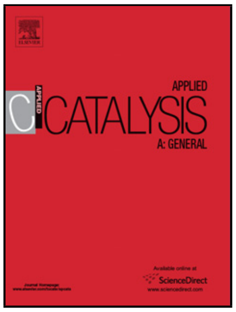

A new triazine based covalent organic polymer for catalytic applications

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A new triazine based covalent organic polymer for catalytic applications

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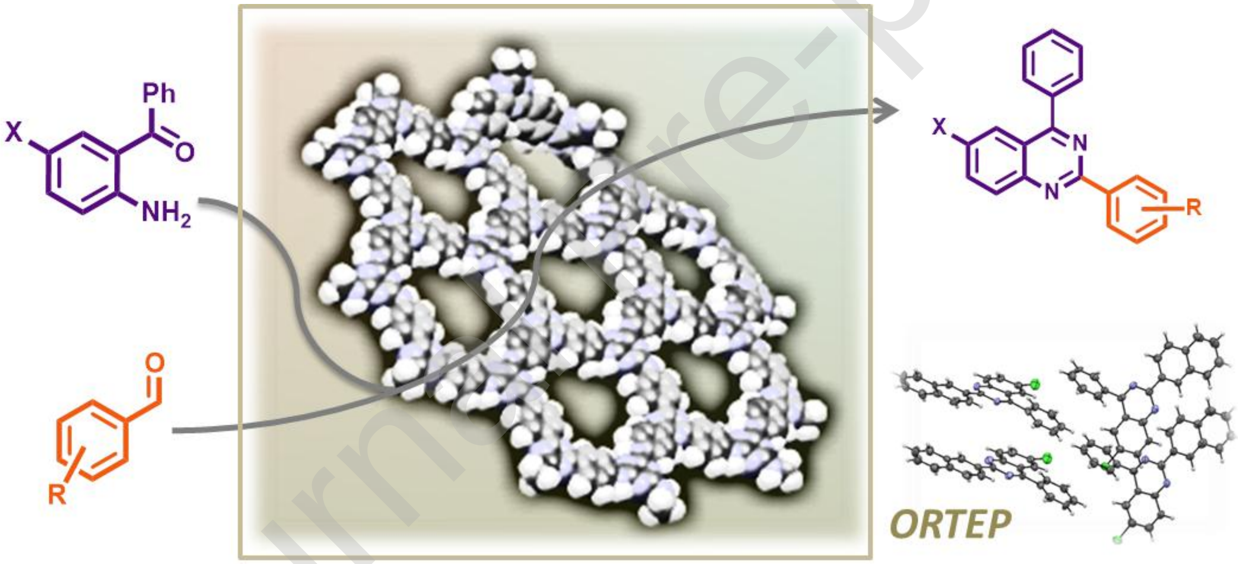
Graphical Abstract



Highlights

- A new triazine based COP has been synthesized and evaluated for catalytic applications.
- HR-TEM shows aggregation of particles with varying diameter.

- CC-TAPT-COP is metal-free, economic and sustainable heterogeneous catalyst.
- CC-TAPT-COP acts as robust catalyst for quinazolines with enhanced response.
- Single Crystal-XRD confirmed the synthesis of quinazoline.

ABSTRACT

A triazine based covalent organic polymer (CC-TAPT-COP) was designed and synthesized via nucleophilic substitution reaction between 1,3,5-*tris*-(*p*-aminophenyl) triazine and cyanuric chloride under refluxing conditions with bottom-up approach. The structural and morphological properties of CC-TAPT-COP were well characterized by various spectroscopic cum analytical techniques. The CC-TAPT-COP appeared as irregular block morphology (SEM) and possesses remarkable thermal stability. The physical properties like insolubility, chemical and thermal stability of CC-TAPT-COP provide a sustainable alternative to classical metal and homogeneous catalysts. In this report, we have explored CC-TAPT-COP as a heterogeneous catalyst for expedient access to the substituted quinazoline, a family of N-containing biopharmaceutical active heterocyclic compounds, at ambient conditions. Moreover, the present work not only supports COPs for their synthesis, but also paves an opportunity for catalytic applications as heterogeneous media.

