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Communications

Metal–Organic Frameworks

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Tandem Postsynthetic Modification of a Metal–Organic Framework by Thermal Elimination and Subsequent Bromination: Effects on Absorption Properties and Photoluminescence**

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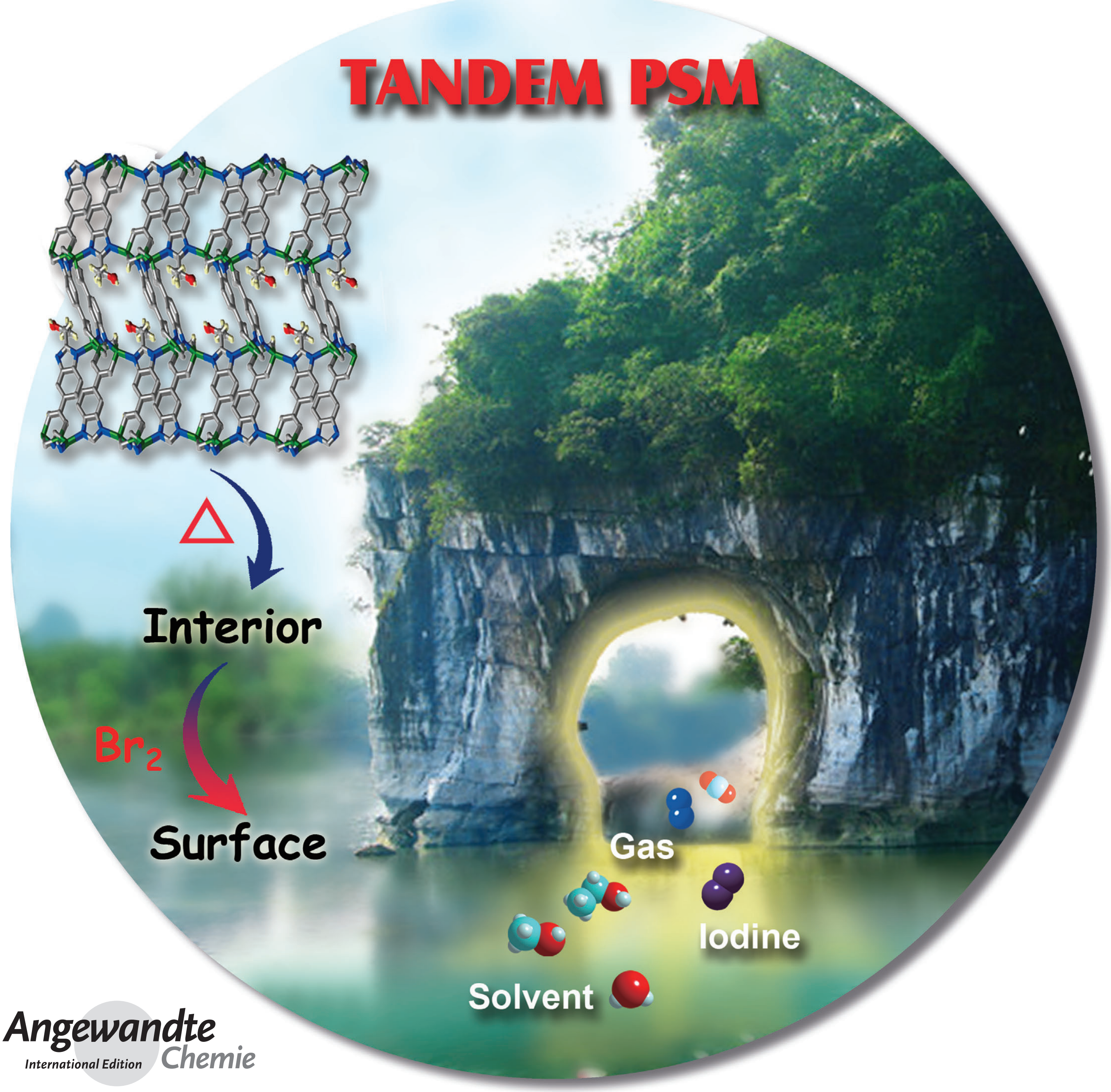

