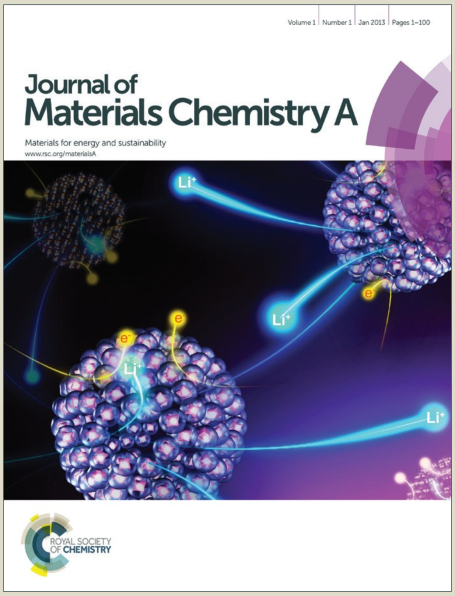
Journal of Materials Chemistry A

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/materialsA

Journal of Materials Chemistry A

COMMUNICATION

Pore Surface Engineering in Porous, Chemically Stable Covalent Organic Frameworks for Water Adsorption

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Bishnu P. Biswal,[a,b] Sharath Kandambeth,[a,b] Suman Chandra,[a,b] Digambar Balaji Shinde,[b] Saibal Bera,[a,b] Suvendu Karak,[a,b] Bikash Garai,[a,b] Ulhas K. Kharul[c] and Rahul Banerjee*[a,b]

Herein, we have explored the possibility of a class of covalent organic frameworks (COFs) as water adsorbing material. We have selected, synthesized 12 chemically stable functionalized Schiff base COFs and thoroughly studied their water uptake behaviour. Further, a deep understanding was developed with these COFs towards effects of condensation pressure of water, hydrophilic/hydrophobic groups present in the COF pores on water absorption capacity and ultimately, their recyclability. Among all reported COFs, TpPa-1 shows a highest water uptake of 30 wt % (368 cm^{3}g^{-1}; 17 mmolg^{-1}) at $P/P_0 = 0.3$, which is also comparable with the recently reported carbon materials and few well known MOFs. This study also reveals that the overall water uptake of COFs can be tuned systematically based on chemical functionality and pore size in a wider window of relative pressures.

Water adsorption in porous materials is an important field of research because of their usage in electric dehumidifiers, adsorption-driven heat exchangers and adsorption based heat pumps.[1-5] The energy efficiency and working humidity range of these processes depend on the water adsorption properties of the adsorbent. It has been well documented that, for real life applications, water capture by porous materials at low relative pressures is essential ($P/P_0 < 0.1$).[6-8] Hence, the search for a new, efficient water adsorbing materials is highly important. Among the existing solid materials, silica gel and zeolites have good affinity towards water at lower relative pressures ($P/P_0 < 0.1$) and thus commonly used as the water adsorbing material.[9,10] However, the strong interaction of water molecules with the zeolite framework implicates a requirement of high temperature to desorb water molecules and to regenerate the adsorbent for further use. More recently, metal-organic frameworks (MOFs) have emerged as promising candidates for effective water adsorption.[11-16] However, among the quantity and diversity of MOFs, except few, water sensitivity of many MOFs has been well documented in the literature and stability in actual operational environments is largely considered to be a major challenge particularly for the water capture application perspective. Notably, MOFs containing carboxylate–metal bonds have varying degrees of water stability and usually unstable in the presence of water vapor.[17-20] Hence, an alternative porous material with engineered pore walls, balance of hydrophilic and hydrophobic groups, tuneable pore size and volume is highly essential. Such materials are expected to display not only hydrolytic stability but also the durability with high water adsorption capacity.

Covalent Organic Frameworks (COFs)[21-25] are MOF alike porous, crystalline materials but covalently linked via lighter elements (H, B, C, Si, N, O). These materials have attracted immense interest with excellent properties like gas adsorption, catalysis, sensing and electronics owing to their highly ordered and low density framework (don't contain metals unlike MOFs), with an opportunity to incorporate various functional groups. However, the water instability was considered to be a serious drawback for COFs and hence, they were not explored for water adsorption studies except one very recent report.[26-27] Moreover, we had developed combined reversible and irreversible Schiff base reactions to synthesize chemically stable COFs[29-35] and reported their water adsorption data.[35] However, the rationale behind the factors affecting water adsorption, has not been properly understood yet. Hence, we decided to explore the water uptake behaviour of a series of chemically stable COFs with engineered pore walls for the development of new desiccant materials. Moreover, a detailed study was made on the structural stability, optimum uptake capacity, recyclability and change in porosity after water adsorption. More importantly, role of functionality, surface area, hydrophilicity-hydrophobicity and the intermolecular interaction between adsorbed water molecules with the COF pore walls is analysed and discussed. These COFs do posses the crystallinity and porosity like MOFs and chemical stability similar to carbons, which could be an ideal platform for water

