nitrophenyl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carbonitrile: Yellow powder; mp= 227-229 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 8.29-8.27 (m, 1H), 8.24 (d, J = 8.6 Hz, 2H), 8.21 (brs, 2H, NH_2), 8.11-8.09 (m, 1H), 7.98-7.97 (m, 2H), 7.82 (d, J = 8.6 Hz, 2H), 6.31 (s, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): 157.4, 154.3, 151.3, 151.5, 148.0, 146.6, 134.9, 134.6, 129.4, 129.0, 128.7, 128.0, 126.0, 124.4, 116.6, 62.8 ppm; IR (KBr): υ= 3440, 3326, 3079, 2165, 1662, 1560, 1520 cm $^{-1}$.

3-Amino-1-(3-methoxyphenyl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2 carbonitrile: Yellow powder; mp = 247-249 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 8.27-8.25 (m, 1H), 8.12-8.10 (m, 3H, NH_2, H), 8.0-7.96 (m, 2H), 7.27 (t, J = 7.6 Hz, 1H), 6.99–6.97 (m, 2H), 6.90 (dd, J = 8.0, 1.6 Hz, 1H), 6.12 (s, 1H), 3.76 (s, 3H, OCH_3) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): 160.0, 156.9, 153.8, 150.9 137.8, 134.4, 129.7, 129.2, 129.1, 128.9, 127.2, 126.9, 124.3, 119.3, 114.0, 112.9, 64.1, 55.7 ppm; IR (KBr): υ = 3363, 3261, 3060, 2193, 1655, 1567 cm $^{-1}$.

3-Amino-1-(3-chlorophenyl)-5,10-dioxo-5,10-dihydro-1Hpyrazolo[1,2-b]phthalazine-2 carbonitrile:Yellow powder; mp = 264-266 ^{o}C. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 8.25-7.38 (10H, m, Ar and NH_2). 6.13 (1H, s, CH) ppm, ^{13}C NMR (100 MHz, DMSO-d_6): 157.4, 154.0, 151.5, 140.9, 135.7, 135.0, 134.1, 129.0, 129.1, 128.3, 127.9, 127.0, 125.8, 122.4, 117.3, 63.0, 61.2 ppm; IR (KBr) υ = 3363, 3265, 2202, 1670, 1660 cm^{-1}.

3-Amino-1-(2-nitrophenyl)-5,10-dioxo-5,10-dihydro-1Hpyrazolo[1,2-b]phthalazine-2-carbonitrile Yellow powder; mp = 262-264 ^{o}C. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 8.29-7.60 (10H, m, Ar and NH_2). 6.64(1H, s, CH) ppm, ^{13}C NMR (100 MHz, DMSO-d6): 156.8, 154.2, 151.9, 148.5, 135.0, 134.5, 134.2, 133.4, 129.8, 129.2, 129.0, 128.5, 127.4, 126.9, 124.4, 16.0, 59.4, 57.8 ppm; IR (KBr) υ = 3385, 3175, 2198, 1701, 1655 cm^{-1}.

4. Conclusion

Here in, for the first time, using a new and facile strategy, SBA@BiPy^{+2} 2Cl$^-$ nanocomposite has been synthesized. Characterization and its catalytic activity as a novel environmentally safe heterogeneous nanoreactor towards the preparation of 1H-Pyrazolo[1,2-b]phthalazine-5,10-dione derivatives through three-component one-pot synthesis under solvent-free conditions have been described. The method offers several advantages including high yields, application of an inexpensive catalyst, short reaction times, easy workup and performing multicomponent reaction under solvent-free conditions that is considered to be relatively environmentally benign.

Acknowledgements

We gratefully acknowledge the support of this work by Shahid Chamran University Research Council.

Notes and references

Chemistry Department, College of science, Shahid Chamran University, Ahvaz, 61357-4-3169, Iran
Tel/Fax: (+98) 611-3331746, Email: akiasat@scu.ac.ir

1. C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature.*, 2013, **359,** 710.
2. S. Rostamnia, E. Doustkhah and A. Nuri, *J. Fluor. Chem.*, 2013, **153**, 1.
3. W. Zhang, H. Wang, J. Han and Z. Song, *Appl. Surf. Sci.,* 2012, **258**, 6158.
4. J. Davarpanah and A. R. Kiasat, *Catal. Commun.*, 2013, **42**, 98.
5. R. Ghorbani-Vaghei, S. Hemmati and H. Veisi, *J. Mol. Catal. A: Chem.*, 2014, **393**, 240.
6. S. Brauch, S. S. Van Berkel and B. Westermann, *Chem. Soc. Rev.*, 2013, **42**, 4948.

7. T. Nakamura , M. Sato , H. Kakinuma , N. Miyata , K. Taniguchi , K. Bando , A. Koda and K. Kameo*, J. Med. Chem.,* 2003, **46**, 5416.
8. O. Prakash, R. Kumar and V. Parkash*, Eur. J. Med. Chem*., 2008, **43**, 435.
9. M. A. F. Vera-DiVaio, A. C. C. Freitas, H. C. Castro, S. de Albuquerque, L. M. Cabral, C. R. Rodrigues, M. G. Albuquerque, R. C. A. Martins, M. G. M. O. Henriques and L. R. S. Dias, *Bioorg. Med. Chem*., 2009, **17**, 295.
10. M. J. Genin, C. Biles, B. J. Keiser, S. M. Poppe, S. M. Swaney, W. G. Tarpley, Y. Yagi and D. L. Romero, *J. Med. Chem.,* 2000, **43**, 1034.
11. F. Wei, B. X. Zhao, B. Huang, L. Zhang, C. H. Sun, W. L. Dong, D. S. Shin and J. Y. Miao, *Bioorg. Med. Chem. Lett.,* 2006*,* **16**, 6342.
12. Y. Xia, Z. W. Dong, B. X. Zhao, X. Ge, N. Meng, D. S. Shin and J. Y. Miao, *Bioorg. Med. Chem*., 2007, **15**, 6893.
13. P. C. Lu, J. Sun, Y. Luo, Y. Yang and H. L. Zhu, *Bioorg. Med. Chem. Lett*., 2010, **20**, 4657.
14. A. R. Kiasat and J. Davarpanah, *J. Mol. Catal. A: Chem*., 2013, **373**, 46.
15. M. R. Nabid, S. J. Tabatabaei Rezaei, R. Ghahremanzadeh and A. Bazgir, *Ultrason. Sonochem*., 2010, **17**, 159.
16. D. S. Raghuvanshi and K. N. Singh, *Tetrahedron Lett*., 2011, **52**, 5702.
17. H. R. Shaterian and M. Mohammadnia, *J. Mol. Liq.,* 2012, **173,** 55.
18. G. Karthikeyan and A. Pandurangan, *J. Mol. Catal. A: Chem*., 2012, **361**, 58.
19. S. H. Song, J. Zhong, Y.H. He and Z. Guan, *Tetrahedron Lett*., 2012, **53**, 7075.
20. M. Veeranarayana Reddy and Y. Tae Jeeong, *Tetrahedron Lett.*, 2013, **54**, 3546.
21. J. Safaei-Ghomi, H. Shahbazi-Alavi, A. Ziarati, R. Teymuri an, M. R. Saberi, *Chin. Chem. Lett*., 2014, **25**, 401.
22. V. Meynen, P. Cool and E. F. Vansant, *Micropor. Mesopor. Mater*., 2009, **125**, 170.