Keywords: Covalent organic polymers; triazine; heterogeneous catalysis; quinazoline; MCRs

1. Introduction

Covalent organic polymers (COPs) are a well-known class of highly cross-linked porous materials having amorphous to semi-crystalline nature, substantially formed by strong covalent linkage [1, 2]. These materials are usually formed by organic building blocks consisting light elements such as nitrogen and carbon, *in-situ* during the synthesis of 2/3D- ordered porous materials [3]. In the recent research, COPs have been widely employed and categorized as covalent triazine frameworks (CTFs) [4, 5], polymers of intrinsic micro porosity (PIMs) [6] and conjugated micro/meso-porous polymers (CMPs) [7]. Unlike conventional porous materials such as zeolites and porous carbon [8], COPs possess high surface area, integrated adsorptive sites, flexibility, insolubility, low density, high thermal and chemical stability [9]. Subsequently, these kind of functional materials have encouraging advantages such as catalysis [10], CO_2 storage [11, 12], oxygen reduction [13], gas sensors [14] and detection of nitro-aromatics [15].

In general, the conventional approaches for the synthesis of COPs include Schiff's base formation, nucleophilic substitution reaction and C-C coupling methodology [16-19]. Therefore, for building up such rigid organic architectures, a task specific organic substrate is always of paramount significance [20]. The architectures of COP depend upon the geometry of reactive groups present in an altered fashion. Several research reports are available depending upon their pore size and topology; they are categorized as triangular or hexagonal, which usually limit the scope for the development of such networks [21]. Thus, we worked to find task specific and functional sites bearing reactive groups in the core structure of COPs. Further, this approach provides an alternative solution which results in broadening a bird's view for monomers and also encourage the development of COPs [22].

Recently, imine-linked covalent organic architectures have been thoroughly studied in heterogeneous catalyst application because of promising advantages in comparison with other supported materials such as Silica and graphene oxide [23-25]. COPs, in general, have low-density, high thermal resistance and insolubility in organic solvents which make them alternative catalytic materials for various organic transformations. COPs endowing triazine core with high surface area and N-rich architecture provide sustainable and environmentally friendly alternative to their homogeneous analogues with respect to stability, selectivity, ease of separation and recyclability. Moreover, the N-rich active sites are beneficial to hold the reactants and also provide the solid supports to enhance the catalytic activity. Despite this, COPs not being only act as support materials but they can be helpful in base-catalyzed reactions.

In trend, a diversified range of covalent organic polymers were already reported for heterogeneous catalysis and a broad scope of various organic transformations has been successfully implemented by COPs [2]. Among all, many of COPs were used as support materials, which show significant advantages over traditional methods. Pitchumani et al reported the metal immobilized COP as catalyst for Mizoroki-Heck cross-coupling reactions [26]. Recently, Yadav et al reported the first synthesis of unsymmetrical covalent organic polymer as demonstrated its metal free action as sustainable catalyst for non-classical catalytic amide synthesis [27]. Nonetheless, the COPs catalyzed transformations are less practiced and hunted in the field of heterogeneous catalysis and MCRs. To the best of our knowledge, a range of COP based catalysts have been developed but nowhere used for one pot multi-component reactions (MCRs) for the synthesis of substituted quinazoline.

Quinazolines, an important class of N-heterocycles with ubiquitous structure have significant utilization in bio- [28] and pharma industries [29]. The substituted derivatives of quinazoline are varyingly found in numerous natural products and have several implications as pesticides and drugs [30]. Modern methods for the synthesis of quinazoline are well established but these methods have some limitations such as solubility of catalyst and formation of by-products. Therefore, these routine challenges always promote material chemists to find a complementary method by the development of schematic and smart approach for the synthesis of quinazoline.

So, there is always a step ahead to develop a generous synthetic method to deal with such difficulties.

Herein, we have designed and synthesized a triazine based covalent organic polymer and successfully employed, for the first time, as promising heterogeneous catalyst to demonstrate efficient one pot synthesis of highly functionalized quinazoline derivatives. It was found that CC-TAPT-COP acts as robust approach for an easy and quick access to functionalized quinazoline.