---

[a] *Academy of Scientific and Innovative Research (AcSIR), New Delhi, India.*
[b] *Physical/Materials Chemistry Division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pune-411008, India.*
[c] *Polymer Science and Engineering Division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pune-411008, India.*

†Electronic Supplementary Information (ESI) available: [General Remarks, PXRD, N_2 and Water Adsorption, FT-IR, TGA, SEM and TEM. See DOI: 10.1039/x0xx00000x

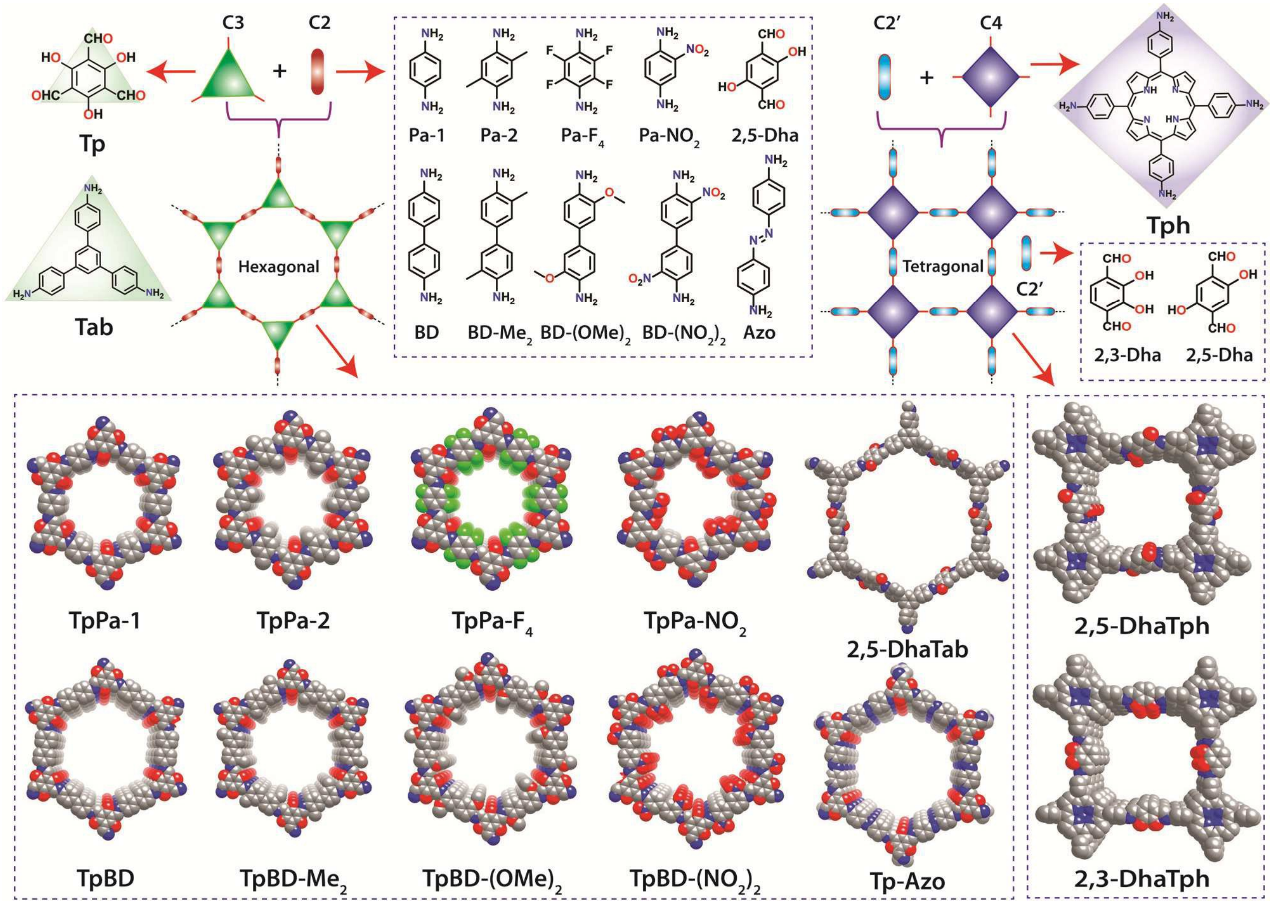


Figure 1. A library of functionalized chemically stable Schiff base COFs (Hexagonal-Series and Tetragonal-Series) synthesized using (C2, C3 and C4) aromatic amines and (C2, C3) aldehydes.

adsorption.

