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N-rich porous organic polymer as heterogeneous organocatalyst for the one-pot synthesis of polyhydroquinoline derivatives through Hantzsch condensation reaction

Sabuj Kanti Das,[a] Sujan Mondal,[a] Sauvik Chatterjee,[a] and Asim Bhaumik*,[a]

Abstract: Incorporation of nitrogen functionality onto the high surface area porous polymeric network are very demanding in designing suitable heterogeneous organocatalyst having surface basicity. Here we report the synthesis of a new aminal-linked triazine based microporous organic polymer (TrzMOP) through a simple and efficient condensation pathway involving the reaction between 1,4-bis(4,6-diamino-s-triazin-2-yl)-benzene (SL-1) and 2,5-thiophene dicarboxaldehyde. The material has been characterized by using powder XRD, FTIR spectroscopy, solid state magic-angle spinning ^{13}C NMR, CHN analysis, FESEM, CO_2-TPD and N_2 adsorption/desorption techniques. This nitrogen-rich new porous organic polymer showed very high catalytic efficiency for one-pot proficient synthesis of polyhydroquinoline derivatives via microwave assisted condensation reaction. As little as 8 mg of catalyst was found to be effective under the optimum reaction conditions. In addition, TrzMOP catalyzed synthesis of biologically active polyhydroquinoline derivatives are very cost effective, scalable, less time consuming, and environmentally benign compared to those of currently used as heterogeneous catalysts.

Introduction

Multi-component reactions (MCRs) are very useful chemical reactions where three or more starting materials take part in a single step at a time in the presence of a suitable heterogeneous catalyst to form a product, where most of the reactive atoms contribute in the formation of the final product.[1] For being atom economy and environmentally benign MCRs are very powerful and proficient tool for the synthesis of fine chemicals. In addition, MCRs reduce reaction time, minifies the reaction and purification steps, save raw materials and there is no complexity to isolate the product. Polyhydroquinoline synthesis through Hantzsch condensation applying MCR procedure is an economically favorable, time efficient, high yield and easily separable pathway.[2]

Polyhydroquinoline derivatives are precursor to several important class of drugs. Those possess a variety of biological activities like treatment of cardiovascular diseases as the chain cutting agent (nifedipine, nicardipine, amlodipine) for factor IV channel and modulation agonist-antagonist activities of calcium channel (L-type calcium channel blocker).[3-7] Hence, synthesis of polyhydroquinoline derivatives are drawing a significant attention for last few decades. Extensive analysis of these derivatives has revealed that they can play various important medicinal functions such as vasodilator, bronchodilator, antiatherosclerotic, antitumor, geroprotective, hepatoprotective, neuroprotectant, antidiabetic agents.[8-11] Platelet anti-aggregatory and cerebral antischemic activity in the treatment of Alzheimer's disease and chemosensitizing activity in tumor therapy have been explored with these kind of compounds.[12-13] Along with the above mentioned various important roles, from the biological point of view, substituted 1,4-dihydropyridines compounds are analogue of NADH coenzymes which have the potential application for reductive amination by supplying hydride.[14-15] All these advantages including medicinal and biological importance, synthesis of this heterocyclic nucleus have attracted huge attention to the synthetic chemists and a large number of synthetic roots for the synthesis of valuable molecules have been reported for last few decades.

One-pot condensation of an aldehyde, β-ketoester and ammonia in acetic acid or ethanol was first reported by Arthur Hantzsch, in 1882. [2] A prolonged reaction time was required for this process. Followed by this so many researchers have reported advance methodology to reduce reaction time, increase yield, minimise the drastic reaction conditions. Many research groups used heterogeneous solid acid like sulfonated porous nanomaterials,[16] p-toluenesulfonic acid (p-TSA),[17] ionic liquids,[18-20] $Yb(OTf)_3$,[21] $HClO_4$-SiO_2,[22] metal triflates,[23] vanadium ion doped titania nanoparticles,[24] sulfonated CMP[25] etc. as efficient catalyst for the synthesis of polyhydroquinolines. But no group ever used heterogeneous solid base as a catalyst in the synthesis of polyhydroquinoline derivatives through the Hantzsch reaction. Heravi et al.[26] have employed morpholine as a homogeneous organocatalyst for this reaction, but the catalyst can't be recycled for the sustainable operation.

