Molecular Catalysis 497 (2020) 111198

Contents lists available at ScienceDirect

Molecular Catalysis

journal homepage: www.journals.elsevier.com/molecular-catalysis

Porous organic polymer bearing triazine and pyrene moieties as an efficient organocatalyst

Sabuj Kanti Das, Avik Chowdhury, Debabrata Chakraborty, Utpal Kayal, Asim Bhaumik *

School of Materials Sciences, Indian Association for the Cultivation of Science, 2A & 2B Raja S. C. Mullick Road, Jadavpur, Kolkata, 700032, India

ARTICLE INFO

Keywords:
Porous organic polymer
Surface area
Heterogeneous catalysis
Multi component reaction
Biginelli reaction

ABSTRACT

Materials with high specific surface area and bearing abundant basic sites at their pore surface are very demanding as heterogeneous catalyst for the eco-friendly base catalyzed reactions. Here we have developed a new secondary amine linked triazine and pyrene containing microporous organic polymer (TrzPyPOP) through a simple polycondensation reaction between tetramine1,4-bis(4,6-diamino-s-triazin-2-yl)-benzene (SL-1) and monoaldehyde pyrene-1-carboxaldehyde. This new porous organic polymer TrzPyPOP is very rich in N-content with high BET surface area (1016 $m^2 g^{-1}$). High surface area and N-rich surface basic sites have been explored in its potential as heterogeneous organocatalyst for the synthesis of dihydropyrimidones via Biginelli condensation involving three-component coupling reaction. Only a very little amount of catalyst was effective for the synthesis of dihydropyrimidones derivatives (yields = 88–99 %) together with high recycling efficiency under the optimum reaction conditions.

1. Introduction

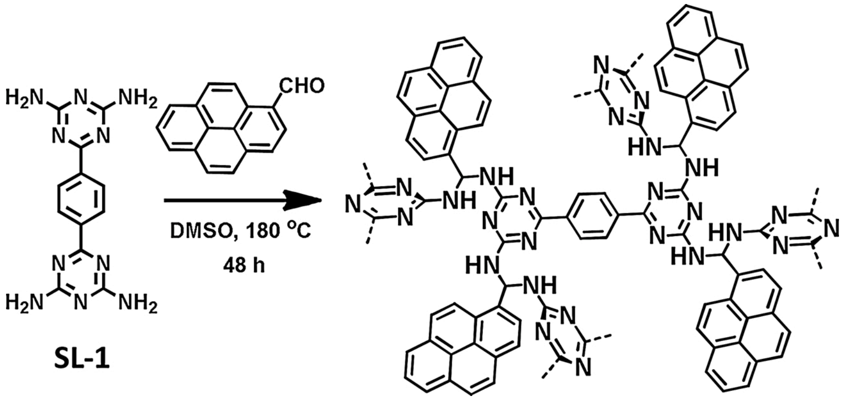
Convenient and eco-friendly strategies for the synthesis of dihydropyrimidones (DHPMs) [1] have attracted considerable attention over the years in medicinal chemistry as these compounds worked efficiently for the treatment of cardiovascular diseases [2]. DHPMs show close structural as well as compositional resemblance with nifedipine, often used to regulate high blood pressure. Further, the activity of the DHPMS can be tuned by changing the axial aromatic group, which bisect the boat conformation [3]. Thus, continuous research efforts are directed for the modification of the reactants and reaction conditions [4] for better yield of DHPMs together with its high purity in shorter reaction time. In this context, multicomponent condensation reaction between reactive small organic molecules in the presence of suitable catalyst can offer viable route for the synthesis of DHPM derivatives. In synthetic organic chemistry multicomponent reactions (MCR) [5] are very demanding especially in the discovery of novel drug molecules. In the year 1891, Italian chemist Petro Biginelli [6] has introduced a one-pot multicomponent reaction featuring the condensation between ethyl acetoacetate, benzaldehyde and urea. This reaction has versatile potential for the synthesis of a series of DHPM derivatives. The reaction can easily be carried out by heating the reactants in the presence of solvent with catalytic amount of hydrochloric acid at the refluxing temperature. Being a one-pot process involving multiple reactants, the products obtained from the MCR are economically favorable too. However, under this reaction conditions often moderate yields of the products are obtained together with no scope for recyclability.

Subsequently scientific community has paid huge attention to develop several homogeneous and heterogeneous catalytic systems for synthesizing analogous heteroatom containing chemicals [7] by exploring different synthetic routes. Several heterogeneous catalysts can catalyzes the modified Biginelli reactions with good recyclability, easiness in separation of the catalysts from reaction mixture together with enhanced purity of the product, leaching of active metal sites are the major issues in these cases for prolonged operation. In this context metal-free heterogeneous base catalyst or organocatalysts [8] bearing reactive organic functional groups at the catalyst surface can be utilized to carry out this MCR for the synthesis of value added DHPMs. Biginelli condensation reaction has been conducted over a large variety of homogeneous and heterogeneous catalysts such as $Fe(NO_3)_3.9H_2O$ [9], 12-molybdophosphoric acid [10], Fe(III)/Si-MCM-41 [11], poly (2-acrylamido-2-methylpropane sulphonic acid) [12], polystyrene-supported Al(III) [13], Ce-MCM-41 [14] etc. The magnetic Fe_3O_4 nanoparticles supported imidazolium-based ionic liquids [15] and many more surface functionalization strategies [16–20] have been undertaken for catalyst modification as well as enhancement of the rate

---

* Corresponding author.
E-mail address: msab@iacs.res.in (A. Bhaumik).

https://doi.org/10.1016/j.mcat.2020.111198
Received 1 July 2020; Received in revised form 26 August 2020; Accepted 29 August 2020



Scheme 1. Synthesis of TrzPyPOP material through the polycondensation of tetramine and monoaldehyde.

of this reaction. Previously we had reported the Fe_3O_4 nanoparticles supported functionalized SBA-15 [21] as magnetically recoverable nanocatalyst for carrying out the Biginelli condensation reaction. But optimization of the product yields under mild reaction conditions and purity concern are still remained as major issues for this reaction. Moreover, only few basic organocatalysts are reported so far for this Biginelli condensation reaction.