A veriety of chemically stable COFs with diverse range of functional groups decorated inside the pores were chosen for the water adsorption study (Figure 1). This include salient COFs, like TpPa-1 and TpBD, without any functional groups, as well as functionalised COFs, like TpPa-2 and TpBD-Me$_2$ containing hydrophobic –CH$_3$ groups decorating each COF pore. Among the functionalised COFs, we also report, TpPa-NO$_2$, TpBD-(NO$_2$)$_2$ and TpPa-F$_4$ containing –NO$_2$ groups, and 12 –F groups dangling towards the COF pores and DhaTab, TpBD-(OMe)$_2$ containing 6 –OH and –OMe$_2$ groups respectively. Tp-Azo contains the polar dynamic –N═N– linkages within the hexagonal COF cavities. The COFs such as 2,5-DhaTph and 2,3-DhaTph consist of hydrophobic porphyrin cores with –OH functionality. We have classified all the above mentioned COFs into two categories based on their pore structures. The COFs formed by the combination of C3 and C2 symmetry linker pairs (aldehyde and amines) such as TpPa-1, TpPa-2, TpPa-NO$_2$, TpPa-F$_4$, Tp-Azo, TpBD, TpBD-(NO$_2$)$_2$, TpBD-Me$_2$, TpBD-(OMe)$_2$ and DhaTab belongs to hexagonal series (H-Series). Whereas those formed by the combination of C4 and C2 symmetry, 2,5-DhaTph and 2,3-DhaTph is included in the tetragonal series (T-Series). The COF pores of both the series have been intentionally engineered with diverse functionality to fine tune the overall porosity, hydrophobicity and hydrophilicity for the pressure dependent water uptake.

The synthesis of COFs reported in this paper were carried out using an already reported solvothermal protocol[29-35] by reacting a suitable aromatic [C3 or C2] di- or trialdehydes (0.3 mmol) and the corresponding aromatic [C2, C3 or C4] di, tri or tetra-amines (0.45 mmol) in the presence of selective organic solvents (in particular ratio) in a Pyrex tube at 120 ºC for 3 days. After Soxhlet purification, these COFs were dried at 120 ºC under vacuum for 12 h to give a colored powder in ~80% isolated yield (Section S2, ESI†). The synthesized COFs were at first examined *via* PXRD to ensure their purity. As revealed from PXRD, these COFs show good crystallinity similar to our previously reported ones.[29-35] The TpPa-series COFs show first and the most intense peak at a low angle ∼4.7° (2θ) corresponding to the (100) reflection planes, along with other minor peaks at ∼8.1°, 11.1°, and 27° (2θ) correspond to 200, 210 and 001 planes. Similarly, TpBD-series COFs and the Tp-Azo COF, the first and most intense peak become visible at ∼3.3° (2θ) (100 plane), with other minor peaks at ∼6.3° (200),

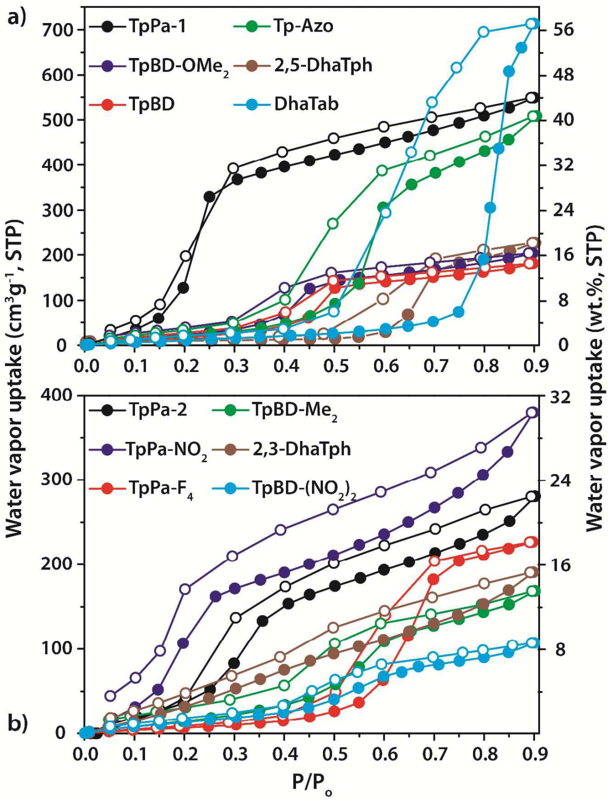


Figure 2. (a) and (b) Water adsorption isotherms (STP) of COFs of both Hexagonal-series and Tetragonal-series. The large portion of water uptake capacity indicates that the pore filling or condensation occurs at higher pressure range. Filled symbols corresponds to adsorption and un-filled are for desorption.