Porous organic materials/polymers (POPs)[27] materials are intensively studied over the years due to their wide range of applications like gas storage,[28] separation,[29] energy applications,[30-32] photocatalysis[33] and heterogeneous catalysis.[34-40,c,d] These versatile properties lead those materials to perform different type of acidic,[41] basic[42] as well as stereo selective[43] catalytic reactions. These POPs are generally synthesized through the condensation polymerization reaction between two reactive monomers in the presence of porogenic solvent molecules.[44] Thus the introduction of aminal-linkages through the amine and triazine containing monomeric units can

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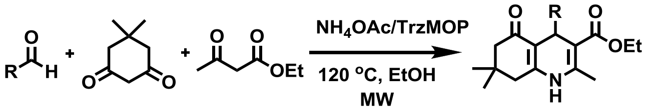
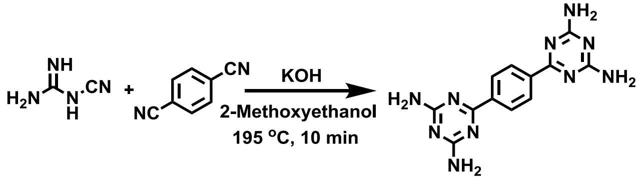
Supporting information for this article is given via a link at the end of the document.((Please delete this text if not appropriate)) offer great opportunities heterogeneous basic organocatalysis. In comparison to the intensive usage of solid acid catalysts in chemical technology, solid bases are not lagging far behind. There are various solid bases that have been studied as heterogeneous catalyst for a wide variety of catalytic reactions.[45] Herein, we are demonstrating a successful fabrication of new aminal-linked microporous triazine based organic polymer (TrzMOP) by a simple condensation pathway. We are exploiting the activity of newly developed porous polymer TrzMOP as an efficient heterogeneous organo-catalyst to synthesize polyhydroquinoline derivatives. To the best of our knowledge first time we are reporting here microporous heterogeneous solid base catalyzed one-pot proficient synthesis of polyhydroquinoline derivatives under microwave irradiation conditions (Scheme 1).



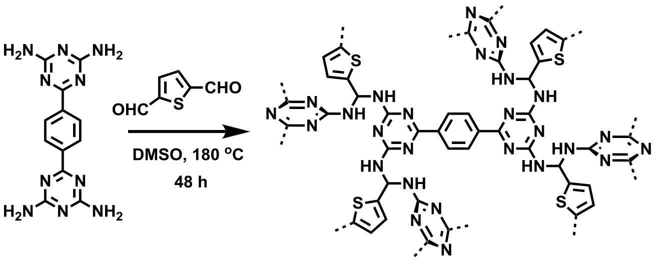
Scheme 1. Multi-component reactions for the synthesis of polyhydroquinone derivatives using TrzMOP as catalyst.

Results and Discussion

Triazine based tetra armed amine compound (SL-1) was synthesized from terepthalonitrile in basic medium under microwave irradiation for 10 min (Scheme 2). Then the Schiff base condensation has been carried out between SL-1 and 2,5-thiophenedicarboxaldehyde to synthesize porous organic polymer (TrzMOP) catalyst (Scheme 3). Elemental analysis of TrzMOP material reveals C, H, N and S content in the polymer are 51.3 %, 4.2 %, 32.4 % and 7.3 % respectively.



Scheme 2. The synthetic scheme of polyhydroquinone derivatives.



Scheme 3. Synthetic scheme of porous organic polymer TrzMOP.

Spectroscopic analysis: To investigate the bonding connectivity presence in the polymer network, the FTIR spectral analysis has been done with both monomer units and TrzMOP material from 4000 to 400 cm^{-1} which is represented in ESI, Figure S1 and ESI, Figure S2. The attenuation intensity of the sharp aldehydic C=O stretching peak at 1666 cm^{-1} and -NH$_2$ deformation band between 1650-1657 cm^{-1} confirms the condensation reaction between two monomer units. The presence of a sharp IR band at 1540 cm^{-1} in both the SL-1 monomer and TrzMOP material indicates the presence of triazine moiety in the polymer. Absence of imine (-C=N) stretching band at 1620 cm^{-1} and presence of a very broad band at 3417 cm^{-1} in TrzMOP confirmes about the formation of (-CH-NH-) bond.[46] FTIR spectrum of TrzMOP catalyst and recycled catalyst after 7th cycle is displayed in ESI, Figure S3. Both of the FTIR spectra remain unaltered which indicates no structural breakage occurred during the catalytic reaction. The Solid state ^{13}C CP MAS NMR spectrum of TrzMOP material was represented in Figure 1. The down field resonance signal appeared at 166 ppm is due to the presence of carbon atom in triazine ring. And the sp^2 hybridized aromatic carbon atoms (Phenyl and thiophene ring) adjacent to triazine ring gave the resonance signals at 128, 141 ppm.[47] The Schiff base condensation reaction can generate two type of C-N linkage like aminal (-NH-CH-NH-) or iminal (-C=N-) linkage.[48,49] The signal appeared at around 57 ppm is attributed to the formation of aminal linkage in TrzMOP.

