

# Metal–Organic Frameworks Containing (Alkynyl)Gold Functionalities: A Comparative Evaluation of Solvent-Assisted Linker Exchange, *de Novo* Synthesis, and Post-synthesis Modification

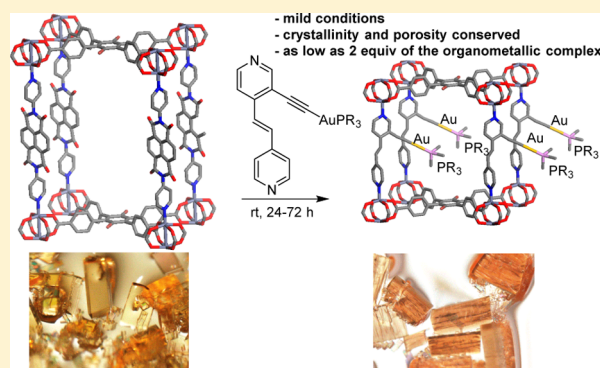
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## S Supporting Information

**ABSTRACT:** A series of metal–organic framework (MOF) materials containing Au<sup>I</sup>–carbon covalent bonds was prepared by solvent-assisted linker exchange (SALE) between (alkynyl)gold–(phosphine)–functionalized bipyridine linkers and the bipyridyl naphthalene tetracarboxydiimide struts in Zn pillared–paddlewheel MOFs. These new materials could not be obtained by the authors through *de novo* synthesis or post-synthesis modification, both of which lead to the decomposition of the organometallic complex. In contrast, the SALE process occurs readily under mild conditions that preserve the integrity of both the pillared–paddlewheel structure and the organometallic complex. For bipyridine linkers with similar basicities, the rate of the SALE exhibits a strong inverse dependence on the size of the phosphine ligand in the incoming (alkynyl)gold(phosphine)–functionalized linker, with smaller ligands reacting faster.



## ■ INTRODUCTION

Over the past decade, as the number of published metal–organic framework (MOF) structures exponentially increased, MOFs containing organometallic functionalities also began to appear in high numbers. Interestingly, the majority of these functionalities have been stable metal–carbonyl species,<sup>1–8</sup> ferrocene derivatives,<sup>9–16</sup> and late metal–*N*-heterocyclic carbene moieties.<sup>17,18</sup> Given the relatively high temperature and acidic reaction media often used for MOF syntheses, it is not surprising that MOFs containing less-stable metal–hydrocarbyl moieties have been relatively rare.<sup>19–22</sup> While post-synthesis modification (PSM) strategies can potentially be used to prepare metal–hydrocarbyl-containing MOFs,<sup>23–26</sup> they are hampered by the low accessibility of the reactive sites in the parent MOF and/or the need to use multiple reactions to arrive at the desirable organometallic-functionalized framework. As such, we were interested in the possible application of solvent-assisted linker exchange (SALE)—a concept that was originated by Choe,<sup>27–29</sup> and expanded by Cohen,<sup>30–32</sup> us,<sup>33–37</sup> and others,<sup>38–40</sup>—to synthesize MOFs containing non-carbonyl organometallic functionalities. Given the ability of SALE to afford a number of MOF materials that would likely be difficult to synthesize by *de novo* synthesis and PSM, we hypothesized that SALE would be particularly attractive for this purpose given its mild conditions and broad solvent spectrum.<sup>40</sup>

Herein, we describe the high-yield preparation of a series of MOFs containing (alkynyl)gold(phosphine) functionalities through SALE between (alkynyl)gold(phosphine)-functionalized bipyridine linkers with the bipyridyl naphthalene tetracarboxydiimide struts in an easily accessible Zn pillared–paddlewheel MOF.<sup>41</sup> The use of an (alkynyl)gold(phosphine)-functionalized bipyridine linker, which is shorter than the “parent” bipyridyl naphthalene tetracarboxydiimide strut and has more basic pyridine moieties, allows SALE to reach completion with a small amount of the incoming organometallic ligand (as few as 2 equiv) under ambient conditions. Significantly, in our hands, the product MOF materials could not be prepared using either *de novo* or PSM methods: the former led to the decomposition of the organometallic species, while the latter can be taken to completion only after destruction of the parent MOF crystals via grinding.