~11.7° (210), and ~25° (001) (2θ). The porphyrin-series COFs, on the other hand, show the intense peak at ~3.5° (100 plane) with minor peaks at ~6.7° and ~20–23° (2θ), which corresponds to the 200 and 001 planes. Further, the centre-to-centre pore distance ranges from ~1.5 to 3.7 nm and the π–π stacking distances between the layers were calculated as ~3.4–4.4 Å. The 2D COF models were built with the Self-Consistent Charge Density Functional Tight-Binding (SCC-DFTB) method.[36,37] The experimentally obtained PXRD patterns resemble well with the simulated one of the proposed eclipsed (AA) stacking model for all these COFs. We have also characterised all COFs presented here *via* FT-IR, TGA, N_2 adsorption, SEM and TEM to confirm the reproducibility, structural integrity and to identify their physical properties (ESI†).

Nitrogen adsorption isotherms were collected at 77K to check the architectural rigidity, pore size distribution and permanent porosity of these COFs (Section S9, ESI†). All the COFs displayed typical reversible isotherms. As these COFs have permanent porosity and a defined pore window decorated with a wide variety of functionality (hydrophobic and hydrophilic), we have decided to check their water uptake capacity at 298K. The COFs belong to H-series display S shaped type II isotherm profile with hysteresis in the water adsorption isotherms indicating that the COF pores are open and allow the inclusion of water molecules (Kinetic Diameter: 2.6 Å) (Figure 2). The water uptake is low at lower vapor pressure ($P/P_0 < 0.2$) for most of the COFs except TpPa-1, which could be due to the poor affinity of the water molecules to the COF pores and low surface area. However, for all the COFs reported here, at higher water vapor pressure, the water uptake increases due to the pore filling and the presence of hydrophilic N and O sites. Surprisingly, TpPa-1 shows maximum water uptake (368 cm^3g^{-1}; 17 $mmolg^{-1}$; 30 wt %) at 0.3 $P/P_{0,}$ which could be due to its good crystallinity and surface area (984 m^2g^{-1}).[35] This water uptake value for TpPa-1 is comparable with recently reported carbon material PCC-1[6] (~330 cm^3g^{-1}; 14 $mmolg^{-1}$ and 26.5 wt % at P/P_0 = 0.3) and MOF-801-P[12] (~380 cm^3g^{-1}; 17 $mmolg^{-1}$ and 30 wt % at P/P_0 = 0.3). Moreover, it also outperforms some of the well known MOFs and porous materials such as MOF-801-SC (270 cm^3g^{-1}), MOF-804 (235 cm^3g^{-1}), CAU-6[16] (335 cm^3g^{-1}), Basolite A300 (260 cm^3g^{-1}), in terms of water uptake at P/P_0 =0.3.[12] On the other hand, Tp-Azo and DhaTab[38], which has large pore diameter of 2.7 nm and 3.7 nm respectively, does not take up water till the pressure reaches to P/P_0 = 0.5 (Tp-Azo) and P/P_0 = 0.8 (DhaTab). Once the water uptake begins, it reaches a total water adsorption capacity value of 508 cm^3g^{-1} (41 wt %) for Tp-Azo and 713 cm^3g^{-1} (57 wt %) for DhaTab at P/P_0 = 0.9. Such high water uptake capacity at higher relative pressure designates a fare relationship between porosity of these COFs and pore condensation of water within the COF pore. The maximum uptake of both TpPa-2 and TpPa-NO_2 is 280 (22 wt %) and 380 cm^3g^{-1} (30 wt %), which is comparatively moderate and could be due to the presence of hydrophobic methyl and nitro groups.[39] As all these COFs possess one type of pores and hence they show only one step water adsorption isotherm by filling of the respective cavities present in the framework. Similarly, the COFs made up of benzidine or substituted linkers, the pore diameters are bigger as compare to those synthesized from *p*-phenylenediamine or substituted linkers. The maximum water uptake of TpBD, TpBD-Me_2, and TpBD-$(OMe)_2$ are 181 cm^3g^{-1} (15 wt %), 168 cm^3g^{-1} (14 wt %) and 204 cm^3g^{-1} (16 wt %), respectively at P/P_0 = 0.9. On the other hand, TpPa-F_4 and TpBD-$(NO_2)_2$ show low water uptake 226 cm^3g^{-1} (18 wt %) and 107 cm^3g^{-1} (9 wt %) even at higher water vapor pressure. This is due to the high hydrophobicity of fluorine and nitro groups present in the frameworks, which doesn’t allow the water molecules to enter inside the cavities easily. Further, the COFs that belongs to T-Series show a type V sigmoid isotherm profile (Figure 2). The COFs in this group show relatively very low uptake at P/P_0 = 0.3, compared to the H-Series COFs. 2,5-DhaTph has a maximum uptake of 213 cm^3g^{-1} (17 wt %) at P/P_0 = 0.9, while 2,3-DhaTph have a maximum uptake of 190 cm^3g^{-1} (15 wt %). In belief, the hydroxyl (–OH) functional groups as present in 2,5-DhaTph and2,3-DhaTph pores should enhance the overall affinity of the framework for water molecules, and should result higher water uptake capacity at lower range of pressures. However, it has been found that in porphyrin based COFs (T-Series COFs) due to the presence of highly hydrophobic porphyrin core in the framework results in to very low overall water uptake and

