

Dual functionalization of porous aromatic frameworks as a new platform for heterogeneous cascade catalysis†

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Dual functionalization of porous aromatic frameworks (PAFs) has been illustrated in the context of incorporating two antagonistic sites of strong acid and strong base into the highly porous and highly robust PAF-1 via stepwise post-synthetic modification. The resulting bifunctionalized PAF-1 exhibits excellent performances in catalyzing a series of cascade reactions and demonstrates superior chemical stability compared to the counterparts of mesoporous silica and MOFs, thereby opening the door for dual functionalization of PAFs as a new platform for heterogeneous cascade catalysis.

The capability of enzymes to immobilize different catalytically active sites or mutually incompatible catalytic groups on a single molecule in a site-isolation manner maintaining their independent function yet acting cooperatively to catalyze one step in a multistep reaction sequence¹ has spurred intense interest in developing catalysts containing multiple types of active centers for cascade reactions.² The driving force for the keen pursuit of cascade catalysts lies in that cascade reactions can allow a consecutive series of reactions to proceed in a concurrent fashion without isolation of intermediates and self-quenching of catalysts, thus offering enormous economical advantages.³ Given the important role in chemical industries, great attention has been paid to the development of bi/multi-functional solid catalysts for heterogeneous cascade catalysis, which however is challenged by the controlled spatial arrangement of a high-density yet continuous range of different active sites.⁴ Extensive efforts have been devoted to grafting bi/multi-functional groups onto the surfaces of mesoporous silica materials.⁵ However, the limited amount of silanol groups on the surface inevitably dilutes the density of active sites for mesoporous silica-based bi/multi-functional catalysts,^{5/6} and the instability of mesoporous silica in basic solutions also represents a potential limitation for their application in a wide range of catalytic systems.⁷

Albeit bi/multi-functionalization has been demonstrated in metal-organic frameworks (MOFs)⁸ with some investigated for cascade catalysis,⁹ the issue of water/chemical stability¹⁰ remains to be addressed for the majority of MOFs before MOF-based bi/multi-functional catalysts could meet the stringent industrial requirements. A bifunctional porous polymer incorporated with strong acidic sites and weak basic sites was reported recently,¹¹ but the weak basicity together with low surface area thereby exterior surface catalysis limits its performance in tandem reactions, particularly those that require the co-existence of both a strong acidic site and a strong basic site.

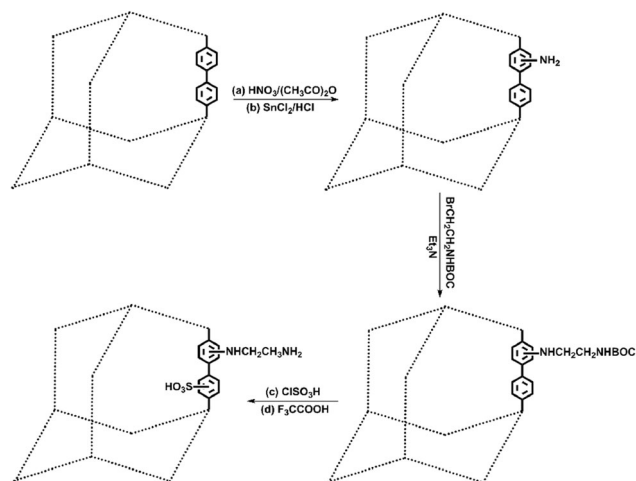
Therefore, there is still a need to search for new types of platforms for heterogeneous cascade catalysis. Several attributes have been delineated for an ideal platform to afford bi/multifunctional solid catalysts: (i) a high surface area with a high-density and continuous range of spatially arranged different active sites to afford high catalytic efficiency, (ii) a robust framework structure with high water/chemical stability to sustain framework integrity under typical reaction conditions, (iii) ease of functionalization to facilitate the tailoring of active sites.

It has been well documented that the phenyl ring can be functionalized with different groups through various established organic reactions.¹² Porous aromatic frameworks (PAFs),¹³ a subclass of porous organic polymers¹⁴ that are constructed from phenyl ring-derived building blocks, feature high surface area and robust structure with high water/chemical stability. These features make them a promising platform to afford bifunctionality for heterogeneous cascade catalysis.

