REVIEW

Fluorine-functionalized metal–organic frameworks and porous coordination polymers

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Fluorine, the element with the highest electronegativity and low electric polarizability, can produce a variety of characteristics, including specific adsorption sites for molecules as well as flexibility to the host materials. In this review, we will introduce fluorine-functionalized metal–organic frameworks/porous coordination polymers that show unique and unprecedented structures, structural transformations, and gas and vapor adsorption/separation properties derived from the fluorine characteristics.

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INTRODUCTION

During the last two decades, metal–organic frameworks (MOFs)/porous coordination polymers (PCPs) composed of metal ions and organic bridging ligands as main building units and, in some cases, inorganic ligands, have been investigated extensively because of their versatile structural diversity, high structural controllability (pore size, shape, dimension, flexibility and surface environment), high crystallinity, and their potential porous properties/functionalities in a variety of research fields such as storage and separation, catalysis, drug delivery and sensing ability.^{1–3} The porous properties of MOFs/PCPs can be finely tailored by not only chemical modification of organic ligands and judicious choice of components but also a variety of techniques such as solid solution formation, defect engineering, core-shell structure, crystal morphology and size control, and so on. For example, the appropriate combination of organic bridging ligands provided the Zn(II) MOF, $[\text{Zn}_4\text{O}(\text{bte})_4(\text{bpdc})]$ (bte = 4,4',4''-[benzene-1,3,5-triyl-tris(ethyne-2,1-diyl)]tribenzoate, bpdc = biphenyl-4,4'-dicarboxylate), with ultra-high Brunauer–Emmett–Teller and Langmuir specific surface areas close to 6000 and 10 000 $\text{m}^2 \text{g}^{-1}$, respectively.⁴ Unlike porous inorganic zeolites and porous carbon materials, MOFs often give flexible structures. As coordination bonds, hydrogen bonds and van der Waals interactions that are used to assemble each component are weaker (bonding energies are 10–200 kJ mol^{-1}) than covalent and ionic bonds (200–1000 kJ mol^{-1}), reversible rotation, bending and breaking of these weaker bonds easily occurs, resulting in structural changes. One representative of flexible MOFs is $[\text{Cr}(\text{OH})(1,4\text{-bdc})]$ (MIL-53(Cr), 1,4-bdc = 1,4-benzenedicarboxylate), in which local reorientation of the coordination bond triggered by guest adsorption/desorption induced the structural transformation between narrow pore and large pore forms.⁵ In addition, many MOFs show high crystallinity as with porous inorganic zeolites, which is advantageous for understanding deeply the structure–property relationship using single-crystal and powder X-ray diffraction techniques. For example, the unprecedented highly selective CO sorption from a CO/N_2 mixture, which is

difficult to separate, was achieved using the flexible Cu(II) MOF, $[\text{Cu}(\text{aip})]$ (aip = 5-azidoisophthalate).⁶ Successful determination of the crystal structures of the dried and CO-adsorbed forms using powder X-ray diffraction demonstrated that the synergetic effect of the interaction between CO and the Cu(II) axial sites and a structural transformation contributed to such high selectivity.

At present, it is all but impossible to comprehend completely the reports on MOFs because of the huge, ever-growing number of reports that have been published. In this review article, therefore, we focused on fluorine-functionalized MOFs/PCPs due to their fluorine-specific, interesting porous properties. A fluorine atom has discriminating characteristics, the highest electronegativity and small electric polarizability, which causes the development of a variety of unique characteristics, such as low boiling point, fluorous phase, selective gas absorbability, hydrophobicity and high chemical stability, in fluorine-containing molecules/materials. One of the best-known fluorine-containing materials is polytetrafluoroethylene, an organic polymer containing only carbon and fluorine atoms invented by the DuPont company. Polytetrafluoroethylene exhibits high thermal and chemical stability, low dielectric constant, high insulation property, high water and oil repellency, and non-adhesive property, all of which are caused by fluorine atoms, and is used extensively in our society.

In 2014, Pachfule and Banerjee⁷ published an excellent review article on fluorine-functionalized MOFs/PCPs, in which MOFs/PCPs with a variety of fluorine-containing building blocks and their structure–property (gas adsorption and separation) relationships were introduced. Herein, we provide a comprehensive review of fluorine-functionalized MOFs/PCPs including not only latest results on the basis of the kinds of fluorinated building blocks but also a much wider range of fluorine-related properties (hydrophobicity, adsorption/separation, perfluoroarene–arene interaction, structural flexibility, ionic conductivity and low-energy C–F bond). The fluorinated components, crystal structures and porous properties of fluorine-functionalized MOFs/PCPs are discussed with the relations between

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Figure 1 Fluorine-substituted organic ligands with the pyridine coordination sites reported by Fujita and colleagues.^{8,47}

Figure 2 Crystal structure of $[\text{Cd}(\text{NO}_3)_2(2,6\text{-bpfn})_2] \cdot 2(p\text{-dimethoxybenzene})$. (a) Top view of the two-dimensional sheet. The guest *p*-dimethoxybenzene molecules are coloured red. (b) View of the intermolecular hydrogen bonds. Reproduced from Kasai *et al.*⁸

porous properties and fluorine characters. The papers that did not discuss on fluorine-porous property relationships in fluorine-functionalized MOFs/PCPs are not covered here. Table 1 summarizes fluorine-functionalized MOFs/PCPs introduced in this review.

MOFS CONTAINING FLUORINE- AND TRIFLUOROMETHYL-SUBSTITUTED ORGANIC LIGANDS

It is well known that a perfluoroarene unit forms an intermolecular face-to-face perfluoroarene–arene interaction (the origins of which are van der Waals and quadrupole–quadrupole interactions) with an arene unit.⁴⁶ Fujita and colleagues^{8,47} reported the crystal structures of a large number of Cd(II) MOFs with fluorine-functionalized organic ligands, as shown in Figure 1. The observed MOFs formed one-, two- and three-dimensional porous structures with non-fluorinated

aromatic guest molecules, some of which formed intermolecular arene–perfluoroarene interactions between fluorinated ligands and non-fluorinated aromatic guests. For example, the two-dimensional MOF, $[\text{Cd}(\text{NO}_3)_2(2,6\text{-bpfn})_2] \cdot 2(p\text{-dimethoxybenzene})$ (2,6-bpfn = 2,6-bis(4-pyridylmethyl)hexafluoronaphthalene, Figure 1c), exhibited face-to-face interactions between the perfluoroarene rings and the guest arene rings with the shortest C...C distance of 3.411 Å inside the grids (Figure 2a).⁸ In addition, the guest afforded the weak C–H...F hydrogen bond (H...F distance = 2.653 Å and C–H...F angle = 126.1°) with the neighboring two-dimensional sheet (H27A...F2 in Figure 2b).⁴⁸

