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A Metal−Organic Framework with Covalently Bound Organometallic Complexes

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Abstract: A procedure for making covalently linked organometallic complexes within the pores of metal−organic frameworks (MOFs) has been described. An *N*-heterocyclic carbene precursor containing link **L0** was prepared and then constructed into a MOF-5-type structure (IRMOF-76). Attempts to produce covalently bound organometallic complexes in IRMOF-76 were unsuccessful. An alternative way of linking the first metalated link, **L1**, into the desired metalated MOF structure, IRMOF-77, was successful. IRMOF-76 and -77 were characterized by single-crystal X-ray studies. Demonstration of permanent porosity and successful substitution of the pyridine coligand in IRMOF-77 are also described.

Metal−organic frameworks (MOFs) are ordered porous solids in which inorganic building units are joined by organic links.[1] An important aspect of their chemistry is the ability to build structures with functionalized pores. This is achieved either by (1) employing an appropriately functionalized link in the assembly of the structure or (2) functionalizing the links after the structure has formed.[2] Although these approaches have been employed to yield MOFs with pores that are functionalized by organic units and noncovalently or covalently bound coordination complexes,[3] strategies for introducing covalently bound organometallic complexes in which metal ions are directly bound to carbon atoms remain largely undeveloped. The first approach works only in cases where the functional unit does not interfere with the assembly of a given structure,[4] and the second one is limited by the overall stability of the framework under the reaction conditions necessary for postsynthetic functionalization.

In this report we show how to make covalently linked organometallic complexes within the pores of MOFs. We initially prepared a link containing an *N*-heterocyclic carbene (NHC)[5] precursor (**L0**, Scheme 1) and then assembled it into a MOF-5 type structure (IRMOF-76, Scheme 1). After unsuccessful attempts at producing a covalently bound organometallic complex in the MOF, we metalated the link first (**L1**) and then assembled it into the desired metalated MOF structure (IRMOF-77, Scheme 1). Here we describe the synthesis and structural characterization of IRMOF-76 and -77 and report the permanent porosity and the successful substitution of the pyridine coligand in IRMOF-77 without affecting the integrity of the MOF.

Our strategy, which targeted a structure based on the well-known primitive cubic MOF-5, required the use of a linear ditopic carboxylate link that could accommodate an NHC−metal complex or its precursor. It is not easy to predict the final atomistic connectivity if bent links are employed, which in many cases leads to the lack of accessible space in the framework even for small molecules.[6,7] Therefore, we established a convergent synthetic route for new links utilizing cross-coupling reactions as the key step to combine the imidazolium core with the carboxylate modules (Scheme 1).

The synthesis of 4,7-bis(4-carboxylphenyl)-1,3-dimethylbenzimidazium tetrafluoroborate (**L0**) starts from the known 4,7-dibromobenzthiaziazole (**1**).[8] Cobalt-catalyzed reduction with sodium borohydride[9] followed by acid-catalyzed condensation with triethyl orthoformate converted thiaziazole to benzimidazole.

Successive *N*-methylation produced a dibromobenzimidazole core (**2**). Pd(0)-catalyzed Suzuki−Miyaura cross-coupling between **2** and 4-(*tert*-butoxycarbonyl)phenylpinacolborane (**3**)[10] resulted in the diester-terminated linear terphenyl strut **4**. In particular, for the synthesis of **L0**, the module possessing a *tert*-butyl ester as a masked carboxylic acid was selected because of improved solubility and feasible late-stage unmasking of carboxylic acid. Treatment with an excess of methyl iodide produced **5**, possessing the *N*,*N*′-dimethylbenzimidazolium moiety. **L0** was then obtained by deprotection of two *tert*-butyl esters using HBF_4 concomitant with counteranion substitution from I^- to BF_4^-. All conversions were feasible on a gram scale.[10]

The synthesis of IRMOF-76 was carried out using a mixture of 3 equiv of $Zn(BF_4)_2 \cdot xH_2O$, 10 equiv of KPF_6, and **L0** in *N*,*N*-dimethylformamide (DMF). The mixture was heated at 100 °C for 36 h, whereupon colorless crystals of IRMOF-76 $[Zn_4O(C_{23}H_{15}N_2O_4)_3(X)_3$, X = BF_4, PF_6, OH] were obtained.[10]

Single-crystal X-ray diffraction analysis[11] revealed that IRMOF-76 is isoreticular with MOF-5.[12] Here, Zn_4O units are connected to six **L0** links to form a cubic framework of **pcu** topology[13] (Figure 1a). IRMOF-76 is a non-interpenetrated cationic MOF possessing imidazolium moieties (NHC precursors) on each link.[7] ICP analysis and ^{19}F NMR spectroscopy of digested IRMOF-76 reveal that both BF_4^- and PF_6^- are included as counteranions of the imidazolium moieties.

