Journal of Materials Chemistry A

ROYAL SOCIETY OF CHEMISTRY

EDITORIAL

View Article Online
View Journal | View Issue

Cite this: J. Mater. Chem. A, 2024, 12, 8613

Introduction to functional framework materials

Paolo Falcaro, *[a] Patricia Horcajada [b] and Dan Li [c]

DOI: 10.1039/d4ta90056a

rsc.li/materials-a

[a]Institute of Physical and Theoretical Chemistry, Graz University of Technology, Graz, 8010, Austria. E-mail: paolo.falcaro@tugraz.at

[b]Advanced Porous Materials Unit, IMDEA Energy Institute, 28935 Móstoles-Madrid, Spain. E-mail: patricia.horcajada@imdea.org

[c]College of Chemistry and Materials Science, Jinan University, Guangzhou, China. E-mail: danli@jnu.edu.cn

Over the past decade, the exploration of functional framework materials – with notable examples that include metal–organic frameworks (MOFs), covalent–organic frameworks (COFs), hydrogen bonded-organic frameworks (HOFs) and porous organic polymers (POPs) – has generated new research areas in chemistry and materials science.[1–5] The driving force to explore these materials is based on their unprecedented structural tunability and physicochemical properties. These materials stand at the forefront of scientific research due to their promising functionalities in separation, catalysis, energy conversion/storage, sensing, and medicine, to name a few relevant applications.[3,6–15] We note that, over the last decade, these applications have attracted increasing scientific

Paolo Falcaro

Paolo Falcaro is a professor of Bio-based Materials Technology at the Institute of Physical and Theoretical Chemistry at Graz University of Technology (TU Graz, Austria). He holds a PhD in materials engineering from the University of Padova and Bologna (supervisor, Prof. P. Innocenzi). His early career included research and managerial roles at industrial-oriented research facilities (Civen and NanoFab, Italy) and a team leader role at CSIRO (Australia, Supervisor A. Hill, Mentor R. Hannink). At TU Graz, he was awarded an ERC Consolidator Grant for developing porous material-based films and patterns with anisotropic properties. A salient part of his research is focused on metal–organic frameworks (MOFs) for biotechnology. He is currently co-leading a Lead Project initiative at TU Graz named Porous Materials@Work for Sustainability (PMWS – LP-03) to enhance the scope of porous materials for sustainable aspects. He aims to progress the practical applications of emerging porous materials including functional framework materials.

Patricia Horcajada

With an unconventional multidisciplinary background (Pharmacy BC and Material Science PhD), Patricia Horcajada joined the Institut Lavoisier (France) as CNRS researcher in 2007. Since 2016, she has been a senior researcher and Head of the Advanced Porous Materials Unit at IMDEA Energy (Spain). Her research activity is focused to the development of new multifunctional materials (e.g. metal organic frameworks, perovskites, composites) and their application in strategic fields, including energy (H_2 production, fuels from wastes), environment (CO_2 conversion, water purification, agrochemicals) and health (drug delivery, detoxification). She was ranked in the top 2% worldwide researchers (2020–2022, Stanford University) and has been awarded with several prizes (e.g. "Doctora de Alcala" 2023, Silver Medal IAAM 2023, "Young Female Talent" Spanish Royal Society of Sciences 2022, "Young Researcher Leading Groups" Spanish Royal Society of Chemistry 2020, "Leonardo award" 2017, "Miguel Catalan" 2016).