## ■ RESULTS AND DISCUSSION

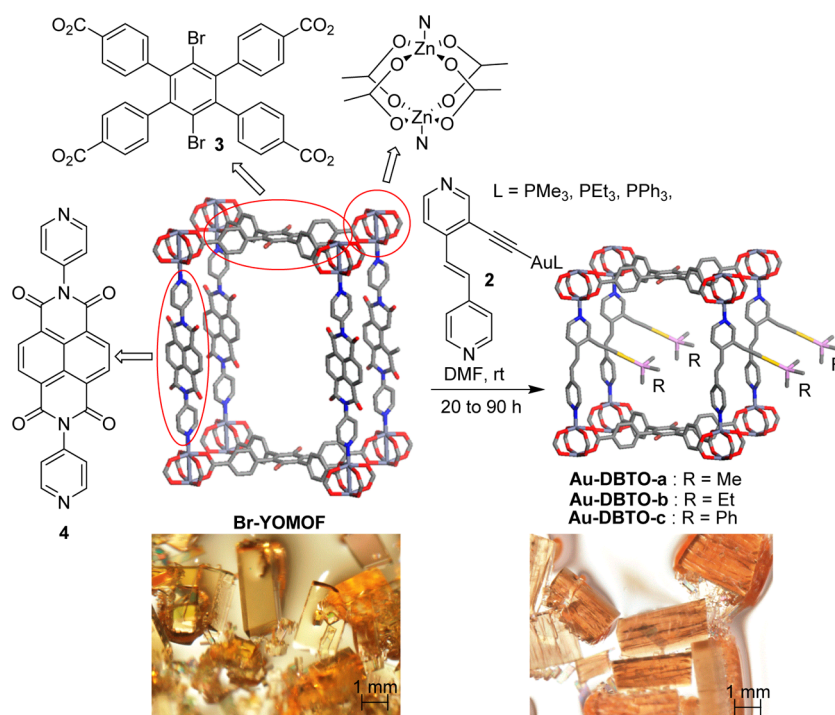
We chose (alkynyl)gold(phosphine) complexes as a model system to test the utility of SALE in the preparation of organometallic-functionalized MOFs because their Au–C bonds are relatively more stable (even to chromatography)

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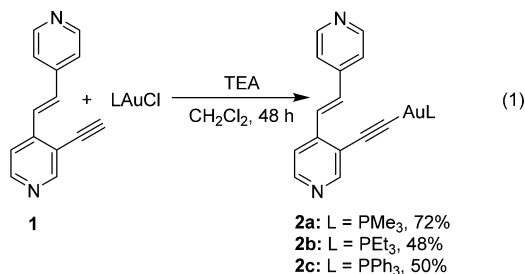




**Figure 1.** Synthesis of **Au-DBTO-a,b,c** MOFs through SALE (the structures were generated by Materials Studio from the known **DBTO** MOF structure<sup>45</sup>). The pictures below each MOF structure, taken of the corresponding DMF-solvated materials, illustrate that the SALE process preserves the crystalline nature of the materials.

than other transition metal-hydrocarbonyl species. In addition, the broad range of steric environments provided by phosphine ligands would allow us to explore the scope of SALE against **Br-YO** MOF,<sup>41</sup> a non-catenated Zn pillared-paddlewheel MOF containing the dibrominated octaoxygenated strut **3** and *N,N'*-di(4-pyridyl)-1,4,5,8-naphthalenetetracarboxydiimide (**4**) pillar (Figure 1). This orange-colored MOF has been shown to readily undergo SALE with a broad range of dipyridyl struts,<sup>35</sup> due to the facile exchange of the coordinated Zn-pyridine bonds with external pyridyl ligands. In addition, its large pore diameter ( $\sim 28$  Å)<sup>41</sup> should allow for the reagents **2** ( $\sim 9 \times 14$  Å) to penetrate and undergo exchange with **4**. Both of these features can work to our advantage in the preparation of the desired (alkynyl)gold(phosphine)-functionalized MOFs under significantly milder conditions than the *de novo* synthesis, which typically requires prolonged heating and added acid modulators.

**Preparation of (Alkynyl)gold(phosphine) Complexes 2a–c.** The (alkynyl)gold(phosphine) complexes **2a–c** were prepared by a modification of previously reported procedures (eq 1, see Section S3 in the Supporting Information (SI) for



experimental details).<sup>42–44</sup> The desired product was isolated in 48–72% yield after column chromatography over basic

alumina. The use of the (chloro)gold(phosphine) complexes is critical as the strong gold–phosphine bond is not susceptible to being displaced by the pyridine moieties of **1**. Indeed, in our hands, (chloro)gold(phosphite) and (chloro)gold-(tetrahydrothiophene) complexes all formed an intractable mixture upon being treated with **1** in the presence of triethylamine. The isolated complexes were characterized by multinuclear nuclear magnetic resonance (NMR) spectroscopies and electrospray-ionization mass spectrometry (ESI-MS) (see Section S3 in the SI).