We then aimed to produce an NHC or its metal complex in IRMOF-76 by a postsynthetic approach. However, none of the conditions examined (treatment with Brönsted base/Ag_2O/Ag_2CO_3, or formation of CN/CCl_3/alkoxide adducts followed by thermal α-elimination) were successful for this system.

These results led us to seek an alternative strategy using a link possessing a metal−NHC complex.[14] The metal−NHC bond is generally stable even under mild acidic conditions, and chemoselective NHC coordination avoids undesired reactions with metal sources in the construction of secondary building units, which, in many cases, relies on oxygen−metal coordination.[15] Specifically, we used [4,7-bis(4-carboxylphenyl)-1,3-dimethylbenzimidazol-2-

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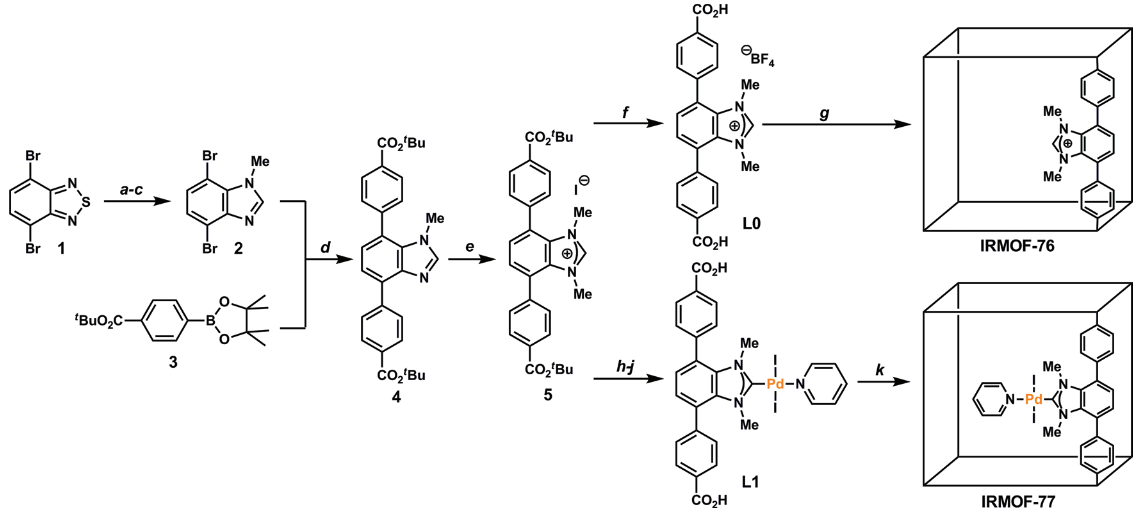
Scheme 1. Convergent Synthesis of New Dicarboxylic Acid Links **L0** and **L1** and Preparation of IRMOF-76 and -77[a]



[a] Conditions: (a) $CoCl_2$ (1 mol %), $NaBH_4$, EtOH/THF, reflux; (b) $HC(OEt)_3$, sulfamic acid (5 mol %), MeOH, 52% (two steps); (c) MeI, K_2CO_3, EtOH, reflux, 100%; (d) $Pd(PPh_3)_4$ (5 mol %), K_2CO_3, dioxane/H_2O, 100 °C, 62%; (e) MeI, CH_3CN, reflux, 94%; (f) $HBF_4 \cdot OEt_2$, CH_2Cl_2, 100%; (g) $Zn(BF_4)_2 \cdot xH_2O$ (3 equiv), KPF_6 (10 equiv), DMF, 100 °C, 36 h; (h) $Pd(CH_3CN)_2Cl_2$, NaI, K_2CO_3, pyridine, reflux, 88%; (i) TMSOTf, CH_2Cl_2; (j) pyridine, $CHCl_3$/MeOH; 74% (two steps); (k) $Zn(NO_3)_2 \cdot 6H_2O$ (3 equiv), DEF/pyridine (75:1), 100 °C, 30 h.