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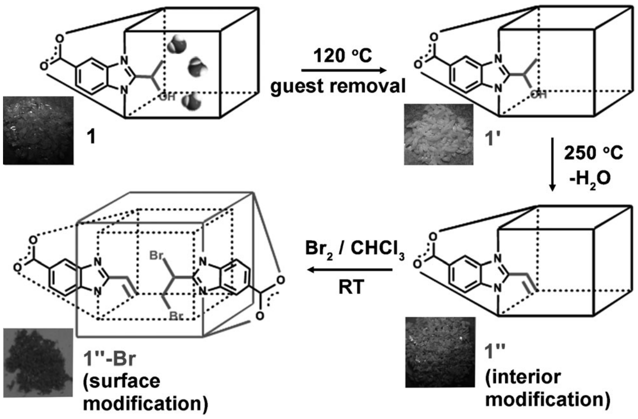
Metal–organic frameworks (MOFs) make up a topical subsection of coordination chemistry. Because they display a range of chemical and physical properties, they have potential applications, for example, in sorption, catalysis, and sensors.[1] A MOF having accessible open spaces can be subjected to postsynthetic modification (PSM) by chemical reaction.[2] PSMs are of major interest to scientists from different fields of research.[2] Cohen has classified several types of PSMs.[2a] For example, when the reaction involves a covalent bond of the organic linker it is termed a covalent PSM and when it occurs at the metal centers it is referred to as a dative PSM. The former has been more developed due to the possibility of having a pendant tag group at which the reaction can take place without perturbing the framework structures,[3] though there have been cases of the latter especially when vacant coordination sites at the metal are available.[4]

Following the "one-step" covalent and dative PSMs, "serial" or "tandem" modification of MOFs has since been gaining increasing interest.[2] It was first reported by Wang and Cohen, and then by Gamez et al.[5] Several functional groups can be introduced into MOF structures by clever postsynthetic strategies (Table S1 in the Supporting Information).[6–8] So far only well-known MOFs have been employed,[7] in particular those with only two different kinds of functionalized linkers based on dicarboxylate and bipyridine groups, either separately or together.[8] Tandem modification has been rarely reported because of the requirement for a rational multistep strategy; for example, a MOF is partially modified with one reagent and subsequently modified with another reagent on the remaining reactive sites and has higher stability than the precursor.[5–8] Tandem postsynthetic modification of MOFs showing various types of reaction behavior and different kinds of modification effects, in the interior and on the surface, is a new challenge in this domain.[2]

On the other hand, the principal aim of PSM is the functionalization of MOFs to endow them with specific properties.[9] In MOFs it is possible to tune the size of the channels and windows to be specific for different types and strengths of molecular interactions. The rational choice of tag groups and utilization of different guest probes, especially colored entities such as iodine, is of major importance in the study of the influence of PSM on host–guest interactions.[10] Iodine is known to be an interesting instant visual probe to study host–guest interactions and it can also introduce electrical conductivity.[11] Studying the absorption of gas molecules, solvents, and iodine in MOFs may contribute to the deeper understanding of the structural changes during PSM and may also lead to other applications.

Our original goal was to devise a MOF that contains both carboxylate and imidazolate groups and we therefore synthesized 2-(1-hydroxyethyl)-1*H*-benzo[*d*]imidazole-5-carboxylic acid (**H_2L**). We expected both the carboxylate and the imidazolate groups would be involved in the formation of a completely new MOF-ZIF structure while the hydroxyethyl group would be free for further reactions. The reaction of **H_2L**, $Zn(NO_3)_2\cdot 6H_2O$, and triethylamine in an ethanol/water mixture under solvothermal conditions resulted in colorless rhombus-shaped crystals of $\{Zn_3[(L)_2(\mu_2\text{-}OH)_2]\cdot 6H_2O\}_n$ (**1**) (Scheme 1). Indeed, the crystal structure determination confirms the successful realization of a MOF with channels containing water of crystallization surrounding the uncoordinated hydroxyethyl groups. Herein we describe unusual tandem PSM reactions on **1**; the gas, solvent, and iodine absorption of this compound demonstrates its unique properties relative to those of known MOFs.