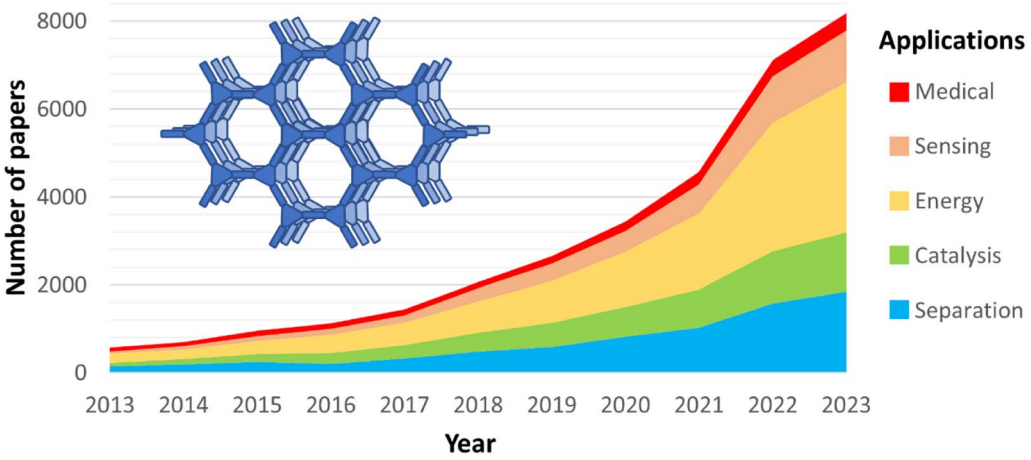

Fig. 1 Stack area chart showing the number of papers published over the last 10 years on selected framework materials for specific applications. Scopus was used with (MOFs OR COFs OR HOFs OR POPs) AND the listed application on March 7th 2024.

interest as shown by the stack area chart in Fig. 1.

With their typically ordered framework, high surface area, and tunable pore size, framework materials exhibit a uniquely high propensity to structural and functional customization, making them versatile platforms for tackling some of the most pressing global challenges for sustainability (see United Nations' 17 Sustainability Goals).[16]

The current themed collection, "Functional Framework Materials," presents a meticulously curated set of over 70 papers (including 5 review articles and 2 communications), each contributing to the progress of this dynamic field.

The theme focuses on the design of new framework materials spanning from their synthesis, *via* traditional solvothermal and unconventional methods, to device fabrication and applications. We note that the use of unconventional synthetic approaches (*e.g.* vapor deposition, mechanochemistry) and the development of protocols for device fabrication, will progress the practical application of framework materials.[17–20] Equally important in this collection, is the use of advanced computational and characterization methods that underscore the need for new tools for a deeper understanding of the material properties.[21,22] This collection places a significant focus on MOFs, which are discussed in 44% of the papers. This emphasis reflects the established attention to their specific combination of organic and inorganic building blocks, yielding unique functional properties. COFs and porous polymers/cages, known for their robustness and designable structures, are the subject of 18% of the contributions, further illustrating the scientific community's effort to explore and expand the boundaries of organized organic structures. In addition to MOFs, COFs, and POPs, the collection encompasses a diverse array of materials including HOFs, carbon-based structures, zeolites, and more, expanding the scope to other extended materials.

The collection reveals the promising role of functional frameworks in energy: 37% of the papers are related to renewable energy production and storage. Catalysis and separation account for 22% and 20% of the contributions, respectively, highlighting the materials' efficiency in facilitating chemical transformations and purifying essential resources. Additionally, the collection includes valuable insights into sensing (6.6%), environmental remediation (3.3%), and biomolecule protection (3.3%), showcasing the broad applicability of these materials in detecting environmental pollutants, mitigating ecological impacts, and protecting valuable biomacromolecules.

This diversity of preparation methods, materials, and applications underscores the interdisciplinary nature of this research field that combines aspects of chemistry, physics, materials science, and engineering.

To highlight the quality of the collected studies, here we briefly discuss three selected examples.

Example 1: Vicent-Luna and Calero and colleagues (**https://doi.org/10.1039/**

Dan Li

Dan Li is a professor of chemistry at the College of Chemistry and Materials Science in Jinan University (Guangzhou, China) and the Director of Guangdong Provincial Key Laboratory of Functional Supramolecular Coordination Materials and Applications. He obtained his PhD in inorganic chemistry from the University of Hong Kong (supervisor, Prof. Chi-Ming Che). His research interest is the design and fabrication of supramolecular coordination assemblies including metal–organic clusters, cages and frameworks that are utilized to embrace luminescent, chiral and porous functionalities. He was a recipient of the National Science Fund for Distinguished Young Scholars of China in 2008, Fellow of the Royal Society of Chemistry (FRSC) in 2014 and Fellow of the Chinese Chemical Society (FCCS) in 2024.