Porous organic materials have attracted significant interest in solving several issues of energy and environment in the recent times. Covalent organic frameworks (COFs) [22–24], covalent triazine frameworks (CTFs) [25], conjugated microporous polymers (CMPs) [26, 27] and related other porous organic polymers (POPs) [28–31] are intensively studied in several frontline applications like catalysis [32–34], selective gas adsorption [35], water purification [36], light harvesting [37] and so on. Among all these porous organic materials, POPs have more flexibility in the synthesis due to their high specific surface area, ease of synthesis in bulk quantities, ease of the introduction of the desired functional group and high chemical stability. As POPs are insoluble in all common organic solvents, they can be used as a heterogeneous catalyst for a series of organic transformation and after reaction the catalyst can be easily isolated, which offer high recyclability of catalyst after several reaction cycles. Further, abundance of aminal linkages in the POP network is helpful for carrying out the base catalyzed reactions [38]. Herein we report the facile metal-free base catalyzed Biginelli reaction over a new triazine and pyrene containing porous organic polymer TrzPyPOP as a heterogeneous organocatalyst synthesized through a very convenient polycondendation reaction between 1,4-bis(4,6-diamino-s-triazin-2-yl)-benzene and pyrene-1-carboxaldehyde as shown in Scheme 1.

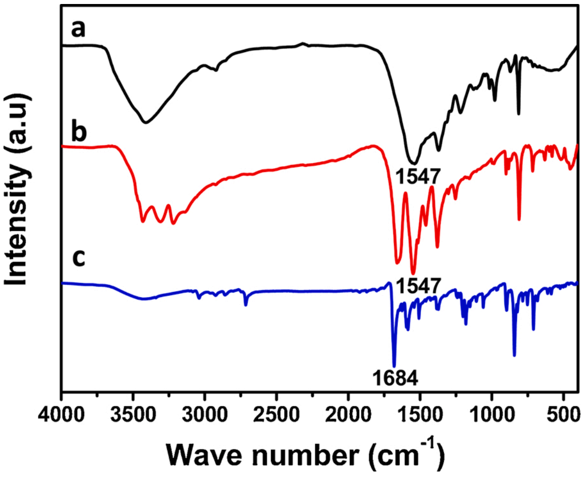


Fig. 1. FT-IR spectra of pyrene-1-aldehyde (a), SL-1 (b) and TrzPyPOP (c).

2. Experimental section

2.1. Chemicals

Terephthalonitrile, dicyandiamide, 1-pyrene-carboxaldehyde and the aldehydes used as substrates for the catalytic reactions, like 4-methylbenzaldehyde, 4-bromobenzaldehyde, 4-chlorobenzaldehyde, 4-formylbenzonitrile, 4-nitrobenzaldehyde and furan-2-carbaldehyde, were purchased from Sigma-Aldrich. Ethyl acetoacetate, ethyl cyanoacetate were received from Loba Chemie, whereas thiourea and urea were procured from Merck India. Organic solvents such as 2-metoxyethanol, dimethylsulphoxide (DMSO), ethanol, tetrahydrofuran (THF) and acetonitrile were purchased from Spectrochem, India.

2.2. Material characterizations

The amine monomer SL-1 had been synthesized by Antonpaar Monowave 300, microwave synthesis reactor. We have used Perkin-Elmer Spectrum 100 spectrophotometer for investigating the bonding connectivity through FTIR spectroscopy. The crystalline or amorphous nature of the powder POP material was analyzed by using wide angle PXRD data taken in a Bruker AXS D-8 Advanced SWAX diffractometer, where Cu-Kα (λ =0.15406 nm) radiation was used as X-ray source. After synthesizing the TrzPyPOP material it was solvent extracted for 3 days through a Soxhlet apparatus using equimolar mixture of THF and methanol to remove the adsorbed guest molecules occupied inside the pores of the material. The porosity and BET surface area of TrzPyPOP was investigated by analyzing N_2 adsorption/desorption isotherm at -196 °C taken in an Autosorb-iQ of Quantachrome Instruments, USA. Before the BET analysis the TrzPyPOP material was degassed at 150 °C for 4 h. The pore size distribution profile was obtained from the sorption isotherm by employing non-local density functional theory (NLDFT).

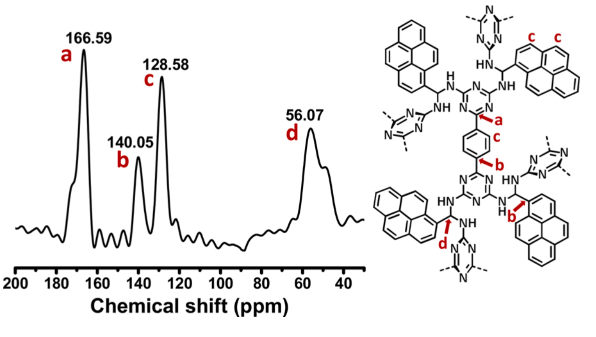


Fig. 2. ^{13}C CP/MAS NMR spectrum of TrzPyPOP. ^{13}C signals are marked with the corresponding colors of the carbon atoms drawn in the model framework of TrzPyPOP.