Single-crystal X-ray diffraction shows that **1** crystallizes in the monoclinic space group *C*2/*c* and is a three-dimensional framework constructed by linear trimeric Zn^{II} secondary building units (SBUs) (Figure 1 and Table S2 in the Supporting Information). The central Zn2 atom is located on a twofold axis and has a distorted tetrahedral geometry with two μ_2-hydroxide (Zn2–O4 = 1.895(6) Å), and two carboxylate oxygen atoms (Zn2–O1 = 1.951(5) Å) from two L^{2-} units. The two terminal Zn atoms also have tetrahedral coordina-



Scheme 1. Transformations of **1**: postsynthetic elimination of H_2O from the hydroxyethyl groups in the channels to form vinyl groups and subsequent bromination at the surface.

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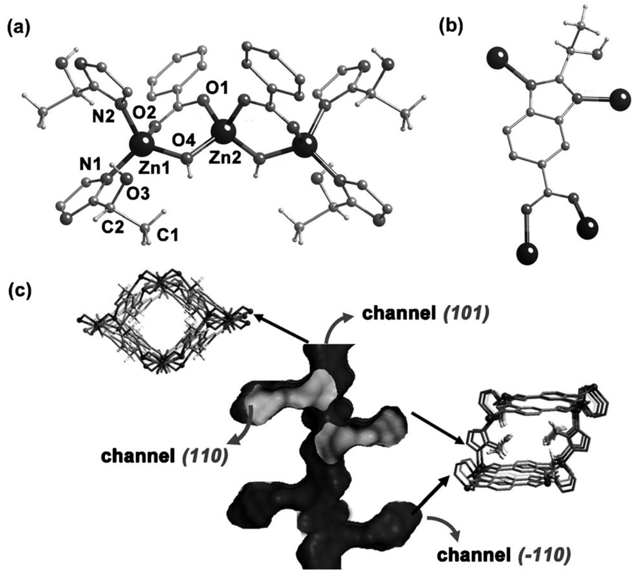

Figure 1. a) Coordination environment of the Zn atoms. b) The coordination model of the ligand in **1**. c) The interconnected channels in **1** and the windows along the *101*, *110* and *−110*.

tion geometry made up of a μ_2-hydroxide (Zn1–O4 = 1.926(5) Å), a carboxylate oxygen atom (Zn1–O2 = 2.044(4) Å) from L^{2-}, and two nitrogen atoms (Zn1–N1 = 1.983(6) Å, Zn1–N2 = 1.992(6) Å) from two L^{2-} units. The central Zn atom is linked to the terminal Zn atoms by μ_2-hydroxide and *syn,syn* μ_2-1,3-carboxylate mixed bridges (Zn1···Zn2 = 3.238(1) Å, Zn1-O-Zn2 = 115.9(3)°) to form a slightly bent Zn_3 unit. The trimeric units are almost parallel to each other and are bridged by the two nitrogen atoms of the imidazole group through the *ab* plane to form an infinite layer with irregular hexagonal windows with dimensions of roughly 6.4 Å and 5.9 Å, taking the van der Waals radii into consideration. The framework is formed by a pairwise connection of inverted L^{2-} units between adjacent layers at a distance of approximately 7.8 Å. The two different types of one-dimensional channels along the *110* and *−110* directions intersect at 132° to form the three-dimensional network of channels (Figure 1 and Figure S1 in the Supporting Information). The hydroxyethyl groups are interlaced in the channels. Then, the 1D channel penetrates the layer along the *101* direction. PLATON indicates that **1** has a potential void volume of 30.7 % of the unit cell without the water.[12]

Single-crystal X-ray diffraction analysis of the dehydrated form (**1′**), prepared by heating crystals of **1** at 120 °C within the first plateau (100–200 °C according to thermogravimetric analysis (TGA); Figure S2 in the Supporting Information), indicates no change in the space group; the key features of the framework are similar to those of the as-synthesized **1**, apart from slight structural deformation and reduction of the estimated void volume to 31.5 % for **1′**. The results suggest the ruggedness of the present framework. The water molecules are absent and the hydroxyethyl tag group is free in the channel. It should be noted that, though desirable as groups for tuning the sorption performance, noncoordinated hydroxy groups within MOF are rarely observed.[13] In our work, $\mathbf{H_2L}$ was only doubly deprotonated, at the carboxylic acid and at the imidazole, and the hydroxyethyl tag group does not take part in the coordination of the metal atoms. In addition, the formation of the long trimeric unit favors a mode of packing that can sustain channels filled with water molecules and the tag group. It should be noted that this is the first time that such a hydroxyethyl tag group is found in a postsynthetically modified MOF.[2]