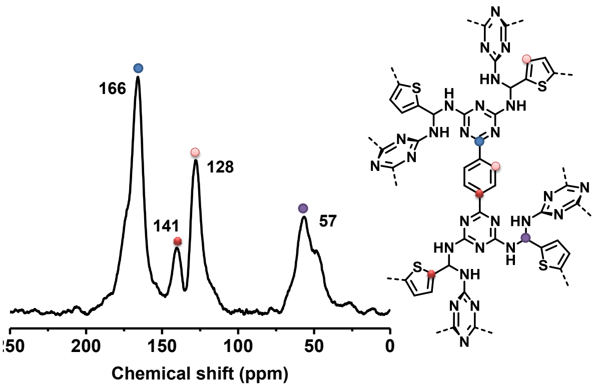


Figure 1. ^{13}C CP MAS NMR of polymeric network TrzMOP.

Porosity and surface area analysis: The nitrogen adsorption/desorption analysis was performed to analyze the specific surface area with architectural rigidity and permanent porosity of TrzMOP. The N$_2$ adsorption/desorption isotherm of TrzMOP and recycled TrzMOP matrix were represented in Figure 2 and ESI, Figure S4 which displayed the features of both type I and IV isotherms according to IUPAC nomenclature.[47] At the very low pressure region isotherm shows a sharp increase of adsorbed N$_2$ volume which indicates the presence of microporosity in the polymeric material. Further, at very high pressure region a small hysteresis loop together with large nitrogen uptake suggested the existence of mesoporosity in this material. This type of typical isotherm was generated probably due to the disordered packing[48] of very small size polymer

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particles as observed in the electron microscopic images (Figure 3). This nitrogen adsorption-desorption isotherm suggested the Brunauer-Emmett-Teller (BET) surface area of TrzMOP material as 792 m^2 g^{-1} with total pore volume 1.27 cc g^{-1} at P/P_0 0.9913. High surface area and pore volume of this porous polymer suggested its huge scope in heterogeneous catalysis. Non local density functional theory has been employed in this adsorption/desorption isotherms to obtain the pore size distribution (PSD) of TrzMOP and this is shown in the inset of Figure 2. PSD plot suggested peak pore width of TrzMOP was 1.55 nm. Other peaks at 2.8, 4.7 and 8.2 could be attributed to the presence of interparticle mesopores in TrzMOP material. During the course of catalytic reactions organic catalyst TrzMOP showed retention of structural integrity as seen from the FTIR spectrum (ESI: Figure S3). Further, after using this TrzMOP material for seven consecutive catalytic cycles the BET surface area of the material was 785 m^2 g^{-1}. This confirmed that surface nanostructure of TrzMOP is quite stable and the catalyst can be reused for several reaction cycles.

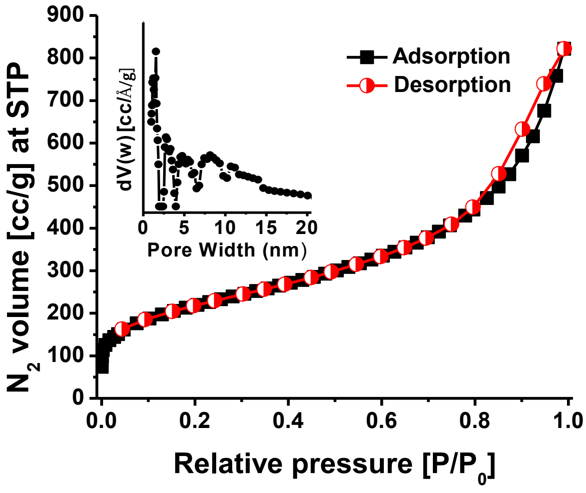


Figure 2. N_2 adsorption/desorption isotherm and pore size distribution of TrzMOP.