2. Experimental Section

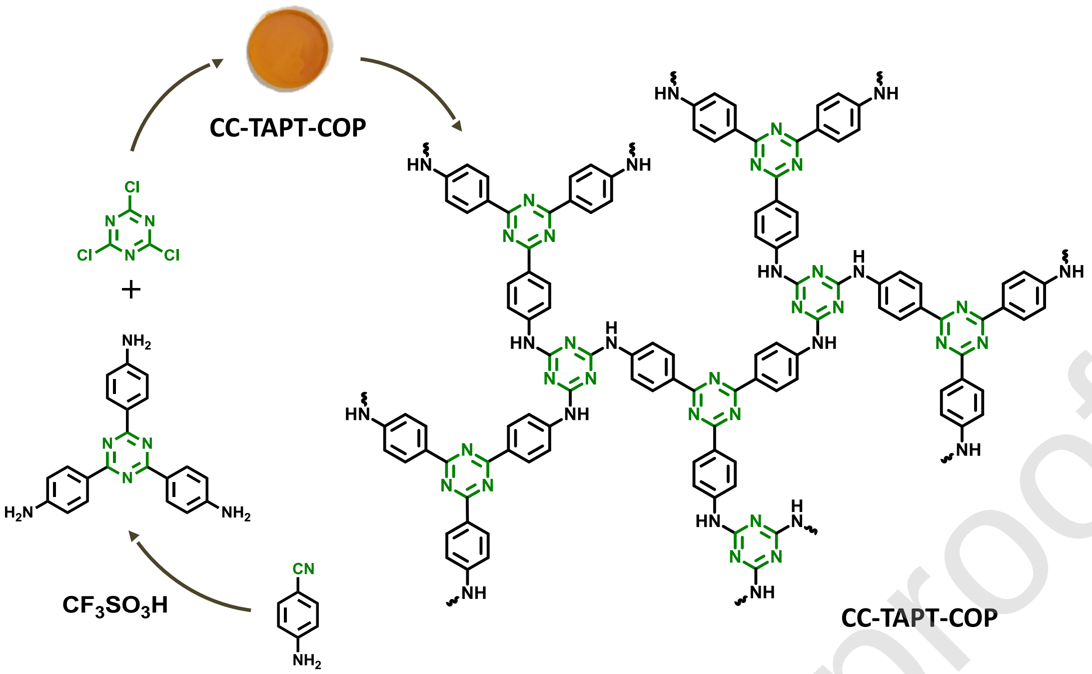
2.1 Materials *p*-amino benzonitrile was purchased from Alfa Aesar Pvt. Ltd. and cyanuric chloride was purchased from SigmaAldrich Pvt. Ltd. Both tetrahydrofuran and methanol were of A.R. grade obtained from SpectroChem. Pvt. Ltd. All the solvents and chemicals were used as received. Double deionised water was obtained from USIC, University of Delhi, India. The instrumentation, general procedure, optimization and recyclability are listed in sections (SI, Page S3).

2.2 Synthesis of CC-TAPT-COP A solution of cyanuric chloride **1** (208 mg, 1.128 mmol) was prepared in THF (10 mL). 2, 4, 6-*tris*-(*p*-aminophenyl)-1,3,5-triazine (TAPT) was synthesized as per procedure with slight modification (Fig. S1) [12]. In an oven-dried R.B. flask, a solution of TAPT **2** (400 mg, 1.128 mmol) in THF (10 mL) was taken followed by addition of DIPEA (589µL, 3.38 mmol). Then, the solution (**1**) was added dropwise to the above reaction mixture (**2**) over a period of 30min with constant stirring and kept on reflux for next 24h. The resulting precipitate was filtered through G4 crucible, and washed successively with THF, methanol and double deionised water, dried at 80°C in *vacuo.* Color: Orange-Yellow; Yield 430 mg.

Results and Discussions

The synthesis route for triazine based CC-TAPT-COP was driven by poly-(N-arylation) of cyanuric chloride with 2, 4, 6-*tris*-(*p*-amino phenyl) triazine under refluxing conditions in THF for 24h (Scheme 1). The as-synthesized CC-TAPT-COP and starting precursors were characterized by FT-IR to probe the bonding feature of polymers (Fig. 1a).

The N-H stretching of newly formed C-NH-C bond was observed as a broad band between 3450-3050 cm^{-1} with disappearance of two characteristic peaks (3322 and 3213 cm^{-1}) of $–NH_2$ group of TAPT and an intense C-Cl str. at 845 cm^{-1} confirmed the successful attempt for the synthesis of CC-TAPT-COP [31, 32]. The peaks observed at 1285, 1358 and 1578 cm^{-1}, respectively can be assigned to triazine core unit present in COP and starting precursors (Fig. 1a) [33]. A characteristic peak of aromatic C=C str. was observed at 1488 cm^{-1}. The rise of a new peak at 1235 cm^{-1} may be attributed to C-N bond str. in as-synthesized polymer (Fig. 1a). The breathing mode of imine (C=N) of triazine core was observed at approx. 810 cm^{-1} [34]. The possible chemical transformation can be easily interpreted in the respective FT-IR of organic polymer.



Scheme 1. Synthesis route of CC-TAPT-COP.

