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# Mesoporous poly-melamine-formaldehyde (mPMF) – a highly efficient catalyst for chemoselective acetalization of aldehydes†

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**A mesoporous poly-melamine-formaldehyde polymer with a high surface area, good porosity and a high density of amine and triazine functional groups was investigated as a highly efficient hydrogen-bonding catalyst. This porous organic polymer was found to be highly effective in catalyzing chemoselective acetalization of aldehydes, without the consumption of any dehydrating agents. The turnover frequency of mesoporous poly-melamine-formaldehyde is hundreds of times higher than melamine monomer, and this high efficiency is due to the high density of aminal (–NH–$CH_2$–NH–) groups and triazine rings in the polymer network, which provides an inherently powerful system with multiple hydrogen bonds. This unique characteristic imparts mesoporous poly-melamine-formaldehyde polymer with a very high activity as a heterogeneous organocatalyst. The polymer is also low cost, and easy to be synthesized and recycled.**

## Introduction

The search for alternative technologies that are greener, safer and environmentally friendly is a research priority, especially for the chemical and pharmaceutical industries. In particular, the use of recyclable catalysts for organic synthesis to minimize waste production and optimize catalyst efficiency is of great interest.[1,2] Porous organic polymers (POPs), a class of highly crosslinked amorphous polymers possessing nanopores, have recently emerged as a versatile platform for catalysts due to their high structural stability. The bottom-up synthesis for POPs provides an opportunity to design polymeric frameworks with various functionalities for use as catalysts or ligands.[3] Current strategies for the design of porous heterogeneous catalysts include: (i) surface modification and catalyst immobilization,[4] (ii) incorporation of ligands into the framework and then introducing the catalytic centers *via* ligands,[5] and (iii) directly using catalytic centers as monomers or building blocks in the synthesis of porous materials.[6] Although these strategies have been studied for many years, their inherent drawback in catalytic activity as compared to the original small molecular catalysts has remained a challenge. Herein we report a novel mesoporous poly-melamine-formaldehyde (mPMF) material that exhibits superb activity in catalyzing the acetalization of aldehydes, even when compared to melamine. The high activity of mPMF is attributed to its condensed network structure with a multifunctional hydrogen bonding system.

Protection of carbonyl compounds such as aldehydes and ketones by acetal formation *via* reaction with alcohols or diols is a common and useful technique for multistep synthesis in drug design, organic and carbohydrate chemistry, and the pharmaceuticals, cosmetics and fragrances industries.[7] Many types of catalysts, including conventional acids (*e.g.* HCl, trifluoroacetic acid (TFA) and *p*-toluenesulfonic acid (*p*-TSA)[8]), solid acids,[9] functionalized silica,[10] acidic polymers,[11] Lewis acids,[12] metal catalysts,[13] small organic molecules,[14] and natural materials[15] (such as kaolinitic clay), have been reported to catalyze the acetal protection of carbonyls. Although acetalization has been widely reported and well-investigated, it suffers from drawbacks such as the use of a corrosive acid catalyst,[16] the need for an excess amount of drying agents, poor chemoselectivity, and incompatibility with substrates containing acid-sensitive functional groups. There is increasing interest in developing an acetalization protocol that is mild, greener, chemoselective, cost-effective and atom-efficient, with ease of catalyst recycling and no excessive use of water scavenging reagents.[17]

## Results and discussion

Recently, Kotke and Schreiner reported the acetalization of carbonyl compounds catalyzed *via* double hydrogen bonding using an electron-deficient thiourea derivative in the presence

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of trialkyl orthoformate as a water scavenger.[18] The electron-deficient thiourea catalyst was designed to be capable of 'partial protonation' of carbonyl compounds *via* hydrogen bonding. Herein we propose the use of melamine, which has a low $pK_a$ value (5.3) and both hydrogen donating and accepting sites, as a catalyst for aldehyde acetalization. Our preliminary studies demonstrated melamine-catalyzed cinnamaldehyde acetalization with methanol (Table S1†), but the activity was very low. The reaction was sluggish at room temperature over 10 mol% melamine (<5% yield for 24 h). At 60 °C, 31% yield was obtained in 24 h without using any water scavenger. Although this melamine-catalyzed acetalization reaction was not practical due to the low activity, it convinced us of the potential of a more powerful hydrogen-bonding system for catalyzing acetalization reactions.