We selected PAF-1,¹⁵ which possesses a hypothetical diamondoid-topology structure with very high surface area and exceptional stability in water and acidic-basic media, for “proof-of-concept” studies. To achieve dual functionality in PAF-1, two different types of functional groups can be readily grafted to the phenyl rings *via* stepwise post-synthetic modification¹⁶ using selected organic reactions (Scheme S1, ESI†). In this contribution, we demonstrate how two antagonistic sites of strong acid and strong base can be incorporated into PAF-1 to afford a highly effective and highly stable bifunctional solid catalyst for acid-base catalyzed tandem reaction, thereby paving a way

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Scheme 1 Illustration of stepwise post-synthetic modification of PAF-1 to graft the two antagonistic functional groups of a strong acid and a strong base to afford PAF-1-NHCH₂CH₂NH₂-SO₃H.

for dual functionalization of PAFs as a new platform for heterogeneous cascade catalysis.

In order to graft the two antagonistic functional groups of strong acid and strong base onto PAF-1 (Scheme 1), the freshly prepared PAF-1 was first nitrated and then reduced to PAF-1-NH₂, which was further modified by *N*-BOC-bromoethylamine to afford PAF-1-NHCH₂CH₂NHBOC. Sulfonation of PAF-1-NHCH₂CH₂NHBOC followed by deprotection gave rise to the desired bifunctional catalyst PAF-1-NHCH₂CH₂NH₂-SO₃H in which the aliphatic amine group can serve as the strong basic catalytic site and the sulfonic group can act as the strong acidic catalytic site.

Elemental analysis suggested that PAF-1-NHCH₂CH₂NH₂-SO₃H contains ~1.66 mmol g⁻¹ of aliphatic amine groups and 0.79 mmol g⁻¹ of -SO₃H groups. The FT-IR spectra (Fig. 1) of PAF-1-NO₂ show two asymmetric and symmetric stretching vibrations of the nitro group at 1528 cm⁻¹ and 1344 cm⁻¹,¹⁷ indicating the successful modification of nitro groups onto the framework of PAF-1. The disappearance of the nitro group bands in PAF-1-NH₂

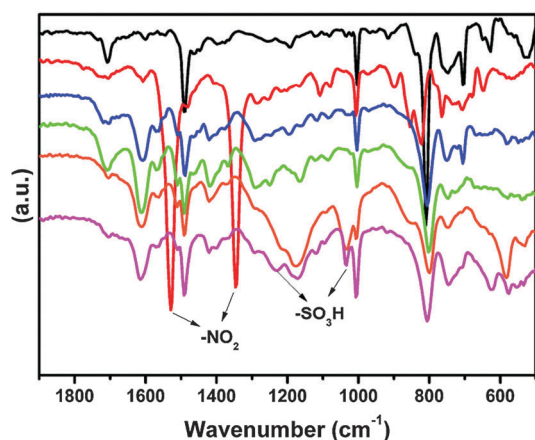


Fig. 1 FT-IR spectra of PAF-1 (black), PAF-1-NO₂ (red), PAF-1-NH₂ (blue), PAF-1-NHCH₂CH₂NHBOC (green), PAF-1-NHCH₂CH₂NHBOC-SO₃H (orange), and PAF-1-NHCH₂CH₂NH₂-SO₃H (magenta).

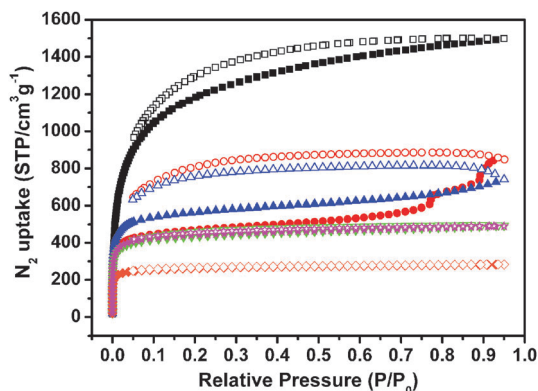


Fig. 2 The N₂ adsorption isotherms (solid symbols: adsorption; open symbols: desorption) at 77 K for: PAF-1 (black); PAF-1-NO₂ (red), PAF-1-NH₂ (blue), PAF-1-NHCH₂CH₂NHBOC (green), PAF-1-NHCH₂CH₂NHBOC-SO₃H (orange), and PAF-1-NHCH₂CH₂NH₂-SO₃H (magenta).

can be attributed to the reduction of the nitro group to the amino group. The existence of sulfonic groups in PAF-1-NHCH₂CH₂NHBOC-SO₃H and PAF-1-NHCH₂CH₂NH₂-SO₃H is confirmed by the appearance of absorption peaks at 1229 cm⁻¹ and 1033 cm⁻¹, the characteristic bands of SO₃H.¹⁸

