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Hydrogen Bond Reformation in Tetracarboxylic Acid-Based Organic Frameworks with Square Lattice Topology

Haruka Tsuji[a] and Ichiro Hisaki*[a]

The weak and reversible nature of hydrogen bonds endows porous materials with structural flexibility. In this article, we highlight structural transformations involving the cleavage and reformation of hydrogen bonds—termed H-bond reformation. To enable control over H-bond reformation through molecular design, we examine and discuss key structural features.

Particular attention is given to tetracarboxylic acids bearing 4,4′-dicarboxy-o-terphenyl moieties as scaffolds for inducing H-bond reformation. These insights are expected to guide the rational design of dynamic porous materials with tunable properties and stimuli-responsive behavior.

1. Introduction

The flexibility of porous organic materials has garnered significant interest for over the past two decades, as it can lead to fascinating properties and functions.[1,2] Significant progress has been made in the fields of representative porous organic materials such as metal-organic frameworks (MOFs)[3] or porous coordination polymers (PCPs),[4,5] covalent-organic frameworks (COFs),[6] and porous organic cages (POCs).[7] In these systems, various transformation patterns have been investigated, and structural studies[8,9] have contributed to expanding the scope of their applications. Examples of their flexible behavior include structural transformations such as shrinkage or expansion of the voids–referred to as breathing,[10–12] changes in stacking or interpenetration manners,[13–15] and local dynamics driven by molecular isomerization[16,17] or conformational flexibility.[18–20]

Hydrogen-bonded organic frameworks (HOFs) [21–23] have emerged as a promising flexible porous materials in recent years. HOFs are formed through hydrogen bonds (H-bonds) and other molecular interactions. Typically, HOFs are constructed by crystallization using guest solvents, which help to make porous frameworks by occupying the void space.[24,25] In early studies, guest removal frequently led to framework collapse due to the weakness of H-bonds. In 2011, Chen and coworkers investigated the transformation of **HOF-1** by observing changes in powder X-ray diffraction (PXRD) patterns, which indicated that **HOF-1** showed shrinkage of its voids upon removal of the guest molecules.[26] After that, their group also sug-

gested the crystal structure of **HOF-5** after the transformation by Rietveld refinement analysis.[27] Hisaki and coworkers reported a series of layered HexNet HOFs (**Tp-1**, **T12-1**, **T18-1**, and **Ex-1**). They demonstrated that HOFs **Tp-1** and **T12-1** undergo layer sliding upon guest solvent release, as revealed by crystal structure prediction and Rietveld refinement analyses.[28] In 2019, Chi and coworkers revealed the structures of **8PN** frameworks before and after transformations by single-crystal X-ray diffraction (SXRD) analysis.[29] Over the past few years, some HOFs have been known to show single-crystal-to-single-crystal transformations.[30,31] The atomic-level structures before and after transformations provide us with the opportunity to establish a strategy for designing transformable HOFs.

The weak and reversible nature of H-bonds can impart a unique type of transformation, involving the cleavage and reformation of H-bonds. Here, we refer to such transitions as "H-bond reformation." Details and illustrative examples are presented in the next section and Figure 1.

To program H-bond reformation by designing building block molecules, it is crucial to identify the key structural features that control the transformations. In this article, we discuss the common features of H-bond reformation reported in previous studies. In particular, our attention is directed to tetracarboxylic acid-based HOFs, which are a common platform for observing H-bond reformation as described in section 3.

2. Classification of H-Bond Reformation

The reformation can be classified into two types depending on guest–framework interactions: guest-mediated or guest-independent H-bonds. Representative examples are illustrated as schematic diagrams in Figure 1.