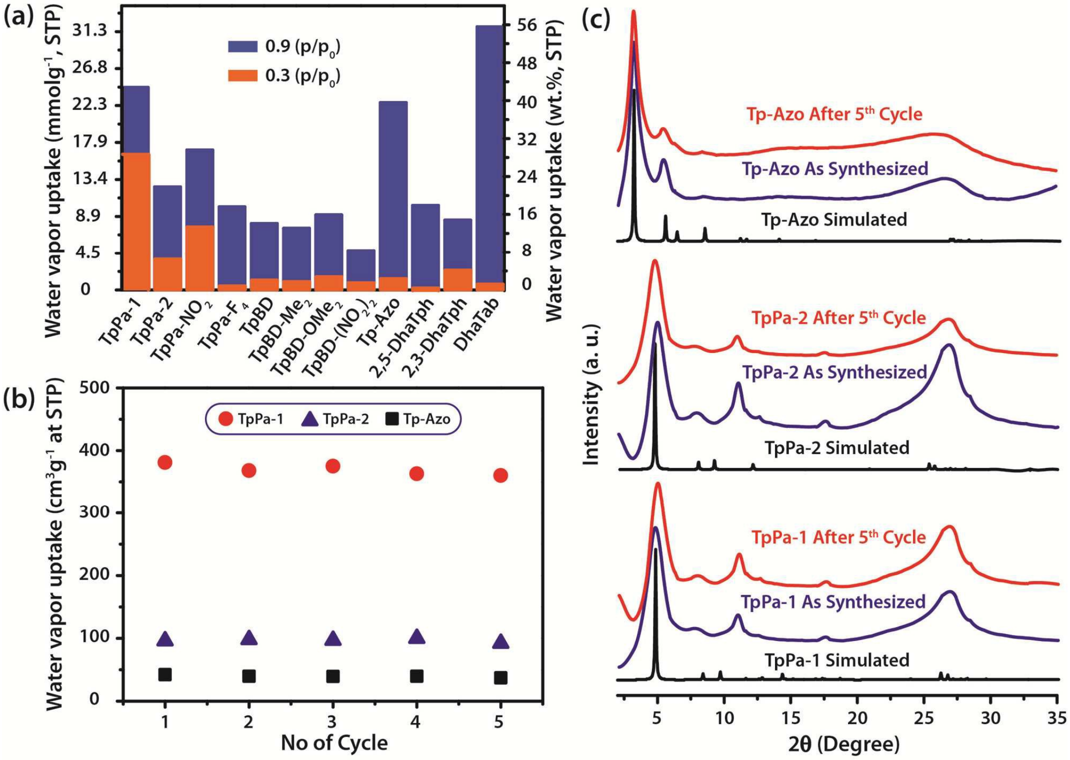


Figure 3. (a) Water uptake capacity of COFs in different pressure ranges; (b) 5 cycles of water vapor adsorption at 25 ºC, showing the uptake at $P/P_0 = 0.3$; (c) PXRD patterns of as-synthesized COFs (TpPa-1, TpPa-2 and Tp-Azo) before and after the water adsorption study (consecutive 5 cycles), showing excellent hydrolytic stability.