N₂ sorption measurements at 77 K reveal the preservation of permanent porosity during the stepwise dual functionalization process of PAF-1 even under harsh conditions (Fig. 2). Nitration of PAF-1 leads to a significant decrease in the Brunauer-Emmett-Teller (BET) surface area from 4162 m² g⁻¹ for PAF-1 to 1764 m² g⁻¹ for PAF-1-NO₂, whereas the reduction of the NO₂ group to the NH₂ group results in an increase of the BET surface area to 2129 m² g⁻¹ for PAF-1-NH₂. Steady reduction of the BET surface area was observed during the process of modifying PAF-1-NH₂ with *N*-BOC-bromoethylamine followed by sulfonation, as indicated by the values of 1637 m² g⁻¹ and 1003 m² g⁻¹ for PAF-1-NHCH₂CH₂NHBOC and PAF-1-NHCH₂CH₂NHBOC-SO₃H respectively. Deprotection of PAF-1-NHCH₂CH₂NHBOC-SO₃H affords a BET surface area of 1672 m² g⁻¹ for the bifunctional PAF-1-NHCH₂CH₂NH₂-SO₃H, which however is much higher than the BET surface areas of similar bifunctional mesoporous silica⁵ and porous polymers¹¹ reported previously.

Given the high surface area together with the high density of strong basic and strong acidic sites, we evaluated the performances of PAF-1-NHCH₂CH₂NH₂-SO₃H as a bifunctional solid catalyst in the context of acid-base catalyzed tandem reaction involving the deacetalization and subsequent Henry reaction (Table 1). Remarkably, PAF-1-NHCH₂CH₂NH₂-SO₃H can effectively catalyze benzaldehyde dimethyl acetal (1) into 2-nitrovinyl benzene (3) in almost quantitative yield in 24 h (Table 1, entry 1). In contrast, the employment of the monofunctional PAF-1-SO₃H with strong acidity as a catalyst afforded only the product of benzaldehyde (2) (Table 1, entry 2) and a negligible amount of 3 was obtained when the reaction was catalyzed by the monofunctional PAF-1-CH₂NH₂ with strong basicity (Table 1, entry 3). In addition, a negligible amount of 3 was also observed when the bifunctional PAF-1-NH₂-SO₃H with a weak basic site was used (Table 1, entry 4). These results therefore suggest the requirement of co-existence of a strong

Table 1 One pot deacetalization–Henry reaction^a

Entry	Catalyst	Conv. of 1 [%]	Yield of 2 [%]	Yield of 3 [%]
1	PAF-1-NHCH ₂ CH ₂ NH ₂ -SO ₃ H	100	2	97.2
2	PAF-1-SO ₃ H	100	100	0
3	PAF-1-CH ₂ NH ₂	Trace	Trace	Trace
4	PAF-1-NH ₂ -SO ₃ H	100	100	Trace
5	Ethylamine + <i>p</i> -toluene sulfonic acid	Trace	Trace	Trace
6	PAF-1-NHCH ₂ CH ₂ NH ₂ -SO ₃ H + ethylamine	Trace	Trace	Trace
7	PAF-1-NHCH ₂ CH ₂ NH ₂ -SO ₃ H + <i>p</i> -toluene sulfonic acid	100	100	Trace
8 ^b	PAF-1-NHCH ₂ CH ₂ NH ₂ -SO ₃ H	100	5	94.7

^a Reaction conditions: benzaldehyde dimethyl acetal (1.0 mmol), CH₃NO₂ (5.0 mL), 90 °C, 24 h. ^b Treatment with NaOH (2 M) and HCl (2 M).

acidic site and a strong basic site as in the bifunctional PAF-1-NHCH₂CH₂NH₂-SO₃H for effectively catalyzing the one-pot deacetalization–Henry reaction; and also indicate the tailorability of active sites in bifunctionalized PAF-1. Mixing equal amounts of free acid of *p*-toluene sulfonic acid with free base of ethylamine cannot drive the deacetalization–Henry reaction due to the rapid neutralization in the homogeneous system (Table 1, entry 5). Moreover, only a trace amount of 3 could be detected when a stoichiometric amount of ethylamine or *p*-toluene sulfonic acid was added to PAF-1-NHCH₂CH₂NH₂-SO₃H due to the formation of ion pairs thereby quenching the active acid or basic sites (Table 1, entries 6 and 7). These results highlight PAF-1 as an excellent solid support capable of fixing and spatially separating the two antagonistic sites of strong acid and strong base. The applicability of PAF-1-NHCH₂CH₂NH₂-SO₃H as a bifunctional catalyst to other types of cascade reactions has been illustrated in the tandem deacetalization–Knoevenagel reaction, which PAF-1-NHCH₂CH₂NH₂-SO₃H can catalyze with high efficiency (Scheme S2, Fig. S2, ESI†). It is noteworthy that the initial catalytic activity of PAF-1-NHCH₂CH₂NH₂-SO₃H was higher (~2 times) than physical mixtures of PAF-1-SO₃H and PAF-1-CH₂NH₂ (Fig. S2, ESI†). We attribute this enhancement of activity to the lack of proximity of catalytic sites in a physical mixture.