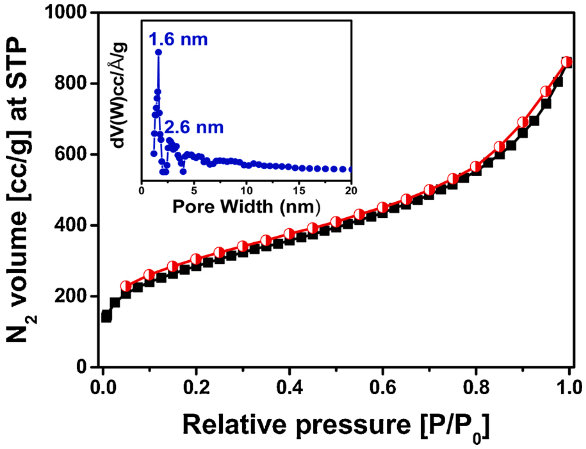


Fig. 3. N_2 adsorption (black field square)/desorption (red half field circle) isotherm of TrzPyPOP at 77 K. Respective pore size distribution is shown in the inset.

Bruker Advance II spectrometer was used to investigate the ^1H and ^{13}C NMR using deuterated NMR solvents. The ^{13}C CP MAS NMR of insoluble polymeric material was taken in 8 kHz magic angle spinning frequency using a 4 nm MAS probe. The particle size and morphological analysis of the TrzPyPOP polymer have been carried out by collecting HRTEM images with JEOL JEM 2010 at an accelerating voltage of 200 kV. Thermal stability of TrzPyPOP was investigated by thermogravimetric analysis using TA-SDT Q-600 of TA Instruments, USA. The elemental composition (*i.e.* carbon, hydrogen and nitrogen) of the TrzPyPOP material has been investigated by Perkin Elmer 2400 Series II CHN analyzer.

Synthesis of 1, 4-Bis(4, 6-diamino-s-triazin-2-yl) benzene (SL-1)

The targeted tetradented ligand (SL-1) was synthesized following our previously reported literature [39]. In this typical synthesis, at first 640 mg of terephthalonitrile (5 mmol, 640 mg), dicyandiamide (10 mmol, 841 mg), and KOH (1.75 mmol, 100 mg) were taken into a microwave G-30 vial followed by addition of 15 ml of 2-methoxyethanol solvent. Then the reaction vial was placed into the microwave reactor and reaction was carried out at 195 °C for 10 min. After that the reaction mixture was cooled down and it was placed into hot water. Then the product was filtered off and washed with plenty of water followed by methanol and finally with acetone to get pure tetraammine ligand SL-1. 75 % yield of the SL-1 product was obtained. The ^{13}C and ^1H NMR analysis of SL-1 compound are: ^{13}C NMR (100 MHz, DMSO-d6) δ = 170.10, 167.59, 139.57, 127.24 ppm. ^1H NMR (400 MHz, DMSO-d6) δ = 8.35 (s, 4H, Ar), 6.81 (br s, 8H, NH_2).

2.3. *Synthesis of TrzPyPOP*

The TrzPyPOP was synthesized by the simple polycondensation between pyrene-1-aldehyde (3 mmol, 420.48 mg) and SL-1 (3 mmol, 891 mg) in 25 ml of dimethylsulphoxide (anhydrous), the under N_2 atmosphere at 180 ℃ (Scheme 1). The reaction has been continued for 48 h and the material is obtained as buff color precipitate. The mixture was cooled to room temperature and then it was filtered followed by washing with water, methanol, THF and finally by acetone. The product was filtered for another 3 days by a mixture of MeOH and THF (1:1) by using Soxhlet's apparatus the crude product is dried under vacuum at 180 °C for 24 h thus finally pyrene containing triazine based guest free porous organic polymer (TrzPyPOP) obtained with isolated yield of 70 %.

2.4. *Catalytic reactions over TrzPyPOP*

In a typical catalytic reaction a mixture of aldehyde (1.0 mmol), ethyl acetoacetate (1.1 mmol) and 10.0 mg of TrzPyPOP was taken in a desired solvent in a two neck round bottomed flask and the reaction mixture was heated for 30 min at different temperature (40–80 ℃). Then 1.3 mmol of urea was added into the reaction mixture and it was refluxed for 2-7 h at elevated temperatures. After the reaction, the products were collected through filtration and purified to obtain the respective isolated products. All the reaction products were fully characterized by NMR spectroscopy (ESI, Section S1 and Figure S1-S7). After completion of the catalysis, the reaction mixture was allowed to cool at room temperature. Then the catalyst was removed from the reaction mixture by filtration. This was followed by solvent evaporation under reduced pressure. Then the product was taken in 50 mL of water in a 100 mL beaker and stirred for 30 min. Then the solid product was collected by filtration. Solid compound was further washed three times by 15 mL of hexane (each time). Finally, the pure product was obtained by recrystallization from ethanol and characterized by ^1H NMR.

3. Results and discussion

We have synthesized the triazine based four armed amine functionalized ligand (SL-1) by microwave assisted thermal condensation (at 195℃) between terepthalonitrile and dicyandiamide under alkaline medium (Scheme 1). This is followed by the polycondensation reaction between SL-1 with pyrene-1-carboxaldehyde under refluxing conditions to yield TrzPyPOP. The as synthesized material has been characterized by several characterization tools and these are summarized below.