the isotherms shift more towards higher P/P_0 range (0.2 to 0.8) compared to the H-Series COFs (Figure 2a). The real life applicability of these COF materials could be better evaluated by the ease of restoration and the hydrolytic stability. To evaluate these two important factors, we have freshly collected the water adsorption isotherms for the best perfuming COFs *viz*. TpPa-1, TpPa-2 and Tp-Azo up to five consecutive cycles. These COF materials show excellent recyclability as well as repeatability; as concluded by their almost identical water adsorption isotherms for all five cycles (Figure 3b and Figure S6, ESI†). Further, to examine the hydrolytic stability of COF samples which were exposed to humid conditions (after multiple water adsorption cycles), we have collected PXRD data and compared with the as-synthesized profiles (Figure 3c). Notably, it has been already shown in our previous reports that the keto-enamine based COFs are highly stable in boiling water (under hydrothermal condition), acidic and basic medium for more than 7 days period.[29-35] The local structural retention was also confirmed *via* FT-IR, which display the identical spectra for all three COFs (TpPa-1, TpPa-2 and Tp-Azo) even after multiple water adsorption cycles. Further support of the framework stability analysis is confirmed by BET surface area analysis of the initial and reactivated samples (Table 1). It is to be noted that the slight loss of surface area in COF materials could be related to water molecules strongly interact with the COF framework. Since these COF materials are highly stable under humid environment (even in water, acid and base) and have potential interacting sites for water molecules, it is anticipated that their water adsorption capacity will not to be strongly affected by the restoration conditions. The above results endow with important insight into the water adsorption behaviour of such class of porous solids. We presume that the water molecules do interact with the hydrophilic cavities of COFs by means of weak hydrogen bonding.[40-44] The crystallinity, surface area, the geometry and pore surface functionality are other deciding factors for the overall water uptake capacity in COF based porous materials.

In summary, we have selected, synthesized, and characterized a series chemically stable COFs and evaluated the water adsorption ability of all these COFs with an intension of finding new sort of desiccant materials. Among them, TpPa-1 show excellent performance while considering all important criteria that required for effective water adsorption: TpPa-1 takes up 30 wt % (368 cm^3g^{-1}; 17 $mmolg^{-1}$) of water at $P/P_0 = 0.3$ and exhibit high water uptake of 549 cm^3g^{-1} ($P/P_0 < 0.9$) respectively with excellent recyclability. This value is comparable with the recently reported carbon material PCC-1(381.5 cm^3g^{-1}; 14 $mmolg^{-1}$ and 26.5 wt % at $P/P0 = 0.3$) and some well known MOFs. These uptakes are sharp and almost constant after consecutive five cycles where these COF materials are easily regenerated with expense of low energy and operational cost. Due to these potential characteristics, it has been found that TpPa-1 is a good candidate and has

Table 1. Summary of pore aperture, water uptake and BET surface areas of studied COFs.

COFs	Pore diameter (nm) (From AA models)	Water uptake (cm^3g^{-1}) at $P/P_0 = 0.9$	BET (m^2g^{-1}) (Before Water Adsorption)	BET (m^2g^{-1}) (After Water Adsorption)
TpPa-1	1.8	549	984	855
TpPa-2	1.5	280	460	452
TpPa-NO_2	1.6	380	457	415
TpPa-F_4	1.7	226	529	440
TpBD	2.4	181	341	265
TpBD-$(OMe)_2$	2.3	204	365	248
TpBD-$(NO_2)_2$	2.2	107	90	70
Tp-Azo	2.7	508	942	921
2,5-DhaTph	2.0	545	1112	1058
2,3-DhaTph	2.0	190	659	580

sufficient potential to be used in capture and release of water present in the atmosphere. These results signify that the structural features such as size of the COF pores, hydrophobic/hydrophilic groups' present, surface area, crystallinity and hydrogen-bond formation between neighbouring water molecules decides the optimum water uptake in this class of porous materials. Moreover, the hydrolytic stability and recyclability offered by these keto-enamine COFs are outstanding in comparison to all reported porous materials for water capture till date. Hence, we believe that the understanding generated out of this work would help to develop new desiccant materials with high water capture capacity at ambient conditions for wider range of applications in near future.