2.1. Guest-Mediated H-Bonds

Polar guest solvents like alcohols or amines sometimes make H-bonds with building block molecules. Ejecting guest molecules from guest-mediated H-bonds is a reasonable way to induce

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changes in bonding motifs (Figure 1a). For one of the pioneering studies, Jiang, Chen and coworkers reported that **HOF-30(M)**, **HOF-30(E)**, and **HOF-30(P)** transformed to **HOF-30a**.[32] **HOF-30(M)**, **HOF-30(E)**, and **HOF-30(P)** have *dia*-networks formed by guest-bridged H-bonds between a carboxylic acid dimer and two alcohol molecules bridging the dimer (Figure 1d left). The H-bonds were cleaved by evaporating alcohol molecules, resulting in **HOF-30a**, which retains *dia*-networks but is formed by self-complementary H-bonds of a carboxylic acid dimer (Figure 1d right). PXRD measurements showed that soaking **HOF-30a** into alcohol resulted in the recovery of original HOFs, indicating reversible transformations.

Reformable HOFs formed through guest-mediated H-bonds are not restricted to specific network types but are widely observed across various bonding units. Reformation of other bonding motifs has also been reported—for example, between phosphonic acid groups and amines in **BPPA**,[33] sulfonic acid, amines, and water in **iHOF-10** and **iHOF-11**,[34] carboxylate anions, ammonium cations, and water in **GC-1**.[35] In some cases, transitions from MOF to HOF have also been observed (Figure 1e).[36]

In another case, guest molecules can block the H-bonding sites of building block molecules. Upon evaporation of these guests, the sites become accessible again, allowing H-bond reformation (Figure 1b).[37] Transformation caused by NH_3 capture has been demonstrated by Li, Chen, and coworker.[38] They constructed **FDU-HOF-3** through self-complementary H-bonds of a carboxylic acid dimer (Figure 1f left) and confirmed that the HOF can retain its structure after activation. The HOF transformed into an amorphous state upon NH_3 gas capture and recovered its original structure through mild heating to remove NH_3. The H-bonds between carboxylic acid and NH_3 (Figure 1f right) were suggested based on FT-IR spectroscopy and DFT calculation. **HOF-NBDA (DMA)** [39] reported by Wu and coworkers has *hcb*-network formed by truncated carboxyl dimers (Figure 1g left). The one oxygen atom of terminal carboxylic acid in the

building block **NBDA** is bound to dimethylamine (DMA), and the other one makes a H-bond with another **NBDA**. Removal of DMA changed **HOF-NBDA (DMA)** to **HOF-NBDA**, which was formed by self-complementary H-bonds of a carboxylic acid dimer (Figure 1g right).

Desolvation or guest exchange involving guest-mediated H-bonds can readily induce reformations in HOFs, often leading to reversible H-bond cleavage and reformation. While this approach allows access to diverse bonding motifs, it remains challenging to predict the resulting structures. Furthermore, such transformations often yield nonporous or amorphous frameworks.[40]