The polar C–F bond may be useful for a preferable gas adsorption site. Cheetham and colleagues⁹ found an enhanced enthalpy of H₂ adsorption in the three-dimensional fluorinated MOF, $[\text{Zn}_5(\text{triazole})_6]$

Table 1 Summary of fluorine-functionalized MOFs/PCPs^a

MOFs/PCPs	Type of fluorinated ligands	Type of structures	Properties	References
[Cd(NO ₃) ₂ (2,6-bpfn) ₂ ·2(<i>p</i> -dimethoxybenzene)]	2,6-bpfn, organic bridging ligand	2D	Perfluoroarene-arene interaction	8
[Zn ₅ (triazole) ₆ (tetrafluoroterephthalate) ₂ (H ₂ O) ₂]	Tetrafluoroterephthalate, organic bridging ligand	3D	High enthalpy of H ₂ adsorption	9,10
[Ni _{0.5} (tpb) _{0.5} (R-opa) _{0.5} (H ₂ O) _{0.5}]	R-opa ²⁻ , organic bridging ligand	3D	Enhanced H ₂ and CO ₂ adsorption capacity	11
[Zn ₂ (L1)(4-(trifluoromethyl)pyridine) ₂]	4-(Trifluoromethyl)pyridine, organic terminal ligand	3D	Enhanced CO ₂ /N ₂ and CO ₂ /CH ₄ selectivity	12
[Zn(L2)]	L2 ²⁻ , organic bridging ligand	3D	Selective adsorption of hydrophobic heptane	13
[Cu ₄ (L3) ₄]	L3 ²⁻ , organic bridging ligand	2D	High hydrophobicity, high tolerance to water, oil/water separation	14
[Ag ₆ (tz) ₆]	tz, Organic bridging ligand	3D	High hydrophobicity, high tolerance to water, high C6–C8 hydrocarbon adsorption capacity	15,16
[Zr ₆ O ₆ (OH) ₂ (tdc) ₄ (RCOO) ₂] (RCOO ⁻ = trifluoroacetate, 4-(trifluoromethyl)benzoate and pentafluorobenzoate	RCOO ⁻ , organic terminal ligand	3D	High tolerance to water	17
[Zn(SiF ₆)(4,4'-bpy) ₂]	SiF ₆ ²⁻ , inorganic bridging ligand	3D	—	18
[Cu(SiF ₆)(4,4'-bpy) ₂] (SIFSIX-1-Cu)	SiF ₆ ²⁻ , inorganic bridging ligand	3D	High CH ₄ adsorption capacity, high CO ₂ /CH ₄ selectivity, C ₂ H ₂ /C ₂ H ₄ separation	19–21
[Cu(TiF ₆)(4,4'-bpy) ₂] (TIFSIX-1-Cu)	TiF ₆ ²⁻ , inorganic bridging ligand	3D	C ₂ H ₄ separation	22
[Cu(SnF ₆)(4,4'-bpy) ₂] (SNIFSIX-1-Cu)	SnF ₆ ²⁻ , inorganic bridging ligand	3D	High CO ₂ /N ₂ and CO ₂ /CH ₄ selectivity	22
[Cu(SiF ₆)(1,2-bis(4-pyridyl)ethylene) ₂] (SIFSIX-2-Cu)	SiF ₆ ²⁻ , inorganic bridging ligand	3D	High CO ₂ /N ₂ and CO ₂ /CH ₄ selectivity	20
[Co(SiF ₆)(4,4'-dipyridylacetylene) ₂] (SIFSIX-2-Co)	SiF ₆ ²⁻ , inorganic bridging ligand	3D	C ₂ H ₂ /C ₂ H ₄ separation	21
[Cu(SiF ₆)(4,4'-dipyridylacetylene) ₂] (SIFSIX-2-Cu-i, i = interpenetrated)	SiF ₆ ²⁻ , inorganic bridging ligand	3D	CO ₂ /N ₂ , CO ₂ /CH ₄ and C ₂ H ₂ /C ₂ H ₄ separation	21,23
[Cu(TiF ₆)(4,4'-dipyridylacetylene) ₂] (TIFSIX-2-Cu-i)	TiF ₆ ²⁻ , inorganic bridging ligand	3D	C ₂ H ₂ /CO ₂ separation	24
[Cu ₂ (PF ₆)(NO ₃)(4,4'-bpy) ₄ ·2PF ₆]	PF ₆ ⁻ , inorganic bridging ligand and inorganic guest	3D	—	25
[Zn(SiF ₆)(pyz) ₂] (SIFSIX-3-Zn)	SiF ₆ ²⁻ , inorganic bridging ligand	3D	CO ₂ /N ₂ , CO ₂ /CH ₄ and C ₂ H ₂ /C ₂ H ₄ separation	21,23,26
[Ni(SiF ₆)(pyz) ₂] (SIFSIX-3-Ni)	SiF ₆ ²⁻ , inorganic bridging ligand	3D	CO ₂ /N ₂ and C ₂ H ₂ /C ₂ H ₄ and CO ₂ /C ₂ H ₂ separation	21,24,26
[Cu(SiF ₆)(pyz) ₂] (SIFSIX-3-Cu)	SiF ₆ ²⁻ , inorganic bridging ligand	3D	CO ₂ /N ₂ separation	26
[Co(SiF ₆)(pyz) ₂] (SIFSIX-3-Co)	SiF ₆ ²⁻ , inorganic bridging ligand	3D	CO ₂ /N ₂ separation	26
[Fe(SiF ₆)(pyz) ₂] (SIFSIX-3-Fe)	SiF ₆ ²⁻ , inorganic bridging ligand	3D	—	27
[Cu ₃ (4-(pyridin-4-yl)acrylate)(SiF ₆)] (fsc-2-SIFSIX)	NbOF ₅ ²⁻ , inorganic bridging ligand	3D	High CO ₂ /N ₂ and CO ₂ /CH ₄ selectivity	28
[Ni(NbOF ₅)(pyz) ₂]	NbOF ₅ ²⁻ , inorganic bridging ligand	3D	CO ₂ /N ₂ and propylene/propane separation	29,30
[Cu(BF ₄)(4,4'-bpy) ₂] (ELM-11)	BF ₄ ⁻ , inorganic terminal ligand	3D	Gate sorption	31
[Cu(CF ₃ SO ₂)(4,4'-bpy) ₂]	CF ₃ SO ₂ ⁻ , inorganic terminal ligand	2D	Gate sorption	32
[Cu(PF ₆)(4,4'-bpy) ₂]	PF ₆ ⁻ , inorganic terminal ligand	2D	Gate sorption, high CO ₂ /X (X = N ₂ , O ₂ , CH ₄ and Ar) selectivity	33
[Co(CF ₃ SO ₂)(4,4'-bpy) ₂]	CF ₃ SO ₂ ⁻ , inorganic terminal ligand	2D	Gate sorption	34
[Cu(PF ₆)(bpe) ₂]	PF ₆ ⁻ , inorganic terminal ligand	1D	Gate sorption, 2-butanone/EtOH and 2-butanone/MeOH separation	35,36
[Cu(BF ₄)(bpy) ₂]	BF ₄ ⁻ , inorganic terminal ligand	1D	Gate sorption, CO ₂ /CH ₄ and CH ₄ /C ₂ H ₆ separation	37,38
[Cu(PF ₆)(bpy) ₂]	PF ₆ ⁻ , inorganic terminal ligand	1D	Gate sorption, CO ₂ /CH ₄ separation	39
[Cu(CF ₃ SO ₂)(bpy) ₂]	CF ₃ SO ₂ ⁻ , inorganic terminal ligand	1D	Gate sorption	40
[Cu(CF ₃ SO ₂)(bpy) ₂ ·PF ₆]	CF ₃ SO ₂ ⁻ , inorganic bridging ligand; PF ₆ ⁻ , inorganic guest	2D	—	41
EMI-TSFA@[Zn(MeIm) ₂] (EMI-TSFA@ZIF-8)	PF ₆ ⁻ , inorganic guest	3D	High ionic conductivity	42
[Co(NCS) ₂ (L4) ₂]	TSFA ⁻ , inorganic guest	2D	High fluorophilicity	43
[Cu(bpbtp)(L5)]	L4, organic bridging ligand	2D	Preferential CO ₂ and O ₂ adsorption over N ₂ , Ar and CO	44
[Zr ₆ (μ ₃ -OH) ₄ (OH) ₄ ·0.6(TBAPY)(C ₆ F _{2x+1} COO) _{4-3.4}] (x = 3, 7 and 9)	bpbtp and L5, organic bridging ligand; C ₆ F _{2x+1} COO ⁻ , organic terminal ligand	3D	Enhanced enthalpy of CO ₂ adsorption	45

