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A Comparison of Two Isoreticular Metal-Organic Frameworks with Cationic and Neutral Skeletons: Stability, Mechanism, and Functionality

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ABSTRACT: Although many ionic metal-organic frameworks (MOFs) have been reported, people still know few about how the charge of skeleton affect the entire properties of MOF materials. We here for the first time report that the chemical stability of MOFs can be substantially improved through embedding electrostatic interactions in structure. As demonstrated, MOF with a cationic skeleton is impervious to extremely acidic, oxidative, reductive, and high ionic strength conditions such as 12 M HCl (301 days), aqua regia (86 days), H_2O_2 (30 days), and seawater (30 days), which is surprisingly unprecedented in MOFs. Density functional theory calculations suggested that the cationic framework shows repulsive interaction and large steric hindrance toward the positively charged species in microenvironments, thus protecting the vulnerable dative bonds in structure to achieve high chemical stability. Diverse functionalities can be simultaneously bestowed by substituting the counterions of the charged framework with identically charged functional species, which broadens the horizon in the design of MOFs adaptable to a demanding environment with specific functionalities.

Metal-organic frameworks (MOFs) have attracted significant attention across many disciplines in material chemistry due to their high porosity, well-crystallinity, and the liberty of tuning on structure and components[1]. However, their practical applications have been hampered by relatively low chemical stability. Considering that most metal-ligand bonds have much lower bonding energies than those of C-C, C-N and C-O covalent interactions in ligands[2], the most intuitive strategy for enhanced stability is to reinforce the coordination bonds, the weakest point in MOF structure[3]. Along this line, tremendous research has been directed to the construction of MOFs with the guidance of hard and soft acid and base theory[4], integration of hydrophobic groups on ligands[5], hydrophobic polymer coatings[6], and so on[7]. Although enhanced stability has been achieved with the advent of these methodologies, there are barely MOFs surviving extremely harsh conditions, for example, the concentrated acid or high ionic strength solution engaging in the processes of the nuclear fuel cycle and seawater extraction[8]. Therefore, the exploration of simple and yet effective strategies for the design of robust MOFs is still a long-term challenge.

Electrostatic interaction, omnipresent in nature, is one of the dominant forces responsible for the stability of many materials such as biomolecules, membranes, and colloids[9]. In fact, this type of interaction also exists in ionic MOFs where the skeletons are either cationic or anionic with counterions inside of pores[10]. The charged skeleton might exhibit attractive or repulsive interactions toward the guest species in the microenvironment and affect the stability of MOF materials. However, the charge backbones and the existed electrostatic interaction have yet to arouse broad attention of chemists in MOF field. If one can take advantage of the repulsive interaction to limit the access of competing reagents to the vulnerable dative bonds, can the stability of MOFs be significantly improved? This speculation inspires our interest to unveil the chemistry between electrostatic interaction and MOF stability, which is convoluted and uncertain to date although many ionic MOFs have been reported. A convincing conclusion can be only made from a direct comparison between the MOFs with identical dative bonds and topology but different charge natures, which, unfortunately, are absent in the existing MOFs until now.

Thanks to the structural tailorability of MOFs, herein we designed two isoreticular MOFs with identical dative bonds, space group, and topology, but bearing cationic and neutral frameworks, namely PFC-8 and PFC-9, respectively (PFC = Porous materials from FJIRSM CAS). Very strikingly, the obtained PFC-8 with a cationic skeleton is impervious to extremely acidic, oxidative, reductive, and high ionic strength conditions. This exceedingly high stability is unprecedented in previously reported MOFs[3],[11]. In sharp contrast, PFC-9 maintains structure integrity only in aqueous solutions with a narrow pH range. Density functional theory (DFT) calculation illustrates that the neutral ligands in PFC-8 have a lower affinity toward protons and higher positive charges on metal centers, which protects metal-ligand bonds from the approach of attacking or reactive species. These results unveil for the first time that the chemical stability of MOFs can be dramatically improved by creating an ionic skeleton. Accompanying with the ionic backbones is the prospect of functionalizing MOFs in a convenient, cost-efficient and mild synthetic condition by substituting unbonded counterions with identically charged functional species. As a representative example, we show that PFC-8 can be readily functionalized by exchanging counterions with $PdCl_4^{2-}$ followed with reduction to fabricate MOF composite as a catalyst for formic acid dehydrogenation. This work may open a new pathway to regulate both the stability and functionality of MOFs for diverse applications.