Specifically, we have designed mPMF with the goal of deriving a high density of triazine and aminal ($–NH–CH_2–NH–$) functional groups. By mixing melamine and paraformaldehyde in hot DMSO,[19] we derived a POP with a high surface area of 930 $m^2\ g^{-1}$ and an average pore size of 15.7 nm (see ESI Fig. S1–S4†). A foam-like interconnected mesoporous network structure was observed under transmission electron microscopy (TEM), while scanning electron microscopy (SEM) revealed that the mPMF consisted of aggregates of submicron-sized spherical particles (Fig. 1(b) and (c)). mPMF was rich in aminal ($–NH–CH_2–NH–$) and triazine groups (Fig. 1(a)), which would provide a powerful and highly dense hydrogen-bonding system. The high surface area and mesoporous structure of mPMF would be highly desirable for applications in heterogeneous catalysis.

Preliminary studies showed that the reaction of aldehyde with methanol to form dimethyl acetal proceeded well over the mPMF catalyst (Table 1, entries 1–3). *trans*-Cinnamaldehyde was chosen as the model substrate as it contains an α,β-unsaturated C═C bond, which is sensitive to acidic conditions, and can undergo carbon–carbon double bond isomerization. mPMF was found to catalyze the formation of dimethyl acetal from *trans*-cinnamaldehyde and methanol without *cis*–*trans* isomerization.[20] The reaction reached equilibrium with 65% yield in 8 h at room temperature using 2 mg of mPMF (Table 1, entry 1). mPMF was superior in activity to melamine. Further increase in reaction time or reaction temperature did not lead to increased yield (Table 1, entries 1 and 2), probably due to the presence of the water by-product. The addition of trimethyl orthoformate as a water scavenger increased the yield to 84% (Table 1, entry 3). Without the mPMF catalyst, no reaction was observed after 8 h (Table 1, entry 4).

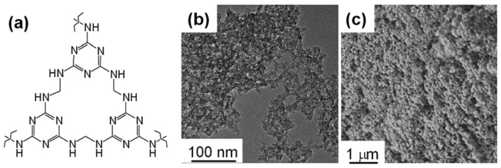


**Fig. 1** (a) Chemical structure, (b) transmission electron microscopy (TEM) and (c) scanning electron microscopy (SEM) images of mPMF.

**Table 1** Acetalization of *trans*-cinnamaldehyde over mPMF[a]

| Entry | mPMF (mg) | Alcohol | Temp. (°C) | Time (h) | Yield[b] (%) |
|---|---|---|---|---|---|
| 1 | 2 | $CH_3OH$ | 25 | 8 | 65 |
| | | | | 24 | 68 |
| 2 | 2 | $CH_3OH$ | 40 | 8 | 64 |
| 3[c] | 2 | $CH_3OH$ | 25 | 8 | 84 |
| 4 | — | $CH_3OH$ | 25 | 8 | 0 |
| 5 | 2 | PDO | 25 | 4 | 46 |
| | | | | 8 | 62 |
| | | | | 24 | 83 |
| 6 | 2 | PDO | 40 | 8 | 85 |
| 7 | 10 | PDO | 25 | 8 | 77 |
| 8 | 50 | PDO | 25 | 8 | 81 |

[a] Reaction conditions: 1 mmol of *trans*-cinnamaldehyde in 25 mmol of methanol or 13 mmol of PDO. [b] Gas chromatography (GC) yield. [c] Trimethyl orthoformate (1.65 eq.) was used.