D3TA05258C) utilized molecular simulations to evaluate the effectiveness of five different metal–organic frameworks (MOFs) in adsorption-driven heat pumps with methanol and ethanol as working fluids. Their approach involved a detailed analysis of adsorption data along with a thermodynamic model to determine key properties such as coefficient of performance, working capacity, and specific heat. This research emphasizes the significance of enhancing the efficiency of adsorption-based heat pumps (AHPs) and adsorption cooling systems (ACSs) in order to decrease energy usage through the utilization of MOFs. Specifically, MAF-6 emerges as a promising candidate based on the findings presented in this study. The methodology presented in this work elucidates the operating mechanisms of the adsorption-driven heat pumps for heating and cooling with light alcohols as working fluids and the potential of MOF materials in such applications.[23,24]

Example 2: the Farha's group (https://doi.org/10.1039/D3TA07163D) proposed a new modification strategy to prepare Zr-phosphonate MOFs. This two-step post-modification method consists of replacing carboxylate linkers with phosphinate linkers, to then post-synthetically oxidize them to phosphonates. Indeed, the phosphonate-based hydroxyl group remains uncoordinated, resulting in more hydrophilic materials with increased Brønsted acidity. This modification platform provides an easy strategy to obtain versatile and tunable isoreticular robust Zr_6-phosphinate/phosphonate MOFs, being potentially extended to other MOF families and/or benefiting from the digital reticular chemistry.[25]

Example 3: Patterson and co-workers (https://doi.org/10.1039/D3TA05397K) studied the influence of protein folding in prenucleation clusters on the efficiency of enzyme@MOF composites, particularly focusing on glucose oxidase and catalase encapsulated into zeolitic imidazolate frameworks-8 (ZIF-8). Through electron microscopy and spectroscopy analyses, the author reveals that the interaction between enzymes and MOF precursors during initial cluster formation is crucial for retaining enzyme activity. This research offers a new perspective on enzyme immobilization, emphasizing the importance of enzyme-MOF precursor interactions, potentially advancing industrial-scale enzyme@MOF applications. This work represents a milestone for the advancement of encapsulation and protection of enzymes[26] as a way to improve sustainability aspects.[27,28] We posit that similar investigations will be beneficial to other classes of protective matrices (*e.g.* HOF materials).

As we stand on the brink of a new era in materials science, the articles selected for this collection reflect the current advancement of framework materials research and provide directions for future investigations by highlighting their role in sustainable development. This editorial invites readers to explore the depths of functional framework materials, encouraging a multidisciplinary approach to harness their full potential in addressing some of the most pressing challenges of our time.