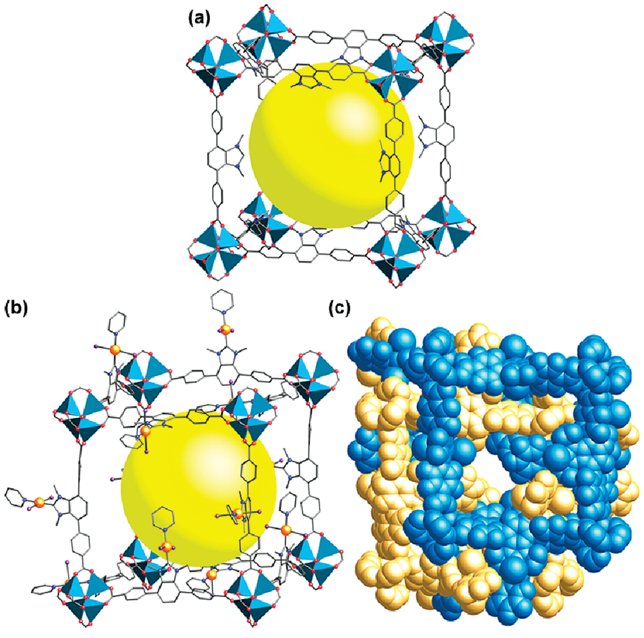


Figure 1. (a) Single-crystal structure of IRMOF-76 [$Zn_4O(C_{23}H_{15}N_2O_4)_3(X)_3$, X = BF_4, PF_6, OH]. (b) Single-crystal structure of IRMOF-77 [$Zn_4O(C_{28}H_{21}I_2N_3O_4Pd)_3$] shown with only one **pcu** net. Atom colors: blue tetrahedron, Zn; purple, I; orange, Pd; red, O; blue sphere, N. The yellow spheres represent the largest spheres that would occupy the cavity without contacting the interior van der Waals surface for IRMOF-76 and the single framework of IRMOF-77 (ca. 19 and 15 Å, respectively). All hydrogen atoms, counteranions (X), and guest molecules have been omitted for clarity. (c) Space-filling illustration of IRMOF-77. Two interwoven **pcu** nets are shown with blue and gold colors, respectively.

ylidene](pyridyl)palladium(II) iodide (**L1**, Scheme 1), which is potentially attractive as a catalyst homologous to known homogeneous catalyst systems.[5c]

L1 was prepared from intermediate **5** (Scheme 1). The benzimidazolium moiety of **5** was converted to the NHC$-$PdI$_2$(py) complex when refluxed in pyridine with a Pd(II) source, a base (K_2CO_3), and an iodide source (NaI). Deprotection of the *tert*-butyl esters was achieved with trimethylsilyl trifluoromethanesulfonate (TMSOTf). The covalently formed Pd(II)$-$NHC bond was surprisingly stable, even under the strongly Lewis acidic conditions for deprotection. However, the pyridine coligand was removed to form dimeric complexes.[10] Adding pyridine as a ligand was necessary to produce **L1** possessing a monomeric NHC$-$PdI$_2$(py) moiety.

The synthesis of IRMOF-77 was conducted using $Zn(NO_3)_2 \cdot 6H_2O$ and 3 equiv of **L1** in a solvent mixture of *N*,*N*-diethylformamide (DEF) and pyridine (75:1). The mixture was heated at 100 °C for 30 h, whereupon orange crystals of IRMOF-77 [$Zn_4O(C_{28}H_{21}I_2N_3O_4Pd)_3$] were obtained.[10]

X-ray single-crystal structure analysis[11] reveals that IRMOF-77 is also isoreticular with MOF-5.[12] The X-ray crystal structure verifies the presence of the NHC$-$PdI$_2$(py) moiety (Figure 1b). The Zn ions used for the construction of the framework are not involved in binding with the metal$-$NHC moiety.[6] Measured elemental compositions in accordance with the expected values[16] confirm the absence of undesired metal exchange on NHC. The observed Pd$-$C distance (1.925 Å) and coordination geometry match well with those found in the Cambridge Structural Database for NHC$-$PdX$_2$ (py) (X = halide) complexes.[17] The presence of the Pd(II)$-$NHC bond was further confirmed by the solid-state ^{13}C cross-polarization magic angle spinning (CP/MAS) NMR spectrum (δ = 154.1 ppm for N-**C:**-N).[18] NHC$-$Pd(II) moieties are positioned on every face of the cubic cage within the framework. Two interwoven frameworks were formed with ca. 7 Å offset distance (Figure 1c), presumably to mitigate the interference of the metal$-$NHC moieties with each other, with 4.06 Å shortest distances between two methyl carbons from two frameworks. As a result, the catenation is different from that of IRMOF-15,[12] whose link length is the same as in **L1**. Due to the interwoven nature of the structure, the pore aperture is ca. 5 Å × 10 Å. All immobilized Pd(II) centers protrude into the pores without blocking each other.

To confirm the presence of void space and the architectural stability of IRMOF-77, the permanent porosity was demonstrated by the N_2 adsorption isotherm of the guest-free samples.[10] The isotherm shows steep N_2 uptake in the low-pressure region, which indicates that the material is microporous (Figure 2). The Langmuir and BET surface areas of activated IRMOF-77 are calculated to be 1610 and 1590 $m^2\ g^{-1}$, respectively. The amount of N_2 uptake in the pores (P/P_0 = 0.9) corresponds to 46 N_2 molecules per formula unit, or 552 per unit cell.