When acetalization was conducted in 1,3-propanediol (PDO) to form 1,3-dioxane-protected cinnamaldehyde, a good yield of 83% was achieved within 24 h at room temperature without the use of drying agents or water scavengers (Table 1, entry 5). The equilibrium was shifted to the product due to the formation of a more stable 6-membered cyclic 1,3-dioxane structure, instead of dimethyl acetal, which would be more prone to hydrolysis. When the reaction temperature was increased to 40 °C, a yield of 85% was attained in a shorter reaction time of 8 h (Table 1, entry 6).

For a reaction to be feasible for industrial application, a recyclable heterogeneous catalyst and a short reaction time would be highly attractive.[21] Table 1 shows that a product yield of 77% could be achieved in 8 h at room temperature over 10 mg of mPMF (entry 7). This yield could be further increased to 81% when 50 mg of mPMF was used (Table 1, entry 8). Furthermore, it was found that the reaction rate could be remarkably increased by increasing the reaction temperature. Fig. 2 shows that 90% yield of acetal was obtained in less than 1 h at 60 °C. The short reaction time associated with the use of mPMF allowed for the possibility of industrial application in flow reactors. Hence, the stability of the mPMF catalyst was further examined. mPMF was a solid powder that could be easily filtered and separated from the reaction mixture. This

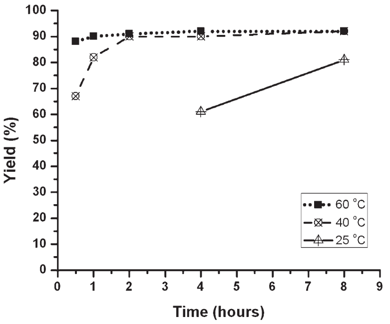


**Fig. 2** Effect of reaction temperature on acetalization of *trans*-cinnamaldehyde with mPMF. Reaction conditions: 1 mmol of *trans*-cinnamaldehyde in 1 ml of PDO, 50 mg of the mPMF catalyst.

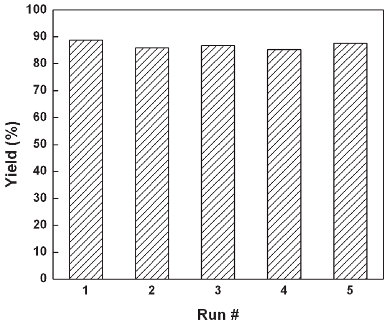
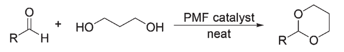
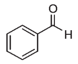
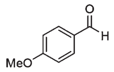
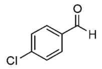
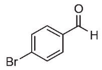
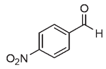
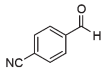
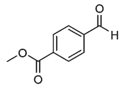
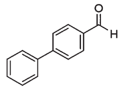
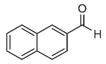
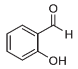
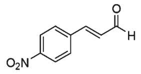
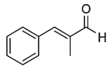
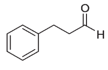
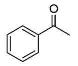
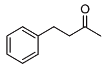


**Fig. 3** Recycling of the mPMF catalyst. Reaction conditions: 2.5 mmol of *trans*-cinnamaldehyde in 2.5 ml of PDO, 5 mg of mPMF, 25 °C, 48 h.

**Table 2** Acetalization of various substrates in PDO over the mPMF catalyst[a]



| Entry | Substrate | Temp. (°C) | Yield[b] (%) |
|---|---|---|---|
| 1 |  | 25 | 94 (90) |
| 2 |  | 25 | 85 (78) |
| 3 |  | 40 | 76 (74) |
| 4 |  | 40<br>60 | 48 (75) |
| 5 |  | 40<br>60<br>80 | Trace<br>71<br>97 (94) |
| 6 |  | 40<br>60<br>80 | Trace<br>58<br>97 (90) |
| 7 |  | 60 | 99 (98) |
| 8 |  | 60<br>80 | 54<br>96 (90) |
| 9 |  | 40 | 97 (94) |
| 10 |  | 40 | 84 (79)[c] |
| 11 |  | 40 | 87 (73) |
| 12 |  | 25<br>40 | 52<br>97 (94) |
| 13 |  | 40<br>60 | 29<br>95 (87) |
| 14 |  | 40 | —[d] |
| 15 |  | 40 | —[d] |