Microscopic analysis: The morphological and nanostructural features of the porous polymer have been analyzed through field emission scanning electron microscopy (FESEM) and high resolution transmission electron microscopic (HRTEM) techniques. The FESEM images of TrzMOP polymer have been represented in the Figure 3a and 3b. The FESEM images show spherical morphology. The average particle diameter is found to be between 15-25 nm. The HRTEM images of TrzMOP before and after catalysis were displayed in the Figure 3c and 3d and ESI, Figure S5 respectively. HRTEM analysis also confirms the sphere like particle morphology and with average particle size of ca. 19.04 nm for this porous organic polymer. After 7th catalytic reaction cycles we did not observe any morphological deformation.

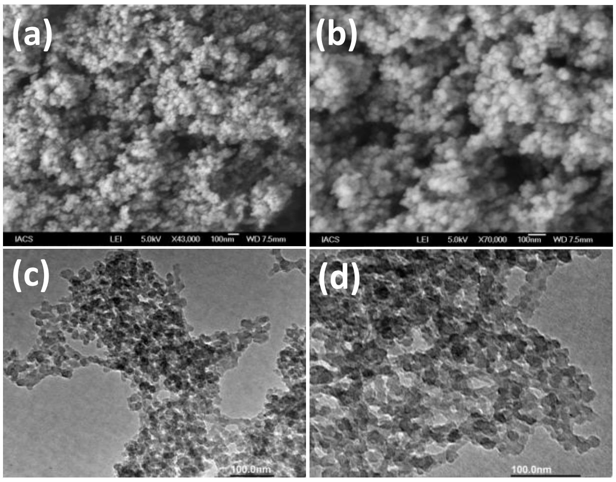


Figure 3. FESEM & HRTEM images of TrzMOP.

Thermal stability and PXRD analysis: Thermal stability of the porous organic network is important to explore their potential in catalysis.. To investigate the thermal stability of TrzMOP porous polymer and the used catalyst after the reaction the thermogravimetric analysis was performed at 10 ^oC/min ramp under N_2 flow in the temperature range of 25-800 ^oC. TGA profile diagram is shown in Figure 4. The polymeric network of the organic catalyst is thermally stable upto 400 ^oC. The sharp weight loss below 100 °C can be assigned due to the surface adsorbed water molcucles or trapped solvents in the porous networks. The TGA profile diagram of recycled catalyst is also very similar to that of the unused catalyst, which suggested high structural stability and huge scope of TrzMOP as a recyclable catalyst. The wide angle powder X-ray diffraction pattern of TrzMOP material is shown in ESI, Figure S6. A broad peak appeared between 2θ value of 20 to 30 degree as a characteristic PXRD pattern of amorphous material.[50]

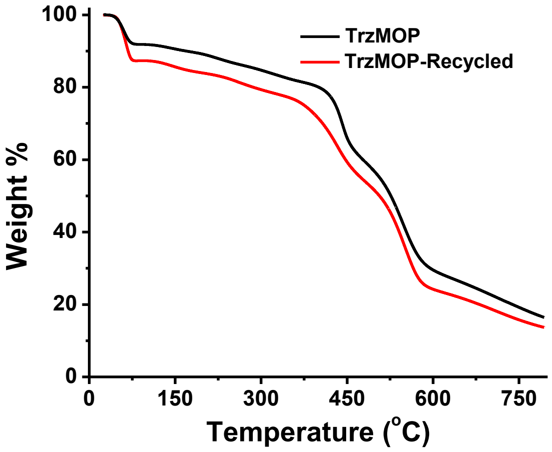


Figure 4. Thermogravimetric (TG) plot of TrzMOP and recycled TrzMOP catalysts.