Abbreviations: 1D, one-dimensional; 2D, two-dimensional; 3D, three-dimensional; MOF, metal-organic framework; PCP, porous coordination polymer.

^a 2,6-bpfn, 2,6-bis(4-pyridylmethyl)hexafluoroisophthalate; tpt, 2,4,6-tris(4-pyridyl)-1,3,5-triazine; H₂R-opa, phthalic acid with different functional groups; H₄L1, 4,4',4''-benzene-1,2,4,5-tetrayl(tetrabenzic acid); H₄L2, 4,4'-(hexafluoroisopropylidene)bis(benzic acid); H₄L3, 4,4'-(3,5-bis(trifluoromethyl)phenylazanediyl)benzoic acid; tz, 3,5-bis(trifluoromethyl)-1,2,4-triazolate; H₄tdc, 2,5-thiophenedicarboxylic acid; 4,4'-bpy, 4,4'-bipyridine; pyz, pyrazine; bpe, 1,2-bis(4-pyridyl)ethane; bpp, 1,3-bis(4-pyridyl)propane; H₂MeIm, 2-methylimidazole; EMI-TSFA, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide; L4, 1,3-bis(4-pyridyl)ethynyl-2-(3,4,4',5,5',6,6',7,7,8,8-tridecafluoroethoxy)benzene; H₂bpbtp, 2,5-bis(perfluorobutyl)terephthalic acid; L5, 2,5-bis(perfluorobutyl)-1,4-bis(4-pyridyl)benzene; TBAPY, 1,3,6,8-tetrakis(*p*-benzoic acid)pyrene.

Figure 3 Molecular structures of organic ligands with fluorine or trifluoromethyl substituents, (a) tetrafluoroterephthalic acid, (b) 3-fluorophthalic acid, (c) 3,6-difluorophthalic acid, (d) 3,4,5,6-tetrafluorophthalic acid, (e) 4-(trifluoromethyl)pyridine, (f) 4,4'-(hexafluoroisopropylidene)bis(benzoic acid), (g) 4,4'-bis(3,5-bis(trifluoromethyl)phenyl)azanediyldibenzoic acid, (h) 3,5-bis(trifluoromethyl)-1,2,4-triazole, (i) trifluoroacetic acid, (j) 4-(trifluoromethyl)benzoic acid and (k) pentafluorobenzoic acid.

(tetrafluoroterephthalate)₂(H₂O)₂•4H₂O}, using commercially available fluorinated tetrafluoroterephthalic acid (Figure 3a). This MOF had a small pore and fluorine atoms exposed on the pore surface (Figure 4a), which was expected to cause high enthalpy of H₂ adsorption (−8 kJ mol^{−1} at low coverage, Figure 4b), comparable to MOFs with coordinatively unsaturated metal centers that considerably increase this value. After this report, the H₂ adsorption sites were closely investigated using inelastic neutron scattering spectroscopy and molecular simulation by Space and colleagues.¹⁰ Theoretical calculation is a powerful tool to support and predict intermolecular interactions between coordination frameworks and guest molecules. The inelastic neutron scattering spectroscopy and simulation results concluded that the most favorable adsorption site is the vicinity of the Zn-coordinated H₂O, the fluorine and the carboxylate oxygen atoms of tetrafluoroterephthalate ligands in small pores as shown in Figure 4c. To elucidate the effect of fluorination on the gas-sorption properties of MOFs, a systematic investigation was performed by Bu and colleagues¹¹ using the three-dimensional MOFs, {[Ni_{0.5}(tpt)_{0.5}(R-opa)_{0.5}(H₂O)_{0.5}]•x(guest)} (tpt = 2,4,6-tri(4-pyridyl)-1,3,5-triazine and H₂-R-opa = phthalic acid with different functional groups), in which each phthalate and tpt ligand bridges two and three Ni(II) ions, respectively, to form the porous framework. The increase in the number of fluorine atoms from 3-fluorophthalic acid, 3,6-difluorophthalic acid to 3,4,5,6-tetrafluorophthalic acid (Figure 3b–d) resulted in the positive effect of fluorine on H₂ and CO₂ adsorption capacity. Snurr and colleagues¹² succeeded in the enhancement of CO₂/N₂ and CO₂/CH₄ selectivities in the three-dimensional

MOF, [Zn₂(L1)] (H₄L1 = 4,4',4'',4'''-benzene-1,2,4,5-tetrayltetrabenzoic acid), using the fluorinated 4-(trifluoromethyl)pyridine terminal ligand (Figure 3e). The as-synthesized sample had paddlewheel Zn₂ dimers and the *N,N*-dimethylformamide (DMF) molecules were coordinated to their axial sites. Using the post-synthetic modification approach, the coordinated DMF could be successfully exchanged with the bigger 4-(trifluoromethyl)pyridine. Although this exchange led to a lower specific surface area (800 vs 390 m² g^{−1}), the CO₂/N₂ and CO₂/CH₄ selectivities increased, especially remarkably higher CO₂/N₂ selectivity at low pressure (22 vs 42 (ideal adsorbed solution theory (IAST) selectivity for equimolar binary mixture)), at the same time. The authors proposed that this enhancement in selectivity can be attributed to (1) the attractive interaction between the polar CF₃ group and CO₂ and (2) the formation of smaller pores by the introduction of more bulky 4-(trifluoromethyl)pyridine ligands.