[a] Reaction conditions: 1 mmol of substrate in 13 mmol of PDO, 2 mg of mPMF catalyst, 24 h, unless otherwise specified. [b] GC yield; isolated yield in parentheses. [c] Reaction time: 8 h. [d] No reaction.

heterogeneous organocatalyst exhibited excellent stability in recycling, with no loss in catalytic activity over at least 5 runs (Fig. 3). The use of the mPMF catalyst is advantageous over conventional acetalization protocols in industrial reactors because it is non-corrosive, does not require the use of a co-solvent, is compatible with acid-sensitive substrates, has minimal chemical waste, and provides ease of catalyst recovery and reuse. While polymer-supported catalysts and reagents have been around for decades,[22] they still have a long way to go before they move to industrial applications due to their high costs. As remarked by Nicolaou and Snyder, "Every synthetic technology … has a drawback. For solid-supported reagents, it is their cost."[23] In this case, however, the ease of synthesis, low cost of production, high activity, high stability, and mild reaction conditions make mPMF a promising catalyst for large-scale acetalization of aldehydes.

The substrate scope for acetalization in PDO over mPMF was examined (Table 2). The reaction was found to be chemoselective to aldehydes, and did not occur with ketones (Table 2, entries 14 and 15). Thus, this mild protocol could be useful for the protection of aldehydes in the presence of ketones and acid-sensitive groups. Generally, the protocol worked well for various aryl aldehydes (Table 2, entries 1 to 10). For the more challenging substrates with electron-withdrawing groups, higher reaction temperatures (*e.g.* 80 °C) were required to give satisfactory yields (>95%) (Table 2, entries 5 and 6). Good yields were also obtained at 40 °C for derivatives of *trans*-cinnamaldehyde, such as 4-nitrocinnamaldehyde (Table 2, entry 11) and α-methyl-*trans*-cinnamaldehyde (Table 2, entry 12). Importantly, the reaction also worked well for aliphatic aldehydes. As an example, 95% of acetal yield was achieved for hydrocinnamaldehyde at 60 °C (Table 2, entry 13).

The mechanism of mPMF and related molecules in the acetalization of aldehydes was studied. Firstly, melamine and other small molecules with similar hydrogen bonding functionalities were examined as catalysts in the model reaction (Table S1†). With 3-aminopyridine, which has an amine group in close proximity to the nitrogen on the pyridine ring, a moderate product yield of 53% was obtained at 60 °C after 24 h. With 4-aminopyridine, almost no reaction was found. Reaction over 2-aminopyridine resulted in decomposition, yielding a dark brown mixture. With 2-aminopyrimidine as a catalyst, 47% yield was obtained. The 2-pyridinol catalyst led to a moderate yield of 52%, despite its high p$K_a$ value of 11.7. The results here suggested that hydrogen bonding activation could play a major role in aldehyde activation (Fig. S5†) and acetal formation. The acetalization reaction proceeded with 2-pyridinol, but not with 4-aminopyridine probably because the latter did not favor the synergistic double hydrogen bonding model with its amino group in the *para*-position

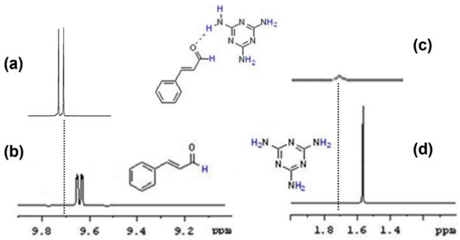


**Fig. 4** $^1$H NMR spectra of (a) *trans*-cinnamaldehyde and (c) melamine when these two compounds are mixed, (b) pure *trans*-cinnamaldehyde, and (d) pure melamine in $CDCl_3$.