Basicity measurement: Prior to base catalyzed reaction basicity of TrzMOP material has been estimated. To investigate the surface basicity, temperature programmed desorption (TPD) of CO_2 has been performed in the range of 25-350 ^oC and a broad peak with desorption maxima at 64 ^oC was observed (ESI, Figure S7). The Lewis basicity measured from CO_2-TPD profile suggested total basic strength of 0.35 mmol g^{-1}, which can be considered as mild surface basicity for this porous polymer material.[51] Further, to understand the total base strength of the TrzMOP catalyst, we have carried out the acid-base titration, which suggested the total basic strength of 0.6445 mmol/g (ESI, Section 1). Since the interaction of N-sites of the TrzMOP network with the acidic CO_2 molecules are not strong enough, the basic strength estimated from this titration method is considered as the correct quantification of surface basic sites over CO_2-TPD measurement.

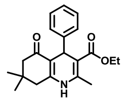
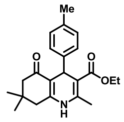
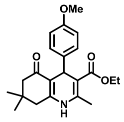
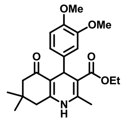
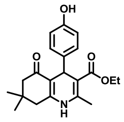
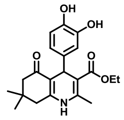
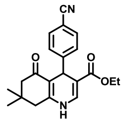
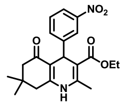
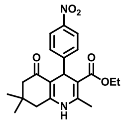
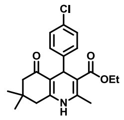
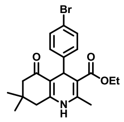
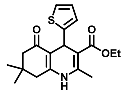
Heterogeneous Catalysis

TrzMOP material was used to examine catalytic performance in four-component one-pot Hantzsch coupling synthesis of polyhydroquinoline derivatives. The scope and generality of this catalytic reaction is illustrated with various substituted aldehydes (Table 1). We started our exploration with an optimization study for the catalytic activity of TrzMOP in single step reaction between benzaldehyde (1 mmol), dimedone (1 mmol) and ethyl acetoacetate (1 mmol) with variation in the amount of ammonium acetate as well as TrzMOP. The reaction was carried out in ethanol under microwave irradiation and benzaldehyde and ethyl acetoacetate are selected as the model reactants for the synthesis of corresponding polyhydroquinoline derivatives.

The impact of temperature was studied by carrying out the model reaction in presence of TrzMOP under microwave irradiation. We began our study at 80 ^oC and then temperature was raised to 100 and 120 ^oC under the identical reaction conditions. The product yield has been improved from 84 to 98 % (Table 1, entry 1). Upon further increase in temperature to 140 ºC no significant increase in yield was observed. To achieve the optimal amount of NH_4OAc, the model catalytic reaction was treated with different amount of NH_4OAc and the results are shown in Table 2. Our experimental data suggested that the reaction using 2 mmol of NH_4OAc was found to be the best for the synthesis of polyhydroquinoline derivatives. On the basis of literature precedents,[18,52] polar solvents are much better than the non-polar solvent and we choose ethanol as the reaction medium for its fast reaction rate, high yield, economic viability and environmental acceptability.

The catalytic efficiency of TrzMOP in four component Hantzsch condensation reaction was evaluated with different catalyst loading for a fixed amount of aldehyde. In absence of TrzMOP a very less amount of reaction yield (<2%) was obtained. But use of just 1 mg of catalyst is enough to run the reaction forward. Reaction product yield was gradually increased from 51% to 98 % up on use of 8 mg and then there was no significant

Table 1. TrzMOP catalyzed synthesis of polyhydroquinoline derivatives through Hantzsch reaction.

Entry	Ar-CHO	Product	Yield (%)	TON[a]
1	-Ph		84 (80 ^oC) 93 (100 ^oC) 98 (120 ^oC) 98.1 (140 ^oC)	300.00 332.14 350.00 350.36
2	4-CH_3-Ph-		96	342.86
3	4-CH_3O-Ph-		95	339.28
4.	3,4,-$(OMe)_2$-Ph-		92	328.57
5.	4-OH-Ph-		96	342.86
6	3,4,-$(OH)_2$-Ph-		91	325.00
7	4-CN-Ph-		96	342.86
8	3-NO_2-Ph-		90	321.43
9	4-NO_2-Ph-		90	321.43
10	4-Cl-Ph-		95	339.28
11	4-Br-Ph-		94	335.71
12	2-thienyl-		72	257.14

[a]TON: Turn Over Number= moles of substrate converted per mole of active site of the catalyst.

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improvement of yield with high catalyst loading (Figure 5a). We optimized the reaction time to get maximum yield of product.