3.1. *Spectroscopic analysis*

The bonding connectivity in TrzPyPOP has been investigated by

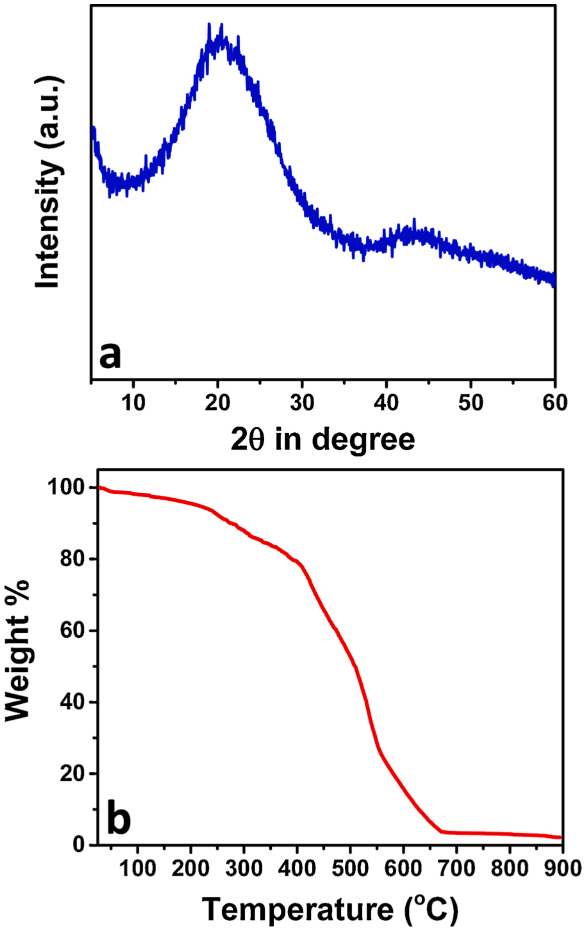


Fig. 4. Wide angle PXRD (a) and TGA profile diagram (b) of TrzPyPOP.

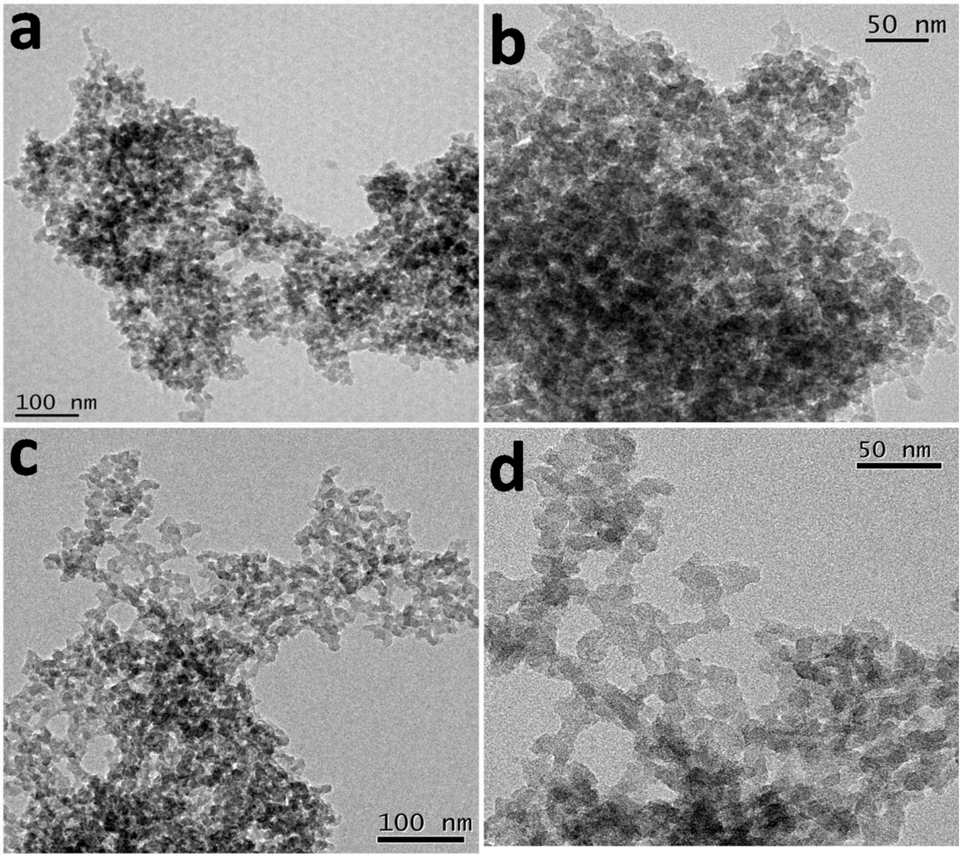
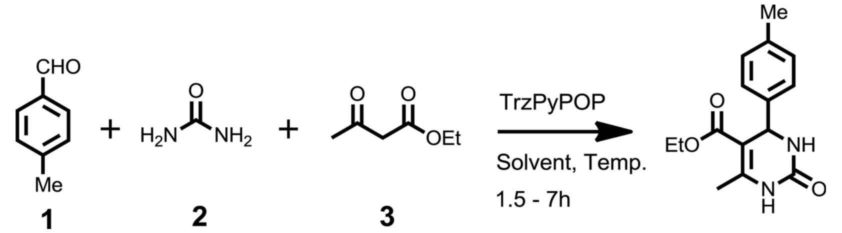


Fig. 5. HR-TEM images of as synthesized TrzPyPOP (a and b) and those after sixth catalytic cycle (c and d).

Table 1
Optimization of the Biginelli reaction conditions catalyzed by TrzPyPOP a: Pure isolated product yield.