2.2. Reformations of Guest-Independent H-Bonds

Unlike guest-mediated H-bonds, guest molecules are not always directly involved in H-bonds. Even in this case, guest removal can trigger H-bond reformation (Figure 1c).
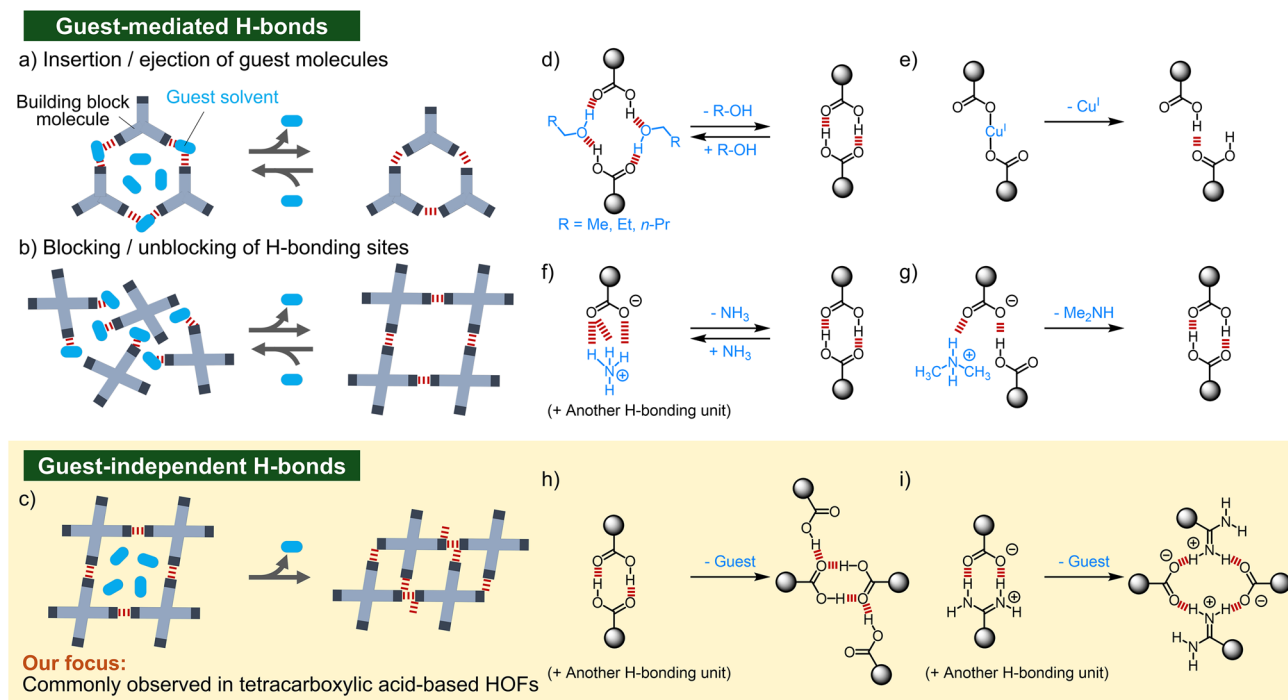
In 2021, **PFC-77(PFC-78)**,[41] **CP-PP-1**,[42] and **HOF-BrPQ-1**[43] were reported one after another as the HOFs showing reformation. By coincidence, all these HOFs were constructed using tetracarboxylic acid derivatives with a planner π-conjugated core. They have similar *sql*-networks formed by H-bonds of a carboxylic acid dimer, which are stacked in layers. Guest exchange in **PFC-77** and **PFC-78**, and partial guest removal in **CP-PP-1** and **HOF-BrPQ-1** induced reformation of the H-bonds into alternative motifs. Guest exchange was achieved by immersing **PFC-77** or **PFC-78** in CH_2Cl_2 for 10 minutes, whereas partial guest removal was carried out by heating **CP-PP-1** at 142 °C and **HOF-BrPQ-1** at 120 °C. It is notable that their void spaces were shrunk, but still existed. After these reports, similar behaviors have been observed in other tetracarboxylic acid-based HOFs. After reformation, the motifs of H-bonds were not all the same in these HOFs, but some of them were formed among four carboxylic acid groups (Figure 1h right).
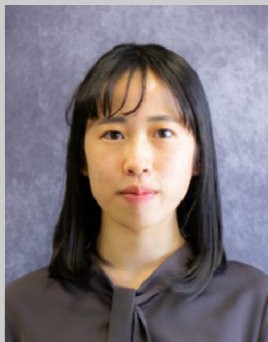
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Figure 1. H-bond reformations triggered by removal or exchange of guest solvents. a) Insertion or ejection of guest molecules into guest-mediated H-bonds, b) blocking or unblocking of H-bonding sites, and c) reformation between guests-independent H-bonds. d–i) Examples of H-bonding motifs of each H-bond reformation.

As another example, White and coworkers constructed the charge-assisted HOFs from tetraamidinium and tetracarboxylate.[44] A terminal amidinium group and a terminal carboxylate group were dimerized through H-bonds (Figure 1i left). The H-bonded networks were sixfold interpenetrated, resulting in HOF α-$\mathbf{1}^{C/C}$. Upon heating, α-$\mathbf{1}^{C/C}$ transformed to β-$\mathbf{1}^{C/C}$, where the H-bonds became slightly shorter. Further heating lets β-$\mathbf{1}^{C/C}$ change into γ-$\mathbf{1}^{C/C}$ by breaking and reforming H-bonds. In γ-$\mathbf{1}^{C/C}$, the H-bonds were formed among four terminal groups, including two amidinium groups and two carboxylate groups (Figure 1i right).