The as synthesized CC-TAPT-COP exhibits amorphous nature as indicated by three broad patterns observed in PXRD measurements (Fig. 1b) [35]. A broad diffraction pattern at $2\Theta=26.1^{0}$ may be assigned to π-π stacking between the layered structure of CC-TAPT-COP (Fig. 1b). The angular strain between precursors prevent formation of symmetric framework of polymer and consequently, we have observed broad peaks for amorphous CC-TAPT-COP [36]. The thermal stability is promising requirement for the development of materials, a TGA experiment was performed which was further categorized into three major stages. The initial degradation starts with removal of guest solvents loss (~5.72% around 100°C), successive weight loss of ~15.8% between 150°-290°C was observed due to degradation of triazine core (Fig. 1c). The last stage shows sharp degradation of ~77.8% between 460-630°C due to degradation of organic polymers till complete carbonization (Fig. 1c) [37].

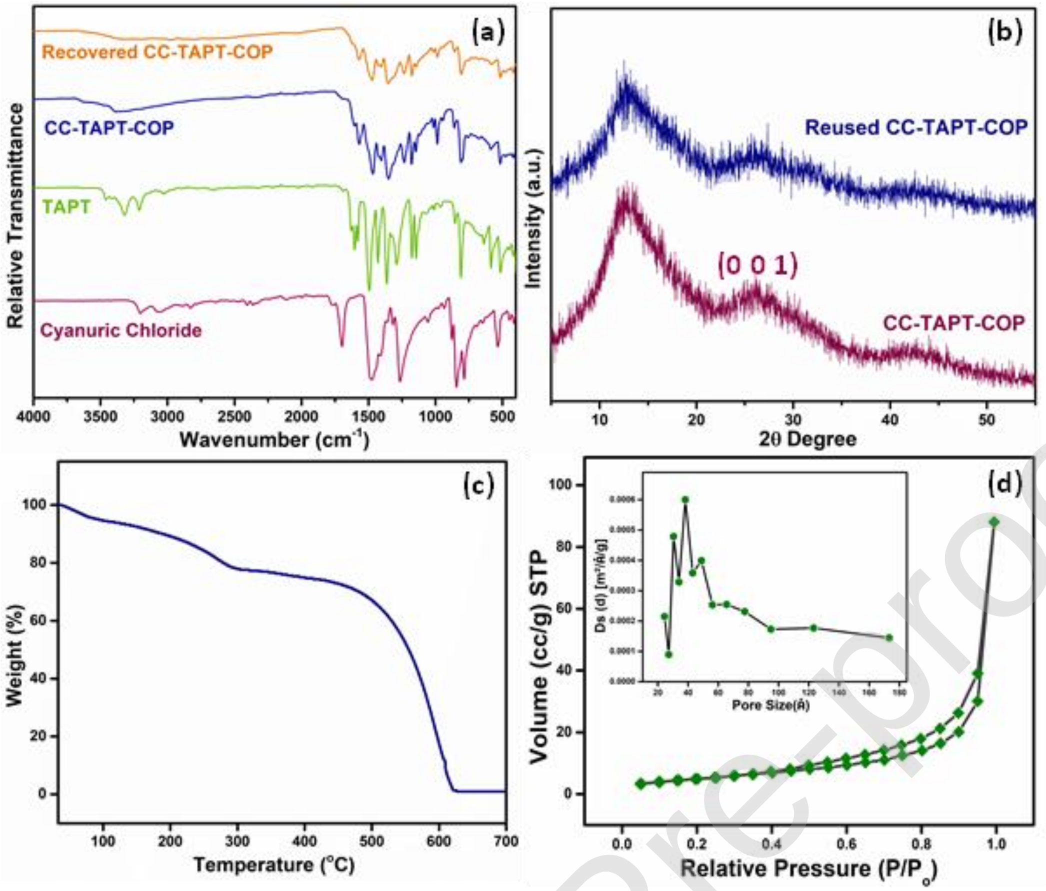


Fig.1. (a) FT-IR of precursors, CC-TAPT-COP and recovered CC-TAPT-COP, (b) PXRD of CC-TAPT-COP and Reused CC-TAPT-COP. (c) TGA and (d) N_2 sorption isotherm of CC-TAPT-COP [Inset: Pore size distribution of CC-TAPT-COP].

The porosity and textural features of CC-TAPT-COP were evaluated by N_2 adsorption/desorption experiment at 77 K. The significant uptake of relative pressure p/p_0 of 0.995 indicated type III isotherm [38]. Thus, the BJH surface area, pore volume and average pore diameter were found to be as 26.7 $m^2\ g^{-1}$, 0.139 $m^3\ g^{-1}$ and 28.6 Ǻ, respectively (Fig. 1d) [39]. The featured agglomeration of small and regular size particles directed towards the pore distribution, which further tells us about the mesoporous nature of CC-TAPT-COP (Fig. 1d).