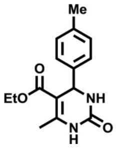
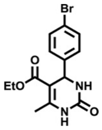
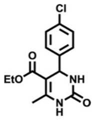
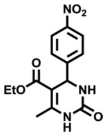
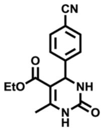
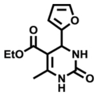
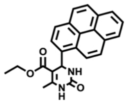


Entry	Solvent	Time(h)	Temperature	Yield[a] (%)
1	THF	24	RT	–
2	CH_3CN	24	80	34
3	DCE	24	80	20
4	THF	1.5	65	98
5	EtOH	24	70	40
6	THF	24	50	30
7	DCM	24	40	–

[a] Pure isolated product yield.

using Fourier-transform infrared spectroscopy (Fig. 1). The peak at 1547 cm^{-1} in SL-1 amine as well as in TrzPyPOP indicates the presence of triazine moiety in TrzPyPop. Further, peak at 1684 cm^{-1} in pyrene-1-carboxaldehyde is absent in the final TrzPyPOP material, which confirm the absence of C=O moiety in material, and thus the polycondensation reaction proceeds completely. The absence of IR band at around 1640 cm^{-1} also confirms the imine (C=N) bond is not formed in the TrzPyPOP, whereas the signal at around the (1645–1660) cm^{-1} confirms the presence of deformation band of aminal linkage (-NH-). The absence of imine moiety, presence of -NH- deformation band and the presence of hump at 3300 cm^{-1} confirms the presence of aminal-linkages [40] as of our predicted framework model shown in Scheme 1. To investigate the bonding and structural integrity of the organocatalyst, FT-IR spectrum of TrzPyPOP has been collected after 6th cycles (ESI, Figure S9), where we could not observed any significant changes in the spectral pattern. This result suggested high robustness of the porous network in TrzPyPOP. To confirm the formation of the organic framework of TrzPyPOP and the chemical environment of different carbon atoms in it, ^{13}C CP MAS NMR spectroscopic analysis has been performed (Fig. 2). The spectrum consist of four sharp and intense peaks at 166.59, 140.05, 128.58 and 56.07 ppm. The NMR signal at 166.59 ppm confirms the presence of triazine moiety [39]. ^{13}C signal appeared at 140.05 ppm

Table 2
Substrate scope for the TrzPyPOP catalyzed MCR in THF.

Entry	Aldehyde	Urea	Ester	Product	Time	Yield[h]
1.	1a	2	3		2.0	98
2.	1b	2	3		1.5	98
3.	1c	2	3		2.0	99
4.	1d	2	3		7.0	77
5.	1e	2	3		6.5	88
6.	1f	2	3		1.5	98
7.	1g	2	3		2.0	99

1a: R = 4-tolyl, 1b: R = 4-bromophenyl, 1c: R = 4-chlorophenyl, 1d: R = 4-nitrophenyl, 1e: R = 4-ciyanophenyl, 1f: R = 2-furyl, 1g: R = pyrene, h: pure isolated yield. 2: urea, 3: ethyl acetoacetate.

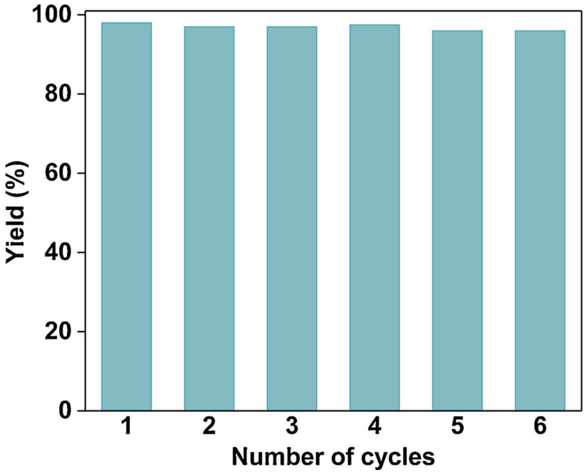


Fig. 6. Recycling efficiency of TrzPyPOP for the Biginelli condensation between 4-methylbenzaldehyde, urea and ethyl acetoacetate.

is responsible for the aromatic carbons attached with the triazine ring and aliphatic carbon atom adjacent to 'N' atom of secondary amine linkage [39]. Broad peak at 128.58 ppm is an indication the rest of the carbon atoms come from aromatic pyrene moiety. The aliphatic carbon atoms between the aminal linkages of TrzPyPOP material give up-field signal in 56.07 ppm.

3.2. Nanostructure and porosity analysis

The porosity and surface area of the TrzPyPOP is investigated by measuring volumetric N_2 adsorption/desorption and the corresponding isotherm at liquid N_2 temperature is shown in Fig. 3. This isotherm indicates high uptake of N_2 at low relative pressure (<0.1 P/P_0) confirming the presence of microporous nature of the polymeric network together with a steady increase in N_2 uptake at high pressure (>0.9 P/P_0) is due to the interparticle voids formation between the polymeric nanoparticles [41,42]. Thus, this isotherm suggested the presence of both type I and type IV BET sorption isotherms according to IUPAC classification [43]. The BET (Brunauer-Emmett-Teller) surface area calculated from the N_2 adsorption/desorption isotherm is 1016 m^2 g^{-1}, and the pore size distribution graph (inset of Fig. 3) indicated the presence of hierarchical porosity with peak pore sizes of 1.6 and 2.6 nm. The high BET surface area and microporosity along with some mesoporosity is the organic framework is very demanding as it could overcome the diffusional limitation that faced by the microporous materials when used alone in heterogeneous catalysis [44]. To investigate the structural integrity of organocatalyst TrzPyPOP, surface area and porosity analysis has been conducted with the reused catalyst after sixth reaction cycle following above method (ESI, Figure S10). The BET surface area of this used catalyst was 1012 m^2 g^{-1}, which is almost same as that of the fresh catalyst. Pore size distribution of the reused material also remained unchanged with reference to fresh TrzPyPOP. This result suggested high structural integrity of the polymer network.