These transformations suggest that H-bond reformation can be regulated through molecular design. The HOFs described above feature directional H-bonds, which can yield stable and highly crystalline frameworks even after reformation. The building block molecules of these HOFs share common characteristics, notably being tetracarboxylic acids. Moreover, although the voids undergo significant changes in size and shape during transformation, they often remain intact. In the following section, we highlight H-bond reformation in tetracarboxylic acid-based HOFs and explore the relationship between their structural features and transformation behavior.
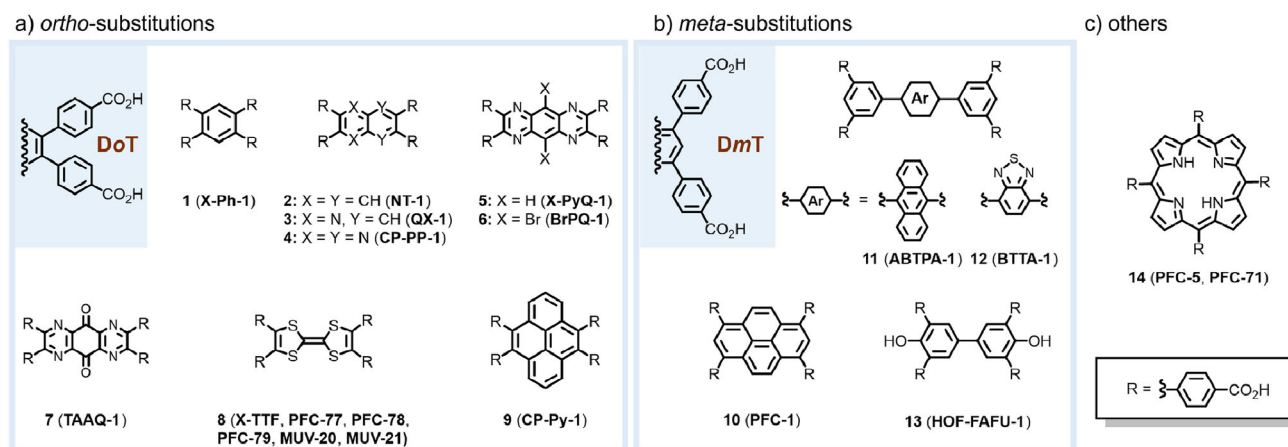
3. Reformable HOFs Based on Tetracarboxylic Acids

3.1. Tetracarboxylic Acid for Reformable *Sql*-HOFs

A tetracarboxylic acid bearing four 4-carboxyphenyl groups on a planar π-conjugated core has been utilized for constructing lay-ered *sql*-networks. Figure 2a illustrates tetratopic building block molecules that have been used in reformable layered *sql*-HOFs. As an example of the simplest tetracarboxylic acid-based component, benzene-cored derivative **1** has been reported in 2017 to form layered *sql*-networks, **X-Ph-1**,[45] through H-bonds of a carboxylic acid dimer. Although transformation of **1** was suggested by variable-temperature PXRD, the resulting structure has yet to be elucidated.

A series of bicyclic aromatic-cored derivatives **2**, **3**, and **4** have been demonstrated to construct isoreticular *sql*-networks.[46] All these HOFs (**NT-1**, **QX-1**, and **CP-PP-1**) exhibited H-bond reformation, however, the reformed H-bond motifs were different. These studies have shown that the molecular core plays a key role in modulating H-bond reformation in HOFs. Another set of isoreticular *sql*-networks comprises three frameworks, each constructed from one of the tricyclic aromatic-cored building blocks (**5**, **6**, or **7**). Their HOFs (**X-PyQ-1**,[45] **HOF-BrPQ-1**, and **TAAQ-1**,[47] respectively) also have been known to transform, although the transformed structure from **HOF-X-PyQ** has yet to be elucidated due to a significant decrease in crystallinity. Both **HOF-BrPQ-1** and **TAAQ-1** exhibited the same reformed H-bond motif: a cross-shaped carboxylic acid tetramer composed of a carboxylic acid dimer and two additional carboxy groups.