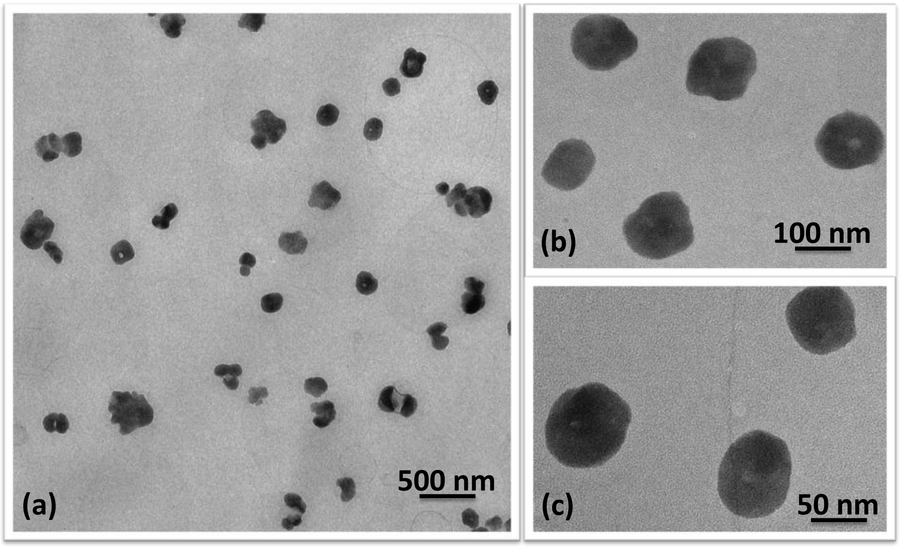


Fig. 2. High Resolution-TEM images of CC-TAPT-COP (**a**) 500 nm, (**b**) 100 nm and (**c**) 50 nm.

The morphological behaviour of CC-TAPT-COP was examined by SEM and TEM spectroscopy. From FESEM micrograph, the CC-TAPT-COP attained supramolecular self-assembling to form agglomerated particles with average diameter range of ~50-100 nm which was found in consistency with TEM results (Fig. S2) [40]. The HR-TEM images at different resolution indicated that approx. ~50-100 nm of particle size upon agglomeration results in formation of as-synthesized CC-TAPT-COP (Fig. 2). However, the irregular morphology was also observed in similar COPs [36].

Further, to study the bonding correlation in CC-TAPT-COP, the sample was analysed by XPS. XPS complete survey spectrum confirms C, N and O elements (Fig. 3a). The appearance of O element was well expected due to presence of guest solvents in CC-TAPT-COP. In deconvoluted C1s, the three peaks with binding energy at 284.6, 285.2 and 288.8 eV can be assigned to C=C, C-N and C=N, respectively (Fig. 3b) [41, 42]. In N1s, the deconvoluted spectra reveals two significant peaks with binding energy at 401.8 eV and 403.2 eV attributed to triazine N and pyrrolic N respectively (Fig. 3c) [43, 44]. In deconvoluted O1s, two peaks with binding energy at 530.08 eV and 531.66 eV attributed to C-O-H and C-O-C bond, respectively (Fig. S3). The elemental mapping of CC-TAPT-COP also confirmed C and N elements (Fig. 3d).