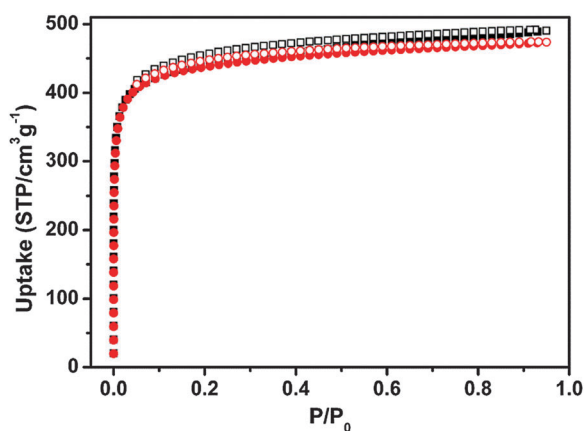


Fig. 3 N₂ sorption isotherms of PAF-1-NHCH₂CH₂NH₂-SO₃H (black) and PAF-1-NHCH₂CH₂NH₂-SO₃H after treatment with 2 M NaOH and then with 2 M HCl (red).

The accelerated reaction rate that results from a shortened mass transfer path underscores PAF-1 as a platform for imparting a continuous range of spatially arranged antagonistic active sites.

We tested the stability of PAF-1-NHCH₂CH₂NH₂-SO₃H under harsh chemical conditions (*i.e.* very high pH and very low pH media), which represents an issue for mesoporous silica and MOF-based bifunctional catalysts. Immersing PAF-1-NHCH₂CH₂NH₂-SO₃H into aqueous solutions of 2 M NaOH and 2 M HCl sequentially led to neither a substantial loss of catalytic activity (Table 1, entry 8) nor a significant decrease in surface area (Fig. 3), in striking contrast to MOF MIL-101-Cr¹⁹ and the mesoporous silica MCM-41,²⁰ both of which have been widely employed for dual functionalization but would be decomposed under similar treatments. These observations thus highlight PAF as a robust and chemically stable platform superior to mesoporous silica and MOF-based platforms for applications in heterogeneous cascade catalysis in a broad range of reaction media.

To examine the potential of microporous dual functionalized PAF-1 for size/shape catalysis, PAF-1-NHCH₂CH₂NH₂-SO₃H was assessed in the context of catalyzing the Knoevenagel reaction using two substrates with different sizes/shapes (Scheme S3, ESI†). It was observed that PAF-1-NHCH₂CH₂NH₂-SO₃H can efficiently catalyze the small sized substrate of benzaldehyde with 99% yield; in contrast, only 8% yield was obtained for the large sized/shaped substrate of benzophenone under the same reaction conditions.

PAF-1-NHCH₂CH₂NH₂-SO₃H can be readily recycled after three runs without observable loss of catalytic activity (Fig. S3, ESI†), which could be attributed to the covalent anchoring of catalytically active sites as well as framework robustness. In addition, after removal of PAF-1-NHCH₂CH₂NH₂-SO₃H from the solutions, the reaction would stop immediately, indicating no leaching of catalytically active species. These results therefore confirm the heterogeneous nature of PAF-1-NHCH₂CH₂NH₂-SO₃H as a bifunctional catalyst for cascade reactions.

In summary, we have illustrated the incorporation of two antagonistic sites of strong acid and strong base into the high surface area and highly robust porous aromatic framework, PAF-1. The resulting bifunctional PAF-1-NHCH₂CH₂NH₂-SO₃H not only exhibits excellent performance in catalyzing a series of cascade reactions, but also demonstrates superior chemical stability compared to mesoporous silica and MOFs. Our studies therefore lay a solid foundation for dual functionalization of

PAFs as a new platform for heterogeneous cascade catalysis. Ongoing work in our laboratory includes introducing other types of functional groups into PAF-1 and bifunctionalizing other PAFs for cascade catalysis.

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