3.3. Powder XRD, thermogravimetric and elemental analysis

For sustainable catalytic operation, thermal and chemical stability of the catalyst is very essential. The amorphous nature of the polymeric material TrzPyPOP could be attributed to random co-polymerization between the monomer units (SL-1 and pyrene-1-aldehyde) and this has been revealed by a very broad hump obtained between 12° to 30° in the wide angle ($2\theta = 2°$ to $60°$) PXRD pattern (Fig. 4a). [36] Further, thermal stability of the TrzPyPOP material has been evaluated from the thermogravimetric analysis (TGA) under N_2 atmosphere from 25 to 900 °C with continuous ramping rate of 10 °C (Fig. 4b). The TGA profile diagram showed a sharp weight loss after 450 °C, which concludes the material decomposed after this temperature. The CHN elemental analysis data on the other hand suggested the presence of 76.44 % carbon, 19.38 % nitrogen and 4.18 % hydrogen in TrzPyPOP.

3.4. Morphological analysis

The morphological features of the TrzPyPOP material is obtained from high resolution transmission electron microscopic (HR-TEM) analysis. The microscopic images of the as-synthesized material and recycled catalyst after six reaction cycles are shown in Fig. 5. The HR-TEM images show sphere like particle morphology with particle size ranging 15–20 nm. The TEM images of recycled materials clearly suggested that the morphology remains unchanged after catalytic reactions. Thus, HR-TEM analysis suggested no structural deformation during liquid-phase catalysis.

3.5. Basicity measurement

For performing the heterogeneous base catalyzed Beginelli condensation reaction, measurement of the total basic strength of the catalyst is very much necessary. Direct acid-base titration method has been employed to measure the basicity of the TrzPyPOP catalyst. From the volumetric acid-base titration we have measured the basicity of TrzPyPOP as 0.5432 mmol g^{-1}. Detail calculation is represented in ESI, section S2.

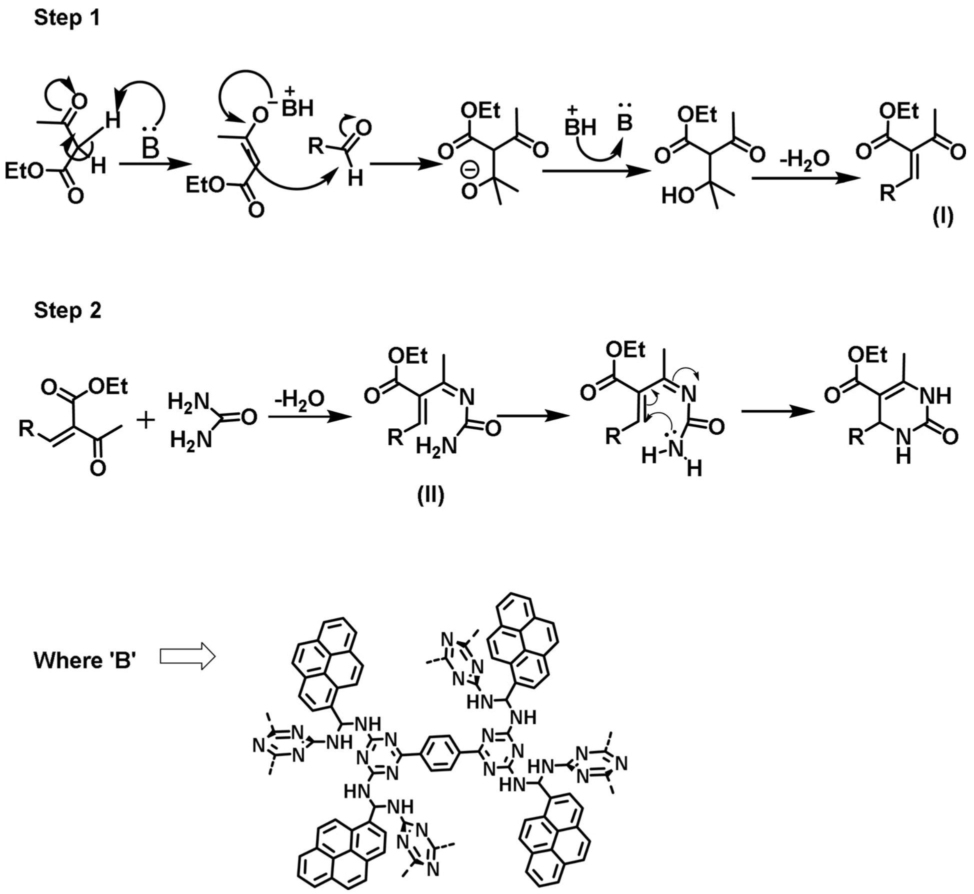


Fig. 7. Probable mechanistic pathway for the Biginelli condensation catalyzed by N-rich POP TrzPyPOP.

3.6. *Heterogeneous organocatalysis over TrzPyPOP*

3.6.1. *Optimization of catalytic reactions*

To optimize the catalytic activity of TrzPyPOP, we have started our catalytic reaction with 4-methylbenzaldehyde (1a), urea (2) and ethyl acetoacetate (3) as model reactants to synthesize ethyl 6-methyl-2-oxo-4-(p-tolyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylate in various solvents and catalyst-solvent combinations. We have also varied the reaction temperature to obtain optimum yield of DHPM. We have observed that at 65 °C the reactants give 98 % yield of the corresponding DHPM in tetrahydrofuran (THF) medium within 1.5 h. Detailed optimization results are summarized in Table1.