Acknowledgements

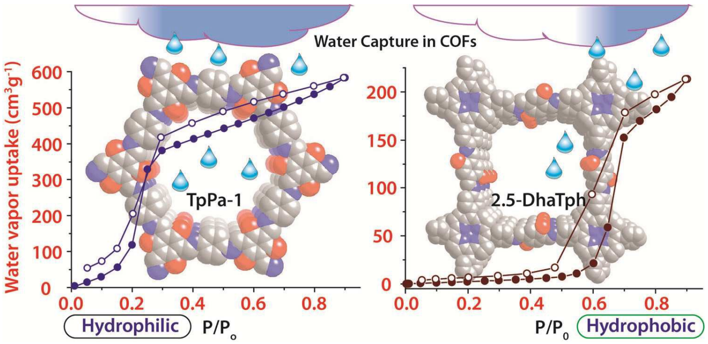
B. P. B, Sa. K, S. C, S. B, Su. K and B. G acknowledge UGC and CSIR, New Delhi, India, for fellowship. U. K and R. B acknowledge Five Year Plan Project (CSC0122 and CSC0102) and DST (India)-A*STAR (Singapore) (INT/SIN/P-05) for funding.

Notes and references

1 S. K. Henninger, H. A. Habib, C. Janiak, *J. Am. Chem. Soc.*, 2009, **131**, 2776.
2 E. Kang, G. S. Jeong, Y. Y. Choi, K. H. Lee, A. Khademhosseini, S. H. Lee, *Nat. Mater*. 2011, **10**, 877.
3 H. Yang, H. Zhu, M. M. R. M. Hendrix, N. J. H. G. M. Lousberg, G. de With, A. C. C. Esteves, J. H. Xin, *Adv. Mater*. 2013, **25**, 1150.
4 M. N. Golubovic, H. D. M. Hettiarachchi, W. M. Worek, Int. *J. Heat Mass Transfer* 2006, **49**, 2802;
5 D. Fröhlich, S. K. Henninger, C. Janiak, *Dalton Trans.*, 2014, **43**, 15300.
6 G.-P. Hao, G. Mondin, Z. Zheng, T. Biemelt, S. Klosz, R. Schubel, A. Eychmller, and S. Kaskel, *Angew. Chem. Int. Ed*. 2015, **54**, 1941.
7 S. Narayanan, X. Li, S. Yang, I. McKay, H. Kim, E. N. Wang, *Proceedings of the ASME 2013 Heat Transfer Summer Conference* 2013, HT2013.
8 M. Thommes, J. Morell, K. A. Cychosz, M. Fröba, *Langmuir* 2013, **29**, 14893.
9 S. K. Henninger, F. Jeremias, H. Kummer, C. Janiak, *Eur. J. Inorg. Chem*. 2012, 2625.
10 S. G. Wang, R. Z. Wang, X. R. Li, *Renewable Energy* 2005, **30**, 1425.
11 P. Kusgens, M. Rose, I. Senkovska, H. Frçde, A. Henschel, S. Siegle, S. Kaskel, *Microporous Mesoporous Mater*. 2009, **120**, 325.
12 H. Furukawa, F. Gandara, Y.-B. Zhang, J. Jiang, W. L. Queen, M. R. Hudson, O. M. Yaghi, *J. Am. Chem. Soc*. 2014, **136**, 4369.
13 P. M. Schoenecker, C. G. Carson, H. Jasuja, C. J. J. Flemming and K. S. Walton, *Ind. Eng. Chem. Res*. 2012, **51**, 6513.
14 A. Khutia, H. U. Rammelberg, T. Schmidt, S. Henninger and C. Janiak, *Chem. Mater*. 2013, **25**, 790.
15 J. Canivet, A. Fateeva, Y. Guo, B. Coasne and D. Farrusseng, *Chem. Soc. Rev.,* 2014, **43**, 5594.
16 H. Reinsch, B. Marszalek, J. Wack, J. Senker, B. Gil, N. Stock, *Chem. Commun*. 2012, **48**, 9486.
17 G. Akiyama, R. Matsuda, S. Kitagawa, *Chem. Lett*. 2010, **39**, 360.
18 Y. -K. Seo, J. W. Yoon, J. S. Lee,Y. K. Hwang, C.-H. Jun, J. -S. Chang, S. Wuttke, P. Bazin, A. Vimont, M. Daturi, S. Bourrelly, P. L. Llewellyn, P. Horcajada, C. Serre, G. Férey, *Adv. Mater*. 2012, **24**, 806.
19 N. C. Burtch, H. Jasuja, and K. S. Walton, *Chem. Rev*. 2014, **114**, 10575.
20 J. B. DeCoste, G. W. Peterson, B. J. Schindler, K. L. Killops, M. A. Broweb and J. J. Mahleb, *J. Mater. Chem. A*, 2013, **1**, 11922.
21 A. P. Côté, A. I. Benin, N. W. Ockwig, A. J. Matzger, M. O'Keeffe, O. M. Yaghi, *Science* 2005, **310**, 1166.
22 X. Feng, X. Dinga, D. Jiang, *Chem. Soc. Rev*. 2012, **41**, 6010.
23 J. F. Dienstmaier, D. D. Medina, M. Dogru, P. Knochel, T. Bein, W. M. Heckl, M. Lackinger, *ACS Nano* 2012, **6**, 7234.
24 P. Kuhn, M. Antonietti, A. Thomas, *Angew. Chem., Int. Ed*. 2008, **47**, 3450.
25 M. Dogru, M. Handloser, F. Auras, T. Kunz, D. Medina, A. Hartschuh, P. Knochel, T. Bein, *Angew. Chem., Int. Ed*. 2013, **52**, 2920.
26 L. M. Lanni, R. W. Tilford, M. Bharathy, J. J. Lavigne, *J. Am. Chem. Soc*. 2011, **130**, 11872.
27 E. Spitler, M. Giovino, S. White, W. Dichtel, *Chem. Sci*. 2011, **2**, 1588.
28 L. Stegbauer, M. W. Hahn, A. Jentys, G. Savasci, C. Ochsenfeld, J. A. Lercher and B. V. Lotsch, *Chem. Mater.*, 2015, DOI: 10.1021/acs.chemmater.5b02151.