The hydrophobic character of the fluorinated pore surface provides a preferable adsorption and a high capacity of hydrophobic guests. Monge *et al.*¹³ reported the three-dimensional MOF [Zn(L2)] (H₂L2 is shown in Figure 3f), in which the helical Zn(II)-carboxylate chains are connected by the L2 ligands to form two kinds of very different parallel channels. One of the channels had walls formed by CF₃ substituents of ligands. The as-synthesized sample included guest H₂O molecules in the other hydrophilic channels but the desolvated form selectively took in hydrophobic heptane guests within its CF₃-decorated channels. Ghosh and colleagues¹⁴ found that the desolvated form of the two-dimensional MOF, {[Cu₄(L3)₄(DMF)₄]•3DMF} (H₂L3 is shown in Figure 3g), exhibited excellent water-

Figure 4 (a) Crystal structure of $[\text{Zn}_5(\text{triazole})_6(\text{tetrafluoroterephthalate})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ viewed down the *b* axis. Guest H_2O molecules are omitted to show one-dimensional pores down the *b* axis. (b) H_2 adsorption isotherms at 77 K (black) and 87 K (red), and Q_{st} plot. Reproduced from Hulvey *et al.*⁹ (c) Depiction of an adsorbed H_2 molecule (orange) on the most favorable adsorption site as determined from simulation. Carbon atoms are depicted in cyan, hydrogen in white, nitrogen in blue, oxygen in red, fluorine in pink and zinc in silver. Reproduced from Forrest *et al.*¹⁰

repellent and oil/water separation properties derived from CF_3 substituents on the L3 ligand. The fluorinated MOF, $[\text{Ag}_6(\text{tz})_6]$ ($\text{tz} = 3,5\text{-bis(trifluoromethyl)-1,2,4-triazolate}$, Figure 3h), reported by Omary and colleagues,⁴⁹ showed the three-dimensional porous framework consisting of tetranuclear $[\text{Ag}_4(\text{tz})_6]$ clusters connected by three-coordinate $\text{Ag}(\text{I})$ centers and had both large semi-rectangular channels (~ 12.2 and 7.3 Å) and small diamond-shaped cavities (~ 6.6 and 4.9 Å) coated with CF_3 groups of the fluorinated tz ligands (Figure 5a). Because of its CF_3 -coated channels and cavities, this MOF adsorbed a negligible amount of water even under almost 100% relative humidity condition and retained its original porous structure after soaking in water for several days.¹⁵ In contrast, a high adsorption amount of C6–C8 hydrocarbons such as benzene, toluene, *p*-xylene, cyclohexane and *n*-hexane, the most common oil components, was observed (Figure 5b). Such hydrophobic character is effective in the field of oil-spill clean-up. A hydrophobic space derived from fluorine atoms was also suitable for investigating properties of water clusters themselves due to the negligible interaction of water molecules with the pore walls. Omary and colleagues¹⁶ reported water cluster confinement in the hydrophobic cavities using the same fluorinated MOF, $[\text{Ag}_6(\text{tz})_6]$. From Raman and IR spectroscopy and theoretical calculations, it was suggested that a small number of pentamer water clusters were formed in the large pores and the binding energy between the water clusters and the CF_3 -decorated walls was weak.

A hydrophobic nature of fluorine-containing materials contributes to a high stability to water. Senkovska and colleagues¹⁷ succeeded in the incorporation of the hydrophobic fluorinated monocarboxylate ligands such as trifluoroacetate, 4-(trifluoromethyl)benzoate and pentafluorobenzoate (Figure 3i–k, respectively) to the three-dimensional Zr MOF of $[\text{Zr}_6\text{O}_6(\text{OH})_2(\text{tdc})_4(\text{HCOO})_2]$ (DUT-67-Fa, $\text{H}_2\text{tdc} = 2,5\text{-thiophenedicarboxylic acid}$) using the solvent-assisted ligand incorporation technique.⁴⁵ The exchange of HCOO^- for these fluorinated monocarboxylates was performed by immersing the parent DUT-67-Fa in a DMF solution of the respective carboxylic acid. The tolerance of the obtained carboxylate-exchanged materials toward the removal of adsorbed water could be significantly enhanced compared with the parent DUT-67-Fa MOF.

MOFS FUNCTIONALIZED WITH INORGANIC FLUORINATED ANIONS

Inorganic fluorinated anions as illustrated in Figure 6 are also good building blocks for the construction of fluorine-functionalized MOFs/PCPs. AF_6^{2-} anions ($\text{A} = \text{Si, Ge, Sn}$ and Ti) can be used as bridging ligands for MOFs due to their high density of negative charge on fluorine atoms.^{18–27,29,50} There are many AF_6^{2-} -bridged MOFs, $[\text{M}(\text{AF}_6)(\text{L})_2]$, in which M is Fe(II) , Co(II) , Ni(II) , Cu(II) or Zn(II) cations, and L is pyrazine (pyz) or bipyridine-type neutral ligands, and their prototypes are $[\text{M}(\text{SiF}_6)(4,4'\text{-bpy})_2]$ ($\text{M} = \text{Zn(II)}$ or Cu(II) , $4,4'\text{-bpy} = 4,4'\text{-bipyridine}$), which form the three-dimensional porous

Figure 5 (a) Crystal structure of $[\text{Ag}_6(\text{tz})_6]$. In the right figure, the small cavities are denoted by black circles that surround the large channels. (b) Adsorption/desorption isotherms for benzene, toluene, *p*-xylene, cyclohexane and *n*-hexane. Closed and open symbols indicate adsorption and desorption, respectively. Reproduced from Yang *et al.*^{15,49}

Figure 6 Inorganic fluorinated building units.