The reaction of 1,4-Di(1H-pyrazol-4-yl)benzene (H_2DPB) with $Ni(CH_3COO)_2 \cdot 4H_2O$ resulted in cubic crystals PFC-9. Single-crystal X-ray diffraction (SCXRD) analysis reveals that DPB^{2-} ions coordinate with Ni^{2+} ions forming a neutrally charged framework[12]. Ni(II) centers are square-planar coordinated by four N atoms to create an infinite metal chain. DPB^{2-} ligands further connect adjacent metal chains to construct a three-dimensional network while leaving a quadrilateral channel with a size of 21×12 Å. To create an isoreticular cationic framework, 1,4-Bis(4H-1,2,4-triazol-4-yl)benzene (BTAB) was designed and successfully synthesized, which has the same geometry and length with H_2DPB but serves as a neutral ligand to coordinate with metal ions. The self-assembly of BTAB with Ni^{2+} cations resulted in PFC-8 with net positive charge on metal nodes attracting Cl^- counterions in channels for charge balance (Scheme 1). SCXRD analysis of PFC-8 reveals that Ni(II) ions are square-planar coordinated by four N atoms and axial-occupied by two bridging Cl^- to form a Ni(II) metal chain. As expected, the obtained PFC-8 and PFC-9 present the same space group (*Imma*) and topology

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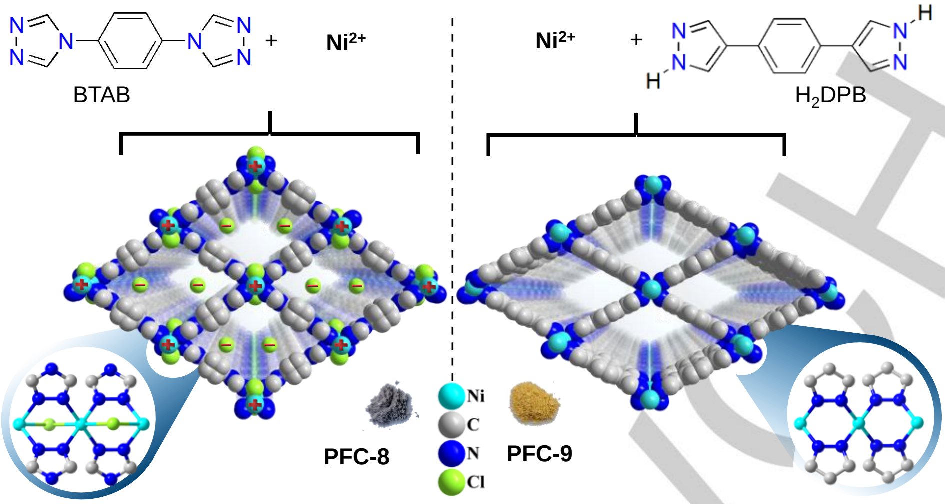
(seh-4,6-Imma)[13] but positively and neutrally charged skeletons, respectively. The



Scheme 1. Schematic representation of the structures of cationic PFC-8 and neutral PFC-9