(Fig. S5(c)†). Small molecules with both hydrogen bond donation and accepting sites in adjacent position might bring the reactants together and promote the acetalization reaction (Fig. S5(a) and (b)†). The presence of hydrogen bonding was also observed in nuclear magnetic resonance (NMR) studies (Fig. 4 and S6†). The NMR spectrum of the mixture of *trans*-cinnamaldehyde and melamine in $CDCl_3$ showed a downfield shift in the doublet peak of aldehyde (–CHO) proton from 9.630–9.655 ppm to 9.703–9.723 ppm. At the same time, both a downfield shift and a broadening of melamine ($-NH_2$) protons from 1.566 ppm to 1.712 ppm in $CDCl_3$ were observed (Fig. 4). The downfield shift and broadening of proton peaks indicated the presence of hydrogen bonding interactions between the aldehyde substrate and melamine.

Generally, the reactions using small amine-based catalysts were sluggish (Table S1†). In contrast, mPMF provided superior activity (Tables 1 and 2). Structurally, the mPMF catalyst contained a high density of triazine rings and aminal groups. It could provide two types of hydrogen bonding models for both aldehyde and alcohol (Fig. 5 and 6). One involved a bridged hydrogen bonding between the oxygen atom of the aldehyde and the two –NH functional groups of the aminal group; the other involved hydrogen bonding between methanol and triazine. The electron-deficient aminal groups in mPMF might have partially protonated carbonyl compounds *via* hydrogen bonding.[18] The formation of hydrogen bonding activated the carbonyl substrate and stabilized the negative charge of the carbonyl oxygen in the transition state during acetalization. At the same time, alcohols were also stabilized and activated by triazine groups *via* hydrogen bonding interactions. Such a synergistic hydrogen bonding effect could be the reason for the superior activity of mPMF in the acetalization reaction. Density functional theory (DFT) modeling at B3LYP/6-31G(d,p) level also indicated favorable hydrogen bonding between *trans*-cinnamaldehyde with melamine (Fig. 5(a)) and mPMF (Fig. 5(b)). Interestingly, the hydrogen bonding energy in the mPMF system (38.19 kcal mol$^{-1}$) was much higher than that in the melamine system (7.76 kcal mol$^{-1}$). This might also explain the superior activity of mPMF as compared with melamine. Fig. 6 illustrates the proposed mechanism for aldehyde activation over the mPMF catalyst. mPMF consisted of a high density of aminal ($-NH-CH_2-NH-$) groups and triazine rings, which presented dual functionalities of Brønsted acidity and Lewis basicity. This unique characteristic of mPMF enabled multiple types of hydrogen bonding interactions. The synergistic effect of these hydrogen bonding interactions promoted the acetalization reaction in a highly efficient manner.

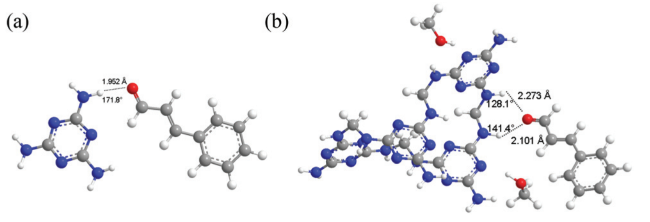


**Fig. 5** DFT modeling for *trans*-cinnamaldehyde with (a) melamine (binding energy = 7.76 kcal mol$^{-1}$) and (b) mPMF (binding energy = 38.19 kcal mol$^{-1}$).