primitive cubic structure constructed from two-dimensional $[\text{M}(4,4'\text{-bpy})_2]_n$ sheets and inorganic SiF_6^{2-} pillars.^{18,19} The Cu(II) compound, $[\text{Cu}(\text{SiF}_6)(4,4'\text{-bpy})_2]$ (SIFSIX-1-Cu), was shown to have permanent pores and exhibit a high uptake of CH_4 (6.5 mmol g^{-1} at 298 K and 36 atm) and selective CO_2 uptake over CH_4 (10.5 (IAST CO_2/CH_4 (50:50) selectivity) at 298 K and 1 atm), and selective C_2H_2 uptake over C_2H_4 (8.37 (IAST $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ (50:50) selectivity) at 298 K and 1 atm).^{19–21} In general, this type of MOF with Co(II), Ni(II) and Zn(II) is obtained in non-aqueous condition because H_2O is preferentially coordinated to these metal centers instead of the weak Lewis base SiF_6^{2-} ($\text{p}K_a = 1.92$).²¹ In contrast, the Cu types can be prepared even in the presence of H_2O . Cu(II) complexes have longer axial coordination bonds than equatorial bonds because of a Jahn–Teller effect and, therefore, there is a relatively large contribution of electrostatic interaction to the axial coordination bonds, which enables the preferential coordination of a SiF_6^{2-} dianion to the Cu(II) axial

site compared with a neutral H_2O molecule. Use of the Cu(II) axial sites permitted even a stable bridge of metal centers by an inorganic fluorinated PF_6^- monoanion. We succeeded in the synthesis of the three-dimensional MOF, $\{[\text{Cu}_2(\text{PF}_6)(\text{NO}_3)(4,4'\text{-bpy})_4] \cdot 2\text{PF}_6\}$, in which the PF_6^- and NO_3^- anions alternately bridged the Cu(II) axial sites of adjacent two-dimensional layers with Cu–F and Cu–O distances of 2.676(4) and 2.320(5) Å, respectively (Figure 7a).²⁵ In fact, this MOF was stable after the removal of guest molecules and the desolvated form showed a type I adsorption isotherm for N_2 at 77 K with a Brunauer–Emmett–Teller specific surface area of $559 \text{ m}^2 \text{ g}^{-1}$, suggesting the presence of stable micropores (Figure 7b). The SiF_6^{2-} pillars had an important role in the formation of favorable MOF-sorbate interactions via non-coordinated F atoms, which was confirmed using modeling studies, and X-ray and neutron diffraction analysis.^{21,23,26} The exceptional CO_2 separation ability of the three-dimensional MOF, $[\text{Zn}(\text{SiF}_6)(\text{pyz})_2]$ (SIFSIX-3-Zn, pyz = pyrazine), was reported by Nugent *et al.*,²³ in which the modeling studies revealed close interactions between electropositive carbon atoms of CO_2 molecules and four negatively charged fluorine atoms of SiF_6^{2-} pillars. Xing and colleagues²¹ crystallographically characterized the C_2D_2 -adsorbed structure of SIFSIX-1-Cu using the powder neutron diffraction technique. C–D $\cdots$ F hydrogen bonds (2.063 Å) were observed between C_2D_2 and SiF_6^{2-} dianions, and the other D interacted with a neighboring C_2D_2 molecule with C–D $\cdots$ C distances of 3.063 and 3.128 Å, which synergistically contributed to high selective C_2H_2 separation from a $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ mixture (Figure 8). Space and colleagues²⁸ recently found that the SiF_6^{2-} anion connected other type of cationic two-dimensional sheets, $[\text{Cu}_3(4\text{-(pyridin-4-yl)acrylate})]$, to form the neutral three-dimensional $[\text{Cu}_3(4\text{-(pyridin-4-yl)acrylate})]$.

Figure 7 (a) Porous structure with bridged PF_6^- anions (the non-coordinated PF_6^- anions are omitted for clarity in the central figure) and (b) N_2 adsorption isotherms at 77 K in $[\text{Cu}_2(\text{PF}_6)(\text{NO}_3)(4,4'\text{-bpy})_4] \cdot 2\text{PF}_6$. Reproduced from Noro *et al.*²⁵

yl)acrylate)(SiF_6)] (fsc-2-SIFSIX) with both coordinatively unsaturated Cu(II) and SiF_6 fluorine sites for a CO_2 gas trapping. Computational studies revealed that a primary CO_2 adsorption site was the two Cu(II) cations of adjacent paddle-wheel $[\text{Cu}_2(\text{CO}_2\text{R})_4]$ moieties and a secondary adsorption site was the two equatorial SiF_6^{2-} fluorine atoms.

In contrast to the organic fluorinated ligands, it is very difficult to modify inorganic fluorinated ligands at will. However, Eddaoudi and colleagues^{29,30} succeeded in the preparation of a fine-tuned fluorinated MOF by modification of the inorganic fluorinated anions. They used a NbOF_5^{2-} dianion instead of SiF_6^{2-} to afford the three-dimensional MOF, $[\text{Ni}(\text{NbOF}_5)(\text{pyz})_2]$. Because of its longer Nb–F bond length (1.899(1) Å) than the Si–F bond (1.681(1) Å) and greater Lewis basicity, this MOF provided an appropriate pore space for capturing trace CO_2 , separating propylene from propane and enhanced water stability.

Inorganic fluorinated monoanions such as PF_6^- , BF_4^- , CF_3SO_3^- and $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ have been used as counter anions of ionic liquids.⁵¹ As the negative charge of these anions is delocalized by fluorine atoms, electrostatic interaction between these anions and cations is weaker than that between non-fluorinated anions and cations, which causes low melting points. The same situation, that is, weaker intermolecular interactions, should be observed between fluorinated anions and neutral molecules. In addition, the poor metal-bridging ability of these monoanions contributes to the lowering of a framework dimensionality from three dimensions to two and one dimension. Therefore, the introduction of inorganic fluorinated monoanions to MOFs/PCPs may afford flexible materials showing gate-sorption/breathing behaviors.