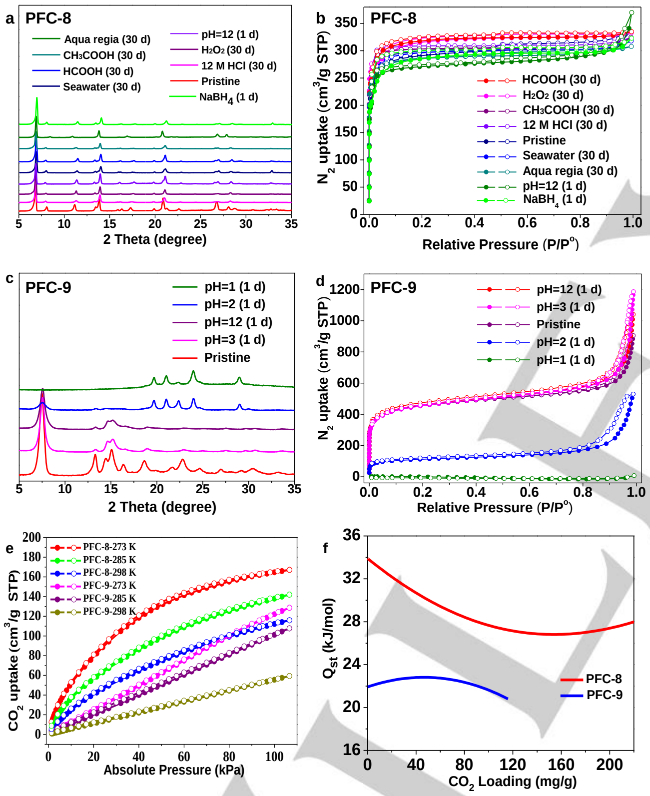


Figure 1. PXRD patterns and N_2 isotherms collected at 77 K for (a, b) PFC-8, (c, d) PFC-9 after various treatments (aqueous solutions with different pH were prepared using HCl). (e) CO_2 isotherms of PFC-8 and PFC-9 at 273 K, 285K, and 298 K. (f) Q_{st} of CO_2 for PFC-8 and PFC-9.

reaction of the same ligands with Cu ions generated another pair of isoreticular MOFs: Cu-btab and Cu-dpb with cationic and neutral framework, respectively (Fig S6.6) [12].

To achieve an accurate analysis, the chemical stability of MOFs in this study was assessed by a combination of PXRD patterns, N_2 isotherms, and single-crystal X-ray diffraction. Figures 1a and 1b show that PFC-8 survives extremely harsh condition including concentrated HCl (301 days), H_2O_2 (30 days), seawater (30 days) and even aqua regia (86 days), which was unprecedented in MOFs (more details in SI, Section 6). It is noted that PFC-8 was still qualified for SCXRD even after being immersed in aqua regia for two days, again confirming its high chemical stability (Table S1). In sharp contrast, PFC-9 can only maintain intact in aqueous solution with pH from 3 to 12 (Fig. 1c-d), comparable to previously reported water/moisture-resistant MOFs[14], but much inferior to PFC-8. A plausible explanation of such a huge disparity on chemical stability can be advanced to the contribution of the cationic framework where the electrostatic repulsion presents between the positive PFC-8 skeleton and the positive ions in solution, therefore saving the labile metal-ligand bonds from being attacked. This hypothesis has been further proved by the DFT calculation discussed later in this manuscript. Additional experimental evidence came from the observation that stabilities of PFC-8 and PFC-9 are on a par with each other in alkaline solutions (up to pH = 12) where the positively charged backbones fail to repel the OH^- ions. Chemical stability studies of the other pairwise MOFs (Cu-btab and Cu-dpb) presents the same trend that the cationic framework is more acid-resistant than the neutral one (Fig S6.6). It's worthwhile to mention that previously reported ionic MOFs did not exhibit excellent stability mainly because they are usually based on weak coordination bonds being sensitive to moisture (for example, Zn-O, Ni-O, and Cu-O)[10],[11], making the electrostatic interaction effect being to no avail. However, in this work, the metal-N bonds possess adequate strength, which allows for the further improvement on stability by taking advantage of the electrostatic interaction in structure. Meanwhile, the corresponding neutrally charged structures, based on the same coordination bonds, components, and topology, are absent in the MOF library for comparison, leaving the contribution of skeleton's charge an open question and unclear to date.

Towards a better understanding of the factors accounting for MOF's collapse, the chemical stability of PFC-8 in other commonly used acids was further investigated. Since protons in the solution could attack the metal-ligand bonds and drive the framework collapse, an intuitive speculation is that the smaller acid dissociation constant (pKa) the acidic species has, the more corrosive effect it causes to MOFs (in the brønsted acid concept). However, we found that the stability of PFC-8 actually does not relate to the pKa values of the brønsted acid (Table S2). A typical example is that HCl has the smallest pKa but does not damage the integrity of PFC-8. It turns out that the strength of the corresponding Lewis base, formed by losing the proton of the acid, is strongly indicative of the corrosive effect of the acid toward PFC-8. A possible reason is that the Lewis base inclines to coordinate with Ni(II) center (as a Lewis acid) and thus causes Ni-N bond dissociation[15]. Of particular note, other factors might also

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affect the stability of MOFs, such as the π-π interaction, hydrogen-bonding, as well as the size/shape/geometry of the lewis base (or the attacking species) [16]. However, here we only focus on the general trend revealed by these experiments. As shown in Table S2, PFC-8 exhibits structural integrity in HCl, HCOOH, CH_3COOH, and aqua regia, detracted porosity in HNO_3, complete decomposition in H_2SO_4 and H_3PO_4.