Table 2. Effect on product yield with variation of added NH_4OAc.

Entry	NH_4OAc (mmol)	Product yield (%)
1	1	88
2	1.5	95
3	2	98
4	2.5	98

Table 3. Comparative study of methods for synthesis of polyhydroquinolene.

Entry	Catalyst	Nature of Catalyst	Reaction Condition	Yield (%)	Reference
1	Silica Sulfuric Acid	Acidic (heterogeneous)	Solvent free (60 °C, 45min)	93	16
2	SBA-15 supported solid acids	Acidic (heterogeneous)	Solvent free (110 °C, 2h)	92	17
3	p-TSA	Acidic (homogeneous)	EtOH (RT, 2h)	93	18
4	[hmim]BF_4	Ionic liquid (homogeneous)	Solvent free (90 °C, 10min)	95	19
5	([$(CH_2)_4SO_3$HMIM][HSO_4])	Ionic liquid (homogeneous)	EtOH (78 °C, 57min)	90	20
6	Yb$(OTf)_3$	Acidic (homogeneous)	Solvent free (RT, 5 h)	90	21
7	$HClO_4$-SiO_2	Acidic (heterogeneous)	Solvent free (90 °C, 8 min)	95	22
8	Sc$(OTf)_3$	Acidic (homogeneous)	EtOH (RT, 4h)	93	23
9	V-TiO_2	Nanoparticle (heterogeneous)	Solvent free (80 °C, 10 min)	85	24
10	SPPN	Acidic (heterogeneous)	EtOH (120 °C, MW, 5 min)	96	25
11	Morpholine	Basic (homogeneous)	Solvent free (RT, 60 min)	95	26
12	TrzMOP	Basic (heterogeneous)	EtOH (120 °C, 10 min) EtOH (120 °C, 30 min)	57 79	This Work
13	TrzMOP	Basic (heterogeneous)	EtOH (120 °C, MW, 10 min)	98	This Work

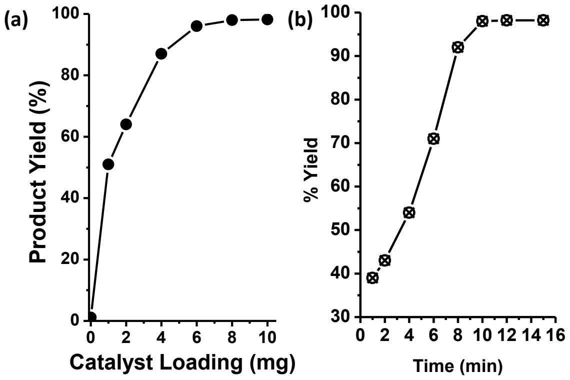


Figure 5. (a) Reaction profile of TrzMOP catalyst at variable catalyst loadings (a). Reaction conditions: benzaldehyde (1 mmol), t = 10 min, T=120 °C, microwave irradiation, NH_4OAc (2.0 mmol), ethyl acetoacetate (1 mmol), dimedone (1.0 mmol) and EtOH (2 mL). Yield of reaction against time (b). Reaction conditions: benzaldehyde (1 mmol), T=120 °C, microwave irradiation, NH_4OAc (2.0 mmol), ethyl acetoacetate (1 mmol), dimedone (1 mmol), TrzMOP catalyst (8 mg), and EtOH (2 mL).

Under the identical reaction condition product yield was increased from 39% to 98% with increasing reaction time from 1 to 10 min. There is no considerable change in yield was observed at longer reaction times (Figure 5b).

In order to investigate the versatility and generality of this catalytic process we have taken a series of other aldehydes to achieve the corresponding polyhydroquinoline derivatives and this method has the ability to tolerate a variety of functional groups with electron rich and electron-deficient substituents as well as heterocyclic aldehyde. As seen from Table 1, we achieved good to excellent yields (72-98%) in most of the cases. TON of the TrzMOP catalyst are obtained 257.14 - 350.36, shown in Table 1 and calculation is represented in ESI, Section 2. All the polyhydroquinoline products were characterized by ^{1}H-NMR spectroscopy (ESI, Figure S8 to S19).