The two-dimensional MOF $[\text{Cu}(\text{BF}_4)_2(4,4'\text{-bpy})_2]$ (ELM-11; ELM, elastic-layer-structured MOF) was the first flexible material with inorganic fluorinated anions.³¹ This Cu(II) MOF, which was prepared by dehydration of the precursor one-dimensional coordination polymer $[\{\text{Cu}(\text{BF}_4)_2(4,4'\text{-bpy})(\text{H}_2\text{O})_2\}] \cdot 4,4'\text{-bpy}$,⁵² had a two-dimensional square-grid framework with weakly coordinated BF_4^- anions at the Cu (II) axial sites (Figure 9a) and showed gate-sorption behaviors for CO_2 with interlayer expansion/shrinkage (Figure 9b).^{31,53} After this finding, the derivatives $[\text{M}(\text{A})_2(4,4'\text{-bpy})_2]$ ($\text{M} = \text{Cu}$, $\text{A} = \text{CF}_3\text{SO}_3^-$; $\text{M} = \text{Cu}$, $\text{A} = \text{PF}_6^-$; $\text{M} = \text{Co}$ and $\text{A} = \text{CF}_3\text{SO}_3^-$) were separately reported.^{32–34} These MOFs formed similar two-dimensional square-grid frameworks with weakly coordinated CF_3SO_3^- and PF_6^- (Cu), and coordinated CF_3SO_3^- (Co) monoanions but showed different sorption behaviors from the parent ELM-11; there were two sorption events: the first uptake was a micropore filling and the second uptake was caused by a gate-sorption process with an expansion of the interlayer distance and sliding between the layers. Using these anions, it is also possible to fabricate one-dimensional flexible MOFs exhibiting gate sorption.^{35–40,54} We reported the one-dimensional flexible MOF, $[\text{Cu}(\text{PF}_6)_2(\text{bpetha})_2]$ (bpetha = 1,2-bis(4-pyridyl)ethane).^{35,36,54} This MOF exhibited doubly linked one-dimensional chain structures consisting of Cu(II) ions and bent bpetha ligands with weakly coordinated PF_6^- monoanions at its axial sites. CO_2 and C_2H_2 gases were selectively adsorbed to this MOF with structural changes.³⁵ The coordination state of the PF_6^- monoanions was retained during the change in structures and the adsorbed CO_2 gas may interact with the fluorine atoms of weakly coordinated PF_6^- monoanions. This MOF also showed selective uptake of a larger 2-butanone guest from 2-butanone/EtOH and 2-butanone/MeOH

mixtures.³⁶ The 2-butanone guest with an sp^2 coordinated oxygen atom could coordinate to the Cu(II) axial sites instead of the PF_6^- monoanion, whereas the EtOH and MeOH guests with a sterically crowded sp^3 coordinated oxygen atom were hard to coordinate to the sterically crowded Cu(II) axial sites that are formed by the coordination

Figure 8 (a) Crystal structure and (b) experimental column breakthrough curves for C_2H_2/C_2H_4 (50:50) separation at 298 K and 1 atm in $[Cu(SiF_6)(4,4'-bpy)_2]$ (SIFSIX-1-Cu). SIFSIX-2-Cu-i is $[Cu(SiF_6)(4,4'-dipyridylacetylene)_2]$ (i = interpenetrated). Reproduced from Cui *et al.*²¹

of four bpetha pyridine moieties from the equatorial direction, which was the origin of the high selectivity for the larger 2-butanone guest.

Ionic liquids with inorganic fluorinated monoanions have been found to adsorb CO_2 gas selectively over other gases through $F\cdots CO_2$ interactions. In some MOFs with inorganic fluorinated monoanions, selective CO_2 adsorption and separation were observed.^{33,37,39} We reported selective CO_2 adsorption over CH_4 in the one-dimensional MOF, $[Cu(PF_6)_2(bpp)_2]$ ($bpp = 1,3$ -bis(4-pyridyl)propane).³⁹ The bent bpp ligands and the Cu(II) ions formed a doubly linked chain with weakly coordinated PF_6^- anions at the axial sites (Figure 10a). At 298 K, this MOF adsorbed CO_2 gas but CH_4 and H_2O were hardly adsorbed (Figure 10b), suggesting an availability for separation of the CO_2/CH_4 mixture under dry and even humid conditions. In fact, it was experimentally proven that this MOF showed high equilibrium and kinetic separation for CO_2 over CH_4 under realistic conditions, using a mixed gas at room temperature and in a humid environment (Figure 10b and c). The moderate heat of CO_2 adsorption ($Q_{st} = -18$ to -31 kJ mol⁻¹), which was experimentally determined, and the calculated interaction energy using a model structure (Figure 10d)³² suggested that the fluorine atoms of the weakly coordinated PF_6^- anions contribute to the interaction sites with adsorbed CO_2 molecules. To elucidate the interactions between inorganic fluorinated monoanions and guest molecules in detail, it is important to determine the crystal structures with adsorbed guest molecules. Recently, the CO_2 -adsorbed structures of ELM-11 and one-dimensional MOF $[Cu(BF_4)_2(bpp)_2]$ ³⁸ showing CO_2 gate sorption were successfully determined from synchrotron powder X-ray diffraction data.^{55,56} In the CO_2 -adsorbed ELM-11 ($ELM-11 \supset 2CO_2$), one CO_2 interacted with two neighboring BF_4^- anions with $F\cdots C$ distances of 2.918 and 2.932 Å,⁵⁵ whereas the CO_2 -adsorbed one-dimensional MOF, $\{[Cu(BF_4)_2(bpp)_2] \cdot 0.7CO_2\}$, formed $F\cdots CO_2$ interactions ($F\cdots C = 2.61(6)$ Å, see Figure 11a).⁵⁶ If single crystals of MOFs with inorganic fluorinated monoanions have permanent micropores and retain their single crystallinity after removal of guest molecules, they could be available for determining guest-adsorbed structures and discussing interactions between inorganic fluorinated monoanions and guest molecules by single-crystal X-ray diffraction measurements. However, such permanent single crystals are difficult to synthesize,

Figure 9 (a) Two-dimensional structure and (b) change in the sample volume on increasing CO_2 pressure (from the left, 0, 6.66, 13.3, 26.7, 34.7, 45.3 and 101 kPa) at 273 K in $[Cu(BF_4)_2(4,4'-bpy)_2]$. Reproduced from Kondo *et al.*³¹

Figure 10 Structure and gas separation properties of [Cu(PF₆)₂(bpp)₂]. (a) Schematic view of the structure. (b) Single-gas and mixed-gas equilibrium adsorption properties at 298 K under dry and humid conditions. The single-gas adsorption isotherms for CO₂ and CH₄ are shown in filled red circles and blue squares, respectively. The open black circles and triangles indicate the CO₂, CH₄ and total adsorption amounts, respectively, for the mixed gas of CO₂:CH₄=40:60 (mol). The filled black symbols correspond to their adsorption amounts for the mixed gas of CO₂:CH₄:H₂O=39.98:59.96:0.06 (mol), in which each adsorption amount is calculated according to the hypothesis that water is hardly adsorbed at all. The mixed-gas adsorption measurements were repeated five times. (c) Breakthrough curves of CO₂/CH₄ mixture (measurement condition: CO₂:CH₄=40:60 (mol), the measurement temperature=298 K, the total pressure=800 kPa and the space velocity=3 min⁻¹). The red circles represent CO₂ and the blue squares represent CH₄. (d) Optimized structure of [Cu(PF₆)₂(pyridine)₄] and CO₂. Reproduced from Noro *et al.*^{33,39}

because the inorganic fluorinated monoanions often give flexible MOFs. We succeeded in the preparation of a stable single crystal of the two-dimensional MOF, {[Cu(CF₃SO₃)(bpp)₂]}•PF₆, using an anion-mixing method.⁴¹ Two coexistent types of inorganic fluorinated anions, CF₃SO₃⁻ and PF₆⁻, with different Lewis basicities, enabled the formation of a higher dimensional, in this case two-dimensional, framework compared with the corresponding one-dimensional MOFs with only one type of anion, [Cu(A)₂(bpp)₂] (A=CF₃SO₃ and PF₆). In the acetone-including crystal {[Cu(CF₃SO₃)(bpp)₂]}•PF₆•acetone, the guest acetone molecules located in micropores formed weak hydrogen-bonding interactions with the bridged CF₃SO₃⁻ (C•••O=