References

1 H. Furukawa, K. E. Cordova, M. O'Keeffe and O. M. Yaghi, *Science*, 2013, **341**, 1230444.
2 H. S. Sasmal, A. Kumar Mahato, P. Majumder and R. Banerjee, *J. Am. Chem. Soc.*, 2022, **144**, 11482–11498.
3 R. Freund, O. Zaremba, G. Arnauts, R. Ameloot, G. Skorupskii, M. Dincă, A. Bavykina, J. Gascon, A. Ejsmont, J. Goscianska, M. Kalmutzki, U. Lächelt, E. Ploetz, C. S. Diercks and S. Wuttke, *Angew. Chem., Int. Ed.*, 2021, **60**, 23975–24001.
4 R.-B. Lin, Y. He, P. Li, H. Wang, W. Zhou and B. Chen, *Chem. Soc. Rev.*, 2019, **48**, 1362–1389.
5 R. Dawson, A. I. Cooper and D. J. Adams, *Prog. Polym. Sci.*, 2012, **37**, 530–563.
6 C. Petit, *Curr. Opin. Chem. Eng.*, 2018, **20**, 132–142.
7 K. Adil, Y. Belmabkhout, R. S. Pillai, A. Cadiau, P. M. Bhatt, A. H. Assen, G. Maurin and M. Eddaoudi, *Chem. Soc. Rev.*, 2017, **46**, 3402–3430.
8 S. Yuan, X. Li, J. Zhu, G. Zhang, P. Van Puyvelde and B. Van Der Bruggen, *Chem. Soc. Rev.*, 2019, **48**, 2665–2681.
9 X. Zhao, Y. Wang, D. Li, X. Bu and P. Feng, *Adv. Mater.*, 2018, **30**, 1705189.
10 X. Liu, D. Huang, C. Lai, G. Zeng, L. Qin, H. Wang, H. Yi, B. Li, S. Liu, M. Zhang, R. Deng, Y. Fu, L. Li, W. Xue and S. Chen, *Chem. Soc. Rev.*, 2019, **48**, 5266–5302.
11 L. Wang, Y. Han, X. Feng, J. Zhou, P. Qi and B. Wang, *Coord. Chem. Rev.*, 2016, **307**, 361–381.
12 L. Jiao, Y. Wang, H. Jiang and Q. Xu, *Adv. Mater.*, 2018, **30**, 1703663.
13 I. Stassen, N. Burtch, A. Talin, P. Falcaro, M. Allendorf and R. Ameloot, *Chem. Soc. Rev.*, 2017, **46**, 3185–3241.
14 M. Giménez-Marqués, T. Hidalgo, C. Serre and P. Horcajada, *Coord. Chem. Rev.*, 2016, **307**, 342–360.
15 J. Yang and Y. Yang, *Small*, 2020, **16**, 1906846.
16 J. Tollefson, *Nature*, 2023, DOI: 10.1038/d41586-023-02970-2.
17 T. Stolar and K. Užarević, *CrystEngComm*, 2020, **22**, 4511–4525.
18 R. Bo, M. Taheri, B. Liu, R. Ricco, H. Chen, H. Amenitsch, Z. Fusco, T. Tsuzuki, G. Yu, R. Ameloot, P. Falcaro and A. Tricoli, *Advanced Science*, 2020, **7**, 2002368.
19 V. Rubio-Giménez, M. Galbiati, J. Castells-Gil, N. Almora-Barrios, J. Navarro-Sánchez, G. Escorcia-Ariza, M. Mattera, T. Arnold, J. Rawle, S. Tatay, E. Coronado and C. Martí-Gastaldo, *Adv. Mater.*, 2018, **30**, 1704291.
20 J.-L. Zhuang, A. Terfort and C. Wöll, *Coord. Chem. Rev.*, 2016, **307**, 391–424.
21 Y. G. Chung, E. Haldoupis, B. J. Bucior, M. Haranczyk, S. Lee, H. Zhang, K. D. Vogiatzis, M. Milisavljevic, S. Ling, J. S. Camp, B. Slater, J. I. Siepmann, D. S. Sholl and R. Q. Snurr, *J. Chem. Eng. Data*, 2019, **64**, 5985–5998.
22 V. Bon, E. Brunner, A. Pöppl and S. Kaskel, *Adv. Funct. Mater.*, 2020, **30**, 1907847.
23 M. F. De Lange, K. J. F. M. Verouden, T. J. H. Vlugt, J. Gascon and F. Kapteijn, *Chem. Rev.*, 2015, **115**, 12205–12250.
24 W. Li, X. Xia, M. Cao and S. Li, *J. Mater. Chem. A*, 2019, **7**, 7470–7479.
25 L. Gagliardi and O. M. Yaghi, *Chem. Mater.*, 2023, **35**, 5711–5712.

26 W. Liang, P. Wied, F. Carraro, C. J. Sumby, B. Nidetzky, C.-K. Tsung, P. Falcaro and C. J. Doonan, *Chem. Rev.*, 2021, **121**, 1077–1129.
27 S. Giaveri, A. M. Schmitt, L. Roset Julià, V. Scamarcio, A. Murello, S. Cheng, L. Menin, D. Ortiz, L. Patiny, S. Bolisetty, R. Mezzenga, S. J. Maerkl and F. Stellacci, *Adv. Mater.*, 2021, **33**, 2104581.
28 R. A. Sheldon, A. Basso and D. Brady, *Chem. Soc. Rev.*, 2021, **50**, 5850–5862.