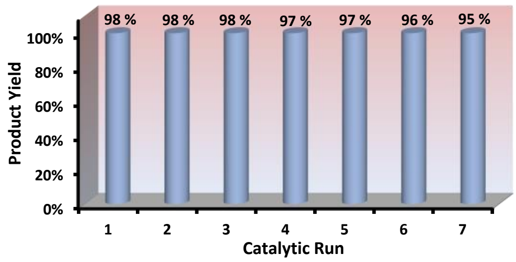
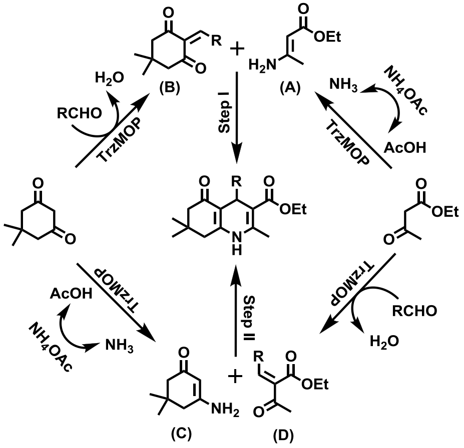


Figure 6. Recycling efficiency of the TrzMOP catalyst in the multi-component reaction.

A comparative study (Table 3) was done for this reaction with other reported catalysts, both homogeneous and heterogeneous, to show the catalytic efficiency of TrzMOP. This reaction was mostly reported with acidic catalysts with very high yield, upto 95%. Morpholine, the only basic moiety used as homogeneous catalyst for the same reaction, shows 95% product yield. TrzMOP, however, shows 98% yield for this one pot MCR. A controlled reaction has been carried out under same condition in absence of microwave irradiation. We achieved comparatively low yield (Table 3, entry 12) of the product when the heating source is changed from microwave to oil-bath. To explore the recyclability of TrzMOP catalyst, it was separated from the reaction mixture through centrifugation then the recovered catalyst was thoroughly washed with hot methanol and THF, well dried under vacuum at 120 °C for 6h. Recovery and reusability of TrzMOP catalyst were evaluated with the reaction of benzaldehyde (1 mmol), dimedone (1mmol), ethyl acetoacetate (1mmol), and ammonium acetate under optimized reaction condition. We reused the catalyst up to 7 consecutive cycles and it was noticed that upto 3rd catalytic run the reaction yield remained same such as fresh catalyst (figure 6). After the 7th cycle the product yield was declined by 3%.

A reasonable pathway for the formation of polyhydroquinoline derivatives have been proposed in scheme 4. On the basis of the above explanations and the literature precedents polyhydroquinoline is formed through Hantzsch-like Conjugate addition mechanism. In presence of basic surface sites of TrzMOP cyclization of enamine to the corresponding enone product takes place. The mechanism is gone through either step I or step II. According to step I conjugate addition of enamine intermediate (A) with enone product (B) and according to step II conjugate addition of enamine intermediate (C) with enone product (D) leads to the formation of polyhydroquinoline derivatives followed by cyclization.



Scheme 4: Probable mechanistic pathway for the TrzMOP catalyzed synthesis of polyhydroquinolines.

Conclusions

Here we have developed a new aminal-linked triazine based microporous organic polymer having high BET surface area (792 m^2g^{-1}) through simple condensation reaction between 1,4-bis(4,6-diamino-s-triazin-2-yl)-benzene (SL-1) and 2,5-thiophene dicarboxaldehyde. Owing to such high surface area and aminal linkages, this porous polymer displayed excellent catalytic activity and recycling efficiency as a heterogeneous basic organocatalyst for the synthesis of polyhydroquinoline derivatives. This protocol offers benefits such as clean reaction, high yields of products, low catalyst loading, short reaction times, high sustainability. Thus, this multicomponent reaction over novel porous organic polymer based organocatalyst have huge scope to explore for the reactions involving various structurally analogous aldehydes for the synthesis of a wide range of polyhydroquinoline derivatives.

Experimental Section

Materials. Terephthalonitrile, 2,5-thiophenedicarboxaldehyde and dicyandiamide were purchased from Sigma Aldrich. Ammonium acetate was procured from Merck, India, ethyl aceoacetate from Loba chemicals and dimedone from from TCI. The organic solvents viz. dimethylsulphoxide (DMSO) and 2-methoxyethanol were used as received from Spectrochem, India and ethanol from Bengal Chemicals. All reactions were performed without further purification.