3.34(2) Å) and non-coordinated PF₆⁻ anions (C•••F=3.11(2) Å), as shown in Figure 11b. After the removal of acetone guests, the single crystallinity was unchanged and we could determine the crystal structure of the completely desolvated form {[Cu(CF₃SO₃)(bpp)₂]}•PF₆. As this MOF adsorbed CO₂, a direct visualization of the interaction between fluorinated monoanions and adsorbed CO₂ may be possible using a single-crystal X-ray diffraction technique.

Ionic liquids including inorganic fluorinated monoanions are good candidates as safe electrolytes in electrochemical devices because of their flame resistance, extremely low volatility, high thermal and electrochemical stability, and high ionic conductivity. However, their

Figure 11 (a) CO₂-adsorbed structure in {[Cu(BF₄)₂(bpp)₂]·2CO₂} (ELM-11) (2CO₂). Reproduced from Tanaka *et al.*⁵⁵ (b) Crystal structure and view of the interaction between the acetone guest and inorganic fluorinated CF₃SO₃[−] and PF₆[−] anions in {[Cu(CF₃SO₃)(bpp)₂]·PF₆·acetone}.

ionic conductivity dramatically decreases below their freezing points. Kitagawa and colleagues⁴² reported a low-temperature ionic conductor obtained by the incorporation of the ionic liquid, EMI-TSFA (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide) within the three-dimensional MOF, [Zn(MeIm)₂] (ZIF-8, HMeIm = 2-methylimidazole). The ionic conductivity of EMI-TSFA@ZIF-8 was higher than that of bulk EMI-TSFA below 250 K because there is no freezing transition of the nanosized ionic liquid formed in the restricted pore space.

PERFLUOROALKANE-FUNCTIONALIZED MOFs

As is the case with previously introduced fluorine-containing MOF building units, perfluoroalkanes can provide polar adsorption sites. Furthermore, the assembly of these substituents is useful for the construction of a specific fluorophilic field and preferential adsorption field for O₂ and CO₂. There are two methods to adopt perfluoroalkyl substituents into MOFs; one is to use bridging ligands with their substituents and the other is the use of terminal ligands bearing them. The two-dimensional MOF, {[Co(NCS)₂(L4)₂]·x(guest)} (guest is ethylene glycol or C₆F₁₄ and L4 is 1,3-bis(4-pyridylethynyl)-2-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)benzene shown in Figure 12a), with the pendant perfluoroalkyl C₆F₁₃ chains were synthesized by Fujita and colleagues.⁴³ The stacking of the distorted two-dimensional grid frameworks created pores occupied by the C₆F₁₃ chains and the guest molecules. When ethylene glycol guests (boiling point: 471 K) were included, they started to be removed from the pores around 313 K, similar to neat ethylene glycol. On the other hand, the clathrated perfluorohexane (boiling point: 329 K) began to evaporate at around 268 K, which was much higher than neat perfluorohexane (~223 K), indicating high fluorophilicity and organophobicity. Matsuda and colleagues reported the densely perfluorobutyl-functionalized two-dimensional MOF, {[Cu(bpbtp)(L5)(DMF)]·DMF} (H₂bpbtp = 2,5-bis(perfluorobutyl)terephthalic acid, L5 = 2,5-bis(perfluorobutyl)-1,4-bis(4-pyridyl)benzene, Figure 12b and c), in which its pore surface was covered with perfluorobutyl substituents. The installation of

Figure 12 Structures of organic bridging and terminal ligands with perfluoroalkane substituents, (a) 1,3-bis(4-pyridylethynyl)-2-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)benzene, (b) 2,5-bis(perfluorobutyl)terephthalic acid, (c) 2,5-bis(perfluorobutyl)-1,4-bis(4-pyridyl)benzene and (d) perfluoroalkane carboxylic acid.

perfluorobutyl groups to both neutral and anionic bridging ligands enabled the formation of densely fluorinated pores (Figure 13a). The desolvated form of this MOF was found to show preferential adsorption for CO₂ and O₂ over N₂, Ar and CO with hysteresis, which may be caused by the high dissolving ability of perfluoroalkanes for CO₂ and O₂. Using the solvent-assisted ligand incorporation technique, Snurr and colleagues⁴⁵ succeeded in the incorporation of terminal perfluoroalkane carboxylate (Figure 12d) within the three-dimensional Zr-based MOF, [Zr₆(μ₃-OH)₈(OH)₈(TBAPy)₂] (NU-1000, H₄TBAPy = 1,3,6,8-tetrakis(*p*-benzoic acid)pyrene), as shown in Figure 13b. The octahedral Zr₆ cluster has eight terminal -OH ligands, which can be exchanged with a variety of monocarboxylate ligands, including perfluoroalkane carboxylate, without destruction of the framework. Detailed sorption measurements and theoretical modeling confirmed that (1) the NU-1000 functionalized with a perfluoroalkane carboxylate exhibited a systematically higher value

Figure 13 (a) Crystal structure of $[\text{Cu}(\text{bpbtp})(\text{L5})(\text{DMF})]\cdot\text{DMF}$. Perfluorobutyl groups are coloured blue. Reproduced from Jeon *et al.*⁴⁴ (b) Crystal structure and solvent-assisted ligand incorporation in $[\text{Zr}_6(\mu_3\text{-OH})_8(\text{OH})_8(\text{TBAPy})_2]$ (NU-1000). Reproduced from Deria *et al.*⁴⁵

for the heat of adsorption than the parent NU-1000 with increasing the length of the perfluoroalkane chain and (2) the Zr_6 cluster and perfluoroalkane synergistically acted as the primary CO_2 adsorption sites. The C–F dipole in the perfluoroalkane carboxylate contributed to the favorable C–F $\cdots$ CO_2 interaction.