H-bond reformation in HOFs based on functional π-conjugated cores, such as tetrathiafulvalene (TTF) and pyrene has also been explored. **8** has been known to construct various *sql*-networks in response to crystallization conditions.[41,45,48] Cao and coworkers have constructed **PFC-77** and **PFC-78**. Both have *sql*-networks formed through H-bond of a carboxylic acid dimer, while their stacking manners were different. These HOFs were found to transform into **PFC-79** upon immersion in CH_2Cl_2. The

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Figure 2. Tetracarboxylic acids forming a layered *sql*-HOFs bearing a) 4,4′-dicarboxy-*o*-terphenyl (D*o*T) moieties, b) 4,4′-dicarboxy-*m*-terphenyl (D*m*T) moieties, and c) four 4-carboxyphenyl groups at the *meso* positions. Compounds **1**, **8**, **10**, and **14** are known to form some polymorphic structures depending on crystallization conditions; however, in this article, we focus exclusively on those forming representative layered *sql*-HOFs.

reformed H-bond motif in **PFC-79** is a cross-shaped carboxylic acid tetramer, which is identical to the motifs observed in **NT-2**, **HOF-BrPQ-2**, and **TAAQ-2**. Pyrene-cored *sql*-networks **CP-Py-1**[49] has been reported to exhibit H-bond reformation, resulting in **CP-Py-3**. **CP-Py-3** had 1D H-bonded chain structure formed through a carboxylic acid dimer.

Taken together, these studies suggest that 4,4′-dicarboxy-*o*-terphenyl (D*o*T) moiety is a key structural feature for controlling H-bond reformation. We now turn to a comparison of this structure with other related frameworks.

3.2. Comparison of *Ortho*- and *Meta*-Terphenyl Moieties

Tetracarboxylic acids bearing 4,4′-dicarboxy-*m*-terphenyl (D*m*T) moieties, which can also construct *sql*-networks, are presented in Figure 2b. Anthracene-cored derivative **11** has been reported to form a solvated HOF, **ABTPA-1**.[50] Upon desolvation, **ABTPA-1** transformed into **ABTPA-2** accompanied by a change in stacking manners, while retaining the H-bonded *sql*-topology. A geometrically analogous compound **12** also has constructed a layered *sql*-HOF **BTTA-1**,[51] which can retain its structure up to 270 °C. Biphenyl-based derivative **13** has been confirmed to form the robust network **HOF-FAFU-1**,[52] which retains its structure after guest exchange with *n*-hexane followed by degassing. Notably, the pyrene-based compound **10** bearing D*m*T moieties formed a robust HOF **PFC-1**,[53] in contrast to compound **9**, which features D*o*T moieties and yielded a reformable HOF as described in the previous section. In addition, porphyrin-based compound **14**, functionalized with four 4-carboxyphenyl groups at the *meso* positions, has been employed in the construction of *sql*-HOF **PFC-5** [54] or **PFC-71**.[55] **PFC-5** was revealed to retain its structure at least up to 90 °C. Above 120 °C, broadened peaks were observed in the variable-temperature PXRD pattern. The structure of this high-temperature phase remains unidentified. These comparisons suggest that tetracarboxylic acids bearing D*o*T moieties are more likely to undergo H-bond reformation.