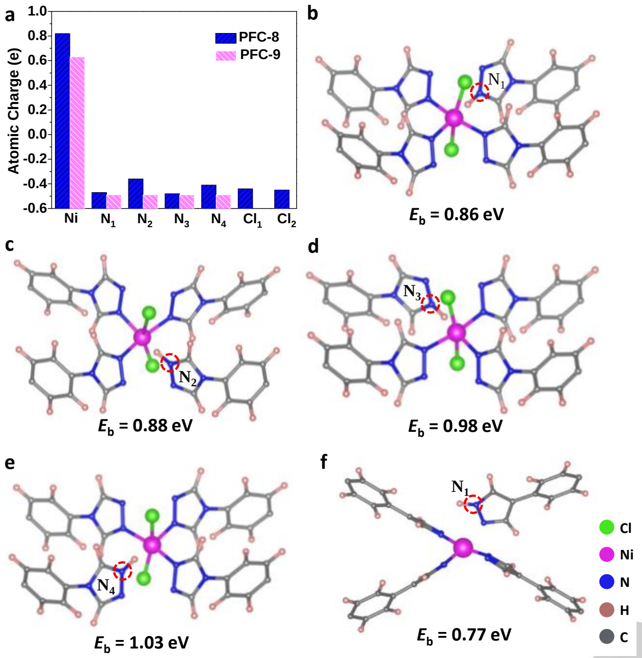

Figure 2. (a) Bader charge analyses for the Ni(II) center and the coordinated nitrogen, chlorine in PFC-8 and PFC-9. Computational optimized configurations and binding energies of a proton with the ligands in PFC-8 (b-e) and PFC-9 (f).

Having obtained the experimental chemical stability of PFC-8 and PFC-9, we turned to theory to gain a deep insight into the influence of charge on structural stability at the atomic level. First-principles calculations were performed at the spin-polarized DFT level using the Vienna ab initio Simulation Package. Geometric optimization reveals that the Ni(II) center in PFC-9 adopts square planar geometry as a low spin complex in a strong crystal field. While in PFC-8, two extra Cl^- ions are coordinated on axial positions, leading to an octahedral geometry occupying the high-spin state in the weak crystal field. Although the existence of Cl^- counterions weakens the Ni-N interaction (experimental evidence of the greater average bond length of 2.05 Å for PFC-8 than 1.86 Å for PFC-9, Fig. S7.3), the large steric hindrance of the octahedral geometry in PFC-8 could effectively protect the Ni(II) center from the attack of reactive species. Meanwhile, Bader charge analysis shows that the Ni(II) center in PFC-8 possesses more positive charges than that in PFC-9, as reflected by the differential charge distribution (Fig. 2a, Section 7). Thus, PFC-8 holds strong repulsive interactions toward the positive guest species in microenvironments.

The binding energies were also calculated to demonstrate the affinity of the positively charged species toward PFC-8 and PFC-9 respectively. Taking proton as an example here, with adding a proton near Ni(II) center, the proton preferentially binds with N atoms of the ligand, consequently dissociating Ni-N bonds. In PFC-8, due to the existence of isolated Cl^- ions, four N atoms connected to the Ni(II) center possess differential charges, resulting in different binding energies (E_b) of 0.86 eV (N_1), 0.88 eV (N_2), 0.98 eV (N_3) and 1.03 eV (N_4). In contrast, the N atoms in symmetrical PFC-9 exhibit even charge distribution and equally low binding energy of 0.77 eV (Figs. 2b-f). This indicates that PFC-9 is more preferential to associate with protons and hence more labile in acidic conditions, coincident with the experimental observation. Therefore, we infer that the high stability of PFC-8 can be ascribed to that the skeleton shows repulsive interaction and large steric hindrance toward the positive guest species, and the neutral ligands of the framework are less likely to be protonated.