The second step in the TGA is an endothermic weight loss of 3.9 % between 250–310 °C before another plateau up to 340 °C.[14] The percentage weight loss corresponds to one unit of water (calculated 3.8 %). So, we associate this loss with the elimination of H_2O from the hydroxyethyl group to give a vinyl group (see NMR spectra later). Crystals of **1″** were then prepared by heating the as-synthesized crystals of **1** at 250 °C for 12 h under dynamic vacuum. Unfortunately, the high temperature degrades the quality of the crystals for further single-crystal X-ray characterization. However, powder X-ray diffraction (PXRD) indicates the framework is still present and stable (Figure S3 in the Supporting Information). Given that the lattice water has been removed at low temperature and the oxygen atoms of carboxylic group are coordinated to Zn ions, we consider that the hydroxyethyl group (-CHOHCH$_3$) has been transformed to the vinyl group (-CH=CH$_2$). Thus **1″** is a new MOF with vinyl group in the channels.

To confirm this thermal elimination of water during the transformation from **1′** to **1″**, we conducted multiple characterizations. The PXRD patterns of **1″** are very similar to those of **1** and **1′**, which indicates that the framework remains intact during this transformation. Secondly, the well-matched solid-state ^{13}C NMR spectra of **1** and **1″** indicate that the carbon backbone of the organic ligand is still present (Figure 2). The formation of a vinyl-group-modified organic linker was demonstrated as follows: crystals of **1″** were digested in aqueous 0.0125 M NaOH solution and analyzed by liquid chromatography mass spectrometry (LC–MS) (Figure S4 in the Supporting Information). Two peaks at retention times of 1.20 and 1.45 min were observed, which correspond to *m*/*z* values of 207 and 189, respectively, and were assigned to $\mathbf{H_2L}$ ($[M+H]^+ = 207.1$) and 2-vinyl-1*H*-benzo[*d*]imidazole-5-carboxylic acid ($\mathbf{H_2L''}$, $[M+H]^+ = 189.1$). Thirdly, the ^{1}H NMR spectrum of digested **1″** show three extra sets of peaks at 6.98, 6.78, and 6.35 ppm, which correspond to the three different hydrogen atoms in the vinyl group (-CH=CH$_2$) (Figure S5). According to the LC result, the content of $\mathbf{H_2L}$ is about six times that of $\mathbf{H_2L''}$, which indicates that base-catalyzed addition reaction of the vinyl group giving the hydroxyethyl group occurs during the digestion under basic aqueous conditions. This also explains the weak ^{1}H NMR signals of the vinyl group.

It was surprising to note that the simple molecule 2-vinyl-1*H*-benzo[*d*]imidazole-5-carboxylic acid ($\mathbf{H_2L''}$) has not been reported before as there is no entry for it in the Scifinder database.[15] Consequently, our attempt to synthesize $\mathbf{H_2L''}$ under synthesis conditions similar to those described above using the cyclization of 3,4-diaminobenzoic acid with acrylic acid was unsuccessful (Figure S6 in the Supporting Information).[16] It may not be possible to prepare $\mathbf{H_2L''}$ because