3.3. Retained or Reformed H-Bonds in a Transformation

To explore design principles for reformable HOFs, we examined the molecular conformations and packing arrangements in these frameworks. The carboxyl O···O distance of H-bond (d_{O1} and d_{O2} in Figure 3b; d_{O1}' and d_{O2}' in Figure 3c) and the dihedral angle between the core and peripheral phenylene groups (φ_1 and φ_2 in Figure 3b; φ_1' and φ_2' in Figure 3c) are listed in Table 1. Except for the cases of **QX-1** and **NT-1**, the molecules adopt a conformation characterized by two phenylene rings with distinct dihedral angles ($\varphi_1 \simeq 20°$ and $\varphi_2 \simeq 60°$). In **QX-1** and **NT-1**, the steric hindrance of the aromatic hydrogen atoms in the core prevents the dihedral angle from being small. The carboxylic acid dimers and their corresponding O···O distances, linked through the phenylene rings oriented at φ_1 and φ_2 are denoted as dimer-1 (d_{O1}) and dimer-2 (d_{O2}), respectively. In all systems, d_{O1} is slightly elongated to d_{O1}' during the reformation. This corresponds to a destabilization of approximately 30 kJmol^{-1}, as evaluated by intermolecular interaction energy.
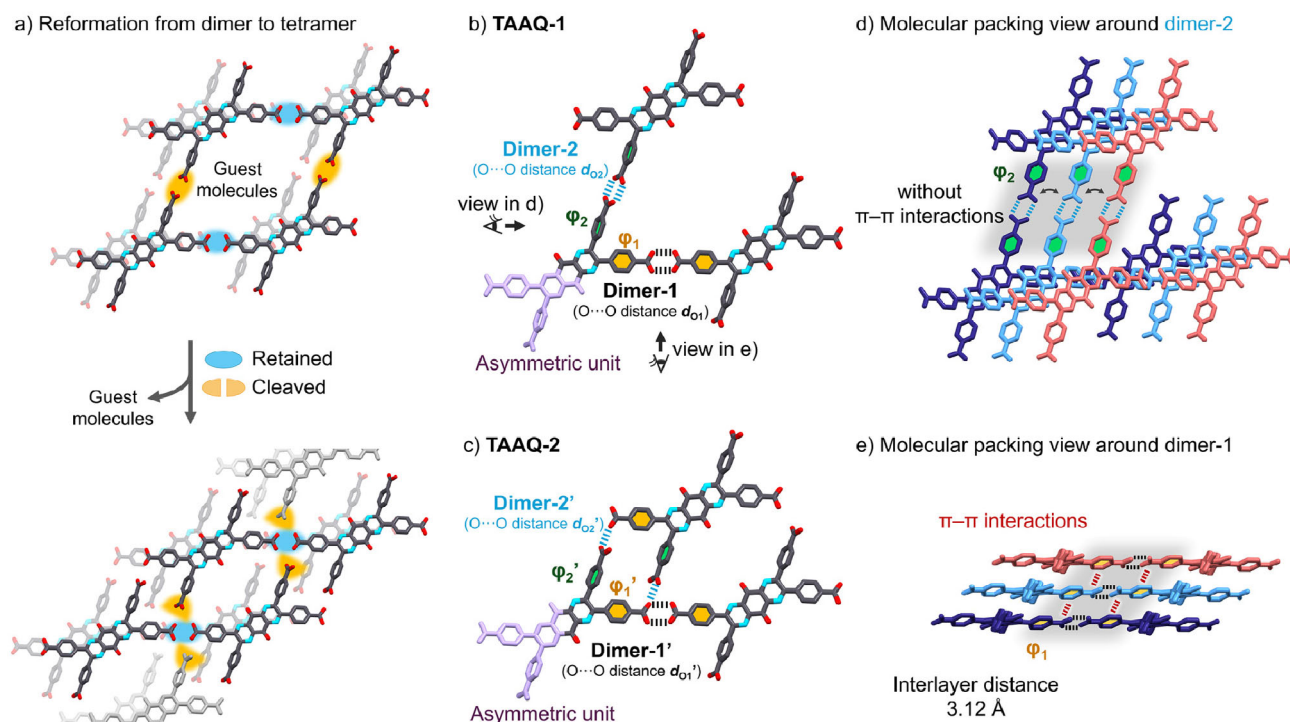
Interestingly, in all HOFs, dimer-1 was retained, whereas dimer-2 was cleaved and reformed. Analysis of the crystal packing shows that dimer-1 is stabilized by π–π stacking with surrounding molecules (Figure 3e), whereas dimer-2 lacks such stabilizing interactions (Figure 3d).