POSTSYNTHETIC TRIFLUOROMETHYL MODIFICATION OF MOF USING A PLASMA-ENHANCED CHEMICAL VAPOR DEPOSITION

Decoste *et al.*⁵⁷ reported a unique technique to modify an internal pore surface of MOF with trifluoromethyl groups. The postsynthetic treatment of the famous three-dimensional hydrophilic MOF, $[\text{Cu}_3(\text{btc})_2]$ (HKUST-1, $\text{H}_3\text{btc} = 1,3,5\text{-benzenetricarboxylic acid}$),⁵⁸ with a plasma-enhanced chemical vapor deposition of perfluorohexane yielded a hydrophobic form of HKUST-1 (herein referred to as ‘HKUST-1 plasma’). The HKUST-1 plasma got CF_3 groups on the surface of the pores with maintenance of the overall crystal structure of HKUST-1 and the presence of the CF_3 groups had an important role in perfluorohexane loading. Thus, the HKUST-1 plasma with perfluorohexane guests showed an enhanced stability to ammonia and

water and an enhanced ammonia adsorption capacity compared with untreated HKUST-1.

CONCLUSION AND OUTLOOK

In this review article, we organized the structures and porous properties of MOFs/PCPs decorated with fluorinated building blocks such as fluorine- or trifluoromethyl-functionalized organic bridging ligands, inorganic fluorinated anions and perfluoroalkane-functionalized organic ligands. The manipulation of porous structures using fluorine-containing building blocks leads to fascinating porous properties such as high hydrophobicity, preferable adsorption for targeted gases, flexible pores and specific perfluoroarene–arene interaction. In addition, we expect that fluorine functionalization has great potential to give other novel and beneficial properties to MOFs/PCPs.

The existence of high-energy C–H and/or O–H oscillators in luminescent coordination compounds causes a decrease in emission intensity. Utilization of fluorinated organic ligands with low-energy C–F bonds is effective for reducing/eliminating the non-emissive process associated with vibrational relaxation. Chen *et al.*⁵⁹

compared the luminescent properties of two three-dimensional MOFs, $\{[\text{Er}_2(1,4\text{-bdc})_3(\text{DMF})_2(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}$ and $\{[\text{Er}_2(\text{tetrafluoroterephthalate})_3(\text{DMF})(\text{H}_2\text{O})]\cdot\text{DMF}\}$. The partially desolvated fluorinated MOF $\{[\text{Er}_2(\text{tetrafluoroterephthalate})_3(\text{DMF})]\cdot\text{DMF}\}$ showed higher Er(III)-based emission intensity than the desolvated non-fluorinated MOF $[\text{Er}_2(1,4\text{-bdc})_3]$. The hfa (hexafluoroacetylacetonate) chelating ligand is also a good building unit for the construction of MOFs exhibiting strong emissions. Hasegawa and colleagues⁶⁰ reported the one-dimensional Eu(III) coordination polymers, $[\text{Eu}(\text{hfa})_3(\text{L})]$ (L = bidentate phosphane oxide ligands). In particular, a high-emission quantum yield ($\Phi_{\text{Ln}} = 83\%$ in the solid state) was observed in $[\text{Eu}(\text{hfa})_3(\text{dppcz})]$ (dppcz = 3,6-bis(diphenylphosphoryl)-9-phenylcarbazole). Although the luminescent properties given in this paragraph are not related to porous properties, it is expected that this strategy to use fluorinated ligands is available for the construction of luminescent MOFs showing a significant guest-responsive change in emission properties in future sensing devices.

Fine control of framework flexibility is one of the challenging issues in MOF/PCP chemistry. A solid-solution approach based on organic bridging ligands such as substituted dicarboxylates has been applied to tune the flexibility.^{61,62} Inorganic fluorinated monoanions have the potential to endow MOFs/PCPs with flexibility and the degree of flexibility is dependent on the kind of these monoanions. For example, we found inorganic monoanion-dependent acetone adsorption properties of porous assemblies of coordination complexes, $[\text{Cu}(\text{A})_2(\text{pyridine})_4]$ (A = PF_6^- , BF_4^- , CF_3SO_3^- and CH_3SO_3^-).⁶³ The desolvated forms had no pores and showed no N_2 and CO_2 adsorption at all. However, the adsorption isotherms for acetone at 283 K clearly indicated that the porous assemblies of coordination complexes with PF_6^- or BF_4^- monoanions took in acetone guests with structural changes, whereas the porous assemblies of coordination complexes with CF_3SO_3^- or CH_3SO_3^- monoanions exhibited no response to acetone. Furthermore, these monoanions are often coordinated to the metal centers in a monodentate manner, which is effective in an unalterable framework topology during complete or partial anion displacement. We believe that these characteristics in inorganic fluorinated monoanions contribute to the controllable flexibility in MOFs/PCPs by mixing more than two kinds of monoanions.

Charge- and electron-transfer MOFs/PCPs composed of electron donor and acceptor units may show fascinating electronic properties (magnetic, conductive and ferroelectric properties) coupled with porous properties.⁶⁴ Modification of organic ligands by fluorine atom with the highest electronegativity and small van der Waals radius enables to drastically change the degree of charge/electron transfer with less effect in steric hindrance, resulting in a fine tuning of electronic structures and properties. A series of electronically active carboxylate-bridged paddle-wheel Ru dimers can be utilized as an electron-donor building unit in MOFs/PCPs frameworks with electron-acceptor building units.

In addition, it is important to provide new synthetic methods to obtain fluorine-functionalized MOFs/PCPs. Partial incorporation of fluorine-containing molecules into pores of MOFs/PCPs may be a new approach to obtain fluorine-dominated porous properties. Uemura and colleagues⁶⁵ hint at the possibility of this synthetic approach. Oligo(vinylidene fluoride) was confined in $1 \times 1 \text{ nm}^2$ pores of the three-dimensional MOF, $[\text{Tb}(1,3,5\text{-benzenetrisbenzoate})]$,⁶⁶ without any fluorine substituents to elucidate the dynamics of oligo(vinylidene fluoride) in restricted space. Although the parent MOF showed a typical type I N_2 isotherm with the Brunauer–Emmett–Teller specific surface area of $730\text{--}930 \text{ m}^2 \text{ g}^{-1}$, the obtained composite adsorbed negligible amount of N_2 gas, indicating no accessible pores after the

incorporation of oligo(vinylidene fluoride). However, we expect that if pores can be filled with an appropriate amount of fluorine-containing molecules, the composite may retain sufficient accessibility for other guests with a fluorine-modified pore surface. Partial incorporation of ionic liquids with inorganic fluorinated anions into MOFs/PCPs is also effective for creating a fluorine-modified pore surface.⁴²

Finally, we anticipate that this review will attract much attention among not only MOF/PCP scientists but also many researchers involved in other scientific fields and provide opportunities to investigate new and/or reported fluorine-functionalized MOFs/PCPs towards future applications.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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