Characterization techniques. To check crystalline nature of the material powder X-Ray diffraction patterns of the porous polymers was analyzed by using a Bruker AXS D-8 Advanced SWAX diffractometer using Cu-Kα (λ = 0.15406 nm) radiation. The Quantachrome Autosorb 1-C was used to obtain the nitrogen adsorption/desorption isotherms of the TrzMOP polymer at 77 K. Prior to N_2 sorption measurement of the material, Solvent extraction was performed in Soxhlet apparatus for 3 days with MeOH and activated for 24 h at 180 °C temperature under vacuum to get rid of any adsorbed solvent molecule occupied in the pore. Pore-size distribution of TrzMOP material was calculated from adsorption isotherm by employing Non-Local Density functional Theorem (NLDFT). To analyze the bonding connectivity FTIR spectrum of the powder sample was taken using Nicolet MAGMA-FTIR 750 Spectrometer Series II. The liquid state ^{1}H and ^{13}C NMR spectra of the SL-1 and all catalysis products were taken in a 400/500 MHz Bruker Advance II spectrometer. The solid state ^{13}C MAS NMR spectrum of the polymer was obtained from 500MHz Bruker-Avance II spectrometer at a mass frequency of 8 kHz using a 4 nm MAS probe. To investigate the structural morphology as well as particle size of the sample FE-SEM and HRTEM images were taken from JEOL JEM 6700 and JEOL 1400 Plus respectively. Thermal stability of the polymer network was investigated by thermal analyzer TA-SDT Q-600 under nitrogen flow with temperature ramp of 10 °C/min. Perkin Elmer 2400 Series II CHN analyzer was used for elemental analysis of the TrzMOP polymer. For determination of surface basicity of the material CO_2-TPD was analyzed by using a Micromeritics ChemiSorb 2720 with a thermal conductivity detector.

Synthetic procedure of 1, 4-Bis(4,6-diamino-s-triazin-2-yl) benzene (SL-1). Following a literature procedure,[53] at first terephthalonitrile (640mg, 5mmol), dicyandiamide (841mg, 10mmol) and KOH (100mg, 1.75 mmol) were taken into a microwave (G-30) vial. 15 ml of 2-methoxyethanol solvent was poured immediately into the vial and the reaction was carried out at 195 ºC under microwave irradiation for 10 min (Scheme 2). After cooling down, the reaction mixture was poured into in hot water then filtered off under hot conditions and washed with plenty of water followed by methanol and finally with acetone to obtain 75 % yield. ^{1}H and ^{13}C NMR spectra with details of SL-1 are provided in ESI, Figures S20 and S21.

Synthetic procedure of TrzMOP. The TrzMOP material has been synthesized using Schiff-base condensation polymerization method.[54] The reaction was carried out with 2,5-thiophenedialdehyde (420.48mg, 3 mmol) and SL-1 (891 mg, 3 mmol) in 25 mL of anhydrous DMSO solvent under N_2 atmosphere at 180 ^oC (Scheme 3). With the increase of temperature starting materials get dissolved and clear solution appeared, after 10-12 h slowly precipitation took place then the reaction was allowed to continue for about 45 to 48 h. After completion, reaction mixture was allowed to cool at RT, filtered off and washed with water, methanol, THF, acetone. Finally, solvent exchange using Soxhlet apparatus had been carried out with the MeOH and THF mixture (1:1) for 3 days and dried under vacuum at 180 °C for 24 h to obtain guest free triazine based aminal-linked microporous organic polymer.

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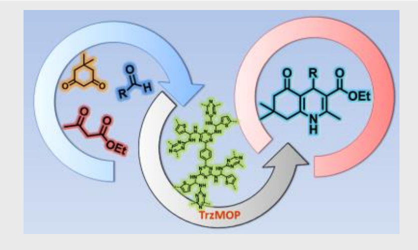
FULL PAPER

A new aminal-linked microporous triazine based organic polymer (TrzMOP) with high BET surface area (792 m^2g^{-1}) has been synthesized and used as an efficient heterogeneous basic organocatalyst for the synthesis of polyhydroquinoline derivatives via Hantzsch condensation reaction.



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N-rich porous organic polymer as heterogeneous organocatalyst for the one-pot synthesis of polyhydroquinoline derivatives through Hantzsch condensation reaction