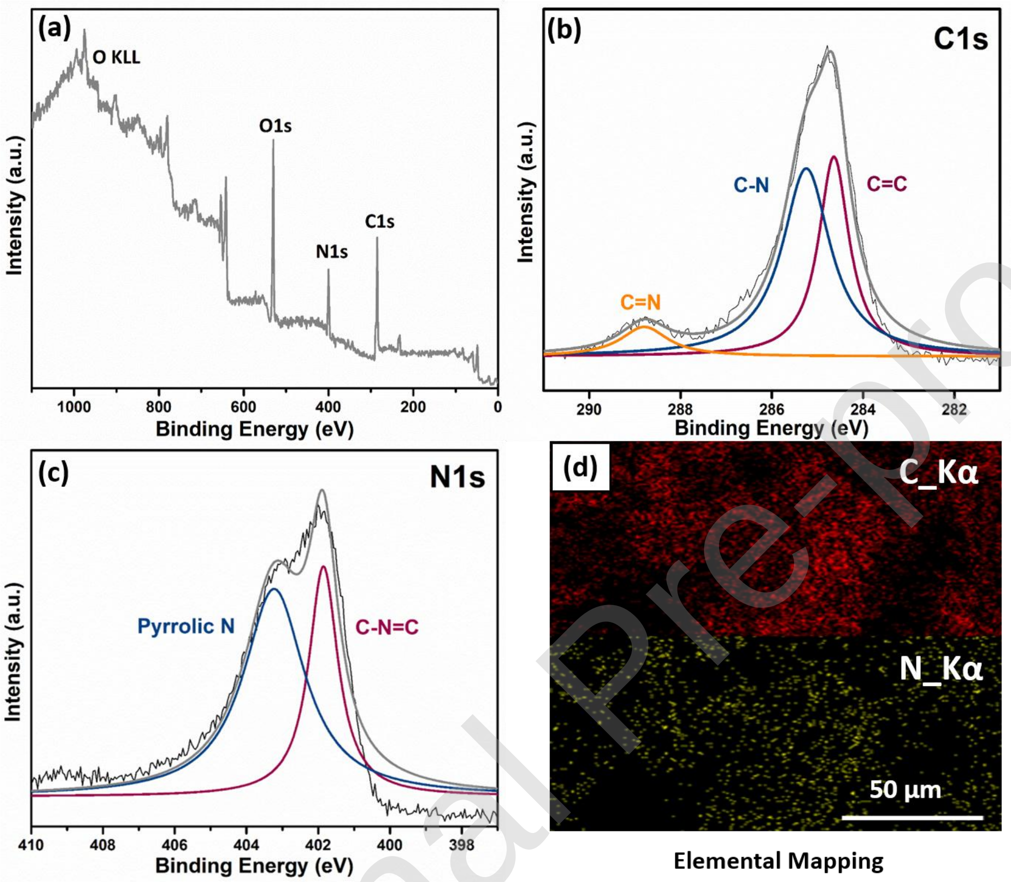


Fig. 3. (a) Complete XPS survey spectrum, deconvoluted (b) C1s and (c) N1s of CC-TAPT-COP. (d) Elemental mapping of CC-TAPT-COP.

With an interest for catalytic application of COPs, we choose multi-component reaction (MCR) to evaluate its catalytic efficiency. The idea of MCR always encouraged us to perform such reaction because of their efficient advantages such as one pot analogy, minimum reaction time and easy work-up methods [45]. Multi-component reaction involves the consecutive synthetic approach of all the reactants, solvent and catalyst together in a vial through one pot approach, which further attain a supramolecular assembly and results in crowding of reactants over the surface of catalyst, the method is known as cascade synthesis [46, 47]. The purpose for this approach is to obtain high efficacy under cleaner reaction conditions. Above all, only a few literature reports are presented by organic chemists in respect to above considerations. With this prediction, we believe that the present catalytic system could act as a smart heterogeneous catalyst for one pot synthesis of highly congested substituted quinazoline.

Table 1. Optimization of reaction conditions.[a]

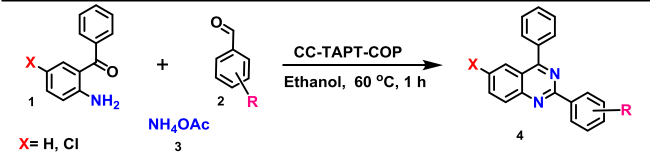
Solvent	**COP**	**Temp/°C**	**Time/h**	**Yield[b]**
EtOH	CF[c]	80	2	17
SF*	10	100	3	-
CH_2Cl_2	10	45	2	72
THF	10	50	2	68
EtOAc	10	70	2	48
CH_3CN	10	84	2	57
Toluene	10	110	2	75
H_2O	10	50	3	22
H_2O	10	100	3	65
EtOH	10	50	2	93
EtOH	10	RT	2	70
EtOH	10	60	0.7	88
EtOH	10	60	1	96
EtOH	10	60	2	96
EtOH	10	70	1	96
EtOH	15	60	1	95

[a]Reaction conditions: 2-amino-5-chlorobenzophenone (1 mmol), *p*-chlorobenzaldehyde (1 mmol), NH_4OAc (2 mmol), CC-TAPT-COP (10 mg), solvent (10 ml). [b]Isolated yields (%). [c]Catalyst Free. *Solvent Free.