**Solvent-Assisted Ligand Exchange (SALE).** The SALE between **Br-YO** MOF and **2a** occurs efficiently at room temperature with as little as 2 equiv of the latter complex, presumably due to the large difference between the lengths and basicities of the (alkynyl)gold(phosphine)-containing linker and the naphthalene tetracarboxydiimide pillar **4**.<sup>35,36</sup> The progress of SALE can be qualitatively observed by a gradual color change of the orange **Br-YO** MOF crystals to bright yellow (**Au-DBTO** MOFs) (**D** and **T** indicate the deprotected TMS-acetylene-containing strut **1**, and **B** and **O** indicate the brominated octaoxygenated strut **3**, following notations in a previous report on similar materials<sup>45</sup>) (Figure 2) or quantitatively monitored using inductively coupled plasma atomic emission spectroscopy (ICP-AES) analyses of Au/Zn and P/Zn ratios. Full conversion to the  $\text{PMe}_3$ -functionalized **Au-DBTO-a** MOF was achieved within 24 and 168 h in the presence of **4** and 2 equiv of **2a**, respectively.

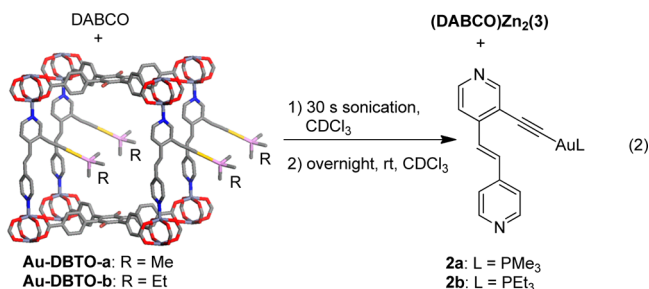
**Characterization of (Alkynyl)gold-Containing MOFs Au-DBTO-a.** The powder X-ray diffraction (PXRD) pattern for DMF-solvated **Au-DBTO-a** is very similar to that of the parent **DTO** MOF (Figure S11 in the SI),<sup>45</sup> indicating that the materials are isostructural with similar unit cells. Single crystals of the **Au-DBTO-a** were of sufficient quality for X-ray structure determination. The structure clearly shows conversion from



**Figure 2.** Light-orange Br-YO MOF crystals become bright yellow as this material is converted to Au-DBTO-b MOF over the course of SALE. From right to left: samples correspond to 7, 15, 27, 40, 58, and 95% conversion, respectively. The solution of the starting (alkynyl)gold(phosphine) complex **2b** is colorless. Complete crystal to crystal transformation was also verified by comparing the powder X-ray diffraction (PXRD) pattern of the product to that of Br-YO MOF (Figure S11 in the SI).

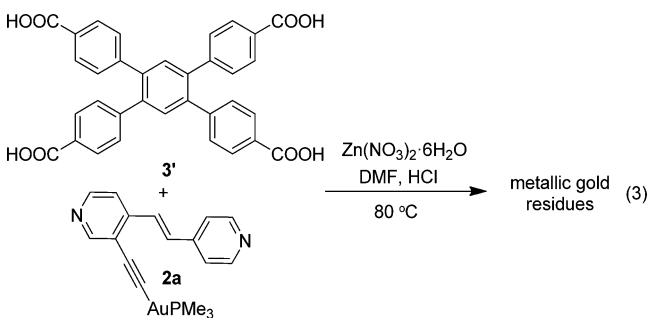
naphthalene tetracarboxydiimide pillar **4** to the dipyriddy ligand **2** backbone (Figure S12 in the SI); however, the  $\equiv\text{C-AuPMe}_3$  moieties were disordered over several crystallographic positions and could not be precisely located from the residual electron density. As such, solvent-masking procedures were used to remove the contributions of these ligands and other disordered solvents. The total number of electrons so removed is sufficient to account for the C–Au–P(Me)<sub>3</sub> moiety and disordered solvent (see section S8 in the SI for further discussion).