29 S. Kandambeth, A. Mallick, B. Lukose, V. M. Mane, T. Heine, R. Banerjee, *J. Am. Chem. Soc*. 2012, **134**, 19524.
30 B. P. Biswal, S. Chandra, S. Kandambeth, B. Lukose, T. Heine, R. Banerjee, *J. Am. Chem. Soc*. 2013, **135**, 5328.
31 S. Chandra, S. Kandambeth, B. P. Biswal, B. Lukose, S. M. Kunjir, M. Chaudhary, R. Babarao, T. Heine, R. Banerjee, *J. Am. Chem. Soc*. 2013, **135**, 17853.
32 S. Kandambeth, D. B. Shinde, M. K. Panda, B. Lukose, T. Heine and R. Banerjee, *Angew. Chem. Int. Ed.,* 2013, **52***,* 13052.
33 D. B. Shinde, S. Kandambeth, P. Pachfule, R. R. Kumar and R. Banerjee, *Chem Commun.*, 2015, **51**, 310.
34 S. Kandambeth, V. Venkatesh, D. B. Shinde, S. Kumari, A. Halder, S. Verma, R. Banerjee, *Nature Commun.,* 2015, **6**, 6786.
35 The water adsosption isotherms has been reported as supporting information of ref. 28-33, but not analysed intermes of their chemical functionlity modification.
36 B. Lukose, A. Kuc, T. Heine, *Chem. —Eur. J*. 2011, **17**, 2388.
37 Heine, T.; Rapacioli, M.; Patchkovskii, S.; Frenzel, J.; Koester, A. M.; Calaminici, P.; Escalante, S.; Duarte, H. A.; Flores, R.; Geudtner, G.; Goursot, A.; Reveles, J. U.; Vela, A.; Salahub, D. R. *deMon-nano*; Jacobs University Bremen: Bremen, Germany, 2009.
38 Once again we have freshly prepared all these COFs (except DhaTab; for which we have used the old data for comparative study), characterized and studied the water adsorption behaviour with respect to functionality and surface area.
39 N. Sagawa and T. Shikata, *Phys. Chem. Chem. Phys.,* 2014, **16**, 13262.
40 G. R. Desiraju, T. Steiner, The Weak Hydrogen Bond in Structural Chemistry and Biology, Oxford University Press, Oxford, 1999.
41 R. Banerjee, P. M. Bhatt, M. T. Kirchner, G. R. Desiraju, *Angew. Chem., Int. Ed*., 2005, **44**, 2515.
42 A. Kovacs, A. Szabo, I. Hargittai, *Acc. Chem. Res*. 2002, **35**, 887.
43 G. R. Desiraju, *Chem. Commun*., 2005, 2995.
44 G. R. Desiraju, *Acc. Chem. Res*. 2002, **35**, 565.

TABLE OF CONTENT GRAPHIC



In this investigation, we have explored the possibility of a class of chemically stable covalent organic frameworks (COFs) as water adsorbing material. We have synthesized keto-enamine and imine based functionalized COFs through pore engineering and thoroughly studied the condensation pressure of water in the COF pores, optimum uptake capacity, and recyclability.