Therefore, the catalytic activity of CC-TAPT-COP as heterogeneous catalyst was evaluated for the synthesis of substituted quinazoline, which are classical base-mediated MCRs [48]. Subsequently, the reaction conditions were optimized to support the evaluation under the essence of typical loading, time, temperature and % yields (Table 1). Initially, we step up using procedure of model reaction (Section 1.2, SI), the aforementioned MCRs proceeded efficiently to yield the desired products with CC-TAPT-COP. Whereas, the blank experiment was forwarded without catalyst resulted in negligible amount of product (Table 1). It was clearly observed that the use of polar/non-polar organic solvents resulted in varied range of yields, but only ethanol resulted in remarkable yield (Table 1). The further studies revealed that the reaction was not efficient at room temperature and upon increasing the temperature to 60°C, resulted in better yields, whereas prolonged heating for 2h was found insignificant. Therefore, the optimal bestowed reaction conditions were used where a satisfactory conversion to quinazoline was achieved.

After the careful evaluation for the optimization of reaction conditions with or without COP, we alternatively drive down in order to extend the scope of present COP as a sustainable catalyst to get an easy access to the library of highly congested quinazoline derivatives. Therefore, a range of substituted aromatic aldehyde having electron rich/deficient functional groups was used to investigate the scope of reaction which resulted in the formation of desired products with varied yields (Table 2). Upon careful investigation, we found that with electron-withdrawing substrates, the % yield was obtained in the range of 93-96%, comparatively higher than the electron donating substrates where the % yield was observed in the range of 90-93% (Table 2). This trend suggested that the reaction proceeded smoothly with electron withdrawing (EW) groups instead of electron-donating (ED) substituents, which directed towards an idea that the –C=O (aldehyde) group is more prone to the nucleophilic attack by –NH_2 group. At last, the CC-TAPT-COP catalyst comes up with an enhanced catalytic response, in support with above hypothesis.

Table 2. CC-TAPT-COP catalysed synthesis of quinazoline derivatives.[a]



Product[c]	X	R	Yield[b]
4a	-Cl	-H	95
4b	-Cl	*m*-CH_3	92
4c	-Cl	*p*-CH_3	93
4d	-Cl	*p*-OH	94
4e	-Cl	*p*-OMe	95
4f	-Cl	*p*-NMe_2	92
4g	-Cl	p-F	93
4h	-Cl	*o*-Cl	93
4i	-Cl	*m*-Cl	94
4j	-Cl	*p*-Cl	96
4k	-Cl	*m*-Br	94
4l	-Cl	*p*-Br	93
4m	-Cl	*p*-CN	94
4n	-Cl	*p*-NO_2	93
4o	-Cl	*m,p*-OMe	90
4p	-Cl	*o,p*-Cl	90
4q	-Cl	*m*-F, *p*-Cl	91
4r	-Cl	*o*-F, *m*-NO_2	91
4s	-Cl	2-Napthaldehyde	91
4t	-Cl	Cuminaldehyde	92
4u	-H	*m*-Cl	94
4v	-H	*p*-Cl	94
4w	-H	*p*-F	92
4x	-H	*o*-F, *m*-NO_2	90
4y	-H	2-Napthaldehyde	90

[a]Reaction conditions: 2-amino aryl ketone (1 mmol), substituted aromatic aldehyde (1 mmol), NH_4OAc (2 mmol), CC-TAPT-COP (10 mg), Ethanol (10 mL). Temperature 60°C. [b]Isolated yield (%). [c]Products were characterized by $^1H/^{13}C$- NMR and ESI-HRMS.

Further, the synthesis of substituted quinazoline is also supported by single crystal X-ray structure of **4s** (Fig. 4). The crystal packing diagram of **4s** at 50% probability level is presented in Fig. S4. The associated details of other crystallographic parameters, bond length, bond angle and hydrogen atom coordinates are listed in Table S1-S6.

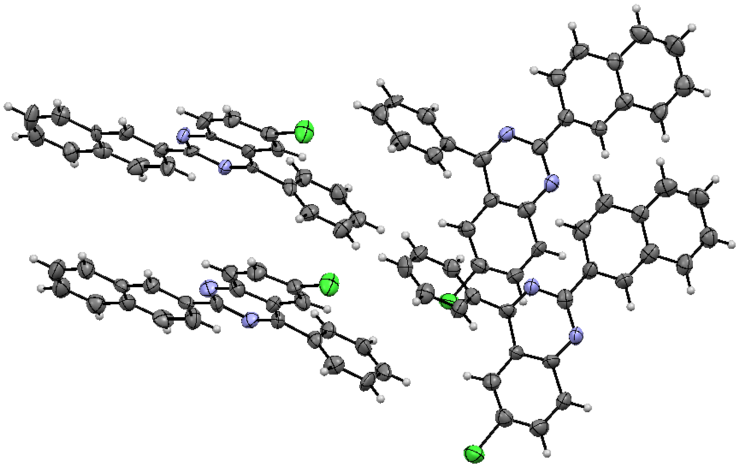


Fig.4 ORTEP diagram of **4s** at 50% probability level.