To verify that the (alkynyl)gold(phosphine) functionalities were indeed incorporated into Au-DBTO-a without decomposing, we subjected the MOF to a second SALE experiment with 1,4-diazabicyclooctane (DABCO) in CDCl<sub>3</sub> (eq 2).<sup>46</sup>



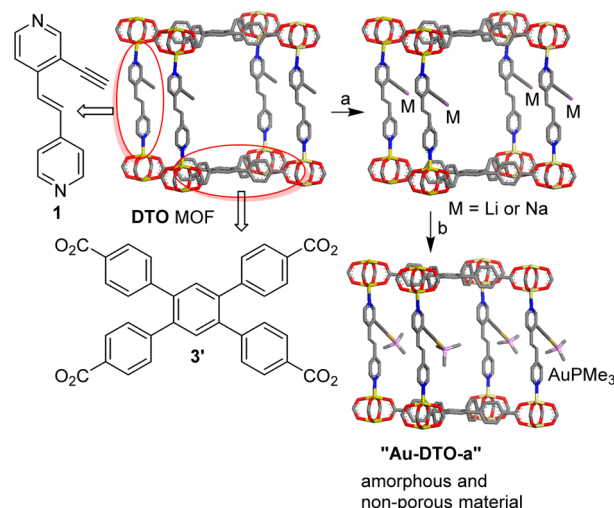
After a brief sonication and stirring overnight, the NMR spectrum of the filtered mother liquor matched perfectly with that of complex **2a** (Figure S7 in the SI), with no trace of the demetallated strut **1**, confirming that the (alkynyl)gold-(phosphine) moiety is completely preserved over the course of both SALEs.

In contrast to the smooth SALE, both *de novo* synthesis and PSM failed, in our hands, to afford Au-DTO-a (as previously stated, **D** and **T** indicate the deprotected TMS-acetylene-containing strut **1**, and **O** indicates the non-brominated octaoxygenated strut **3'** (eq 3), following notations in a



previous report on similar materials<sup>45</sup>). As anticipated, the relatively harsh conditions (acidic DMF, 120 °C) of the *de novo* synthesis led to the decomposition of ligand **2a** (eq 3). While the Humphrey<sup>47,48</sup> and van Bokhoven<sup>21</sup> groups had successfully carried out the PSM of phosphine-containing MOFs with (SMe<sub>2</sub>)AuCl and (THT)AuCl complexes through a one-step

ligand displacement reaction, modifying our acetylene-containing MOF would require a two-step procedure (Figure 3):



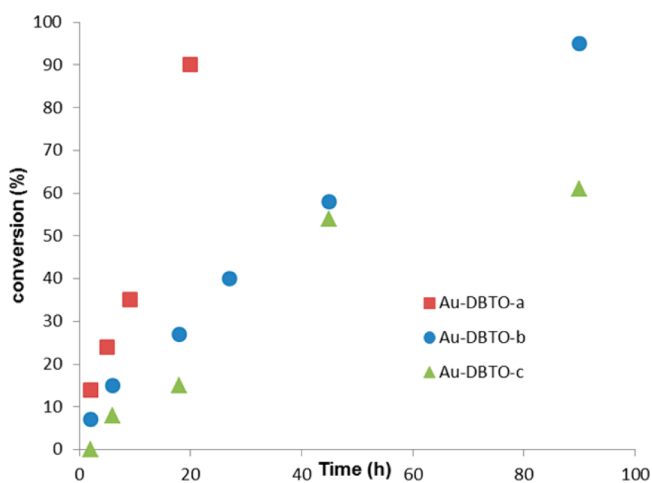
**Figure 3.** Attempts to prepare Au-DTO-a through PSM (the structures were generated by Materials Studio) a) LiNMe<sub>2</sub> or NaOMe in THF, rt, 12 h. b) (PMe<sub>3</sub>)AuCl in CH<sub>2</sub>Cl<sub>2</sub> or TEA and (PMe<sub>3</sub>)AuCl in CH<sub>2</sub>Cl<sub>2</sub>.