Accompanying the framework robustness, of equal importance is the feature that the counterion of PFC-8 can be substituted by other identical charged exogenous species, which offers an opportunity to functionalize MOFs in a mild, convenient, and low-cost synthetic route. This feature is representatively demonstrated here through fabricating ultrafine Pd nanoparticles (NPs) immobilized in PFC-8 for selective formic acid (FA) dehydrogenation[17],[18], which is considered as an excellent pathway for energy supply (H_2) with the advantages of high energy density, nontoxicity, and safety[19]. We substituted Cl^- with $PdCl_4^{2-}$ ions followed by reduction to fabricate PFC-8 supported Pd nanocatalysts (denoted as Pd@Nano-PFC-8). PFC-9 in nanosize was also investigated for comparison. Along with the addition of aqueous K_2PdCl_4 solution into Nano-PFC-8 (dispersed in hexane), noticeable phase separation was observed in 4 minutes, which, however, did not occur in PFC-9 suspension (video 1 and 2 in SI). These phenomena suggested that the electrostatic driving force existing in PFC-8 accelerated the ion-exchange process and therefore increased the hydrophilicity of particles and finally resulted in the phase separation in hydrophobic hexane. Without this electrostatic force, PFC-9 underwent a much slower ion-exchange process, and no visible hydrophilicity change was observed. Correspondingly, after reducing by $NaBH_4$ solution, ultrafine Pd NPs were evenly dispersed in PFC-8 with the mode value of the particle size about 1.75 nm. In contrast, Pd NPs were mainly observed around the periphery of PFC-9 particles as indicated by transmission electron microscopy analysis, energy dispersive X-ray spectroscopy mapping (Fig. 3). A small amount of Pd^{2+} species was observed in the composite as revealed by X-ray photoelectron spectroscopy (Fig S8.6), which probably caused by the incomplete reduction of $PdCl_4^{2-}$ or the partial oxidation of Pd nanoparticles during the washing and drying process. The successful preparation of ultrafine Pd nanoparticle dispersed PFC-8 can be ascribed to the porous cationic charged skeleton which a) allows for the even encapsulation of $PdCl_4^{2-}$ precursor, b) withstands the harsh reductive condition in $NaBH_4$, and c) provides confinement effect preventing nanoparticles from aggregation.

The resulted Pd@PFC-8 exhibited high catalytic activity for hydrogen generation from FA with high turnover frequency (TOF_{Pd} = 5141 h^{-1}, Pd content: 1.13×10^{-6} mol), high selectivity and conversion efficiency (> 99%), which was of an outstanding MOF-supported catalyst for FA decomposition (Fig. 4a, Section 9 in SI)[20]. Although the reaction proceeded in a very harsh condition with high acidity and high ionic strength, Pd@nano-PFC-8 only show a slight decrease on activity in five runs (probably caused by the sample loss during the recycle process) and the Pd NPs remained the original size and even distribution as revealed by TEM analysis (Fig. 4b and 4c). In contrast, Pd@PFC-9 showed much lower conversion (32.7%) and H_2 production rate (TOF_{Pd} = 2443 h^{-1},Pd content: 6.6×10^{-7} mol) and failed to catalyze the reaction from the second run due to the fragile PFC-9 structure (Fig. 4d and Fig. S8.9).

In conclusion, by harnessing the structural tailorability of MOFs, cationic PFC-8 and neutral PFC-9 with identical dative bond, topology, and space group have been successfully synthesized. The postively charged structure PFC-8 exhibits far superior chemical stability than PFC-9 and can survive various extremely harsh conditions. Such high stability has never been achieved in MOFs.