In order to determine the active catalytic sites of CC-TAPT-COP, control experiments were performed using CC-TAPT-COP and TAPT (precursor). Precisely, the 75.3% conversion of benzaldehyde was observed with CC-TAPT-COP (Table S7). It was observed that TAPT act as homogeneous catalyst, showing conversion of benzaldehyde along with the formation of by-products, whereas CC-TAPT-COP exhibited good catalytic efficiency with selective transformation to quinazoline. In addition, it was inferred that the presence of -NH- (primary/secondary) group may encourage the reaction to get proceed. By considering the fact that the secondary amine groups are widely present in core structure of COPs, TAPT consists of -NH_2 groups, which further suggested that secondary amine of COPs could be identified as the active sites for this specific transformation.

Then after, the dimension and molecular sizes of precursor and product were calculated using Gauss view 5.0 [49] and compared with CC-TAPT-COP in order to ensure the influence of porosity on its catalytic efficiency. Unfortunately, the results showed that the porosity is nowhere relevant for being the main factor to the catalytic activity. Above all, the skeleton of COP, the effects of pore size, surface area and other plausible factors may contribute to encourage the catalytic activity, so the future research on this issue will be critically evaluated later [50].

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In order to understand the plausible mechanism, we have envisioned roughly by probing the theoretical aspects into it. Initially, the N-rich catalytic active sites of as-synthesized COP act as soft center which increase the electrophilic character for –C=O group of substituted benzaldehyde. Initially, the nucleophillic attack of –NH_2 group (2-aminoaryl ketone) to the activated –C=O (benzaldehyde) encourages the formation of aldimine intermediate. Then, the aldimine intermediate reacts with NH_4OAc to form ketimine intermediate which upon ring-transformation and subsequent dehydration yield desired product upon tautomerization under air.

It is always in interest to discuss about the recyclability and stability of any material because of some parameters such as being green and sustainable which is in synthetic interest for industrial applications. After completion of reaction, the CC-TAPT-COP could be easily separated from the reaction mixture without any expected difficulty due to its awakening insoluble behaviour and could be subsequently used for next catalytic runs. Then, the recovered CC-TAPT-COP was washed with ethanol, ethyl acetate and dried. Above all, it was clearly seen that CC-TAPT-COP could be recycled after six runs without prominent loss in its catalytic activity, which was identified by the yield of the desired product (Table S8).

Further, we have studied the direct monitoring of reaction using UV-Vis spectroscopy, we have opted for an on-site sampling during the course of reaction after every 3 min interval over 1h (Fig. S5). In addition, it was observed that CC-TAPT-COP was insoluble in a variety of solvents. The collected samples were subjected to UV-Vis study which indicated that the conversion was efficient with respect to time (Fig. S6).

In connection to find the novelty of our present work, we have compared the present material CC-TAPT-COP with other reported catalytic materials used for the synthesis of substituted quinazoline varied in accordance with reaction conditions and yields (Table S9). Further, this can be explained on fact that *n*-channels allow the precursors to stay and clubbed together in order to orient a feasible geometry and desired product formation via pre-organisation concept through nano-channels. However, the present material CC-TAPT-COP acts as a robust heterogeneous material which could proceed organic transformation in its ability to cope with high temperature, which may increase the flux between the reactants. In addition, supramolecular host-guest interaction thorough π-channels may assist the reaction and could make the material more promising and valuable. Therefore, CC-TAPT-COP is presented as a smart catalyst for MCRs in the synthesis of substituted quinazoline.

3. Conclusions

In summary, we have successfully synthesized a new triazine based CC-TAPT-COP by poly-(N-arylation) between TAPT and cyanuric chloride using bottom-up approach. CC-TAPT-COP shows irregular block morphology and good thermal stability along with average pore diameter of 2.86 nm. Further, we found that CC-TAPT-COP acts as propitious heterogeneous catalyst for synthesis of substituted quinazoline which was confirmed by single crystal X-ray crystallography. CC-TAPT-COP shows robust recovery and efficacy with intriguing catalytic activity. Moreover, this study opens up a new horizon for catalytic application of COPs in MCRs other than novel applications viz. biomedical applications which will be discussed in our future research work.

Conflict of Interest

The authors declare no conflict of interest.

Acknowledgements

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