4. Summary and Outlook

In this article, we have explored the structural features that trigger H-bond reformation in HOFs. In the first part, we discussed the role of guest molecules in H-bond reformation, contrasting guest-mediated and guest-independent H-bonding motifs. Both types can undergo cleavage and reformation into alternative H-bonding motifs.

In particular, we showed that guest-independent H-bond reformation tends to occur in layered 2D *sql*-HOFs constructed from tetracarboxylic acids bearing D*o*T moieties. In most robust

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Figure 3. a) H-bond reformations in *sql*-HOF **TAAQ-1** composed of tetracarboxylic acid **7**. H-bonding motifs b) before and c) after reformation. Each label (d_{O1}, d_{O2}, φ_1, and φ_2 corresponds to the values listed in Table 1. Molecular packing view around d) dimer-1 and e) dime-2.

Table 1. Structural information of H-bonds and molecular conformation before and after transformation.

Initial structure					Transformed structure				
	d_{O1} / Å	d_{O2} / Å	φ_1 / °	φ_2 / °		d_{O1}' / Å	d_{O2}' / Å	φ_1' / °	φ_2' / °
CP-PP-1	2.62	2.62	19.7	55.9	**CP-PP-2**	2.63	–[b]	21.8	55.9
HOF-BrPQ-1	2.64	2.63	22.7	63.9	**HOF-BrPQ-2**	2.70	2.80	27.5	63.9
PFC-77	2.61	2.64	25.2	66.3	**PFC-79**[a]	2.72	2.83	17.4	66.3
TAAQ-1	2.60	2.59	19.5	62.5	**TAAQ-2**	2.69	2.81	19.5	62.5
QX-1	2.61	2.60	42.4	46.9	**QX-2**	2.63	–[b]	28.6	42.4
NT-1[a]	2.61	2.62	49.2	50.7	**NT-2**	2.64	2.70	37.4	50.4

[a] In **NT-1** and **PFC-79**, asymmetric unit contains one building block molecule, having four phenylene rings with distinct dihedral angles (φ_1, φ_2, φ_3 and φ_4). The average dihedral angles of the 4-carboxyphenyl groups forming dimer-1 and dimer-2 are listed as φ_1 and φ_2, respectively.
[b] These HOFs are formed through H-bonds different from those of a carboxylic acid tetramer (**CP-PP-2**: formed through OH···N H-bonds, **QX-2**: formed through weak interaction between a carboxylic oxygen atom and a hydrogen atom on phenylene groups).

layered 2D frameworks, coplanarity between the core and peripheral phenylene rings is favored to maximize interlayer $\pi-\pi$ overlap. By contrast, in tetracarboxylic acids bearing D*o*T moieties, steric repulsion between the *ortho*-linked phenylene rings prevents both from adopting a coplanar conformation with the core ($\varphi_1 \simeq 20°$ and $\varphi_2 \simeq 60°$). Thus, H-bonds stabilized by interlayer $\pi-\pi$ interactions tend to be retained ($\varphi_1 \simeq 20°$), whereas those lacking $\pi-\pi$ interactions are more readily cleaved ($\varphi_2 \simeq 60°$). This key structural feature leads to H-bond reformation upon guest removal.

The field of functional HOFs exploiting the weak and reversible nature of H-bonds is rapidly growing. Realizing control over H-bond reformation would enable molecular-level functional modulation of flexible HOFs and broaden the

potential of dynamic porous materials for stimuli-responsive applications.

Acknowledgments

Conflict of Interest

The authors declare no conflict of interest.

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Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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