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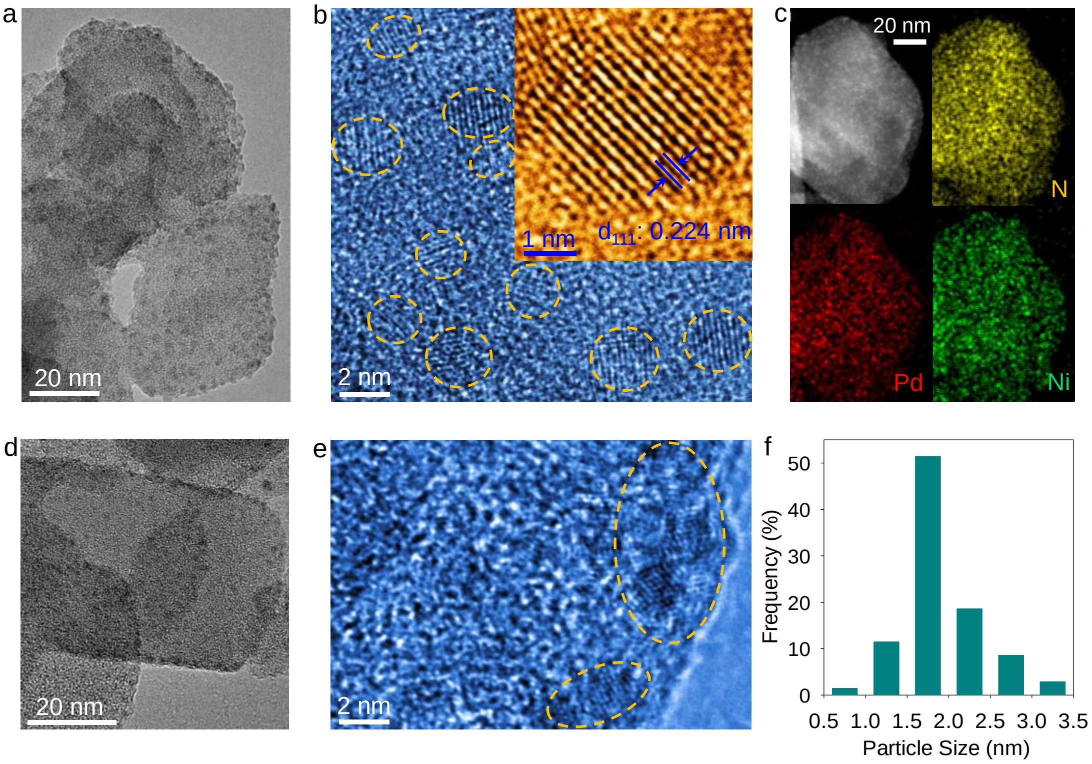

Figure 3. (a, b) HRTEM images and (c) Dark-field TEM-EDX mapping of Pd@Nano-PFC-8, Pd NPs are circled in yellow. (d, e) HRTEM images of Pd@PFC-9. (f) Pd particle size distribution in Pd@Nano-PFC-8.

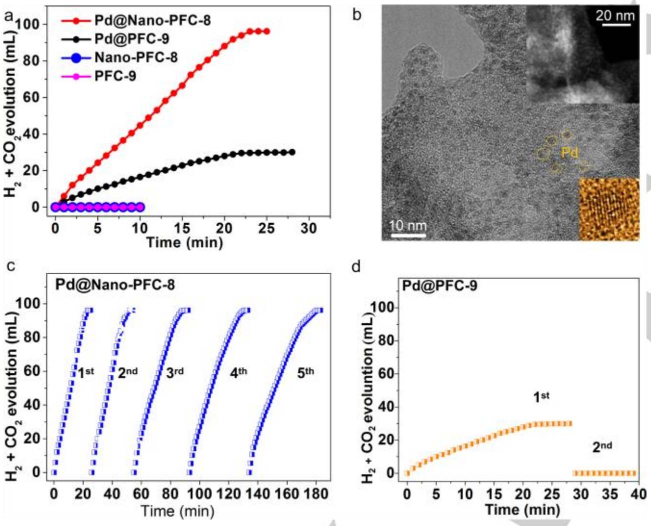

Figure 4. (a) Gas evolution with Pd@Nano-PFC-8 and Pd@PFC-9 catalysts. (b) TEM images of Pd@Nano-PFC-8 after five recycling runs. Insets show the dark-field TEM image (top) and HRTEM image (down). The recyclability of (c) Pd@Nano-PFC-8 and (d) Pd@PFC-9 for FA dehydrogenation. Pd contents are 1.20 wt% for Pd@Nano-PFC-8 and 0.70 wt% for Pd@PFC-according to the inductively coupled plasma analyses.

The charged skeleton further enables the integration of functional species into the structure through an ion-exchange methodology for MOF functionalization. Overall the discovery considerable new insight into the structural stability of MOFs and expands our ability to design MOFs adapted to a demanding environment with specific functionality. Many intriguing questions still remain and will be subject to further research, including the exploration of other strategies for fabricating MOFs with cationic or anionic skeletons, the synergism between a charged skeletons and guest species.

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Table of Contents