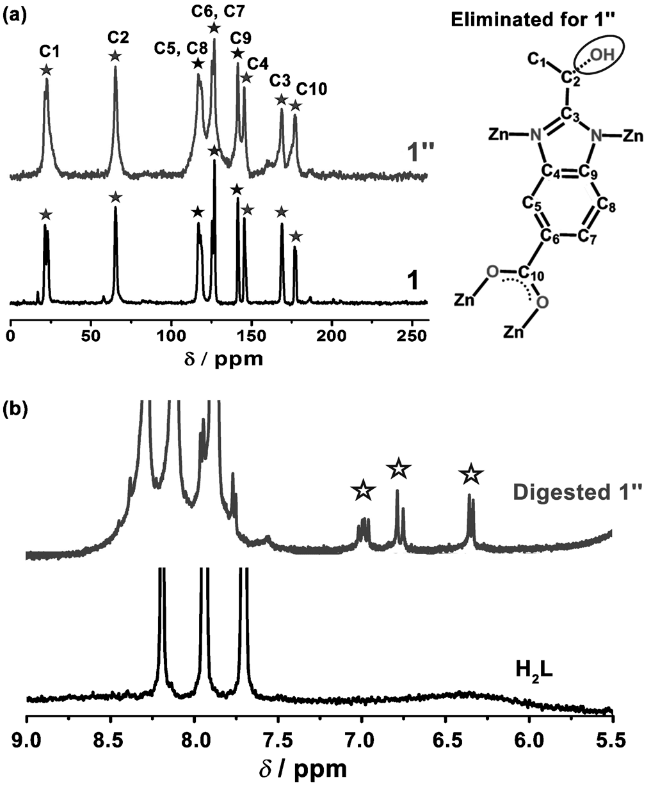

Figure 2. a) Solid-state ^{13}C NMR spectra of **1** and **1″**. b) Liquid-phase ^{1}H NMR spectroscopy of **H$_2$L** and digested **1″**. Powder of **H$_2$L** and **1″** was dissolved in D$_2$O/[D$_6$]DMSO/DCl and then the solution was measured. The three peaks (marked with stars) in the range of 6.0–7.0 ppm correspond to the characteristic signals of a vinyl group.

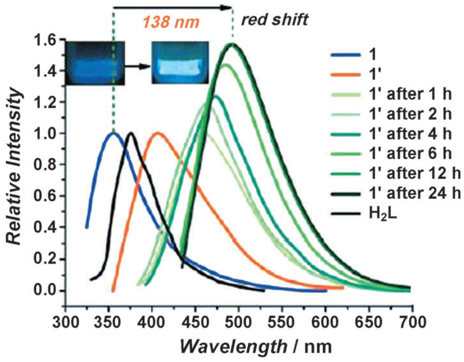

Figure 3. Fluorescence emission spectra recorded during the transformation of **1** to **1′** and **1″** .

acrylic acid polymerizes in acidic media and at high temperature.[17] In comparison, we investigated the thermal decomposition behavior of **H$_2$L** (Figure S7). We found that the decarboxylation of the carboxyl group and dehydration of the hydroxyethyl group occur simultaneously, which explains the unsuccessful preparation of **H$_2$L″**. Thus, the synthesis of **H$_2$L″** is possible only in the framework because of the protection of the carboxylate group and the deprotonation of the imidazole through coordination.

Owing to the strong photoluminescence (PL) of the ligand, it was possible to monitor the solid-to-solid transformations of the organic components of the the framework (Figure 3). The PL spectrum ($\lambda_o = 310$ nm) of the deprotonated ligand in the framework displays a blue-shift to 355 nm for **1**. In contrast, a major red-shift of the band to 407 nm was observed for **1′** upon dehydration of **1** at 120 °C, suggesting a decrease of the π–π^* transition energy upon removal of the hydrogen-bonding interactions with the water molecules.[18] While **1′** is heated at 250 °C, this band is progressively red-shifted to 459 nm after one hour and to 490 after 12 h, and does not change further after 24 h, as **1′** is transformed to **1″**. This is in good agreement with the increase in conjugation the transformation of the hydroxyethyl to the vinyl group.[19] This transformation is accompanied by a lowering of energy due to the formation of π-bonds. Compared to characterizing the PSM products and determining the conversion by solution-phase ^{1}H NMR spectroscopy, this tracking of the solid-to-solid transformation through luminescence changes was a very simple, direct to monitor the PSM of the MOFs without destroying the MOFs.[2]

Moreover, the presence of a vinyl group is an invitation to perform an addition reaction with a halogen molecule. We reacted **1″** with Br$_2$ in CHCl$_3$ for 30 min and obtained a brown powder of **1″-Br** (Figures S8 and S9 in the Supporting Information). The PXRD pattern indicates that the framework is preserved. After digestion of **1″-Br** in anhydrous MeOH with dry NH$_3$ gas, the collected ligand was analyzed by ESI-MS. The negative-ion signals at 344.88, 346.88, and 348.89 were assigned to the dibrominated ligand 2-(1,2-dibromoethyl)-1*H*-benzo[*d*]imidazole-5-carboxylic acid (**H$_2$L″-Br**). Meanwhile, the two peaks at 264.95 and 266.96 correspond to the monobrominated ligand. Furthermore, after digestion of **1″-Br** in D$_2$O/DCl/[D$_6$]DMSO, the ^{1}H NMR spectra showed new resonances between 6.4 and 7.0 ppm (Figure S10), which is consistent with the formation of **H$_2$L″-Br**. However, it should be noted that both the ESI-MS and ^{1}H NMR signals for **H$_2$L″-Br** are very weak which suggests the reaction of vinyl group with bromine is partial. Since only a very small amount of brominated ligand in **1″-Br** was observed, we undertook further experiments which indicate that the quantity depends on the crystal size: the smaller the crystals, the more brominated ligand was observed (Figure S11). This led us to conclude that the bromination is only at the surface and thus it closes the windows preventing further reaction.[8] There are only two examples of the bromination the tag group in MOFs in the literature and in both cases it occurs both in the interior and the surface of the crystals.[5a,20] Such surface modification in our case resulting from bromination of the tag group differs from previous examples and also has severe consequences on the absorption properties (see below).