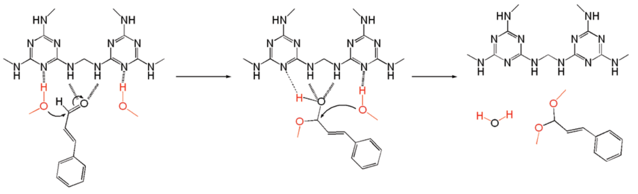


**Fig. 6** Proposed mechanism for aldehyde activation over the mPMF catalyst *via* synergistic double hydrogen bonding.

## Conclusions

mPMF-catalyzed acetalization of aldehydes is a green and chemoselective protocol. The reaction was highly efficient, compatible with acid-sensitive substrates, and did not require any dehydrating agents. A variety of substrates including aliphatic and aromatic aldehydes were reacted with good-to-excellent yields. A synergistic hydrogen bonding activation mechanism for the acetalization reaction was proposed. The high density of aminal ($-NH-CH_2-NH-$) groups and triazine rings in the mPMF network and the inherently powerful multiple hydrogen bonding system were responsible for the high activity of this novel POP, as compared to its melamine monomer. In addition, mPMF was attractive for its low cost, ease of synthesis and excellent reusability. This material demonstrated great potential for the application of functionally tailored POPs as highly efficient heterogeneous catalysts.

## Experimental

### General information

GC-mass spectrometry (GC-MS) was performed with Shimadzu GC-2010 coupled with GCMS-QP2010. $^1$H and $^{13}$C NMR spectra were obtained using a Brucker AV-400 (400 MHz) spectrometer. Nitrogen sorption analysis was conducted on a Micromeritics Tristar 3000 at 77 K. Elemental analysis (C, H, N, S) was performed on Elementar Vario Micro Cube.

### Synthesis and characterization of mPMF

Melamine (0.378 g, 3 mmol) and paraformaldehyde (1.8 eq, 0.162 g, 5.4 mmol) were mixed with 3.36 ml (overall concentration of 2.5 M) of dimethyl sulfoxide (DMSO) in a 15 ml Teflon container secured in a steel reactor. The reaction mixture was heated to 120 °C in an oven for 1 h. The reactor was then carefully removed from the oven for stirring on a magnetic stirrer plate to obtain a homogeneous solution. It was then heated in the oven to 170 °C for 72 h. The reaction was allowed to cool to room temperature, and the obtained solid was crushed, filtered, and washed with DMSO, acetone, tetrahydrofuran (THF) and $CH_2Cl_2$. The resulting white solid was dried under vacuum at 80 °C for 24 h. Elemental analysis: C 33.90%, H 4.83%, N 39.61%, S 5.05%. The resulting white polymer has a BET surface area of 930 $m^2\ g^{-1}$, an average BJH pore width of 15.7 nm, a total pore volume of 1.90 $cm^3\ g^{-1}$, and a micropore volume of 0.21 $cm^3\ g^{-1}$, as analyzed by $N_2$ sorption at 77 K.

### General acetalization procedure

The glassware used was dried in the oven at 100 °C. 2 mg of the mPMF catalyst was used with 1 mmol of carbonyl substrate and 1 ml of a solvent (methanol (anhydrous, 99.8%) or PDO (98%)). The reaction mixture was stirred at room temperature or heated to reaction temperature, and monitored by GC-MS. The product was extracted using $CH_2Cl_2$, washed with $H_2O$ and brine, and dried over $Na_2SO_4$. The organic layer was concentrated *in vacuo*, and column purification on silica gel was performed using hexane–ethyl acetate in 1% triethyl amine to obtain the product and its isolated yield. The purified product was characterized by $^1H$ and $^{13}C$ NMR spectroscopy, and GC-MS.

### Recycling of the mPMF catalyst

2.5 mmol of *trans*-cinnamaldehyde was reacted with 2.5 ml of PDO with 5 mg of the mPMF catalyst at room temperature. After reaction, the reaction mixture was filtered. The filtrate was collected, extracted with $CH_2Cl_2$, washed with $H_2O$ and brine, and dried over $Na_2SO_4$. The organic layer was concentrated *in vacuo*, and NMR was conducted with mesitylene as the internal standard. The recovered solid catalyst was directly used for subsequent runs.

### Calculation method

The DFT calculations were performed with Gaussian 03 software.[24] The exchange-correlation functional theory that we employed is dubbed Becke, three-parameter, Lee–Yang–Parr (B3LYP),[25] which includes a fraction of Hartree–Fock exchange to reduce the self-interaction error. In this study, the 6-31(G)(d,p) basis sets were used. After the structure of each compound was fully optimized, its total energy was obtained.

## Acknowledgements

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