Substrate scope for the synthesis of 3, 4-dihydropyrimidinones over TrzPyPOP

After optimization of the reaction conditions, a mixture of 1.0 mmol of aldehyde, 1.1 mmol of ethyl acetoacetate and 10.0 mg of TrzPyPOP was taken in THF and heated for half an hour, then urea (1.3 mmol) was added and refluxed for 2 h at 65°C. The reaction mixture was cooled and poured into ice cold water with stirring, then crude product was filtered followed by washed with cold water, dried and purified. We have varied carried out this MCR with different aromatic aldehyde of tolyl, bromophenyl, chlorophenyl, nitrophenyl, ciyanophenyl, furyl and pyrenes. Results are summarized in Table 2. As seen from this table that apart from electron withdrawing nitro and cyano groups the DHPM yields were very high for all the substrates. Turnover numbers have been calculated for different DHPM derivatives, and the values are ranging from 143 to 183. Detailed calculation procedure and values are shown in ESI, Section S3 and Table S1. This result suggested very high catalytic activity of TrzPyPOP for the synthesis of DHPMs for a wide range of activated aromatic aldehydes. Further, we have performed the same catalytic reaction using 4-methyl benzaldehyde and thiourea (instead of urea) and we got desired product ethyl-6-methyl-2-thioxo-4-(p-tolyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylate in 73 % yield. This product has been identified by ^{1}H NMR spectroscopy. (ESI, Figure S8).

3.6.2. *Recyclability and possible mechanism*

Recyclability of the heterogeneous catalyst is a very essential parameter for its sustainable operation. We have carried out the recycling experiment by using 4-methylbenzaldehyde as the aldehyde precursor and in Fig. 6 we have plotted the product yields in six consecutive cycles. As seen from this plot that the product yields have only decreased from 98 % to 96 %. This result suggested high recycling efficiency of the TrzPyPOP organocatalyst. A plausible mechanism for this MCR over TrzPyPOP is shown in Fig. 7, where we have proposed that the acidic hydrogen from ethyl acetoacetate get deprotonated by our N-rich base catalyst (TrzPyPOP) under the reaction conditions [45]. This is followed by the attack of the nucleophile generated to the electrophilic carbonyl carbon of the aldehyde to yield the intermediate I. These intermediate moieties I reacts with one equivalent of urea and give Schiff base adduct II with the release of one equivalent of water. Finally through the intramolecular cyclization of adduct II produces involving hydride transfer to form the desired DHPM derivatives [46].

4. Conclusions

Our experimental observations suggested that a novel hierarchically porous organic polymer TrzPyPOP bearing pyrene and triazine moieties can be synthesized through a convenient polycondensation reaction between four armed amine and pyrene aldehyde. TrzPyPOP showed hierarchical porous polymeric structure with BET surface area 1016 m^2 g^{-1}. By virtue of its high specific surface area, hierarchical porosity in nanoscale, and mild surface basicity due to presence of aminal linkages, this porous polymer can act as a very efficient orgnocatalyst for the one-pot synthesis of DHPM derivatives via base catalyzed Biginelli reaction under mild reaction conditions. Due to high structural robustness of the porous polymeric network this triazine and pyrene containing POP showed excellent recyclability for the synthesis of DHPMs. Highly porous organic polymer bearing triazine, pyrene moieties and aminal linkages together with their high recycling efficiency for the synthesis of value added bioactive molecules presented herein may open new opportunities in heterogeneous organocatalysis in future.

CRediT authorship contribution statement

Sabuj Kanti Das: Methodology, Data curation, Formal analysis, Writing - original draft. **Avik Chowdhury:** Data curation, Formal analysis, Writing - original draft. **Debabrata Chakraborty:** Data curation, Formal analysis. **Utpal Kayal:** Data curation, Formal analysis. **Asim Bhaumik:** Supervision, Funding acquisition, Writing - review & editing.

Declaration of Competing Interest

There are no conflicts to declare.

Acknowledgements

SKD wishes to thank UGC New Delhi and IACS for his senior research fellowship. AC wishes to thank CSIR, New Delhi for a senior research fellowship. DC wishes to thank DST-INSPIRE for a senior research fellowship. AB wishes to thank DST-SERB, New Delhi for a core research grant (Grant number CRG/2018/000230).

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2020.111198.