The absorption of gases (N$_2$ and CO$_2$), solvents (water, methanol, and ethanol), and iodine by **1′**, **1″**, and **1″-Br** was studied to explore the influence of the postsynthetic modifications on the pores (Figure 4 and Figures S12–16 and Table S3 in the Supporting Information). Considerable difference in the amount of gas or solvents was observed for the three different compounds, decreasing in the order **1′** > **1″** ≫ **1″-Br**. MOFs **1′** and **1″** absorb iodine from a C$_6$H$_{12}$ solution

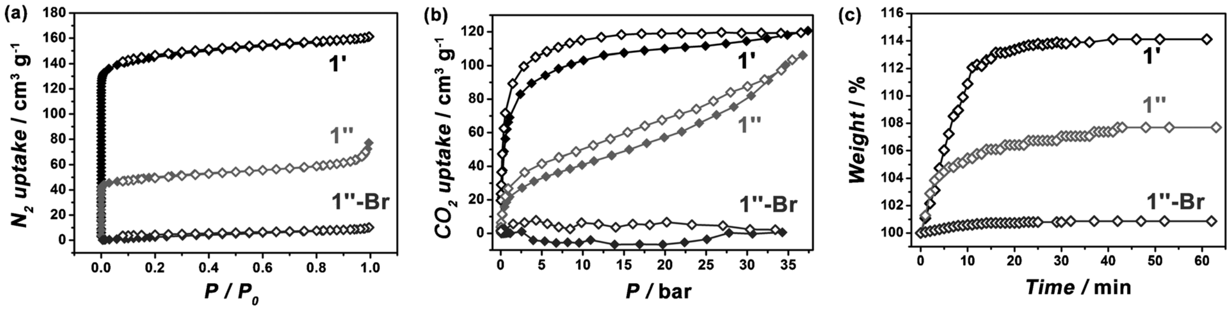

Figure 4. a) The low-pressure N_2 sorption isotherms at 77 K of **1′**, **1″**, and desolvated **1″-Br**. b) The high-pressure CO_2 sorption isotherms at 298 K of **1′**, **1″**, and desolvated **1″-Br**. c) Plots of the weight change of **1′**, **1″**, and desolvated **1″-Br** in air under 25 °C and a humidity of 60%.

saturated with iodine and the color of the crystals changed from colorless to yellow, then brown, and finally black. From the photos, we can infer that the iodine sorption rate of **1′** is quicker than that of **1″**. However, TG and titration consistently confirm the maximum iodine uptake of **1′** and **1″** is comparable, with a value of about 0.28 and 0.26 g I_2 per gram of desolvated crystals. In the absence of regular aromatic channels, this value is far less than that for the reported double-walled MOF $\{[Zn_3(\text{DL-lac})_2(\text{pybz})_2]\cdot 3\,\text{DMF}\}_n$ (DL-lac = lactate, pybz = 4-pyridine benzoate), which shows extremely high iodine sorption ability and cooperative electrical conductivity.[11] However, the iodine sorption of **1″-Br** cannot be detected. Furthermore, we monitored the release of iodine in methanol and confirmed that the release rate of loaded **1′** is about 2.8 and 2.4 times greater then that of iodine-loaded **1″** at 298 and 323 K, respectively (Figure 5 and Figures S15–17).