deprotonation to generate an acetylide intermediate followed by metallation with an LAuCl reagent (L = SMe<sub>2</sub>, THT (tetrahydrothiophene), and PMe<sub>3</sub>). To evaluate the PSM approach, we employed large (2–5 mm) crystals of DTO MOF,<sup>45</sup> the non-metallated analogue of Au-DTO-a but with the non-brominated octaoxygenated strut **3'** (as previously, **D** and **T** indicate the deprotected TMS-acetylene-containing strut following a notation in a previous report on similar materials.<sup>45</sup> Treating DTO MOF with BuLi or Me<sub>2</sub>Mg only led to the deprotonation of the surface and near-surface acetylene groups, presumably due to the large sizes of the oligomeric base species present in solution for these reagents. Using smaller bases such as LiNMe<sub>2</sub> or NaOMe allowed for “deeper” deprotonation into the DTO MOF crystals, but these reactions never reached completion. Direct reaction of DTO MOF with a mixture of NEt<sub>3</sub> and (PMe<sub>3</sub>)AuCl<sup>49</sup> only afforded surface metallation, as verified by ICP-AES and NMR spectroscopy. As such, we conclude that after being metallated, the pores near the surface of a DTO MOF crystal are narrowed and limit the diffusion of the relatively large gold reagent deeper inside. Indeed, grinding DTO MOF crystals to a fine powder led to complete functionalization, but the crystallinity and the porosity of the final material was lost. Details of these *de novo* and PSM experiments are given in the SI (Sections S5 and S6).

**Dependence of the SALE Rate on the Size of the Ligand.** While the rate and extent of SALE reactions have been shown to depend on the Lewis basicity of the incoming linker,<sup>34,35</sup> it is reasonable to expect that the size of the



incoming linker will also play a role. To this end, we examined the SALE of Br-YO MOF with linkers **2a–c**, which have similar basicity but possess phosphine ligands of different sizes. As anticipated, the rate of SALE showed a strong inverse dependence on the size of the phosphine ligand on the Au center: in the presence of 4 equiv of incoming linkers, the SALE of **2a** was complete within 24 h, while that for the slightly bulkier,  $\text{PET}_3$ -ligated **2b** took almost 4 days to complete (Figure 4). The SALE of the bulkiest  $\text{PPH}_3$ -ligated **2c** only reaches 60%



**Figure 4.** Conversion of Br-YO MOF to Au-DBTO-a-c through SALE in the presence of 4 equiv of the incoming linkers **2a–c**, as monitored by ICP-AES analysis of the MOF materials (based on P/Zn and Au/Zn ratios).<sup>50</sup>

conversion after 4 days and remains unchanged even after the linker solution is replaced with fresh solution. The incomplete exchange of **2c** is most likely due to its limited transport into the center of the Br-YO MOF crystals once the linkers **4** of the outside layers have been exchanged away.

The complete exchange of Br-YO MOF into Au-DBTO-b was confirmed by PXRD patterns, and the complete incorporation of linker **2b** was verified by a second SALE with DABCO (eq 2).<sup>46</sup> The relative amount of physisorbed DMF, as obtained by thermogravimetric analysis (TGA) also correlates well with the size of the phosphine ligand: as-synthesized Au-DBTO-b took up slightly less DMF than as-synthesized Au-DBTO-a (Figure S9 in the SI).

## CONCLUSIONS

In summary, we have shown that SALE can be used to prepare non-catenated Zn pillared-paddlewheel MOFs containing moderately sensitive metal-hydrocarbyl complexes such as (alkynyl)gold(phosphine). The SALE-prepared MOFs retained their crystallinity and porosity and the (alkynyl)gold(phosphine) complexes in the linkers remained intact during the SALE. Additionally, the reactions can be carried out at room temperature and in neutral solvents, making SALE an attractive strategy for preparing MOFs containing organometallic functionalities that cannot be easily accessed through *de novo* and PSM methods.<sup>51</sup> Lastly, complete exchange can even be achieved with as few as 2 equiv of the incoming linkers, pointing to a potential advantage when the incorporation of a high-molecular-weight, expensive organometallic compound into an MOF is desired.

## ASSOCIATED CONTENT

### Supporting Information

Crystallographic information file. S1. General information. S2. General procedures and materials. S3. Preparation of alkynyl-gold functionalized linkers **2a–2c**. S4. General procedure for SALE experiments. S5. *De novo* approach. S6. PSM approach. S7. Characterization of Au-DBTO materials. S8. Single-crystal X-ray diffraction data for Au-DBTO-a. S9. References. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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- (49) The (SMe<sub>2</sub>)AuCl and (THT)AuCl complexes decomposed into metallic Au residues under these conditions. See Section S6 in the SI.
- (50) That these plots do not quite match typical exponential profiles for ligand exchanges reflects the fact that the MOF crystals tend to develop cracks over the course of SALE, which can allow for faster diffusion of the incoming linkers inside the pores. Such cracks are visible in the bottom right image shown in Figure 1.
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