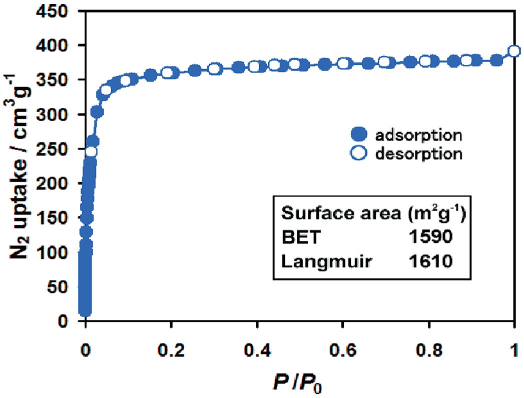


Figure 2. N_2 isotherm for IRMOF-77 measured at 77 K.

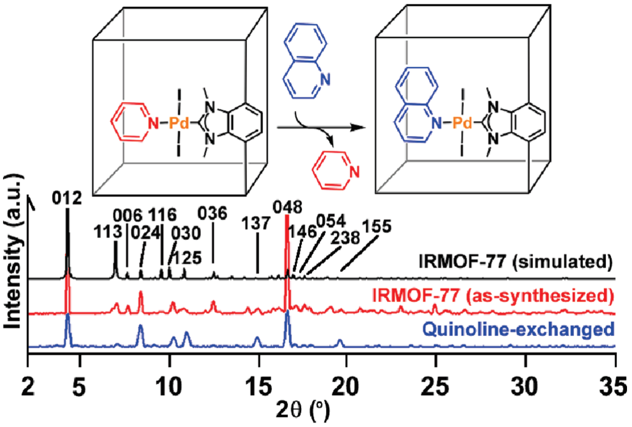


Figure 3. PXRD patterns of as-synthesized IRMOF-77 (red) and quinoline-exchanged IRMOF-77 (blue) and simulated PXRD pattern from single-crystal X-ray structure (black).

To examine the reactivity of the immobilized Pd(II) centers of IRMOF-77, ligand exchange experiments were carried out by immersing as-synthesized crystals of IRMOF-77 in 4% v/v quinoline/DMF solution for 1 day at room temperature. A comparison between the powder X-ray diffraction (PXRD) patterns before and after exchange reveals that the framework remains intact during the exchange process (Figure 3), which is also supported by porosity measurements.[10] No signal from the pyridine protons is observed in the ^{1}H NMR spectrum of the digested MOF after ligand exchange. Only the signals from quinoline are observed, with the expected molar stoichiometry (carboxylate link:quinoline = 1:1).[10] Retention of the NHC−Pd bond is confirmed by the ^{13}C CP/MAS solid-state NMR spectrum (before, 154.1 ppm; after, 152.9 ppm). These results indicate the presence of an NHC−PdI_2(quinoline) complex after ligand exchange.[18]

In conclusion, the structures of IRMOF-76 and -77 demonstrate the successful application of our strategy to immobilize Pd(II)−NHC organometallic complexes in MOFs without losing the MOF's porosity and its structural order.

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Supporting Information Available: Detailed experimental procedures, including synthesis of **L0** and **L1**, crystallographic data (in CIF format), PXRD, TGA of IRMOF-76 and -77, and detailed sorption studies of IRMOF-77 and quinoline-exchanged IRMOF-77. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Crystal data after SQUEEZE (Cu Kα radiation, $\lambda = 1.54178$ Å): IRMOF-76, $Zn_4O(C_{23}H_{15}N_2O_4)_3$, $M_r = 1427.59$, cubic $Fm\bar{3}m$, $a = 42.9245(2)$ Å, $V = 79088.9(6)$ Å^3, $Z = 8$, $D_c = 0.240$ g cm^{-3}, 1260 independent reflections observed, $R_1 = 0.0549$ ($I > 2\sigma(I)$), $wR_2 = 0.2166$ (all data), and GOF = 0.912; IRMOF-77, $Zn_4O(C_{28}H_{21}I_2N_3O_4Pd)_3$, $M_r = 2748.51$, trigonal $R\bar{3}c$, $a = b = 31.0845(4)$ Å, $c = 71.018(2)$ Å, $V = 59427(2)$ Å^3, $Z = 12$, $D_c = 0.922$ g cm^{-3}, 3946 independent reflections observed, $R_1 = 0.0560$ ($I > 2\sigma(I)$), $wR_2 = 0.1389$ (all data), and GOF = 0.950.

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