From these results, we can easily infer that the absorbing behaviors of the postsynthetically modified MOF for different guest probes are different from those of the as-synthesized MOF. For gas molecules such as N_2 and CO_2, the random orientation of the tag group and the partial distortion in modified **1″** hinders restoration. For solvent molecules, small water or methanol molecules are completely restored in the channels, while big ethanol molecules are only partly restored in the channels. The restoring ability of I_2 is similar to that of water or methanol, though the host–guest interaction is stronger in **1′** than in modified **1″**. Interestingly, after surface modification, the brominated tag group apparently acts as a gate, which prevents the inclusion of N_2, CO_2, and I_2 and slows down the inclusion and release of H_2O, MeOH, and EtOH molecules.[21] With these easy-to-perform stepwise synthetic operations, we can fine-tune the internal molecular environments of MOFs. This provides unprecedented opportunities to systematically evaluate and improve the performance of MOF materials.

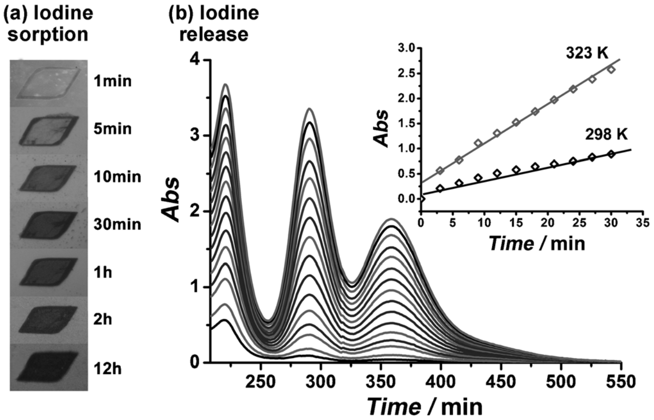

Figure 5. a) Photos showing the iodine sorption of **1′** from a saturated solution of iodine in cyclohexane. b) Absorbance spectrum showing telease of iodine from iodine-loaded crystals of **1′** in methanol. Insert: plot of the release iodine from iodine-loaded crystals in methanol at different temperatures.

In summary, a novel MOF has been synthesized with a trifunctional (carboxylate, imidazolate, and hydroxyethyl groups) tag and it exhibits single-crystal to single-crystal transformation. After dehydration of the MOF, two consecutive postsynthetic modifications—elimination and bromination—were realized on the tag group within the highly crystalline solid. The modifications have dramatic effects on the absorption of gases (N_2, CO_2), solvents (H_2O, CH_3OH, C_2H_5OH, C_3H_7OH), and I_2 and on the luminescence properties. The convenient methods of characterization employed may prove useful in the further evolution of MOFs. The elimination of water from the hydroxyethyl group to generate the vinyl group is unique to this framework and this appears to be the only synthesis of the modified ligand 2-vinyl-1*H*-benzo[*d*]imidazole-5-carboxylic acid (**H$_2$L″**) in the literature. Consequently, the rational design of new MOFs along with PSMs may be effective for the synthesis of new organic compounds difficult to prepare by traditional methods because coordination to the framework provides protection of thebreactive groups.

Experimental Section

Colorless crystals of **1** were obtained from the solvothermal reaction of $Zn(NO_3)_2\cdot 6H_2O$ (0.5 mmol), and **H$_2$L** (0.125 mmol) in 3.5 mL ethanol, 3.5 mL water, and 0.125 mL triethylamine at 140 °C for 3 days (average yield: 55% based on Zn). Elemental analysis (%): Observed, C: 32.33; H: 4.10; N: 7.55; Found, C: 32.17; H: 4.05; N: 7.50. IR: $\tilde{\nu}$ =3386(*s*), 1585(*w*), 1535(*s*), 1481(*w*), 1397(*s*), 1293(*w*), 1114(*w*), 1064(*w*), 792(*s*), and 757 cm^{-1}(*w*).

Crystals of **1′** were obtained by degassing the crystals of **1** at 120 °C for 6 h under dynamic vacuum. Crystals of **1″** were obtained by degassing the crystals of **1** at 250 °C for 12 h under dynamic vacuum. The resulting crystals of **1″** were immediately soaked in 10 mL bromine/$CHCl_3$ solution (10 wt %) and the reaction mixture was kept in darkness for 30 min. Then, the crystals 1″-Br were obtained by filtering and washing with $CHCl_3$ and dried in the air.

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