References

[1] J.P. Wan, Y. Pan, Mini Rev. Med. Chem. 12 (2012) 337–349.
[2] L.H.S. Matos, F.T. Masson, L.A. Simeoni, M. Homem-de-Mello, Eur. J. Med. Chem. 143 (2018) 1779–1789.
[3] B. Jauk, T. Pernat, C.O. Kappe, Molecules 5 (2000) 227–239.
[4] R. Kaur, S. Chaudhary, K. Kumar, M.K. Gupta, R.K. Rawal, Eur. J. Med. Chem. 132 (2017) 108–134.
[5] A.R. Moosavi-Zare, M.A. Zolfigol, V. Khakyzadeh, C. Boettcher, M.H. Beyzavi, A. Zare, A. Hasaninejad, R. Luque, J. Mater. Chem. A 2 (2014) 770–777.
[6] P. Biginelli, Ber. Dtsch. Chem. Ges 24 (1891) 1317–1319.
[7] M.J. Hulsey, H.Y. Yang, N. Yan, ACS Sustain. Chem. Eng. 6 (2018) 5694–5707.
[8] H. Xu, J. Gao, D. Jiang, Nat. Chem. 7 (2015) 905–912.
[9] L.W. Xu, Z.T. Wang, C.G. Xia, L. Li, P.Q. Zhao, Helv. Chim. Acta 87 (2004) 2608–2612.
[10] M.M. Heravi, K. Bakhtiari, F.F. Bamoharram, Catal. Commun. 7 (2006) 499–501.
[11] V.R. Choudhary, V.H. Tillu, V.S. Narkhede, H.B. Borate, R.D. Wakharkar, Catal. Commun. (2003) 449–453.
[12] A. Pourjavadi, H. Salimi, S. Barzegar, Acta Chim. Slov. 54 (2007) 140–143.
[13] L. Wang, C. Cai, J. Heterocycl. Chem. 45 (6) (2008) 1771–1774.
[14] P. Vadivel, R. Ramesh, A. Lalitha, J. Catal. 2013 (2013), 819184.
[15] Z. Zarnegar, J. Safari, J. Nanopart. Res. 16 (8) (2014) 2509.
[16] S.Z. Dalil Heirati, F. Shirini, A.F. Shojaei, RSC Adv. 6 (2016) 67072–67085.
[17] E.S. Diarjani, F. Rajabi, A. Yahyazadeh, A.R. Puente-Santiago, R. Luque, Materials 11 (2018) 2458.
[18] S. Verma, M. Nandi, A. Modak, S.L. Jain, A. Bhaumik, Adv. Synth. Catal. 353 (2011) 1897–1902.
[19] J. Ortiz-Bustos, M. Fajardo, I. del Hierro, Y. Perez, Mol. Catal. 475 (2019), 110501.
[20] A. Nakhaei, A. Davoodnia, S. Yadegarian, Russ. J. Gen. Chem. 86 (2016) 2870–2876.
[21] J. Mondal, T. Sen, A. Bhaumik, Dalton Trans. 41 (2012) 6173–6181.
[22] A.P. Côté, A.I. Benin, N.W. Ockwig, M. O'Keeffe, A.J. Matzger, O.M. Yaghi, Science 310 (2005) 1166.
[23] S.-Y. Ding, W. Wang, Chem. Soc. Rev. 42 (2013) 548–568.
[24] E.M. Johnson, R. Haiges, S.C. Marinescu, ACS Appl. Mater. Interfaces 10 (2018) 37919–37927.
[25] M. Liu, L. Guo, S. Jin, B. Tan, J. Mater. Chem. A 7 (2019) 5153–5172.
[26] Y. Xu, S. Jin, H. Xu, A. Nagai, D. Jiang, Chem. Soc. Rev. 42 (2013) 8012–8031.
[27] S. Wang, Y. Liu, Y. Yu, J. Du, Y. Cui, X. Song, Z. Liang, New J. Chem. 42 (2018) 9482–9487.
[28] W. Lu, D. Yuan, D. Zhao, C.L. Schilling, O. Plietzsch, T. Muller, S. Brase, J. Guenther, J. Blumel, R. Krishna, Z. Li, H.C. Zhou, Chem. Mater. 22 (2010) 5964.
[29] A. Modak, M. Nandi, J. Mondal, A. Bhaumik, Chem. Commun. 48 (2012) 248–250.
[30] F.M. Wisser, P. Berruyer, L. Cardenas, Y. Mohr, E.A. Quadrelli, A. Lesage, D. Farrusseng, J. Canivet, ACS Catal. 8 (2018) 1653–1661.
[31] X.K. Chen, W.L. Wang, H.J. Zhu, W.S. Yang, Y.J. Ding, Mol. Catal. 456 (2018) 49–56.
[32] P. Kaur, J.T. Hupp, S.T. Nguyen, ACS Catal. 1 (2011) 819–835.
[33] K. Huang, J.Y. Zhang, F.J. Liu, S. Dai, ACS Catal. 8 (2018) 9079–9102.
[34] J.-J. Kim, C.-R. Lim, B.M. Reddy, S.-E. Park, Mol. Catal. 451 (2018) 43–50.
[35] S.K. Das, P. Bhanja, S.K. Kundu, S. Mondal, A. Bhaumik, ACS Appl. Mater. Interfaces 10 (2018) 41303–41313.
[36] A.B. Hu, W.J. Zhang, Q.L. You, B. Men, G.Y. Liao, D.S. Wang, Chem. Eng. J. 370 (2019) 251–261.
[37] B.P. Biswal, H.A. Vignolo-Gonzalez, T. Banerjee, L. Grunenberg, G. Savasci, K. Gottschling, J. Nuss, C. Ochsenfeld, B.V. Lotsc, J. Am. Chem. Soc. 141 (2019) 11082–11092.
[38] T. Yokoi, Y. Kubota, T. Tatsumi, Appl. Catal. A Gen. 421 (2012) 14–37.
[39] S.K. Das, S. Mondal, S. Chatterjee, A. Bhaumik, ChemCatChem 10 (2018) 2488–2495.
[40] M.G. Schwab, B. Fassbender, H.W. Spiess, A. Thomas, X. Feng, K.C. Mullen, J. Am. Chem. Soc. 131 (2009) 7216–7217.
[41] S.K. Kundu, A. Bhaumik, ACS Sustain. Chem. Eng. 3 (2015) 1715–1723.
[42] D. Chandra, A. Bhaumik, J. Mater. Chem. 19 (2009) 1901–1907.
[43] P. Schneider, Appl. Catal. A Gen. 129 (1995) 157–165.
[44] D.P. Serrano, J.M. Escola, P. Pizarro, Chem. Soc. Rev. 42 (2013) 4004–4035.
[45] N. Aider, A. Smuszkiewicz, E. Perez-Mayoral, E. Soriano, R.M. Martin-Aranda, D. Halliche, S. Menad, Catal. Today 227 (2014) 215–222.
[46] S.H.S. Azzam, M.A. Pasha, Tetrahedron Lett. 53 (2012) 7056–7059.